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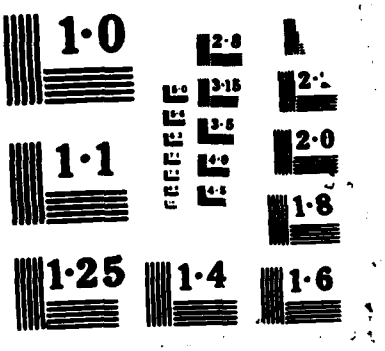
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PROBLEM DEFINITION STUDY ON TECHNIQUES AND METHODOLOGIES FOR EVALUATING THE CHEMICAL AND TOXICOLOGICAL PROPERTIES OF COMBUSTION PRODUCTS OF GUN SYSTEMS, VOL. 1

FINAL REPORT

March 1988

Robert H. Ross
Bimal C. Pal
Roswitha S. Ramsey
Roger A. Jenkins
Simon Lock
Wayne H. Griest
Michael R. Guerin

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Gun exhaust is a complex mixture of both organic and inorganic chemical species. Similar to other mixtures, it has both vapor and particulate phases. This report contains information concerning the chemical characterization of gun exhaust and offers recommendations for its chemical and toxicological investigation.

Propellant compositions used in munitions are all nitrocellulose based but are categorized by the inclusion of the other major ingredients (i.e., single-base propellants contain nitrocellulose only, double-base propellants contain nitrocellulose and nitroglycerin, and triple-base propellants contain nitrocellulose, nitroguanidine, and nitroglycerin). The principal decomposition products present in gun exhaust are carbon monoxide, hydrogen, carbon dioxide, water, and nitrogen (approximately 99% by volume). A number

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of minor products have been reported to be present in gun exhaust including nitrogen oxides, ammonia, inorganic particulates (e.g., lead and copper), and polycyclic aromatic hydrocarbons (of unknown origin).

Sampling and analytical chemistry methods routinely used to examine combustion products from other complex mixtures (e.g., diesel exhaust and tobacco smoke) should be applicable to gun exhaust due to similarity of constituents. Drawbacks to a thorough chemical characterization of gun exhaust include a lack of information on organic emissions in the vapor and particulate phases and the fact that standard methods do not exist for producing the exhaust for compositional evaluation.

Complex mixtures can be toxicologically investigated in one of three ways: (1) whole-mixtures testing, (2) testing of fractions, and (3) single-compound testing. Each of these methods has proven useful in the investigation of the health effects of mixtures such as diesel exhaust and tobacco smoke. However, at present the ability to test gun exhaust as a whole mixture in a manner that simulates human exposure is not possible. This is a serious limitation to the investigation of the toxicology of gun exhaust since it is only through testing of the mixture that the investigator can be confident that observed results are representative of potential interactive effects among chemicals (i.e., additive, synergistic, or antagonistic). Many of the chemicals that have been at least tentatively identified in gun exhaust are toxicologically well studied compounds (e.g., carbon monoxide) and evaluation of the health effects data on these can provide an insight into the toxicology of gun exhaust. However, this single-compound approach must be used with caution since possible interactive effects are not taken into consideration. There is a limited number of studies that have investigated the health effects of combined pollutants, but, in general, these have not proved very useful in the assessment of the toxicology of gun exhaust.

Once the capability to test gun smoke as an intact mixture is developed, then a wide range of acute and subchronic tests should be employed, designed primarily to detect performance degrading effects. Chronic toxicity testing is not recommended since it is unlikely that exposure to Army personnel will be anywhere near lifetime. The possibility of delayed effects should, however, be investigated. Special attention should be given to behavioral modification and to possible male reproductive effects.

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EXECUTIVE SUMMARY

Emissions from rifles and large-caliber guns are a complex mixture of chemical species that have undergone only limited chemical characterization and toxicological investigation. The chemicals arise mainly as a result of the combustion process occurring during the firing of a round. The process begins with the detonation of the primer mix, followed by ignition of the igniter (igniters are only used in large-caliber rounds) and detonation of the propellant, and ending with the ejection of the projectile from the gun barrel. All propellants are nitrocellulose based -- single-base propellants contain nitrocellulose; double-base propellants contain nitrocellulose and nitroglycerine; and triple-base propellants contain nitrocellulose, nitroguanidine, and nitroglycerin as the major ingredients.

Available information indicates that the major decomposition products in gun exhaust are carbon monoxide, carbon dioxide, hydrogen, water, and nitrogen, constituting approximately 99 percent by volume. A number of minor chemical species have been identified including ammonia, nitrogen oxides, sulfur dioxide, methane, inorganic particulates (lead, antimony, barium, copper, and zinc), and polycyclic aromatic hydrocarbons (of unknown origin). There is a specific lack of information on organic emissions in the vapor and particulate phases, including the contribution of classes to the total exhaust. Evaluation of the chemical characterization data is complicated by the fact that no standard method exists for producing the exhaust. A test environment where temperature, concentration, humidity, background, and other variables can be accurately controlled is needed. Emphasis should be placed on collecting gases from the breech compartment since these products will in all likelihood be the major source of exposure. The results of these investigations can then be correlated with results from field studies.

Recommendations are given for analytical and sampling methods for chemical species reported to be present or likely to be present in weapons exhaust. The methods selected were chosen because they have been found to be valid for determining combustion products from other complex mixtures (i.e., gasoline and diesel exhaust and tobacco smoke) or are standard methods for monitoring exposure. Examples include (1) capture of particulates by filtration followed by solvent extraction and analysis of the extracts by high-performance liquid chromatography using fluorescence detection for polycyclic aromatic hydrocarbons and carbon monoxide and (2) gas analysis either by a portable monitor or by the use of sample bags to capture samples for subsequent analysis by gas chromatography using a thermal conductivity detector.

There are three principal methods for investigating the toxicology of a complex mixture: (1) whole-mixture testing, (2) fractionation and subsequent testing of fractions, and (3) single-compound testing.

Testing of the whole mixture is the most desirable since this simulates human exposure. Intact-mixture testing also takes into account

interactive effects between chemicals (i.e., additive, synergistic, or antagonistic) that can alter the toxicity of single components.

Testing of various fractions can define those components that have the greatest potential for causing toxicological effects. For cigarette smoke and diesel exhaust (reference complex mixtures used in the report), the most commonly investigated fraction is the particulate matter. Mutagenic evaluation of solvent extracts has shown that a number of genotoxic chemicals are adsorbed to the particulates. However, the expression of this mutagenicity in vivo may be curtailed through binding to or metabolism by physiological fluids and phagocytosis by alveolar macrophages, and thus caution should be used in extrapolating from in vitro to in vivo conditions.

Since a considerable amount of health effects data exists for some of the more significant chemicals present in gun exhaust (e.g., carbon monoxide), evaluation of the toxicology data of single compounds can provide an insight into the toxicology of gun exhaust. In addition, a few studies are available that investigate the interactive effects of chemicals found in gun exhaust (e.g., carbon monoxide/carbon dioxide and carbon monoxide/hydrogen cyanide). The results of such studies, however, must be evaluated with regard to their applicability to gun exhaust since no or limited (for the two-compound studies), interactive effects are considered. Actual testing of single compounds should perhaps only be conducted when the results could be used to reformulate a propellant such that toxic chemical species could be eliminated.

The principal effect of concern from exposure to gun exhaust is performance degradation resulting from short, high-level, intermittent exposures. Therefore, investigations of the chronic toxicity of gun exhaust are not recommended. Tests that are recommended include a full range of acute and subchronic assays with special attention to behavioral modification. Reproductive effects tests can probably be limited to males, although the possibility of women being exposed during training exercises could extend testing to females. The use of nose-only or head-only exposure methods seems appropriate since the amount of generated test mixture may be small, and these methods eliminate the possibility of dermal or oral exposure (through grooming) that can occur during whole-body exposure.

In summary, developing the ability to generate gun exhaust for toxicological investigations in a manner that simulates human exposure is vitally important. Although the testing of fractions of gun exhaust and the consideration of what is known concerning the toxicology of single compounds or limited compound interactions are ways to gain an insight into the toxicology of gun exhaust, whole-mixture testing is the only way to ensure that the results encompass the wide range of possible interactive effects. Standardization of generation and collection procedures for gun exhaust is needed to facilitate both analytical and toxicological investigations.

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1. INTRODUCTION AND BACKGROUND

1.1 PURPOSE AND MILITARY OBJECTIVES

Rifles and large-caliber guns generate exhaust emissions as a result of combustion of propellant mixtures. Combustion occurs under high temperature and pressure inside the gun until the projectile is ejected from the barrel. The exhaust emissions are a complex mixture of chemical species, similar in many respects to other exhaust emissions (e.g., diesel exhaust and tobacco smoke) in terms of complexity, but also probably in terms of potential threat to human health.

The rifle and gun are ubiquitous to the military. Every soldier has had some exposure to weapons exhaust products and some receive almost daily exposure. When the exhaust is discharged into the enclosed space of an armored vehicle, a soldier can be expected to inhale significant quantities of the material prior to removal through the ventilating system.

Unfortunately, information about the chemical and toxicological properties of the weapons exhaust mixture is limited. This is so, in part, because laboratory duplication of the gun environment, particularly for large-caliber weapons, is an untested but inherently complex task. In order to efficiently focus research efforts, a literature evaluation of techniques and methodologies was undertaken.

1.2 LITERATURE REVIEW APPROACH

Initial efforts focused on a review and analysis of the literature that presented information concerning the chemical characterization of gun exhaust. Although somewhat fragmented (and in many cases inconclusive) these data identify the major chemical species and several of the minor components of gun exhaust.

With this knowledge it was possible to focus on the toxicology and analytical methods for selected chemicals. Once this was accomplished, review efforts were concentrated on the real question -- what about gun exhaust as a complex mixture? This is the central issue, especially with regard to toxicology, since knowledge of the potential health effects of the individual chemicals, while informative, does not permit a valid assessment of the toxicology of the mixture. Interactive effects (i.e., additive, synergistic, or antagonistic) and competition for receptor sites in vivo can not be adequately assessed by examination of the data for individual chemicals.

Appropriate strategies and methodologies for investigating the analytical and toxicological properties of gun exhaust were, therefore, reviewed. Since it was known from the outset of the project that the literature discussing gun exhaust as a complex mixture was extremely limited - especially with respect to toxicology - it was decided that examination of the health effects and analytical chemistry data for

other complex mixtures that had been well characterized and tested would be conducted. Those selected were tobacco smoke, diesel and gasoline exhaust, and polymer combustion products. Analogy to these well-studied mixtures and use of the limited information concerning gun exhaust, as well as general principles of toxicology and analytical chemistry, permitted development of strategies and methodologies for investigating the analytical and toxicological properties of gun exhaust.

1.3 SCIENCE OF EVALUATING COMPLEX MIXTURES

1.3.1 Introduction

It is a logical assumption that most adverse health and environmental effects associated with occupational and ambient environments are the result of exposure to complex mixtures. Even in those cases where a single agent is responsible for the effect, it is seldom present as a single entity in an otherwise pristine environment. The causative agent(s), once released into an environment, is (are) subject to chemical transformation and to physical or chemical interactions with constituents already in that environment. More importantly, products and by-products of most chemical and physical processes are themselves complex mixtures. This is especially so for fuel processing and combustion and for military-specific concerns such as those related to conventional weapons firing, battlefield obscurants, and missile propellants.

It is extensively documented (e.g., Committee 1982, 1983; Rosin 1982; USEPA 1986) that the toxicological potency of a chemical is influenced by the mixture in which it is found. The mixture can increase its potency (as when a tumor initiator is accompanied by tumor promoting agents) or decrease its potency (as when a carcinogen is irreversibly bound by the mixture such as to be biologically unavailable). It is also logical that a mixture might contain a variety of constituents that affect different organ systems or produce a variety of toxicological effects. A mixture that may not contain an acutely toxic constituent may contain constituents that produce a long-term effect.

The importance of complex-mixtures toxicology and associated risk assessment has been recognized by many federal agencies and scientific advisory bodies. The National Academy of Sciences/National Research Council is currently deliberating strategies to address the toxicology of complex mixtures. The U.S. Environmental Protection Agency (EPA) has issued (USEPA 1986) "Proposed Guidelines for Health Risk Assessment of Chemical Mixtures." The U.S. Department of Energy (DOE) currently (USDOE 1986) funds a program on the toxicology of complex chemical mixtures as a follow-up to its extensive (e.g., Cowser 1984) previous program to define the toxicological properties of synthetic fuels. In general, these and other organizations recognize the importance of complex mixture toxicology and seek to identify or develop the experimental strategy or database required to generate reliable risk assessments.

1.3.2 Related Past Program Examples

Military-specific materials, effects, and exposure sequences of concern are generally unique. The subject of this document, by-products of conventional weapons firing, is an example. The principal effect of concern is performance degradation during battlefield operations and training exercises where exposures tend to be for short periods of time to highly concentrated contaminants. While research efforts in the civilian sector seldom address these same concerns, experiences gained in these programs may provide guidance to experimental designs suitable for military-specific concerns. The Smoking and Health Program sponsored by the National Cancer Institute and the Synthetic Fuels Program sponsored by the DOE are discussed below as examples of past toxicology research dealing with complex mixtures.

The National Cancer Institute Smoking and Health Program was initiated in approximately 1968 and continued as a carefully integrated and highly funded program through 1976. (The program continues today but as a smaller grant-oriented effort addressing specific issues identified by the research community.) The program was coordinated by an advisory body consisting of independent researchers, tobacco industry scientists, and National Cancer Institute staff. It was based upon strong epidemiological evidence of an association between cigarette smoking and lung cancer. In the absence of legislative or societal mandates to control smoking, the program sought to determine whether a less hazardous cigarette could be formulated.

The approach (e.g., USDHEW 1980) taken combined engineering design, toxicological and chemical testing, and fundamental research on bioassay development and on the identification of causative agents. In the course of the program, several million of each of approximately one hundred cigarette types of systematically varied composition were manufactured. Variables included tobacco types, tobacco processing methods, major additives, and cigarette paper characteristics. The cigarettes were smoked by machine using puff parameters thought to mimic the human situation, and smoke was collected as condensate in large cold traps. Kilogram quantities of smoke condensate were generated from each cigarette, and the condensate was subjected to mouse skin painting to determine its carcinogenicity. Fresh batches were prepared every 6 weeks to reduce the likelihood of errors due to aging of the condensate. Portions of the condensate were subjected to chemical analysis as a quality control measure and to provide a database for correlation with carcinogenicity. In addition, the cigarette filler was analyzed for parameters commonly used by the tobacco industry to establisy cigarette characteristics. A smaller number of cigarettes were also smoked using analytical smoking machines to determine their deliveries of tar, nicotine, carbon monoxide, and a variety of other constituents of the particulate and gas phases.

The result was an extensive database allowing correlations between tobacco chemistry, cigarette construction characteristics, smoke chemistry, and carcinogenicity of smoke condensate. The general conclusion was that modifications in cigarette design that yielded a significantly

lower carcinogenicity increased the yields of other noxious constituents or were known to be unacceptable to the consumer. Important findings were that total dose was more determinant than specific carcinogenicity of the condensate and that nicotine itself may contribute to carcinogenicity.

Subsequent research focused on the development of inhalation exposure instrumentation and animal models. Dogs, mice, rats, hamsters, baboons, and pigeons were used to study a variety of cigarettes and issues but not systematically as was done by skin painting. Acute toxicity associated with nicotine and carbon monoxide proved to be a serious impediment to achieving sufficiently large doses of tar to clearly elicit respiratory tract tumors in a time frame practical for inhalation study of a large variety of cigarettes.

The DOE program on synthetic fuels toxicology addressed a different question than did the smoke program and thus utilized a different approach. The first objective of the program was to determine whether there were any unsuspected (in magnitude or kind) hazards associated with the production of gaseous and liquid fuels from coal and oil shale. The only samples available initially were those generated in small-scale experimental facilities of questionable relevance to eventual commercial facilities. As such, no sample was viewed as sufficiently relevant to warrant expensive long-term toxicological study. In addition, a large variety of conversion processes were being considered and each produced a large variety of materials of possible concern.

The approach taken was to screen a large variety of samples using the Ames mutagenicity assay and chemical analyses for selected carcinogens. Results were generally compared with those simultaneously generated on petroleum-derived equivalents of the synthetic fuel samples. As the toxicology and conversion technology programs advanced, mouse skin carcinogenesis, other toxicological endpoints, and sophisticated chemical analyses were included.

An important general feature of the program was its extensive use of integrated chemical class fractionation and biological testing. In this approach, the sample of interest is first bioassayed as a whole. An aliquot is also subjected to chemical class or physical separation and each of the resulting fractions is bioassayed. If the objective was to identify the bioactive constituents, the fraction(s) exhibiting the highest biological activity was (were) further separated and the subfractions were bioassayed. The process was repeated until bioactivity could not be further concentrated, and then the fraction was analyzed chemically.

One important result of this "bio-directed chemistry" (e.g., Schuetzle and Lewtas 1986) approach was the unexpected finding (Guerin et al. 1980; Wilson et al. 1980) that polycyclic aromatic primary amines were the principal contributors to the Ames mutagenicity of coal liquids. This explained a later observation that it was possible to eliminate mutagenicity without reducing carcinogenicity because different constituents were responsible for each of the effects. Also

important, it was found that class separation often allowed the detection of mutagenicity in a sample that appeared inactive when the mixture was tested as a whole. It is also true that some types of mixtures that test positive are negative or only weakly positive after class separation. Class separation served to concentrate the biologically active constituents and to free them of matrix constituents which interfered with the assay.

Both the National Cancer Institute Smoking and Health Program and the Department of Energy Synthetic Fuels Program relied on comparative toxicology to assess progress and set directions. The smoke program compared the toxicological properties and chemical characteristics of the cigarettes under study to those of a reference cigarette designed to mimic those in common use in the 1950s. The synthetic fuels program compared the properties before and after treatment and to petroleum counterparts currently in the marketplace.

1.3.3 Complicating Characteristics of Complex Mixtures

Complex mixtures are especially difficult to evaluate toxicologically for three principal reasons. First, the mixtures commonly consist of a relatively small number of chemicals present at parts per hundred quantities and an ever increasing number of constituents at successively lesser concentrations. The chemicals present at higher concentrations generally determine the acute toxicity properties of mixtures, but those present at lesser concentrations may lead to long-term health effects. The large variety of chemicals present requires that a large variety of endpoints and organ systems be considered for a thorough health risk assessment. Second, the physical and chemical composition of the mixture is highly influenced by the conditions of its production. A diesel engine at idle produces an exhaust different from that produced under full load, and a new weapon is likely to produce a compositionally different smoke than is a weapon highly stressed by recent intense action. Third, complex mixtures change composition with time as a result of dilution in the environment, interactions with ambient environmental constituents, and interactions with other components of the original mixture.

Products of incomplete combustion are especially subject to these complications. Cigarette smoke, for example, is known (Norman 1982; Dube and Green 1982) to consist of respirable-sized liquid particulate matter in a matrix of air, carbon monoxide, carbon dioxide, nitrogen oxides, water, and a great variety of volatile organic chemicals. Its composition is dependent on the properties of the cigarette and how it is smoked. At least 4,720 constituents have been identified (Dube and Green 1982) in cigarette smoke at concentrations ranging from volume percent (e.g., carbon dioxide, carbon monoxide) to parts per billion (e.g., selected N-nitrosamines). The distribution of the constituents between particulate matter and gas phase depends upon the water solubility and volatility of the constituents, and upon the age and distribution of the smoke. Nicotine, almost solely a particulate phase constituent in mainstream smoke, is found (Eudy et al. 1985) almost solely in the gas phase of environmental tobacco smoke. Similar dependence on time and dilution might be expected of the constituents of gunsmoke.

Such considerations require that experimental evaluations of mixtures be carried out with caution and understanding. Studies of condensed cigarette smoke or of collected diesel exhaust particulates, for example, are important for detecting constituents of concern and relating product or process modifications to one another but do not measure the toxicological effect of inhalation exposure to the materials as wholes. Collection of atmospheres containing principally inorganic constituents such as the one of concern in this report is an especially suspect approach because the constituents are very likely to transform to a chemical state in solution different than their natural state in the aerosol.

Toxicological interactions in complex mixtures are currently poorly understood. A comingled constituent might activate or deactivate an enzyme system required to convert another constituent to its biologically active form. The constituent might competitively bind to sites on DNA, making them unavailable for binding to the constituent(s), which would otherwise result in cancer. Toxins may be present that result in lethality before the bioassay system can respond to the more subtle challenge.

It is unlikely that advances in the sciences of toxicological and chemical interactions will occur sufficiently soon as to allow a fundamental approach to risk assessment for complex mixtures. Strategies for chemical characterization and for comparative and empirical toxicological assessments of risk are summarized below.

1.3.4 General Approaches to Chemical Characterization

The chemical characterization of complex mixtures for toxicological evaluation is generally approached in one of three ways. These are (a) through a comprehensive mass balance, (b) through the measurement of major constituents, or (c) by analyzing the mixture for the presence and quantities of preselected "indicator" chemicals or chemical classes. A mixture that has been characterized toxicologically and chemically can serve as a reference material for comparison with related mixtures. Comparative gross properties measurements and multielement and/or multicomponent screening is often sufficient to detect similarities and differences suggesting whether toxicological study is required.

General features of combustion products are that they are highly complex chemically and physically and that their precise composition is dependent on the exact conditions of their formation. Field conditions (e.g., ambient temperature and humidity extremes, weapon maintenance, recent action, ammunition history) influencing either the formation chemistry or the fate of emissions immediately following formation are highly variable and generally undefined. As a result, a set of controllable and defined conditions are best selected so as to mimic a realistic field condition and constitute a standard or reference method for generating an experimental test atmosphere. Conditions are chosen to allow laboratory generation of the atmosphere whenever possible. This is done to allow the use of sophisticated physical and chemical measurement instrumentation that is difficult to place in the field.

Results obtained in the laboratory are compared with those obtained using less sophisticated methods in the field under a number of common conditions or under conditions representing the range of those expected to be encountered.

The mass balance approach to chemical characterization is used relatively rarely because it is time-consuming and costly. Examples of successful use include the study of mainstream cigarette smoke (Norman 1977) and of synthetic fossil fuels (Guerin et al. 1981). Cigarette smoke characterization has included the identification of individual constituents, and the fuels work has generally been limited to establishing mass balance by chemical class. The advantage of the approach is that it allows an accounting of the quantity of material characterized. The approach becomes less useful as trace contaminants become important because each constituent identified contributes little to the mass balance.

Characterization by measurement of major constituents, physical components, and physical properties is often the first step in studying a completely unknown mixture. The selection of constituents for measurement is generally made based upon what is known about the "fuel" and the process leading to the formation of the mixture of concern. Where toxicology is of concern, gases such as carbon monoxide, oxides of nitrogen, hydrogen cyanide, and hydrogen sulfide are commonly sought. For propellant mixtures, permanent gases and inorganic oxidants are also measured. Gross measurements also commonly include respirable and non-respirable particulate matter, total organic carbon, and vapor phase organics. The objectives of the approach are to identify and quantitate the major components of possible toxicological concern as rapidly as possible.

The most common chemical characterization strategy is to measure selected constituents of known toxicological concern or thought to be indicative of the presence of toxicologically important constituents. Gases such as carbon monoxide and nitrogen oxides are determined regardless of whether they are major or trace constituents. Benzene, formaldehyde, and methylene chloride might be determined as indicators of vapor phase organic hazards. Benzo(a)pyrene and 3-naphthylamine are commonly determined as carcinogenic hazard indicators. This approach provides a rapid assessment of commonly known hazards but misses unexpected hazards and often accounts for a very small percentage of the total material present.

Advances in analytical technology have made multielement and multicomponent screening a common component of mixture characterization. The presence and approximate quantities of most elements in the periodic table can be assessed rapidly using techniques such as inductively coupled plasma spectroscopy and neutron activation analysis. Gas chromatography and gas chromatography-mass spectrometry are commonly used to profile a wide range of volatile organics. The elemental distributions and the relative quantities of organic chemicals detected chromatographically may be used empirically for comparison with related mixtures.

Two limitations of current analytical chemical technology require special mention. First, highly reactive chemicals can seldom be sampled for analysis with certainty that they have not reacted with other chemicals in the mixture or the environment. This problem is generally overcome by employing sophisticated instrumental monitors and is a major reason why laboratory test atmospheres are preferred. Second, it is currently very difficult to identify organic chemicals isomerically when they are present at trace levels. This problem is often reduced by comparative chromatographic or mass spectrometric profiling so that the number of constituents requiring identification is minimized.

The most practical approach to chemical characterization involves the measurement of toxic constituents suspected to be present as a result of what is known about fuel composition and formation chemistry. Furthermore, multielement and multicomponent analyses provide a cost-effective survey of the composition of the mixture that can identify unsuspected hazards. Studies must be carried out using a controlled experimental atmosphere in order to ensure applicability of the most reliable measurements technology. Results must then be compared with those acquired under a variety of field conditions using the most suitable field methods.

1.3.5 General Approaches to Toxicological Assessment

The toxicological properties of a complex mixture are generally measured in one of three ways: (a) by subjecting the mixture as a whole to biological testing, (b) by subjecting major fractions of the mixture to biological testing, or (c) by identifying and quantitating the individual constituents of the mixture and subsequently determining (usually through the literature) their individual toxicities. Biological testing is carried out either in a highly directed manner (e.g., USDHEW 1980) or using a tier approach (e.g., Jaworski 1979; Merrill 1979). Directed testing involves a definitive measurement of the effect (e.g., carcinogenesis) of interest using the most suitable protocols available. The tier approach involves the application of successively more complex or definitive tests chosen on the basis of results from the earlier tests. Typical tiers include chemical analysis, acute toxicity, chronic effects screening (e.g., mutagenicity as an indicator of carcinogenicity), subchronic toxicity and finally chronic toxicity. The tier approach is most commonly and efficiently applied to mixtures for which little is known and a variety of effects are of possible concern.

The results of biological testing may be used (USEPA 1986) in the same manner as results of testing of single compounds are used to assess risk. A common alternative is to compare the results of biological testing with those for closely related mixtures. Such comparative measures may be especially suitable for new formulations leading to a product similar to that in common use and of generally known toxicological characteristics.

1.3.5.1 Bioassay of Whole Mixtures

As shown by EPA guidelines (see USEPA 1986 in Appendix A), data on the mixture as a whole is generally preferred for risk assessment, because all the constituents involved in human or environmental exposure are presented to the biological test system. The result of the exposure presumably represents the net toxicity of the mixture as a whole and accounts for additive, synergistic, and antagonistic properties characteristic of the mixture.

It is generally difficult (and sometimes impossible) to both maintain the integrity of a mixture and prepare it in a form suitable for biological testing. This is especially the case for aerosols and trace airborne contaminants. Sampling required to accumulate sufficient material for many bioassay systems collects only that material for which the collection medium is designed. Particulate matter is commonly collected while vapor phase constituents escape the trap, for example. Further, extraction or dissolution of the collected material in an organic solvent for skin painting or other bioassay removes only that portion of the material that is soluble in the solvent used. Such difficulties are compounded when both inorganic and organic constituents are of concern because a given solvent is seldom applicable to both classes and because of the reactivity between the classes (for example, halogen acids or inorganic oxidants and aromatic organics).

Aerosols and airborne contaminants in general are preferably bioassayed as a whole when risk assessment is intended. To do so, however, generally requires that a laboratory-scale aerosol generator be developed to produce a test material that accurately mimics that of concern in actual human exposure or environmental contamination. This in turn requires that considerable chemical and physical analyses be carried out to define the nature of the test material. Furthermore, field sampling and analyses must be carried out to define the nature of the actual material that is to be mimicked by the test material.

This is often a time-consuming and expensive component of the toxicological study. Once such a system is in place, however, it may be used not only for inhalation bioassay but also as a source for other routes of exposure (e.g., skin absorption, drinking water contamination) and for environmental testing. The atmosphere itself may be studied as a function of environmental (e.g., temperature and humidity) conditions in the search for toxicologically relevant chemical or physical changes. Chemical and physical characterization of aerosols from candidate replacement formulations or processes may be sufficient (e.g., Brazell et al. 1984) to determine whether toxicological study of the new material is required.

1.3.5.2 Fractionation and Bioassay

Biological testing of only a portion of a mixture is often done when the portion of concern is known. Study (USDHEW 1980; Hoffmann et al. 1983) of cigarette smoke condensate was thought to be adequate because carcinogenic activity was thought to be associated with smoke

"tars" and not the gas phase of smoke. Particulate matter from diesel engine exhausts commonly (e.g., Schuetzle and Lewtas 1986) receives the most extensive chemical and biological study partly because the major gas phase components have been identified and their toxicological properties are relatively well known. Such a practice is important for identifying constituents of concern and for comparative toxicological evaluation but remains questionable for overall risk assessment.

Studies of only a portion of a mixture are often dictated more by experimental practicality than by choice. Biological test systems suitable for the study of liquids and solutions may not be applicable to gaseous or highly volatile constituents. In other cases, acute toxins (e.g., inorganic acids, carbon monoxide, hydrogen cyanide) present in major quantities might have to be eliminated in order to study more subtle toxicological effects. High costs and long time-frames associated with generating test atmospheres and carrying out inhalation bioassays frequently require that less definitive approaches be taken.

Systematic chemical or physical class fractionation coupled with biological testing is an alternative to testing whole mixtures that has some advantages. It is an effective approach to identifying causative chemicals (e.g., Guerin et al. 1980; Schuetzle and Lewtas 1986) and can allow (e.g., Guerin et al. 1978) measurement of low-level biological activity that is undetectable by testing the mixture as a whole. It has been used most successfully for organic mixtures posing cancer hazards following skin contact or deposition in the respiratory tract. Cigarette smoke condensate (Hoffmann et al. 1983), diesel exhaust particulates (Schuetzle and Lewtas 1986), and hydrocarbon fuels (Wilson et al. 1980) are among the materials studied using this "bio-directed chemistry" approach. It appears that the toxicological study of fractions important from the standpoint of chronic effects may be justified by the existence of a threshold for acute effects when it is suspected that the chronic effects have a very low (or no) threshold. The proportion of chronically affected test animals would be impractically low if the test mixture exposures were low enough to be under the acute-effects threshold.

The most extensive experience (e.g., Cowser 1984) with this approach is the DOE's work on the microbial mutagenicity of synthetic fossil fuels. Samples were separated either by boiling range (Wilson et al. 1982) or by chemical extraction and chromatography (Guerin et al. 1981), and each of the resulting fractions was subjected to Ames mutagenicity testing. The sum of the specific mutagenicities of each chemical fraction weighted for their mass contributions to the whole mixture was found (Guerin et al. 1978) to be a reasonable estimate of the activity of the whole mixture. Results obtained by summation for a series of related mixtures that were also tested as wholes were found (Ma et al. 1983) to correlate well with one another.

Chemical class fractionation carried out with the intent of computing activity by summation must meet stringent requirements. First, the method must allow complete recovery of the starting material so that all of its parts can be tested. Second, the method must be gentle enough that chemical transformations do not occur as a result of the separation itself. Third, the method must often be applicable to sample sizes of several grams or more in order to generate sufficient quantities of the minor fractions for biological testing. Lastly, fractions generated must be chemically homogeneous. Contamination of a major (by mass) inactive chemical class fraction with a small amount of a highly active chemical of another class results in a large error upon summing weighted class contributions to compute the activity of the mixture as a whole.

1.3.5.3 Chemically Directed Assessment

Chemical and physical characterization is often an early step in toxicological assessments of mixtures. If the mixture contains only a relatively small number of constituents of well-known toxicity, their identification and quantitation may be sufficient to assess the toxicity of the mixture as a whole. This is especially so if the constituents are chemically inert toward one another.

Most mixtures of interest in military applications are too complex to allow toxicological assessment from chemical measures alone. Chemicals resulting from weapons firing, for example, are highly reactive. Mixtures resulting from fuel combustion contain such a large variety of gaseous and organic chemical constituents as to make positive identification and quantitation of each impractical. Organic analytical technology is currently incapable of identifying trace organics with the isomeric specificity required for toxicological assessment without a major expenditure of time and resources.

Chemical and physical measures are most useful for determining levels of exposure and for supporting toxicological assessments. Measures of the major constituents of a mixture can suggest acute toxicity concerns to be considered. Selected carcinogens such as benzo(a)pyrene and β-naphthylamine are frequently measured to assess the need for carcinogenicity testing. A most important use of chemical analysis is to assess the similarity of the mixture of interest to other mixtures that may have already been characterized toxicologically. Physical and chemical properties, chemical class compositions, and multicomponent chromatographic or spectrometric measures of the unknown and known mixtures may be compared to assess their similarity without requiring identification and quantitation of each constituent.

1.3.5.4 Relationship to Gunsmoke

Most experience with complex-mixtures toxicology has involved the study of materials where relatively common gases and/or complex mixtures of organic chemicals were of concern. Gun smoke contains reactive inorganic constituents as well as gases and organic chemicals. Methods of chemical class separation and in vitro bioassay preparation that were successful for fuels and smoke condensate are unlikely to be equally

useful for gun smoke since sampling methods used to accumulate material for bioassay or chemical analysis are likely to be accompanied by chemical transformations. Laboratory generation of intact gun smoke appears to be the only definitive approach to establishing its toxicological properties. Some information might be gained by biological study of major gases and inorganic constituents alone or in mixture.

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2. CHARACTERIZATION OF COMBUSTION PRODUCTS OF PROPELLANTS

2.1 INTRODUCTION

The following discussion is arbitrarily limited to certain small-caliber weapons (M-16, M-242, 20-mm cannon) and to certain large-caliber weapons (105-mm cannon, 120-mm cannon, 155-mm Howitzer, and 8-in. Howitzer). In this section the discussion focuses on: (1) mechanism of combustion of propellants including the role and composition of primers and igniters; (2) composition, physicochemical parameters, and combustion products of propellants; (3) mechanism of combustion of propellants; (4) current methods for protecting the gun crews against exposure to gun exhausts; (5) physicochemical parameters affecting the composition of the exhaust emission from guns; and (6) minor constituents of gun exhaust with special reference to Snelson's report (Snelson et al. 1983). Section 2.2 presents a more detailed analysis of gun exhaust products.

2.1.1 Firing Mechanism - Composition of Primers and Igniters

Of the three types of mechanical initiators--percussion primers, stab detonators, and friction primers--the discussion in this section is limited to percussion primers because of their wide use in gun systems. In small arms ammunition such as the M-16 rifle, a relatively small amount of sensitive primer mix, upon being struck by a firing pin, causes ignition of the propellant. However, in large-caliber rounds an igniter usually composed of black powder is inserted between the primer and the propellant to act as a booster. The arrangement is shown schematically in Figure 2.1 (Ciccone 1978).

The primers in use today are of nonmercuric and nonchlorate composition. Mercury fulminate is no longer used because of its inherent instability. The use of chlorate is undesirable since it decomposes to form corrosive chloride. The compositions of conventional priming mixtures used in different types of primers are shown in Table 2.1 (Ciccone 1978).

The military percussion primers are usually of the centerfire type with the ammunition containing a primer located centrally in the head of the cartridge case. The more commonly used boxer primer and battery primer are shown schematically in Figure 2.2. The boxer primer consists of a metallic cup and anvil, both made from brass alloy Cu-Zn (70:30). Compressed priming mixture is placed between the cup and the anvil (Ciccone 1978).

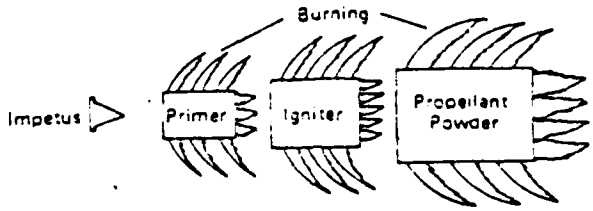


Figure 2.1. Schematic representation of propelling charge explosive train.
Adapted from Ciccone (1978).

TABLE 2.1. STANDARDIZED PRIMING MIXTURES

Ingredients	PA100 (%)	PA101 (%)	793 (%)	NOL160 (%)	NOL130 (%)	FA956[b] (%)
Lead styphnate, basic	-	53	39	60	40	-
Lead styphnate, normal	38	-	-	-	-	37.0±5
Barium nitrate	39	22	44	25	20	32.0±5
Lead azide	-	-	-	-	20	-
Tetrazene[a]	2	5	2	5	5	4.0±1
Lead dioxide	5	-	-	-	-	-
Calcium silicide	11	-	14	-	-	-
Aluminum powder	-	20	-	-	-	7.0±1
Antimony sulfide	5	10	-	10	15	15.0±2
PETN	-	-	-	-	-	5.0±1
Gum arabic	-	-	-	-	-	0.2

a. The German name 'Tetrazene' is used to avoid confusion with the polycyclic aromatic hydrocarbon, tetracene.
b. The primer used in the M-16 rifle system in Snelson's study (Snelson et al. 1983) and that used in the XM-19 rifle (Rocchio and May 1973) fall in this category.

Adapted from Ciccone (1978).

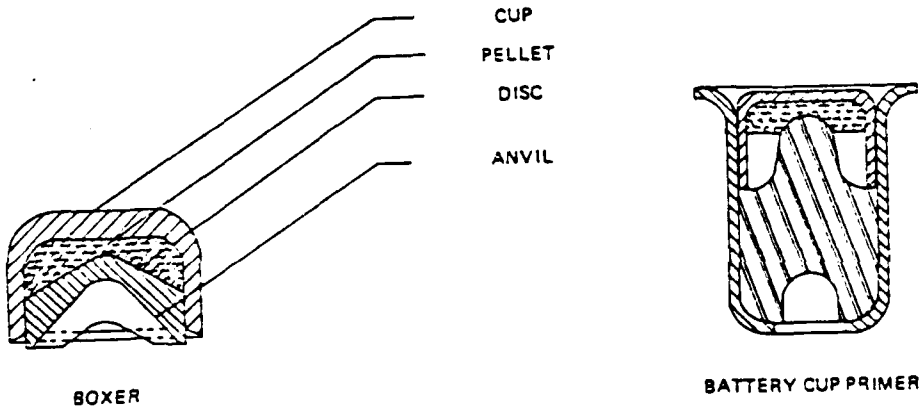


Figure 2.2. Boxer primer and battery cup primer.
Adapted from Ciccone (1978).

Igniters are used in large-caliber weapons and act as intermediates between the primary charges and propellant charges. The most commonly used igniter materials used by the United States are: black powder, CBI (clean-burning igniter) made of porous nitrocellulose, and benite [extruded material consisting of 50:50 mixture of black powder and nitrocellulose; according to Lindner (1980), it is a 60:40 mixture of black powder and nitrocellulose]. Advantages of black powder are (1) easy to ignite even at low temperature, (b) very stable on long storage under dry conditions, and (c) low gas and hot particle output; brisance is controlled by granulation. Powerful igniter impact may shatter propellant grains, especially at low temperature where the grains may be brittle (Stiefel 1985). The composition of most current military black powders is between the following limits: potassium nitrate, 74 to 78 percent; charcoal, 12 to 16 percent; and sulfur, 10 to 12.5 percent. Requirements for the U.S. Armed Forces are covered by specification JAN-P-223A for black powder (potassium nitrate, 74.0 percent; charcoal, 15.6 percent; sulfur, 10.4 percent; ash content, 0.80 percent maximum) (Fedoroff and Sheffield 1962).

Sketches of various types of artillery ammunition showing the location and function of primer-igniters have been presented by Fedoroff and Sheffield (1969). Besides the percussion primer discussed above, electric primers, i.e., primers initiated by an electric current, are used in several gun munitions. Combination electric/percussion primers have been studied but have not come into use (Stiefel 1985).

2.1.2 Composition and Physicochemical Parameters of Propellants

All gun propellants in use are nitrocellulose based. Common ingredients used in these gun propellants and their functions are given in Table 2.2.

Nitrocellulose-based propellant compositions used in guns have been reported by Lindner (1980) and by Roth and Capener (1978). These data are given in Table 2.3. Single-base propellants contain nitrocellulose but no nitroglycerin or nitroguanidine. Double-base propellants contain nitrocellulose and nitroglycerin but no nitroguanidine, and triple-base propellants contain nitrocellulose, nitroglycerin, and nitroguanidine. This is also a class of double-base propellants that may contain diethyleneglycol dinitrate and nitroglycerin or nitrocellulose (Holleman et al. 1983).

Thermochemical, thermodynamic, and performance characteristics of nitrocellulose gun propellants are given in Table 2.4 (Lindner 1980). Composition of the major combustion products constituting about 99 percent of the exhaust is also included. The characteristics of black powder and approximate composition of reaction products of black powder are given in Tables 2.5 and 2.6 respectively. The approximate composition and properties of typical nitrocellulose-base cast propellants as used in rockets are shown in Table 2.7. The composition of the combustion products of these propellants is also included. The justification for including the data on rocket propellants in this document on gun propellants is that they provide pertinent information on methodology and analysis that may be applicable to the investigation of gun exhaust.

TABLE 2.2. TYPICAL COMPONENTS OF NITROCELLULOSE PROPELLANTS AND THEIR FUNCTION

Component	Application
Nitrocellulose Polyglycol diols	Energetic polymeric binder
Nitroglycerin, metriol trinitrate, diethylene glycol dinitrate, triethylene glycol dinitrate, dinitrotoluene	Plasticizers: Energetic
Dimethyl, diethyl or dibutyl phthalates, triacetin	Plasticizers: fuels
Diphenylamine, diethyl centralite, 2-nitrodiphenylamine, magnesium oxide[a]	Stabilizers
Organic and inorganic salts of lead; e.g., lead stannate, lead stearate, lead salicylate	Ballistic modifiers[b]
Carbon black	Opacifier
Lead stearate, graphite, wax	Lubricants
Potassium sulfate, potassium nitrate, cryolite[c] (potassium aluminum fluoride)	Flash reducers
Ammonium perchlorate, ammonium nitrate	Oxidizers Inorganic[b]
RDX, HMX, nitroguanidine and other nitramines	Organic[b]
Aluminum[d]	Metallic fuels Cross-linking Catalysts
Lead carbonate Tin	Defouling agent

a. MgO is perhaps the most efficient inorganic stabilizer for nitroglycerin (Urbanski 1983). Lack of its use in the gun propellant compositions used in the U.S. Army is a surprise (see Table 2.1). However, according to Stiefel (1985), the Army may not use MgO because double-base propellants are stabilized well by organic materials such as ethyl centralite. Inorganic materials are not desirable. Their products have high molecular weight and they may produce fouling and smoke.

b. Ballistic modifiers are very sparingly used in gun propellants. Ammonium perchlorate, ammonium nitrate, RDX, and HMX are not used in gun propellant formulas (see Table 2.1).

c. Cryolite used in the U.S. Army propellants has always been sodium aluminum fluoride (Freedman 1986).

d. Aluminum is not used in gun propellants. It is used only in rocket propellants (Freedman 1986) and primer mix (Ko et al. 1985) (Kapeel and Lohner [illegible]).

TABLE 2.3. GUN PROPELLANT COMPOSITIONS[a] (wt %)

Component	M1	M2	M5	M6	M8	M9	M10	M14	M15	M16	M17	M26	M30	M31	NACO[b] type 1	IMR[c]
Nitrocellulose	85.0	77.5	82.0	87.0	52.2	57.8	98.0	90.0	20.0	55.5	22.0	67.5	28.0	20.0	93.6	100.0
(nitrogen, %)	(13.15)	(13.25)	(13.25)	(13.15)	(13.25)	(13.25)	(13.15)	(13.1)	(13..5)	(12.6)	(13.15)	(13.15)	(12.6)	(12.6)	(12.0)	(13.15)
Nitroglycerin		19.5	15.0		43.0	40.0			19.0	27.5	21.5	25.0	22.5	19.0	34.90	
Nitroguanidine									54.7		54.7		47.7	54.7		
Ethyl centralite		0.6	0.6		0.6	0.70			6.0	4.0	1.5	6.0	1.5			1.2
Diphenylamine	1.0[d]			1.0[d]			1.0	1.0[d]								0.7[d]
2 Nitrodiphenylamine														1.5		
Dinitrotoluene	10.0			10.0				8.0		10.5						8.0[e]
Dibutyl phthalate	5.0			3.0	3.0			2.0						4.5		
Potassium nitrate		0.7	0.7		1.2	1.50				0.5		0.75				
Barium nitrate		1.4	1.4									0.75				
Potassium sulfate	1.0[f]			1.0[d]			1.0								1.2	1.0[d]
Lead carbonate	1.0[f]														1.0[g]	
Cryolite								0.3			0.3		0.3	0.3		
Graphite		0.3	0.3			0.10[d]	0.10[d]				0.15[d]					
n-Butyl stearate															3.0	
Lead stearate										0.5						

a. All compositions are solvent extruded as grains except M8, which is solventless-rolled as sheet.

b. NACO Navy Cool Propellants.

c. IMR Improved Military Rifle (Pdr) (Brit).

d. On added basis.

e. Added as a coating.

f. If required, on added basis.

g. As basic lead carbonate.

Adapted from Lindner (1980) and Roth and Capener (1978).

TABLE 2.4. THERMOCHEMICAL, THERMODYNAMIC, AND PERFORMANCE CHARACTERISTICS OF NITROCELLULOSE GUN PROPELLANTS[a]

Characteristics	Designation												
	M1	M2	M5	M6	M8	M9	M10	M15	M17	M26	M30	M31	IMR[b]
Heat of explosion, J/g[c]	3140	4522	4354	3182	5192	5422	3936	3350	4019	4082	4082	3370	3601
Heat of formation, ΔH, J/g[c]	2261	2366	2407	2261	1989	1989	2533	1256	1361	2114	1549	1465	2366
Flame temperature, K, Tv	2435	3370	3290	2580	3760	3800	3040	2555	2975	3130	3090	2600	2835
Impetus, J/g[c]	911	1121	1091	956	1181	1142	1031	980	1088	1082	1090	1000	1007
Heat capacity, Cv, J/(gK)[c]	1.46	1.51	1.46	1.46	1.42	1.51	1.42	1.51	1.51	1.46	1.51	1.51	1.46
Mean heat capacity products, J/(moleK)[c]	1.84	1.76	1.76	1.80	1.76	1.72	1.80	1.88	1.80	1.80	1.80	1.88	1.80
Mean mol wt of products, g/mole	22.0	25.1	25.4	22.6	26.8	26.4	24.6	21.5	23.1	24.1	23.2	21.6	23.9
Specific heat ratio of gases	1.26	1.22	1.22	1.25	1.21	1.21	1.23	1.25	1.24	1.24	1.24	1.25	1.24
Gas volume, mole/g	0.045	0.040	0.040	0.044	0.038	0.038	0.041	0.046	0.043	0.042	0.042	0.044	0.042
Burning rate at 20°C, cm/s at 137.9 MPa[d]	7.6	12.7	14.0	8.4	17.8	23.0	11.4	10.2	14.0	11.4	12.2	7.9	
Pressure exponent	0.66	0.73		0.66	0.81	0.85	0.67	0.66	0.60	0.85	0.70	0.65	
Compositions of combustion products, mole/g x 10^2													
CO	2.33	1.54	1.61	2.24	1.28	1.13	1.81	1.45	1.15	1.89			1.79
CO_2	0.19	0.51	0.48	0.22	0.66	0.74	0.40	0.14	0.25	0.33			0.32
H_2	0.88	0.31	0.34	0.78	0.19	0.15	0.44	0.92	0.57	0.52			0.55
H_2O	0.64	1.10	1.08	0.72	0.11	0.09	0.99	0.83	1.07	0.95			0.90
N_2	0.44	0.49	0.48	0.45	0.54	0.54	0.46	1.29	1.30	0.50			0.46

a. At loading density of 0.2 g/cm³.

b. IMR - Improved Military Rifle.

c. To convert J to cal, divide by 4.184.

d. To convert MPa to psi, multiply by 145.

Adapted from Lindner (1980).

TABLE 2.5. CHARACTERISTICS OF BLACK POWDER

Characteristics	Value
Flame temperature, K (isochoric)	ca 2800
Moles of gas per gram	0.0128-0.0159
Heat of explosion (H_2O, liq), J/g[a]	3015-3140
Impetus, J/g[a]	239-284
Burning rate, cm/s at 6.9 MPa[b]	ca 1 to 1.5
Temperature coefficient of pressure, %/°C	0.4
Pressure exponent	0.25-0.5
Ignition temperature, °C	450
Activation energy, kJ/mole[a]	(87.9)

a. To convert J to cal, divide by 4.184.
b. To convert MPa to psi, multiply by 145.

Adapted from Lindner (1980).

TABLE 2.6. APPROXIMATE COMPOSITION OF REACTION PRODUCTS OF BLACK POWDER

Component	Wt %
Gases	
Carbon dioxide	49
Carbon monoxide	12
Nitrogen	33
Hydrogen sulfide	2.5
Methane	0.5
Water	1
Hydrogen	2
Total	44
Solids	
Potassium carbonate	61
Potassium sulfate	15
Potassium sulfide	14.3
Potassium thiocyanate	0.2
Potassium nitrate	0.3
Ammonium carbonate	0.1
Sulfur	9
Carbon	0.1
Total	56

Adapted from Lindner (1980).

TABLE 2.7. APPROXIMATE COMPOSITION AND PROPERTIES OF TYPICAL NITROCELLULOSE-BASE CAST PROPELLANTS USED IN ROCKETS

	Type		
	Low energy	High energy	
	A	B	C
Composition, wt %			
Nitrocellulose (12.6%N)	59.0	20.0	22.0
Nitroglycerin	24.0	30.0	30.0
Triacetin	9.0	6.0	5.0
Dioctyl phthalate (Di-2-ethylhexyl phthalate)	3.0		
Aluminum		20.0	21.0
HMX		11.0	
Stabilizer	2.0	2.0	2.0
Ammonium perchlorate		11.0	20.0
Lead stearate	3.0		
Ballistic properties			
Specific impulse, N·s/kg[a]	2062	2651	2602
Burning rate at 6.9 MPa[b] at 20°C, cm/s	0.65	1.40	2.00
Pressure exponent		0.45	0.40
Pressure coefficient		0.025	0.04
Thermochemical-thermodynamic properties			
Heat of explosion (J/g)[c]	2931	7718	7432
Heat of formation, - ΔH J/g[c]		1570	1842
Flame temperature, K	1925	3850	3900
Mean heat capacity, (J/g·K)[c]			
Products	1.80	1.76	1.76
Gases	1.80	1.26	1.21
Mean molecular weight, g/mole			
Products	21.8	27.9	28.9
Gases	21.8	30.9	21.0
Specific heat ratio, gas	1.27	1.18	1.17
Combustion products composition, mole/100 g[d]			
C	2.12		
CO_2	0.31	0.05	0.07
CO	2.12	1.30	1.15
H_2	1.06	0.75	0.66
H_2O	0.66	0.27	0.33
N_2	0.43	0.49	0.38
Pb	0.004		
Al_2O_3		0.35	0.37
H		0.20	0.23
OH		0.05	
Other		0.15	
HCl			0.10

a. To convert from N·s/kg to lbf/lb, divide by 9.82.

b. To convert MPa to psi, multiply by 145.

c. To convert J to cal, divide by 4.184.

d. Major products only.

Adapted from Lindner (1980).

2.1.3 Mechanism of Combustion of Propellant in Gun Systems

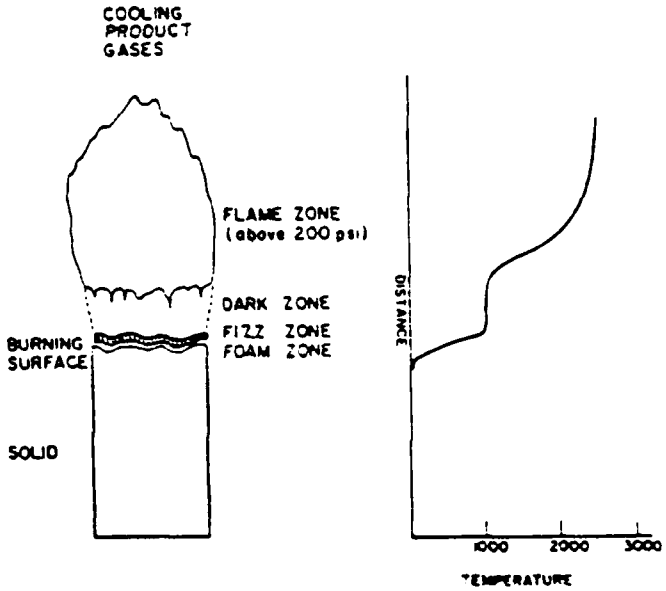
According to Piobert's law of combustion, when a solid grain of a propellant is ignited in air, each surface burns independently and progressively in parallel layers and at the same rate. The law is valid only for nonporous powders that deflagrate but do not explode. Hence it does not apply to porous black powder, nongelatinized compressed nitrocellulose, etc. (Kaye 1978). The law also fails in the case of perforated grains depending on the length and diameter of the perforation, because a stream of hot gases passing through the channels causes the channel surface to burn faster than the external surface of the same grain. This effect is known as erosive burning (Fedoroff and Sheffield 1962a). However, according to Stiefel (1985) the law does work if the burning surface area of the pores is taken into account. In perforated stick propellant where the grains are very long, the gas produced in the perforations is restricted from moving out, resulting in pressure build-up and rise in the velocity of the exit gas leading to erosive burning. The problem is solved by using a slotted stick where a thin slot runs along the stick leading to the perforations, thereby permitting the escape of the gases through the slots. Most multiperforated gun propellant granulations have been found to burn quite normally when tested using an interrupted bomb technique (Mitchell 1986).

The complex interacting physical and chemical processes that occur during the ignition and combustion phase of the interior ballistics cycle of a gun are not completely understood. The ignition phase is still a subject of active research (Irish 1985). Various flame zones, temperature profile, and probable species distribution for nitrate ester propellants at low pressure are shown in Figure 2.3 (Fifer 1984). At high pressures, the zones are greatly compressed and thus are not visible. The processes indicated, however, occur nevertheless (Stiefel 1985).

The linear rate of burning of a propellant is defined as the rate r (in mm/s, cm/s, or ins/s), at which the burning surface of the propellant recedes and the mass burning rate, m (in lbs/s, g/s), equals $r \cdot \rho \cdot A$, where ρ = density of propellant and A = burning surface area. There are several physicochemical factors that can influence the mass rate of burning--size, shape, and web thickness of grains, porosity and surface treatment of propellants, pressure of confinement, and composition of propellant (Fedoroff and Sheffield 1962a). The effect of grain geometry is discussed below. For single perforated grains, the web thickness is equal to half the difference between the outside diameter and the diameter of the perforation; the larger the web thickness, the slower is the propellant. Porous grains are faster burning than nonporous grains. The higher the pressure of confinement, the higher is the rate of burning, and the higher the nitrogen content of nitrocellulose, the higher is the rate of burning of nitrocellulose based propellants.

Control of the total burning surface can be achieved by establishing the number of grains to be used, their geometrical configuration, and in the case of rocket propellants, the cementing of

NITRATE ESTER AND NITRAMINE PROPELLANTS



Subsurface Reaction		Fizz-Zone Reaction		Flame Zone Reaction	
$RO\text{-}NO_2$	⟶	$R'CHO + NO_2$ etc.	⟶	$NO + HCHO + CO + CO_2$ $H_2O + H_2$ etc.	⟶	$N_2 + CO + CO_2$ $+ H_2O + H_2$ etc.
		Surface Products		Fizz Dark Zone Products		Flame Zone Products

Figure 2.3. Reaction zone structure, temperature profile, and probable species distribution for nitrate ester propellant. Adapted from Fifer (1984).

noncombustible inhibitors on grain surfaces to prevent their burning and bonding the exterior surfaces to the motor wall. The effect of grain geometry on burning surface area is shown in Figure 2.4. (Lindner 1980).

The relationship between pressure, distance traveled by the projectile, and velocity of the projectile is shown in Figure 2.5 (Ryan 1982). On firing, the burning charge produces gases at a very high pressure to propel the projectile through the barrel until it leaves the muzzle at a predetermined muzzle velocity. Initially the rate of burning increases very fast, causing a rapid rise in pressure until the gas reaches "shot start pressure," at which point the projectile starts to move forward. For spin stabilized projectiles, a major cause of the shot start pressure is the resistance to motion during engraving of the projectile rotating band. Pressure quickly reaches its maximum value and then starts to fall as more space becomes available owing to projectile movement along the barrel. The projectile continues to accelerate even after the gases are all burnt. However, the rate of acceleration decreases until retardation occurs just outside the muzzle due to air drag. About 25 to 35 percent of the energy produced by the charge is consumed during the projectile's travel in the bore of the gun. The remainder is dissipated into the atmosphere after the projectile leaves the muzzle. The "all burnt" position is usually located well inside the barrel. If it is too far forward in the barrel, the likelihood of a muzzle flash increases. If it is outside the barrel, there is, in addition to wastege of propellant, a danger that the breech may be opened before all the propellant has been consumed.

The combustion of gun propellants, particularly measurement of linear burning rate vs pressure, is studied in closed bombs. Traditionally, measurement of linear burning rates have been made with bombs loaded to a density of 0.2 g/mL and producing pressures of about 30 kpsi (Stiefel 1985). This loading density is still used for testing of existing common propellants, but loadings that produce pressures of 100 kpsi or even higher are frequently used with new propellant formulations. (Mitchell 1986).

As pointed out by Fedoroff and Sheffield (1962a), the conditions of burning propellants in a closed bomb and a gun are not the same. In the closed system the gas generated flows along the normal to the burning propellant surface if the charge is not concentrated near one end of the vessel; the gas velocities parallel to the burning surface are negligible. In a gun, movement of the gas stream from the breech to the muzzle takes place with a relative velocity of hundreds of feet per second. In essence, the propellant burning in a gun initially resembles that in a closed bomb and then shows a rate of burning greater than that found in a closed vessel at the same pressure. It would be difficult to use closed chamber data on the relative amounts of trace gases to predict the amounts of those same gases to be expected from gun firings (Freedman 1986).

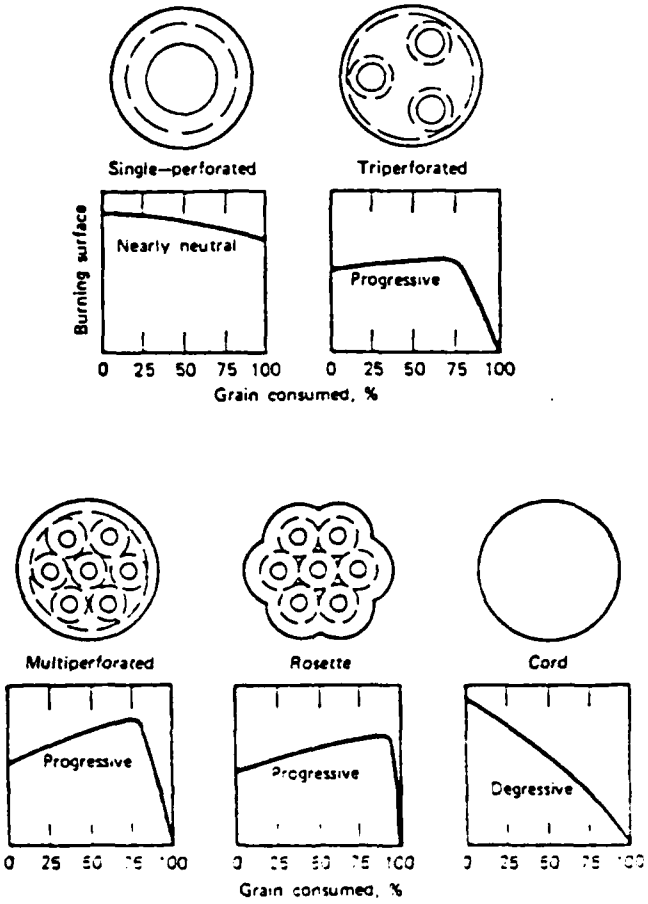


Figure 2.4. Effect of grain shape on surface exposed during burning of gun propellants.
Adapted from Lindner (1980).

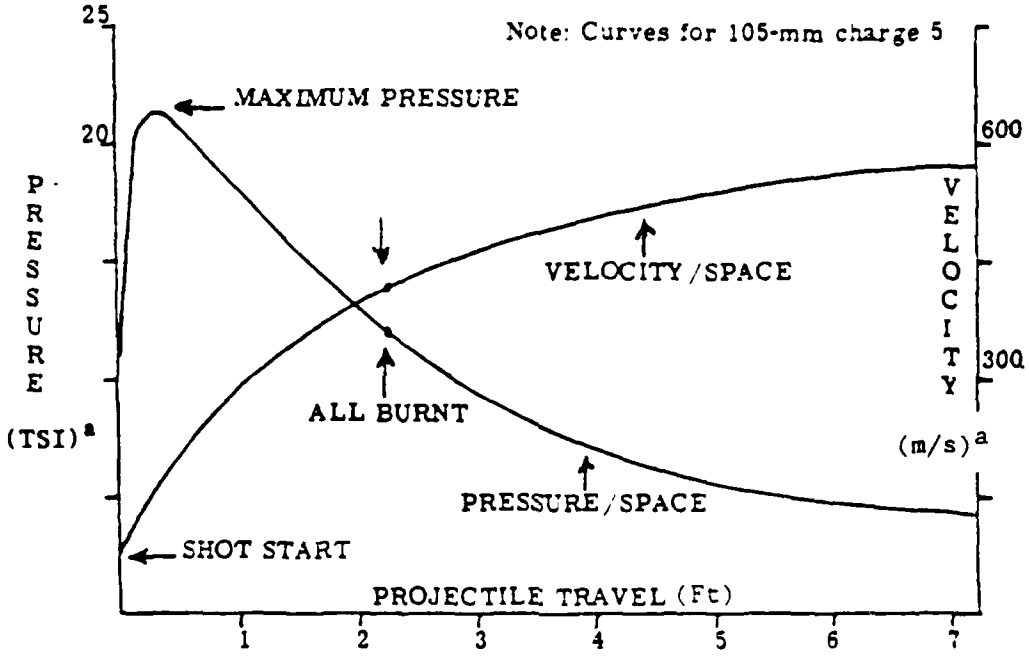


Figure 2.3. Pressure/velocity/space curve.

[a]TSI - tons per square inch.
m/s - meters per second.

2.1.4 Physical and Chemical Parameters Affecting the Composition of the Exhaust Emission from Guns

The composition of the exhaust emission from guns depends on many factors--composition of the propellant, igniter, primer, temperature and pressure in the barrel, and erosion of the gun barrel and combustion chamber.

According to Urbanski (1983) the products of decomposition of propellants resemble the products of decomposition of their individual constituents taken separately. The chief products of decomposition of explosives are combustible gases CO and H_2 and noncombustible gases CO_2, H_2O, and N_2; these constitute about 99 percent by volume of the exhaust. The amount of CO_2 and H_2O formed from nitroglycerin is higher than the amount formed from nitrocellulose due to the more favorable oxygen balance in the former. The primary minor constituents are CH_4 and NH_3. There are numerous very minor constituents occurring at far below 0.1 percent by volume (Section 2.1.5).

Generally speaking, the pressure in the powder chamber and in the bore of the gun profoundly affects the composition of the decomposition products of smokeless powder. Pressure is mainly dependent on the density of loading. The amounts of CO_2 and CH_4 increase and those of CO and H_2 decrease as the loading density increases (see Table 2.8) according to the following:

$$CO + 3H_2 \rightarrow CH_4 + H_2O + 57.8 \text{ kcal} \qquad (1)$$

Decomposition products of a given powder differ at different distances from the muzzle since the temperature and pressure decrease considerably with the movement of the projectile along the bore (Urbanski 1983). The equilibrium shifts when the gas expands and cools as the projectile moves down the barrel. At some point in the expansion, the equilibrium freezes, however, and the composition then remains essentially constant. One of the uncertainties in predicting the gas composition via computer is the pressure at which the equilibrium freezes (Stiefel 1985). Temperature and pressure changes along the length of the barrel have been reported for the German M/38 rifle (Table 2.9).

In addition to reaction (1), the following reactions also take place:

$$2CO_2 \rightarrow 2CO + O_2 - 135.2 \text{ kcal} \qquad (2)$$
$$2H_2O \rightarrow 2H_2 + O_2 - 115.6 \text{ kcal} \qquad (3)$$

In reactions (2) and (3), a rise in temperature favors the shift of the equilibrium to the right and a rise in pressure favors the shift in the other direction (Urbanski 1983).

According to Urbanski (1983) pressure affects the system more than temperature, so the content of CO_2 in the combustion products grows and that of CO falls as the projectile moves towards the muzzle. Apparently reaction (2) is not the only reaction that determines the concentration of CO_2 in the barrel. The view that pressure affects the system more than temperature is contradicted by Freedman (1986).

TABLE 2.8. AMOUNTS OF DECOMPOSITION PRODUCTS OF POWDER IN RELATION TO DENSITY OF LOADING (Δ)

Δ	Pressure (kg/cm^2)	CO_2	CO	CH_4	H_2	N_2	H_2O
0.1	730	9.6	44.8	0.7	20.7	10.3	13.9
0.3	3,200	16.4	38.4	5.5	13.2	13.3	13.2

Adapted from Urbanski (1983).

TABLE 2.9. VARIATION OF TEMPERATURE AND PRESSURE ALONG THE LENGTH OF THE BARREL OF THE GERMAN M/88 RIFLE

Travel of the base of the projectile (mm)	Temperature of gases (°C)	Pressure (kg/cm^2)
200	1,426	1,385
300	1,202	834
400	1,060	577
500	965	434
600	877	339
693 (muzzle)	818	280

Adapted from Urbanski (1983).

There is another noteworthy reaction taking place inside the bore (Urbanski 1983):

$$CO + H_2O \rightarrow CO_2 + H_2 + 9.83 \text{ kcal} \qquad (4)$$

A rise in temperature shifts the equilibrium of this exothermic reaction to the left.

The nitrogen present in the form of nitro groups in the ingredients of the propellant is mostly converted into molecular N_2 in the final combustion products. However, traces of NO_x may be formed. Ammonia formed by the following exothermic reaction has been detected in gun exhaust (Urbanski 1983):

$$N_2 + 3H_2 \rightarrow 2NH_3 + 22.0 \text{ kcal}$$

This reaction is catalyzed by iron particles in the exhaust.

The heat of explosion and consequently the temperature reached depend on the composition of the propellant. The higher the nitrogen content of nitrocellulose, the higher is the heat of explosion (Urbanski 1983a), and the higher the nitroglycerin content of the propellant, the higher is the heat of explosion (Table 2.10) (Urbanski 1983).

Potassium nitrate or potassium sulfate is often incorporated in propellant formulations (see Table 2.3). Potassium has been shown to be very efficient in suppressing secondary flame (Urbanski 1983). A report by Klingenberg and Heimerl (1982) on the effect of flash suppressants shows that the active species is KOH, which is formed by chemical reaction in the gas phase from the corresponding nitrate or sulfate. It is hypothesized that the mechanism of flash suppression is free radical scavenging by the hydroxyl radical.

Hydrogen, oxygen, and carbon monoxide (present in the exhaust) can enter into following chain reactions at high temperatures, giving rise to free radicals (Urbanski 1983):

$$H_2 + O_2 \rightarrow 2OH$$
$$OH + H_2 \rightarrow H_2O + H$$
$$H + O_2 \rightarrow OH + O$$
$$O + H_2 \rightarrow OH + H$$
$$CO + OH \rightarrow CO_2 + H$$

Examination of the course of gaseous explosive reactions by kinetic absorption spectroscopy indicates that potassium ions promote the following chain-breaking reactions to reduce the concentration of free radicals, thereby causing suppression of the secondary flame:

$$H + H \rightarrow H_2$$
$$H + OH \rightarrow H_2O$$
$$O + O \rightarrow O_2$$
$$CO + O \rightarrow CO_2$$

TABLE 2.10. HEAT OF EXPLOSION OF PROPELLANTS AND VOLUME OF GASES EVOLVED

Composition of propellants (%)	1	2	3	4	5	6
Nitroglycerin	30	36	40	47	58	-
Nitrocellulose	65	52	50	53	37	100
Other nonexplosive ingredients (centralite, petroleum, etc.)	5	12	10	-	5	-
Volume of gases, V_0 (l./kg)	913	910	900	810	875	934
Heat of explosion (kcal/kg)	1,030	935	1,005	1,090	1,250	924
Temperature, t (°C)	2,470	-	-	2,850	2,825	2,230

Adapted from Urbanski (1983).

Erosion of the gun barrel and chamber contributes to the gun exhaust in the form of particulates (smoke) that, in part, come from the barrel material due to erosion, from the gilding metal jacket on small-caliber projectiles, and from the rotating band on larger-caliber projectiles. Erosion may be thermal, chemical, or mechanical. Nitroglycerin in propellants causes more thermal erosion than nitrocellulose because the former generates a higher flame temperature. This can be countered by incorporating inert materials (e.g., petrolatum, centralite) or an active substance of a lower heat of explosion (e.g., nitroguanidine). Another type of thermal erosion is known as gas wash erosion. In the initial phase of firing, the cartridge case expands and seals the breech. On ignition of the charge, the projectile leaves the cartridge and moves into the barrel where, via engraving of the rotating band or of the bullet jacket, it comes to fit tightly in the rifling of the barrel. Before the projectile is fully seated and engraved, gun gas may flow past the projectile causing increased heat transfer and high surface temperatures. This may cause melting and wipe-off of the steel at the barrel surface near the origin of rifling, as shown in Figure 2.6 (Smith and Haslam 1982).

According to Urbanski (1983), chemical erosion in the barrel can be a problem and is caused by decarburization of steel at high temperature according to the reaction:

$$CO_2 + C \rightarrow 2CO$$

The decarburization increases the porosity of the metal. The absorption of gases in the pores under high temperature and pressure followed by expansion will blow up the pores causing severe corrosion (Urbanski 1983). However, gun barrel erosion due to decarburization is now discounted according to Freedman (1986).

2.1.5 Minor Constituents of Gun Exhaust Emission

There are very few documents which examine the minor (<1 percent by volume) constituents of gun exhaust in depth. Tompa (1985) reported the formation of other toxic gases (HF, HCl, H_2S, HCN, NO, Pb, SO_2, COS, CH_2O, and NH_3) besides CO in the combustion products of three propellants and three LOVA (low vulnerability ammunition) compositions. Small amounts of CH_4, C_2H_2, and C_2H_6 were also formed.

Results of recent studies on the combustion products formed on firing an M16 rifle and 105-mm gun have become available (Snelson et al. 1983, Ase et al. 1985). A large number of chemical species were found: 90 and 70, from the M16 rifle and 105-mm gun exhausts respectively. As many as 11 polynuclear hydrocarbons including benzo[a]pyrene have been identified. It is not known if these polynuclear hydrocarbons arise from the aromatic components in the propellant or are formed by condensation and cyclization of simple molecules. Most of the polynuclear hydrocarbons are attached to the particulates (Ase et al. 1985).

Five metals have been found in significant quantities in the inhalable metal particulate fraction from the M16 rifle study (Ase et

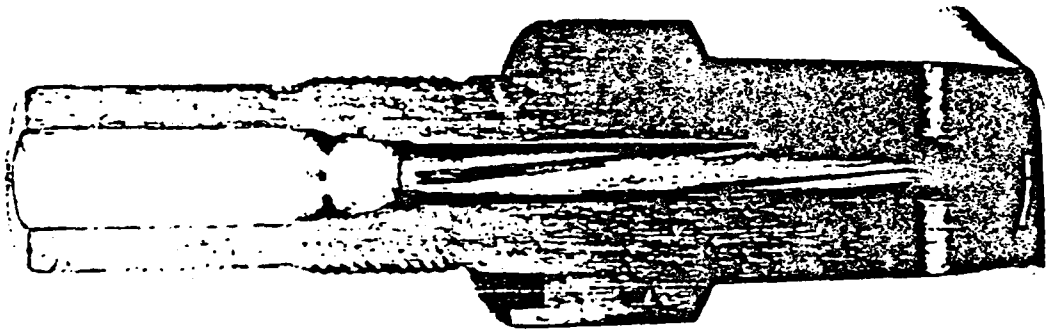


Figure 2.6. Wear inside a machine gun barrel.
Adapted from Smith and Haslam (1982).

al. 1985). These are Pb, Sb, Ba, Cu, and Zn. Lead constitutes about half of the total amount of inhalable (<10 μ) metal particulates; Cu constitutes about one-third and Sb, Ba, and Zn together constitute about one-twentieth. It has been speculated that most of this Pb probably comes from the copper-coated lead slug used in the rifle. It is worthwhile to mention here that large-caliber artillery weapons use lead foil as a "decoppering agent" to remove copper residues left by the projectile rotating bands on the gun bore. As much as 290 g of lead foil are used in some 8-in. howitzer propelling charges; smaller amounts are used in some 155-mm and 105-mm propeller charges. This foil is the major source of lead fumes from artillery weapons (Herud 1985). Copper and zinc are present in the brass bullet case. Lead, barium, and antimony are present in the primer. This topic is addressed in more detail in Section 2.2.

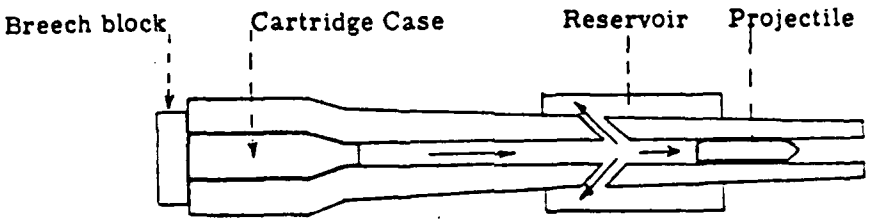
2.1.6 Existing Methods for Protecting Gun Crews Against Exposure to Gun Exhaust Fumes

Two systems have been reported in the literature for protection of gun crews in closed vehicles or aircraft against exposure to fumes--the bore evacuator or fume extractor, and the ventilator system.

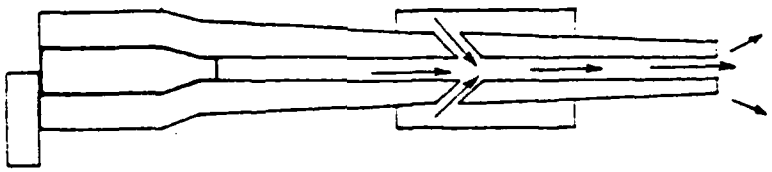
According to Ryan (1982), bore evacuators are cylinders fitted to a segment of the barrel to form an additional reservoir for the gun exhaust. Ports or nozzles are drilled in the barrel and are inclined towards the muzzle. The gas flow to the reservoir stops when the pressure in the reservoir equals the pressure in the barrel. The operation of the bore evacuators is shown schematically in Figure 2.7.

A closed breech scavenger system, M81, was developed in the late 1960s to overcome the shortcomings of the previously used bore scavenger system in dealing with the problems of toxic fumes, burning residues, or flareback conditions resulting from incomplete combustion of the combustible case ammunitions or missile (Swank 1969; Daffron Jr. 1968; Musick 1969). The closed breech scavenger system utilizes an inert gas at 3,000 psi to flush out the exhaust and residual material from the gun tube and chamber. The carbon monoxide concentration at each of the crew positions (commander, gunner, driver, and loader) was monitored by a Model 200 or 300 Lira analyzer. It was concluded that the M81 closed breech scavenger system along with the ventilation system will eliminate hazardous levels of toxic gas and smoke and will eliminate or significantly reduce the possibility of a flareback condition (Swank 1969).

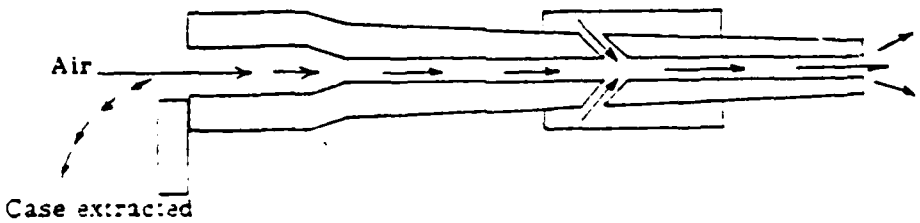
The promises of the closed breech scavanger system (Swank 1969; Daffron Jr. 1968; Musick 1969) were apparently not realized in practice and the principal protection of the gun crew in a confined space, such as an armored vehicle, continues to be the ventilation system. There are many types, ranging from those that exhaust the entire crew compartment to those that exhaust the breech of individual weapons.



1. Gas drawn into reservoir as projectile passes.



2. Projectile ejected from muzzle and gas drawn from reservoir and expelled from muzzle.



3. Breech opened cartridge case ejected (if used). Air drawn into bore through breech and expelled from muzzle. Reservoir purged of gas.

Figure 2.7. Operation of a bore evacuator. Adapted from Ryan (1982).

2.2 PROPELLANT EXHAUST PRODUCTS UNDER AMBIENT CONDITIONS AND FROM COMBUSTION CHAMBERS AND OTHER DEVICES

The major gaseous constituents identified in gun and rifle exhaust are discussed from a general standpoint in Section 2.1. This portion of the report focuses on specific studies that have examined exhaust products from a more detailed chemical or toxicological perspective. Since combustion conditions influence product formation, the methods used to generate and analyze the various constituents are described. The propellant formulations are also given if available.

The studies that are most relevant in terms of evaluating or identifying potential toxic hazards to personnel exposed to gun exhausts are those that examine the composition under actual exposure conditions. Analysis of ambient air in indoor rifle ranges falls in this category and has been reviewed. Since it may be experimentally difficult to examine exhaust products under all exposure conditions (especially in the case of large-caliber weapons) some investigators have devised combustion chambers to generate and collect the combustion products for subsequent analysis. Confinement chambers also serve to concentrate the samples, which facilitates the determination of trace constituents. These studies are classified according to the conditions used for smoke collection (i.e., atmospheric versus other environmental regimes). Included in this discussion are a few reports on the characterization of rocket exhausts. They have been added because they provide information on methodology used for a complete chemical description or define some problems encountered in analysis that may also pertain to gun propellant exhaust. A final section of this chapter (2.2.5) deals with reports that have examined reactive intermediate species or methods of determining these species.

2.2.1 Analysis of Ambient Air in Indoor Firing Ranges

Various industrial hygiene studies have been conducted at firing ranges and indoor rifle ranges to determine personnel exposure levels to ammunition combustion products during shooting exercises. In these studies, samples are generally collected by drawing ambient air, with the aid of personal sampling pumps, through adsorption tubes or across filters that extract and retain particulates or vaporized organics. Carbon monoxide and nitric oxide levels have been monitored with direct-reading analyzers that indicate ambient levels. Low-molecular-weight organics that are not retained on adsorbent cartridges have been collected in evacuated cylinders, although this method does not provide data on exposure levels over an extended time period. Both general area and breathing zone samples can be obtained; the latter are more related to inhalation levels. Exposures are, of course, dependent on local exhaust ventilation and firing activity.

Several of the studies have been conducted by the National Institute for Occupational Safety and Health (NIOSH) and have examined inorganic lead exposures. The primary source of lead and other metals in ambient air in indoor ranges arises from vaporization of the bullet cases and bullets. A comparison of lead emissions from lead vs zinc

bullet ammunition (Lee 1982) at one indoor range showed that lead concentrations can be reduced by at least a factor of 40 with the use of zinc bullets. The range where the study was conducted was 75 ft long, 19 ft wide, and 8 ft high. The ventilation system supplied 7000 cubic feet of air per minute (cfm) and exhausted 520 cfm. Air flow at the firing line was reported to be turbulent and erratic with velocities ranging from 20 to 400 cfm. Breathing zone (BZ) samples were collected from guards during qualification exercises where 30 rounds of 100-grain zinc wadcutter ammunition were fired in 5 to 10 min. Results for both lead and zinc determinations are shown in Table 2.11. The low concentrations for lead contrast to the time-weighted average (TWA) values (average 160 $\mu g/m^3$) when lead target bullets have been used at the same range under similar conditions. Current Occupational Safety and Health Administration (OSHA) environmental standards for lead and zinc oxide (8-hr TWA) are 50 and 5,000 $\mu g/m^3$, respectively.

Wadcutter ammunition has been reported to produce lead exposures greater than OSHA standards while copper-jacketed controlled-expansion bullets (CEBs) result in exposures significantly less than OSHA standards (Kronoveter 1983). The indoor range where this study was conducted was approximately 15 ft wide, 9 ft high, and 12 ft in length. A ventilation survey showed that 6,000 cfm of air was supplied and 6,700 cfm was exhausted from the range. Results from personal air samples (shown in Table 2.12) indicate that lead levels decreased as the ammunition was changed to the controlled expansion bullets. An examination of four different weapon types also showed that a 0.38 caliber revolver produced the greatest concentration of airborne lead (1.66 mg/m^3) and a 0.22 caliber rifle produced the least (0.20 mg/m^3) (Gill and Madill 1981). The range surveyed was 80 ft long, 16 ft wide, and 12 ft high. The air intake and exhaust were 908 and 943 cfm, respectively. Firing conditions, ammunition, and weapons used over the 5-day test survey are described in Table 2.13. Air samples were collected from fixed locations on the range and from the breathing zone of individual shooters. The results show a significant increase in lead emissions for the 0.38 special. The increased firing rate and the difference in bullet weights contribute to the difference in lead emissions from this weapon compared with either of the 0.22 caliber weapons. Compared with the 9-mm pistol however, where the firing rates are the same and there is only a 21 percent reduction in bullet weight, a 2.5 times greater lead emission was still found for the 0.38 caliber weapon. This difference was attributed to basic weapon design. Samples were also collected and analyzed for CO and NO_2 in this study. The results indicated that concentrations did not exceed the occupational exposure limit. The NO_2 concentrations were also below the detection limit of the method used for analysis (i.e., 1 ppm on Draeger tubes).

The combustion products generated during tracer firing in an indoor range have been characterized in detail (USAEHA 1984). Compounds found in significant concentrations [i.e., at least 1/2 of the OSHA permissible exposure level (PEL) or threshold limiting value] were carbon monoxide, copper, lead, particulates, and formaldehyde. Copper was the only species found in concentrations exceeding the PEL. Other constituents determined but found in low concentrations include NO, NO_2, SO_2, various elemental species, acetaldehyde, aromatic and aliphatic hydrocarbons.

TABLE 2.11. SAMPLING RESULTS FOR INORGANIC LEAD AND ZINC

Location	Sample Type	Sampling Time	Lead Concentration in $\mu g/m^3$ (& 8-hr TWA)	Zinc Concentration in $\mu g/m^3$ (& 8-hr TWA)
Booth 2	Guard BZ[a]	10:01-10:10 am	N.D.[b]	300 (6)
Booth 4	Guard BZ	10:13-10:21 am	N.D.	200 (3)
Booth 2	Guard BZ	10:20-10:30 am	N.D.	1500 (10)
Booth 4	Guard BZ	10:30-10:30 am	N.D.	200 (4)
Booth 2	Guard BZ	10:40-10:45 am	400 (4)	1500 (2)
Booth 4	Guard BZ	10:40-10:45 am	N.D.	300 (3)
Booth 2	Area Sample	10:50-11:00 am	N.D.	100
Booth 4	Area Sample	10:50-11:00 am	N.D.	5
Desk	Rangemaster BZ	10:20-10:50 am	50 (3)	200 (10)
OSHA Standard (8-hour TWA)			50	5000

a. BZ = Personal breathing zone sample.
b. N.D. = nondetectable (about 200 $\mu g/m^3$ for a 10-min sample).

Adapted from Lee (1982).

TABLE 2.12. PERSONAL AIR SAMPLE RESULTS FOR LEAD

Sample Time	Sample Description	Ammunition Type	Air Concentrations of Lead ($\mu g/m^3$) Actual	8-hr TWA[a]
0847-1048	Range Master		790	
1117-1214	Range Master		210	220
0847-0910	Shooter 1: Booth 1	Wadcutters[b] & CEBs[c]	1,600	
0918-0933	Shooter 1: Booth 2	Wadcutters	2,100	140
0847-0910	Shooter 2: Booth 2	Wadcutters & CEBs	830	
0918-0933	Shooter 2: Booth 1	Wadcutters	2,100	
1006-1019	Shooter 2: Booth 1	CEBs	650	
1037-1048	Shooter 2: Booth 2	CEBs	270	130
1006-1020	Shooter 3: Booth 2	CEBs	540	
1037-1047	Shooter 3: Booth 1	CEBs	450	25
1116-1134	Shooter 4: Booth 1	CEBs	280	11
1116-1133	Shooter 5: Booth 1	CEBs	320	11
1155-1215	Shooter 6: Booth 2	CEBs	180	8
1155-1215	Shooter 7: Booth 1	CEBs	280	12
OSHA Standard				50

a. Calculated 8-hr time weighted average exposures (assumes zero exposures when outside of the shooting range).
b. Wadcutter bullets - 38 Special, 148 grain.
c. Controlled Expansion Bullets - 38 Special, 110 grain, jacketed hollow point.

Note: Each shooter used 60 rounds of ammunition for each qualification attempt. The revolvers used were Smith & Wesson, Model 15, 6-in. barrel J. Series, 38 Specials.

Adapted from Kronoveter (1983).

TABLE 2.13. DESCRIPTION OF WEAPONS, AMMUNITION, AND FIRING CONDITIONS FOR AN INDOOR RANGE STUDY

Weapons

0.22 Rifle	Canadian Military Bolt Action, Single Shot Rifle, 0.22 Caliber, Barrel length - Approximately 23 in.
0.22 Revolver	Colt Police Positive Revolver, 0.22 Caliber, Barrel Length - 6 in.
0.38 Special	Smith and Wesson Revolver, 0.38 Special Caliber, Barrel Length - 3 in..
9-mm Pistol	Browning High Power, Caliber 9-mm (Parabellum), Barrel Length - 4 5/8 in.

Ammunition

0.22 Long Rifle	Bullet Weight - 40 grains lead
0.38 Special	Bullet Weight - 158 grains Metal Point
9-mm (Parabellum)	Bullet Weight - 125 grains Miltary Ball

Rate of firing and weight of bullets expended

	Rounds/hr	Total Rounds	Total Weight of Rounds g
0.22 Revolver	120	480	1,152
0.22 Rifle	120	480	1,152
9-mm Pistol	160	640	4,800
0.38 Special	160	640	6,067

Adapted from Gill and Madill (1981)

benzonitrile, oxygenated compounds, and chlorinated hydrocarbons. Specific details regarding the analytical procedures used to identify or quantitate these species were not given. Exhaust ventilation was available at the weapons but was not studied in depth. To provide maximum protection of workers to the combustion products, a ventilation system that removes and prevents re-entry of contaminated air and provides clean make-up air was recommended.

From these studies conducted in indoor ranges it is apparent that the concentrations of various chemical species are dependent upon many factors including the type of ammunition fired (e.g., Pb- vs. Zn- vs. Cu-coated expansion bullets), the type of weapon or weapon design, the overall firing activity or number of rounds fired per unit time, and the ventilation available at the firing line. Differences in these factors make it difficult to compare the individual studies. In at least one case the ventilation rate was not even reported (USAEHA 1984). Samples from the studies were also often analyzed for different compounds, although all examined lead concentrations. Overall, the results do indicate that significant levels of lead can be generated when lead bullets are used as ammunition. These levels can be reduced by using Zn- or Cu-jacketed expansion bullets. For other species that may be present (e.g., CO, Cu, particulate matter) there have been too few studies to determine whether they may pose a significant exposure problem.

2.2.2 Analysis of Ambient Air in Crew Compartments of Armed Vehicles

A limited number of reports are available on the analysis of emissions from the firing of weapons in actual crew compartments of armed vehicles. The data presented in these documents are varied, indicating in some cases high concentrations of toxic compounds and in others very low concentrations that would not pose any significant health risk. The studies do not provide a comprehensive examination of the compounds present. The conditions under which the analyses were conducted are also not well documented, making it difficult to compare results or derive conclusions concerning the hazards associated with exposure. Brief descriptions of the studies are given below.

Carbon monoxide levels have been measured in the cabins of the UH-1B and CH-47A helicopters during weapons firing (Hody and Shane 1966). The UH-1B was equipped with an XM-21 armament subsystem that contains a group of seven rocket tubes on each side of the aircraft and a General Electric 30-caliber minigun mounted above each rocket tube. The CH-47A Chinook was equipped with five interchangeable machine guns (7.62-mm or 50-caliber) mounted within the cabin (except for the barrels), an M-3 40-mm grenade launcher that is fired from the nose, and outboard mounts on each side of the aircraft containing a 20-mm cannon. Information on the chemical composition of the propellants was not given in the report. Carbon monoxide levels were determined with colorimetric indicating tubes and an MSA (mine safety appliance) carbon monoxide meter. Tests were conducted with cabin doors opened and closed. Samples were collected between the pilot and co-pilot seats and near the rear doors. The results on the UH-1B show that the highest concentrations are present immediately following firing of the rockets. A concentration of 500 ppm

was obtained after seven pairs of rockets had been fired but was cleared in approximately 90 sec with the cabin doors open. The machine guns were reported to produce less than 50 ppm of carbon monoxide. It should be noted that information on ventilation or the number of rounds fired and the rate of fire were not provided in the report. Results from the Chinook are given in Table 2.14. The authors conclude that significant contamination of the cabin atmosphere can result from the weapons systems.

The toxic hazard due to weapons firing in the UH-1B helicopter was reported by Hody (1969). Carbon monoxide levels were determined and metal particulates were sampled during actual flight testing where several thousand rounds of M-60 and minigun ammunition, 10 rounds of S-11/M-22 wire-guided missile, and 42 pairs of 2.75-in. folding fin aircraft rockets (FFARs) were fired. A continuous record of the carbon monoxide concentration in the aircraft was obtained with a specially constructed analyzer. Measurements were also made with colorimetric indicating tubes. Metal particulates were collected on filter discs for later analysis by atomic emission spectroscopy. Sampling probes were placed on the pilot's shoulder harness and on the flight suit of a rear-seat occupant. The maximum levels of carbon monoxide measured during firing of the machine guns and wire-guided missiles are given in Table 2.15 and the exposure associated with firing of the 2.75-in. rocket is shown in Table 2.16. Firings with the doors opened were generally found to yield higher concentrations of carbon monoxide, although for shorter time periods. It was also noted that changes in wind and flight directions would be expected to produce large variations in concentrations from test to test, as the gas may be swept eiether into or away from the cabin. Dose estimates for metal particulates (assuming a mean pulmonary air flow of 30 L/min) are given in Table 2.17. The overall results indicate that toxic levels of CO or metal particulates were not present during practical mission profiles. Since low concentrations of CO were detected, however, it was advised that crew members avoid exposure to other sources of toxic materials (e.g., tobacco smoke) since the effects could be additive.

Schumaker and Pollard (1977) measured the accumulation of toxic gases in the the crew compartment of the UH-60 helicopter resulting from the firing of two 7.62-mm machine guns under a variety of flight conditions. As representative examples of gases that could accumulate in the aircraft, carbon monoxide and nitrogen dioxide/nitric oxide were monitored continuously. An on-board mass spectrometer was used to analyze rapidly decaying toxic compounds. Samples were also collected for later analysis by a high resolution, high sensitivity mass spectrometer. The number of rounds fired, ventilation (on or off), and airspeed (40 to 100 knots) were varied. Information on the location of the sample collection devices or instrumentation in the aircraft was not provided in the report. Carbon monoxide levels were found to range from 0 to 20 ppm, with the highest concentration present at the lowest airspeed (40 knots). Nitric oxide and nitrogen dioxide were not detected. Mass spectrographic analysis on two separate grab samples collected at the lowest airspeed and with both guns at maximum firing rate provided the data shown in Table 2.18. Trace quantities of other compounds were

TABLE 2.14. CARBON MONOXIDE LEVELS IN THE CH-47A CHINOOK CABIN DURING WEAPONS FIRING

Weapon Tested	Sampling Location	Carbon Monoxide Concentration (ppm)	Approximate Duration of Contamination (seconds)
M5	Cockpit and near ammo bet	0	-
20 mm	Cockpit	0	-
	Right rear cabin	50-100	30-60
	Left rear cabin	0-50	30-60
50 cal in pairs (except tail ramp)	Cockpit Right rear cabin Left rear cabin Right front cabin Left front cabin	Maximum 40	Maximum 60
50-cal tail ramp alone	Extreme rear cabin	40	60
7.62 mm in pairs (except tail ramp)	Cockpit Right rear cabin Left rear cabin Right front cabin Left front cabin	Maximum 140	40
7.62-mm tail ramp alone (200 rounds)	Extreme rear cabin	1,000	60

Adapted from Hody and Shane (1966).

TABLE 2.15. CARBON MONOXIDE EXPOSURE DURING FIRING OF MACHINE GUNS AND WIRE-GUIDED MISSILES (MAXIMUM LEVELS MEASURED) IN UH-1B HELICOPTERS

Weapon Tested	Flight Condition	Door Condition	Maximum CO Concentration (ppm)	Maximum Exposure Time (min)	Product of Concentrations and Time (ppm/min)
M-60 Machine Gun (Quad)	Hover	Open	<50	<0.2	<10
M 60 Machine Gun (Quad)	Forward Flight	Open/Closed	No Detectable Levels (Less than 25 ppm at all times)		
Minigun (Dual)	Hover	Open	<50	<0.2	<10
Minigun (Dual)	Forward Flight	Open/Closed	No Detectable Levels (Less than 25 ppm at all times)		
Wire-Guided Missile	Hover and Forward Flight	Closed	<25	<0.2	<5

Adapted from Hody (1969)

TABLE 2.16. CARBON MONOXIDE EXPOSURE ASSOCIATED WITH FIRING OF THE 2.75-in. FOLDING FIN AIRCRAFT ROCKET (FFAR)

	Doors Open	Doors Closed	Units
Mean air concentration	25	50	ppm/pair[a]
Standard deviation of above	11	25	ppm/pair
Typical "dose" (concentration-time product)	5	5	ppm min/pair
Typical exposure after firing salvo of 48 pair	240	240	ppm min
48-pair exposure assuming worst concentration and longest exposure time	5,300	2,600	ppm min
Permissible exposure (If received within 1 min)	8,000		ppm min

a. Concentration related to the firing of a single rocket pair.

Adapted from Hody (1969).

TABLE 2.17. MINERAL AEROSOL INHALATION DURING VERY ACTIVE 1-DAY ARMED HELICOPTER MISSION

Metal	Dose (mg/day)
Lead	0.03
Copper	0.008
Magnesium	0.02
Aluminum	0.02
Silicon	0.03

A breathing rate of 30 L/min is assumed for man.

Adapted from Hody (1969).

TABLE 2.18. MASS SPECTROGRAPHIC ANALYSIS OF GASEOUS EMISSIONS FROM 7.62-mm MACHINE GUNS IN THE UH-60 HELICOPTER[a]

Gas	Sample 1 (ppm)	Sample 2 (ppm)	OSHA Standard Based on 8-Hr/Day, 40 Hr/Week, Weighted Exposure Level (ppm)[2]
NO	None detected	None detected	5
NO_2	None detected	None detected	5
SO_2	24	8.5	5
HCN	18	21.0	10
H_2S[b]	126	63.0	50

a. Accuracy is ± 25%.
b. OSHA standards only allow one 10-min exposure of 50 ppm H_2S in any 8-hr period as opposed to the other gases in the table, which are based on weighted averages.

Adapted from Schumaker and Pollard (1977).

detected but could not be positively identified. It should be noted that hydrogen sulfide was found to exceed the OSHA maximum ceiling for a 10-min exposure. Sulfur dioxide and hydrogen cyanide were also present in significant amounts, although for a one-time exposure they would not exceed the 8-hr TWA values.

Yamazaki et al. (1974) measured the quantities of noxious gases (CO, NO_x, and NH_3) produced in tank gun turrets from the firing of 90-mm antitank tracer projectiles used in Type 61 90-mm tank-mounted weapons. Three different propellant formulations were used: a conventional triple-base propellant, a propellant mixed with DL-α-alanine as an erosion control agent, and a propellant containing calcium pyroglutanate as an erosion control agent. Gas measurements were conducted with Draeger detection tubes. Samples were collected following the firing of five projectiles with each propellant and with the tank gun turret hatch closed with no ventilation and with forced ventilation. All three propellants were found to produce little or no noxious gases in the tank turret. Details regarding sample collection, location, and ventilation were not given in the report.

2.2.3 Exhaust Products Determined from Test Chambers at Atmospheric Conditions

One of the earliest reports to provide any information on weapons exhaust was that of Scharf et al. (1967), in which data from 7.62-mm and 0.5-in.-caliber machine guns were presented. These weapons are used in armed helicopters with semi-enclosed crew compartments. Combustion products generated from the firing of these weapons may therefore present a toxic hazard to the crew. The composition of the propellants and the charge weights for the weapons are given in Table 2.19. In this study a test stand was constructed to hold the weapons and accumulate the exhaust gases in a stainless steel cylinder through which the weapons were fired. All gas samples were obtained at atmospheric pressure. The contents of the cylinder were then sampled in evacuated containers or in a condensation train for analysis by infrared spectrometry (IR) and mass spectrometry (MS). The gases were also analyzed directly with a rapid scan infrared spectrometer equipped with a gas flow cell. Data for the various constituents were presented as partial pressures and as the ratio of component to carbon monoxide partial pressure. Compounds detected include CO, CO_2, CH_4, NH_3, HCN, cyanogen, acetaldehyde, carbonyl sulfide, benzene, acetylene, NO_2, Cu, and Pb.

The chemical composition of gases released from the firing of XM-1 rifles with XM-645 flechette rounds has been studied by Rocchio and May (1973). The composition of the XM-645 is given in Table 2.20 along with the composition of the primer. It differs from conventional rounds in that it contains a fiberglass sabot and rubber gas seal. To collect the exhaust gases the rifle was placed on a test stand with the muzzle held in a confinement cylinder (1.02-m x 0.1-m diameter). The far end of the cylinder was covered with a rubber membrane that would allow the flechettes to pass through but still maintain a gas seal. Samples were collected in evacuated cylinders and by drawing the gases from the confinement cylinder through a condensation train. Two sets of firings

TABLE 2.19. AMMUNITION AND PROPELLANT DATA

Weapon	7.62-mm machine gun	Caliber 0.50 machine gun	2.75-in. FFAR
Ammunition	Cartridge, 7.62 mm, NATO Ball:M80	Cartridge, Caliber .50, Ball:M33	
Propellant	WC 846	WC 860	N-5
Charge Weight	2.92 g	15.99 g	2.68 kg
	% Component		
	WC 846	WC 860	N-5
Nitrocellulose	82.61[a]	80.54[a]	49.7
% nitrogen	13.12	13.15	12.6
Nitroglycerin	9.86[a]	8.79[a]	35.2
Diphenylamine	0.97[a]	0.94[a]	
Dinitrotoluene	0.57[a]		
Graphite	0.2	0.2	
Moisture	0.62	1.13	
Volatiles	0.37	0.37	
Dibutylphthalate	5.07[a]	8.11[a]	
Diethylphthalate			10.5
2-nitrodiphenylamine			2.0
Wax			0.2
Sodium sulfate	0.07[a]	0.12[a]	
Calcium carbonate	0.62[a]	0.49[a]	
Potassium nitrate		0.73[a]	
Lead salicylate			1.3
Lead 2-ethylhexoate			1.1

a. Reported on a volatiles-free basis.

Adapted from Donaldson et al. (1967) as cited in Stiefel and Hody (1970).

Table 2.20. COMPOSITION OF XM-645 PROPELLANT[a]

Component	Wt %	% of total wt[b]
Nitrocellulose	85.0	82.6
Nitroglycerin	9.4	9.1
Diphenylamine	0.9	0.88
Dinitrotoluene	0.7	0.68
Dibutylphthalate	2.8	2.7
Potassium sulfate	0.5	0.48
Moisture & volatiles	0.7	0.68
Weight = 1.3 g		
Composition of Primer[a]		
Lead styphnate	37 ± 5	1.02
Tetrazene	4 ± 1	0.11
Barium nitrate	32 ± 5	0.89
Antimony sulfide	15 ± 2	0.41
Aluminum powder	7 ± 1	0.19
PETN	5 ± 1	0.14
Weight = 0.037 g		2.8
Total[b]	1.337 g	100%

a. Nominal composition.
b. Total weight of propellant and primer.

Adapted from Rocchio and May (1973).

(12 rounds each) were used to obtain samples. Analyses were conducted by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

The concentrations of constituents determined are given in Table 2.21. Other gases (NO, N_2O) were detected but could not be quantitated because of their low concentrations. Carbon monoxide was identified as the major exhaust component of toxicological importance due to its elevated concentration. Cyanogen and carbonyl sulfide (other toxic constituents) were found to be present at <0.1 percent of the CO concentration. It should be noted that analyses were restricted to uncondensed gaseous species. Higher-molecular-weight organics that may be present in the aerosol were not analyzed. In this study the combustion products determined experimentally were also compared with products predicted from equilibrium thermodynamic calculations. Values for CO_2, COS, and CH_4 concentrations were found to agree with theory, while calculations indicated that significant amounts of H_2S, HCN, SO_2, and NH_3 should have been formed, though these were not determined experimentally. The measured concentration of $(CN)_2$ was also much greater than the calculated results indicated. The theoretical predictions are discussed in greater detail in the following section (2.3).

Wohlford and Sheets (1971) measured carbon monoxide levels from the firing of small arms automatic weapons in a closed 63-ft^3 test chamber. Weapons tested were the H60C, M60E2, M219, M85, M2HB, M37, M16, M14, XM207E1, and M134. Measurements were made with on-line carbon monoxide analyzers. The report provides extensive data on concentration levels from the firing of these weapons under a variety of conditions including the position and mounting of the weapons in the chamber, total number of rounds fired, and the firing rate. Overall, the data were correlated to show that the amount of gas expelled from the firing of a weapon of a given caliber is a function of dwell time--the time from the primer initiation to complete unlocking of the bolt.

The combustion products formed from firing an M16 and a 105-mm caliber gun were examined by Ase et al. (1985) to identify chemical species present in the gas and particulate phase. Samples from the M16 rifle were obtained from an enclosed test chamber through which the weapon was fired, and exhausts from the 105-mm gun were obtained by drawing samples into an evacuated cylinder through a probe placed into the breech end of the gun following firing. Purified air was used to pressurize the M16 chamber and to provide make-up gas as the samples were withdrawn. Uniform mixing and exponential dilution were assumed. The composition of the propellants and primer or igniter used in this study are shown in Table 2.22. Analyses were conducted for a variety of chemical compounds including the major gaseous constituents, H_2S, HCN, metal particulates, polyaromatic hydrocarbons (PAHs), and trace volatile compounds. The PAHs were solvent extracted from filters on which they were collected and analyzed by HPLC and GC-MS. Trace volatiles were collected on Tenax adsorbent cartridges and analyzed by GC-MS.

Quantitative data were presented for 14 volatile compounds detected in the M16 and 105-mm gun exhausts (see Table 2.23). This listing

TABLE 2.21. EXHAUST GASES DETERMINED FROM THE FIRING OF XM-19 RIFLES WITH XM-645 FLECHETTE ROUNDS

Component	Concentration (ppm) Relative to Air[a]	R^b
Carbon monoxide	15,500	(1000)
Carbon dioxide	5,500	355
Cyanogen	4	0.25
Carbonyl sulfide	4	0.25
Methane	21	1
Acetylene + ethylene	19	1
Propene	15	1
Propane	<1	<0.1
Allene or propyne	<1	<0.1

a. From 12 rounds in containment vessel.
b. R = (concentration of component/concentration of CO) $\times 10^3$.

Adapted from Rocchio and May (1973).

TABLE 2.22. COMPOSITION OF PROPELLANT AND PRIMER OR IGNITER FOR THE M-16 RIFLE AND 105-mm CALIBER GUN

M-16 Propellant (5.56-mm Ammunition, Olin WC 844, 1.65 g)		Primer	
Components	Weight %	Components	Weight %
Nitrogen in nitrocellulose	13.05-13.20	Lead styphnate	35 ± 5
Graphite	0.4	Tetrazene	4 ± 1
Sodium sulfate	0.5	Barium nitrate	32 ± 5
Calcium carbonate	0.2	Antimony sulfide	15 ± 2
Nitroglycerin	8.0-11.0	Al powder	7 ± 1
Diphenylamine	0.75-1.50	PETN	5 ± 1
Dibutylphthalate	3.0-6.0	Organic binder	Small
Total volatiles	<2.0		
Nitrocellulose	Balance		

105-mm-Caliber Gun Propellant (12 lb)		Igniter (M-83, 0.07 lb)	
Components	Weight %	Components	Weight %
Nitrocellulose	28.55	Nitrocellulose	60.0
Nitrogen in nitrocellulose	12.6	Black powder[a]	40.0
Nitroglycerin	22.23		
Nitroguanidine	47.00		
Cryolite	0.31		
Ethyl centralite	1.54		
Ethanol	0.24		
Carbon	0.13		

a. The specific composition of the unmixed black powder was not defined. Black powder compositions typically lie in the following ranges: charcoal, 14-18%; sulfur, 10-16%; and potassium or sodium nitrate, 70-74%. The composition and amount of primer were not given. The primer mass would probably be ≤0.1 g and would have a negligible impact on the overall combustion product distribution.

Adapted from Ase et al. (1985).

TABLE 2.23. SOME GASEOUS CHEMICAL SPECIES QUANTITATED IN COMBUSTION PRODUCTS OBTAINED FROM FIRINGS OF AN M16 RIFLE AND 105-mm-CALIBER GUN

Compound name	M16 Rifle		105-mm-Caliber Gun	
	Grams of Compound per Gram of Propellant Burned	% Standard Deviation of the Mean	Grams of Compound per Gram of Propellant Burned	% Standard Deviation of the Mean[a]
Benzene	1.74×10^{-4}	18	9.2×10^{-5}	41
Acrylonitrile	2.36×10^{-5}	57	8.5×10^{-6}	59
Toluene	1.82×10^{-5}	9	2.2×10^{-5}	28
Cyanobenzene	9.91×10^{-6}	26	$0\text{-}3.1 \times 10^{-6}$	b
Crotonitrile	1.43×10^{-6}	24	$0\text{-}1.3 \times 10^{-4}$	b
Furan	1.10×10^{-6}	90	$0\text{-}4.6 \times 10^{-7}$	b
Dimethylnitrosamine	8.5×10^{-7}	39	$0\text{-}3.0 \times 10^{-7}$	b
Methacrylonitrile	7.6×10^{-7}	38	$0\text{-}1.4 \times 10^{-6}$	b
Quinoline	5.1×10^{-7}	50	$0\text{-}1.4 \times 10^{-7}$	b
Nitrobenzene	4.5×10^{-7}	44	$0\text{-}2.3 \times 10^{-8}$	b
2-Furfural	3.5×10^{-7}	52	0	b
Carbon disulfide	1.8×10^{-7}	56	5.2×10^{-6}	69
Hexane	1.7×10^{-7}	60	5.5×10^{-7}	50
Indane	3.0×10^{-8}	73	1.1×10^{-7}	69

a. In those cases where a range of values is indicated rather than the standard deviation of the mean, the range covers minimum and maximum values measured.
b. No attempt at measurement.

Adapted from Ase et al. (1985).

includes a wide variety of organic compounds (e.g., nitriles, a nitrosamine, heterocyclic aromatics, aromatics, aliphatic hydrocarbons, sulfur compounds, etc.). Considerable variability in concentration was found from the different analyses as evident from the standard deviations. This is likely due to the sampling and analytical methodology. For example, it is unlikely that carbon disulfide would be quantitatively retained on Tenax or that chromatographic conditions were optimum for analyzing each of these compounds. Qualitative analysis by GC-MS led to the identification of an additional 70 to 90 organic compounds. A number of PAHs were also detected in the M16 exhaust. Four of these (fluoranthene, pyrene, benz[a]anthracene, and chrysene) were found at concentrations significantly greater than the blank values. Inhalable metal particulates (i.e., particle diameters <10 μm) determined from the M16 included Sb, As, Ba, Cu, Pb, and Zn. The authors note that Sb, Pb, and Ba are constituents of the primer and that copper-plated slugs were used in the ammunition. Erosion of the brass bullet case was the probable source of zinc particulates. Overall the authors conclude that many of the species identified are toxic (at some concentration level) and present the potential for adverse health effects if personnel are exposed for extended periods to these combustion products. A more detailed description of this work was presented in the report by Snelson et al. (1983), and is summarized in Appendix A.

Johnson et al. (1983) examined the products from the detonation of trinitrotoluene in air and in nitrogen at atmospheric pressure. The nitrogen atmosphere simulates underwater detonation. Relatively large quantities of TNT (approximately 1.5 kg) were exploded in steel chambers (35 m^3 or larger). Samples were collected on adsorbent cartridges or cold traps and analyzed by GC-MS. Despite sampling and analytical difficulties, a number of high-molecular-weight compounds were identified. Benzonitrile, naphthalene, dinitrotoluene, trinitrotoluene, and phenanthrene were detected in both air and nitrogen atmospheres. Higher percentages of particulates and nonvolatile compounds were found from the detonations in nitrogen as compared to air. This result would be predicted for incomplete combustion in nitrogen.

Some compositional information on the particulate residue remaining following the firing of black and smokeless powders has been obtained from forensic studies (Yinon and Zitrin 1981). Solid decomposition products are primarily carbonaceous particles, nitrites, and nitrates. Metals originating from the primer may also be present. A variety of analytical methods including colorimetry, atomic absorption, neutron activation analysis, electron microscopy with energy-dispersive X-ray analysis, and X-ray fluorescence and luminescence have been used to examine metallic residues. Nitrates and nitrites have been determined by color reactions and organic residues have been examined by GC, MS, thin-layer chromatography (TLC), or by colorimetric procedures.

Overall, the studies conducted in test chambers indicate that gun exhaust is a highly complex mixture of compounds. Whereas the studies conducted in indoor firing ranges or enclosed crew compartments principally focused on gaseous species and metals, these studies provide compositional information on higher-molecular-weight compounds.

Most notably, from a toxicological standpoint, aromatic and polycyclic aromatics were detected. Again, there are insufficient data (especially quantitative data) to determine the significance of some of the findings. Additional studies are certainly required to validate the results and to enable extrapolations from the test chamber environment to acutal field conditions.

2.2.4 Exhaust Products Generated in Test Chambers Under Non-atmospheric Conditions

It should be noted in the following discussion that external conditions (pressure, temperature, environment) affect combustion processes that in turn influence the composition of the final combustion products. A closed or sealed vessel, for example, will limit the amount of oxygen available for combustion, which could result in incomplete oxidation of the products and a higher concentration of carbon monoxide than would be expected if the propellant were burned in the open atmosphere.

The toxic gases produced by propellant actuated devices in aircraft escape systems were investigated by Stiefel and VanArtsdalen (1965). The propellants examined and the exhaust gases they generate are listed in Table 2.24. Mixtures of boron and potassium nitrate or barium nitrate and zirconium were used as igniters. XM87 initiator or XM173 cartridge housings were used to contain the various propellant igniter combinations in firing tests. The devices were placed in an enclosed container which was then evacuated to collect the exhaust gases. Samples were then taken from the container in evacuated glass bulbs for analysis by mass spectrometry. To assure that the propellants burned correctly, ballistics data were also recorded.

Large concentrations of carbon monoxide were generated with the HES 6405, HES 6635, and AMOCO 14 and 15 charges. It should also be noted that the ammonium and potassium perchlorate propellants did not produce any measurable quantities of chlorine gas or hydrogen chloride. These compounds were believed to react with potassium from the potassium nitrate to form solid potassium chloride or with the metal in the apparatus. The effects of the igniters on the combustion products were found to be dependent upon the propellant used. Carbon monoxide concentrations, for example, were reduced when HES 6573 was used with the boron/potassium nitrate igniter and when AMOCO 14 was used with the zirconium-containing igniter. The other toxic gas detected in some systems was nitric oxide. The authors note that this gas remained stable in the sampling bulbs due to the exclusion of air. In the atmosphere, NO is converted to NO_2 which can react further with oxygen and moisture to form nitrous and nitric acids. The composition of the exhaust products was also determined by computational analysis. These result are discussed in greater detail in the following section (2.3).

Lenchitz et al. (1974) conducted high-pressure (to 100,000 psi) combustion studies on single-, double-, and triple-base propellants (M10, T-28, and T-34, respectively). These studies are important because of their applicability to high-velocity guns. Experiments were conducted in a high-pressure closed vessel and gases produced following

TABLE 2.24. GASES PRODUCED BY PROPELLANT IGNITER MIXTURES IN AIRCRAFT ESCAPE SYSTEMS

Propellant		Igniter	
HES 5808	Ammonium perchlorate/cellulose acetate	A	15% B-85% KNO_3
HES 6405	Ammonium perchlorate/hycar	B	10% B-90% KNO_3
HES 6573	Potassium perchlorate/hycar	C	41% Zr-59% $Ba(NO_3)_2$
HES 6635	Ammonium perchlorate	D	25% Zr-75% $Ba(NO_3)_2$
AMOCO No. 14	Ammonium nitrate/cellulose acetate (proprietary)	E	U.S. Flare 2K
AMOCO No. 15	Ammonium nitrate/cellulose acetate (proprietary)	F	45% KNO_3
AMOCO P-1	Ammonium nitrate/binder (proprietary)		20% Zr-30% $Ba(NO_3)2$-5% B
AMOCO P-1A	Ammonium nitrate/binder (proprietary)	G	U.S. Flare 2D
AMOCO P-1B	Ammonium nitrate/binder (proprietary)		

Concentration (percent)

Propellant	Igniter	CO	CO_2	N_2O	H_2	NO	N_2	O_2	CH_4	H_2O	Ar
HES 5808	A	0.5	53.8		0.8	0.3	41.0	3.2		0.5	Trace
HES 5808	A	0.0	50.1		0.8	0.4	43.5	3.8		1.4	Trace
HES 5808	A	0.2	56.5		0.3	0.3	37.8	4.3		0.7	Trace
HES 5808	B	0.0	51.2		0.0	0.8	41.6	6.4		0.1	Trace
HES 5808	B	0.0	55.3		0.6	0.7	38.4	3.8		1.2	Trace
HES 5808	B	0.5	50.5		0.4	0.8	42.6	4.5		0.7	Trace
HES 5808	C	0.0	60.1	2.5	0.5	0.9	33.8	1.4		1.1	Trace
HES 5808	C	0.0	52.9		1.7	0.0	41.1	3.1		1.1	Trace
HES 5808	C	0.0	66.1	2.1	0.3	0.5	29.3	0.0		1.7	Trace
HES 6405	B	6.7	51.7		5.2		30.0	1.2		5.1	Trace
HES 6405	B	4.1	54.3	2.2	5.3		34.8	0.5		1.0	Trace
HES 6405	B	6.2	47.3		7.4		33.3	2.1		3.7	Trace
HES 6573	B	1.2	69.5		0.3		15.2	8.4		5.4	Trace
HES 6573	B	0.0	67.0		0.0		16.1	6.5		0.4	Trace
HES 6573	B	0.6	78.7		0.3		11.1	4.0		2.5	Trace
HES 6573	F	4.5	67.1		0.3		13.9	8.1		6.1	Trace
HES 6573	F	4.5	73.3		0.2		12.6	8.1		1.1	Trace
HES 6573	F	1.9	69.4		0.5		15.5	8.7		4.0	Trace
HES 6573	F[a]	3.9	67.3		0.3		16.8	4.7		6.9	0.1
HES 6573	F[a]	2.1	68.4		0.2		18.6	6.1		4.5	0.1
HES 6573	F[a]	1.9	64.1		0.5		26.2	4.5		2.7	0.1
HES 6573	F[a]	2.8	70.8		0.1		20.1	3.0		3.1	0.1
HES 6573	F[b]		65.0		0.1		21.8	6.5		6.5	0.1
HES 6573	F[b]	2.4	64.5		0.1		22.4	5.9		4.6	0.1
HES 6573	F[b]	3.2	61.9		0.7		22.6	2.0		9.0	0.1
HES 6573	F[b]	3.1	69.0		0.2		20.6	3.7		3.3	0.1
HES 6573	F[c]	0.5	71.2		0.1		19.7	4.2		4.3	0.1
HES 6573	F[c]	1.1	65.1		0.2		24.2	7.1		2.3	0.1
HES 6573	F[c]	2.5	70.4		0.2		13.8	4.8		3.1	0.1
HES 6573	F[c]	2.8	62.0		1.3		24.3	3.3		6.3	0.2
AMOCO No. 14	B[d]	18.8	15.9		16.1		37.4	0.1		1.6	Trace
AMOCO No. 14	B[d]	19.1	22.9	2.2	15.6		39.0	0.1	1.2	2.1	Trace
AMOCO No. 14	B[d]	21.0	22.4		15.9		36.5	0.2		1.7	Trace
AMOCO No. 14	C[d]	8.0	18.6		21.3		45.2	1.4	0.6	4.9	Trace
AMOCO No. 14	C[d]	0.0	23.6		1.7		60.3	1.6		2.2	Trace
AMOCO No. 14	C[d]	13.8	23.7	1.5	14.8	0.4	43.4	0.1	1.1	1.2	Trace

TABLE 2.24. GASES PRODUCED BY PROPELLANT IGNITER MIXTURES IN AIRCRAFT ESCAPE SYSTEMS (cont'd)

		Concentration (percent)									
Propellant	Igniter	CO	CO_2	N_2O	H_2	NO	N_2	O_2	CH_4	H_2O	Ar
AMOCO No. 15	B[d]	4.3	31.4		9.4		53.1	1.3		0.5	Trace
AMOCO No. 15	B[d]	4.1	32.0		9.4		53.5	0.3	4.0	0.6	Trace
AMOCO No. 15	B[d]	2.3	28.6		5.7		54.7	3.1		0.6	Trace
AMOCO P-1	B[d]		24.2	1.2	0.5		60.5	6.9		7.9	Trace
AMOCO P-1	B[d]		30.2		0.4		57.1	7.6		3.5	Trace
AMOCO P-1	B[d]	0.6	26.4		0.2		60.3	8.7		3.8	Trace
AMOCO P-1A	F[d]	2.2	23.5		0.3		66.1	6.8		1.2	Trace
AMOCO P-1A	F[d]	1.3	26.6				63.8	3.1		3.2	Trace
AMOCO P-1A	F[d]	1.8	24.6		0.1		64.5	7.2		1.8	0.1
AMOCO P-1A	F[d]	0.5	25.2		0.1		65.5	7.5		1.1	Trace
AMOCO P-1B	F[e]		25.1		0.3	10.5	62.7	Trace	0.4	0.9	0.1
AMOCO P-1B	F[e]		24.0		0.2	6.9	65.0			3.5	
AMOCO P-1B	F[e]		26.4		Trace	7.7	64.7	Trace		1.2	
AMOCO P-1B	D[e]		23.6			7.3	63.1	0.1		5.9	0.1
AMOCO P-1B	D[e]		24.3		0.2	9.3	61.5	0.3	0.3	4.1	
AMOCO P-1B	D[e]		25.0			6.6	65.3	0.4		2.8	
HES 6573	C	7.1	68.7		1.9		12.8	2.5		7.2	
HES 6573	C	1.5	21.5		0.4		58.8	14.7		3.2	
HES 6573	C		72.2		1.7		18.1	2.4		5.6	
HES 6573	D	4.5	76.4		1.2	0.4	14.0	1.9		1.7	
HES 6573	D	5.4	72.4		2.9		14.0	2.3		2.7	
HES 6635	B	32.0	36.1			0.4	17.7	0.4	0.6	4.5	0.2
HES 6635	B	34.0	33.7				17.7	0.4	0.8	4.0	Trace
HES 6635	B	17.0	51.5			0.6	10.5	0.4	0.6	9.0	
None	E	42.9	3.4				36.7	0.6	1.3	3.2	
None	E	38.2	1.0				34.9	0.5	1.4	1.2	
None	C	21.5	1.5		38.0	0.1	38.1	0.2	0.6	1.2	
None	C	23.7	3.0		37.4	0.1	36.3	0.2	1.0	0.9	
None	C	23.8	0.4		31.4	0.2	41.5	0.2	1.0	1.4	
HES 5808[f]	C	1.4	43.0		3.5	0.1	42.9	7.8			
HES 5808[f]	C	0.2	61.0		2.9		33.5	2.0			
HES 6573[f]	C	0.9	70.0				7.9	19.3			
HES 6573[f]	C	2.2	72.0				3.0	17.8			1.0

a. With aminoguanidine carbonate coolant.

b. With melamine coolant.

c. With oxamide coolant.

d. 0.2 gram of HES 5808 added as ignition aid.

e. 0.15 gram of HES 6573 added as an ignition aid.

f. 8.3 grams propellant used.

NOTES: Igniter weight was 0.7 g in all cases except that 2.4 grams was used for U.S. Flare 2K and U.S. Flare 2D. Propellant weight was 2 g except in the case of HES 6573, where 2.8 g was used.

Adapted from Stiefel and VanArtsdalen (1965).

firings were analyzed by MS. The data showed that the concentration of H_2 and CO decreased with loading density for all three formulations. For the T-34 propellant, CO_2, H_2O, and CH_4 were significantly correlated (at the 5 percent level) with density but were found to increase in concentration. These changes may cause increased heats of reaction and variations in flame temperature that could affect the composition or concentration of other products. Table 2.25 shows the results for CH_4, H_2, CO, CO_2, and H_2O expressed in moles/g as a function of loading density.

Patrick and Floyd (1976) compared the gaseous by-products generated from a triaminoguanidine nitrate (TAGN) gun propellant with those produced from standard nitrocellulose (NC) based propellants, with the objective of identifying potential hazards to personnel exposed to these gases during testing or actual firing conditions. The TAGN-containing propellant (RGP-150, Rocketdyne) was an experimental formulation proposed for use in weapon systems using high-density, armor-piercing penetrators. The formulations of all the propellants investigated in this study are given in Table 2.26. They were burned in a Parr Adiabatic Calorimeter at atmospheric pressure and also at high pressures in an impulse bomb (Technoproducts Model 601) (i.e., approximately 12,000 and 28,000 psi to simulate conditions during firing of an actual weapon). Samples were collected in evacuated stainless steel cylinders and analyzed by gas chromatography using a thermal conductivity detector (TCD). The results of the study are presented in Table 2.27. Significant quantities of carbon monoxide and methane were produced by all the formulations at elevated pressures (up to 60 and 12 percent, respectively). Deflagration at atmospheric pressures resulted in less carbon monoxide and methane, which can be attributed to the greater amount of oxygen available for more complete combustion of the propellant ingredients. Qualitatively the various formulations produced similar products with the exception of the triple-base propellant, which, in addition to the major components, also produced small amounts of ethylene and nitrous oxide. Quantitative differences were explained as resulting from the increased nitrogen content and reduced oxygen availability in some formulations, promoting nitrogen and methane formation. Overall, when these propellants are used in actual firing situations, the authors believe that the gases produced should be considered hazardous (based upon the amount of carbon monoxide and methane present) in confined areas lacking ventilation to dissipate concentrations to permissible levels.

Lenchitz et al. (1965) examined the effects of TiO_2-wax additives for gun propellants on erosion reduction. M-2 and T-36 propellants containing TiO_2, paraffin wax, or both were burned in a closed bomb. The quantity of gas evolved and CO-to-CO_2 ratios were measured to indicate changes in chemistry resulting from the additives. The wax was found to interact with the propellant gases, resulting in an increase in CO-to-CO_2 ratios, reducing the heat of explosion but increasing the volume of gas produced; TiO_2 showed no effects on the chemistry based upon the experiments performed. The TiO_2-wax mixture gave results similar to those from wax alone.

TABLE 2.25. ANALYSIS OF COMBUSTION PRODUCTS OF M-10, T-20, AND T-34 PROPELLANTS

Loading Density g/cm^3	Concentration (Moles/g of propellant)				
	CH_4	H_2	CO	CO_2	H_2O
	Single-Base Propellant (M-10)				
0.10	0.692	8.052	13.189	7.425	5.082
0.20	0.775	4.174	13.129	8.841	7.355
0.25	0.789	6.739	12.820	12.774	1.124
0.30	0.860	5.540	11.162	13.673	2.869
0.32	1.220	5.211	9.412	11.463	6.078
0.34	1.059	4.093	7.113	9.413	12.028
0.36	1.331	4.053	7.710	11.974	8.093
0.38	1.219	3.547	6.735	11.197	10.688
	Double-Base Propellant (T-20)				
0.15	0.742	7.502	13.349	7.787	5.608
0.20	1.824	5.861	13.460	9.205	2.473
0.24	2.032	6.672	11.853	7.789	4.060
0.27	1.234	3.895	7.257	6.048	15.569
0.32	2.049	4.012	8.659	8.948	8.703
0.42	0.827	3.515	7.502	12.050	10.922
	Triple-Base Propellant (T-34)				
0.05	1.06	12.99	10.308	3.554	0.0
0.10	1.069	11.23	12.43	4.431	0.58
0.15	0.994	11.25	11.02	5.603	1.61
0.20	1.412	9.016	9.368	5.308	5.06
0.25	1.309	7.689	7.870	5.840	7.74
0.30	1.593	6.546	7.784	5.909	8.05
0.36	1.667	5.403	6.447	8.211	7.81
0.41	1.694	4.185	5.029	8.274	10.57
0.465	2.052	3.750	4.822	9.074	9.20

Adapted from Lenchitz et al. (1974).

TABLE 2.26. COMPOSITION OF NITROCELLULOSE-BASED PROPELLANTS AND TAGN EXPERIMENTAL FORMULATION

Propellant	Chemical Composition	Percent of Total
Hercules' GAU-8 Extract	Nitrocellulose (NC)	82.30
	Nitroglycerin (NG)	9.37
	Dibutylphthalate (DBP)	4.17
	Diphenylamine (DPA)	0.54
	Potassium nitrate (KNO_3)	0.56
	Hercote ($C_{5.142}H_{8.750}1.838$)	3.06
Rocketdyne's RGP-150	Nitrocellulose (NC)	19.00
	Triaminoguanidine nitrate (TAGN)	45.00
	Cyclotetramethylene tetranitramine (HMX)	30.00
	Isodecyl pelargonate (IDP)	5.00
	Resorcinol	1.00
M-10	Nitrocellulose (NC)	97.40
	Diphenylamine (DPA)	1.00
	Graphite glaze	0.10
	Carbon black	0.50
	Potassium sulfate (K_2SO_4)	1.00
Triple Base	Nitrocellulose (NC)	28.04
	Nitroglycerin (NG)	20.12
	Ethylcellulose (EC)	1.00
	Potassium sulfate (K_2SO_4)	0.25
	Nitroguanidine (NG)	50.59
WC-870	Nitrocellulose (NC)	80.23
	Nitroglycerin (NG)	9.66
	Diphenylamine (DPA)	1.06
	Potassium nitrate (KNO_3)	0.50
	Dibutylphthalate (DBP)	7.38
	Potassium sulfate (K_2SO_4)	0.38
	Dinitrotoluene (DNT)	0.52
	Calcium carbonate ($CaCO_3$)	0.05
	Sodium sulfate (Na_2SO_4)	0.12
	Graphite	0.10

Adapted from Patrick and Floyd (1976).

TABLE 2.27 PERCENTAGES OF GASES PRODUCED FROM SELECTED PROPELLANTS WHEN BURNED UNDER HIGH AND LOW PRESSURE

Propellant	Pressure (psi)	H_2	N_2	O_2	N_2O	CO	CO_2	CH_4	C_2H_4	H_2O
RGP 150	Atm		84.0	8.7			5.8			1.5
RGP 150	13,000	0.2	42.2	tr		40.0	6.4	4.6		6.6
RGP 150	31,000	0.3	41.3	0.1		31.4	10.0	12.7		4.2
GAP 8 Extract	Atm		43.5	7.4		5.8	28.9	tr		14.4
GAP 8 Extract	11,500	0.3	15.3	0.3		50.9	14.8	2.3		16.1
GAP 8 Extract	28,000	0.3	12.7			42.0	20.8	7.1		17.1
M 10	Atm		51.0	15.7		1.6	22.2			9.5
M 10	13,000	0.1	16.2			57.7	20.4	1.3		4.0
M 10	30,000	0.2	15.6			40.9	30.2	3.2		9.9
WC 870	Atm		60.6	5.1		4.0	20.2			10.1
WC 870	12,000	0.3	16.2			60.6	16.3	2.4		4.2
WC 870	27,000	0.2	16.6	0.3		49.0	25.4	4.9		3.6
Triple Base	Atm		62.9	17.5	tr	5.5	4.1		2.6	7.4
Triple Base	13,000	tr	37.8			38.7	12.5	2.0		9.0
Triple Base	27,000	tr	35.9			38.9	14.2	2.1		8.9

adapted from Patrick and Floyd (1976).

Tompa (1985) examined the combustion products of three conventional propellants and three low vulnerability ammunitions (LOVAs). The materials were combusted in a bomb calorimeter and trace (ppm) level gaseous products were analyzed by GC-MS. In addition to the experimental work, theoretical compositions were calculated using a thermochemical computer program (discussed in Section 2.3). Details regarding the sampling and analytical methodology were not provided nor were the compositions of the various propellants given. Carbon monoxide was identified as the toxic product generated in the greatest concentration. Hydrogen sulfide and carbonyl sulfide were found in some formulations containing potassium sulfate, and hydrogen cyanide was detected in some LOVA compositions. The theoretical analysis predicted a number of other species.

Propellants used in the large solid rocket and Sprint missiles were combusted under laboratory conditions to chemically characterize the exhaust gases (Nole and Moss 1966). The work was conducted to demonstrate that propellants can be fired on a laboratory scale to evaluate potential toxic hazards. Although the study examines rocket propellants, the methodology, especially that of sample collection and preconcentration, may also provide information useful for analysis of gun exhaust in combustion chambers. Approximately 50-gram samples of the rocket propellants were burned in a Crawford bomb. The gases that were generated were then concentrated by passing them through successive traps at dry ice-acetone and liquid nitrogen temperatures. Analyses were conducted by GC using a flame ionization detector and MS. The major constituent was found to be CO_2. Smaller amounts of water, HCl, COS, and CS_2 (present only in the Sprint propellant containing sulfur) and trace levels of organic compounds were also detected. Attempts to identify these organics were only partially successful since they could not be fully resolved from the water and CO_2 present in the samples using standard gas chromatoraphic techniques. Efforts to remove these major constituents allowed some additional determinations for 10 compounds ranging from methane to pentane. This technique was not entirely satisfactory, however, since it also resulted in the removal of some organics. The most difficult task for performing trace organic determinations was separation of the compounds from the interfering effects of H_2O, HCl, and CO_2. The use of cryogenic techniques did allow the separation of the materials into dry ice-acetone, liquid nitrogen, and noncondensible fractions. It also provided a 6-fold and 10^4-fold concentration factor for the liquid nitrogen and dry-ice acetone fractions, respectively, permitting identification for some of the constituents. It should be noted that sorbent resins are available today to concentrate organic vapor phase samples without retention of major gases (see Section 3). This would eliminate some of the problems encountered in this study. A complete list of the compounds that were identified and their estimated concentrations is given in Table 2.28. The conclusion drawn by the authors based upon their findings was that the concentration of the organics released in an actual test firing will be extremely small. No actual toxicity data were provided in the report.

TABLE 2.28. COMPOUNDS IDENTIFIED IN SPRINT AND LARGE SOLID ROCKET COMBUSTION GASES

Compound	Estimated Concentration[a]	
	Large Solid Rocket	Sprint
CO_2	5.2%	7.9%
H_2O	x	x
HCl	x	x
CH_4	0.1%	0.2%
Ethane	x	x
Ethylene	x	x
Propane	x	x
Propylene	x	x
Butane	x	x
Butylene	x	x
Isobutene	x	x
Pentane	x	x
Hexane	x	x
Heptane	x	x
Dioxane	x	x
Benzene	3 ppm	14 ppm
Toluene	x	0.7 ppm
3-methyl-1-hexene	0.8 ppm	x
2-methyl-2-butene	7 ppm	15 ppm
CH_2Cl_2	x	
Cyclohexane	1 ppm	[illegible] ppm
Carbonyl sulfide	x	
Carbon disulfide	x	
Sulfur dioxide	x	
Hydrogen sulfide	x	

a. x=concentration was not estimated

Adapted from Nole and Moss (1964).

Goshgarian (1969) designed a system for the direct analysis of exhaust products of solid rocket propellants immediately following combustion that may also have some application for gun propellants. He notes that most experimental determinations are made by trapping or collecting the gaseous samples in containers for subsequent analysis. Because some of the products are highly reactive, the results in these situations may not adequately reflect the actual composition immediately following combustion. The importance of this should not be overlooked. Reactive toxic species (e.g., NO_x) in gun exhaust may require direct or real-time analysis for accurate determination. The system designed by Goshgarian includes a micromotor combustor (shown in Figure 2.8) that simulates combustion conditions of normal-sized motors. The exhaust gases are vented into a controlled atmospheric chamber. A differentially pumped sampling system is then used to introduce samples directly in a mass spectrometer for analysis. The concentration profile of major reaction species formed from the combustion of a composite modified double-base propellant (15 percent Al, 30 percent ammonium perchlorate, and 55 percent binder) could be monitored with this system over an extended time period.

Goshgarian (1976) has also monitored the concentration of H_2O, CO, N_2, CO_2, and HCl as a function of burn time for solid rocket propellant formulations. A micromoter combustion chamber was used to burn the propellants and a molecular beam mass spectrometer was used to continuously analyze the exhaust gases by introducing them directly into the orifice of a water-cooled sampling cone. All gases were found to increase in concentration as the pressure at the sampling orifice increased, with the exception of CO_2, which remained relatively constant.

A study was performed by Farr and Goshgarian (1976) to develop analytical procedures suitable for examining the combustion products of solid rocket propellants containing acoustic stability additives. These additives stabilize the combustion process although the manner by which it is accomplished is not fully understood. The four propellants examined were TPH-8046 (Thiokol Chemical Corporation), ANB-3513 (Aerojet Solid Propulsion Company), TMS-26, and AMS-35. The latter two formulations were prepared at the Air Force Rocket Propulsion Laboratory (AFRPL) from Thiokol and Aerojet propellants. Their compositions are given in Table 2.19. A micromotor combustor was used to burn the materials, and samples were collected in evacuated glass collection cylinders. The analytical methods and approach may have some applicability for gun propellants.

Analyses were conducted for noncondensible combustion gases, water, HCl, particle size distribution, and condensed phase products. The gases were analyzed by GC using a thermal conductivity detector, and water and chloride were determined by Karl-Fischer titration and constant current coulometry, respectively. Particle size analyses of the solid combustion products were performed on an image analyzer, and X-ray emission and diffraction were used to identify elements and crystalline solids.

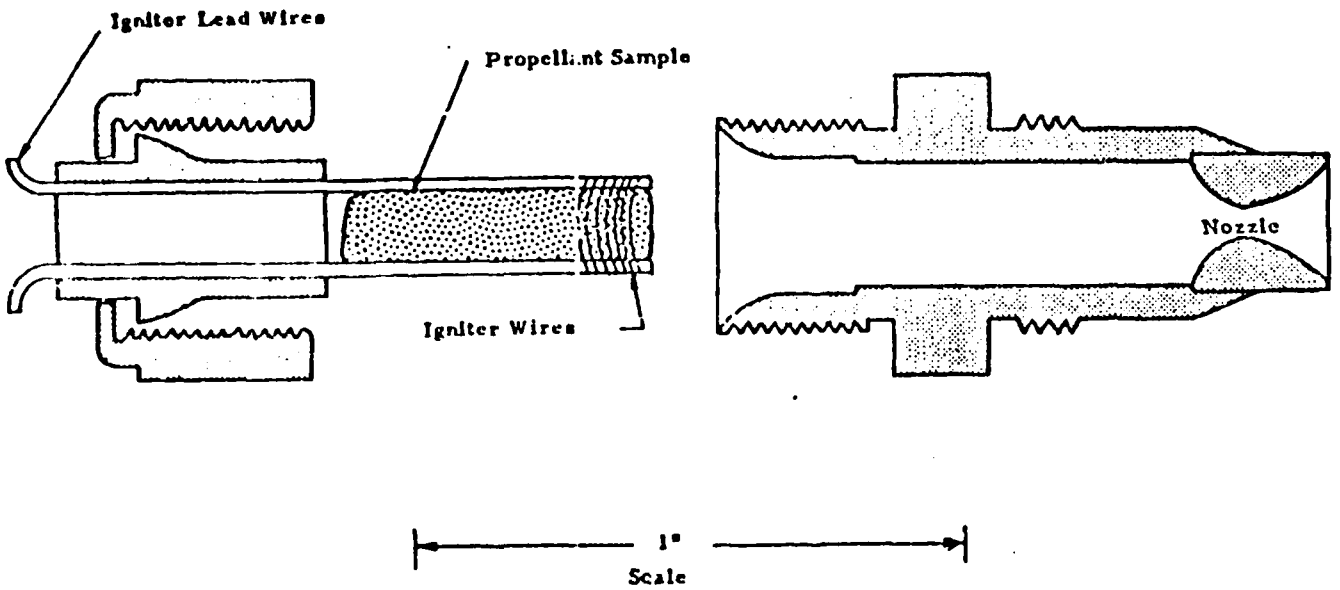


Figure 2.8. Micromotor design.
Adapted from Goshgarian (1969).

TABLE 2.29. COMPOSITION OF REDUCED SMOKE SOLID PROPELLANTS

Ingredients	TMS-26	AMB-3513	AMS-35	TPH-8246
Binder (hydroxyterminated polybutadiene prepolymer and isocyanate curing agent)	X	X	X	X
NH_4ClO_4	X	X	X	X
Additives				
ZrC	X	X	X	-
C	X	X	X	X
Al_2O_3	X	-	-	X

Adapted from Farr and Goshgarian (1976).

Carbon dioxide, CO, H_2, N_2, CH_4, and traces of acetylene were found in all samples. Hydrogen concentrations were related to the amount of graphite and zirconium carbide, both combustion stability additives, in the formulations. For example, less hydrogen was found in TPH-8246, which contains no ZrC and the least amount of graphite relative to the other propellants. The explanation the authors offer is that higher graphite and ZrC favor a reducing atmosphere and nonequilibrium conditions in the combustion chamber, which results in an increased production of hydrogen and carbon monoxide at the expense of carbon dioxide. The nitrogen produced relative to the amount of CO_2 was also found to be slightly greater than predicted. The difference may be due to sampling methods or the formation of organo-nitrogen compounds.

Water concentrations in the collected samples were found to change as a function of time. The authors reason that the change may be due to the reaction of HCl with the solvent (methanol) used to transfer the condensed phase from the collection cylinders (i.e., $CH_3OH + HCl \rightarrow CH_3CL + H_2O$). This reaction, however, proceeds slowly and may not fully explain large increases in water concentration. It is recommended that analyses for water be performed immediately following collection. Hydrogen chloride present in the gaseous phase of the combustion products was dissolved in methanol, which was then analyzed for total chloride. No errors due to incomplete transfer were expected in the analysis. X-ray diffraction performed on the solids detected graphite and ZrO_2. No ZrC was found, indicating that it was completely oxidized. Scanning electron microscopy also detected Al_2O_3 in the particulate phase. It should be noted that no attempt was made to determine the concentration of condensible organics.

These studies conducted in closed bombs or test calorimeters are believed to partially simulate conditions during the firing of an actual weapon. The products generated should then relate to actual gun exhaust. If this is the case, then closed bombs may provide a convenient and relatively inexpensive method of generating combustion products from different formulations, permitting comparisons and evaluation of potential toxic hazards from a chemical standpoint. It is unlikely, however, that the products will be identical. Incomplete combustion and oxidation may lead to elevated concentrations of some products or even the formation of different products under some circumstances. While comparisons of the experimental data with theoretical predictions (see Section 2.3) indicate close agreement for the major combustion products, there is poor agreement for minor constituents (Tompa 1985; Stiefel and Hody 1970; Rocchio and May 1973). There have been no studies reported in the open literature that have examined the trace level compounds produced in closed bombs. The data that can be obtained from these devices, however, may indicate which components should be examined in greater detail either in the field or in chambers where an actual weapon is fired. Additional studies are required to determine if the closed bomb approach would be valid.

2.2.5 Identification of Reactive Intermediate Species

The chemistry involved in the combustion of propellants under gun or rocket conditions is very difficult to determine experimentally because of the speed and complexity of the reactions and the extreme physical conditions involved (i.e., high temperatures and pressures). In the case of guns and rifles the processes are believed to involve almost entirely transient reactions. While a broader understanding of these could aid in solving ballistic-related problems or in predicting product composition, few studies have been undertaken to examine the chemical species generated. White and Reynolds (1975) have developed a molecular beam sampling system coupled to a time-of-flight mass spectrometer for studying transient species produced in interior ballistic combustion processes. They cite the study of the ignition and combustion under ambient conditions of caseless ammunition as an example of practical application of the method that could lead to a rationale for selecting additives for reducing the vulnerability of this type of ammunition. The report only describes the system and does not present any experimental data.

An extensive review on nitramine propellant decomposition and combustion was written by McCarthy et al. (1976). Nitramine oxidizers such as cyclotetramethylene tetranitramine (HMX) and cyclotrimethylene trinitramine (RDX) in gun propellants offer the advantage of high impetus due to high energy and large quantities of gas produced on combustion. These desirable properties, however, have been countered by objectionable ballistic properties (i.e., slow ignition and either high peak pressure or low projectile velocity, depending upon charge design). An objective of this review was to develop a broader understanding of nitramine combustion and establish criteria for controlling the ballistic properties. Nitrous oxide (N_2O) and formaldehyde were identified as the initial decomposition products and potential reactions in the CH_2O/N_2O flame were listed. Nitrous oxide decomposes to form N_2 and atomic oxygen at high activation energies. In the presence of atomic hydrogen, N_2 and hydroxyl radical are formed at a much lower activation energy. The addition of Table 2.12 atomic hydrogen would therefore accelerate burning and free radical traps would inhibit burning. It should be noted that decomposition products formed at low pressures may not indicate final products generated at high pressures.

Klein and Keller (1979) reviewed analytical methods that are capable of providing information on the spatial and temporal distribution of reaction products and intermediate species in the three reaction zones (foam, fizz, and flame) of burning propellants. They note that to accurately model the combustion process, spatial and temporal descriptions of heat and the various species produced during the reaction sequences are required. To obtain this information, a high degree of resolution is needed. Techniques that are capable of providing kinetic data are recognized as being suitable.

Measurements that can be obtained with probes are deficient because they are invasive and provide an average over the area of the probe. If the area is large an error will be introduced into the measurement.

Techniques that involve removal of the material from the reaction region for subsequent analysis are also difficult because species may continue to react prior to measurement. Mass spectrometry requires such sampling but may be useful in detecting and identifying some species. Optical spectroscopic methods are judged as being most suitable (i.e., laser excited fluorescence, inverse, and coherent anti-Stokes Raman spectroscopy).

Since reactive intermediate species formed in the combustion process of gun propellants have very short lifetimes and the information obtainable from such species could only aid in predicting final product composition, sampling and analysis for this class does not seem necessary at this time for evaluating the toxicological properties of gun exhaust.

2.3 EMISSION PRODUCTS THAT CAN BE PREDICTED FROM PROPELLANT COMPOSITIONS

In the past 25 years the computation of high-temperature chemical equilibria has become an important application of high-speed digital computers (Cruise 1979). Several computer programs have been developed and modified from time to time to solve ballistic problems. Since detailed treatment of the computer programs is beyond the scope of the present document, discussion is limited to the application of some of these programs to simulate the situation in a gun and predict the composition of the exhaust gases.

Important features of the computer programs used to predict the composition of the gun exhaust are (Steifel 1985):

a. The computer program will calculate the product composition for a given condition, i.e., chamber pressure or loading density. Then the gas is allowed to expand isentropically. The same entropy is imposed as obtained in the first calculation but the composition is calculated at lower and lower pressures.

b. A major unknown is the pressure at which the equilibrium freezes.

c. Another important limitation is that the calculation will only predict compositions on the basis of data supplied for each of the possible combustion species. If no data are supplied for a species that actually occurs, the program will, of course, not predict its pressure.

Stiefel and Hody (1970) compared the experimental results of chemical analysis of the exhaust with the computer predictions from propellants WC846 (7.62-mm machine gun), WC860 (caliber 0.50 machine gun), and N-5 (2.75-in. FFAR). The computer program used was developed by American Cyanamide Corporation under an Advanced Research Project Agency contract. The composition of the propellants is given in Table 2.20.

TABLE 2.30. COMPARISON OF RECONCILED COMPUTER AND EXPERIMENTAL RESULTS FOR SELECTED EXHAUST COMPONENTS OF THE 7.62-mm MACHINE GUN USING WC846 PROPELLANT

	Results (mole fractions)							
	Calculated[a]						Experimental	
Component	50K	25K	10K	5K	1K	14.7	Mean	Maximum
CO	0.82E-00	0.80E-00	0.78E-00	0.74E-00	0.63E-00	0.28E-00	0.66E-00	0.81E-00
CO_2	0.18E-00	0.20E-00	0.22E-00	0.25E-00	0.34E-00	0.68E-00	0.26E-00	0.42E-00
CH_4	0.91E-03	0.14E-02	0.35E-01	0.84E-02	0.39E-00	0.46E-01	0.10E-01	0.15E-00
NH_3	0.12E-02	0.98E-03	0.83E-03	0.76E-03	0.51E-03	0.11E-03	0.38E-02	0.10E-00
NO_2	Exponents range from -11 (50K psi) to -30 (14.7 psi)							
HCN	0.65E-03	0.36E-03	0.18E-03	0.10E-03	0.25E-04	0.23E-06	0.55E-03	0.10E-00

a. Pressure (psi) used in calculations.

Adapted from Steifel and Hody (1970).

TABLE 2.31. COMPARISON OF RECONCILED COMPUTER AND EXPERIMENTAL RESULTS FOR SELECTED EXHAUST COMPONENTS OF THE CALIBER 0.50 MACHINE GUN USING WC860 PROPELLANT

	Results (mole fractions)							
	Calculated[a]						Experimental	
Component	50K	25K	10K	5K	1K	14.7	Mean	Maximum
CO	0.83E-00	0.82E-00	0.79E-00	0.73E-00	0.60E-00	0.24E-00	0.65E-00	0.85E-00
CO_2	0.15E-00	0.17E-00	0.21E-00	0.24E-00	0.34E-00	0.67E-00	0.27E-00	0.59E-00
CH_4	0.68E-02	0.11E-01	0.23E-01	0.37E-01	0.67E-01	0.55E-01	0.65E-02	0.93E-02
NH_3	0.21E-02	0.17E-02	0.13E-02	0.11E-02	0.56E-03	0.12E-03	0.28E-02	0.80E-02
NO_2	Exponents range from -12 (50K psi) to -30 (14.7 psi)							
HCN	0.10E-02	0.55E-03	0.24E-03	0.13E-03	0.25E-04	0.20E-06	0.28E-03	0.88E-03

a. Pressure (psi) used in calculations.

Adapted from Steifel and Hody (1970).

TABLE 2.32. COMPARISON OF RECONCILED COMPUTER AND EXPERIMENTAL RESULTS FOR SELECTED EXHAUST COMPONENTS OF THE 2.75-in. ROCKET USING N-5 PROPELLANT

	Results (mole fractions)						
	Calculated[a]					Experimental	
Component	1200	1000	500	100	14.7	Mean	Maximum
CO	0.83E-00	0.83E-00	0.81E-00	0.76E-00	0.65E-00	0.21E-00	0.57E-00
CO_2	0.16E-00	0.16E-00	0.18E-00	0.23E-00	0.34E-00	0.52E-00	0.70E-00
CH_4	0.73E-06	0.89E-06	0.13E-05	0.16E-05	0.37E-02	0.60E-02	0.26E-00
NH_3	0.33E-04	0.31E-04	0.26E-04	0.24E-04	0.41E-04	0.70E-02	0.11E-00
NO_2	Exponents range from -10 (1,200 psi) to -26 (14.7 psi)						
HCN	0.19E-04	0.16E-04	0.94E-05	0.30E-05	0.11E-05	0.30E-02	0.38E-00

a Pressure (psi) used in calculations.

Adapted from Steifel and Body (1970).

Calculated and experimental values for selected components (CO, CO_2, CH_4, NH_3, HCN) in the combustion products from WC846, WC860, and N-5 are given in Tables 2.30, 2.31, and 2.32, respectively. Samples were analyzed by conventional infrared spectroscopy and high-resolution mass spectrometry. Accuracies of ±10 percent were obtained for sample components with partial pressures higher than 10 torr. This may partially explain examples of species predicted by computation but not detected by chemical experiments (Table 2.33). Components detected by chemical analysis but not predicted in the computation results are listed in Table 2.34. The same computer program was used by Stiefel and VanArtsdalen (1965) to develop a potassium perchlorate composite propellant with a binderless boron/potassium nitrate igniter composition for use in an aircraft escape system with minimum production of toxic gases. There was close agreement between the predicted and experimentally determined composition of the major combustion products as shown in Table 2.35.

Rocchio and May (1973) investigated the exhaust composition from XM-19 rifles and compared the experimental data with those calculated from a computer program. The program is code-named "Blake" and is based on the "Tiger" code developed by Stanford Research Institute (now known as SRI International) and modified by Eli Freedman (1982). The composition of the XM-645 round used in firing the XM-19 rifle is given in Table 2.20. Experimental and calculated product concentrations from the X-2374.13 propellant are shown in Table 2.36.

Tompa (1985) investigated the combustion products from three propellants and three LOVA compositions and compared the experimental data with those calculated by using a program developed by Cruise (1979). He found general agreement between the observed and calculated values for major constituents of the combustion products.

Snelson et al. (1983) characterized the combustion products from propellants WC844 and compared the experimental data with those calculated by using the "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incipient and Reflected Shocks and Chapman-Jonquet Detonation" by Sandford Gordon and Bonnie J. McBride of the NASA Lewis Research Center (see Table 2.37).

Snelson (1983) observed that in calculations of equilibrium composition during expansion, the major factor affecting the product distribution is the temperature, with pressure having an almost negligible effect. This is true even for minor constituents (CH_2O, COS, HCN, H_2S, NH_3). Data also clearly indicate that starting with propellants having similar elemental composition, one can expect similar major and minor combustion products. The theoretical calculations predict the order of magnitude of major species formation to within a factor of ≈2 or less and for the minor species, a factor ≈30 or less. Computer programs have been successful in predicting the ballistic properties of propellants and associated major product distributions. However, the reliability of the theoretical prediction for the minor products is both qualitatively and quantitatively less certain. This conclusion is supported by the observations of Stiefel and Hody (1970) and Rocchio and May (1973).

However, in the current context, chemical measurements and computer data should be viewed as complementary methods that should be used together to improve the accuracy of toxic hazard prediction in the military environment. Computer calculations are also useful in alerting the chemist to species they may encounter during analysis. Computer data also suggest that more effort should be spent in evaluating the contribution of reactive species such as free radicals to the overall toxicity of the exhaust products (Stiefel and Hody 1970). However, this view is now discounted. Instead, more attention needs to be given to the problem caused by interaction of the exhaust with the surrounding air. If the reaction is rapid, it may be accompanied by secondary flash. Absence of visible flash does not preclude reaction. The computer programs usually stop at the point where the bullet exits the muzzle and have not been extended to include the muzzle gas/air interaction. Some of the discrepencies between predicted and experimental results can probably be traced to this (Stiefel 1985).

TABLE [illegible] SPECIES PREDICTED BY COMPUTATION BUT NOT DETECTED BY CHEMICAL EXPERIMENTS

Component	Typical Mole Fraction Predicted	Pressure Used for Calculation psia[a]	Propellant
[illegible] Hydrogen	[illegible]	14.7	N-5
[illegible]	[illegible]	10,000	WC 846
[illegible]	[illegible]	14.7	N-5
[illegible]	[illegible]	14.7	N-5
[illegible]	[illegible]	10,000	WC 846
[illegible]	[illegible]	[illegible]	WC 846
[illegible]	[illegible]	[illegible]	WC 846
[illegible] Methane	[illegible]	[illegible]	WC 846
[illegible] Methane	[illegible]	[illegible]	WC 846
[illegible]	[illegible]	[illegible]	WC 846
[illegible] Ammonia	[illegible]	[illegible]	WC 846
[illegible]	[illegible]	[illegible]	WC 846
[illegible]	[illegible]	[illegible]	WC 846

a. Pressure [illegible].

Adapted from a Stanford [illegible] 1[illegible]

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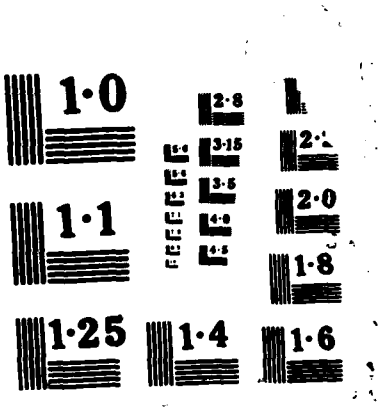
1·0
2·8
3·15
3·5
4·0
4·5
1·1
2·0
1·8
1·25
1·4
1·6

TABLE 2.34. COMPONENTS REPORTED BY CHEMICAL ANALYSIS BUT NOT PREDICTED IN THE COMPUTATION RESULTS

Component	Typical Mole Fraction	Weapon
Cyanogen	0.50 E-03	All
Carbonyl sulfide	0.10 E-03	Both machine guns
Benzene	0.10 E-04	7.62-mm machine gun
Acetaldehyde	0.50 E-03	Caliber 0.50 machine gun
Hydrogen chloride	Trace	Rocket plume only
Sulfur dioxide	Trace	Rocket plume only
Copper and lead	50 mg/m^3 urban air	Both machine guns

Adapted from Stiefel and Hody (1970).

TABLE 2.35. COMPARISON OF COMPUTED AND OBSERVED GAS COMPOSITIONS

	Results (mole fraction)				
	Computed Results				
	1.0 atm	Adjusted for Condensation	Without Condensibles and Oxygen	Mass Spectrometer Results	Standard Deviation
			A-1 Composition		
HCl	0.1140				
H_2O	0.3794				
CO_2	0.1929	0.4722		0.535	
O_2	0.0771	0.1887		0.038	
N_2	0.1353	0.3312		0.408	
BHO_2	0.0291				
KCl	0.0605				
K_2CL_2	0.0085				
B_2O_3	0.0470				
			M10 Propellant[a]		
N_2	0.118	0.137		0.180	0.025
CO_2	0.230	0.267		0.213	0.025
CO	0.316	0.366		0.368	0.051
H_2	0.199	0.231		0.220	0.025
J_2O	0.138			0.008	
			B-3 Composition		
H_2O	0.2263			0.028	
CO_2	0.3229	0.5267	0.8324	0.717	
O_2	0.2252	0.3673		0.065	
N_2	0.0560	0.0913	0.1443	0.141	
KOH	0.0645				
KCl	0.0626				
K_2Cl_2	0.0288				
$K_2O_2H_2$	0.0047				

a. Mass Spectrometer results are for M10 black powder.

Adapted from Stiefel and VanArtsdalen (1965).

TABLE 2.36. COMPARISON OF EXPERIMENTAL AND CALCULATED PRODUCT CONCENTRATIONS FOR X-2374.13 PROPELLANT[a]

Species	Calculation	Measured	Species	Calculation	Measured
CO	1,000	1,000	C_2H_2	2.86×10^{-5}	>1[b]
H_2O	476	dnm[c]	C_2H_4	3.60×10^{-5}	
H_2	389		CNCN	1.57×10^{-8}	0.25
N_2	289	dnm	OH	5.97×10^{-4}	
CO_2	364	380	CN	1.45×10^{-8}	
KOH	3.34		HS	3.73×10^{-3}	
H_2S	1.65		SO	8.27×10^{-5}	
NH_3	3.66×10^{-1}	dnm	CH_3	$2.28 \times 1-^{-4}$	
HCN	3.69×10^{-2}	dnm	H	1.01×10^{-2}	
K	1.97×10^{-2}		KO	8.43×10^{-7}	
CH_2O	1.98×10^{-2}		O	1.28×10^{-8}	
COS	1.18×10^{-1}	0.25	N	3.10×10^{-10}	
NO	1.08×10^{-5}	dnm	C_3H_4	NI[d]	<0.1
SO_2	3.35×10^{-4}		C_3H_6	NI	0.1
CH_4	3.56×10^{-1}	1	C_3H_6	NI	<0.1
S	8.29×10^{-6}		C_2H_6	NI	dnm
O_2	7.27×10^{-9}	dnm			

a. Values are normalized to CO. [(Concentration of component/concentration of CO) x 10^3]
b. Measured value includes both C_2H_2 and C_2H_4.
c. Detected, but did not quantify.
d. Not included in these calculations.

Adapted from Rocchio and May (1973).

TABLE 2.37. COMPARISON OF THE EXPERIMENTAL AND THEORETICAL COMBUSTION PRODUCT DISTRIBUTION FOR SOME OF THE SPECIES FORMED FROM FIRING THE WC844 PROPELLANT IN THE VENTED TEST FIXTURE

	Expt. Data		Frozen Composition		Equilibrium Composition			
Species	$2x10^4$psi	$5x10^4$psi	$2x10^4$psi	$5x10^4$psi	$2x10^4$psi[a]	$5x10^4$psi[a]	$2x10^4$psi[b]	$5x10^4$psi[b]
H_2	18.12	18.04	15.50	15.16	15.50	15.17	20.56	16.59
N_2	11.30	12.60	10.80	10.79	10.80	10.79	11.11	11.32
CO	43.40	44.60	47.08	46.94	47.07	46.93	24.55	22.44
CO_2	12.23	12.55	9.41	9.59	9.43	9.59	24.99	25.55
H_2O	14.46	11.98	16.82	16.90	16.82	16.90	19.19	12.86
CH_4	0.309	0.127	0.077	0.140	0.018	0.140	1.31	2.27
NH_3	$2.11x11^{-2}$	$4.9x10^{-2}$	$3.7x10^{-2}$	$10.7x10^{-2}$	$3.7x10^{-2}$	$10.7x10^{-2}$	$0.6x10^{-2}$	$1.1x10^{-2}$
NO	$7.2\ x10^{-1}$	$8.3x10^{-1}$	$<5x10^{-4}$	$<5x10^{-4}$	$<5x10^{-4}$	$5x10^{-4}$	$<5x10^{-4}$	$<5x10^{-4}$

a. These product compositions were calculated at the stated pressures and a temperature of ~2,280 K at the rocket chamber exit without any exhaust gas expansion.

b. The product compositions were calculated for the stated initial pressures in the rocket combustion chamber but with subsequent expansion to almost atmospheric pressure and a temperature in the range of 950-1000 K.

Adapted from Snelson et al. (1983).

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3. ANALYTICAL AND SAMPLING METHODS FOR DETERMINING COMBUSTION PRODUCTS

This section includes a description of the techniques and methods for sampling and analyzing combustion products of various materials, namely tobacco, diesel fuel, and gasoline. In general, these substances yield highly complex and reactive combustion products. It should be noted, however, that combustion processes in a diesel or gasoline engine or in a burning cigarette are very different from those of a propellant fired by a weapon. A major difference noted by Klein and Keller (1979) between propellant combustion and other types of combustion processes is that the fuel and oxidizer are homogeneously distributed in a gun propellant so that mixing and reactant distribution apply only to intermediate species produced during the reaction. In a gasoline or diesel engine the fuel and oxidizer (air) are added separately, mixed, and then burned in a combustion chamber. The temperatures, pressures, and other conditions of combustion are also greatly different. A modern gun propellant can reproducibly release heat in excess of 1 kJ/g, generate temperatures in excess of 2,700°C, and pressures greater than 350 MPa in less than a millisecond (Klein and Keller 1979). Chemical transformations are very rapid and the reactions are complex oxidations and reductions.

Despite the differences in the combustion processes of different materials, similar products may be formed, and the methods for determining the various constituents or compound classes will be similar. In general, automobile exhaust and the smoke generated from cigarettes have been well characterized; the combustion products of gun propellants have not. Further, irrespective of the source of the combustion products, all determinations involve detection, identification, and quantitation of the individual constituents. Sensitive, accurate methods that can resolve the various compounds are required.

This chapter specifically focuses on analytical and sampling methodology used to determine the composition of the combustion products of the materials mentioned, with emphasis on methods for constituents that may be present in gun exhaust. The review is not designed to provide a comprehensive listing of all available methods but rather of the most recent commonly used techniques. Problems that have been encountered or areas that still require additional attention are noted. The chapter concludes with recommendations for techniques that appear to be most suitable for determining the chemical composition of weapons exhaust.

3.1 GASOLINE ENGINE EXHAUST EMISSIONS

The incomplete combustion of fuels used in automotive vehicles results in emissions of unburned hydrocarbons, carbon monoxide, oxides of nitrogen, sulfur compounds, and particulates including lead compounds. These are all considered to be pollutants and are hazardous depending upon concentrations and exposure levels. Other compounds are also formed in the gasoline combustion engine (water vapor, hydrogen, carbon dioxide, etc.), but these are in general not of significant concern and are not addressed in this report. The mechanisms for the formation of these various constituents and their emission rates are

related to a variety of factors including engine type (carburetor-type spark-ignition, port-fuel-injection spark ignition, cylinder fuel-injection spark-ignition) and engine operating conditions (transient vs. steady state, for example). A detailed discussion of these factors is beyond the scope of this work. Instead the reader is referred to a text that reviews the chemistry (kinetics and mechanism) of combustion processes and emission formation in various engines (Springer and Patterson 1973). However, some general statements can be made concerning exhaust emissions. The engine itself may be thought of as a chemical reactor with most of the undesirable chemical compounds being formed as a result of arrested chemical reactions. Most hydrocarbons, for example, derive from an air-fuel mixture that is too rich or too cool for complete oxidation. Nitric oxide is found in the exhaust because of low oxygen concentrations and the rapid decrease in temperature of the post-flame gases. Carbon monoxide is also a result of low oxygen concentrations and slow kinetics during expansion of the post-flame gases. It should be noted that similar conditions (i.e., limited oxygen availability) are responsible for the generation of the same types of compounds in gun exhaust. Some of the major exhaust components of gasoline and diesel engines are listed in Table 3.1 (Colgrove 1980).

Gasoline itself is composed of C_4 to C_{12} hydrocarbons and has a lower and upper explosive limit of 1.3 to 6 percent (volume) in air, respectively (Windholz et al. 1983). Commercial grades contain saturated hydrocarbons, olefins, and aromatics and are obtained by cracking heavy petroleum fractions. Gasolines sold in the United States also may contain small quantities of tetraethyl lead (3 mL gal of fuel or less). Commercial grades of tetraethyl lead (TEL) contain approximately 63 percent TEL and 35 percent ethylene dichloride or dibromide, which help remove lead combustion products from the engine. Other compounds may also be blended in with the material (e.g., benzene or ethanol). The composition of the fuel affects vehicle exhaust composition. Tetraethyl lead has been determined to influence the combustion of other fuel constituents (either promoting or inhibiting various reactions) and specifically leading to the production of lead compounds. Polynuclear aromatic content in the exhaust may also be associated with the aromatic content of the fuel (Springer and Patterson 1973).

3.1.1 Sampling Methods

Springer and Patterson (1973) have described three commonly used sampling methods for collecting exhaust emissions: total sample collection, constant volume sampling, and variable-rate proportional sampling. The most direct method involves total collection of the gases produced during a test period. In general, the exhaust is collected in an inflatable plastic bag from which samples for individual analyses are then removed. Although the method is simple, difficulties may be encountered in collecting and handling large sample volumes, maintaining sample integrity, and minimizing contamination. In constant-volume sampling (CVS) the exhaust is continuously mixed with a diluent gas (usually air) at a rate that maintains a constant total flow. Measurements are then made on samples withdrawn at a constant rate from the diluted exhaust stream. For direct "on-line" analyses the signals

TABLE 3.1. SOME OF THE EXHAUST COMPONENTS OF GASOLINE AND DIESEL ENGINES

Component	Gasoline Engine	Diesel Engine
Carbon monoxide	0.5-12 vol %	0.01-0.50 vol %
Aldehydes	0-0.2 mg/L	0.001-0.009 mg/L
Hydrocarbons	0.2-3.0 vol %	0.009-0.5 vol %
Nitrogen oxides (as N_2O_5)	0-0.8 vol %	0.0002-0.5 vol %
Water vapor	3-5.5 vol %	0.5-4.0 vol %
Carbon dioxide	5-12 vol %	1-10 vol %
Soot	0-0.04 g/m^3	0.01-1.1 g/m^3
3,4-Benzpyrene	10-20 $\mu g/m^3$	0-10 $\mu g/m^3$

Adapted from Colgrove (1980).

are integrated, time-averaged, and combined with volumetric data to obtain average concentration values. An advantage of this sampling method is that total gas-volume emission measurements can be easily obtained using calibrated pumps. The gases, however, need to be handled at constant temperature and pressure, and the diluent gas must be free from interfering impurities. In variable-rate sampling (VRS) the exhaust is withdrawn at a rate proportional to the exhaust flow so that the volume of sample collected is a fixed fraction of the total exhaust volume during the sampling period. It requires sensors to provide signals of engine air-intake rates and sample withdrawal rates, an electrical network to compare the two, and a servo system that will automatically regulate sample to air flow. The exhaust gases are collected in sampling bags partially filled with dry nitrogen to minimize possible further reactions of the products. This sampling procedure is relatively complex and is used primarily in research operations. Both CVS and VRS systems require a continuously generated exhaust stream. Since gun exhaust is produced itermittently in short bursts as a weapon is fired, these sampling methods are not appropriate for gun emissions.

Other sampling methods that have been used involve the collection of a particular fraction (e.g., gaseous vs. particulate phase), compound class, or compound and are discussed in greater detail in the analysis sections. References for various sampling methods may also be obtained from Colgrove (1980).

3.1.2 Particulate Emissions

Samples may be collected directly from the exhaust system or from the atmosphere outside of the exhaust system. In the latter case the effects of fuel composition and various engine parameters cannot be ascertained directly since emissions from other sources may contribute to the sample. The method does, however, provide general information (e.g., variations in total particulate matter as a function of traffic volume in a given area). In the case where the exhaust is sampled directly, several factors must be taken into consideration (Springer and Patterson 1983). The gas velocity in the sampling probe must be equal to that of the stream at the inlet of the probe (i.e., isokinetic) to minimize bias in the collection of smaller or larger particulates. Losses of particulates and condensation in the sample probe and sample line should also be avoided. This requirement may necessitate placing the sample probe in a constant temperature chamber. Finally, the sampling time must be of sufficient duration to provide representative results. Figures 3.1, 3.2, and 3.3 show three sampling arrangements for collecting particulates from auto exhaust.

Total particulate emission rates are generally expressed in terms of weight per unit distance traveled (g/mile). They have been shown to vary with engine operating conditions (e.g., cold start vs. continuous operation, engine speed, acceleration vs. deceleration, exhaust gas temperature) and fuel composition (e.g., leaded vs. unleaded). The particles are believed to be formed primarily in the exhaust stream as a result of vapor phase condensation with some enhancement from coagulation. The smaller particles are emitted directly; larger ones may

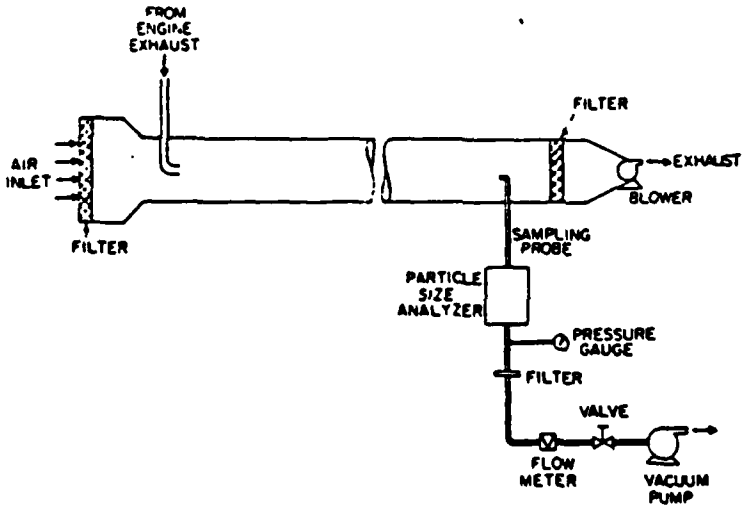

Figure 3.1. Schematic of apparatus for collecting particulates from exhaust diluted with air. Source: Springer and Patterson (1973).

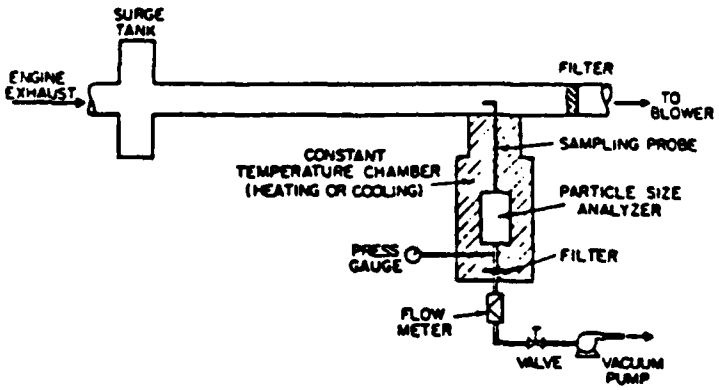

Figure 3.2. Schematic of apparatus for sampling the exhaust directly. Source: Springer and Patterson (1973).

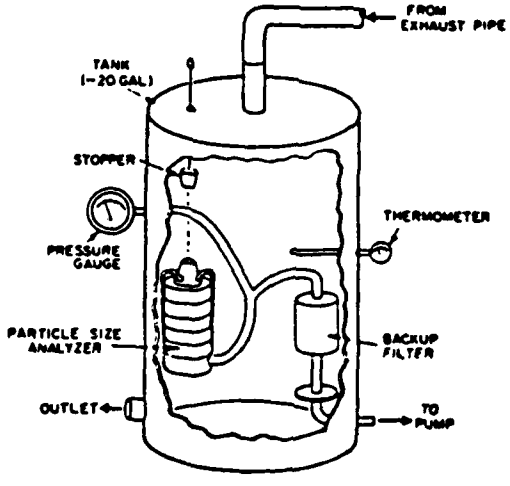

Figure 3.3. Schematic of apparatus for sampling undiluted auto exhaust directly from the exhaust pipe. Source: Springer and Patterson (1973).

settle on the walls of the exhaust system, where they may be removed with sudden changes in flow rate (as during acceleration). Solid particulates may also be formed on the combustion chamber walls from dehydrogenation and polymerization of the fuel, followed by agglomeration. Particle shape has not been extensively investigated although micrographs show evidence of both single crystals and aggregates. Particle diameters may be determined from inspection of micrographs, from the intensity and direction of scattered light off the particles, or from particle deposition on the various stages of a cascade impactor. The size distribution has also been shown to be a function of various engine and fuel parameters. The mass median equivalent diameter (MMED) is determined from the log-normal size distribution of the particles.

3.1.3 Chemical Analysis of Particulate Matter

The particulate exhaust from automobiles is composed of both organic and inorganic constituents. In fuels with lead additives, lead comprises the largest weight fraction. Other constituents include bromine, chlorine, carbon, various elements (primarily iron and zinc), and organic compounds. Lead is present not only in elemental form but also as lead halide and complexes of ammonium halide and lead halide (Springer and Patterson 1983). The various metals and metal compounds are ordinarily collected on membrane filters, digested in acid solution, and determined by atomic absorption or inductively coupled plasma spectroscopy (NIOSH 1984). The organics are also sampled on filters, which are then solvent extracted (Soxhlet or batch procedures). They may then be fractionated into chemical classes by liquid chromatography and finally analyzed by GC, HPLC, or GC-MS. More detail on the analysis of organics in particulates, including PAHs and nitro-PAHs, is given in Section 3.2.

3.1.4 Carbon Monoxide

The standard method for measuring CO emissions and for certifying some automotive exhausts is by nondispersive infrared absorption spectroscopy. Principles of operation of a nondispersive infrared (NDIR) analyzer and calibration methods are discussed in Patterson and Henein (1972) and Springer and Patterson (1973). Other gases, namely water vapor, CO_2, and organic vapors, present in the exhaust may interfere with CO determinations, especially at low CO levels (i.e., below 0.2 percent). This can generally be overcome by using an optical filter. The method can provide continuous analysis and has a detection limit of approximately 1 mg/m^3.

Greater specificity can be obtained with gas chromatographic methods. A thermal conductivity detector will provide sensitivity in the low ppm range. Alternatively, catalytic reduction of CO to methane followed by flame ionization detection can be used.

3.1.5 Oxides of Nitrogen

The oxides of nitrogen emitted from gasoline engines are primarily nitric oxide (NO) and nitrogen dioxide (NO_2). They can be readily

determined with a chemiluminescence analyzer (Springer and Patterson 1973). In this instrument NO is reacted with ozone to produce NO_2, a certain amount of which will be present in an excited state. These excited molecules decay to ground state with the emission of light. The intensity of the emission is measured with a photomultiplier and is proportional to the concentration. The sum of NO and NO_2 (NO_x) is determined in the same manner after the initial reduction of NO_2 to NO. The difference between the NO_x and the NO measurements provides NO_2 concentrations. Sub-ppm levels can be determined with this method. The effects of other chemiluminescent reactions that may interfere in the analysis such as ozone with CO, ethylene, or other compounds may be eliminated by filtering wavelengths shorter than 0.6 μm. Nitric oxide has also been determined by NDIR, although water vapor strongly interferes and the sample must be dried prior to measurement. Concentrations of NO_2 above 5 ppm can be determined by nondispersive ultraviolet absorption. Chemiluminescence, however, remains the most sensitive and selective method. Portable chemiluminescent monitors are commercially available.

3.1.6 Hydrocarbons

The exhaust from automobiles can be sampled directly and continuously for total hydrocarbon analysis. Other sampling methods include absorption of the gaseous organic vapors on adsorbents (such as Tenax), cryogenic trapping, or collection in containers. A general discussion on the sampling and identification of organics in air is given by Schlitt et al. (1980). The standard method for determining total hydrocarbons is by flame ionization detection. It offers high sensitivity and a wide dynamic range (10^6). Greater detail on the composition of the exhaust may be obtained by various gas chromatographic methods or by GC-MS analysis. The greatest resolution is obtained with small-bore capillary columns. The organic exhaust component has been found to contain hundreds of constituents including about 50 percent aliphatic compounds, 5 percent PAHs, and 30 percent oxygenated compounds (Colgrove 1980). The hydrocarbons are primarily in the C_1 to C_{12} range. Some specific compounds that have been identified are listed in Table 3.2 (Colgrove 1980). References on the effects of automobile engine parameters (e.g., air fuel ratio, engine speed, spark timing, intake manifold pressure, etc.) on the hydrocarbon emissions can be found in (Colgrove 1980).

3.1.7 Oxygenated Compounds

Of the several classes of oxygenated organic compounds, the aldehydes are quantitatively the most important in engine exhaust (Springer and Patterson 1973). They are produced as a result of the partial oxidation of hydrocarbons, primarily during the low-temperature preflame reactions within the combustion chamber (Patterson and Henein 1972). The predominant species are formaldehyde and acrolein. Collection procedures for the oxygenates generally involve passing a known volume of exhaust through scrubbers or impingers that contain reactive derivitizing reagents (NIOSH 1984; Seizinger and Dimitriades 1972; Melcher and Langhorst 1985). The resulting complexes can often be analyzed

TABLE 3.2 SOME HYDROCARBONS FOUND IN GASOLINE ENGINE AUTOMOBILE EXHAUST

Hydrocarbon	Hydrocarbon
Methane	3-Methyl-trans-2-pentene and/or
Ethane	3-Methyl-cis-2-pentene
Ethylene	Methylcyclopentane
Acetylene	2,4-Dimethylpentane
Propylene	2,2,3-Trimethylbutane
Propane	3,4-Dimethyl-1-pentene
Cyclopropane	4,4-Dimethyl-cis-2-pentene
Propadiene	3,3-Dimethylpentane
Methylacetylene	Benzene
Isobutane	Cyclohexane
Isobutylene and/or 1-Butene	3,Ethyl-1-pentene
1,3-Butadiene	5-Methyl-1-hexene
n-Butane	4-Methyl-1-hexene
trans-2-Butene	2-Methylhexene and/or
cis-2-Butene	2,3-Dimethylpentane
3-Methyl-1-butene	Cyclohexene
Isopentane	3-Methylhexane
1-Pentene	2,2,4-Trimethylpentane
2-Methyl-1-butene	1-Heptene
n-Pentane	trans-3-Heptene
2-Methyl-1-1,3-butadiene	n-Heptane
trans-2-Pentene	cis-3-Heptene and/or
cis-2-Pentene	3-Ethyl-trans-2-pentene
2-Methyl-2-butene	2,4,4-Trimethyl-1-pentene and/or
2,2-Dimethylbutane	trans-2-Heptene
Cyclopentene	cis-2-Heptene
4-Methyl-1-pentene and/or	2,5-Dimethyl-trans-3-hexene
3-Methyl-1-pentene	*Methylcyclohexane*
Cyclopentane	2,4,4-Trimethyl-2-pentene
2,3-Dimethylbutane	4-Methylcyclohexene
2-Methylpentane	2,4-Dimethylhexane and/or
4-Methyl-cis-2-pentene	2,5-Dimethylhexane
3-Methylpentane	2,2,3-Trimethylpentane
2-Methyl-1-pentene and/or	4-Methylheptane
1-Hexene	2,3,4-Trimethylpentane
2-Ethyl-1-butene	Toluene
n-Hexane	2,3,3-Trimethylpentane
trans-3-Hexene	2,5-Dimethyl-trans-2-hexene
trans-2-Hexene	2-Methyl-3-ethylpentane and/or
2-Methyl-2-pentene	2,3-Dimethylhexane
cis-3-Hexene	3,4-Dimethylhexane and/or
cis-2-Hexene	3-Methylheptane
2,2,5-Trimethylhexane	1-Methyl-2-ethylbenzene
1-Octene	t-Butylbenzene
trans-2-Octene	1,2,4-Trimethylbenzene
Dimethylheptane	Isobutylbenzene
cis-2-Octene	sec-Butylbenzene
cis-1,2-Dimethylcyclohexane	1-Methyl-3-isopropylbenzene
Ethylcyclohexane	n-Decane
Ethylbenzene	1,2,3-Trimethylbenzene
m-Xylene and p-Xylene	1-Methyl-4-isopropylbenzene
o-Xylene	1,3-Diethylbenzene
2-Methyloctane	n-Butylbenzene and/or
n-Nonane	1-Methyl-4-n-propylbenzene
Isopropylbenzene	1,3-Dimethyl-5-ethylbenzene and/or
n-Propylbenzene	1,2-Diethylbenzene
1-Methyl-4-ethylbenzene and/or	1-Methyl-2-n-propylbenzene
1-Methyl-1,3-ethylbenzene	Durene
1,3,5-Trimethylbenzene	1-Dodecene

Adapted from Colgrove (1980).

spectrophotometrically. Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) has been extensively used to determine formaldehyde. Aromatic hydrocarbons may interfere in the analysis, but the effects can be reduced by adding 1 percent sodium bisulfite to the absorbing solution. The Girard-T method with polarographic measurement and the 3-benzyloxazolidine method with gas chromatographic-flame ionization detection (GC-FID) can also be used. All three methods have validated by NIOSH (1984) for determining formaldehyde in air. Acrolein can be trapped on XAD-2 resin coated with 2-(hydroxymethyl)piperidine and determined by GC with a nitrogen-specific detector (NIOSH 1984). Total aliphatic aldehydes can be determined by derivatization with 3-methyl-2-benzothiazolone hydrazone (MBTH) or with 2,4-dinitrophenylhydrazine (DNPH) (Opresko et al. 1984). Detection limits are 0.04 and 0.2 ppm, respectively. Individual aldehydes can also be determined by generating the DNPH derivatives followed by GC or HPLC. Other oxygenates that have been identified in the exhaust from gasoline fuels include ketones, alcohols, ethers, esters, nitroalkanes, and phenols. Methods for estimating levels of carbonyl and noncarbonyl compounds have been developed (Seizinger and Dimitriades 1972).

3.1.8 Sulfur Compounds

Dietzmann et al. (1979) have described analytical procedures for determining sulfur-containing compounds in automotive emissions. Sulfur dioxide is collected in impingers containing a hydrogen peroxide solution as the absorbing reagent and determined as sulfate by ion chromatography. Sulfate already present in the exhaust is removed with a Fluoropore filter during sample collection to eliminate its interfering effects. Hydrogen sulfide is determined by a colorimetric procedure. A sample is bubbled through a zinc acetate absorbing solution, which is then treated with N,N-dimethylparaphenylenediamine sulfate and ferric ammonium sulfate. The formation of methylene blue, which is detected by visible absorption spectroscopy, indicates the presence of H_2S. Total sulfate is measured by use of a barium chloroanilate procedure. Samples are collected on particulate filters, leached from the filter, and analyzed by ion exchange HPLC using a post-column reaction detector. Organic sulfides (e.g., carbonyl sulfide, methyl sulfide, and ethyl sulfide) are trapped on sorbent resin (Tenax) cartridges, which are then thermally desorbed for analysis by GC with flame photometric detection.

3.2 DIESEL ENGINE EXHAUST

Diesel fuel (DF) differs from gasoline in several important respects, both chemically and physically. Bulk properties of a reference fuel (DF-2) are compared with two representative naphthas or gasolines in Table 3.3. The DF is a more dense, more viscous, higher-boiling mixture than are the naphthas. The density is 0.06 to 0.11 g/cm^3 greater, and the average and final boiling points are approximately 100°C greater than those of the naphthas. The flash point of DF also is much higher than those of the naphthas. However, the aromaticity of DF, as defined by a fluorescent indicator assay, falls within the range of the naphthas.

TABLE 3.3. COMPARISON OF BULK PROPERTIES OF A REFERENCE DIESEL FUEL AND NAPHTHAS[a]

	Phillips Reference DF-2[b]	API Light Catalytically Cracked Naphtha	UOP Reformed Light Arabian Naphtha
Density, g/cm^3 25°C	0.844	0.730	0.781
Viscosity, cSt 25°C	3.35	0.57	0.67
Flash Point, °C	74	<-35	-22
Simulated Distillation,[c] °C			
IBP	186	148	152
ABP	271	154	167
FBP	320	197	223
FIA[c]			
Aromatics	29.1[d]	20.3[e]	54.2[f]
Olefins		29.6[e]	0.8[f]
Paraffins + Naphthenes		50.0[e]	45.0[f]

a. Guerin 1978, unless otherwise noted.
b. Data from Jenkins et al. 1983.
c. IBP = initial boiling point (0.5% distillation point).
ABP = average boiling point (50% distillation point).
FBP = final boiling point (99.5% distillation point).
FIA = Fluorescence Indicator Assay
d. Data supplied by the Phillips Chemical Company, Bartlesville, OK.
e. Data from the American Petroleum Institute, Washington, DC.
f. Data from the Universal Oil Products, Inc. (now Signal Research Center, Inc.), Des Plaines, IL.

The chemical differences account for these physical differences. The DFs are basically composed of higher-boiling compounds, whereas gasoline consists largely of C_4-C_{11} branched and normal chain alkanes, alkenes, and benzene and C_1-C_3 alkylated benzenes (Rooney 1978; Guerin 1978). The major components of DF are C_8-C_{25} normal alkanes at concentrations of <0.1 to 3 weight percent (each component) (Jenkins et al. 1983; Griest et al. 1985; Petrovic and Vitrovic 1976). Less concentrated major components in DF consist of numerous C_3-C_5-benzenes, naphthalene, C_1-C_4-naphthalenes (especially 2-methylnaphthalene, 1-methylnaphthalene, and several dimethylnaphthalenes), C_1-C_3-biphenyls/acenaphthenes, fluorene, and phenanthrene, and C_1-C_3-phenanthrenes (Jenkins et al. 1983; Griest et al. 1985; Reinhard et al. 1976). An important difference between DF refined from shale oil versus that from petroleum is that the former contains lower levels of alkylated two- and three-ring aromatic hydrocarbons. Both shale oil- and petroleum-derived DF contain sub-ppm concentrations (0.03-0.8 ppm) of benzo(a)pyrene (Griest et al. 1985); unleaded gasolines and reformed naphthas may contain slightly higher concentrations of 1-3 ppm (Guerin 1978).

Methodology for sampling and analysis of diesel engine exhaust appears to have some potential for the characterization of the exhaust from projectile weapons firing. The combustion products of both are aerosols consisting of gaseous (vapor) and particulate phases. The discussion in this section specifically focuses on organics in the vapor and particulate phases of diesel exhaust. Other gaseous constituents or inorganic compounds that are also present may be determined by methods described for gasoline emissions (see Section 3.1) and are not readdressed here.

The particulate phase of diesel engine exhaust is best sampled currently by filtration on Teflon filter media. Soxhlet solvent extraction followed by normal phase chromatographic separation is used to prepare chemical fractions suitable for analysis by capillary column GC (using both general and compound-type specific detectors), GC-MS, and high-performance liquid chromatography (HPLC) (with ultraviolet absorbance or fluorescence detectors). Compound classes of particulate organic matter identified in diesel engine exhaust include aliphatic hydrocarbons, two- through six-ring PAHs, azaarenes, and nitro- and oxygenated- (and mixed) derivatives of PAH and azaarenes. Much research, however, is needed for improvement of sampling, and analytical procedures, particularly for minimizing artifact formation during sampling and improving the resolution and measurement of trace levels of highly polar organic compounds.

The characterization of organic compounds in the vapor phase of diesel engine exhaust has received less attention. Vapor phase organic compounds are best collected through use of sorbent resins and are analyzed by capillary column GC after thermal desorption or solvent extraction. At the present, XAD-2 resin is used most often for collection of vapor phase PAHs, and more volatile species are better collected on Tenax resin. Quantitative data for the vapor phase are much more

limited than for the particulate phase, and most studies report only qualitative identifications.

Although the distinction between vapor phase and particle phase is often complicated by sorption, evaporation, and sublimation processes, representatives of the same classes of compounds are found in both phases. Vapor phase species identified include branched and straight chain alkanes, alkenes, cycloparaffins, alkylated mono- and diaromatic hydrocarbons, thiophenes, and a host of aldehydes, ketones, phenols, and carboxylic acids.

3.2.1 Characterization of Particulate Phase Organic Compounds

Particulate matter is traditionally collected from diesel engine exhaust by passing a portion of the exhaust stream from an air-dilution tunnel through a filter. Electrostatic precipitation also is used, but much less extensively. The engine exhaust is diluted approximately 10-fold with filtered air in the tunnel and is drawn via a vacuum pump through a filter. Because of the air dilution, the sampling can be conducted at temperatures as low as 37 to 39°C (Gibson et al. 1981; Lee et al. 1980) to reduce evaporation or sublimation of semivolatile organic compounds from the particulate matter. However, even at this temperature, the flow rates (approximately 50 to 900 L/min) and volumes (0.6 to 100 m^3) of gases passing through the filter cause loss of organic matter into the vapor phase. This is not expected to be a serious problem in sampling gun exhaust. In this case the exhaust is not produced continuously but rather in discrete increments when a weapon is fired. Since the exhaust volume is lower, sampling volumes can be reduced accordingly.

Teflon filter media are clearly preferred for their superior inertness (Lee et al. 1980) over glass and quartz media. Pallflex T60A20 Teflon-coated glass fiber filters have emerged as the most popular filter (Obuchi et al. 1984; Schulze et al. 1984; Lee et al. 1980; Bechtold et al. 1984; Henderson et al. 1984; Henderson et al. 1982; Jin and Rappaport 1983; Breuer 1984; Henderson et al. 1983; Clark et al. 1982).

Alteration of the compounds collected on the filter by reaction with gaseous components (especially ozone and oxides of nitrogen) in the exhaust during sampling is a major problem requiring clarification. It is generally accepted that PAH in particulate matter can react with nitrogen oxides to form nitro-PAH. The extent of reaction is a subject of much controversy; some studies (Hartung et al. 1984) suggest that less than 20 percent of 1-nitropyrene is artifactual while others (Gibson et al. 1981) suggest higher percentages of artifact formation. Differences in sampling protocol and exhaust composition complicate the comparison of such studies. Particles collected by electrostatic precipitation (Hartung et al. 1984) reportedly show much higher concentrations of nitro-PAH than do filtered samples, indicating greater artifact formation.

The collected particulate samples are solvent-extracted and analyzed by a variety of chromatographic or spectroscopic methods,

usually with some form of fractionation of the crude extracts before the final analysis is conducted. Both soxhlet (Hartung et al. 1984; Obuchi et al. 1984; Schulze et al. 1984; Gibson et al. 1981; Lee et al. 1979; Swarin and Williams 1980; Lee et al. 1980; Henderson et al. 1984; Henderson et al. 1982) and ultrasonic solvent extraction (Bechtold et al. 1984; Jin and Rappaport 1983; Clark et al. 1982; Tomkins et al. 1984) are used to remove organic matter from the particles. Dichloromethane is the most widely used solvent, but one study (Breuer 1984) indicated that for PAH, toluene is as effective, and others (Swarin and Williams 1980; Williams and Chock 1981) demonstrated that a binary solvent composed of a nonpolar aromatic hydrocarbon and a polar alcohol (benzene:ethanol, 80:20) is more efficient. Extraction recoveries depend on the type of particles extracted and the concentrations of the organic compounds (Tomkins et al. 1984).

Analysis of the crude filter extract for semivolatile compounds is best accomplished by capillary column GC (see Figure 3.4 and Table 3.4). This method is superior to packed column GC or HPLC because of its high efficiency in terms of both resolving power and speed of analysis. It is the method of choice for complex mixtures of organic compounds having thermal stability and volatility. Typically, bonded stationary phase, fused silica columns of 30- to 60-m length and 0.25- to 0.32-mm inside diameter are utilized with helium or hydrogen carrier gases at flow rates of 1 to 2 mL/min and at temperatures programmed from about 80° to 280°C. As shown in Figure 3.4, the major chromatographable organic compounds (those present at levels >0.1 mg/g) present in the crude extract of the particulate filter are readily determined (Griest and Tomkins 1985). The major species are seen to be a series of n-paraffins ranging from C_{15} to at least C_{30} at levels of 0.1 to 7.4 mg/g. Pristane and phytane also are prominent. These components are attributed (Karasek et al. 1974) to unburned fuel in the exhaust. The minor peaks (corresponding to those compounds present at ≤0.1 mg/g) visible in the profile correspond to branched aliphatic hydrocarbons and two- through four-ring PAHs and their alkyl derivatives. The latter also may be partially derived from uncombusted fuel components (Henderson et al. 1984). The unresolved hump in the GC profile corresponds to organic matter that is not particularly amenable to GC analysis and is thought to represent higher-molecular-weight compounds with multiple chemical functional group substitution. This matter appears to be contributed in part by crankcase oil in the engine exhaust (Griest and Tomkins 1985; Williams and Chock 1981). Organic matter with molecular weights exceeding 5,000 (based on polystyrene standardization in gel permeation chromatography) is present on the particles.

Much more detailed analyses of the compounds present in diesel exhaust particulate matter can be achieved by separation of the crude particulate extract into chemically more well defined and relatively less complex fractions. Among the fractionation procedures employed are (1) normal (Hartung et al. 1984; Schulze et al. 1984; Jin and Rappaport 1983) and reverse phase (Obuchi et al. 1984) liquid chromatography on disposable cartridges; (2) semipreparative scale, normal phase

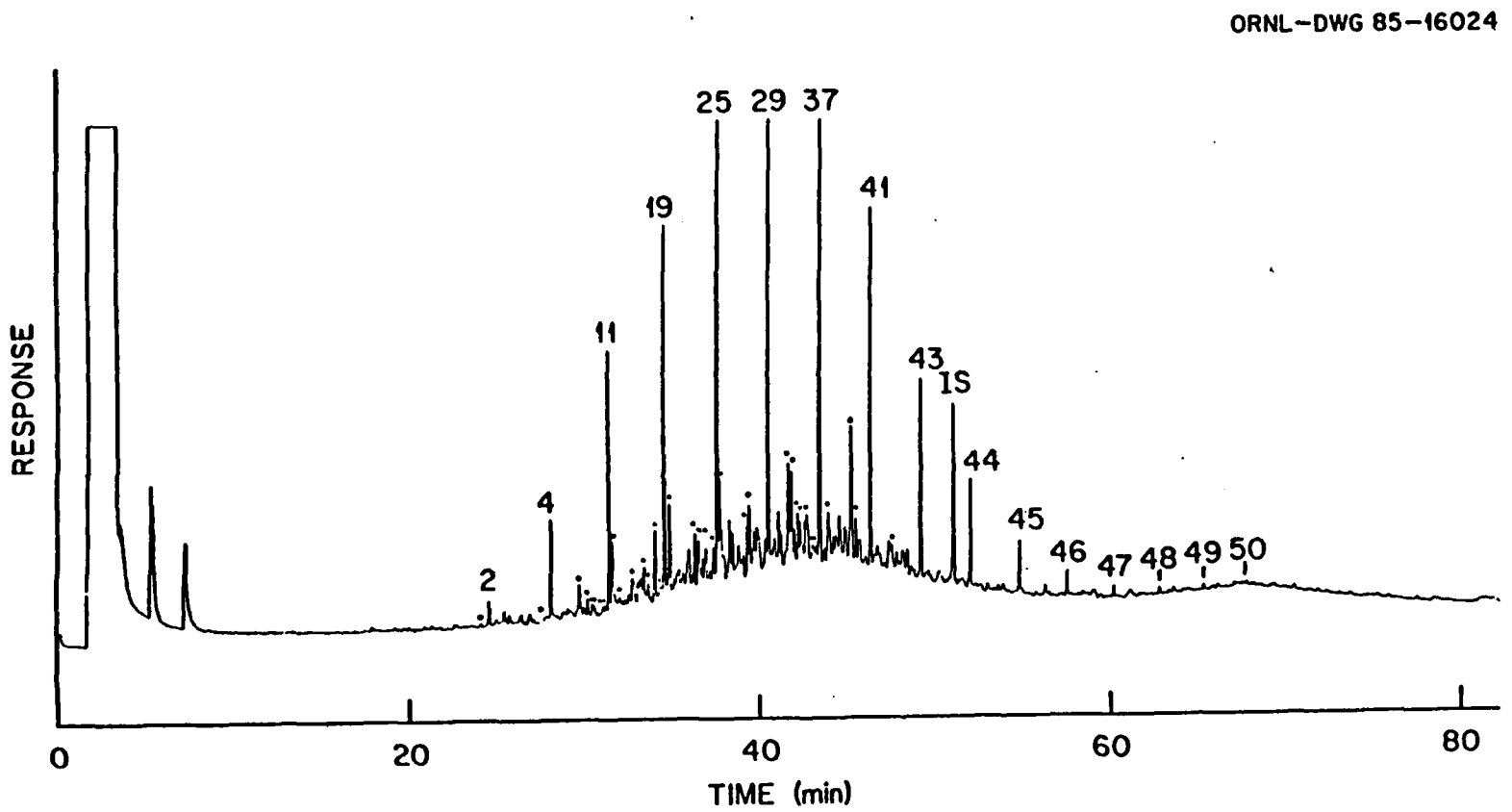

Figure 3.4. Capillary column gas chromatographic determination of major organic compounds in crude solvent extract of diesel engine exhaust particulate (see Table 3.4 for peak identification). Source: Griest and Tomkins (1985).

TABLE 3.4. SUMMARY OF MAJOR CHROMATOGRAPHABLE ORGANIC COMPOUNDS IN DIESEL EXHAUST PARTICULATE MATTER

Chemical Class	Examples		
	Compound	Concentration (mg/g)[a]	Peak Number[b]
Straight-chain alkanes	n-Pentadecane	0.17	2
	n-Hexadecane	1.0	4
	n-Heptadecane	5.3	11
	n-Octadecane	4.5	19
	n-Nonadecane	6.9	25
	n-Eicosane	7.4	29
	n-Heneicosane	7.0	37
	n-Docosane	4.9	41
	n-Tricosane	3.1	43
	n-Tetracosane	1.5	44
	n-Pentacosane	1.0	45
	n-Hexacosane	0.35	46
	n-Heptacosane	0.15	47
	n-Octacosane	<0.1	48
	n-Nonacosane	<0.1	49
	n-Triacontane	<0.1	50
Branched alkanes	Pristane	1.2	12
	Phytane	1.0	20
Di-/Triaromatic hydrocarbons	C_3-Naphthalene	<0.1	1
	Fluorene	<0.1	3
	Phenanthrene	1.5	17
	2-Methyl Phenanthrene	2.2	26
	C_1-Phenanthrene	0.7	24
	C_2-Phenanthrenes	0.3-2	30-32,36
	C_3-Phenanthrenes	1-3	39,40
	C_2-Acenaphthalene or C_1-Fluorene	<0.1	9,10
	Fluoranthene	1.1	33
	Pyrene	1.1	38
	Benzo(b)fluorene	0.5	42
Sulfur-heterocyclics[c]	Dibenzothiophene	0.5	14
	C_1-Dibenzothiophenes	0.7-1	21,23
Oxygenated aromatics[c]	Fluorenone	<0.1	13

a. Milligrams of compound per g of collected particles.
b. See Figure 3.4. Dotted peaks are number sequentially between the numbered peaks.
c. Tentative identification based upon mass spectrum.

Adapted from Griest and Tomkins (1985).

high-performance liquid chromatography (HPLC) (Tomkins et al. 1984); (3) adsorption column chromatography (Karasek et al. 1974); (4) organic solvent partitioning alone (Henderson et al. 1984) or in combination with adsorption thin layer (Mills et al. 1984) or gel permeation column chromatography (Henderson et al. 1982); and (5) acid/base extraction followed by normal phase column chromatography. These procedures are generally used to obtain fractions highly enriched in aliphatic hydrocarbons, PAH, nitro-PAH, and oxygenated PAH. Gas and liquid chromatography are used most often for analysis of these fractions. PAHs are determined by reverse phase HPLC with fluorescence detection (Obuchi et al. 1984; Gibson et al. 1981; Swarin and Williams 1980; Lee et al. 1980; Breuer 1984) and GC-MS (Henderson et al. 1984; Henderson et al. 1983; Karasek et al. 1974; Tong and Karasek 1984). Oxygenated PAHs have been identified and measured by GC-MS (Schulze et al. 1984). A variety of methods have been used for nitro-PAH. These methods should be particularly useful for weapons exhaust characterization because of the nitrocompounds used in the propellants. These methods include GC with the nitrogen-compound sensitive thermionic detector (Hartung et al. 1984) or the nitro-group selective thermal energy analyzer based on chemiluminescence (Tomkins et al. 1984), and by the electron capture detector after reduction to the amine and heptafluorobutyl derivatization (Morita et al. 1982). Microbore HPLC with reductive electrochemical detection (Lee et al. 1979) and triple quadrupole MS (Henderson et al. 1984; Henderson et al. 1982) also have been used. A recent comprehensive review (Tomkins 1986) describes the mechanisms, selectivities, and sensitivities of these detectors.

A summary of the main classes of particulate organic compounds that which have been identified and measured in diesel engine exhaust is presented in Table 3.5. Because of the considerable variability of exhaust composition, these results must be considered as examples. A discussion of the factors contributing to such variability is beyond the scope of this section, but the factors include engine size, speed, load, horsepower, condition, fuel, and lubricants.

3.2.2 Characterization of Vapor Phase Organic Compounds

Much less research has been conducted on the sampling and analysis of vapor phase organic compounds in diesel engine exhaust, but the available studies demonstrate that highly detailed analyses are possible. The available methods range from simple injection of undiluted exhaust into a GC to preconcentration in a solid sorbent resin or cryothermal trap. The sorbent resin methods appear most suited for gun smoke characterization.

The simplest method of analysis consists of drawing an undiluted sample of exhaust into a gas syringe and injecting the sample (via a splitter) onto a capillary column for analysis by GC (Hutte et al. 1984). This is a very simple and direct sampling method, but it lacks the sensitivity of methods relying upon preconcentration. Benzene, toluene, xylenes, and low boiling alkanes and alkenes were identified in diesel engine exhaust. For analysis of the most volatile compounds (e.g., methane and ethane) it is the only practical method.

TABLE 3.5. SUMMARY OF ORGANIC COMPOUNDS IDENTIFIED IN DIESEL EXHAUST PARTICULATE MATTER

Compound Class	Class Concentration	Example of Class		
		Compound	Compound Concentration, μg/g[b]	Reference
Oxygenated Aromatics	7-14[a]			c,d
Aromatic Dicarboxylic		Naphthalene-1,8-Dicarboxylic Acid Anhydride	-	c
Acid Anhydrides		Pyrene-3,4-Dicarboxylic Acid Anhydride	0.3[b]	e
Aromatic Aldehydes		1-Naphthalene Carboxaldehyde	68-168[a]	f
		Naphthalene Acetaldehyde	110-175[a]	f
		Acenaphthene Carboxaldehyde	12-26[a]	f
		Phenanthrene/Anthracene Carboxaldehyde	200-270[a]	f
Aromatic Ketones		9-Fluorenone	645-1,218[a]	f
		9-Xanthone	50-53[a]	f
		7H-Benz(de)anthrone	243-1,281[a]	f
		4H-Cyclopenta(def)phenanthrene-4-one	436-1,033[a]	f
Quinones		Anthraquinone	658-1,010[a]	f
		7,12-Benz(a)anthracene Quinone	75-169[a]	f
Phthalate Esters	1.1-2.7[a]	Bis(2-ethyl hexyl)phthlate	51-1,834[a]	f
		Dioctylphthalate	-	c
Phenols		Phenylpyrocatechol	-	g
		Phenylphenol	-	g
			10[b]	h
Nitrated Aromatic Hydrocarbons		1-Nitropyrene	5.6-8.5[b]	i
		6-Nitrobenzo(a)pyrene	0.9-1.8[b]	i
		1-Methyl-10-nitroanthracene	10[b]	h
		2-Nitronaphthalene	2.5[b]	j
		1,8-Dinitropyrene	0.8-1.2[b]	k
Oxygenated, Nitrated		2,4,7-Trinitro-9-fluorenone	0.4[b]	k
Aromatic Hydrocarbons		3-Nitro-1,8-naphthalic Acid Anhydride	10-23[b]	k
		2-Nitro-9-fluorenone	0.4[b]	k
Sulfur Heterocyclics	1.1-1.6[a]			f
		Dibenzothiophene	1320-540[b]	l
		Methyldibenzothiophene	34-36[b]	l
		Benzo(def)dibenzothiophene	29-40[b]	l
		Benzo(b)naphtho[2,1-d]thiophene	4.4-6.3[b]	l

Table 3.5. (Cont'd)

Compound Class	Class Concentration	Example of Class: Compound	Compound Concentration, μg/g[b]	Reference
Nitrogen Heterocyclics		Dibenz(a,h)acridine	-	m
		7,9-Dimethybenz(c)acridine	-	m
		7,10-Dimethylbenz(c)acridine	-	m
Nitrated Nitrogen Heterocyclics		Nitrobenzocoinnoline	-	n
		Nitroquinoline	-	
Aromatic Hydrocarbons	26-51[a]			f
	0.13[b]			j
		Fluorene	15-20[b]	l
		Phenanthrene	320-540[b]	l
		Fluoranthene	450-810[b]	l
		Pyrene	430-890[b]	l
		Pyrene	96-105[b]	i
		Benz(a)anthracene	60-120[b]	l
		Chrysene	97-170[b]	l
		Benzo(b)fluoranthene	62-122[b]	l
		Benzo(a)pyrene	25-62[b]	l
		Benzo(a)pyrene	7.2-9.2[b]	i
		Benzo(a)pyrene	5.1[b]	o
		Diabenz(a.h)anthracene	6-11[b]	l
		Benzo(ghi)perylene	65-117[b]	l
		Coronene	37-58[b]	l
Aliphatic Hydrocarbons	0.9[b]			j
		Heptadecane	0.4-10[b]	p
		Octadecane	0.5-6[b]	p
		Nonadecane	1.1-6.9[b]	p
		Elcosane	1.0-7.4[b]	p

a. μg/g of extract.
b. μg/g of particles.
c. Hartung et al. (1984).
d. Schulze et al. (1984).
e. Rappaport et al. (1980).
f. Tong et al. (1984).
g. Karasek et al. (1984).
h. Tomkins et al. (1984).
i. Gibson et al. (1981).
j. Liberti et al. (1984).
k. Schuetzle et al. (1983)
l. Tong and Karasek (1984).
m. Handa et al. (1984).
n. Schuetzle et al. (1985).
o. Williams and Chock (1981).
p. Griest and Tomkins (1985).

Much more sensitive and detailed analyses can be achieved by passing diluted exhaust through solid sorbent resins to preconcentrate volatile organic compounds. Tenax (Hawthorne and Miller 1985; Hampton et al. 1982) and XAD-2 resins (Schuetzle 1983; Stenberg et al. 1983a) are used often. The most detailed analysis of engine exhaust was achieved from sampling the air in the Allegheny Mountain Tunnel of the Pennsylvania Turnpike (Hampton et al. 1982). Up to 72 L of air was pumped at 0.3 L/min through a 10-mm OD x 114-mm cartridge packed with approximately 0.6 g of 60/80 mesh Tenax resin. Larger sampling volumes may cause break-through of the most volatile compounds. The compounds collected in the resin were analyzed by GC-MS after a 300°C thermal desorption of the resin and cryogenic focusing of the compounds in a loop at the head of a capillary column. More than 300 compounds were identified by their mass spectra. These included branched and normal chain alkanes from C_4 through C_{26}, alkyl cyclopentanes and cyclohexanes, C_6-C_9 alkenes, alkylated mono- and diaromatics, trichlorobenzenes, C_2-thiophene, benzaldehyde, and phenol. Correlations of analyses with traffic density and makeup (i.e., diesel vs. spark-ignition engines) showed most compounds to be common to both gasoline and diesel exhaust. Sampling was conducted with and without filtration to remove particle-associated organic matter. It was reportedly difficult to define how much of the compounds less volatile than octadecane are truly in the gas phase because of sublimation from the particle phase collected on the filter during sampling. This may not be as much a problem for gunsmoke exhaust sampling because of the shorter sampling periods available. Filtration of the exhaust sample is highly recommended to allow separation and analysis of gas and particle phase organic matter.

The XAD-2 resins are suited more for collection of the less volatile components of the vapor phase such as PAH (Schuetzle 1983; Stenberg et al. 1983a) than for the highly volatile species, which are better collected on Tenax resin. For example, it has been found (Schuetzle 1983) that 40 to 88 percent of the three- and four-ring PAHs reside in the vapor phase of diluted exhaust. The major reason for this difference in sampling application is that XAD resins are much less thermo-stable than is Tenax. The compounds collected on XAD resins usually are recovered via solvent extraction, and highly volatile compounds are readily lost during resin extraction and solvent volume reduction steps. In contrast, the excellent thermal stability of Tenax allows good recoveries to be achieved for the highly volatile species by thermal desorption methods. However, the main drawback of Tenax resin is its reactivity to nitrogen oxide. Small amounts of 2,6-diphenyl-p-quinone are formed in the Tenax resin from reaction with nitric oxide (Neher and Jones 1977). These decomposition products may interfere with the chemical analysis of the collected sample.

It is possible to selectively trap a specific class of compounds on a solid resin. Although this approach has not been utilized in diesel exhaust sampling for compounds other than aldehydes, its success in characterization of cologne essence and tobacco smoke (Picker and Sievers 1981) suggests that it might be a useful tool for gun smoke characterization. Oxygenated compounds in the above sample matrices were trapped in a lanthanide metal chelate precolumn for GC analysis

free of interference from less nucleophilic compounds in the sample matrix.

Selective trapping also can be achieved in solution. Aldehydes are most often collected from diesel exhaust by passing diluted, unfiltered exhaust through a series of impingers containing an aqueous solution of 2,4-dinitrophenylhydrazine (DNPH). Aldehydes reacting with DNPH are trapped as their dinitrophenylhydrazone derivatives and are analyzed by reverse phase HPLC with ultraviolet absorbance detection. Ten aldehydes and ketones, ranging from formaldehyde to hexanal, have been determined in diesel exhaust by this method (Creech et al. 1982). Gas chromatographic analysis of the DPNH derivatives of aldehydes from diesel exhaust (Smythe and Karasek 1973) allowed acrolein to be determined. The DPNH derivatives of acetone interfere with the liquid chromatographic analysis of acrolein (Creech et al. 1982).

Cryogenic collection is another attractive sampling method for the vapor phase of diesel engine exhaust. A cryogenic gradient sampling method has been used (Stenberg et al. 1983a, 1983b) to collect vapor phase PAHs from filtered, diluted diesel engine exhaust. Between 30 and 90 percent of the mass of selected three- and four-ring PAHs was found to be present in the vapor phase. This cryogradient approach also has been used (Hanson et al. 1985) to fractionate volatile compounds vacuum-distilled from diesel exhaust particulate matter. A wide range of aliphatic and aromatic hydrocarbons, phenols, ketones, and carboxylic acids were identified. Most of these compounds also have been identified from vapor phase sampling (Hampton et al. 1982), and their presence in filtered particle phase samples suggests that sorption of vapor phase components by the filtered exhaust particles can occur during sampling. It is not clear if a steady state between sorption and evaporation/sublimation is reached during sampling. For gun exhaust, cryogenic collection methods would only be suitable for controlled chamber studies because of the difficulties of cryogenic trapping in the field.

A summary of the classes of compounds found in the vapor phase of diesel engine exhaust is listed in Table 3.6. This is a qualitative listing because of the relative scarcity of quantitative data for the vapor phase species.

3.2.3 Sulfur Compounds

Sulfur is present in diesel engine exhaust mainly in its oxide forms. The most facile means of determining sulfates is collection of exhaust particles on Teflon filter media, leaching of the particles with water, and measurement by ion chromatography (Perez 1981). Sulfur dioxide reportedly (Perez 1981) is analyzed by drawing exhaust gases through impingers loaded with hydrogen peroxide solution and measuring sulfur dioxide as sulfate by ion chromatography. Obviously, other sulfur oxides such as sulfur trioxide, sulfate and reduced forms of sulfur that can be oxidized to sulfate would also be included in the measurement.

Table 3.6. SUMMARY OF ORGANIC COMPOUNDS REPORTED IN THE VAPOR PHASE OF DIESEL ENGINE EXHAUST

Chemical Class	Example Compounds	Reference
Straight-chain alkanes	Methane	a
	2-Methylbutane	b
	n-Dodecane	b
	n-Hexacosane	b
Branched alkanes	2,3,4-Trimethylpentane	b
	3-Methylnonane	b
	Branched C_{18} or higher alkane	b
Cycloparaffins	Cyclohexane	b
	Decalin	b
	Heptadecylcyclohexane	b
Alkenes	Ethylene	a
	Hexene	b
	1-Nonene	b
Aromatic hydrocarbons	Benzene	b,c
	Toluene	b,c
	Indane	b
	Naphthalene	b
	2-Methyl naphthalene	b
	Heptylbenzene	c
Polycyclic aromatic hydrocarbons	Phenanthrene	d
	Benz(a)anthracene	d
Heterocyclic compounds	Ethylthiophene	b
Chlorinated compounds	Trichlorobenzene	b
Oxygenated compounds	Formaldehyde	e,f
	Benzaldehyde	b,e
	Acrolein	f
	Phenol	b

a. Hutte et al. (1984).
b. Hampton et al. (1982).
c. Hawthorne and Miller (1985).
d. Schuetzle (1983).
e. Creech et al. (1982).
f. Smythe and Karasek (1973).

Sulfur dioxide levels from 3.3 to 85 ppm have been reported (Linnell and Scott 1962) but more recent measurements are closer to 40 ppm (Williams and Chock 1981). Sulfur dioxide appears to be the dominant form of sulfur in diesel engine exhaust and is one to two orders of magnitude more concentrated than sulfate (Perez 1981). Sulfate levels of 1.8 mg/m^3 are reported (Williams and Chock 1981), and sulfuric acid accounts for 90 percent or better of total sulfates (Truex et al. 1980).

Reduced sulfur is very low in concentration, if present at all. A maximum of 0.1 ppm of hydrogen sulfide was estimated (Perez 1981) from colorimetric measurements following trapping of hydrogen sulfide using zinc acetate. Gas chromatography with a sulfur-specific flame photometric detector may be more sensitive and specific.

3.3 TOBACCO SMOKE

Tobacco is a natural material, that, when incompletely burned, gives rise to one of the most complex natural products known, tobacco smoke. Tobacco smoke is a dense (~5 x 10^9 particles per mL) aerosol that results from the rapid condensation of supersaturated vapors of tobacco combustion products. In the sense that it is a chemically complex aerosol arising from combustion processes, it can be considered a model for other combustion derived aerosols, including gun smoke.

An additional similarity to gun smoke is that the bulk material of both tobacco and the explosive component is based on cellulose. The differences between gunpowder combustion and that of tobacco, however, are probably more important than the similarities. First, the pressure, temperature, and rate at which gunpowder combustion occurs is much greater than that of tobacco combustion. The completeness of the combustion of the two systems is indicated by the ratio of the oxides of carbon in the combustion gases. For gun smoke, the overwhelmingly predominant oxide is carbon monoxide. In contrast, the molar ratio of carbon dioxide to carbon monoxide is about 2:1 for mainstream tobacco smoke.

Because of the chemical complexity of tobacco smoke, it is likely to contain many of the species present in gun smoke, although not in the same relative ratios. Tobacco smoke also contains many species not likely to be found in gun smoke, such as the combustion products of leaf waxes and tobacco-specific alkaloids and terpenes. Probably the most relevant comparisons which can be drawn between gun and tobacco smoke involve the procedural aspects of sampling and analytical characterization. Both matrices are complex, combustion-derived aerosols that require relatively sophisticated separation and analytical schemes for the identification and quantitation of various components, especially those present in lesser amounts. This chapter is intended to briefly highlight those aspects of tobacco smoke production and characterization that are likely to be relevant to its consideration as a model for gun smoke exhaust and to point to recent significant reviews in the current literature from which the reader can obtain more detailed information.

3.3.1 Production

Tobacco smoke is generated under two conditions of air flow: puffing and smouldering. During puffing, at which time mainstream (MS) smoke is generated, there is a rapid increase in the air flow through and around the firecone (or coal) for a short duration (1 to 3 sec). During that time, temperatures at or near the char line can reach 900°C. Smoke constituents generated during the burn begin to condense and are drawn through the tobacco rod (and filter, if present) and undergo some adsorption and particulate filtration. Subsequently, they enter the smoker's mouth and lungs.

Sidestream smoke is generated during the smouldering of the cigarette between puffs. Partly because the air moves through at a slower rate, temperatures in the region surrounding the firecone are substantially lower than during puffing (~600°C). In contrast to puffing, which preferentially consumes the peripheral portion of the tobacco rod, the smouldering process tends to consume the axial portion. Because natural convection processes carry it upward and away from the cigarette, sidestream smoke leaves the region essentially unfiltered. The rate of smouldering is controlled by many factors, including air flow, ambient temperature and humidity, packing density of the shredded tobacco, the wrapping paper porosity, and the presence of burn accelerators in the paper or tobacco.

During both active puffing and passive smouldering, several processes occur simultaneously to produce the supersaturated vapors that, when cooled, condense to form the smoke aerosol. One important process is simple evaporation. For example, nicotine is evaporated from the shredded leaf as the firecone approaches. Much of the nicotine present in the smoke arises from this mechanism. Pyrolysis, during which individual molecules are fragmented at high temperatures, also occurs, producing a number of smaller molecules and other reactive species. During pyrosynthesis, some of these reactive species combine, either with themselves, or other molecules. Finally, entrainment results in bits of ash being caught in the air currents and acting as condensation nuclei for the subsequent smoke droplets. The results of all these processes working simultaneously is that the product aerosol contains most of the species present in the tobacco leaf, plus many new compounds not originally present. The smoke production processes have been thoroughly reviewed by several authors (Baker 1980; Johnson 1977; Klus and Kuhn 1982).

3.3.2 Composition

While cigarette smoke contains many thousands of individual constituents, it is important to consider that 90 percent of the mass of the smoke is comprised of nitrogen, oxygen, water, carbon monoxide and dioxide, hydrogen, and argon. The remaining 10 percent of the mass is the organic species that partition themselves between the gas and particle phases of the smoke, depending on the concentration and volatility of individual species.

In addition to the air and combustion gases, the vapor phase of tobacco smoke contains oxides of nitrogen; ammonia; simple saturated, unsaturated, and aromatic hydrocarbons; low-molecular-weight alcohols; aldehydes; and ketones, some esters, nitriles, amines, and nitrosamines. The distinction between the gas and particulate phases of the smoke becomes less clear with increasing molecular weight. Many compounds are found in both phases, which may be dependent on the manner in which the smoke is sampled (see Section 3.3.3).

The most prevalent constituent in the particle phase of mainstream tobacco smoke (other than water and certain humectants that are added to the tobacco to maintain moistness) is nicotine. Present to a smaller extent are other alkaloids, leaf pigments, terpenoids, long chain carboxylic acids, leaf waxes, phenols, catechols, higher-molecular-weight aldehydes, and phytosterols. Present at trace levels are many thousands of compounds, including polynuclear aromatic hydrocarbons, nitrogenous aromatics, nitrosamines, and trace metals. Tables 4.12, 4.13, and 4.14 (Section 4) summarize average mainstream deliveries of several major and trace smoke constituents.

Sidestream smoke is generated under somewhat cooler conditions. It contains more combustion water than mainstream smoke and is considerably more alkaline. Many of the important compositional differences result from these conditions. The carbon dioxide:carbon monoxide ratio is much greater for sidestream smoke, suggesting more complete combustion. The amine content is much higher, with a concomitant increase in nitrosamine levels. The higher pH suggests that a larger fraction of sidestream nicotine is in its unprotonated and thus more volatile form. However, there is considerable debate as to the distribution of nicotine between the liquid and vapor phases of the smoke. In general, however, most of the compositional differences between mainstream and sidestream smoke are differences in relative quantities, rather than qualitative differences. It would be unlikely that compounds found in mainstream would not be found, at least in some quantity, in sidestream smoke, and vice versa.

Environmental tobacco smoke (ETS) is sidestream and exhaled mainstream smoke that has been diluted into an enclosed space. ETS represents the material to which nonsmokers are passively exposed. There is an increasing body of evidence to suggest that smoke, as it is diluted and ages, undergoes some chemical and physical transformation. This results in a material that is no longer simply diluted smoke. The transformation probably occurs as a result of reactions among the more reactive constituents of the smoke and with other airborne contaminants. Light may play an important role in the initiation of these reactions. As a result of these changes, ETS is a poorly defined material. It probably contains many of the constituents of mainstream and sidestream smoke, but most likely not in their original compositional relationship.

There are several excellent recent reviews on the composition of tobacco smoke (Norman 1977; Guerin 1980; Surgeon General 1979). Also, the levels in certain ambient settings due to environmental tobacco smoke have also been reviewed (Sterling et al. 1982).

3.3.3 Sampling

Cigarette smoke is a dense, complex aerosol that has not achieved an equilibrium state before it mixes with the atmosphere. It undergoes physical and chemical transformation upon aging. The liquid droplets coagulate, and thus grow initially, and then shrink as dilution occurs and volatile compounds evaporate. With time, individual constituents react with each other and with other airborne species. Given that most smoke-related studies are conducted with a focus on inhalation toxicology, it is desirable to collect the smoke at a chemical and physical state relevant to the particular exposure in question. (For example, while mainstream smoke should be collected within a few seconds of its generation, it would be inappropriate to collect ETS immediately after its generation.) Unfortunately, the sampling process itself can often exacerbate both chemical and physical changes in the smoke matrix. For example, amines may be converted to nitrosamines if not protected from nitrosation. Nicotine may be evaporated from collected particulate matter with increasing passage of air over the filter (Jenkins et al. 1982). It is thus important for individuals conducting sampling to understand the potential impact of the sampling procedure on the constituent(s) of interest.

For quantitative analytical studies, the conditions of smoke generation have a marked effect on the amounts of constituents produced. Thus, very highly standardized conditions for generation and sample collection have been specified, especially for mainstream smoke. The specific conditions of generation and sampling of mainstream smoke have been thoroughly reviewed (Dube and Green 1982). Briefly, the standard conditions of smoke generation in use in this country consist of one 35-mL, 2-sec duration, sinusoidally shaped puff per minute, until the cigarette is consumed to within 3 mm of the filter overwrap, or to a 23-mm butt for nonfilter cigarettes. A 44-mm-diameter Cambridge filter (Wartman et al. 1959) is installed downstream, immediately behind the butt of the cigarette, to collect the smoke particulate matter. Since the peak volumetric flow through the filter reaches 1.5 L/min, the maximum linear air velocity is about 2 cm/s. While the aerosol and some vapor constituents are collected on the filter, the remaining semivolatiles and gases pass through and are usually collected in gas sampling bags or solid sorbent resin traps.

The generation and collection of sidestream smoke is a much less well-defined activity. First, there is not general agreement on the type of generation/collection apparatus that is most appropriate. Guerin et al. (1987) recently reviewed methods and conditions for sidestream smoke generation/collection.

The problems of sampling ETS are likely related to those of sampling gun smoke exhaust. ETS is a dilute, biphasic material, with many of its constituents distributed into both phases. Because it is so dilute, sampling through filters is even more likely to evaporate constituents from collected particles, especially when long sampling times are used. ETS is also more likely to contain a significant proportion of other (nonsmoke) constituents when compared with mainstream smoke.

Many of the materials and equipment for the sampling of ETS have been reviewed in detail elsewhere (Jenkins and Guerin 1985). Briefly, 44-mm Cambridge glass fiber filter pads have been employed for collection of small samples of particulate matter (>150 mg), whereas large Teflon-coated glass fiber filters (such as the Pallflex T60A20) have been used for collection of larger samples. Their low pressure drop makes the Pallflex filters especially suitable for high-volume sampling, and the inert coating on the fibers reduces artifact formation, especially when long sampling times are employed. Sampling for trace metals in the particulate matter should probably involve a different filter system altogether. Because of the high metal content of most glass fibers, collection on pure Teflon membrane filters would seem more applicable if trace metals are the target constituents.

Solid adsorbents have proven to be the most popular materials on which to collect semivolatile ETS constituents (Jenkins and Guerin 1984; Higgins et al. 1984). The trapped organics can be subsequently removed by thermal desorption (into a gas-liquid chromatograph) or by solvent washing. Unfortunately, not all constituents are retained or subsequently removed with complete efficiency. Thus, it is critical that the retention/desorption characteristics of the constituent(s) in question and the limitations that they place on the analytical accuracy be known prior to sampling. Tenax-GC, XAD-2, and charcoal have all been used for sampling airborne organic compounds (Adams et al. 1977). Charcoal is no longer recommended. Its retention characteristics are good, but quantitative recovery of sorbed materials is difficult.

For constituents that exist solely in the gaseous state at ambient temperatures, concentration on adsorptive resins or condensation in cold traps are usually not viable options. For nonreactive gases, samples can easily be collected in Teflon or Tedlar gas sampling bags. However, there is increasing interest in real-time sampling/analytical procedures for gases whether they are reactive or not. That is, an air sample is drawn directly into the analyzer, and either a chemical reaction is performed or a spectroscopic measurement is made.

3.3.4 Analytical Methods for Tobacco Smoke Constituents

Given the complexity of tobacco smoke, it is probably not an exaggeration to estimate that the number of analytical methods for tobacco smoke constituents is probably equal to the number of constituents identified. A review of all the methods would require volumes and is beyond the scope of this document. There have been several recent reviews on various aspects of tobacco smoke analysis, however (Green et al. 1980; Dube and Green 1982; Bell 1977; Jenkins 1986; Jenkins and Guerin 1984) and the reader is directed toward those reviews for more detail. In general, the methods can be divided into two classes: those directed toward one specific constituent, and those designed to quantitatively determine multiple constituents simultaneously. With advances in gas chromatographic capillary column technology, the number of constituents that can be visualized in a given experiment may be as large as 200. In many cases involving tobacco smoke analysis, the bulk of the effort is directed toward separation of the constituent of interest from

both the matrix itself and from isomerically similar species. Thus, because of the chemical complexity of the smoke, many methods that perform adequately for other matrices are not sufficiently accurate or reliable for tobacco smoke.

The following is a brief review of the current analytical techniques used to quantitatively determine tobacco smoke constituents or compound classes that are believed to be relevant to the problem of gun smoke exhaust analysis. In most cases, reference is made to a published manuscript, to which the reader is directed to more details. However, the citation is only meant as an example, rather than a critical evaluation of the procedure.

3.3.4.1 Permanent Gases

The determination of some of the lower-molecular-weight permanent gases such as CO, CO_2, N_2, CH_4, and O_2 is relatively straightforward. A gas phase sample is chromatographed on a solid adsorbent support, such as molecular sieves or polymer resins. In fact, prepacked GC columns can be purchased to analyze the gases and the lower-molecular-weight (C_1-C_6) hydrocarbons. For ambient concentrations of carbon monoxide, nondispersive infrared analysis (NDIR) may be more useful (Hugod et al. 1978). For oxides of nitrogen (NO, NO_2, NO_x), the method of choice is chemiluminescent analysis (Jenkins and Gill 1980). In most commercial analyzers, the sample gas is mixed with ozone. The NO and O_3 react, producing a product that emits light. In highly concentrated combustion smokes, the sample handling prior to introduction into the analyzer is critical, owing to potential interferences from other combustion gases. For example, collisional deexcitation of the electronically excited NO_2 (from the reaction of NO and O_3) has been reported for a number of compounds, including carbon dioxide, water vapor, and hydrogen (Matthews et al. 1977; Siewert 1975). Rapid side reactions of NO and NO_2 with organic gas phase constituents also act to reduce apparent NO_x concentrations (Phillippe and Hackney 1959; Rathkamp and Hoffman 1970). Rapid dilution of the smoke with ambient air apparently reduces the concentration of these potential interferences to the point at which they are no longer a problem for cigarette smoke analysis (Jenkins and Gill 1980). Potential positive interferences from chemiluminescing lower-molecular-weight organic species is usually eliminated by using a 600-mm optical cut-off filter in the analyzer system.

On-line analytical instrumentation is also commercially available for the primary sulfur gases, H_2S and SO_2. The techniques employed involve either flame-photometric detection (FPD) or UV-induced fluorescence. Gas chromatographic methods have been employed for higher-molecular-weight sulfur containing compounds, usually employing a sulfur specific detector (Horton and Guerin 1974).

3.3.4.2 Ammonia and Hydrogen Cyanide

Hydrogen cyanide (HCN) is distributed equally between the particle and vapor phases of mainstream smoke. It has been determined by a variety of analytical methods, including ion-selective electrodes

(Vickroy and Gaunt 1972), coulometry (Sloan 1980), colorimetry (Griest et al. 1980) and gas chromatography (Brunemann et al. 1977). None of the methods is completely satisfactory; all are either time-consuming or subject to interferences.

Ammonia (NH_3) is present in sidestream smoke at levels approaching those observed in mainstream smoke (Klus and Kuhn 1982). It too has been determined by a variety of analytical methods, including ammonia selective electrodes (Sloan and Morie 1976) or gas chromatography (Brunnemann and Hoffmann 1975). Interestingly, there have been no reports of the determination of ammonia in cigarette smoke by NDIR spectroscopy. This instrumentation, while expensive, should be sufficiently sensitive and selective for NH_3 in tobacco smoke, especially sidestream.

3.3.4.3 Aldehydes

Because of their high degree of reactivity, aldehydes are usually quantitated by first reacting the sample with a derivatizing reagent. The resulting derivatives are usually more stable and more chromatographable. A reagent commonly used is dinitrophenylhydrazine (DNPH). The resulting derivatives, the dinitrophenylhydrazones, can be separated conveniently by HPLC. This approach has been used for mainstream tobacco smokes (Manning et al. 1983), ambient air samples (Grosjean 1982), and diesel exhaust (Lipari and Swarin 1982).

3.3.4.4 Nitroaromatics

Nitroaromatics have been reported in cigarette smoke (Hecht et al. 1977), but the major recent focus on such compounds has been directed toward diesel exhaust. Again, because of their relatively low levels and potential interferences, major analytical effort must be placed in effective separation of these constituents from the smoke matrix. Use of liquid/liquid extraction, followed by liquid chromatography (LC) fractionation, and subsequent gas chromatography with thermal energy analyzer (TEA) detection has been reported (Tomkins et al. 1984). An even more sensitive approach involves the use of reverse-phase HPLC with on-line peroxyoxalate chemiluminescence. In this procedure nitroaromatics are reduced on line to the corresponding aminoaromatic and are subsequently excited by the energy transfer from the decomposition products of the reaction between hydrogen peroxide and bis(2,4,6-trichlorophenyl) oxalate. The excited aminoaromatics are detected using a conventional fluorescence detector with its light source turned off (Sigvardson and Birks 1984).

3.3.4.5 Nitrosamines

Nitrosamines, both the so-called volatile nitrosamines (VNAs) and the tobacco-specific nitrosamines (TSNAs) have received much attention in recent years. They are much more prevalent in sidestream smoke (thus exposing individuals involuntarily to these carcinogens) and can be synthesized in vivo from tobacco and/or smoke related substrates. Because such low levels are present in smoke, artifactual formation during trapping is likely unless specific prevenative measures are used, such as

adding an anti-oxidation compound to the trapping medium. The sample is usually isolated by liquid-liquid extraction, followed by liquid chromatography. Final analytical determination is performed by gas chromatography using a TEA detector under nitrosamine-specific conditions (Brunnemann et al. 1980).

3.3.4.6 Metals

For the determination of individual metallic constituents in cigarette smoke, the particulate matter is collected either on glass fiber filters or as smoke condensate in cold traps. Depending on the specific metal in question, analysis of the particulate matter can be performed by neutron activation analysis (NAA) or atomic absorption (Wescott and Spincer 1974; Abedinzadeh et al. 1977).

3.3.4.7 Polynuclear Aromatic Hydrocarbons

A very large number of PAHs and alkylated PAHs have been reported in cigarette smoke. Isomeric discrimination among the various PAHs is exceedingly important because certain species exhibit carcinogenic and mutagenic properties, while similar species do not. [For example, benzo(a)pyrene (BaP) is carcinogenic, while benzo(e)pyrene is not.] Most of the analytical methods reported employ multistage separations in order to separate nanogram quantities of PAH from the matrix. For example, Tomkins and co-workers have used column liquid chromatography, followed by normal phase HPLC and reverse phase HPLC with fluorescence detection for the determination of BaP in mainstream cigarette smoke (Tomkins 1985). The method has been reported to be accurate to 5 ng per cigarette.

3.3.4.8 Volatile Organics

The gas, or volatile, phase of cigarette smoke is defined rather empirically as that which passes through a standard Cambridge particulate filter. As stated above, the most widely used procedure for analysis of these constituents first requires trapping on a porous polymer resin such as Tenax-GC. The Tenax is then thermally desorbed, and the constituents are cryofocused in a liquid nitrogen cooled trap at the head of the GC column. When the desorption is complete, the liquid nitrogen is removed, and the column oven is heated as it would be for a conventional run. Higgins and co-workers (Higgins et al. 1983, 1984) have used this procedure to simultaneously quantitate more than 30 constituents in the gas phase of cigarette smoke.

3.3.4.9 Particle Phase Constituents

Most of the major constituents of the particle phase of cigarette smoke are polar and semipolar hydrocarbons. Many of these possess hydroxyl or carboxylic acid functional groups and, as such, are not particularly amenable to direct gas chromatographic analysis. One popular approach to multicomponent analysis of such species is to derivatize the particulate matter extract with a powerful silylating reagent, such as N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA). In the

derivatization reactions, all active hydrogens (i.e., those attached to oxygen or nitrogen) are replaced with tri-methyl silyl groups, resulting in a much more volatile compound. The derivatized extract can then be chromatographed, using conventional packed or capillary GC columns. Using capillary columns, more than 80 major constituents of the particulate matter can be readily visualized (Ishiguro and Sugawara 1978).

3.4 INDUSTRIAL HYGIENE SAMPLING METHODS

Some of the most widely used techniques for personal monitoring are briefly covered in this section. Since the methods are applicable to most exposure environments, they are discussed collectively in this section rather than separately for each area. It should be noted, however, that many of the techniques for ambient air analysis discussed for the topics above are also appropriate for industrial hygiene monitoring.

Standard NIOSH methods for the determination of various species in air are available (NIOSH 1984), and reviews covering recent advances in industrial hygiene monitoring have been published in Analytical Chemistry biennially (Melcher and Langhorst 1985, and Melcher 1983). Specific topics in the area of environmental monitoring are also covered in certain American Society for Testing and Materials (ASTM) publications (ASTM 1980; ASTM 1982). The reader is referred to these articles and other reviews on monitoring (Wallace and Ott 1982) for greater detail regarding various techniques. It should also be noted that the U.S. Army Environmental Hygiene Agency (USAEHA) has available an industrial hygiene sampling guide for monitoring various compounds in air (Belkin and Bishop 1982). Included in the manual are recommended sampling methods, sampling volumes, storage and transport procedures, and methods for collecting field blanks.

Environmental contaminants can be classified depending upon their volatility (i.e., substances that are gases, substances of intermediate molecular weight that have appreciable vapor pressures at room temperature, and compounds of low volatility associated with solid particulates). Sampling methods are directed toward each of these classes. The most appropriate technique for a particular application (e.g., monitoring CO levels for individuals exposed to gun smoke) will depend upon a variety of factors including environmental conditions, required sensitivity, time constraints, etc.

Gases can be collected in bags or pre-evacuated cylinders, trapped on various sorbents (see discussion on passive dosimeters below), or determined with direct reading sensors. A disadvantage of container collection is that it may not provide an integrated response over an entire exposure period. Adsorption of the compound of interest on the container surface or loss by diffusion through the bag may also necessitate rapid analysis following collection. In a study conducted by Brown (1985) difficulties encountered in sampling and analyzing reactive gases that are generated during weapons firing (i.e., NO, NO_2, HCN, and HCl) were specifically documented. Nitrogen dioxide was found to dimerize to nitrogen tetroxide at room temperature and nitric oxide was found to react with trace oxygen to form nitrogen dioxide and dinitrogen

trioxide. Hydrogen chloride and hydrogen cyanide were found to rapidly condense at room temperature. These results indicate that these species should be determined directly and not collected for subsequent analysis. Reactions between these compounds and stainless steel sampling cylinders also resulted in significantly reduced concentrations and the formation of artifacts.

Direct reading sensors provide both an early detection warning if exposures exceed permissible levels and immediate quantitation of a contaminant. Colorimetric reactions between a gas or vapor with a chemically sensitive reagent or sorbent (e.g., Draeger tubes and reactive paper tapes) form the basis of one type of sensor. Some factors that must be taken into consideration when using these devices are response time, interferences from other gases or vapors, sensitivity, accuracy, and humidity effects. Instrumental monitors are also available for the direct determination of certain gases (e.g., continuous CO monitors and chemiluminescent NO_x monitors). They offer portability, high specificity, and sensitivity.

Organic vapors (compounds with carbon number from approximately C_5 to C_{20}) are ordinarily sampled on solid sorbents. These are convenient to use and can provide time-weighted average (TWA) exposures. The sample is drawn through a cartridge containing the sorbent with battery operated personal pumps. Charcoal, silica gel, alumina, or porous polymers (e.g., Tenax, XAD resins) are commonly used, although various chemically modified or treated GC packings may provide greater specificity. Once collection has been completed, the trapped substances are eluted from the cartridges, either by thermal desorption or by washing with an appropriate solvent. Aliquots of the solvent washes are then injected into a GC for separation and analysis of the constituents. In the case of thermal desorption, the compounds are usually cryogenically retrapped at the head of a chromatographic column prior to analysis. The sensitivity that can be obtained is dependent upon sampling time and rate, detection method, chromatographic resolution from interfering compounds, and other factors, but is ordinarily in the ppm or even ppb range. Thermal desorption usually provides greater sensitivity, since the entire sample is analyzed. Equipment is commercially available for automated desorption, which interfaces with most GCs. Some estimation of collection and desorption efficiency and breakthrough volume (which are dependent upon sample concentration, sampling rate and time, quantity of sorbent, and efficiency of the cartridge packing) is required. Cartridges are often packed in two sections, separated by a small plug of glass wool. If the constituent of interest is found on the second section, then breakthrough is known to have occurred and quantitation in this case may not be reliable. Other factors that must be considered are compound stability on the sorbent and artifact formation during elution, which could interfere with the overall analysis.

Solid sorbents are also employed in passive dosimeters. These devices provide TWA concentrations and can easily be used to obtain breathing zone levels since they do not require pumps or tubing. Compounds are collected according to principles of mass transport across a diffusion layer or by permeation through a membrane. Since the rate at

which a gas permeates a given membrane is constant, the total mass collected is a function of concentration in air and sampling time. In diffusional dosimeters the gases follow Fick's law from the apertures on the front of the badge through a diffusion space to the collecting medium (Melcher 1983). Design parameters influence sensitivity and range. The relationship between vapor concentration and the weight of material collected is given by (Fick's law): $M = D \times A \times C \times t / L$ where M is the total mass of the compound collected, D is the molecular diffusion coefficient, A is the diffusion path area, C is the environmental concentration, t is the sampling time, and L is the diffusion path length (Melcher 1983). Activated charcoal is most frequently employed as the sorbent. Sampling efficiency, capacity, humidity, competitive sorption by other vapors, and air velocity are factors to be considered in the use of diffusional monitors. Sensitivity for all passive dosimeters can be increased with longer sampling times. They have been used for both long-term sampling (24 hours to 1 week) and for short-term exposures (30 min). Analysis involves solvent extraction or thermal desorption of the sorbent and usually chromatographic determination. Several commercial monitors are available for determining organic vapors, and some have been designed to selectively determine specific compounds (e.g., formaldehyde, ethylene oxide, benzene). Others have been developed to determine inorganic gases (e.g., NO_2, NO_x, SO_2, H_2S, HCN, CO) or heavy metals. These may contain a reactive chemical in a small vial or coated on a solid support. Spectroscopic measurements are often used for determining the inorganic species. Greater detail on specific methods can be obtained from references in the industrial hygiene reviews cited above.

Sampling methods for particulates may be aimed at determining total mass, size, and size distribution or toward determining specific chemical content. Ordinarily the samples are collected with the aid of calibrated pumps followed by filters, impactors, or impingers. Filters of different sizes, porosity, and material (e.g., glass, cellulose, synthetic polymeric, and ceramic fibers) that differ in their collection efficiencies for various particle sizes are available. Total particulate matter (TPM) is most often determined by gravimetric measurements (direct weighing of a filter pad), although microscopic examination with counting techniques is also used. Adsorption of moisture by the filter may influence gravimetric measurements, although controlling the humidity prior to weighing may eliminate problems. High-volume samplers for determining TPM draw air into a covered housing and through a filter (at a rate of 1 to 1.5 m^3/min) by means of a high-volume blower. Once the sample has been collected on a filter, it may then be solvent-extracted for further analyses by liquid or gas chromatography, mass spectroscopy, or other methods. Collection of respirable particulates (i.e., particle size <10 μm) can be accomplished with cyclones and elutriators (see Melcher and Langhorst 1985 for descriptions). Size distribution can be measured by several methods. The two methods most commonly utilized are cascade impaction and optical particle counting. The cascade impactor (CI) instrument draws an air sample through a small orifice sized to admit a desired particle size range. The exiting particles are impinged onto a flat plate or stage (e.g., glass cover slips) that serves as a collector. The collected residues can then be

chemically analyzed or weighed. CI instruments generally contain several stages with a terminal, downstream collection media, and a final filter to collect any undeposited aerosol/particulate matter (Bright and Fletcher 1983). Personal aerosol samplers that collect an inhalable fraction on an impaction stage and the respirable fraction in a filtration stage have been described (Bright and Fletcher 1983). Particle losses in an impactor, generally referred to as wall losses or interstage losses, occur due to deposition of particles on surfaces other than the impaction plate. Currently, no theory exists to predict these losses. Thus, they must be determined experimentally using standard test aerosols and comparative test methods (Marple and Willeke 1984). On the other hand, the optical particle counter (OPC) measures the particle size distributions in real time so that aerosol data may be obtained fairly rapidly and semiautomatically. The OPC determines the optical diameter of the particle based on the intensity of light scattered by individual particles. However, the intensity of the light depends upon the optical properties of the particule and may not be directly related to aerodynamic diameter (Willeke and Liu 1976).

While the CI instrument does measure the aerodynamic diameter of the sample, as deposited, the measurement is not performed in real time. Reactive particles, evaporation effects, coalescing growth, and ricocheting particles can lead to errors in measurement of complex aerosols. Because munitions produce hot, partially oxidized gases and potentially reactive particulate matter, other particle sizing techniques may be more useful for gun smoke characterization. For example, laser-actuated, acoustic relaxation techniques may be utilized for measuring aerodynamic diameters of particulate smokes in real time to supplement or augment CI and OPC measurements.

A single particle aerodynamic relaxation time (SPART) analyzer has been utilized by our laboratories for monitoring process aerosols that are formed by gas phase reactions. Also, aerosol formation by various nucleation processes (e.g., heterogeneously or homogeneously) may be studied with the SPART technique. This instrument, developed by University of Arkansas experimenters (Mazumder and Kirsch 1977), consists of three basic components: (1) a laser Doppler velocimeter (LDV), (2) an acoustic chamber, and (3) electronic signal and data processing circuitry. The LDV is used to monitor the oscillations of an aerosol particle in an applied acoustic field. The aerosol sample is drawn inside the acoustic chamber, where the sensing volume of the LDV is located. The particle motion lags behind the acoustic excitation by an amount that depends upon the particle's aerodynamic diameter. This phase lag may be measured by a fast data processor that performs the computation of the particle's aerodynamic diameter. The instrument can accommodate aerosol flow rates of only 200 particles per second, however. While the dynamic range of size fraction is wide (0.3 to 10.0 μm). the "sharpness of cut" is not as precise as is obtainable with well constructed CI instruments. Calculations of mass concentration are based on the assumption of a spherical particle of unit density. Some other instrumental techniques that may be useful for gun smoke characterization are differential mobility (Alofs and Balakumar 1982), electrical aerosol analysis (Liu

and Whitby 1974), condensation nucleus counting (Sinclair and Hoopes 1975), and piezoelectric crystal mass loading (Sem and Tsurubayaski 1977). These measurements may be applied to provide meaningful aerosol data (Lore and Skeen 1985).

3.5 RECOMMENDED STRATEGIES FOR DETERMINING THE CHEMICAL COMPOSITION OF GUN EXHAUST

Methods used to characterize cigarette smoke and diesel and gasoline exhaust were reviewed in the sections above to identify strategies that may be appropriate for determining gun combustion products. Despite major differences in the combustion processes of these various "fuels" compared to that of a fired weapon, similar products are formed, so sampling and analytical requirements may be the same. From our literature review on weapon's exhaust it was also determined that the compositional information presently available is very limited. The majority of information has been obtained in support of ballistics studies in which thermodynamic properties of the propellants or the performance characteristics of a weapon were the primary factors under investigation. It is from these studies that the major gaseous constituents were determined (i.e., CO_2, CO, N_2, H_2, and H_2O). Few studies have examined the composition from a more detailed perspective or particularly from a toxicological standpoint. The investigations that have been conducted have largely focused on toxic gaseous species. Compounds identified include NO_x, SO_2, NH_3, COS, H_2S, and low-molecular-weight hydrocarbons. In some cases these gases were only detected and not quantitated. Other studies have specifically examined only lead or lead and other metals. The analysis of ambient air in indoor rifle ranges, for example, has been chiefly restricted to inorganic lead determinations.

It is known that the firing of a weapon produces smoke that has a vapor phase and particulate phase component. The particulate matter contains not only metals (erosion products from the gun barrel and chamber or volatilized metal from the projectile) but also uncombusted propellant and propellant transformation products. Very little information is available on the composition of the particles and higher-molecular-weight components in the vapor phase. Perhaps the most comprehensive examination of gun exhaust for a given propellant formulation and weapon type was conducted by Ase et al. (1985) where, in addition to some gaseous constituents and inhalable particulates, volatiles (70 to 90 compounds) in the vapor phase and some specific organics in the particulate phase (PAHs) were determined. The study, however, is not exhaustive and certain important classes of compounds (e.g., nitro-PAHs) were omitted. Difficulties were also encountered in generating the exhaust and in sampling, which may have influenced the results. Further studies are needed to verify their findings.

The studies conducted on gun emissions are also difficult to compare or correlate, since conditions used to generate samples have in most cases been different. There are presently no standard methods for

producing the exhaust for compositional or toxicological evaluation. Combustion conditions are known to influence the final products both qualitatively and quantitatively. This is also the situation for gasoline, diesel, and tobacco products, but in these cases standard methods have been developed. For cigarettes, standard puffing conditions have been specified and data are usually reported for smoke produced under these circumstances. Standard reference cigarettes are also available, allowing methods to be validated and results to be correlated. Currently in the case of gun exhaust, results obtained under one condition are difficult to relate to one another. For example, the products generated in a closed bomb may not represent what is generated by actual firing of a weapon in the field. The absence of a standard method also makes it difficult to determine what precise influence changes in the formulation of the propellant or primer will have on the products.

The military recognizes that certain toxic species (lead, lead compounds, and certain toxic gases) present in weapons exhaust may have short-term debilitating effects for personnel confined to areas where they are in direct proximity to the emission source (e.g., crew personnel in armored vehicles). Accordingly, they have issued test operational procedures (TOP 1984) for measuring certain species during the firing of vehicle armament. The effects (including long-term health effects) of other compounds are unknown. The necessity for evaluating the toxicological properties will depend upon the precise chemical composition of the exhaust. Additional studies are required for a detailed characterization. In particular, information is needed on the contributions of certain compounds or classes of compounds to the total exhaust. There is also a specific lack of data on organics in the vapor and particulate phases.

This document, which has reviewed the available literature on gun exhaust and examined approaches used to characterize other complex combustion products, points to two major areas where additional study or developments are required to fully define the chemical and toxicological properties. Most notable is the need for standardized methods for generating the exhaust products. A test environment where temperature, concentration, humidity, background, and other variables can be accurately controlled should be developed. This may be accomplished by constructing a chamber to contain emissions produced by firing a weapon, similar perhaps to the test stand approach used by Ase et al. (1985). The emphasis should be placed on collecting gases from the breech compartment since these products will in all likelihood be the major source in most exposure cases. Alternatively, a propellant may be burned in a manner that simulates the firing of a weapon and the products contained in a device that would allow sample withdrawal and analysis. Whichever approach is used, the test environment would greatly facilitate the analysis of major constituents (gases, total organic vapor concentration, total particulate concentration, and elemental composition). It would also allow the determination of trace-level compounds of known toxicity. The test environment could also be used to validate sampling methods for field applications or to evaluate methods for removing exhaust in crew compartments. The development of a generator system will be specifically addressed in Volume II of this report.

A second focus should be placed on field studies, which may be conducted concurrently with the controlled chamber experiments. Efforts should be directed toward obtaining samples under worst-case (maximum exposure) conditions (e.g. sustained rates of fire or firing of large caliber weapons). Range-finding field studies that would indicate the maximum exposure under certain conditions would help define the problem. One outstanding feature that is apparent from our review of the literature is that the data available are highly variable and do not give clear indication of the significance of exposures to gun exhaust. Standardized sampling methods that have been successfully used to monitor exposures (NIOSH methods) or methods that have proven reliable for ambient air analysis should be employed (see Table 3.7).

Since it may not be feasible to examine all weapons and propellant combinations, one weapon, munition, etc. could be selected for careful detailed characterization both in the field and chamber. The system chosen for study may be the one most frequently employed under conditions where exposures occur (e.g., guns that are mounted on armored tanks). From these data, then, the charge weight, etc. can be ascertained.

The information that is obtained from either the field or controlled chamber studies can then be used to supplement or modify, if necessary, the other approach. The average concentrations determined in field experiments, for example, may dictate the range of concentrations that should be examined in chamber studies. Sampling and analytical methods for a particular compound that are found to be unreliable in a test environment due to interferences from other species would not be recommended for use in field investigations.

Recommendations for analytical and sampling methods for species reported to be present or likely to be present in weapons exhaust are given in Table 3.7. These methods were selected because they have been found to be valid for determining combustion products from other sources (i.e., gasoline and diesel exhaust and tobacco smoke) or are standard methods for monitoring exposure. Since problems in collection or analysis that are unique to gun exhaust may be encountered, modifications or additional methods development may be required in some cases. The candidate methods do, however, represent techniques that have been successfully applied to complex combustion products and thus have a high probability for successful application to gun exhaust. It should be noted that laboratory studies allow the application of more sophisticated procedures that may offer greater specificity or sensitivity as compared with methods used for field testing where there are constraints of portability and ruggedness for real-time analysis. References are provided for each method. They give details regarding the procedure that may include detection limits, possible interferences, precision, and advantages and disadvantages. These references should be consulted for specific information.

TABLE 3.7. CANDIDATE SAMPLING AND ANALYTICAL METHODS FOR GUN COMBUSTION PRODUCTS*

	Sampling		Analysis	
	Area (Field or Chamber)	Personal	Discreet	Continuous Monitor
Permanent Gases	Evacuated cylinders or sampling bags[1]	Detector tubes for CO_2[2]	GC/TCD[3]	-
CO	Sampling bags[1] or portable monitor[4,5]	Detector tubes[2]	GC/TCD[6] or GC/CFID[43]	NDIR[4] Ecolyzer[5]
NO_x	Portable monitor[7]	Detector tubes for NO_2, NO[2] Passive dosimeter for NO, NO_2[8,9]	Dosimeters analyzed by visible absorption[8]	Portable chemi-luminescence monitors[7,10]
Sulfur Gases				
SO_2	Portable monitor[11,12] Filtration[3]	Detector tubes[2]	Ion chromatography[3]	Portable monitor based on FPD or UV induced fluorescence[11]
H_2S	Portable monitor[13] Molecular sieve cartridges[3]	Detector tubes[2] Molecular sieve cartridges[3]	Cartridges by GC/FPD[3]	Portable monitor based on FPD or UV induced fluorescence[13]
Organic Sulfides	Sorbent cartridges[14,15]	Sorbent cartridges[14,15]	GC/FPD[14]	-
Volatile Organic Compounds	Tenax or XAD-2 cartridges[16,17] Gas syringe[19]	Tenax or XAD-2 cartridges[16,17]	GC/FID[8], GC/MS[16,17] GC/FID[19]	Total hydrocarbon analyzer[18]
PAHs	Filtration (Teflon filter media)[20-22]	Filtration (Teflon filter media)[20,21]	HPLC/Fluorescence[21-23] GC/FID[24] GC/MS[21,25]	-
Nitroaromatics	Filtration (Teflon filter media)[20-22]	Filtration (Teflon filter media)[20,21]	GC/NPD[27] or GC/TEA[26,27] GC/MS[25,27]	-
Metals (including Lead)	Filtration[8]	Filtration[8]	AA, ICP[8]	-
Total Particulate Matter	Filtration (Teflon filter media)[20-22]	Filtration (Teflon filter media)[20,21]	LC fractionation followed by GC GC/MS or HPLC[25]	-

TABLE 3.7 (Cont'd)

	Sampling		Analysis	
	Area (Field or Chamber)	Personal	Discreet	Continuous Monitor
Particle Size	CI[28] Automated analyzer for chamber (SPART, OPC, EAA, PCML, DM CNN)[29-34]	Personal aerosol sampler[28, a]	CI samples by gravimetry	OPC[29] CNC[32] EAA[31] PCML[33] SPART[30] DM[34]
HCN	NaOH impingers for chamber[3]	Passive samplers[35] Detector tubes[2]	Impinger by ion specific electrode[3]	-
NH_3	Portable monitor[36] H_2SO_4 treated silica gel cartridges[3]	Detector tubes[2] H_2SO_4 treated silica gel cartridges[3]	Cartridges by ion specific electrode[3]	NDIR[37]
Oxygenated Compounds				
Formaldehyde	Treated XAD-2 cartridges[4]	Treated XAD-2 cartridges[4]	GC/FID[4]	-
Acrolein	Treated XAD-2 cartridges[8]	Treated XAD-2 cartridges[8]	GC/NPD[8]	-
Vapor Phase aldehydes	DNPH impingers or cartridges for chamber[38-40]	Active or passive badge monitors[41]	HPLC/UV[38-40]	-

a. Portable, personal aerosol monitoring instrumentation has recently been developed by private industry with government support. This equipment has been tentatively approved by the federal authorities (U.S. Department of Labor, Mine Safety and Health Administration; Approval No. 2G-3532-0). The monitor analyzes respirable aerosol/particulate matter (0.1 to 10.0 μm in diameter) by a forward light scattering technique. This miniature, respirable aerosol monitor (MRAM) is described by the instrument manufacturer, GCA Corporation, as measuring the instantaneous, respirable aerosol mass concentration over the range 0.01 to 100 mg/m^3. Independent laboratories, government, and industrial concerns are currently evaluating the MRAM instrument for personal monitoring applications, according to discussions with the manufacturer's technical personnel (Lilenfeld to Lore, 1986).

Table 3.7 (Cont'd)

*Abbreviations:

AA, atomic adsorption
CFID, catalytic flame ionization detector
CI, cascade impactor
CNC, condensation nucleus counter
DM, differential mobility analyzer
DNPH, dinitrophenylhydrazine
EAA, electrical aerosol analyzer
FID, flame ionization detector
FPD, flame photometric detector
GC, gas chromatography
HPLC, high-performance liquid chromatography
ICP, inductively coupled plasma
MS, mass spectrometry
NDIR, nondispersive infrared
NPD, nitrogen phosphorous detector
OPC, optical particle counter
PCML, piezoelectric crystal mass loading analyzer
SPART, single-particle aerodynamic relaxation time analyzer
TCD, thermal conductivity detector
TEA, thermal energy analyzer

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4. REVIEW AND ANALYSIS OF TOXICOLOGICAL APPROACHES TO EVALUATING EXHAUST EMISSIONS

4.1 INTRODUCTION

Propellant combustion products consist of five major gaseous components (CO, H_2, CO_2, H_2O, N_2) (Urbanski 1983) and numerous minor constituents (e.g., methane, hydrogen fluoride). As such, exhaust emissions from gun and rifle systems should be treated as a complex mixture when designing a toxicological testing strategy.

It is always difficult to extrapolate the toxicity data obtained from animal studies to humans. Industrial, accidental, or voluntary human exposure and acclimation data have been very helpful in such cases in setting occupational exposure limits. Epidemiological data have proved useful in evaluating toxicity of some complex mixtures, e.g., cigarette smoke.

Even though the emissions resulting from the firing of guns are a complex mixture of many chemicals, some of the well-known compounds are present in relatively large amounts. Section 4.3, therefore, briefly discusses the toxicity of some of these major combustion products. Section 4.2 provides the reader with some general principles of inhalation toxicology and the remaining sections focus on what is the principal purpose of Section 4, the recommendation of a toxicity testing strategy for emissions from gun systems by analogy to the strategies that have been applied to other complex environmental mixtures. The mixtures chosen for characterization are diesel and gasoline exhaust, cigarette smoke, and polymer combustion products.

4.2 INHALATION TOXICOLOGY

A full discussion of inhalation toxicology is beyond the scope of this project. The reader is referred to publications such as Menzel and McClellan (1980), Phalen (1984), and Ryon and Sawhney (1985). However, some of the basic aspects of inhalation toxicology are briefly discussed below to assist readers who are not inhalation toxicologists.

The air and blood flow in the lung is shown diagrammatically in Figure 4.1. The rate of adsorption of gases in the lung depends on their blood:gas solubility. For very-low-solubility gases such as NO_2, the rate of absorption is highly dependent on blood flow through the lung (perfusion limited); for highly soluble gases such as SO_2, the rate of absorption is highly dependent on the respiratory rate (ventilation limited). There is a transition between the two extremes, which centers around a blood:gas solubility of about 1.2 (Klaassen 1980).

The pulmonary defense system against any toxicant is essentially composed of mucus production, ciliary activity, and activity of phagocytes. Ciliary activity can stand considerable insult, and mucostasis rather than ciliostasis is the early symptom of impairment of the pulmonary defense system (Falk 1970). It is interesting at this point to

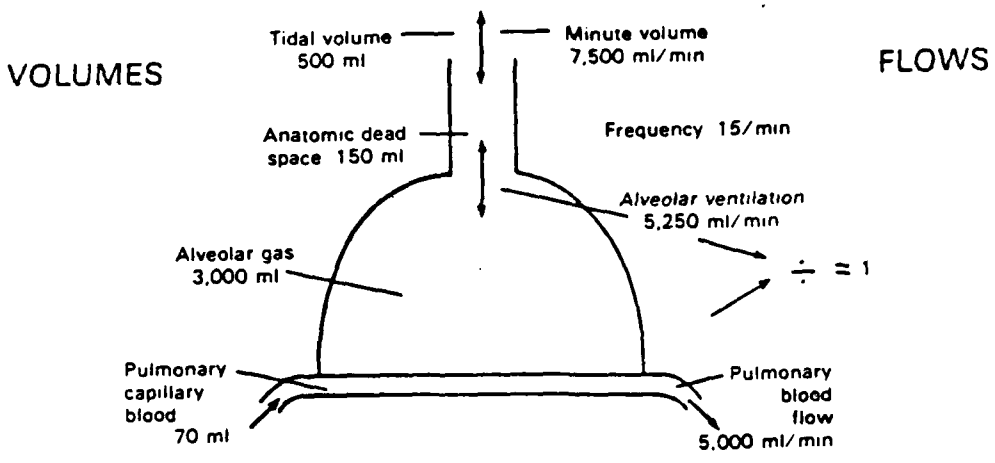

Figure 4.1. Diagram of a lung showing typical volumes and flows. There is considerable variation around these values. Source: West (1974), as cited in Menzel and McClellan (1980).

compare the action of SO_2 and NO_2 on the pulmonary system. Sulfur dioxide is relatively more soluble in blood and is rapidly absorbed in the upper portion of the airway. The less-soluble NO_2, on the other hand, reaches deeper into the lungs and exerts its irritating effect in the lower portion of the respiratory tract. Such irritation can affect the pulmonary defense system adversely and increase the susceptibilty of the exposed animal to infection. This is the basis for several inhalation toxicity studies. Campbell et al. (1980) found enhanced susceptibility to bacterial (Streptococcus) infection in mice after exposure to dilute exhaust from diesel engines. Coffin and Blommer (1967) exposed mice to automobile exhaust containing 0.35 to 0.67 ppm oxidant (measured as ozone) and 100 ppm CO for 4 hr immediately followed by a second exposure to a bacterial aerosol of Streptococcus at the rate of 100,000 organisms per mouse. Fifty-three percent of the exposed animals died compared with eleven percent among the controls (see Section 4.7.4 for further discussion of susceptibility and NO_2).

Pulmonary deposition and clearance of particulates have been subjects of intensive study. Deposition of particulates may occur by interception, impaction, sedimentation, and diffusion (Menzel and McClellan 1980). Interception is an important mechanism by which large particulates (200-μm x 1-μm dia.) are deposited in the bronchial tree. Particles are likely to be deposited by impaction at the airway bifurcation. The impaction probability is determined by a combination of air velocity and the square of the particle mass. Sedimentation of particles takes place in the smaller airways (e.g., the bronchioles and the alveolar spaces) where the velocity of the airflow is low, but is no longer a factor when the aerodynamic diameter reaches about 0.5μm. Diffusion is an important mechanism for the deposition of submicron particles below about 0.5μm. Factors affecting the regional deposition are depicted in Figure 4.2.

Additional physiological or pathological factors may influence deposition of particles in the lung; for instance, during exercise, where large volumes of air are inhaled at high velocities, impaction rate in the large airways and sedimentation and diffusion rate in the smaller airways and alveoli will increase; irritant materials that cause bronchoconstriction will increase the deposition of particles, thus complicating the dose level during exposure. A portion of the particles deposited in the lung is cleared and the rest is retained. Nasopharyngeal and tracheobronchial clearance takes place mainly through mucociliary transport. Pulmonary clearance may follow three different paths: (1) particles after phagocytization may be cleared up the tracheobronchial tree via the mucociliary escalator; (2) phagocytized particles may be removed via the lymphatic drainage; and (3) material may be removed from the surface of the particles by dissolution and carried away in the blood stream or lymphatics (Menzel and McClellan 1980).

As discussed by Menzel and McClellan (1980), both nose- or head-only and whole-body exposure systems have been used in toxicity studies of aerosols; both systems have their merits and demerits. In the nose- or head-only mode, dosimetry is more accurate since there is no

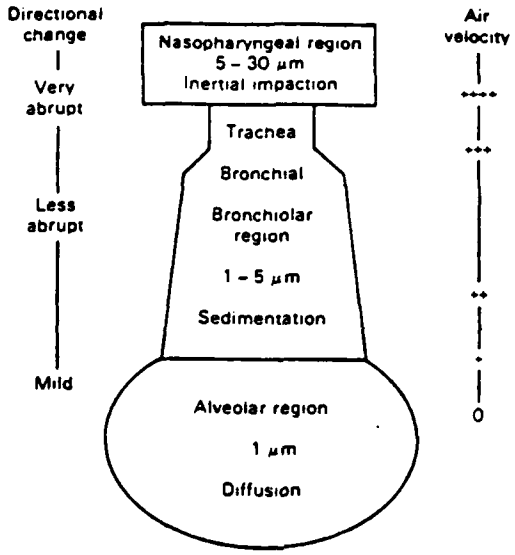

Figure 4.2. Parameters influencing particle deposition. Source: Casarett (1972), as cited in Menzel and McClellan (1980).

deposition that could result in absorption through skin or through the gastrointestinal tract when the animal grooms itself. On the other hand, the animals have to be restrained and relatively few animals can be exposed at once. The whole-body exposure system typically uses a four- or six-sided chamber, the top and bottom of which are mated with a pyramid-shaped section. Animal cages can be arranged in single or multiple tiers and are constructed of wire mesh to minimize any pertubations of airflow.

Species-to-species variation of susceptibility to airborne toxicants has been emphasized by many investigators [e.g., Falk (1970), Legters et al. 1980)]. For example, in one study with NO_2 and with lethality as the endpoint, guinea pigs were the most susceptible of the commonly used laboratory animals, rats were least susceptible, and mice and dogs fell in the middle (Legters et al. 1980). Animals as large as donkeys have been used in inhalation toxicological studies, but for obvious reasons the use of such large animals is not practical.

4.3 PROPELLANT COMBUSTION PRODUCTS

The identity and toxicity of major combustion products from propellants has been recognized for a long time. For example, Knight and Walton (1926) reported the composition of the products formed by burning smokeless powder in two stages in a confined space simulating a naval gun turret as follows:

	Stage 1 (%)	Stage 2[a] (%)
NO	1	-
NO_2	7	1
CO	18	9
CO_2	17	8
H_2	8	-
CH_4	2	-
N_2	37	67
O_2	-	12

[a]With additional air.

The gaseous mixture was found to be very toxic to experimental animals due to the presence of CO and NO_2. Feinsilver et al. (1950) report the toxicity to mice and rats by inhalation of the products of combustion of solid propellant compositions containing a perchlorate-fuel mixture. These propellants were used for assisting the take-off of carrier-based aircraft. The toxic components of the exhaust from the fuel propellant formulations JPL-125, JPL-100-L, and JPL-118 were identified to be H_2S, SO_2, HCl, and CO. Relative toxicities of H_2S, SO_2, and CO in mice were

found to be 100, 50, and 25, respectively. However, of these, carbon monoxide posed the most persistent and greatest hazard because of its high concentration in the exhaust. These combustion products also caused corrosion of Zn- and Cd-plated surfaces of the metal animal cages, which yielded products toxic to living tissues. Mice were found to be more susceptible to the combustion products than rats.

The problem of potential exposure of military personnel to some of the major toxic components of propellant combustion products (i.e., NH_3, CO, SO_2, and NO_x) has recently been summarized by Legters (1980), Nightingale (1980), Normandy et al. (1980), and Morton (1980), respectively. Such exposures may take place during the training of soldiers with various weapon systems or in combat and are likely to be more intense (i.e., intermittent high-level exposure) compared with OSHA standards. OSHA occupational exposure limits are intended to protect against adverse health effects and discomfort in a working lifetime of repeated daily exposure. Military exposure limits, on the other hand, should be based on preventing immediate incapacitation or performance degradation and chronic or irreversible health effects. This is the rationale for the higher exposure limit for military personnel for NH_3 recommended by the Army Environmental Hygiene Agency (Table 4.1).

The following subsections briefly discuss the potential health effects of the four gases noted above: ammonia (NH_3), carbon monoxide (CO), sulfur dioxide (SO_2), and nitrogen oxides (NO_x). Much of the information presented for these gases has been taken from Legters (1980), Nightingale (1980), Normandy et al. (1980), and Morton (1980), respectively, and the reader is referred to these reports for additional information. The health aspects of lead, antimony, barium, copper, and zinc are also briefly discussed since these metals have been reported in the inhalable metal particulate fraction from the M16 rifle; lead constituted about half of the total amount of inhalable (<10 μm) particulates (Ase et al. 1985).

4.3.1 Ammonia

Ammonia (NH_3) is generated by the combustion of propellants, especially those containing nitroguanidine. Some field data are available on exposure of military personnel to ammonia (Legters et al. 1980). A 1943 army report states that during firing of weapons in the M4A4E1 and M7 tanks, the concentrations of NH_3 and CO were so intense that the operation of the weapon was extremely difficult and unreliable. In a 1954 report of the U.S. Army Human Engineering Laboratory on the "relation of toxic gases to equipment design," it is stated that the concentrations of ammonia measured during weapons firing in armored vehicles ranged from 105 to 410 ppm, well above the current ceiling of 100 ppm recommended by the Army Environmental Hygiene Agency (Table 4.1). However, concentrations of ammonia recorded in the main battle tank (XM-1) during development tests at Aberdeen Proving Ground seldom exceeded 100 ppm (Legters 1980).

The upper respiratory tract and eyes are the two organs primarily affected by exposure to ammonia (Legters et al. 1980). High-level

TABLE 4.1. STANDARDS AND GUIDELINES OF SOME MAJOR RIFLE AND GUN SYSTEM COMBUSTION PRODUCTS[a,b]

	All Concentrations in ppm					
Organization	NH_3 (Ammonia)	CO (Carbon Monoxide)	SO_2 (Sulfur Dioxide)	NO (Nitric Oxide)	NO_2 (Nitrogen Dioxide)	PB (Lead)[f]
ACGIH (TLV)	25	50	2	25	3	0.15 mg/m^3
ACGIH (STEL)	35	400	5	-	5	-
OSHA (TWA)	50	50	5	25	5 (C)	0.05 mg/m^3
NIOSH (TWA)	50 (C, 5 min)	35 200 (C)	0.5	25	1 (C, 15 min)	0.10 mg/m^3
EEL	None	None	10 min: 30 30 min: 20 60 min: 10 24 hr: 5	None	5 min: 35 15 min: 25 30 min: 20 60 min: 10	
HEL (APG)	100 (C) 25 (TWA)	COHb, 5%[c,d] COHb, 10%[c,e]				

a. Adapted from Legters et al. (1980); TOP (1984); OSHA (1985); RTECS (1986); ACGIH (1986-1987), except as noted.

b. Abbreviations:

C = Ceiling value

COHb = Carboxyhemoglobin

EEL = Emergency (occupational) exposure limit, recommended by the National Academy of Sciences - National Research Council or American Industrial Hygiene Association

TLV = Threshold limit value; 8-hr time weighted average

TWA = Time-weighted average

STEL = Short-term exposure limit; 15-min ceiling

ACGIH = American Conference of Governmental Industrial Hygienists

HEL (APG) = Human Engineering Laboratory (Aberdeen Proving Ground)

NIOSH = National Institute of Occupational Safety and Health

OSHA = Occupational Safety and Health Administration

c. MIL-STD-1472C, as cited in TOP (1984).

d. All system design objectives and aviation system peformance limits.

e. All other system performance limits.

f. See section 4.3.5 for additional guidelines for lead.

inhalation exposure studies have been carried out with rats, guinea pigs, rabbits, monkeys, dogs, and pigs. Human inhalation exposure studies also have been conducted and threshold levels defined (see Table 4.2). Perhaps the most significant irritant effect from the military standpoint is that exposure at approximately 130 ppm produces lacrimation in 50 percent of uninured subjects and impairs performance standards. In a repeated inhalation study with humans, subjects exposed at levels from 25 to 100 ppm of ammonia for 2 to 6 hours daily, 5 days a week for 6 weeks, showed signs of acclimation and no adverse health effects. However, during excursions above 150 ppm lacrimation was seen in all subjects (Ferguson et al. 1977).

Animal studies provide some information on the relationship of concentration and duration of exposure (Ct) for intermittent exposures. In one study, 6/10 rats exposed to 102 ppm NH_3, 5 hours/day, 5 days/week for 12 weeks (Ct of 30,600 ppm-hours) showed moderately or severely damaged tracheal mucosa, whereas rats exposed to 221 ppm 8 hours/day, 5 days/week for 6 weeks (Ct of 53,040 ppm-hours) showed no effects; and, even more dramatic, rats exposed to 1,100 ppm for this same exposure regime (Ct of 264,000 ppm-hours) showed only nonspecific inflammatory changes in the lungs. These data point to the significance of the overall exposure period and suggest cautious use of concentration and time relationships.

4.3.2 Carbon Monoxide

Carbon monoxide (CO) is the major toxic component of gun exhaust, and concentrations of several thousand ppm have been detected in armored vehicles (Legters et al. 1980). Health effects of carbon monoxide have been discussed by Stokinger [(1975) as cited by Opresko et al. (1984)]. Carbon monoxide has 200 to 300 times more affinity for hemoglobin than oxygen, forming carboxyhemoglobin (COHb) that leads to hypoxia. As noted by Nightingale (1980), the principal organs affected are the heart and brain. The elimination of CO from blood mainly takes place through the lungs and at a slow rate.

There are various factors that should be taken into account in setting the CO-exposure level for military personnel. The normal COHb level for nonsmoking, nonexposed adult humans is less than 1 percent [Stokinger (1975) as cited in Opresko et al. (1984)]. Cigarette smokers, on the other hand, are estimated to have a constant COHb level of 3.8 to 6.8 percent (Mikulka et al. 1970). Evidence of acclimatization of humans to CO exposure has been discussed by Otis (1970). According to Nightingale (1980), sensitive individuals would include subjects with a tendency toward arterial vasospasms, those with a history of myocardial infarcts and anemia, and the pregnant (the target being the fetus).

Stewart (1975) has pointed out that the human brain has a highly efficient mechanism to quickly compensate for any decrease in oxygen-carrying capacity caused by CO and it is doubtful that COHb saturations below 5 percent will have any potential to affect psychomotor and cognitive functions. The effect of low COHb saturations on cognitive tasks (such as arithmatic problem solving, vigilance testing, driving

TABLE 4.2. SUMMARY OF THRESHOLD LEVELS AND RANGES FOR SIGNIFICANT IMMEDIATE REVERSIBLE (MAINLY IRRITANT) EFFECTS OF NH_3 IN MAN[a]

NH_3 Concentration (ppm)	Effects
20-30	Odor "easily noticeable"
50-72	Produces "moderate" irritation of the eyes, nose, and throat in most subjects
110	Tolerated by all uninured subjects for 2 hours
134	Produces lacrimation in 50% of uninured subjects
140	Tolerated by all uninured subjects for 1/2 hour; only by highly motivated subjects for 2 hours
150	Produces lacrimation in subjects previously acclimated at 25-100 ppm for varying durations
150-500	Produces changes in ventilation minute and tidal volume and respiratory rate[b]
1,000	Produces coughing

a. Adapted from Legters (1980).

b. Tidal volume × respiratory rate = minute volume.

performance) is controversial. It has also been pointed out (EPA 1979) that research on the effects of CO on humans has been frought with methodological problems so as to make the data difficult to interpret. These problems include (1) failure to measure blood COHb levels, (2) failure to distinguish between the physiological effects from a CO dose of high concentration and the slow, insidious increment in COHb level over time from lower inhaled CO concentrations, (3) failure to measure the effect of changes in alveolar ventilation volumes on the amount of CO brought to or removed from the lungs, (4) use of small number of experimental subjects, (5) inadequate controls, and (6) poor statistical treatments. Although many of these data are poorly documented, ambiguous, and often in dispute, it has been concluded that cardiovascular effects can be demonstrated with CO exposure as low as 17 to 21 mg/m^3 (15 to 18 ppm CO for an 8-hour exposure; 2.5 to 3.0 percent COHb). Behavioral and central nervous system effects are demonstrable with a minimum of 29 to 34 mg/m^3 CO exposure (25 to 30 ppm CO; 4 to 6 percent COHb). Visual sensitivity may be affected as a continuous dose-response function without an obvious CO threshold, although such data are presently tenuous. A few representative data on the effects of CO on humans are shown in Table 4.3.

Coburn et al. (1965) developed a model known as the CFK (Coburn-Foster-Kane) equation taking into account the physiological variables that determine the blood carboxyhemoglobin concentration in man. They applied the equation to data obtained from normal subjects, male volunteers who breathed 100 percent oxygen for extended periods of time and patients with elevated rates of endogenous CO production. The CFK model has been successfully extended to predict carboxyhemoglobin levels resulting from carbon monoxide exposure of humans at rest and at exercise (Peterson and Stewart 1975; Tikuisis et al. 1987). Modified versions of the CFK equation have been used in predicting carboxyhemoglobin concentration in humans (TOP 1984; NIOSH 1972). It has been pointed out by Tikuisis et al. (1987) that the computation following the NIOSH method results in significant overprediction. This has been ascribed to the omission of water vapor in the lungs when the inspired pressure of CO is considered and to the use of incorrect values of alveolar ventilation.

The basic form of the CFK equation is as follows -

$$\frac{A\,[HbCO]t - BVco - PIco}{A\,[HbCO]o - BVco - PIco} = e(tA/VbB)\text{ , where}$$

$$A = Po_2 / M\,[HbO_2]$$

$$B = 1/DLco + PL/VA$$

$$M = \frac{[COHb]\ Po_2}{[O_2Hb]\ Pco}$$

TABLE 4.3. REPRESENTATIVE DATA ON EFFECTS OF CARBON MONOXIDE ON HUMANS

No. of Subjects	Period of Exposure	COHb	Dependent Variable	Results	References
47	1.33 hr (mean) or 5.5 hr (mean)	Average 35% Average 17%	Aspartate amine transferase (AspAT), lactic acid dehydrogenase activity and lactate level in lighting-gas compared to coal-stove poisonings	Enzymatic changes increase with length of exposure. Changes in enzyme activity and lactate level parallel ECG and clinical changes AspAT activity was increased even without ECG or clinical changes	Bogusz et al.
10	2 hr (50 ppm)	Mean 2.68%	Exercise-induced angina pectoris	Exposure to CO produced symptoms of angina sooner and after less cardiac work	Aronow and Isbell
20	~20 min, depending on subject (50 ppm)	3.17%	Exercise and heat stress	Exposure effectively reduced work time of nonsmokers and elicited changes in respiratory patterns of both smokers and nonsmokers	Drinkwater et al.
16	1 hr (225 ppm)	17-18%	Physical work capacity	No impairment in ability to do heavy work.	Vogel et al.
20	2 hr (50-100 ppm)	3-7.6%	Auditory vigilance	Decreased vigilance performance	Groll-Knapp et al.
9	90 min (50, 175, and 250 ppm)	1.8-7.5%	Visual vigilance	Significant reduction in vigilance	Beard and Grandstaff
10	1-2 1/2 hr (26 and 111 ppm)	2.3 and 6.6%	Visual vigilance	Signal identification performance deteriorated and monotony effect was potentiated	Horvath et al.
52	3 1/3 hr (100+200 ppm)	4.61-12.6%	Vigilance performance (numeric monitoring task)	No effect on vigilance performance	Benignus and Otto
30	4 hr (5-70 ppm)	1-5%	Auditory and visual monitoring	No effects	Putz et al.
18	2 1/2 hr (50-250 ppm)	Estimated 2-3%	Discrimination of short intervals of time	Performance deteriorated increasingly with progressively higher concentrations	Beard and Wertheim
42	2 1/2-8 hr (100 ppm)	7.2-11.6%	Visual perception, ability to learn, manual dexterity	Visual perception was not affected, manual dexterity was diminished, learning performance deteriorated	Bender et al.

$[HbO_2]$ = mL of O_2 STPD (standard temperature and pressure and dry)/mL of blood

$[HbCO]t$ = mL of CO/mL of blood at time t

$[HbCO]o$ = mL of CO/mL of blood at the beginning of the exposure interval

Po_2 = average partial pressure of O_2 in lung capillaries, mm Hg

Pco = average partial pressure of CO in lung capillaries, mm Hg

Vco = rate of endogenous CO production, mL (STPD)/min

DLco = diffusivity of the lung for CO, mL (STPD)/min (mm Hg)

PL = barometric pressure minus the vapor pressure of water at body temperature, mm Hg

Vb = blood volume, mL

PIco = partial pressure of CO in the inhaled air, mm Hg

Va = alveolar ventilation rate, mL (STPD)/min

t = exposure duration, min

It has been pointed out that in the case of large amounts of inspired CO, the assumption that $[O_2Hb]$ is a constant is no longer valid. The decrease in $[O_2Hb]$ can be approximated by

$$[O_2Hb]t = 1.38\ [Hb] - [COHb]t \quad \text{(Peterson and Stewart 1975)}$$

In this situation the CFK equation can be solved numerically, by trial and error or by numerical integration (Tikuisis et al. 1987). Recently Muller and Barton (1987) have further refined the CFK model and developed a non-linear but analytically integrable differential equation which can be used to compute [COHb]t using an interval halving (binary search) algorithm. This method is claimed to be more accurate and almost as convenient to compute as linear approximations.

In the real world, military personnel are exposed not to a constant but to varying concentrations of CO. The level of CO in the blood probably starts with a point near zero concentration, rises steadily to reach a peak, and then falls gradually when the source of CO has been removed. A typical scenario is described in Figure 4.3 (TOP 1984).

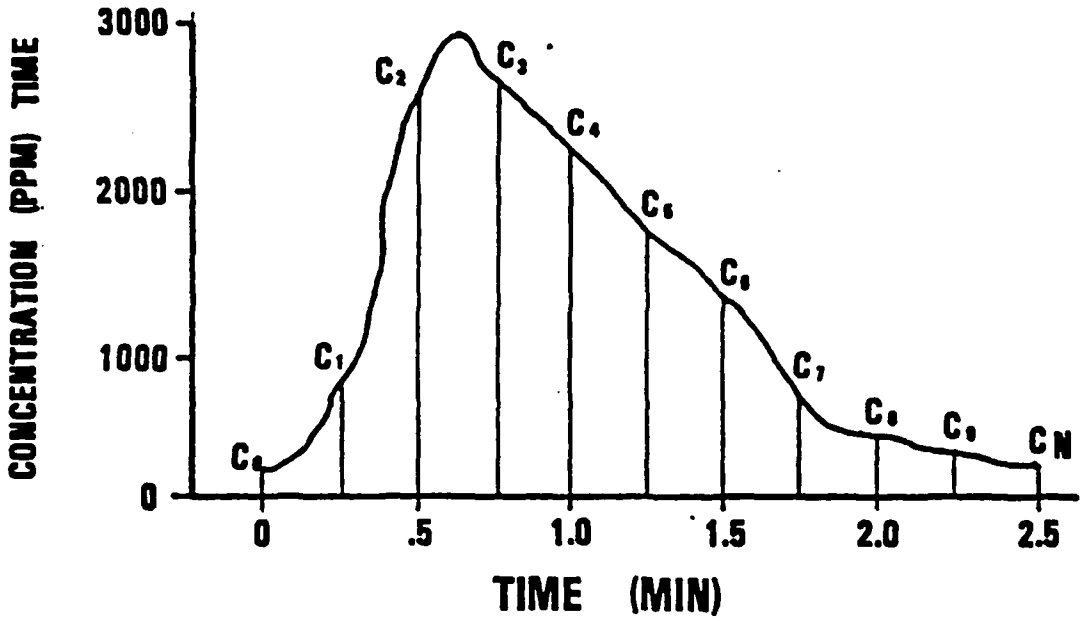

Figure 4.3. Typical exposure-concentration curve for toxic substances, e.g., CO. Adapted from MIL-STD-1472C, as cited in TOP (1984).

Carbon monoxide exposure levels recommended in the past for military, industrial, and spacecraft personnel are indicated in Table 4.4. For nuclear submarine and aviation personnel, CO exposure limits have been set so that the COHb concentration stays below 5 percent (see Tables 4.1 and 4.4). This limit was recommended on the premise that a higher level of CO exposure might compromise the high level of judgment and performance required of pilots, submariners, and space crews. This premise is substantiated in USEPA (1984), which reports decrements in complex sensorimotor performance and driving tasks, e.g., in compensatory tracking (a hand-eye coordination task), at a COHb level of 5 percent. It would seem logical to extend this 5 percent guideline to operators of armored vehicles. For the rest of the military personnel the CO exposure limit has been set at a COHb level of 10 percent (Table 4.1).

The decay time for reduction of COHb in blood can be calculated by the following formula:

$$\text{Decay time (hr)} = (2.582) \times [\ -\ln (COHb_t - 0.0981)/(COHb - 0.0981)],$$

where $COHb_t$ = % of COHb at the end of time period t, and

COHb = % of COHb at the beginning of time period or at the end of consecutive firing episodes.

A decay time of 6.2 hours was calculated for a drop of COHb from 10 to 1 percent.

One other possible health effect that has been studied as a result of CO exposure is interference with normal fibrinolytic activity. However, according to USEPA (1984), the studies in which test subjects were repeatedly exposed were too poorly controlled to confirm any definite effects on the blood coagulation system.

4.3.3 Sulfur Dioxide

Sulfur dioxide (SO_2) may arise in gun exhaust from antimony sulfide used in the priming mixture, sulfur used in the black powder, and potassium sulfate used in the propellant formulations as a flame retardant. There are no data on exposure of personnel in armored vehicles to SO_2 according to Normandy et al. (1980). Physiological effects of SO_2 on humans are summarized in Table 4.5. As stated by Normandy et al. (1980), the neurologic effects are notable since they reportedly occur at concentrations at or below the human sensory threshold; however, the relevance of these subtle effects to performance degradation is not known. Acclimation to the irritant and mechanical effects of SO_2 at concentrations up to 25 ppm have been noted, but this is unlikely to occur with soldiers because of erratic exposure schedules (Normandy et al. 1980).

TABLE 4.4. CARBON MONOXIDE LEVELS THAT HAVE BEEN PREVIOUSLY RECOMMENDED[a,b]

ppm	COHb%	Duration	Exposure Conditions	Subjects	Purpose	Source
1,500		10 min	EEL normal activity	Healthy young adults	Military and space	NRC[c]
1,000		10 min	EEL normal acuity	Healthy young adults	Military and space	NRC
800		30 min	EEL normal activity	Healthy young adults	Military and space	NRC
500		30 min	EEL normal acuity	Healthy young adults	Military and space	NRC
400		60 min	EEL normal activity	Healthy young adults	Military and space	NRC
200		60 min	EEL normal activity	Healthy young adults	Military and space	NRC
200		24 hr	EEL normal activity	Healthy young adults	Military and space	NRC
100		8 hr	MAC	Industrial workers	Industry	USASI
18		8 hr	MAC	Industrial workers	Industry	USSR
50	8-10	7-8 hr/d	TLV: 40 hr/wk	Industrial workers	Industry	ACGIH
25	4-5	90 d	Continuous	Healthy young adults	Nuclear submarine	NRC
15[c]	2-3	90-1,000 d	Continuous	Healthy young adults	Spacecraft	NRC

a. Adapted from DuBois (1970).

b. Abbreviations

EEL = Emergency Exposure Limit

MAC = Maximum Acceptable Concentration

TLV = Threshold Limit Value

NRC = National Research Council

USASI = United States of America Standards Institute

USSR = Union of Soviet Socialist Republics

ACGIH = American Conference of Government and Industrial Hygienists

c. A provisional level for continuous exposure, 12-hr integrated time average.

TABLE 4.5. THRESHOLD LEVELS AND RANGES FOR SIGNIFICANT IMMEDIATE IRRITANT AND NEUROLOGIC EFFECTS IN HUMANS EXPOSED TO SULFUR DIOXIDE

Threshold Level or Range (ppm SO_2)	Effects
0.3 to 1	Lower limit of detectability. Neurological effects, including elevation of optical chronaxy, suppression of dark adaptation, decreased light sensitivity, conditioning of electrocortical reflex, and disruption of alpha brain wave patterns.
1 to 5	Range in which gas becomes detectable by taste and odor. Decreases in tidal volume and increases in respiratory and heart rates occur. Exposure by mouth breathing may cause coughing, throat irritation, increased salivation, bronchoconstriction. Dryness of throat and pharynx, bronchoconstriction, acrid taste, immediate coughing may occur with nasal breathing. Objectionable to some individuals.
6.5 to 10	Definitely identifiable; causes nasal irritation, dryness of throat and pharynx, bronchoconstriction, coughing. May cause moderate to severe eye, nose, and chest irritation.
10 to 12	Objectionable to most human beings; least amount causing pain in nasal area and pharynx, conjunctival pain, rhinorrhea, severe discomfort.
20 to 30	Least amount causing extreme irritation of upper respiratory tract, coughing, epistaxis, chest constriction, hemoptysis, severe bronchoconstriction, copius lacrimation, intense conjunctival pain. Extremely disagreeable.
30 and above	Least amount causing intense nasopharyngeal irritation, sneezing, coughing, epistaxsis; few individuals exceed 15 minutes of exposure.

a. Adapted from Normandy et al. (1980).

The LCt_{50} values from animal studies are given in Table 4.6 (Amdur 1980). Haber's law of concentration-time relationship (C X T = K, where C is the concentration, T is the time, and K is a constant) for mortality does not hold in the case of SO_2 exposure (Normandy et al. 1980). It is evident from animal and volunteer exposures that intensity of response is primarily dependent on concentration and that duration of exposure is less important. This fact is taken into consideration in setting the EEL standards for SO_2 exposure (Table 4.1).

4.3.4 Oxides of Nitrogen

Nitrogen oxides (NO_x) are defined in the context of this discussion as a mixture of nitric oxide (NO) and nitrogen dioxide (NO_2). NO_x may arise in gun exhaust from the decomposition of nitrates and nitrobodies such as nitrocellulose, and nitroglycerin used in propellants. Compared with NO_2, NO is relatively less toxic. It is not an irritant by itself, but it may be oxidized in air to form the more toxic NO_2, although at high dilution (concentrations below 50 ppm), the conversion of NO to NO_2 is slow. It does, however, combine with hemoglobin, having an affinity 1,500 times greater than CO, to form methemoglobin (Kon et al. 1977). No data are available on exposure of personnel in armored vehicles to NO_x according to Morton et al. (1980). The effects of human exposure to NO_2 are summarized in Table 4.7 (Morton 1980). In addition to the effects noted in Table 4.7, NO_2 has been reported to form methemoglobin (Guidotti 1978); however, this effect is secondary to the respiratory system effects noted in Table 4.7. NIOSH has proposed the most stringent ceiling value for exposure to NO_2, 1 ppm for a 15-min exposure (see Table 4.1).

Exposure to NO_2 below the OSHA ceiling level of 5 ppm may cause reversible impairment of respiratory functions, but it is not known how this may affect physical or mental performance (Morton 1980). The effects of a short, high-level exposure may subside and be followed by serious delayed effects including death or incapacitation from infectious pneumonia or obstructive pathologic changes in the lung. Chronic exposure to animals induces cumulative lung damage, reversible or irreversible. There is a clear association between exposure to NO_2 (single or repeated) and an increase in susceptibility to pulmonary infection (Ehrlich et al. 1977; Ehrlich et al. 1979; Ehrlich 1980; and Gardner 1984a). The likelihood of similar responses in human exposure is not known. However, with respect to increased susceptibility to infection, Gardner (1984a) states that the evidence from animal infectivity studies shows that NO_2 was probably the causative agent in the available epidemiological studies reviewed in his report.

As in the case of SO_2, Haber's equation of concentration-time relationship (Amdur 1980) fails in NO_2 exposure even over a short period of time. Here again, the concentration is more important than duration in determining the level of mortality (Morton 1980). However, data suitable for statistical analysis indicate that a modified Haber's relationship, $CT^n = K$, seems applicable. In this expression, C is

TABLE 4.6. LCt_{50} VALUES FROM ANIMAL STUDIES[a]

Species	SO_2 Concentration (ppm)	Time	LCt_{50} (ppm·hours)
Mice	1,337	10.0 min	223
	1,350	10.0 min	225
	1,948	9.8 min	318
	611	59.0 min	601
	610	1 hour	610
	1,375	3.5 min	859
	340	6 hours	2,040
	130	24 hours	3,120
	878.6	217.0 min	3,178
	1,000	4 hours	4,000
	150	847 hours	127,500
Guinea Pigs	1,000	20 hours	20,000
	130	154 hours	20,020

a. Adapted from Normandy et al. (1980).

TABLE 4.7. EFFECTS OF HUMAN EXPOSURE TO NITROGEN DIOXIDE (NO_2)[a]

NO_2 Concentration (ppm)	Time (min)	Effects
1 to 6	15	Threshold for increased airway resistance in bronchitics
4 to 5	10	Lung compliance decreased and airway resistance increased in healthy subjects
5	15	Threshold for decreased arterial partial pressure of O_2 and decreased diffusion capacity for CO in bronchitics
25	5	Pulmonary discomfort
25 to 100	120	Marked mucosal irritation; increase pulse and respiratory rate
45 (with 90 ppm NO)	30	
followed by		Pulmonary edema
20 (with 80 ppm NO)	15	
50	1	Pulmonary discomfort, nasal irritation (more intense than at 25 ppm for 5 min); substernal pain
60	60	Laryngeal irritation; increased respiration rate
70	20	Pulmonary edema
158	10	Intolerable; coughing; irritation of nasal and laryngeal mucosa; lacrimation; headache; nausea, vomiting. No delayed or long-term effect
250	47	Collagen degradation, methemoglobinemia, tightness in chest, dyspnea, nonproductive cough, retrosternal burning sensation

a. Adapted from Morton (1980).

concentration (usually in ppm), T is duration, n is less than unity and is constant for a given species, and K is a constant for a given level of effect (e.g., 50 percent mortality) in that species.

There are several factors that have a bearing on NO_2 toxicity (Morton 1980). Exposure to volunteers has shown that with respect to pulmonary function, the effects of NO_2 are influenced by SO_2 (see Section 4.7.4.4 for more information). Concurrent exposure to NO_2 and inert respirable particles enhanced the toxic effect of NO_2. Inert aerosols have been reported to aggravate the effects of NO_2 on respiratory function. Physical stresses such as pre-exposure chilling or post-exposure exercise may enhance the toxicity of NO_2. Variation in species sensitivity should be taken into account in extrapolating animal data to humans. According to Morton (1980), sensitivity to NO_2 exposure decreases in the following order: guinea pigs > mice/dogs > rats.

4.3.5 Metal Particulates

As indicated in Section 2.1.5, five metals have been found in significant quantities in the inhalable metal particulate fraction from the M16 rifle study (Ase et al. 1985): lead (Pb), antimony (Sb), barium (Ba), copper (Cu), and zinc (Zn). Lead constitutes about half of the total mass of inhalable (<10 μm) metal particulates; Cu is about one-third; and Sb, Ba, and Zn together make up about one-twentieth of the amount of inhalable metal particulates. Comprehensive coverage on the toxicology of these metals of interest is beyond the scope of this document. However, the subject is briefly reviewed below.

4.3.5.1 Lead

Lead (Pb) in gun exhaust may arise from lead carbonate, lead stearate, and lead styphnate used in propellant and primer compositions, but the major source of lead is the copper-coated lead slug used in the rifle (Ase et al. 1985). The propelling charges in artillery weapons normally contain lead foil as a decoppering agent that removes rotating band residues from the weapon bore. The lead is vaporized as the charge burns and is either swept through the tube and out the muzzle or settles in the crew compartment of the armored vehicle firing the artillery.

Indoor exposure to lead in firing ranges has been investigated by NIOSH (1982, 1983). In the NIOSH study involving the Federal Reserve Bank in Cincinnati, OH, (NIOSH 1982) when typical lead target bullets were in use, the shooters were exposed to an average TWA lead concentration of 170 $\mu g/m^3$. Average concentrations of lead were reduced to less than 4.0 $\mu g/m^3$ with the introduction of zinc bullets. In another NIOSH study (1983) involving the U.S. Post Office and Courthouse Building in Cincinnati, OH, the range master had an 8-hour TWA exposure of 220 $\mu g/m^3$ while seven shooters (16 qualification attempts) used wadcutter and CEB (Controlled Expansion Bullets-38 special, 110-grain, copper-jacketed hollow point, +P+) ammunition. Based on single qualification attempts, two shooters using wadcutter bullets had 8-hour time-weighted average daily exposures of 67 $\mu g/m^3$. These are the instances when the exposure level exceeded the OSHA 8-hour TWA daily exposure standard of 50 $\mu g/m^3$.

The USAEHA (1984) study on the determination of composition of combustion products during tracer firing in the Lake City Army Ammunition Plant reported the presence of lead among the combustion products but it was not quantified.

Lead is one of the most intensively studied metals from the toxicological point of view (Hammond and Beliles 1980; Bell et al. 1978). Discussion in this section is limited to the inorganic forms of lead only. The organic forms of lead such as tetraethyl lead have not been reported to be present in gun exhaust and are not discussed.

The most important route of occupational exposure to lead is by inhalation. A relatively minor route is through the ingestion of lead-contaminated food (OSHA 1984). Although details of the mechanism of absorption of lead are not clear, a few important observations can be summarized:

(1) As the respirable particle size decreases, the amount of lead deposited in the lung also decreases; for example, deposition of inhaled lead particles of 1 μm is 60 percent whereas deposition of inhaled lead particles of 0.1 μm is only 40 percent.

(2) On the average, about 30 ± 10 percent of the lead inhaled is absorbed through the lungs.

(3) The degree of absorption is influenced by several factors such as solubility, shape and size of different forms of lead, smoking habits, and the presence of a chronic respiratory disease.

(4) A part of the inhaled lead may be absorbed through the gut. The deposited particles may be phagocytized and cleared up the tracheobronchial tree by the mucociliary escalator and eventually swallowed and dissolved under the acidic conditions in the stomach and then absorbed through the gut.

(5) The gastrointestinal absorption of lead is much higher in children compared with adults.

(6) The presence of food generally lowers lead absorption from the gastrointestinal tract.

(7) About 95 percent of lead in blood is bound to erythrocytes.

(8) About 90 percent of the body burden of lead is present in bones and teeth.

(9) Lead passes through the placenta easily; it also passes through the blood-brain barrier although there is no accumulation of lead in brain.

(10) The elimination of lead takes place mainly through urine (75 to 80 percent) and gastrointestinal secretion (~15 percent). Other routes (hair, nails, sweat) are less than 8 percent (WHO 1980).

The four major target organs and systems are the central nervous system, the peripheral nerves, the kidney, and the hematopoietic system (Hammond and Beliles 1980; Goyer 1986). Toxic effects to these organs/systems are briefly discussed in the following paragraphs.

With respect to the central nervous system, subchronic or chronic exposure to high doses of inorganic lead have reportedly resulted in a severe and often fatal condition known as lead encephalopathy (Hammond and Beliles 1980). Dullness, restlessness, irritability, headaches, muscle tremor, ataxia, and loss of memory are the major signs and symptoms. Residual damage often occurs including epilepsy, hydrocephalus, and idiocy. Subtle behavioral effects, especially in children, have been observed at exposure levels below those causing encephalopathy, e.g., 40 to 80 μg/dL of blood in infants and young children (Hammond and Beliles 1980).

For the peripheral nervous sytem, lead palsy was a frequent occurrence noted in the older literature (Hammond and Belies 1980). Weakness of the extensor muscles is the major manifestation of lead palsy. Even in the absence of palsy, nerve conduction velocity can be slowed. As noted by Seppalainen et al. (1975, as reported in Goyer 1986), motor nerve dysfunction has been observed with blood lead levels in the 50 to 70 μg/dL range or lower.

According to Hammond and Beliles (1980) and Goyer (1986), two distinct types of renal effects have been observed in man. One type of effects are manifestations of damage to the proximal tubules, resulting in a depression of tubular reabsorption of glucose, amino acids, and phosphate. These effects are, however, reversible with chelation therapy. Prolonged exposure to high concentrations of lead leads to the other type of effect. A progressive disease, it is characterized by interstitial fibrosis, sclerosis of vessels, and glomerular atrophy.

The effects of lead on heme metabolism are shown in Figure 4.4. The heme synthesis begins in the mitochondrion with the formation of δ-aminolevulinic acid (ALA) mediated by ALA synthetase (ALAS). A series of additional steps take place initially in the cytoplasm and finally wind up with the formation of heme in the mitochondrion. The rate-limiting step in the heme biosynthetic pathway is the rate of ALA formation, which in turn depends on the rate of ALAS formation controlled by the feedback inhibition of heme. Lead can interfere at several enzymatic steps in the synthesis of heme, particularly by inhibiting the in corporation of iron into protoporphyrin IX by the enzyme ferrochelatase. This inhibiton of heme synthesis coupled with the reduction of the lifespan of circulating erythrocytes (thought to be due to increased mechanical fragility of the cell membrane) leads to the manifestation of anemia, an early symptom of lead poisoning.

The blood lead level is currently regarded as the single most important test for monitoring lead exposure (OSHA 1984). However, this test has one major drawback. A very important component of the total lead body burden is the presence of lead in soft tissue (liver, kidney, and brain). This fraction of the biologically active lead body burden

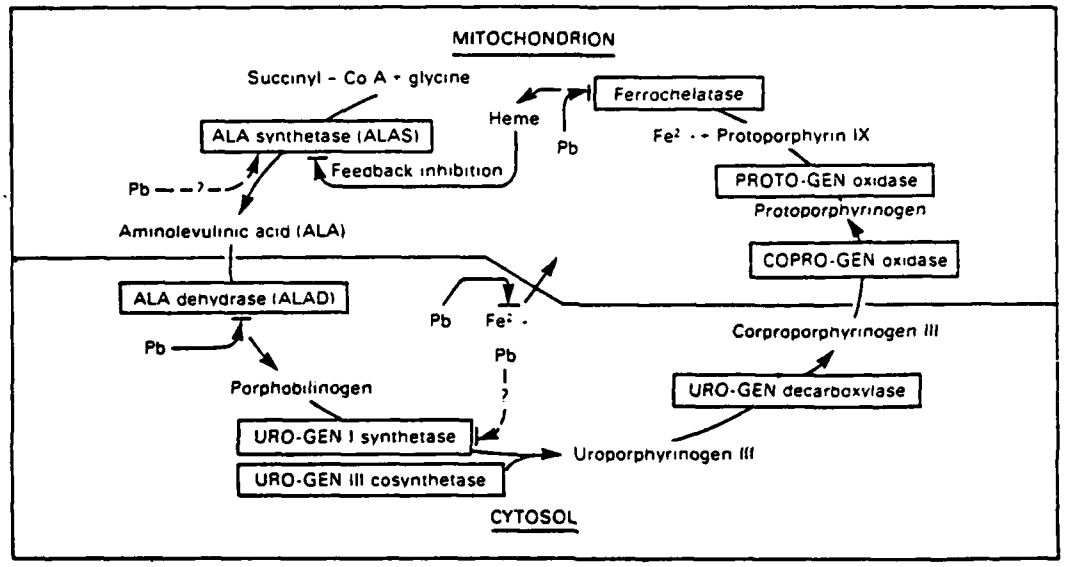

Figure 4.4. Effects of lead on heme metabolism.
Adapted from Hammond and Beliles (1980).

is not entirely reflected by blood lead levels since it is a function of the dynamics of lead absorption, distribution, deposition in bone, and excretion. A supplementary test, the zinc protoporphyrin (ZPP) test has been advocated in OSHA (1984). Zinc protoporphyrin results from the inhibition of the enzyme ferrochelatase (Figure 4.4). Zinc, having a greater affinity for porphyrin, takes the place of the iron-forming ZPP. Zinc protoporphyrin has a characteristic fluroescence spectrum (λmax = 594 nm) detectable with a hematofluorimeter, a portable instrument used in field studies. Although data on blood lead-ZPP correlations and the ZPP levels associated with adverse health effects are limited, ZPP has the potential to be an important diagnostic test for the early detection of lead toxicity. Due to pending litigation it is not required under the standard and remains an ancillary test.

As noted by Goyer (1986), other effects of lead possibly include gametotoxicity, chromosomal defects, and alterations of the humoral immune system. Schlipkoter et al. (1977) reported evidence that lead exhibited cytotoxic effects on alveolar macrophages causing a time- and dose-dependent deterioration of bacterial elimination and the combined pollutants NO_2 and flame-soot affected the mucocilliary system.

A case history of plumbism from airborne lead in a firing range has been well documented to indicate that the blood lead concentration is not a reliable indicator of lead poisoning, especially at a low level (Anderson et al. 1977). A 17-year-old boy developed plumbism while he was working in an indoor firing range. Initially, the blood lead level was reported to be within normal range. However, lead poisoning was clearly documented by several parameters, including characteristic abnormalities of the heme biosynthesis in erythrocytes (inhibited ALAS activity, higher level of protoporphyrin IX, see Figure 4.4) and increased urinary excretion of ALA and coproporphyrin. These abnormalities returned to normal with chelation therapy using calcium disodium edidate (Table 4.8).

The exposure limits for lead during firing are given in Table 4.9. The recommended threshold limit value (8-hr TWA) for inorganic fumes and dust is 0.15 mg/m^3 (ACGIH 1986-87). The current OSHA standard is 0.05 mg/m^3 (OSHA 1985).

4.3.5.2 Copper

Copper (Cu) in gun exhaust arises from the brass bullet case and copper coating on the lead slug used in the rifle (Herud 1985). Copper is an essential element - a part of several enzymes such as tyrosinase (which is necessary for the formation of melanin pigments), cytochrome oxidase, superoxide dismutase, amine oxidases, and uricase. It is also essential for the utilization of iron (Piscator 1979). Manzler and Schreiner (1970, as reported in Goyer 1986), reported that hemolytic anemia resulted from copper poisoning through the use of copper-containing dialysis equipment.

Inhalation of dusts and fumes of metallic copper and its salts causes congestion of nasal mucous membranes, ulceration and perforation

TABLE 4.8. VALUES FOR URINARY δ-AMINOLEVULINIC ACID (ALA) AND COPROPORPHYRIN ERYTHROCYTE δ-AMINOLEVULINIC ACID DEHYDRATASE (ALA-D) AND PROTOPORAPHYRIN, AND BLOOD LEAD IN THE PATIENT BEFORE AND AFTER TREATMENT AND IN AN ASYMPTOMATIC CO-WORKER WITH SUBCLINICAL LEAD POISONING[a]

Subject	Time (± days from start of treatment)	Urine		Erythrocyte			Blood Lead ($\mu g/dL^{-1}$)
		ALA (mg/day^{-1})	Coproporphyrin ($\mu g/day^{-1}$)	Nonactivated ALA-D ($nmole \cdot mL^{-1} \cdot hr^{-1}$)	Activated* ALA-D ($nmole/mL^{-1} \cdot hr^{-1}$)	Protoporphyrin ($\mu g/dL^{-1}$)	
Patient	-77	34.5	...	...	...	588	...
	-27	32.8	2,326	17	438	682	...
	-20	...	...	47	408	516	75
	-6	...	...	92	322	476	61
	1	27.4	4,163	...	...	...	...
	2	7.4	1,042	...	...	...	...
	3	1.4	217	...	...	...	...
	4	2.6	342	...	...	...	...
	5	2.2	629	308	514	488	37
	24	...	...	...	...	...	51
	95	10.3	143	166	414	344	48
Co-worker	...	...	...	31	450	119	69
Normal range	...	0-7	0-161	50-75% of activated	320-900	20-50	1-39

*Activated with 20 mM dithiothreitol.

a. Adapted from Anderson et al. (1977).

TABLE 4.9. EXPOSURE LIMITS FOR LEAD[a]

Airborne Lead Concentrations (mg/m^3)	Maximum Hours of Allowable Exposure	
	Firing 30 or More Days/Year	Firing Less Than 30 Days/Year
0 to 0.03	8	8
0.03 to 0.04	6	8
0.04 to 0.05	4.5	8
0.05 to 0.06	4	6.5
0.07 to 0.08	3	5
0.08 to 0.10	2.25	4
0.10 to 0.15	1.5	2.5
0.15 to 0.20	1	2
0.20 to 0.30	0.75	1.25
0.30 to 0.40	0.5	1
0.40 to 0.50	0.5	0.75
0.50 to 0.75	0.25	0.5
0.75 to 1.00	0.25	0.25
greater than 1.0	0	0

a. Adapted from TOP (1984).

of the nasal septum, and pharyngeal congestion in mammals (Venugopal and Luckey 1978).

Surveys of workers occupationally exposed to copper dust or fumes have not indicated any sign of chronic desease [Cohen (1974), as cited in Piscator (1979)]. Copper fumes and fine dust are known to cause so-called metal-fume fever, an influenza-like syndrome in which the symptoms disappear after 24 hr (Piscator 1979).

The main route of excretion of copper is via bile and feces. Urinary excretion of copper is, however, increased in Wilson's disease and nephrotic syndrome. High intake of molybdenum also increases excretion of copper.

No information is available on the inhalation toxicology of the interaction of copper dust and fumes with the gases such as NO_X, SO_2, NH_3, and CO present in gun exhaust.

The TLV (TWA) for copper fumes and for copper dusts and mists have been recommended at 0.2 and 1.0 mg/m^3, respectively (ACGIH 1986-87). The OSHA standard (8-hr TWA) for copper fumes is 0.1 mg/m^3 and for copper dusts and mists, 1 mg/m^3 (OSHA 1985).

4.3.5.3 Antimony

Antimony (Sb) in gun exhaust arises mainly from antimony sulfide used as a component of the primer (Ase et al. 1985). Industrial exposure may give rise to irritative symptoms in the respiratory tract. Long-term exposure may result in pneumoconiosis, sometimes with obstructive lung diseases, and fatal heart effects. Most of the absorbed antimony is quickly eliminated via urine and feces. A small part of the absorbed antimony may have a long biological half-time. The highest concentrations of antimony are found in the thyroid, adrenals, liver, and kidney after either acute or chronic exposure (Elinder and Friberg 1979). The ACGIH TLV (TWA) and OSHA standard (8-hr TWA) for antimony and antimony compounds (as antimony) is 0.5 mg/m^3 (ACGIH 1986-1987, OSHA 1985).

On the basis of the Fourth Report of the Interagency Testing Committee (ITC), antimony metal, antimony trioxide, and antimony sulfide are given priority testing consideration by the Office of Pesticides and Toxic Substances, Environmental Protection Agency (USEPA 1983a). The ITC recommended testing of these materials for health effects (carcinogenicity, mutagenicity, reproductive effects, teratogenicity) and environmental effects and recommended that epidemiological studies be conducted. It was also pointed out that no techniques are available to chemically distinguish among Sb, Sb_2O_3 or Sb_2S_3.

4.3.5.4 Barium

Barium (Ba) in gun exhaust arises mainly from $Ba(NO_3)_2$ used in the primer (Ase et al. 1985). Water soluble barium compounds are toxic whereas water insoluble barium compounds such as $BaSO_4$ are not because

they remain essentially unabsorbed. The Ba^{2+} ion is a muscle poison causing gastrointestinal, cardiac, and skeletomuscular stimulation followed by paralysis. Barium bioaccumulates in bone and pigmented parts of the eye. It also acts as a physiological antagonist to potassium (Reeves 1979). The TLV (TWA) for soluble compounds of barium has been recommended at 0.5 mg/m^3 (ACGIH 1986-87). This is also the maximum permissible limit set by OSHA (OSHA 1985).

4.3.5.5 Zinc

Zinc (Zn) is an essential element that is a constituent of several enzymes. The biological half-life in humans is about one year - excretion takes place mainly through the gastrointestinal tract. It occurs in high concentrations in prostate, bone, muscle, and liver. Respiratory exposure to freshly generated zinc fumes (mostly ZnO) in high concentrations (>15 mg/m^3) may cause metal fume fever, but chronic zinc poisoning in humans has not been reported (Elinder and Piscator 1979). The TLV (TWA) and short-term exposure limit (STE for ZnO fumes has been L) recommended at 5 and 10 mg/m^3, respectively. In dust form ZnO is regarded as a nuisance particulate and as such has a TLV (TWA) of 10 mg/m^3 of total dust when toxic impurities are not present (ACGIH 1986-87). OSHA adopted the same TLV for ZnO fume in 1968 (Stokinger 1981).

4.4 GASOLINE AND DIESEL EXHAUST EMISSIONS

The toxicological studies available in the literature of gasoline and diesel emissions are geared more towards chronic (mutagenic, carcinogenic) effects as opposed to acute performance degrading effects, whereas, in the case of gun exhausts, one of the primary concerns is performance degradation. In this section it is not intended to present a complete catalog of all the different toxicological studies that have been conducted on gasoline and diesel exhaust, but to emphasize the basic approaches using appropriate examples. Several different approaches for the evaluation of the carcinogenic, mutagenic, and toxicological effects of exposure to diesel and gasoline exhaust emissions have been described in the four symposia held under the auspices of the USEPA (1980a, 1980b, 1982, 1983b). Some of these are cited as examples in the following paragraphs; a more complete characterization of the toxicological testing methods for diesel emissions is given in Appendix B (Table B-1).

4.4.1 Bioassays

Fractionation of the exhaust followed by chemical characterization and short-term toxicological studies of different fractions has been widely followed by many investigators, particularly as an initial phase in determining toxicity. The main objective was to identify the toxic components of the exhaust. A good application of this approach is exemplified by the studies of Rannug et al. (1983). Exhaust samples were taken from gasoline or diesel engines either directly from the tail pipe or after dilution in a dilution tunnel, dilution ratio being 1:10 for

gasoline engines and 1:7 for the diesel engines. The particulate matter was trapped on glass-fiber filters and was extracted with acetone in a Soxhlet apparatus. The extract was concentrated by evaporation and normally 1 mL of extract was equivalent to either 50 L of diesel exhaust or 100 to 150 L of gasoline exhaust. After removal of the particulate phase, the gas phase was fractioned using a cryogradient technique. Three condensers using ice-water, dry ice-ethanol, and liquid nitrogen were used in series. Extracts from the nitrogen condenser contained no polycyclic aromatic hydrocarbons, but showed higher toxicity than the extracts from the other two condensers; consequently, mutagenicity data were not presented. The mutagenic effects of the particulate extract (filter) and extracts from the H_2O condenser and CO_2 condenser on Salmonella typhmurium TA98 and TA100 with and without an S9 metabolizing system (Ames Test) are shown in Figure 4.5. Another interesting observation made by Rannug et al. (1983) is that dilution of the exhaust with air increases the amount of PAHs associated with the particulates (Table 4.10).

Aromatic hydrocarbons present in gasoline and diesel exhaust can be converted into mutagenic nitro-derivatives in the presence of NO_2. Tokiwa et al. (1983) have shown that pyrene is converted into 1-nitropyrene by NO_2. The yield of 1-nitropyrene was 0.02 percent with a low level of NO_2 (1 ppm); 0.37 percent with NO_2 (1 ppm) + SO_2 (7 ppm, flow rate of 0.5 L/min); and 2.85 percent with NO_2 (1 ppm) + HNO_3 (~ 20 ppb) (flow rate of 2.2 L/min) when exposed for 24 hr with a carrier gas (N_2) (flow rate, 2 kg/cm^2). The presence of three nitro compounds, 1-nitropyrene, 3-nitrofluoranthene, and 5-nitroacenaphthene, has been detected by HPLC and MS. All three are carcinogens. It is of interest to note that pyrene, fluroanthene, and acenaphthene have been detected in propellant combustion products (Ase et al. 1985).

Another example of short-term carcinogenesis and mutagenesis bioassays of gasoline and diesel exhaust is the work of Huisingh (1982). This initial screening is useful to (1) demonstrate toxicity or mutagenicity, or provide an indication of possible carcinogenicity of particular fractions or mixture, (2) to biologically direct fractionation and identification of hazardous components, and (3) to compare relative biological activity of similar emissions from other sources. Much of the research has been focused on the organic compounds extracted from the particulates present in the exhaust. The organic extract has been separated into three fractions-acidic, basic, and neutral. The neutral fraction accounted for 34 percent of the mass and was further fractionated into 4 fractions: paraffinic (39 percent, nonmutagenic), aromatic (13 percent, 1.5 percent of the total mutagenic activity), and two most highly mutagenic polar fractions. These two fractions accounted for one third of the mass and over 90 percent of the mutagenic activity in both TA98 and TA1538 strains of Salmonella typhimurium.

Perhaps the most widely used mutagenicity test is the one proposed by Ames et al. (1975) and discussed above using S. Typhimurium with or without metabolic activation. Ames reported that most of the established carcinogens also act as mutagens in his assay system. The current status of mutagenicity and carcinogenicity correlations between

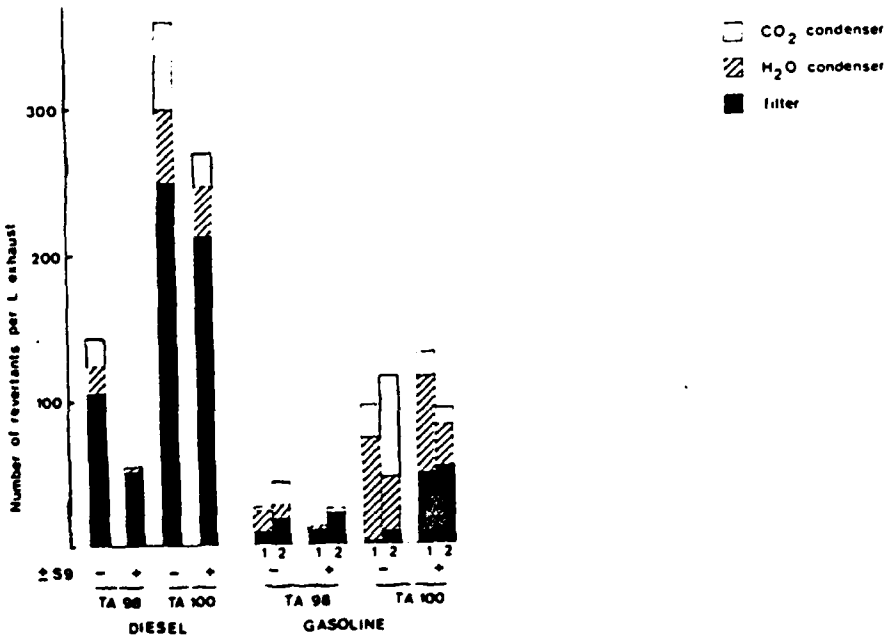

Figure 4.5. The mutagenic effects (revertants per liter exhaust) on Salmonella typhimurium TA98 and TA100 of the particulate phase (acetone extracts) and the gas phase (acetone extracts from H_2O and CO_2 condensers, respectively of exhaust emission from diesel- and gasoline-fueled cars. All samples were tested with and without the addition of a metabolizing system (S9).

Adapted from Rannug et al. (1983).

TABLE 4.10. PARTICLE-ASSOCIATED PAH FROM DILUTED AND UNDILUTED GASOLINE EXHAUST SAMPLED SIMULTANEOUSLY[a]

Type of PAH	Molecular Weight	Amount of PAH ($\mu g/m^3$ exhaust)	
		Undiluted	Diluted
Phenanthrene	178	0.6	6.6
Pyrene	202	3.9	64.6
Benzo(a)anthracene	228	2.9	7.9
Benzo(a)pyrene and 6-H-benzo(cd)pyrene-6-one	252,254	4.3	5.0
Benzo(ghi)perylene	276	12.2	10.6
Coronene	300	10.8	8.2

a. Adapted from Rannug et al. (1983).

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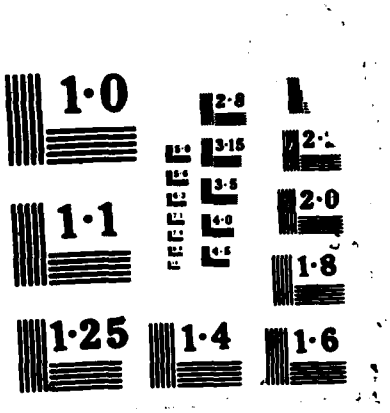
1·0
1·1
1·25
2·8
3·15
3·5
4·0
4·5
1·4
2·0
1·8
1·6

bacteria and rodents has been discussed at length by Brusick (1983). Thus, the Ames test provides a convenient short-term bioassay for mutagenicity and a screening assay for the carcinogenicity of gasoline and diesel exhaust.

Bioassays based on DNA damage (such as the yeast assay for mitotic recombination and unscheduled DNA synthesis and sister-chromatid exchange in mammalian cells) in addition to the carcinogenesis bioassay for morphological oncogenic transformation in the mammalian (BALB/c 3T3) cells have been used with diesel and gasoline exhaust (Huisingh 1982). Skin tumor initiation and promotion studies have been carried out with SENCAR mice (Nesnow et al. 1982). Table 4.11 shows normalized rankings for four bioassays of mobile-source emissions (Huisingh 1982). These assays showed an overall consistency; however, the quantitative results for other complex mixtures (e.g., cigarette smoke condensate and roofing tar) that required metabolic activation did not show agreement among these bioassays. Thus, according to Huisingh (1982), it may not be possible to quantitatively extrapolate from in vitro to in vivo results for all types of complex mixtures.

A great deal of attention has been paid to the particulates in automobile emissions and gun exhaust and a number of interesting and significant observations have been made:

(1) As mentioned before, dilution of the gasoline and diesel exhaust with air increases the amount of PAHs associated with the particulates (Rannug et al. 1983).

(2) About ninety percent of the PAHs in M16 rifle exhaust is associated with particulates (Ase et al. 1985).

(3) Concurrent exposure to NO_2 and inert respirable particles enhanced the toxic effect of NO_2 and other toxicants (Morton 1980); significant interactions between NO_2 and carbon particles resulted in the production of focal destructive pulmonary lesions in Swiss albino mice. [These were localized and severe and were not observed upon inhalation of NO_2 alone (Falk 1970)].

(4) The particulates in gun exhaust are not inert but they are mostly metal particulates, and in the case of M16 rifle exhaust, they have been found to contain Sb, As, Ba, Cu, Pb and Zn (Ase et al. 1985).

(5) Test protocols requiring extraction of particulates with solvents followed by fractionation and concentration do not have any counterpart in natural exposure by inhalation. The CHO (Chinese Hamster Ovary Cells)/HGPRT (Hypoxanthine Guanine Phophoribosyl Transferase) system developed by Hsie et al. (1979) is an example of assays that use the whole particle per se and as such are an improvement over bioassays that use solvent extracts.

Although the major emphasis for short-term bioassays has been placed on bacterial and mammalian cell lines, the use of non-mammalian in vivo systems such as Drosphila, Zea mays, and Tradescantia for

TABLE 4.11. ACTIVITY RANKING FOR MOBILE-SOURCE EMISSIONS[a,b,c]

Activity	Heavy-duty Diesel	Light-duty Diesel			
	Cat	Nissan	Olds	VW Rab	Mustang
Microbial mutation[d]	4.3	100	23	22	25
Sister chromatid exchange[e]	0	100	0	50	1
Mammalian cell mutation[f]	1	100	64	50	36
Rodent skin tumor initiation[g]	0	100	45	1	35

a. Adapted from Huisingh (1982) unless otherwise noted.

b. All data are expressed as a percentage of the Nissan diesel activity, which as assigned a value of 100.

c. Cat is the Caterpillar 3208, 4-stroke cycle engine; Olds is Oldsmobile; VW Rab is Volkswagen Rabbit.

d. S. typhimurium histidine reversion assay; TA98 with S-9 activation (Aroclor-induced).

e. Chinese hamster ovary cell assay with Aroclor-induced S-9 activation.

f. L5178 mouse lymphoma forward mutation assay at the thymidine kinase locus with Aroclor-induced S-9 activation.

g. SENCAR mouse assay using TPA (12-0 tetradecanoylphorbol-13-acetate as the tumor promoter.

environmental mutagen assessment has been advocated by Schairer et al. (1983). Tradescantia blossoms have been used in two ways for mutagenicity assays (primarily the gaseous phase of the auto exhaust): the micronuclei system (Ma et al. 1982, 1983) and the stamen hair system (Schairer et al. 1983). The endpoints are the number of micronuclei in 300 tetrads from a single bud (4 to 10 buds analyzed per treatment) in the micronuclei system and the phenotypic change in pigmentation from blue to pink in mature flowers in the stamen hair system. The experimental setup used by Ma et al. (1983) is shown in Figure 4.6.

In addition to the mutagenicity and carcinogenicity assessments of gasoline and diesel exhaust discussed above, bioassays have been developed for assessment of teratogenicity. A frog embryo teratogenesis assay (Dumont et al. 1983), human serum teratogenicity studies using in vitro cultures of rat embryos (Klein et al. 1983), and a teratology test system that utilizes postnatal growth and viability in the mouse (Chernoff and Kavlock 1983) have been reported.

4.4.2 Inhalation Toxicology

An example of an acute inhalation toxicity study of diesel fuel smokes and/or exhaust is the study of M60A1 tank-generated smokes/exhaust reported by Callahan (1981). Two different diesel fuels (DF1 and DF2), one summer and one winter grade respectively, were used in these tests. Young mature adult Sprague-Dawley rats and Hartley albino guinea pigs were exposed to M60A1 tank-generated DF1 and DF2 smoke and/or vapor in a 20,000-L chamber at levels up to 45,600 mg/m^3 under static air flow conditions for 15 to 300 min. Toxicologic, physiologic, hematologic, blood chemical, and pathologic assessments were made over a 14-day post-exposure period. In the case of DF1, 120- to 300-min exposures to 42,000 mg/m^3 of smoke/exhaust and 60- to 300-minute exposures to 177 mg/m^3 of exhaust caused death in laboratory animals. In the case of DF2, 60- to 300-min exposures to 45,600 mg/m^3 of smoke/exhaust and 280 mg/m^3 of exhaust caused death in laboratory animals. Callahan (1981) stated that the chemical component mainly responsible for the toxicity probably originated from DF1 and DF2 exhaust. Dalbey et al. (1982), in a study of the inhalation toxicology of diesel fuel obscurant aerosol in rats (containing no exhaust component as in the Callahan study) showed that the aerosol can be toxic. In their study, 3 of 10 rats died after 6 hours' exposure to 4,000 mg/m^3 and 10 of 10 died after exposure to 12,000 mg/m^3 for 6 hours.

The large-scale inhalation experiment of Lewis et al. (1974) is significant in the studies of chronic exposure to automobile exhaust. One hundred four beagle dogs were divided into eight groups. A group of 20 dogs served as control. Seven groups of 12 dogs each were exposed to auto exhaust, irradiated auto exhaust, $SO_2 + H_2SO_4$, auto exhaust + SO_2 + H_2SO_4, irradiated auto exhaust + $SO_2 + H_2SO_4$, and a high and a low level of NO_2. A daily exposure for 16 hours was continued for 68 months. Various pulmonary function tests such as carbon monoxide diffusion capacity, dynamic pulmonary compliance, and total expiratory flow resistance were carried out at 61 months following the initiation of exposure.

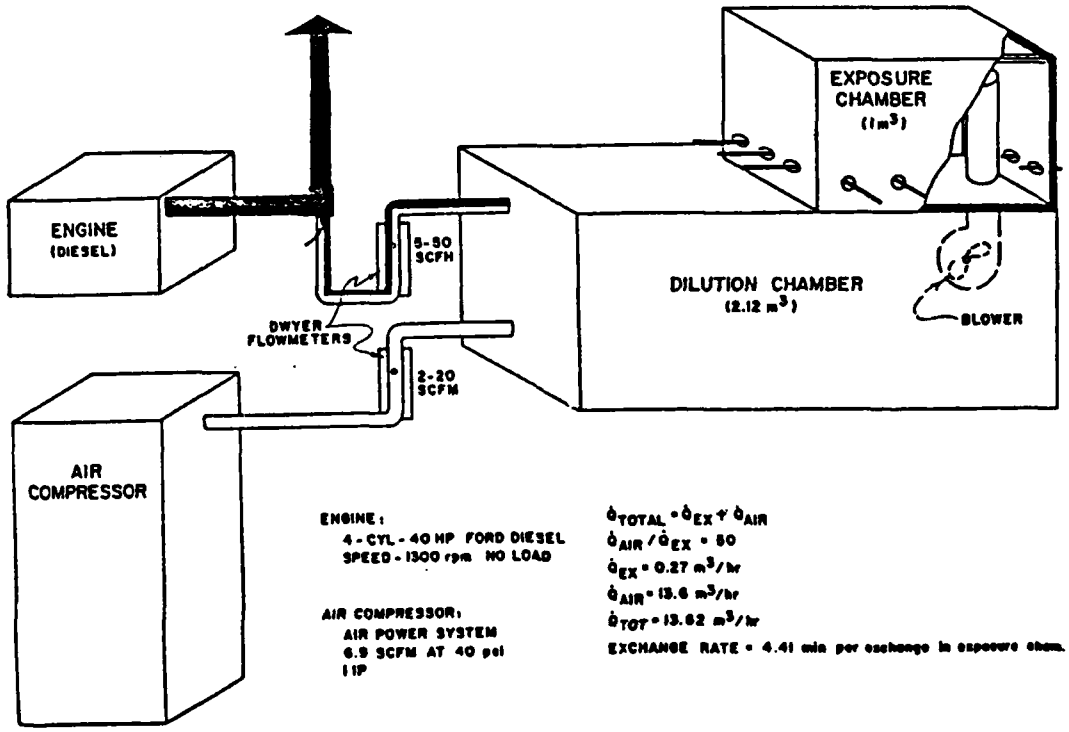

Figure 4.6. Production and measurement of engine exhaust. Adapted from Ma et al. (1983).

Exposure to oxides of nitrogen reduced diffusion capacity and peak expiratory flow. Exposure to auto exhaust and auto exhaust + SO_2 produced pulmonary hyperinflation. Irradiated auto exhaust alone or in combination with oxides of sulfur produced increased expiratory resistance. Irradiated auto exhaust also impaired ventillatory distribution. Two years after the exposure was terminated, the dogs were sacrificed and extensive morphological examination of the lung by light and electron microscopy was undertaken to correlate physiologic and morphologic observations. Two important exposure-related pulmonary lesions were observed; enlargement of air spaces and loss of interalveolar septa in the proximal acinar regions were most severe in dogs exposed to oxides of nitrogen, oxides of sulfur, irradiated exhaust + oxides of sulfur; hyperplasia of nonciliated bronchiolar cells was most severe in dogs exposed to auto exhaust alone or in combination with oxides of sulfur. Amdur (1980) states that these studies indicate alterations in pulmonary function that are reflected in morphologic injury and are persistent in nature following exposure to quite realistic levels of mixed pollution. It is interesting to note the negative findings reported by Gross (1980), who exposed 25 rats to diesel exhaust at a particulate concentration of 1,500 $\mu g/m^3$, for 20 hours/day, 5-1/2 days/week for 267 days. No apparent functionally significant changes occurred in the lungs that could be attributed to the chronic inhalation of diesel exhaust.

4.5 CIGARETTE COMBUSTION PRODUCTS

4.5.1 Introduction

The adverse health effects associated with exposure to tobacco and, in particular cigarette smoke, have been well investigated. Appendix Table B-2 characterizes the types of toxicity testing that have been utilized. Exposure to cigarette smoke is unique in comparison with exposure to the combustion products of diesel and gasoline engines and of rifle and gun systems -- for the most part it is voluntary. Since a significant segment of the U.S. population smokes, there is the opportunity to study the effects directly on humans. As is discussed at some length in the 1979 report of the Surgeon General "Smoking and Health" (USDHEW 1979), epidemiological and clinical studies have been extensively used in the investigation and evaluation of the health effects of cigarette smoking. The use of biological fluids of smokers has also been extensively used in determining the toxicological consequences of cigarette smoking (Yamasaki and Ames 1977; Hollander et al. 1978; Guerrero et al. 1979; Ardito et al. 1980).

4.5.2 Chemical Characterization

The fact that cigarette smoke is a complex mixture of many chemicals is clearly illustrated by Guerin (1980) (Tables 4.12, 4.13, and 4.14). Major chemical constituents of the gas phase that constitute 97 percent of mainstream smoke are shown in Table 4.12. The figures in parentheses indicate the minimum number of components in each category.

TABLE 4.12. CHEMICAL CONSTITUENTS IN THE GAS PHASE OF CIGARETTE SMOKE[a]

Type (Minimum Number)	Largest Representatives: Compound	Quantity: mg/cigt	Quantity: μg/cigt	Quantity: ng/cigt
Inorganic gases (15)	Nitrogen	295		
	Oxygen	67		
	Carbon dioxide	68		
	Carbon monoxide	16		
	Argon	5		
	Hydrogen		700	
	Nitric oxide		300	
	Hydrogen cyanide		300	
	Hydrogen sulfide		90	
	Ammonia		100	
Alkanes (17)	Methane		800	
Alkenes (41)	Ethylene		160	
	Isoprene		400	
Alkynes (5)	Acetylene		25	
Cyclic hydrocarbons (12)	Cyclohexane			300
Aromatic hydrocabons (17)	Toluene		80	
Organohalogen(6)	Methyl chloride		160	
Alcohols (7)	Methanol		180	
Aldehydes (18)	Acetaldehyde		900	
	Formaldehyde		30	
	Acrolein		70	
	Acetone		350	
	Butenone		30	
Esters (14)	Methylformate		30	
	Vinylacetate			400
Heterocyclic oxygen (10)	2-methylfuran		50	
Nitriles (13)	Acetonitrile		140	
Nitrosamines (4)	Dimethylnitrosamine			80
Amines (-)	Methylamine		4	
Miscellaneous (-)	Hydrazine			30
	Vinyl chloride			25
	Methyl nitrate			500
	Water	6		

a. Adapted from Guerin (1980).

TABLE 4.13. MAJOR CONSTITUENTS OF THE PARTICULATE PHASE OF CIGARETTE SMOKE[a]

Chemical	Quantity (mg/cigt)
Water	6.0
Humectants Glycols Propylene glycol	3.0
Alkaloids Nicotine Nornicotine	1.6
Leaf Pigment	1.5
Terpenoids Neophytadiene Limonene	1.5
Carboxylic acids Acetic acid Palmitic acid	1.2
Waxes nC_{31}	1.2
Phenols Phenol Catechol Cresols Hydroquinone	0.6
Aldehydes Furfural Benzaldehyde	0.5
Phytosterols Stigmasterol	0.2

a. Adapted from Guerin (1980).

TABLE 4.14. TRACE CONSTITUENTS OF THE PARTICULATE PHASE OF CIGARETTE SMOKE[a]

Chemical	Quantity (μg/cigt)
Aromatic hydrocarbons	
Naphthalane	3.0
Phenanthrene	0.4
Pyrene	0.1
Fluoranthene	0.1
Benzo[a]pyrene	0.02
Nitrogenous aromatics	
Indole	15
Pyridine	40
Quinoline	2
Anilines	0.2
Napthylamines	0.005
Nitrosoamines	1.5
Nitrosonornicotine	0.5
Nitrosoanatabine	1.5
Trace elements	
Nickel	0.1
Cadmium	0.1

a. Adapted from Guerin (1980).

Carbon monoxide is the major toxic component of the gas phase. Other toxic components present in microgram amounts per cigarette include nitric oxide, hydrogen cyanide, hydrogen sulfide, ammonia, acrolein, acetone, formaldehyde, etc. The particulate phase of cigarette smoke is technically defined as the part of whole cigarette smoke retained by glass-fiber filters capable of collecting 99.9 percent of all particles >0.2μm in diameter. Tar equals the total particulate matter minus water and nicotine. The particulate phase collected by low-temperature condensation is known as cigarette smoke condensate. The particulate phase constitutes about 8 percent of mainstream smoke. The major constituents of the particulate phase are shown in Table 4.13 and include humectants, alkaloids, leaf pigments, turpenoids, carboxylic acids, phenols, waxes, aldehydes, and sterols. Trace organic components and the trace elements Ni and Cd present in μg amounts per cigarette are listed in Table 4.14. Nicotine is the major toxic component that causes problems in long-term carcinogenicity experiments with animals (Wynder and Hoffmann 1967a).

The chemical composition of cigarette smoke does, however, depend on the type of tobacco used, paper ventilation and filtration, and puffing characteristics. Cigarette smoke is a very concentrated and complex aerosol of liquid particles and its physicochemical characteristics change with time (Guerin 1980).

4.5.3 Bioassays of Tobacco Smoke

An excellent review of the genotoxicity of tobaccco smoke has been written by DeMarini (1983). Many of these studies have been characterized in Appendix Table B-2. As can be seen from Table B-2, similar to the testing of gasoline and diesel emissions (see Table B-1) a host of short-term bioassays for genotoxicity have been used including the Ames Assay, and tests to determine the frequency of chromosomal aberrations, sister chromatid exchanges, and cell transformations. The condensate is frequently fractionated for testing as the neutral, basic, and acidic components. Not illustrated in Table B-2 but discussed by DeMarini is the use of the gas phase of tobacco smoke; however, the gas phase is not nearly as extensively used as the condensate or the whole smoke. One example is that of Valadaud-Barrieu and Izard (1979), who investigated the ability of the gas phase of cigarette smoke to induce sister chromatid exchanges (SCEs) in human lymphocytes. These researchers found that the gas phase induced SCEs in a dose-dependent manner and did so in the lymphocytes of both smokers and nonsmokers.

When smoke condensates are tested for their toxicity, the use of fresh material is desirable. As researchers worked with condensates, it became apparent that aging of the material must be considered. As an example, Mizusaki et al. (1977) observed that the mutagenic activity (using TA 1538) decreased to 70 percent of the initial activity (1 hour) 24 hours after the preparation of the smoke condensate, regardless of whether storage was at room temperature or -20°C.

Although skin is not the major target organ, the carcinogenicity of cigarette smoke condensate was first demonstrated on mouse skin [Wynder et al. (1953) as cited in Van Duuren (1980)]. This led Van Duuren to

identify the biologically active components of cigarette smoke condensate by their effects on mouse skin (Table 4.15). Carcinogens, cocarcinogens, initiators, promotors, and tumor inhibitors were found to be present in cigarette smoke condensate. Other skin painting assays used to evaluate the carcinogenicity of tobacco smoke condensate have been conducted by the National Cancer Institute (see NCI 1980).

4.5.4 Inhalation Toxicology of Tobacco Smoke

Dosimetry has always been a problem in inhalation carcinogenesis. Cigarette smoke presents an additional complication in that the nasal passages of the laboratory animals are a very highly effective barrier to the introduction of aerosols ranging in particle size from 0.1 to 1.0μm. In man this defensive system is bypassed since cigarette smoke is actively inhaled into the respiratory system directly through the mouth (Wynder and Hoffmann 1967b).

To avoid the problem of dosimetry and lack of definition of the site of exposure, a number of experimental models have been developed for studying respiratory tract carcinogenesis. The best characterized are the intratracheal instillation model (Saffiotti et al. 1968; Schreiber et al. 1972) and the heterotopic tracheal transplant model (Nettesheim and Griesemer 1978; Pal et al. 1978; Klein-Szanto et al. 1984). In the tracheal transplant model, rodent tracheas are grafted under the skin in the scapular region of the isogenic host. The transplants establish themselves in 3 to 4 weeks and survive indefinitely. These tracheas can then be exposed in a quantitative fashion using controlled-release cylindrical pellets. Thus, the in vivo progress of carcinogenesis in a preselected site of the respiratory tract can be investigated.

In a conventional inhalation toxicology experiment, Dalbey et al. (1980) were able to expose specific-pathogen-free female Fischer-344 rats to cigarette smoke over a lifetime in a regimen considered to result in a maximal tolerated dose. The lifetime nose-only exposures were 7 cigarettes/8-hr day, 5 days/week. After 2.5 years, 30 percent of the exposed rats remained alive. Mortality of the exposed animals was not different from that of untreated and sham-exposed controls. Nine percent of the exposed animals developed tumors in the respiratory tract compared with only one percent tumor incidence among the control animals. Other nonneoplastic changes were observed throughout the respiratory tract. As an aid to dosimetry, cigarettes were labeled by injection with ^{14}C-labeled dotriacontane, which served as a tracer for the particulate phase of the smoke. The method has been discussed in detail by Caton (1979).

Other inhalation toxicology studies have focused on various aspects of lung function (e.g., Witten et al. 1985; Drath et al. 1979), the developmental toxicity of inhaled tobacco smoke (Peterson et al. 1981; Goeringer and Fazel 1983), and cardiovascular disease (USPHS 1976, as reported in USDHEW 1979). Although most research efforts reported in this section have tested either tobacco smoke condensate or whole smoke, some investigators have examined the role of single compounds in the

TABLE 4.15. SOME BIOLOGICALLY ACTIVE AGENTS OF CIGARETTE SMOKE CONDENSATE[a]

Carcinogens	Aromatic hydrocarbons and heterocyclics
Initiating agents	Aromatic, heterocyclic carcinogens, and borderline carcinogens (dibenz[a,c]anthracene, chrysene, etc.)
Promoting agents	Phenol and oleic acid
Cocarcinogens	Catechol, pyrogallol, undecane, tetradecane, pyrene, and fluroanthene
Tumor inhibitors (cocarcinogenesis protocol)	Phenol, resorcinol, hydroquinone, oleic acid, squalene, eicosane ($C_{20}H_{42}$), and octacosane ($C_{28}H_{58}$).

a. Adapted from Van Duuren (1980).

health hazards of tobacco smoke. One example is the study of Astrup (1980), who reported on the contribution of carbon monoxide to the health hazards of cigarette smoking. He concluded that a less hazardous cigarette would result if carbon monoxide levels in the tobacco smoke were reduced.

4.6 PYROLYSIS GASES FROM SYNTHETIC POLYMERS

In recent years, the National Bureau of Standards has developed a standard test method for assessing the acute inhalation toxicity of combustion products of polymers (Levin et al. 1982, 1983). The test method, originally published in 1980 (Birky et al. 1980), was developed by the Products Research Committee consisting of members selected from academia, industry, and government under the auspices of the Federal Trade Commission. The test method has undergone an interlaboratory evaluation in seven laboratories and the revised version has been published (Levin et al. 1982).

The objective of the test method is to ascertain the acute inhalation toxicity of the combustion products of materials for research and screening purposes. While CO is definitely a contributing factor in fire fatalities, other toxicants and/or factors such as heat stress, oxygen deficiency, and prior health problems also play a significant role (Levin et al. 1982).

Briefly, the test method comprises three major components (Levin et al. 1982): (1) a combustion system, (2) a chemical analysis system, and (3) an animal exposure system. The combustion system is a closed design in which the combustion products are generated in a furnace located directly below a 200-L exposure chamber and are kept within the chamber, except that for sample volumes that are withdrawn for chemical analysis and subsequestly returned. Materials are pyrolyzed at 25°C above the materials' autoignition temperature (flaming mode), at 25°C below the autoignition temperature (non-flaming mode), and at 440°C, the temperature at which Douglas fir (the reference material) was tested in the flaming mode (for materials with autoignition temperature above 490°C). The furnace used is a cup style, based on the design of Potts and Lederer (1977, as reported in Levin et al. 1983). It consists of a quartz beaker (usually 300-mL capacity), containing a thermocouple well and surrounded by ceramic with recessed heating elements, all of which are encased in a galvanized steel box. The quartz beaker is heated to a predetermined temperature monitored by a temperature controller. The materials are degraded by a combination of convective, conductive, and radiant heat (Levin et al. 1983).

A portion of the combustion products is pumped from the chamber to analytical instruments for continuous monitoring of CO, CO_2, O_2, and, in some cases, HCN. Monitoring of CO and CO_2 is carried out by non-dispersive IR analyzers and O_2 is monitored by paramagnetic, polarographic, galvanic, or chromatographic techniques; HCN is monitored by a gas chromatograph with thermionic detection or by a specific ion

electrode (Levin et al. 1983). After analysis all products are returned to the chamber. The average concentration of O_2 in the exposure chamber should not be allowed to fall below 16 percent with injection of additional oxygen if necessary. The temperature of the exposure chamber at the nose level of the animal is kept below 35°C.

The animals used in these experiments were male rats (Fischer 344), 3 to 4 months old and weighing 225 to 325 g. They were exposed in "head only" fashion under static condition for 30 min and kept under observation for a 14-day post-exposure period. Blood samples were taken during the exposure by surgically inserting a cannula in the femoral artery of animals designated for this purpose and analyzed for COHb. These animals were not kept for a 14-day observation period. The setup is shown schematically in Figure 4.7.

In the original 1980 test method, the biological endpoints examined were incapacitation and lethality. Incapacitation was measured by the hind-leg flexion conditioned avoidance test developed by Packham et al. (1976). An interlaboratory evaluation of the test method indicated the shortcomings of this incapacitation assay (Levin et al. 1983). It provided less toxicological information (did not detect post-exposure effects), was a less sensitive indicator of acute toxicity (false positives were noted with smoke containing high concentration of irritants), and was a more difficult procedure to measure practically than the biological endpoint of lethality. For these reasons, examination of incapacitation was deleted from the revised test protocol (Levin et al. 1982). The major biological endpoint examined in the test was LC_{50} (30 min exposure + 14-day post-exposure period) in mg/L. In most cases, the reproducibility of LC_{50} values between laboratories for each material in each mode (i.e., flaming, non-flaming, and at 440°C) was within a factor of two. The NBS test protocol has been adopted by several investigators in the acute inhalation toxicity studies of synthetic polymers (e.g., Kaplan et al. 1984; Levin et al. 1986).

Hilado and Machado (1979) reported on the toxicity of pyrolysis gases from synthetic polymers to Swiss Webster male mice. In most of the experiments, pyrolysis gases were generated by heating a 1.00-g sample of the polymer in a quartz tube in a tube furnace to 800°C. The ensuing gases were led to a 4.2-L hemispherical chamber housing four Swiss Webster male mice. Time to death, char yield, and carbon monoxide concentration in the exposure chamber at the time of death of the last surviving animal were recorded. Typical results are given in Tables 4.16 and 4.17. Although no direct measurements have been made, it is speculated that the toxicity of the pyrolysis gases from high-char-yield polymers is due to the presence of highly toxic HCN and COS.

Toxicological evaluations of thermal decomposition products of a variety of synthetic and natural polymers such as polyurethane, polystyrene, phenol-formaldehyde, polyvinyl, and wood have been reported by Alarie and Anderson (1979). For each experiment, four adult male Swiss Webster mice were exposed in "head only" fashion to thermal decomposition products. A continuous recording was made of the respiratory rate of each animal before, during, and after exposure using whole-body

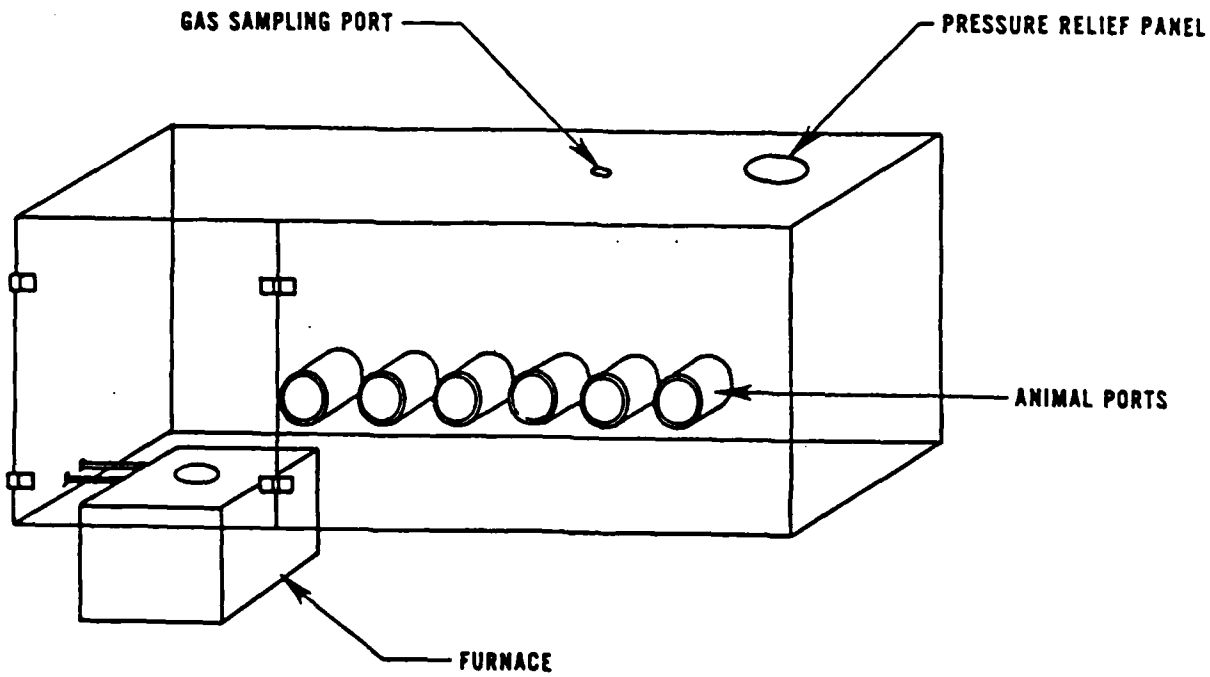

Figure 4.7. Exposure chamber. Levin et al.. (1982).

TABLE 4.16. TOXICITY OF PYROLYSIS GASES FROM NON-CHAR-FORMING POLYMERS TO SWISS WEBSTER MALE MICE[a]

Material	Char yield (%)	Time to death (min)	CO (ppm)
200-800°C rising, 40°C min^{-1}, no forced air flow			
Polyethylene foam, 1	0.3	20.42	12,260
Polyethylene foam, 2	0.7	2.93	8,530
Polymethyl methacrylate	0.4	15.58	-
Polyethylene, 2	0.1	19.84	16,600
Polystyrene, 2	1.3	20.03	-
ABS, 1	1.6	18.52	6,700
ABS, 2	1.3	20.58	-
Polycaprolactam	0.0	21.04	5,480
Polyethylene, 1	0.0	22.66	13,400
Polystyrene, 1	1.6	27.50	8,600
Polystyrene foam	0.5	26.25	5,590
Ethylene propylene diene	0.0	20.66	16,300
Polyisoprene	0.0	22.13	11,200
Styrene/butadiene	0.5	24.11	11,400
800°C fixed, no forced air flow			
Polyethylene foam, 2	0.4	7.91	7,010
Polyethylene foam, 1	0.0	10.16	8,890
ABS, 2	0.4	7.10	3,400[b]
Polyethylene methacrylate	0.0	7.74	6,300
ABS, 1	0.6	9.51	3,600[b]
Polyethylene, 2 2	0.4	9.78	14,200
Polyethylene, 1	0.0	11.72	-
Polystyrene, 2	0.5	19.90	4,500
Polystyrene, 1	3.3	21.84	8,700
Polystyrene foam	1.0	15.39	16,100
Ethylene propylene diene	0.4	10.61	17,700
Polyisoprene	0.6	11.75	-
Styrene-butadiene	0.6	13.82	-

a. Adapted from Hilado and Machado (1979).
b. Carbon monoxide concentration too low to have been lethal.

TABLE 4.17. CHAR YIELD AND TOXICITY OF PYROLYSIS GASES FROM NITROGEN-CONTAINING CELLULAR POLYMERS TO SWISS WEBSTER MALE MICE[a]

Material	Char yield (%)	Time to death (min)	CO (ppm)
Cellular, rising temperature			
Polymethacrylimide	2.7	11.45	4,750
Polyurethane, F8	9.1	22.38	8,530
Polyurethane, F4	9.9	19.41	14,240
Polyurethane, F6	10.6	20.10	14,460
Polyurethane, F1	10.9	20.86	14,070
Polyurethane, F3	10.9	20.49	15,030
Polyurethane, F2	11.0	19.91	10,680
Polyurethane, F5	11.0	19.31	8,890
Polyurethane, F8	11.3	20.73	9,720
Polyurethane, R4	12.6	24.93	7,180
Polyurethane, R3	15.9	25.69	6,380
Polyurethane, R1	19.6	23.92	5,760
Polyurethane, R2	28.6	23.74	5,650
Polyisocyanurate, T1	38.9	21.22	3,220*
Polyisocyanurate, T2	39.5	19.75	4,580
Polybismaleimide	50.7	12.80	4,520
Polyimide	59.6	12.71	2,540*
Cellular, fixed temperature			
Polymethacrylimide	1.7	8.46	8,420
Polyurethane, F8	4.5	9.31	9,720
Polyurethane, F3	7.4	8.25	10,560
Polyurethane, R3	10.2	9.43	3,220[b]
Polyurethane, R4	10.9	12.15	8,250
Polyurethane, R1	12.2	8.70	2,770[b]
Polyurethane, R2	16.8	7.56	3,280[b]
Polyisocyanurate, T1	29.1	5.50	3,450[b]
Polybismaleimide	36.9	3.69	11,070
Polyisocyanurate, T2	38.2	4.97	2,320[b]
Polyimide	56.1	2.70	7,740[b]
Elastomer, rising temperature			
Acrylonitrile rubber	2.5	15.85	5,300
Elastomer, fixed temperature			
Acrylonitrile rubber	2.5	4.34	5,400
Solid, rising temperature			
Polybismaleimide	48.8	11.12	-

a. Adapted from Hilado and Machado 1979.
b. Carbon monoxide concentration too low to have been lethal.

plethysmographs. The four endpoints determined were sensory irritation (RD_{50}), stress index (SI 100), acute mortality (LC_{50}), and concentration range where asphyxiation occurred. Sample sizes necessary to evoke these reponses are given in Table 4.18. The RD_{50} is defined as the sample size necessary to cause a 50 percent decrease in respiratory rate. The stress index takes into consideration the rate of onset and recovery of the respiratory effect as well as the degree of depression of the respiratory rate. For stress index the sample size necessary to evoke a stress index of 100 was calculated (SI 200 is considered as full stress). The LC_{50} and asphyxiation range are self-explanatory. Histopathology of the respiratory tract and other organs was recorded.

4.7 RECOMMENDATIONS FOR TOXICOLOGICAL PROCEDURES AND STRATEGIES FOR EVALUATING GUN EMISSION PRODUCTS

4.7.1 Introduction

This section is divided into four parts. Section 4.7.2 discusses the possible strategies for toxicological investigation of complex mixtures. Section 4.7.3 highlights the pertinent lessons learned during the investigation of other complex mixtures that should be considered when recommending a protocol for the toxicological investigation of gun exhaust which is detailed in Section 4.7.4. Conclusions are presented in Section 4.7.5.

Although the toxicology of polymer combustion products was discussed in Section 4.6, most of the discussion and reference to complex mixtures other than gun exhaust in Section 4.7 is primarily to that of cigarette smoke and motor vehicle exhaust (especially diesel exhaust) since much more research has been conducted on these complex emissions than on polymer combustion products.

4.7.2 Toxicity Testing Strategies for Complex Mixtures

The many years of research that have been devoted to studying the toxicology of cigarette smoke, and more recently, diesel exhaust and polymer combustion products, have contributed substantially to an understanding of the methodology for toxicological investigations of complex mixtures. Three testing strategies have emerged:

(1) testing of the entire mixture,

(2) testing of the fractions of a mixture (e.g., the gas or particulate phase), and

(3) testing of individual components.

Whole-mixture testing of both cigarette smoke and diesel exhaust has been extensively used for the investigation of many different

TABLE 4.18. RESULTS FOR SENSORY IRRITATION (RD_{50}), STRESS INDEX (SI_{100}), ACUTE MORTALITY (LC_{50}), AND CONCENTRATION RANGE WHERE ASPHYXIATION WAS NOTED IN MICE FOR THERMAL DECOMPOSITION PRODUCTS OF POLYMERS TESTED[a]

Samples	RD_{50} (mg)	SI_{100} (g)	Asphyxiation LC_{50}[b] (g)	Range (g)
Flexible polyurethane foam	3.7	1.5	13.0	2-15
Polystyrene expanded	22.0	4.0	5.8	5.3-10
Phenol-formaldehyde	765.0	4.0	6.3	3-6
Urea-formalehyde foam	20.0	0.3	2.5	0.4-1.25
Douglas fir	34.0	4.0	63.8	55-95

a. Adapted from Alarie and Anderson (1979).

b. Calculated from the number of deaths during a 30-min exposure and 10-min recovery as given in the text.

toxicological endpoints (see Appendix B). Similarly, separation of cigarette smoke and diesel exhaust into their gaseous and particulate components with subsequent toxicological testing of each has also been extensively utilized. However, because of the adsorption of organic compounds to particulates, this fraction has received more study than the gaseous component. Further fractionation and testing can more narrowly define the toxic components of the mixture. Appendix B gives several examples of toxicological testing of the particulate fraction and shows that genotoxicity is a common endpoint for investigation.

The testing of individual chemicals identified as present in a mixture is undertaken for two primary reasons: (1) the mixture itself cannot be generated or (2) to determine the chemical(s) responsible for the observed toxic effects of the mixture. Simulated mixtures of two or more chemicals can also be tested to determine if additive, synergistic, or antagonistic effects are occurring. This has recently been done by Levin and co-workers (Levin et al. 1986; Levin et al. 1987a; Levin et al. 1987b) during the investigation of the toxicology of fire combustion products (see Section 4.7.4.4 for further information).

The Environmental Protection Agency has published guidelines on an approach for evaluating data on the subchronic and chronic effects of chemical mixtures (USEPA 1986). As stated in these guidelines, the preferred approach is to use data on the health effects of the mixture of concern. If such data are not available, then it is recommended that health effects data on a similar mixture be used. A similar mixture is defined as "a mixture having the same components but at slightly different ratios or having several common components but lacking one or more components, or having one or more additional components." If comparison with similar mixtures is not possible, then the only other choice is to examine data on the individual components of the mixture. Should health effects data be available only on some of the components of the mixtures, and especially if some components have not yet been qualitatively identified, then any risk assessment of that mixture must be carefully qualified. This is especially true if the health effects data that are available indicate no hazard.

This last mentioned approach leads to an additivity concept. The two approaches given by EPA are dose additivity and response additivity. As defined by EPA, "dose addition assumes that the toxicants in a mixture behave as if they were dilutions or concentrations of each other, thus the slopes of the dose-response curves for the individual compounds are identical, and the response elicited by the mixture can be predicted by summing the individual doses after adjusting for differences in potency; this is defined as the ratio of equitoxic doses." With respect to response addition, EPA states that "this type of joint action assumes that the two toxicants act on different receptor systems and that the correlation of individual tolerances may range from completely negative ($r = -1$) to completely positive ($r = +1$) correlation. Response addition assumes that the response to a given concentration of a mixture of toxicants is completely determined by the responses to the components and the correlation coefficient."

EPA cautions that additivity assumptions can either overestimate or underestimate risk since no provision is made for syngergistic or antagonistic effects.

Pearson et al. (1979) have proposed an approach to the toxicological evaluation of a complex wastewater mixture discharged from 2,4,6-trinitrotoluene (TNT) production facilities. In their discussion they state that the traditional compound-by-compound approach is both technically unacceptable and economically prohibitive. Their approach necessitates the qualitative and quantitative identification of the chemicals present in the complex mixture. They identified 22 compounds present in TNT discharge water above the ppb detection limit and used a mixture of these 22 for detailed toxicological testing. In addition, to identify possible trace constituents with extraordinary toxicological properties, all the compounds identified were subjected to short-term screening testing.

4.7.3 Lessons Learned From Toxicity Studies of Cigarette Smoke, Motor Vehicle Exhaust, and Polymer Combustion Products

Several "lessons learned" from the investigation of well-studied complex mixtures (especially cigarette smoke and motor vehicle exhaust) are applicable to the study of the toxicology of gun exhaust, but the dissimilarities between cigarette smoke (CS) and motor vehicle exhaust (MVE) and gun exhaust should be mentioned. As is illustrated in the preceding sections, the composition of the gaseous and particulate phases of CS and MVE when compared with gun exhaust is basically different, largely due to the nonorganic nature of the latter. Another difference is that the population exposed is much more limited in the case of gun exhaust. Also, the principal concerns for the populations at risk from exposure to CS and MVE are those of chronic toxicity -- especially carcinogenicity -- resulting from exposure to low levels, whereas the primary toxic effect of interest from exposure to gun exhaust is performance degradation resulting from short-term high-level exposures.

A large-scale effort has been expended in the investigation (i.e., methods and equipment development and actual testing) of the toxicology of CS and MVE; most recently, efforts have focused on diesel exhaust. Whole-mixture, fractions (such as gas phase and particulate phase), and single-compound testing have all been used and each has its own merits.

Intact mixtures have been frequently tested (e.g., see Pereria et al. 1980a, Misiorowski et al. 1980; Gross 1980; Heinrich et al. 1980; Rasmussen et al. 1981; Dalbey et al. 1980; Peterson et al. 1981) since this simulates human exposure. The importance of testing the intact mixture cannot be overemphasized. As Lewis et al. (1974) stated, "the complex questions faced by toxicologists studying air pollutants can only be answered by a simulation of the take-it-as-it-is ambient atmosphere to which the epidemiologist can relate." It is only through the testing of whole mixtures that the investigator can be assured that the results are a factor of interactive effects that may have occurred.

Much discussion and effort were given to the appropriate experimental design for health effects testing of CS and MVE. For example, with diesel exhaust it was soon discovered that the composition of the exhaust can vary with fuel, engine type, power output of the engine, emission control devices, and ambient conditions (see Opresko et al. 1984; Huisingh et al. 1978) and, thus, these factors had to be considered in the experimental design of a study evaluating the toxicity of diesel exhaust. For cigarette smoke, Stokely et al. (1979) and Higgins and Stokely (1979) reported that aging itself, i.e., smoke standing in a chamber without animals present, has little effect on most constituents; however, when animals are added to the test chamber, their respiration produces chemical and physical changes in the smoke (Guerin 1979). Thus, it was necessary to devise elaborate exposure systems to ensure that animal exposure simulated human exposure. For polymer combustion products, a test method for assessing acute inhalation toxicity was developed by the Products Research Committee consisting of members from academia, industry, and government under the auspices of the Federal Trade Commission (Levin et al. 1982, 1983).

For both cigarette smoke and diesel exhaust, the testing of the gas phase (e.g., see Valadaud-Barrieu and Izard 1979; Rannug et al. 1983) and especially the particulate phase (e.g., Claxton 1980; Slaga et al. 1980; Hutton and Hackney 1975; DeRaat 1979) was routinely conducted using short-term assays of genotoxicity and potential carcinogenicity. For diesel exhaust, the positive results from short-term assays supported the rationale for conducting long-term tests. Testing of the separate phases also gives an insight into which phase, if not both, is responsible for the effects observed from the intact mixture. A specified fraction of the particulate phase (e.g., acidic, basic, neutral) can also be tested and the components responsible for the toxicity of the mixture can perhaps be more narrowly defined. As the research of Mizusaki et al. (1977) demonstrated using cigarette smoke condensates, the particulate fraction can age and thus fresh material is recommended (see Section 4.5.3).

Single-compound testing of the major chemical species can perhaps link a chemical with a certain effect or establish the chemical's contribution to the potency of the mixture. An example is the study of Astrup (1980), who investigated the contribution of CO to the health hazards of cigarette smoking and concluded that a less hazardous cigarette would result if CO levels in the tobacco smoke were reduced. However, careful extrapolation must be employed since the possibility of antagonistic, synergistic, or additive interactions exists and is not considered in single-compound testing.

When either cigarette smoke condensate or diesel particulates were tested (usually for genotoxicity), it was usually a solvent extract of these materials that was the test agent and the issue of bioavailability quickly arose. Since strong solvents such as dichloromethane extract much more of the toxic constituents than do biological fluids, and since physiological fluids bind and/or metabolize mutagenic chemicals, the potential toxicity of the particulate fraction can be overestimated. This was demonstrated in a study by King et al. (1981), who examined the

release of mutagens from diesel particles in the presence of organic solvents, lung fluids, lung cytosol, and human serum. In contrast to lung lavage fluid and lung cytosol, serum extract did exhibit some mutagenic activity, but far less than the organic solvent extracts. King et al. (1981) found that when the complex organic fraction, previously extracted with the solvent dichloromethane, was mixed with serum or lung cytosol, a significant reduction in mutagenic activity was seen, suggesting that protein binding and/or metabolism of the mutagens is occurring. Thus, removal of mutagens from particles was occurring but expression of mutagenicity was significantly reduced. In a later related study, King et al. (1983) found that lung macrophages have the capability to metabolize mutagenic nitroaromatics found in diesel particulates. Another factor influencing bioavailability and discussed at some length by McClellan (1983) is the deposition and retention of particles. Thus, while toxicity testing with particulate extracts can establish whether these materials have the potential for causing genotoxicity or carcinogenicity, the extrapolation of these data to an in vivo scenario must be carefully done with proper consideration of bioavailability.

Related to the above discussion is the fact that conventional long-term in vivo bioassays of cigarette smoke and diesel exhaust have not been highly successful in demonstrating carcinogenicity of these materials which was either known, based on human epidemiologic data -- as for cigarette smoke -- or suspected, based on short-term in vitro and in vivo genotoxicity and carcinogenicity assays as for diesel exhaust. McClellan (1983) cites a number of long-term studies of the health effects of diesel exhaust in animals that showed only nonneoplastic changes. However, recent research performed at the Lovelace Biomedical and Environmental Research Institute where McClellan is director (Mauderly et al. 1985) has demonstrated lung carcinogenicity in rats. What was termed extreme exposures (0.35, 3.5, or 7.0 mg/m^3 soot concentrations for 7 hr/day, 5 days/week for up to 30 months) was, however, necessary to elicit the carcinogenic response. In exposure groups the time to appearance of first tumors was 710, 574, and 646 exposure days in the low-, middle-, and high-dose groups, respectively.

In general, the same negative results were seen in chronic testing of cigarette smoke (McClellan 1983). Two exceptions are the studies of Dontenwill et al. (1973) and Dalbey et al. (1980). Dontenwill et al. observed an increase in incidence of laryngeal neoplasms in Syrian hamsters whereas Dalbey reported an increase in respiratory tract tumors in Fischer-344 rats (9 percent compared with 1 percent in control animals). A contributing factor for the observed discrepancy between human epidemiological data and the results of animal tests as noted by Wynder and Hoffmann (1967b) is the way in which the smoke is inhaled, by mouth in human smokers and by nose in animal inhalation toxicology experiments. Inhalation by mouth bypasses the defensive system for aerosols provided by the nose. The difficulties experienced in showing carcinogenicity in long-term animal studies for cigarette smoke and diesel exhaust reemphasize the need for careful interpretation of the results of toxicity testing.

A study by Claxton and Barnes (1981) points out that ambient conditions can affect the toxicology of complex mixtures. They discovered that with respect to the mutagenicity of particle-associated organics collected from diesel engines (1) UV light without other mitigating factors was shown to have no influence on the mutagenicity of organics, (2) ozone reduces mutagenicity, and (3) propylene plus nitrogen oxides, sulfur dioxide, and UV light results in a complex array of organics and mutagenicity. Similarly, Tokiwa et al. (1983) showed that aromatic hydrocarbons in the presence of NO_2 can be converted into mutagenic nitro-derivatives.

In summary, the principal lessons learned from the testing of the diesel exhaust and cigarette smoke that are applicable to the toxicity testing of gun exhaust are as follows:

(1) Whole-mixture, fractions, and single-compound testing may each prove useful in defining the toxicology of gun exhaust.

(2) With respect to the design and construction of a suitable generating system for gun exhaust, a considerable effort will undoubtedly be required (Volume II of this report will cover this aspect in detail).

(3) The bioavailability of inhaled chemicals is an important consideration, especially when extrapolating from the results of in vitro tests.

(4) Aging of the test material must be considered.

(5) Ambient conditions can affect the results of an inhalation toxicity study.

4.7.4 Strategies and Considerations for the Toxicological Testing of Gun Exhaust

4.7.4.1 Introduction

Gun exhaust, diesel and gasoline exhaust, and cigarette smoke share in common a number of toxic gaseous components and particle-associated toxic organic constituents. These include CO (major), NO_x, NH_3, SO_2, HCN, H_2S, CH_3CHO, $C_6H_5CH_3$ in the gaseous phase and polycyclic hydrocarbons such as pyrene, fluoranthene, and benzo(a)pyrene in the particulate phase (Ase et al. 1985; Tompa 1985; Guerin 1980; USEPA 1980a). The major gaseous components with significant toxicity in gun exhaust have already been identified and appear to have been investigated in a more or less comprehensive manner (see Section 4.3). Studies with the whole mixture of gases or total gun exhaust are rather limited.

In the military scenario, short-term high-level exposures causing performance degradation among the gun crews are of primary concern. These exposures can occur both in training and combat situations. However, in combat situations the population potentially at risk is male, whereas in training exercises the possibility of exposure to women must be considered. Also, during combat exposure will likely be more intense than during training. Chronic exposure over a significant part of a lifetime is not likely to occur.

At the present time, a suitable system for simulating human exposure to gun exhaust does not exist, i.e., a generating system to simulate the repeated short-term, high-level exposure that is expected when weapons are fired. The following sections discuss the toxicological approaches that might be used if such an exposure system were available and what alternatives would exist if this exposure system were not available.

4.7.4.2 Whole-Mixture Testing

After adequately defining the methods for generating emissions, a multi-dimensional biological program will be required to fully explore the potential hazards associated with gun emission products. In the following sections the outline of such a program is described, starting with some in vitro tests that might be relevant to the circumstance under which human exposures occur; short-term and chronic studies are also outlined briefly with some discussion as to their overall relevance. Since there have already been extensive studies carried out on diesel engine emissions and tobacco combustion products, examples are drawn from the literature for illustrative purposes. Also, where applicable, studies that have used one or more of the individual components of the gun emission products will be used for reference purposes.

4.7.4.2.1 In Vitro Assays.

There are numerous in vitro assays that are used as quick screens for determining the potential for a chemical or a mixture of chemicals to cause mutagenic or carcinogenic effects in mammals. The susceptibility of organs or cells to environmental toxins can also be studied in vitro. In this section, a brief summary of possible carcinogenic/mutagenic screens is given along with a discussion of how cell cultures are used to carry out toxicity assessments in vitro.

4.7.4.2.1.1 Genotoxicity Assays. As illustrated in the genotoxicity testing of complex environmental emissions including diesel exhaust and cigarette smoke, tests to determine gene mutations, chromosomal aberrations, and DNA damage are usually performed (e.g., see Lewtas et al. 1981), and this strategy seems reasonable to propose for gun exhaust. One possible genotoxicity screen could include the Ames test and the Chinese hamster ovary (CHO) cell/HGRPT or V79 cell forward mutation assay for tests of gene mutation, the use of CHO cells for chromosome aberration assays and (to detect possible DNA damage) the unscheduled DNA synthesis assay in rat hepatocytes. As an adjunct to this test battery, an assay for sister chromatid exchanges could be

included and could be conducted in conjunction with the aberration assay in CHO cells.

Although these tests can be used when exposures to the intact mixtures are desired, they have been more commonly used in the investigation of subsamples of mixtures. In addition to indicating the potential genotoxicity of subsamples, these tests have served to reduce the magnitude of the analytical task since chemical fractionation and analysis could focus on those subsamples with biological activity [e.g., diesel exhaust (Huisingh et al. 1978)].

4.7.4.2.1.2 Cell Culture Systems. There are numerous reports in the literature on the use of free cell cultures to determine the toxicity of a gas, extracts of particulates, or the particulates themselves. Since the lung is the primary target organ for most airborne environmental contaminants, many of the studies examine the effects of the compound of interest on the alveolar macrophages. The approaches commonly used for this type of study include determination of (1) changes in the ability of the alveolar macrophages to phagocytize either inert particles or bacteria, (2) viability, and (3) alterations in cellular metabolism as a result of exposure to a toxic agent.

Green and Carolin (1967) have demonstrated that when cigarette smoke was added to a mixture of rabbit alveolar macrophages and Staphylococcus albus there was a significant inhibition of the capacity of the macrophages to inactivate the bacteria. They found that the active components of the smoke were largely contained in the gaseous and filterable phase. Aqueous filtration significantly reduced the toxicity of the smoke. While cell viability per se was unaffected by the smoke, those cells exposed to the cigarette smoke did not adhere to the surface of the flask in which the experiments were carried out. In a similar type of study Vassallo et al. (1973) demonstrated that nitrogen dioxide reduced the rates of entry and killing of Staphylococcus epidermis and Pseudomonas aeruginosa by rabbit alveolar macrophages adherent to a glass surface. This same author also found that nitrogen dioxide and the nitrite ion (NO_2^-) both increase glucose and pyruvate oxidation in resting alveolar macrophages (Vassallo et al. 1973); however, the concentrations required exceed those seen in a normal environmental setting.

Other, and with the exception of one article, more recent techniques have been described by Gardner et al. (1973), Waters et al. (1975), Fisher et al. (1983), Gardner (1984b), Valentine (1985), and Burelson et al. (1987).

Gardner et al. (1973) described a technique using xylene that provided a more accurate assessment of phagocytosis than previously used techniques. This technique was able to more accurately differentiate between mere attachment of particles to macrophages and actual ingestion.

Waters et al. (1975) investigated the metal toxicity for rabbit alveolar macrophages in vitro. The cell viability was one method

$$\frac{\text{total intact cells in test culture}}{\text{total intact cells in controls}}$$

used to assess cytotoxicity. The results of their study also indicated that a consideration of cytotoxicity in a functional or biochemical sense would be appropriate and perhaps a more sensitive indicator. Of the five metal ions studied (Cd^{2+}, V^{3-}, Ni^{2+}, Mn^{2+}, and Cr^{3+}), Ni^{2+} apparently depressed phagocytic activity at a concentration approximately seven times lower than that needed to alter viability. For the other metal ions, the concentrations required to decrease cell viability were similar to those that adversely affected phagocytosis. With respect to biochemical studies, the authors found that the activity of acid phosphatase, a macrophage lysosomal indicator enzyme, was decreased by the five metal ions at concentrations similar to those that caused decreased cell viability.

Fisher et al. (1983) report on the use of bovine alveolar macrophage bioassays in the analysis of the toxicity of complex mixtures. These authors found that bovine alveolar macrophages phagocytize test particles in vitro with kinetics similar to that of alveolar macrophages taken from normal, healthy donors. The measure of toxicity used in this study was inhibition of phagocytic activity.

Gardner (1984b) provides an excellent overview of the methods to assess macrophage function (see Appendix A for more information).

Valentine (1985) describes not a technique but an in vitro system for exposure of lung cells to gases. In his experiments with ozone he concluded that his system provided a realistic simulation of lung cell exposure and afforded ready access to pulmonary alveolar macrophages for the purpose of morphological, biochemical, or functional characterization.

Burleson et al. (1987) have published a method to assess phagocytosis using fluorescent beads.

Since one of the concerns for the military should be the effects that gun emissions might have on the susceptibility of their personnel to infection, the use of in vitro alveolar macrophage preparations might provide some important information on which to base more detailed studies in the whole animal. Two experimental protocols might be considered: the effect that the emissions have on the ability of isolated alveolar macrophages to phagocytize inert particles such as latex particles or yeast and the change in bacterial activity that results from incubating bacteria with macrophages exposed to the gun emissions.

4.7.4.2.2 In Vivo Studies.

In vivo studies can be broken down into two main areas of research for the purpose of these recommendations. The main thrust of the animal experimental work should probably be directed toward classical toxicology studies in which acute and subacute exposures are followed by subchronic exposures carried out to determine the short and repeated

effects of the emissions. Chronic toxicity experiments are not recommended because of the unlikely possibility of individuals being exposed for a significant part of a lifetime. A variety of endpoints should be examined including acute lethal concentrations, histopathology of major organs, and blood and urine chemistries. Along with these traditional tests, additional work in the areas of reproductive toxicology, behavior, pulmonary function, dosimetry, in vivo mutagenesis, and susceptibility of animals to infection might also be considered as adjunct experiments that would provide important information for the assessment of the overall toxicity of the gun emissions.

In addition to the animal studies noted above, information should be collected, when available, concerning the range of exposures encountered by soldiers during their careers.

4.7.4.2.2.1 Acute and Subacute Exposure. In the military scenario the exposures of gun crews to gun exhaust are relatively intense (i.e., above current federal standards for typical civilian occupational exposure), brief (one hour or less), and repeated (up to 6 hours daily for periods up to 14 days). These exposures may take place either in a combat situation or during training. Six 1-hour exposures daily for 14 days was considered to be representative of worst-case military situations (Legters et al. 1980). In this scenario, the impairment of performance is of primary concern; more field data are needed in this area. The ideal scenario encompasses periods when maximum sustained rates of fire are achieved and the crew space ventilation system is maximally stressed to remove gun exhaust. This represents a worst-case operational situation and can occur during stationary fire or fire-and-maneuver exercises (TOP 1984). A firing condition test matrix has been suggested (Table 4.19). These field data can be used as a guide in prescribing an exposure regimen for use in animal inhalation experiments.

A potential reason for the impairment of performance in military personnel is sensory irritation with symptoms of lacrimation, coughing, and respiratory distress. Animal models for studying sensory irritation have been examined and it has been reported that there is a perfect correlation between the observed decrease in respiratory rate in animals and the response in humans consisting of eye, nose and throat irritation (Alarie 1973; Kane et al. 1979). Alarie (1973) used RD_{50} values (exposure concentration necessary to invoke a 50 percent decrease in respiratory rate) obtained in mice to predict the level and type of responses in humans. His data suggest that some sensory irritation would occur at a 0.1 multiple of the RD_{50} but that none would be expected at a multiple of 0.01. Furthermore, when a 0.03 multiple of the RD_{50} (the midpoint on a logarithmic scale between 0.01 and 0.1) was calculated for a series of 23 chemicals and the logarithm plotted against the logarithm of the 1978 TLV-TWA, a correlation coefficient of 0.95 was obtained. Historically, many different species of animals have been used in inhalation studies ranging from mice to animals as large as donkeys. The most extensive data bases are available for rats and mice, although guinea pigs are sometimes used since they are, in many instances, more susceptible to respiratory toxicants. For the purposes of the studies discussed in

TABLE 4.19. FIRING CONDITION TEST MATRIX[a]

Condition No.	Rounds[b] Fired Main Weapon	Firing[b] Rate Rds/min	Rounds[b] Fired Aux Weapon	Firing[b] Rate Rds/min	Main Engine Rpm/off	Aux Engine Rpm/off	Hatches	Crew Ventilator	Crew Heater	NBC Unit
1					Off	Off	Closed	Off	Off	Off
2					Off	Off	Closed	On	Off	Off
3					Off	Off	Open	Off	Off	Off
4					Off	Off	Open	On	Off	Off
5					Idle	On	Closed	Off	On	Off
6					Idle	On	Closed	On	On	Off
7					Idle	On	Open	Off	On	Off
8					Idle	On	Open	On	On	Off
9					Off	Off	Closed	Off	Off	On
10					Off	Off	Closed	On	Off	On
11					Off	Off	Open	Off	Off	On
12					Off	Off	Open	Off	Off	On
13					Off	Off	Open	On	Off	On
14					Idle	On	Closed	Off	On	On
15					Idle	On	Closed	On	On	On
16					Idle	On	Open	Off	On	On
17					Idle	On	Open	Off	On	On
18					Idle	On	Open	Off	On	On
19					Idle	On	Open	Off	On	On
N					Idle	On	Open	Off	On	On

NOTE: In the absence of a specific scenario, the tester may use one similar to the test conditions in this table. The matrix should be altered to conform to the requirements of the system being tested.

a. Adapted from TOP (1984).

b. These columns were blank in TOP (1984).

this section it is recommended that rats and/or mice be used since it will be easier to make comparisons with other particulate studies in the literature and also to assess the role that the gaseous components play in any observed toxicity. The OECD (1981) states that the preferred species is the rat and that commonly used strains should be used.

Although it is recognized that the U.S. military does not currently permit women in active combat roles, they are allowed to perform in areas such as air defense artillery and in training situations. Thus, both males and females of the test species should be included in all of the toxicological tests. This will ensure that any differences between the sexes in terms of their response to the standardized emissions are known.

The initial series of experiments should be to determine the LC_{50} (median lethal concentration) of a standardized emission. Varying exposure durations are suggested ranging from 1 hour to a maximum of 6 hours. A value for the LC_{50} would have to be derived for each exposure duration and for each animal species used. A comparison of the LCt_{50} (where Ct is the product of concentration and time) derived from the various exposure durations should also be made.

There are a number of ways in which animals may be exposed to airborne toxicants. Most frequently, animals are individually caged and then placed in an inhalation chamber that is supplied with air into which the test agent is introduced. Alternative exposure methods include nose-only and head-only systems. The head-only system has been adopted by Levin and co-workers (Levin et al. 1986; Levin et al. 1987a; Levin et al. 1987b) when investigating the toxicology of fire combustion products. Though they are more labor intensive, nose-only and head-only exposure systems do permit experiments to be carried out when there is only a limited supply of the toxicant available or when it is desired to avoid extensive dermal contact with the experimental material. Both during exposure and after, animals should be observed individually at regular intervals, especially for signs of behavioral changes that would be important for determining the potential for performance degradation (see Section 4.7.4.2.2.4 for more discussion of behavioral testing).

Gross necropsy of animals should be carried out where the toxic effects observed indicate the necessity. Particular attention should be paid to the respiratory tract. Where clinical observations have been made that indicate other forms of toxicity, potential target organs should be examined both grossly and microscopically.

Other studies might be carried out simultaneously with the determination of the LC_{50} on additional animals specifically included for that purpose. Blood chemistry parameters might be measured, and a complete hematological screen could be carried out. Derived values such as mean corpuscular volume and mean corpuscular hemoglobin could also be calculated.

A screen of the urine might also be included. If nose-only or head-only is the selected method of exposure, it might be appropriate to

consider performing some measurements on respiratory rate and tidal volume during the course of exposure. This latter will give information on whether these emissions cause a measurable sensory irritation in the selected species.

Having defined the LC_{50} for different intervals of exposure (and hence the LCt_{50}), the next important step would be to examine the effects of repeated exposure to emission concentrations at the lower confidence bounds of 1 percent mortality. A matrix design similar to that described by Dalbey et al. (1982) could be used to examine the relative importance of exposure concentration, duration of exposure, and frequency of exposure. Along with the changes in body weight and the clinical observations described for the acute studies above, parameters that might be examined would include phagocytic activity of alveolar macrophages lavaged from exposed animals, lung function tests, and (depending on the observed causes of death) parameters such as blood cell fragility, tissue edema formation (using radioactive albumin), and liver and kidney function.

4.7.4.2.2.2 Subchronic Exposure. As mentioned previously, exposure of gun crews to gun exhaust is anticipated to be of relatively short duration. However, under extremes of battlefield conditions these crews could be exposed several hours per day with exposure extending over a considerable period of time. Because of this potential for repeated exposure it is important that the toxicology of the emissions be similarly studied over an extended time.

Subchronic studies are defined as repeated daily doses over a part (not exceeding 10 percent) of a life span (OECD 1981). The normal duration for a subchronic study in rats is 90 days.

The organization of a subchronic study is not unlike that used for a subacute study. Several groups of experimental animals (usually rats) would be exposed daily for a defined period of time to the test environment in graduated concentrations. Each group would be exposed to a single concentration for the duration of the study (90 days). The inclusion of interim sacrifices will increase the number of animals required, as will allowing a satellite group of animals to remain alive for a period of time following the last exposure to look for reversibility or persistence or delayed occurrence of toxic effects. Animals would be observed daily for signs of toxicity and any animals that die or are moribund during the exposure period would be necropsied. A detailed microscopic examination of tissues from control and high-exposure groups would be required with particular attention being paid to the respiratory tract. If significant histopathologic changes are observed in the high-exposure group, then an examination of appropriate tissue in the intermediate exposure groups should be implemented. Furthermore, where clinical observations have been made that indicate other forms of toxicity, potential target organs should be examined both grossly and microscopically.

Both during the hours that the animals are being exposed and after the completion of the exposure, animals should be observed individually

at regular intervals. Changes in skin, fur, eyes, and mucous membranes and in respiratory, circulatory, autonomic, and central nervous systems as well as in behavioral patterns should be recorded (see Section 4.7.4.2.2.4 for more discussion of behavioral testing). Particular attention needs to be directed toward tremors, convulsions, lethargy, sleep and coma, salivation, and diarrhea.

Prior to the start of the study, all animals, if possible, should undergo an ophthalmological examination. At the termination of the study the high-dose group and controls should be re-examined; if changes in the eyes are detected all animals should be examined.

If animals are being exposed by the nose-only or head-only method, it would be possible to measure respiratory rate and tidal volume at selected intervals over the course of the subchronic study. This might give some valuable information on whether the animals are able to adapt to frequent sensory irritation or whether they become more sensitive to the emissions with frequent exposure. No additional animals would be required for this in-life study.

At the end of the test period, a complete clinical biochemistry screen should be carried out. Derived values such as mean corpuscular volume and mean corpuscular hemoglobin could also be calculated.

Additional animals might be included in the study so that other experimental parameters might be examined. These could include phagocytic activity of alveolar macrophages lavaged from exposed animals, lung function tests, and, depending on the observed causes of death in the acute studies, parameters such as blood cell fragility, tissue edema formation (using radioactive albumin), and liver and kidney function.

4.7.4.2.2.3 Reproductive Toxicology. In the military environment the majority of personnel exposed to gun emissions are likely to be young, sexually active males. Since germinal cells are frequently more sensitive to toxins than quiescent cells, there is a distinct possibility that the gun emissions could cause toxic effects in the male reproductive tract. These effects may include abnormal sperm, dominant lethal mutations, reduced sperm population, or sterility. To test for these possibilities it would be appropriate to initiate a reproductive study. Popp et al. (1986) have carried out some studies with ethylene oxide (C_2H_4O) that could serve as a model for the experimental protocol. In that study male mice from two different strains (one sensitive to C_2H_4O and other relatively nonsensitive) were exposed 6 hours/day for 5 days/week. Males were mated with nonexposed females on weekends following the 5 days of exposure. While one strain proved to be sterile during the entire course of the exposures (4 weeks) and through an additional 4 weeks without exposure, the other strain remained fertile during the exposure regimen but there were a significant number of dead implants observed in the pregnant females. The sterile males had spermatocytes with necrotic nuclei and there were undifferentiated spermatocytes and Sertoli cells in the lumen of the seminiferous tubules.

While the experiments described above are directed toward fairly gross changes in the male reproductive tract, more subtle changes may be observed by studying sperm motility (Fiscor and Ginsberg 1980) and morphology (Wyrobeck and Bruce 1975). At time of sacrifice, a section of the cauda epididymis is removed and a suspension of sperm made in a drop of warmed tyrode solution on a microscope slide. A number of fields are examined to determine the percentage of motile sperm. To look at sperm morphology a suspension of sperm is prepared and stained with eosin prior to the preparation of smears that are then evaluated microscopically.

Exposure of pregnant females to gun emissions in the military is an unlikely event; however, there might be some justification in carrying out a teratogenic study to determine the risks that would be involved if there were inadvertent exposure of such personnel.

4.7.4.2.2.4 Behavioral Studies. Under battlefield conditions the ability of a soldier to perform well and make rational decisions is of the utmost importance. If sustained exposure to gun emissions caused a significant degradation in performance, substantial risk to life and limb could be engendered. Although there is no ideal substitute for human testing in terms of cognitive skills, there are a battery of animal tests that do permit a fairly accurate determination of even fairly subtle changes in behavior. Norton (1982) has divided behavioral patterns into two major groupings: stimulus oriented and internally generated behavior. Included in the first grouping are conditioned behavior tests such as sensory and motor discrimination tests, active and passive avoidance tests, and unconditional behavior tests such as sensory response and motor response. Internally generated behaviors include exploratory activity, circadian activity, social behavior, consummatory behavior, unique motor acts (Straub tail), walking patterns, etc.

While many of the conditioned behavior tests require extensive training of the animals prior to exposure of a test chemical, the unconditioned responses require no prior training and are thus fairly easy to administer. Similarly, some of the internally generated behavior patterns are relatively straightforward and, thus, lend themselves to be incorporated in a general neurotoxicology screen. Recommended tests in a primary battery would include auditory startle response (sensory reflex), squirrel cage activity (motor response), exploratory behavior, circadian rhythm (using figure-8 maze), and walking patterns (a measure of sensory-motor coordination).

4.7.4.2.2.5 Pulmonary Function Tests. Changes in the lungs as a result of inhaling environmental contaminants can be both reversible and irreversible. For example, aluminum and iron oxides, coal dust, kaolin, and talc are all known to cause pulmonary fibrosis (Menzel and McClellan 1980) while cadmium oxides, oxides of nitrogen, and ozone all cause emphysema. While these changes are irreversible, other chemicals cause transient effects such as edema and irritation, with an associated influx of pulmonary free cells.

While changes in the lung are evident on pathologic examination of the tissue, it is possible to acquire information on how these changes are affecting the performance of the lung in vivo and also to observe the progression of a disease process in individual animals. A battery of pulmonary function tests is available for animals that are modeled on those used to test humans. Likens and Mauderly (1979) and Juhos et al. (1985) have summarized both invasive and noninvasive test procedures for respiratory measurement in small laboratory animals. Briefly, tests that are available include measurement of nitrogen washout (a measure of uneven ventilation of the lung), carbon monoxide diffusing capacity, lung volumes (such as vital capacity, inspiratory capacity, residual volume, and functional residual capacity), and mechanical factors in breathing (such as compliance, total pulmonary resistance, and maximal expiratory volumes).

It is recommended that if there is any evidence that animals exposed acutely to the gun emissions are dying as a result of extreme damage to the lungs, a more detailed survey of lung function during the subchronic study should be made to determine whether there are any changes in pulmonary function as a result of exposure. Reversibility or progression of any changes should also be studied for a period of time after all exposures have been terminated.

4.7.4.2.2.6 Dosimetry. One of the biggest problems associated with inhalation studies is the determination of the actual dose of a material that actually reaches the lung. As well as gaseous components, gun exhaust contains a particulate fraction. Study of the dynamics of the deposition, transmigration, and retention of these particulates in different organs of exposed animals is of importance. Various methods of studying particulate deposition are available. For example, cigarettes labeled with [^{14}C] dotriacontane have been used in inhalation experiments to quantitate the deposition and retention of total particulate matter in the head, larynx, trachea, stomach, and different parts of the lung (right superior lobe, right middle lobe, right inferior lobe, postcaval lobe, and left lobe) (Kendrick et al. 1976). In a more recent study (Jenkins et al. 1983), decachlorobiphenyl was used as an internal marker to study the deposition and retention of a condensation aerosol generated from diesel fuel. Similar techniques using an appropriate marker will be useful in studying the dynamics of the deposition and retention of gun exhaust particulates in different organs of the exposed animals. Use of a radioactive or chemical marker in the propellant formulation may permit enough to survive the combustion process to effectively label the particulate phase of the gun exhaust. Alternatively, the marker could be introduced into the gun exhaust after explosion to tag the particulates.

Furthermore, the amount of solid material deposited or the amount of gaseous material absorbed varies from individual to individual. In fact, the uncertainties of estimating dose in inhalation studies are so severe as to often cast doubts on studies in which no biologic effects are observed (Phalen 1984). It is, thus, important to address the question as to how much material is actually delivered to the subject. With single-chemical entities the approach is fairly straightforward with two

primary methods being applicable: direct assay of the chemical in the tissues of the animals, and use of airborne concentrations along with uptake models. In the former method, the use of radioactive or tracer chemicals can greatly assist in the assessment of the percent of absorbed dose.

Dosimetry should be included in the overall research plan for gun emissions. The major stumbling block that investigators are likely to encounter is determination of a suitable tracer or tracers. Since the gaseous phase of these emissions may play an essential role in their toxicity, it may be necessary to carry out two dosimetry studies: one in which the tracer would be associated with the gaseous phase and the other in which the tracer is combined with the particulates.

4.7.4.2.2.7 In Vivo/In Vitro Mutagenisis. A number of researchers have found that the urine of smokers is mutagenic (see DeMarini 1983). One study is that of Yamasaki and Ames (1977), which found that urine concentrates obtained from human smokers caused a mutagenic effect in *Salmonella typhimurium*, but only with metabolic activiation. Supportive evidence was provided by Guerrero et al. (1979), who found that the urine of smokers (concentration of 5 to 20 percent) in the absence of metabolic activation resulted in a higher frequency of sister chromatid exchanges in human diploid (WI-38) cells after 48-hr incubation than did the urine of nonsmokers.

On the basis of these results, it seems reasonable to recommend that the urine of individuals exposed to gun exhaust be assayed for mutagenicity in the Ames test. Potential confounding factors such as exposure to cigarette smoke or diesel exhaust, which would probably increase the presence of mutagenic compounds in the urine, would have to be considered; the possibility of having each individual serving as his own control is one solution.

4.7.4.2.2.8 In Vivo Mutagenesis. Other than the dominant lethal test and the sperm morphology assay that are recommended as part of the reproductive toxicology protocol (see Section 4.7.4.2.2.3), possible in vivo tests include the mouse-specific locus (including the spot test) and the host-mediated assay for gene mutation, the sister chromatid exchange assay, the micronucleus test, assays for chromosomal aberrations, the heritable translocation test for the determination of chromosomal effects, and unscheduled DNA synthesis as an indication of primary DNA damage.

The most commonly used methods in the study of the genetic toxicology of cigarette smoke and diesel exhaust appear to be assays for chromosomal aberrations, sister chromatid exchanges (SCEs) and micronuclei. In general, these tests have provided negative results. Rees et al. (1973), Nordenson et al. (1978), and Korte et al. (1981) could not find evidence of chromosome aberrations in rats [injected with cigarette smoke condensate (CSC)], smokers, or Chinese hamsters (exposure to cigarette smoke), respectively. The results of studies investigating SCEs among smokers are conflicting. For example, Hollander et al. (1978) found no increase in heavy smokers, while Lambert et al. (1978)

were able to demonstrate a dose response for SCEs among moderate and heavy smokers. With respect to diesel exhaust, Pereria et al. (1980b) were able to find a 50 percent increase in the polychromatic erythrocytes of male Chinese hamsters exposed for 6 months, 8 hr/day, but were unable to find significant increases in SCEs or chromosome aberrations. Tests for significant increases in micronuclei in mice (8 hr/day up to 7 weeks) and in dogs (continuously exposed for 13 weeks) were, however, negative.

The decision whether to employ in vivo genotoxicity assays should, perhaps, not be made until the results of the in vitro tests are available. In the section on reproductive toxicology, it is recommended that the dominant lethal and the sperm morphology assays be conducted as a part of a male reproductive toxicology study; the Army may decide that these assays are sufficient. If further in vivo tests are deemed necessary, then in keeping with the rationale of the proposed in vitro test battery using the SCE assay as an adjunct, the chromosome aberration assay or the micronucleus test could be selected.

4.7.4.2.2.9 Susceptibility to Infection. Over the past few years there has been an increasing awareness and concern about the potential adverse effects of environmental contaminants on the immune system and the ability to resist infection. A number of studies have shown that there is an increased susceptibility to bacterial infection following exposure to ozone (Purvis et al. 1961), nitrogen dioxide (Purvis and Ehrlich 1963; Ehrlich 1966; Ehrlich et al. 1977; Gardner 1984a), gasoline exhaust (Coffin and Blommer 1967), and diesel exhaust (Campbell et al. 1980). The question that is important as far as the military is concerned is whether the emissions from guns are likely to have an impact on the susceptibility of personnel to infection in training or battlefield conditions. To this end it is recommended that a study be carried out in which animals are exposed to the emissions for a number of days and then challenged with a culture of a bacterial pathogen such as Streptococcus or Klebsiella. The endpoint for a study of this nature is mortality, with comparisons being made between animals that have or have not been exposed to the chemical hazard prior to challenge with the nebulized bacterial culture.

4.7.4.3 Testing of Fractionated Gun Exhaust

As discussed in some detail in Sections 4.4 and 4.5, the separation of cigarette smoke and diesel exhaust into their respective gaseous and particulate phases in order to determine the relative toxicity of each fraction was routinely done. Of particular interest were the organic compounds adsorbed onto the cabonaceous particles. Weapons exhaust also is composed of both gaseous components and particle-associated organics that can be similarly tested. Instead of carbonaceous particles, the basic particles are inorganic, consisting of elements such as Pb, Cu, Sb, Ba, and Zn (Ase et al. 1985). As demonstrated in the work of Snelson et al. (1983), it is possible to collect particulates that result from the firing of simulated charges, laboratory firing of small weapons, or actual field firing. As was done with cigarette smoke

condensate or diesel particulates, the organic compounds adsorbed on the particulates can be extracted with solvents.

Genotoxicity or skin painting tests could be conducted as indicators of potential mutagenicity and carcinogenicity (using a similar battery of tests as proposed in Section 4.7.4.2.1.1). Even though long-term exposure to gun exhaust is not likely, the knowledge that possible carcinogenic chemicals exist in gun exhaust would be of interest, especially if the group of animals given subchronic exposure to gun exhaust and allowed to live a significant fraction of their lifetime develop tumors (see Section 4.7.4.2.2.2).

If such tests are conducted on extracts of particulates, the lessons learned regarding bioavailability of the genotoxic components adsorbed to the particles (see Section 4.7.3) should be applied. Also, testing of the gaseous and particulate phases separately does not permit interactions to occur that might influence toxicity. For example, Tokiwa et al. (1983) showed that aromatic hydrocarbons can be converted to mutagens by NO_2 and Legters et al. (1980) noted that concurrent exposure to NO_2 and inert particles enhanced the toxic effect of NO_2.

4.7.4.4 Single-Compound Testing

The toxicology testing of single compounds known to be present in a mixture can be conducted for two reasons: (1) to further define the role of the components in a mixture with respect to the toxicity of the mixture, or (2) to give an insight into the toxicity of a mixture whose toxicity is unknown. As an example of the first reason, Astrup (1980) studied the contribution of carbon monoxide to the health hazards of cigarette smoking and concluded that a less hazardous cigarette would result if carbon monoxide levels in tobacco smoke were reduced. When testing single compounds to satisfy reason two above, the fact that this method does not allow consideration of the possible interactions among chemicals is important to bear in mind. As discussed in USEPA (1986) and in Section 4.7.2, the application of a dose or response additive model when single compounds within a mixture are tested for toxicity is possible. This approach is obviously less desirable than testing a whole mixture or even fractions of a mixture, but if major compounds can be identified and tested for toxicity (if data are not already available), then some insight into the toxicity of the mixture can be achieved. For gun exhaust, it may be practical to consider single-compound testing only when reformulation of the propellant is possible so that a specific toxic compound(s) could be eliminated.

Investigations to date have identified a number of constituents in weapons exhaust (see Snelson et al. 1983; Urbanski 1983; Ase et al. 1985). Some of the major gases are carbon monoxide, carbon dioxide, hydrogen, nitrogen, nitrogen oxides, ammonia, and perhaps sulfur dioxide; principal inorganic particles include lead, antimony, barium, copper, and zinc. Toxicity information is available on all of these chemicals and once reliable quantification for respective gun systems is available, preliminary estimates of the toxicity of the mixtures could be made. The organic compounds (gaseous and adsorbed to particulates)

in weapons exhaust are present at generally lower concentrations than the chemicals mentioned above and their contribution to the toxicological effects of particular interest to the Army, i.e., behavioral or performance degrading effects, is probably limited. It should be stated, however, that assumptions such as the one just made for the role of organic compounds need verification when the capability to test complete mixtures of weapons exhaust is available.

The health effects data that are available concerning the major components can, as noted above, be utilized to gain an insight into the toxicity of the mixture. As examples, consider what is known regarding ammonia (NH_3), carbon monoxide (CO), sulfur dioxide (SO_2), and nitrogen oxides (NO and NO_2). Ammonia (Legters 1980), SO_2 (Normandy et al. 1980), and NO_2 (Morton 1980) are each known to irritate the upper respiratory tract with SO_2 generally recognized as the most irritating (the more important toxicological effects of NO_2 are those in the deep lung). NO is not considered a mucosal irritant but in the presence of oxygen can be converted to NO_2. Some studies have indicated that with nasal breathing approximately 99 percent of inspired SO_2 is absorbed by the nasal mucosa. Nitrogen dioxide is considered to have the greatest potential for penetration into deep lung and has been linked (primarily in animal studies) to increased susceptibility to pulmonary infection.

With respect to eye irritation, both NH_3 and SO_2 are implicated. Sulfur dioxide is a more severe eye irritant causing moderate to severe irritation and intense lacrimation at 10 ppm in humans compared with NH_3 where moderate irritation of the eyes was observed in humans at 50 to 72 ppm.

Carbon monoxide, nitrogen oxide, and nitrogen dioxide (Morton 1980; Nightengale 1980; Opresko et al. 1984) each affect the oxygen carrying capacity of the blood. The formation of carboxyhemoglobin is the mechanism by which CO acts, whereas NO can exert its effects by the formation of methemoglobin. NO is reported to have an affinity for hemoglobin 1,500 times stronger than CO (Kon et al. 1977). The NO_2-mediated formation of methemoglobin is also recognized (Guidotti 1978).

Thus, the data presented above indicate that some of the major pollutants in gun exhaust have similar target sites. If these gases are simultaneously present as in a complex mixture, will one see additive, synergistic, or antagonistic effects? This, of course, is the crux of the matter in any proposed scheme that attempts to evaluate the toxicity of a complex mixture from its components.

There are a few reports providing some insight into possible interactions. Morton (1980) has summarized a study in which a mixture of SO_2 and NO_2 was tested. Five healthy adult male volunteers were successively exposed at 2-week intervals to NO_2 (4 to 5 ppm), and SO_2 (4 to 5 ppm), NO_2 + SO_2 (2.5 ppm each). Subjects breathed each test concentration for 10 min while seated. Effective compliance, inspiratory resistance and expiratory resistance, measurements were made before exposure, immediately after exposure, and 10, 20, and 30 min after exposure. For NO_2 exposures, effects started to appear at the end of the

exposure or 10 min later, then increased linearly. At 30 min after exposure, effective compliance was 59 percent, inspiratory resistance 192 percent, and expiratory resistance 172 percent of initial values. With SO_2, however, a maximal increase in resistance was seen at the end of the exposure period with recovery in 10 to 20 min; no marked change in compliance was observed. It was reported that the mixed gases showed a clear compromise. The change in compliance with NO_2 but not SO_2 was explained on the basis of the ability of NO_2 to reach the deep lung.

Normandy et al. (1980) indicate the possibility of decreased irritancy of SO_2 in the presence of NH_3 due to neutralization. In a study summarized by Morton (1980), concurrent exposure to NO_2 and an aerosol of NaCl increased airway resistance beyond that of NO_2 alone.

The investigations of Levin and coworkers (Levin et al. 1986; Levin et al. 1987a; Levin et al. 1987b) have indicated that when the endpoint is death, toxicological synergism exists between CO and CO_2 and that combinations of CO and HCN act in an additive manner. The 30-min LC_{50} for CO in air is 4,600 ppm (no animals died below 4,100 ppm) and that for CO_2 is greater than 180,000 ppm, but when combined, the presence of 50,000 ppm CO_2 increased the toxicity of CO such that animals died from 30-min exposure to 2,500 ppm. For combinations of CO and HCN (30-min LC_{50} of 160 ppm) it was found that for 30-min exposures the following relationship existed:

$$\text{If } \frac{[CO]}{LC_{50}CO} + \frac{[HCN]}{LC_{50}HCN} \geq 1, \text{ then}$$

some or all of the animals will die (the brackets are test concentrations of the gases). However, if the sum is less than 1, no animals will die. As Levin and co-workers point out, ideally when the equation equals 1, 50 percent of the animals should die.

Consideration of the above data from toxicology studies of the individual chemicals in gun exhaust as well as what little is known concerning toxicant interactions of the major gases is potentially useful, but fails to answer a number of questions.

(1) Will simultaneous exposure of the upper respiratory tract to NO_x, NH_3, and SO_2 result in saturation of the mucosa such that penetration into the deep lung by NH_3 and SO_2 is facilitated?

(2) Are the eye irritation effects experienced after exposure to NH_3 and SO_2 additive?

(3) Are the hypoxic effects seen with CO, NO, and NO_2 additive? and

(4) Will the presence of other chemicals in gun exhaust change the relationship between CO and CO_2 as identified by Levin and

co-workers and will the same relationship be seen for toxicological endpoints other than death?

4.7.4.5 Alternatives to a Continuous Exposure System for Weapons Exhaust

Individual toxicity testing of the major chemical species in weapons exhaust is one alternative if a continuous exposure system is not available, as was discussed in the previous section. A number of methods have been employed for testing the characteristics of propellant detonation and burning and for the collection and analysis of weapons exhaust that have potential application for inhalation toxicology. These include grab samples (Snelson et al. 1983), high-pressure bombs (as used at the Picatinny Arsenal), a laboratory-scale combustor (Snelson et al. 1983), an enclosure designed for the actual firing of an M16 rifle (Snelson et al. 1983), test motors (Feinsilver et al. 1950; Snelson et al. 1983), and a dynagun (Krier and Black 1974). Each of these methods has limitations that will be discussed in Volume II of this report. The only one of these methods that has been used for inhalation toxicity testing is the test motor and that was for an acute toxicity test of the combustion products of perchlorate fuel propellants (see Feinsilver et al. 1950).

One other method that will also be discussed in Volume II is the use of a simulated atmosphere. Since the principal gases present in weapons exhaust have been qualitatively, and in some instances, quantitatively identified (although further characterization is needed), it would be possible to develop a generating system that would enable animals (or human volunteers, if desired) to be exposed to a simulated atmosphere consisting of the major gases. This approach, as an alternative to whole mixture testing, has merit since any performance-degrading effects will likely be due to the gases that are the dominant chemical species present. It might be prudent to add inert or inorganic particulate matter in the size range present in weapons exhaust since there is evidence that particulate matter can influence the toxicity of the major gases (see Section 4.3.4).

4.7.5 Conclusions

The development of a satisfactory generating system for exposing animals to gun exhaust is essential to fully characterize the toxicology of this complex mixture. While useful information can be obtained by testing extracts of collected particulate material or by testing or analyzing existing toxicology information on major chemicals, these methods do not take into consideration the potential interactive effects (additive, synergistic, antagonistic) of one chemical with another. Once the toxicology of the intact mixture is known, then components of the mixture can be examined to determine their contribution to the affected biologic endpoints.

When testing, it is suggested that consideration be given to using either the head- or nose-only exposure route since this minimizes the amount of toxicant needed for testing as well as prohibiting the animal

from ingesting the toxicant by grooming. With respect to tests for reproductive function, the Army must decide if exposure to women during training exercises will occur. If not, then testing can be limited to male reproductive effects. Similarly, if women will not be exposed, then there is no need for teratology testing.

A few information gaps and suggestions for further research in toxicology of NH_3, NO_2, SO_2, and CO have been mentioned by Legters (1980), Morton (1980), Normandy et al. (1980), and Nightingale (1980), respectively. In the case of NH_3, precise threshold limits for immediate irritant effects (lacrimation) in man are not known. The question of reversibility of changes in the respiratory tract caused by repeated short exposures to high levels of ammonia needs to be resolved by animal studies. Pigs are very susceptible animals and have been recommended for this research by Legters (1980); however, problems associated with their size may realistically preclude their use. Although not practical from the technical standpoint, Legters (1980) has suggested an exposure regimen of six 1-hour exposures to concentrations around 400 ppm daily for 14 days, which is thought to be representative of the worst-case military situation. For NO_2, information gaps include (1) adequate study of the rate and completeness of recovery after a single acute exposure, (2) the consequences of intermittent exposure, (3) the extent to which the potentiation of respiratory infection, observed in animals, occurs in man, and (4) cumulative effects of low-level exposure.

Further studies of exposure to SO_2 in combination with other gases and aerosols present in armored vehicles should be conducted. Animal studies need to be carried out to determine the time and concentration necessary for each irreversible effect to occur.

As regards CO exposure, information from firefighters who are professionally exposed to the gas will be valuable to the military. Effects of repeated high-level CO exposure on coronary disease and effects of exposure cofactors such as other gases, cigarette smoking, fatigue, and heat stress on mental and physical performance should be investigated.

The in vitro tests discussed briefly in this section are used to indicate the potential for an agent to cause mutagenesis and possibly carcinogenes is in mammalian systems without having to undergo the lengthy procedures involved with animals. The tests have been sufficiently validated that false positive and false negative results are minimized. The use of these tests to screen the gun and rifle emissions may obviate the need for long-term animal studies; however, if there is evidence that the gun exhausts, at realistic concentrations, do cause mutagenesis and are thus suggestive of potential carcinogenicity, then more extensive animal tests may be necessary. While a classical chronic study is not recommended as a way of verifying positive mutagenic data, it is suggested that an alternative might be to add sufficient animals to the subchronic study and then allow these designated animals to remain with an equivalent group of controls in the animal house for up to 2 years. During the 2-year post-exposure period, a comparison of mortality rate would be made and then at termination of the study all animals would be sacrificed and the tissues closely examined for evidence of malignancy.

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APPENDIX A: REVIEW OF SELECTED REFERENCES

Ehrlich, R., J. C. Findlay, and D. E. Gardner. 1979. Effects of repeated exposure to peak concentrations of nitrogen dioxide and ozone on resistance to streptococcal pneumonia. J. Toxicol. Environ. Health 5:631-642.

Abstract:

Groups of female CD_2F_1 mice were exposed either to peak exposures (3 hr/day, 5 days/wk), or to combinations of continuous (24 hr/day, 7 days/wk), and peak exposures for 1, 2, 3, or 6 months (see Table A-1). Streptococcus infection (via aerosol) occurred within 1 h after termination of the final exposure. Following infection, two groups of experiments were conducted. In one group, exposure was to clean air for 14 days and in the second group animals were exposed to their respective pollutants for an additional 14 days. The measured endpoint was lethality. Tables A-2 and A-3 show the results when exposed to clean air or re-exposed to pollutants, respectively. As these tables indicate, the resistance of mice to streptococcal pneumonia was decreased following exposure; this decrease occurred sooner when mice were exposed to pollutants rather than clean air. The most effective exposure for reducing resistance to infection was peak exposures for 2 to 6 months to a mixture of 0.5 ppm NO_2 and 0.1 ppm O_3.

Analysis:

This study is one of a number of reports that indicate that exposure of animals to airborne substances (most notably, NO_2) results in decreased resistance to bacterial infection. Should this also be true of humans, then the health of individuals could be impaired beyond that otherwise expected for exposure to the pollutant alone.

TABLE A-1. NITROGEN DIOXIDE AND OZONE EXPOSURE PROFILE IN MICE[a]

Continuous exposure (24 hr/day, 7 days/week)	Peak exposure (3 hr/day, 5 days/week)
Filtered air	Filtered air
Filtered air	940 $\mu g/m^3$ (0.5 ppm) NO_2 and 196 $\mu g/m^3$ (0.1 ppm) O_3 mixture
188 $\mu g/m^3$ (0.1 ppm) NO_2	940 $\mu g/m^3$ (0.5 ppm) NO_2 and 196 $\mu g/m^3$ (0.1 ppm) O_3 mixture
Filtered air	940 $\mu g/m^3$ (0.5 ppm) NO_2
188 $\mu g/m^3$ (0.1 ppm) NO_2	940 $\mu g/m^3$ (0.5 ppm) NO_2

a. Exposure was for 1, 2, 3, or 6 months.

Source: Adapted from Ehrlich et al. (1979).

TABLE A-2. MORTALITY AND SURVIVAL TIME OF MICE EXPOSED TO NO_2 AND O_3, CHALLENGED WITH Streptococcus AEROSOL, AND KEPT FOR 14 DAYS IN CLEAN AIR

Concentration ($\mu g/m^3$)						
24 hr/day[a]	3 hr/day[b]		Mortality[d]		Survival time	
NO_2	NO_2	O_3	D/T	%	Days	Change
1 mo						
0	0	0	24/126	19.1	12.3	-
0	940	196	5/99	5.1	13.6	+1.3[c]
188	940	196	21/127	16.5	12.5	+0.2
0	940	0	28/127	22.1	11.7	-0.6
188	940	0	18/127	14.2	12.7	+0.4
2 mo						
0	0	0	21/87	24.1	12.2	-
0	940	196	20/72	27.8	12.0	-0.2
188	940	196	14/80	17.5	12.9	+0.7
0	940	0	24/96	27.1	12.0	-0.2
188	940	0	28/117	23.9	12.1	-0.1
3 mo						
0	0	0	62/156	39.7	11.3	-
0	940	196	94/155	60.7	8.8	-2.5[c]
188	940	196	38/156	24.4	11.9	+0.6
0	940	0	86/169	50.9	9.5	-1.8[c]
188	940	0	39/172	22.7	12.4	+0.9
6 mo						
0	0	0	9/44	20.5	12.8	-
0	940	196	21/44	47.7	11.0	-1.8[c]
188	940	196	18/51	35.3	11.2	-1.6[c]
0	940	0	13/46	28.3	11.8	-1.0[c]
188	940	0	14/42	33.3	11.5	-1.3[c]

a. 24 hr/day, 7 days/week

b. 3 hr/day, 5 days/wk

c. Significant change from corresponding infected mice exposed to filtered air ($p < 0.05$).

d. Number of mice that died/total number of mice.

Source: Adapted from Ehrlich et al. (1979).

TABLE A-3. MORTALITY AND SURVIVAL TIME OF MICE EXPOSED TO NO_2 AND O_3, CHALLENGED WITH Streptococcus AEROSOL, AND REEXPOSED FOR 14 DAYS TO THE POLLUTANTS

Concentration ($\mu g/m^3$)						
24 hr/day[a]	3 hr/day[b]		Mortality[d]		Survival time	
NO_2	NO_2	O_3	D/T	%	Days	Change
1 mo						
0	0	0	0/78	0	14.0	-
0	940	196	2/78	2.6	13.9	-0.1
188	940	196	3/77	3.9	13.8	-0.2
0	940	0	2/78	2.6	13.8	-0.2
188	940	0	1/84	1.2	13.9	-0.1
2 mo						
0	0	0	5/50	10.0	13.2	-
0	940	196	18/52	34.6	12.0	-1.2[c]
188	940	196	11/45	24.4	12.1	-1.1[c]
0	940	0	12.52	23.1	12.5	-0.7
188	940	0	14/67	20.9	12.5	-0.7
3mo						
0	0	0	4/60	6.7	13.4	-
0	940	196	24/60	40.0	10.8	-2.6[c]
188	940	196	16/60	26.7	11.9	-1.5[c]
0	940	0	8/60	13.3	13.2	-0.2
188	940	0	9/60	15.0	12.7	-0.7

a. 24 hr/day, 7 days/week

b. 3 hr/day, 5 days/week

c. Significant change from corresponding infected mice exposed to filtered air ($p < 0.05$).

d. Number of mice that died/total number of mice.

Source: Adapted from Ehrlich et al. (1979).

Gardner, D. E. 1984. Alterations in macrophage functions by environmental chemicals. Environ. Health Perspect. 55:343-358.

Abstract:

Alveolar macrophages play a vital role in the defense of the lung against environmental hazards. This defense role includes activities such as detoxifying and/or removing inhaled particles, maintaining sterility against inhaled microorganisms, interacting with lymphoid cells in immunity, and removing damaged or dying cells. Environmental chemicals have the potential for altering the biochemical, physiological, and immunological functioning of alveolar macrophages, thus compromising one of the body's defense mechanisms. The parameters of number, stability, viability, morphology, function, and biochemistry/metabolism can be used to assess the "health" of the macrophages. The most useful are the determinations based on functional capacity (i.e., phagocytic index, bacteriocidal capacity).

Analysis:

The information presented is a very useful overview of how environmental chemicals can affect alveolar macrophages. For a thorough understanding of the toxicology of inhaled materials it is essential to understand how macrophage function can be affected and what the potential consequences can be from altered function.

Hody, G.L. 1969. Measurement of toxic hazard due to firing the weapons of the UH-1B armed helicopter. USAARL Report NO. 70-5. AD 697765. U.S. Army Aeromedical Research Laboratory, Fort Rucker, AL.

Abstract:

Field investigation of the possible exposure of the UH-1B armed helicopter crew to carbon monoxide (CO) and metal particulates has been reported in this paper. Several thousand rounds of M-60 and minigun ammunition, 10 rounds of 3-11/M-22 wire-guided missiles and 42 pairs of 2.75-in. FFAR (folding-fin aircraft rocket) were fired. A specially modified instrument was used for quantitative monitoring of CO. Typical exposure times in the aircraft were so brief that even the fast responding CO meter did not have sufficient respose time to reach the correct peak readings. These readings were corrected using calibration curves of the transient response of the instrument with time. The overall accuracy of the CO measurement was within ±20 percent at concentrations above 50 ppm. The particulates were collected on a #41H Whatman filter disc with a small electric sampler that drew air at 3 L/min and were analyzed by atomic emission spectroscopy. The CO sample intake probe was located over the pilot's shoulder harness, and the particle sampler was clipped to the flight suit of a rear-seat occupant during the tests. The estimated CO exposures under different flight and door conditions are shown in Table A-4. Inhalation exposures to various metals are given in Table A-5. It was concluded from these results that the helicopter crew was not likely to be exposed to toxic levels of CO or metal particulates during the firing of the M-60 quad machine gun, dual minigun, S-11/M-22 wire-guided missile, or 2.75-in. FFARs.

Analysis:

This paper describes an early field assessment of toxic hazards in an armed helicopter employing instrumentation of very limited capabilities. The results are incomplete in so far as the possible presence of other toxic gases and particle-associated organic materials are concerned.

TABLE A-4. CARBON MONOXIDE EXPOSURE DURING FIRING OF MACHINE GUNS AND WIRE-GUIDED MISSILES (MAXIMUM LEVELS MEASURED)

Weapon Tested	Flight Condition	Door Condition	Maximum CO Concentration (ppm)	Maximum Exposure Time (min.)	Product of Concentration and Time (ppm/min)
M-60 Machine Gun (Quad)	Hover	Open	<50	<0.2	<10
"	Forward Flight	Open/Closed	No Detectable Levels (<25 ppm at all times)		
Minigun (Dual)	Hover	Open	<50	<0.2	<10
"	Forward Flight	Open/Closed	No Detectable Levels (<25 ppm at all times)		
Wire-Guided Missile	Hover and Forward Flight	Closed	<25	<0.2	<5

TABLE A-5. MINERAL AEROSOL INHALATION DURING VERY ACTIVE 1-DAY ARMED HELICOPTER MISSION

Metal	Dose (mg/day)[a]
Lead	0.03
Copper	0.008
Magnesium	0.02
Aluminum	0.02
Silicon	0.03

a. A breathing rate of 30 L/min is assumed.

King, L. C., K. Loud, S. B. Tejada, M. J. Kohan, and J. Lewtas. 1983. Evaluation of the release of mutagens and 1-nitropyrene from diesel particles in the presence of lung macrophages in culture. Environ. Mutagen. 5:577-588.

Abstract:

The principal objective of this study was to investigate the recovery and release of mutagens and 1-nitropyrene from diesel particles after phagocytosis by alveolar macrophages. Rabbit alveolar macrophages were cultured for 40 hr with diesel particles both in the presence and absence of fetal calf serum. For tests, a final diesel-particle concentration of 375 μg of particles/mL was selected when fetal calf serum was a part of the culture. This concentration maximized cellular exposure to diesel particles while minimizing macrophage toxicity. After 40 hr in culture at 375 μg/mL, 80 percent of the diesel particles were phagocitized by the macrophages, less than 7 percent cell lysis was observed, and cell viability was 62.6 ± 7.9 percent of control cultures. For tests in the absence of fetal calf serum, the concentration of diesel particles selected was 200 μg of particles/mL. After 40 hr in culture at this concentration, 68 percent of the diesel particles were engulfed by the macrophages, 24 percent cell lysis was observed, and cell viability was 67.9 ± 12.1 percent of control cultures. The mutagenicity of extracts was determined using the Ames assay. The enhancement of the integrity of the cell membrane observed in the presence of serum proteins and reduced cytotoxicity due to serum protein coating of diesel particles and adsorbed organics are offered as possible reasons for the significantly lower cytotoxicity (as measured by cell viability and sensitive indicators of cellular damage reducti) of diesel particles in the presence of on in adenosine triphosphate levels) serum. With or without fetal calf serum, the exposure of diesel particles to the macrophages in culture resulted in a substantial loss (97 and 98 percent) of the solvent extractable mutagenic activity from diesel particles. The study of King et al. suggests that lung macrophages have the capability to metabolize mutagenic nitroaromatics found in diesel particles.

Analysis:

Similar to the 1981 study (King et al. 1981), this effort also emphasizes the importance of bioavailibility. This study is important because it points out the effectiveness of the body's defense mechanisms and any risk assessment, whether of a single compound or complex mixture, must consider such mechanisms.

King, L. C., M. J. Kohan, A. C. Austin, L. D. Claxton, and J. L. Huisingh. 1981. Evaluation of the release of mutagens from diesel particles in the presence of physiological fluids. Environ. Mutagen. 3: 109-121.

Abstract:

The organic compounds that are adsorbed to diesel particulates have been routinely extracted with organic solvents and have been shown to be mutagenic in short-term assays. Whether or not these organic solvents can be similarly removed by physiological fluids is the subject of the investigation by King et al. The physiological fluids used were human serum, lung lavage fluid, and lung cytosol. Mutagenicity of extracts (from physiological fluids and organic solvents) was tested using the Ames assay. Serum extracts (1-hour sonicate), in contrast to lung lavage fluid and lung cytosol extracts, did show mutagenic activity, although far less than the organic solvents, especially dichloromethane.

Experiments were also conducted to determine the effect of serum and lung cytosol on the mutagenic activity of the dichloromethane extract. Tests showed that mutagenicity was significantly reduced for both serum (80 percent reduction) and lung cytosol (90 percent reduction). Thus, physiological fluids are capable of removing mutagens from diesel particles, but very little mutagenic activity is expressed because of binding to serum and lung cytosol proteins and/or metabolism.

Analysis:

This paper addresses the key issue of bioavailability. Although there is little doubt that the organics adsorbed to diesel particles are mutagenic, the expression of mutagenicity in vivo must be carefully considered. The work of King et al. indicates that the expression of mutagenicity by otherwise mutagenic compounds is compromised by physiological fluids. The same could quite likely be stated for mutagenic compounds present in gun exhaust.

Legters, L. 1980. Biological Effects of Short, High-Level Exposure to Gases: Ammonia. AD 94501. Enviro Control, Inc., Rockville, MD. DAMD17-79-C-9086.

Abstract:

This health effects review on ammonia (NH_3) is one in a series; the other reports are on sulfur dioxide, nitrogen oxides, and carbon monoxide. The eyes and respiratory tract are the organs primarily affected by exposure to NH_3. Although the odor is noticeable, below 50 ppm there are no significant health effects. Irritation of the eyes, nose, and throat is experienced by most people at NH_3 concentrations between 50 and 100 ppm. Acclimation to the irritant effects after 1 or 2 weeks of intermittent exposure to these levels has been indicated. Lacrimation is reported to occur in approximately half of exposed individuals at around 130 ppm.

Analysis:

This review of the toxicology of NH_3 is of interest to the present problem definition study because exposure of personnel to NH_3 from the firing of weapons is possible, and the exposure sequence studied by Legters is what would be anticipated. Information is presented on threshold levels especially as they relate to irritant effects, which are especially relevant in an assessment of potential performance degradation, the principal effect of concern as a result of military-specific exposure to gun exhaust.

Levin, B. C., M. Paabo, J. L. Gurman, and S. E. Harris. 1987a. Effects of exposure to single or multiple combinations of the predominant toxic gases and low oxygen atmospheres produced in fire. Fund. Appl.Toxicol. (submitted)

Levin, B. C., M. Paabo, J. L. Gurman, S. E. Harris, and E. Braun. 1987b. Evidence of toxicological synergism between carbon monoxide and carbon dioxide. Toxicol. Appl. Pharmacol. (submitted)

Abstract:

The principal focus of these two studies is the toxicological interaction of the predominant fire gases and the extent to which the combined action of these gases can explain the toxicity of the thermal degradation products of burning solid materials. The endpoint of investigation was lethality. Fischer-344 rats were exposed for 30 minutes to each gas and to various combinations of the gases and LC_{50} values determined, either at 30 min, 24 hr, or 14 days. The 30-min LC_{50} values for carbon monoxide (CO) were 5,000 ppm for gradual exposures and 4,600 ppm for square-wave exposures. The LC_{50} (square-wave) (14-day observations) for carbon dioxide (CO_2) was >14.7 percent. When animals were exposed to nonlethal concentrations of CO_2 (1.7 to 17.3 percent) in combination with sublethal concentrations of CO (2,500 to 4,000 ppm), some of the animals died either during exposure or 24 hr after exposure. Thus, toxicological synergism was observed. The most toxic combination was 2,500 ppm CO plus 5 percent CO_2 where the rate of carboxyhemoglobin formation was 1.5 times faster than that found in rats exposed only to 2,500 ppm CO.

In contrast, carbon monoxide and hydrogen cyanide (HCN) (30-min LC_{50} of 160 ppm) act in an additive manner such that if

$$\frac{[CO]}{LC_{50}CO} + \frac{[HCN]}{LC_{50}HCN} \geq 1,$$

some or all of the exposed animals will die (the values in brackets are the test concentrations of the gases). When the left-hand side of the equation is less than one, the animals will live. Ideally, when the equation equals one, the LC_{50} is reached. Fifty percent of the animals (3/6) died at the following CO and HCN combinations: 2,392 ppm CO and 92.8 ppm HCN; 1,288 ppm CO and 124.8 ppm HCN; and 1,242 ppm CO and 126.4 ppm HCN. When HCN and CO_2 (at 5 percent) were tested together, the LC_{50} was lower than that of HCN alone [75 ppm compared with 110 ppm (24-hr LC_{50}-30-min exposure plus post exposure)].

When oxygen concentrations were decreased, the toxicity of the mixtures of other fire gases was increased even further.

Analysis:

The research of Levin and co-workers is of interest because many of the gases identified as by-products of fire combustion are also products in gun exhaust (i.e., CO, CO_2, and HCN). Two important questions arise when considering the applicability of the research of Levin et al. to gun exhaust. The first -- and the most significant -- is whether the interactions observed between the major gases when the measured endpoint is lethality would be similar when the endpoint is one associated with performance degradation (e.g., behavior alteration). The second question concerns what influence the other constituents of gun exhaust will have on the toxicity of the major gases. However, until data are available to answer these questions, the interactive effects demonstrated by Levin et al. should be considered as an insight into what might occur in gun exhaust.

Morton, J. D. 1980. Biological Effects of Short, High-Level Exposure to Gases: Nitrogen Oxides. AD A094502. Enviro Control, Inc., Rockville, MD. DAMD17-79-C-9086.

Abstract:

This health effects review on nitrogen oxides is one in a series; the other reports are on sulfur dioxide, carbon monoxide, and ammonia. In the military setting, the nitrogen oxides of most concern are nitrogen dioxoide (NO_2) and nitric oxide (NO). Although NO does react with hemoglobin to form methemoglobin, it is considerably less toxic than NO_2. Nitrogen dioxide is of concern because of the following effects: (1) immediate irritation of the respiratory and other mucosa, (2) delayed tissue damage, principally in the deep lung, and (3) increased susceptibility to infection. One-min NO_2 exposure to 50 ppm or 5-min exposure to 25 ppm are considered to be thresholds of strong sensory discomfort, sufficient to hinder normal activities. Although the effect has not been confirmed in humans, animals show increased susceptibility to respiratory infection after a single exposure to 3.5 ppm NO_2 or several NO_2 exposures of 1.5 ppm. Although somewhat conflicting, the evidence regarding intermittent exposures is that they have an effect similar to continuous exposure at the same concentration providing the exposure is of the same total duration.

Analysis:

This review of the toxicology of nitrogen oxides (NO_x) is of interest because NO_x, primarily NO_2 and NO, are constituents of gun exhaust and the exposure sequence addressed is that expected due to weapons firing. Although NO_2 is undoubtedly of more concern than NO, the adverse effect on oxygen transport could be significant when individuals are simultaneously exposed to carbon monoxide, a compound that also affects oxygen transport.

Nightingale, T. E. 1980. Biological Effects of Short, High-Level Exposure to Gases: Carbon Monoxide. AD 94503. Enviro Control, Inc., Rockville, MD. DAMD17-79-C-9086.

Abstract:

This health effects review on carbon monoxide (CO) is one in a series; the other reports are on sulfur dioxide, nitrogen oxides, and ammonia. The principal effect due to CO exposure is the formation of carboxyhemoglobin (COHb), which results in impaired oxygen delivery and, thus, in adverse effects to the heart and brain. Since CO is not detectable by human senses, the first sign of exposure may be toxicity, beginning as a headache or a sensation of a pounding heartbeat. Rather than defining exposure in terms of concentration, the percentage of COHb formed is used to quantify exposure. Headaches have been first reported in resting males at COHb concentrations ranging from 9.1 to 37 percent, indicating a high degree of variability among individuals. Carbon monoxide impairment of audiovisual performance and motor-coordination-effect parameters of particular military concern has not been well defined.

Analysis:

This review is of special interest to the problem definition study on gun smoke because CO is the principal pollutant (in terms of concentration) in gun exhaust and the exposure sequence is that anticipated during weapons firing.

Normandy, M. J. 1980. Biological Effects of Short, High-Level Exposure to Gases: Sulfur Dioxide. AD 94504. Enviro Control Inc., Rockville, MD. DAMD17-79-C-9086.

Abstract:

This health effects review on sulfur dioxide (SO_2) is one in a series; the other reports are on ammonia, nitrogen oxides, and carbon monoxide. The organ systems primarily affected by short, high-level exposure to SO_2 are the respiratory tract and eyes. No significant irritant or pulmonary effects are observed below 5 ppm, but between 5 and 8 ppm most people will experience coughing; moderate irritation of the eyes, nose, and throat; and bronchoconstriction. Moderate to severe eye irritation, copious lacrimation, and nasal and chest irritation will be observed at SO_2 concentrations of approximately 10 ppm. Sulfur dioxide is water soluble and with nasal breathing about 99 percent is absorbed by the nasal mucosa with only 1 percent penetrating into the lower airways.

Analysis:

The information presented in this report is of interest because of the possible exposure to SO_2 from weapons firing and because the exposure sequence (i.e., short, high-level, intermittent) is the focus of the problem definition study on gun exhaust. The report by Normandy is a good summary of the toxiocology of SO_2, especially with respect to threshold levels for humans.

Rocchio, J. J. and I. W. May. 1973. Analysis of Exhaust Gases from the XM-19 rifle -- An Application of Gas Chromatography/Mass Spectroscopy. Memorandum Report NO 2293. AD 910 937. U.S. Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

Abstract:

A combination of gas chromatography and mass spectrometry has been developed for detection and quantification of the components of exhaust gases from the firing of the XM-19 rifle. (The composition of the primer and propellant used in the rifle is presented in Table 2.20). An exhaust confinement vessel was employed to restrict the diffusion of the exhaust gases in surrounding air. One end of the confinement vessel (an aluminum cylinder 1.02 m x 0.3-m diam.) was covered with an aluminum plate with an opening to accept the muzzle of the rifle. The opposite end was sealed with a replaceable rubber diaphragm. This effectively sealed the gun exhaust while allowing the flechettes to pass through. Exhaust samples were collected through the ports along the length of the cylinder using cryogenic gas condensation traps.

Porapak QS was found to be the most effective packing material for the GC column for separation of all exhaust components except acetylene/ethylene and carbonyl sulfide/cyanogen. The lower limit of detection using TCD (thermal conductivity detector) and FID (flame ionization detector) were ≈20 and <1 ppm, respectively. Unfortunately, most of the permanent gases of interest in this study could not be detected by FID. Gases detected by TCD include air, carbon monoxide, nitric oxide, methane, carbon dioxide, nitrous oxide, [acetylene, ethylene], water, [cyanogen, carbonyl sulfide], propylene, propyne or allene. Gases detected by FID include methane [acetylene, ethylene], ethane, three unidentified components, [cyanogen, carbonyl sulfide, hydrogen cyanide], propylene, propane, propyne or allene. The bracketed components eluted in one peak. Hydrogen sulfide could not be detected in the exhaust. Only a trace of ammonia was detected by infrared spectroscopy but not by GC/MS. The reaction of ammonia with nitrogen dioxide and hydrogen cyanide was presumably the reason for its low concentration in the exhaust. Nitric oxide (but not nitrogen dioxide) was detected by GC/MS. Analysis of nitrogen oxides was less than satisfactory because of its reactivity with the GC column packing and its absorption on the walls of the sampling system or GC columns.

Results of quantitative analysis of the exhaust are presented in Table 2.21. Some of the trace components (nitric oxide, nitrous oxide, and carbonyl sulfide) could not be quantitated because of lack of sensitivity of TCD. The concentration of carbon monoxide was determined by an ultrasonic detector using a 3 m x 3-mm-OD column packed with molecular sieve 5A.

Analysis:

Particulates containing organic matter present in the gun exhaust were not examined. Concentration of cyanogen was 5 orders of magnitude greater than the calculated values. Experimental values of carbon dioxide, carbonyl sulfide, and methane agreed quite well with the calculated values.

Scharf, P.B., B. B. Goshgarian, and G. L. Hody. 1967. The Measurement of the Exhaust Composition of Selected Helicopter Armament. AD 655844. USAARU Report 67-10, AFRPL Report TR-67-203.

Abstract:

A test stand is described for collecting samples of exhaust gases from the firing of the 50-caliber and 7.62-mm machine gun and the 2.75-in. rockets for qualitative and quantitative analysis for toxic hazard prediction. These armaments are typically used in armed helicopters, and the crew members are exposed to the exhaust products from these machine guns and rockets in a semi-closed environment.

Gases and vapors were collected in evacuated stainless steel cylinders and with a three-stage condensation train (salt water-ice, dry ice-trichloroethylene, liquid nitrogen). The system was equipped with a rapid-sequence timer to trigger the solenoid valves for initiating collections at specified times after firing was begun. Sampling duration (usually about 2 sec) was also controlled by the timer to ensure that the samples were taken at atmospheric pressure. A pressure transducer near the gun muzzle provided additional timing information.

Gelman and Staplex samplers fitted with 4-in-diameter millipore SM membranes made of modified cellulose with a nominal pore size (5 ± 1.2 μm) were used for collecting particulates through ports cut in the cylinder surrounding the guns. A protective aircraft-type gate valve was found to be essential to shield the filters during firing. It was electrically opened after the last round had exploded.

Analysis of the exhaust gases was accomplished by a rapid-scan infrared spectrometer (Beckman IR 102) installed close to the weapons to minimize delay and a Consolidated Electrodynamics Corporation Model 21-110 high-resolution mass spectrometer. Methylene chloride extracts of the particulate were analyzed by GC, IR, and MS. The inorganic materials were analyzed by atomic emission spectroscopy. The results were expressed in terms of a dimensionless ratio, R, equal to the partial pressure of the component divided by the partial pressure of carbon monoxide (CO). The R values of selected components of the exhaust are shown in Table A-6. Analysis of the extracts of the particulates was unsatisfactory. The results of analysis of the inorganic particulates are expressed in terms of R_p, which is equal to $C_x \cdot pa/pCO$, where C_x = concentration of the particulate x in mg/m^3, pa = atmospheric pressure, and pCO = partial pressure of CO. $R_p \times 10^{-3}$ can be regarded as units mg/m^3 of x per 1,000 ppm CO. R_p values of some typical elements are given in Table A-7.

TABLE A-6. THE RATIO OF THE CONCENTRATION OF SELECTED COMPONENTS TO CO CONCENTRATIONS[a]

GAS	WEAPON					
	50 Caliber		7.62-mm		Rocket	
	R x 10^3		R x 10^3		R x 10^3	
	Mean	Max	Mean	Max	Mean	Max
Carbon dioxide	390	1,700	400	680	2,800	7,900
Ammonia	5.7	14	12	33	10	25
Nitrogen dioxide	6.0	1 sample	20	25	None Detected	
Hydrogen cyanide	0.4	1.0	1.0	1.2	5.0	10
Cyanogen	0.2	0.5	0.8	2.0	2.0	3.0
Carbonyl sulfide	0.7	2.0	0.3	0.8	None detected	
Acetaldehyde	2.3	10	2.0	1 sample	None detected	
Hydrogen chloride[b]			None detected	None detected	-	4.0
Sulfur dioxide[b]			None detected	None detected	-	3.0

a. Data do not include runs 5 or 15 except for nitrogen dioxide

b. Found only in rocket plume very close to nozzle ("probe" samples).

TABLE A-7. SUMMARY OF R_p ($R_p = C_x \cdot pa/pCO$, WHERE C_x = CONCENTRATION OF THE ELEMENT IN mg/m^3, pa = ATMOSPHERIC PRESSURE, AND pCO = PARTIAL PRESSURE of CO)

Element	$R_p \times 10^{-3}$		
	50-Caliber	7.62-mm	Rocket
Fe	0.06	0.03	88.0
Cu	4.3	1.2	2.6
Pb	1.3	0.4	53.0
Zn	0.7	0.2	-
Al	0.3	0.07	2.0
Mg	0.007	0.004	0.4
Ca	0.8	0.2	-
Si	0.05	0.01	1.0

Analysis:

This important study demonstrates that laboratory study of weapons exhaust composition can provide useful data for assessment of toxicological hazard. This approach to the problem is superior to field analysis of grab samples in so far as the probability of detecting highly toxic components is concerned. Variation in propellant composition and packing density from batch to batch is common because the most rigid specifications for ammunition are ballistic rather than chemical. This partly explains the difficulty in attaining reproducible results.

Schumaker, R. L. and G. D. Pollard. 1977. Toxicologic Gas Evaluation of the Utility Tactical Transport Aircraft System (UH-60). USAARL Report No. 77-18, AD 047801. U.S. Army Aeromedical Research Laboratory, Fort Rucker, AL.

Abstract:

Toxic gases accumulated in the crew compartment of the UH-60 helicopter firing two 7.62-mm machine guns under a variety of flight conditions have been investigated. Carbon monoxide and nitrogen dioxide/nitric oxide were monitored continuously and quantified during the test period. An on-board mass spectrometer was used for analysis of rapidly decaying toxic compounds. Samples were also collected for later analysis using a high-resolution, high-sensitivity JEOL D100 mass spectrometer. The results are shown in Table A-8.

TABLE A-8. MASS SPECTROGRAPHIC ANALYSIS OF GUN CASES[a]

Gas	Sample 1 (ppm)	Sample 2 (ppm)	OSHA standard based on 8 hr/day, 40 hr/week, weighted exposure level (ppm)
NO	None detected	None detected	5
NO_2	None detected	None detected	5
SO_2	24	8.5	5
HCN	18	21.0	10
H_2S[b]	126	63.0	50

a. Accuracy is ±25%.

b. OSHA standards only allow one 10-min exposure of 50 ppm H_2S in any 8-hr period as opposed to the other gases in the table, which are based on weighted averages.

Analysis:

In contrast with other investigators (e.g., Rocchio and May 1973) who used carbon monoxide, Schumaker and Pollard used argon, which has a known concentration in air (0.94 percent or 940 ppm) as an internal reference for quantification. Experimental details such as the type of monitors used and their posssibly limited capacity to detect nitrogen oxides, composition of the primer, and propellants in the munition used in the 7.62-mm machine guns have not been reported.

Snelson, A., P. Ase, W. Bock, and R. Butler. 1983. Characterization of Combustion Products of Military Propellants. Final Report, Vols. I and II. U.S. Army Medical Bioengineering Research and Development Command, Contract NO. DAMD 17-80-C-0019. IIT Research Institute, Chicago, IL.

Abstract:

Three different approaches have been taken to analyze the combustion products from military propellants: computer modeling, laboratory combustion testing, and field weapon testing. Different gun systems and propellants used along with the results of analysis and comments are summarized in Table A-9.

The computer calculations of the composition of combustion products are based on equilibrium chemical thermodynamics. Data input include the chemical formulae of the propellant components and the temperature and pressure of the reaction products in addition to a list of likely combustion products and the associated thermodynamic data (heats of formation, heat capacities, entropies, and thermal phase change properties). Computer calculation of the ballistic performance of propellants has been successful and the prediction of major products distribution has proved to be reliable; however, the reliability of prediction of minor products distribution is uncertain.

In the laboratory combustion experiments, an air-tight, vented test fixture was used for firing cartridges without bullets. The permanent gases were collected in evacuated steel cylinders and nitrogen oxides, sulfur dioxide, ammonia, and hydrogen cyanide were collected in liquid nitrogen traps. Trace gases were collected in Tenax cartridges. Particulates were collected either on Gelman type A/E glass filters or Whatman type 41 cellulose fiber filters by flushing out the sample collection system with air. For aerosol size discrimination, an Anderson six-stage viable particulate sampler was used. The gases were also collected in cylinders containing air at 20 mm Hg to study the effect of air on the combustion products. Samples were collected in a similar fashion from the M16 rifle.

Test motors were used for collecting exhaust samplers from MLRS (Multiple Launch Rocket System). Three mL of 30 percent hydrogen peroxide was used in one set of samples to determine SO_2 and NO_x by oxidizing them to sulfuric acid (H_2SO_4), and nitric acid (HNO_3). Another set of samplers contained 3 mL of 0.5 N H_2SO_4 to absorb ammonia (NH_3). Another set of samplers was used to trap hydrogen cyanide in 3 mL of 0.5 N sodium hydroxide.

Analytical procedures used in this study include gas chromatography, mass spectrometry, ion chromatography, ion specific electrodes, X-ray fluorescence, and plasma emission spectroscopy. Compositions of the gun propellants and the M-16 cartridge primer are given in Tables A-10 and A-11, respectively.

TABLE A-9. ANALYSIS OF COMBUSTION PRODUCTS OF MILITARY PROPELLANTS

Method	Gun system/Combustor	Propellant	Combustion products: Major gas species	Combustion products: Minor gas species	Trace gas species	Particulates
Computer modeling	M16	WC844 M5, M6, M30, MH9A2				
	MLRS (multiple launch rocket system)	Classified (contains Al, ammonium perchlorate)				
Laboratory Combustion Testing	M16[a]	WC 844	H_2, N_2, CO, CO_2, H_2O	CH_4 (4), C_2H_2 (2), C_2H_4, C_2H_6 (4), C_3H_6 (2), C_3H_8 (4), C_4H_{10} (15), C_6H_6 (6), CH_3CN (2), NH_3 (5), NO (7)	~100	Ba, Ca, Cr, Cu, Fe, Pb, Si, Zn
	VTF[b] (vented test fixture) (20, 30, 40, 50 kpsi)	WC 844	H_2, CO, CO_2 (quantified)	CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_6H_6, CH_3CN, NH_3, NO	~70 (semiquantitative data)	Ba, Ca, Cr, Cu, Fe, Pb, Si, Zn
	MLRS/test motor[c]	Classified (contains Al, ammonimum perchlorate)	H_2, CO, CO_2 (quantified), HCl	CH_4, C_2H_2, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_6H_6, NO_x (quantified), Cl_2, N_2H_4	~50	
Field Weapon Testing	M198 howitzer[d]	M119A2	H_2, CO, CH_4, NO_3^-		~35 (not reproducible)	
	25-mm cannon and 7.62-mm machine gun in XM2 infantry fighting vehicle[e]	WC 980 (25-mm cannon WC 846 (7.62-mm machine gun	H_2, CO, CO_2, CH_4, NH_3 (25-mm cannon), H_2, CO, CO_2, CH_4 (7.62-mm machine gun)	C_2H_4, C_2H_6, C_3H_6, C_3H_8 (25 mm cannon), C_2H_4, C_2H_6, C_3H_6, C_3H_8, NH_3 (7.62 mm machine gun)		
	MLRS[f]	Classified (contains Al, ammonium perchlorate)	CO (22%), HCl (13%)			

a. Major combustion products distribution agreed within 27% to the data from VTF (50 kpsi). Minor combustion products distribution disagreed; numbers in parentheses in the minor gas species column indicate the factors by which the two sets of analyses differed. Distribution of metals in the two systems was different.

b. Major combustion products distribution at four different pressures were within ±10% and in agreement with computer modeling data. Minor combustion products distributions were more variable with pressure (±15% for NO, ±100% for CH_3CN) and not in agreement with computer modeling data in many cases.

c. Major products distribution agreed with the computed values.

d. Muzzle exhaust composition was different from the breech exhaust composition because of muzzle flash.

e. Considerable amount of NH_3 from 25-mm cannon exhaust; very little NH_3 from 7.62-mm machine gun exhaust; propellants WC 980 and WC 846 were similar in composition.

f. Crew compartment is sealed to prevent exposure, especially to HCl.

TABLE A-10. COMPOSITION OF THE GUN PROPELLANTS

	7.62-mm machine gun WC846	25-mm cannon WC980	M16 rifle WC844
Nitrocellulose (%)	Remainder	Remainder	Remainder
Nitrogen in nitrocellulose (%)	13.0-13.20	13.00-13.20	---
Dinitrotoluene (% max.)	1.0	1.0	---
Graphite (% max.)	0.4	0.4	---
Carbon black	---	---	0.4
Potassium nitrate (%)	---	0.0-1.50	---
Potassium sulfate (%)	---	0.0-1.50	---
Potassium oxalate (%)	---	0.0-1.50	---
Total potassium salts (% max.)	---	1.50	---
Sodium sulfate (% max.)	0.50	0.50	0.5
Calcium carbonate (% max.)	0.25	0.25	0.2
Nitroglycerin (%)	8.00-11.00	8.50-11.50	11.0
Diphenylamine (%)	0.75-1.50	0.75-1.50	1.5
Dibutyl phthalate (%)	3.50-7.00	4.50-8.50	6.0
Total volatiles (% max.)	2.00	2.00	
Moisture and volatiles (%)	1.00 ± 0.025	1.00 ± 0.25	
Residual solvents	1.20	1.50	

TABLE A-11. COMPOSITION OF THE M16 CARTRIDGE PRIMER[a]

Components	Wt %
Lead styphnate	37 ± 5
Tetracene	4 ± 1
Barium nitrate	32 ± 5
Antimony sulfide	15 ± 2
Aluminum powder	7 ± 1
PETN	5 ± 1
Organic binder	Small

a. Total mass of primer 0.024 g ± 5%.

Field studies were carried out with an XM2 infantry fighting vehicle equipped with a 25-mm cannon and a 7.62-mm machine gun, M198 Howitzer, MLRS, and Stinger shoulder-launched rocket. Internal samples were taken in both the XM2 and MLRS vehicles. The propellant in MLRS contained ammonium perchlorate, which gave rise to copious amounts of HCl in the exhaust. The crew compartment was sealed to prevent exposure. There was a considerable amount of NH_3 in the exhaust from the 25-mm cannon whereas NH_3 was much less noticeable in the exhaust from the 7.62-mm machine gun. This was unexpected since the propellants used in these guns were very similar. Muzzle exhaust composition from the howitzer was different from the breech exhaust composition because of the muzzle flash.

Analysis:

Most of the useful data were obtained from the laboratory combustion testing of the WC 844 propellants using the M16 rifle or vented test fixture. Difficulties and inadequacies in taking field samples have been pointed out. In the case of big guns, it was difficult to obtain muzzle samples, partly because of the muzzle flash; however, breech samples were easily obtained. No attempt was made to correlate the combustion products with the composition of different propellants.

USEPA. 1986. U.S. Environmental Protection Agency. Guidelines for the Health Risk Assessment of Chemical Mixtures (51 FR 34014).

Abstract:

This Federal Register entry is a procedural guide to the evaluation of the subchronic and chronic effects of chemical mixtures (defined as any combination of two or more chemical substances). It is generally recognized that the interaction of toxicants within a mixture may occur during any of the pharmacologic and toxicologic processes that take place with a single compound, i.e., absorption, distribution, metabolism, excretion, and activity at receptor sites. Chemical interactions, yielding a new toxic component or causing a change in the biological activity of the existing component, may occur or chemicals may interact by causing different effects at different receptor sites. Table A-12 lists the risk assessment approach for chemical mixtures. In summary, it states that health effects data on the mixture of concern are desirable; if not available, then health effects data on a similar mixture should be used, and, if none are available, health effects data on mixture components should be used. When examining mixture components, systemic toxicants should be considered separately from carcinogens. Dose additivity and response additivity are the methods discussed to predict the toxic effects of the mixture from its components. Dose additivity assumes that the behavior of the toxicants in a mixture is as though they are dilutions or concentrations of each other; response additivity assumes that the two toxicants act on different receptor systems and that the correlation of individual tolerances may range from completely negative ($r = -1$) to completely positive ($r = +1$).

Analysis:

Although informative, the information presented really does little to clarify the issue of how to assess the toxicity of a mixture when health effects data on the mixture as a whole are not available. The dose additivity and response models do not consider possible toxicant synergistic or antagonistic interactions, and hazard or risk assessments based on them would be tentative at best. As stated by EPA, "Dose-additive and response-additive assumptions can lead to substantial errors in risk estimates if synergistic or antagonistic interactions occur." Furthermore, dose additivity is not the most biologically plausible method if the compounds in a mixture do not have the same mode of toxicity.

TABLE A-12. RISK ASSESSMENT APPROACH FOR CHEMICAL MIXTURES

1. Assess the quality of the data on interactions, health effects, and exposures.

a. If adequate, proceed to Step 2.
b. If inadequate, proceed to Step 14.

2. Health effects information is available on the chemical mixture of concern.

a. If yes, proceed to Step 3.
b. If no, proceed to Step 4.

3. Conduct risk assessment on the mixture of concern based on health effects data on the mixture. Use the same procedures as those for single compounds. Proceed to Step 7 (optional) and Step 12.

4. Health effects information is available on a mixture that is similar to the mixture of concern.

a. If yes, proceed to Step 5.
b. If no, proceed to Step 7.

5. Assess the similarity of the mixture on which health effects data are available to the mixture of concern, with emphasis on any differences in components, as well as the effects that such differences would have on biological activity.

a. If sufficiently similar, proceed to Step 6.
b. If not sufficiently similar, proceed to Step 7.

6. Conduct risk assessment on the mixture of concern based on health effects data on the similar mixture. Use the same procedures as those for single compounds. Proceed to Step 7 (optional) and Step 12.

7. Compile health effects and exposure information on the components of the mixture.

8. Derive appropriate indices of acceptable exposure and/or risk on the individual components in the mixture. Proceed to Step 9.

9. Assess data on interactions of components in the mixtures.

a. If sufficient quantitative data are available on the interactions of two or more components in the mixture, proceed to Step 10.
b. If sufficient quantitative data are not available, use whatever information is available to qualitatively indicate the nature of potential interactions. Proceed to Step 11.

10. Use an appropriate interaction model to combine risk assessments on compounds for which data are adequate, and use an additivity assumption for the remaining compounds. Proceed to Step 11 (optional) and Step 12.

TABLE 12. (CONTINUED)

11. Develop a risk assessment based on an additivity approach for all compounds in the mixture. Proceed to Step 12.

12. Compare risk assessments conducted in Steps 5, 8, and 9. Identify and justify the preferred assessment, and quantify uncertainty, if possible. Proceed to Step 13.

13. Develop an integrated summary of the qualitative and quantitative assessments with special emphasis on uncertainties and assumptions. Classify the overall quality of the risk assessment, as indicated in Table 2. Stop.

14. No risk assessment can be conducted because of inadequate data on interactions, health effects, or exposure. Qualitatively assess the nature of any potential hazard and detail the types of additional data necessary to support a risk assessment. Stop.

Note: Several decisions used here, especially those concerning adequacy of data and similarity between two mixtures, are not precisely characterized and will require considerable judgment. Source: USEPA (1986).

Wohlford, W. and E. Sheets. 1971. Gas contamination test - small arms automatic weapons. AD 887304. Small Arms Systems Laboratory, Rock Island, IL.

Abstract:

Small arms automatic weapons - M60C, M60E2, M219 (control), M85, M2HB, M37, M16, M14, XM207E1, and M134 - were fired in a 63-ft^3 test chamber with the gun barrel protruding through a hole in the chamber. Different sealing methods were used around the barrel and gas evacuator tube. Carbon monoxide (CO) level in the test chamber was determined with a Lira Model 200 carbon monoxide analyzer after sufficient time had elapsed for stabilization (about 2 min after firing) with a circulating fan placed inside the test chamber.

It was found that the most significant factor controlling the gas contamination from the breech of a weapon in the test chamber was the length of the dwell time - the time from primer initiation to complete unlocking of the bolt. Figure A-1 shows CO level as a function of the dwell time. There was a minimum CO output at ca. 1.5 ppm per round fired and dwell times greater than ca. 28 msec had little effect on CO output. The method of sealing of the gun port was also critical to the amount of gas accumulated in a closed compartment such as in a tank. A comparison of stabilized CO concentrations resulting from firing continuous bursts from three different weapons with optimum weapon sealing conditions is shown in Figure A-2.

Analysis:

Although only one component of the small arms automatic weapons exhaust, namely CO, was monitored, the results of this investigation are a good indication of the hazards gun crews are exposed to in a confined space.

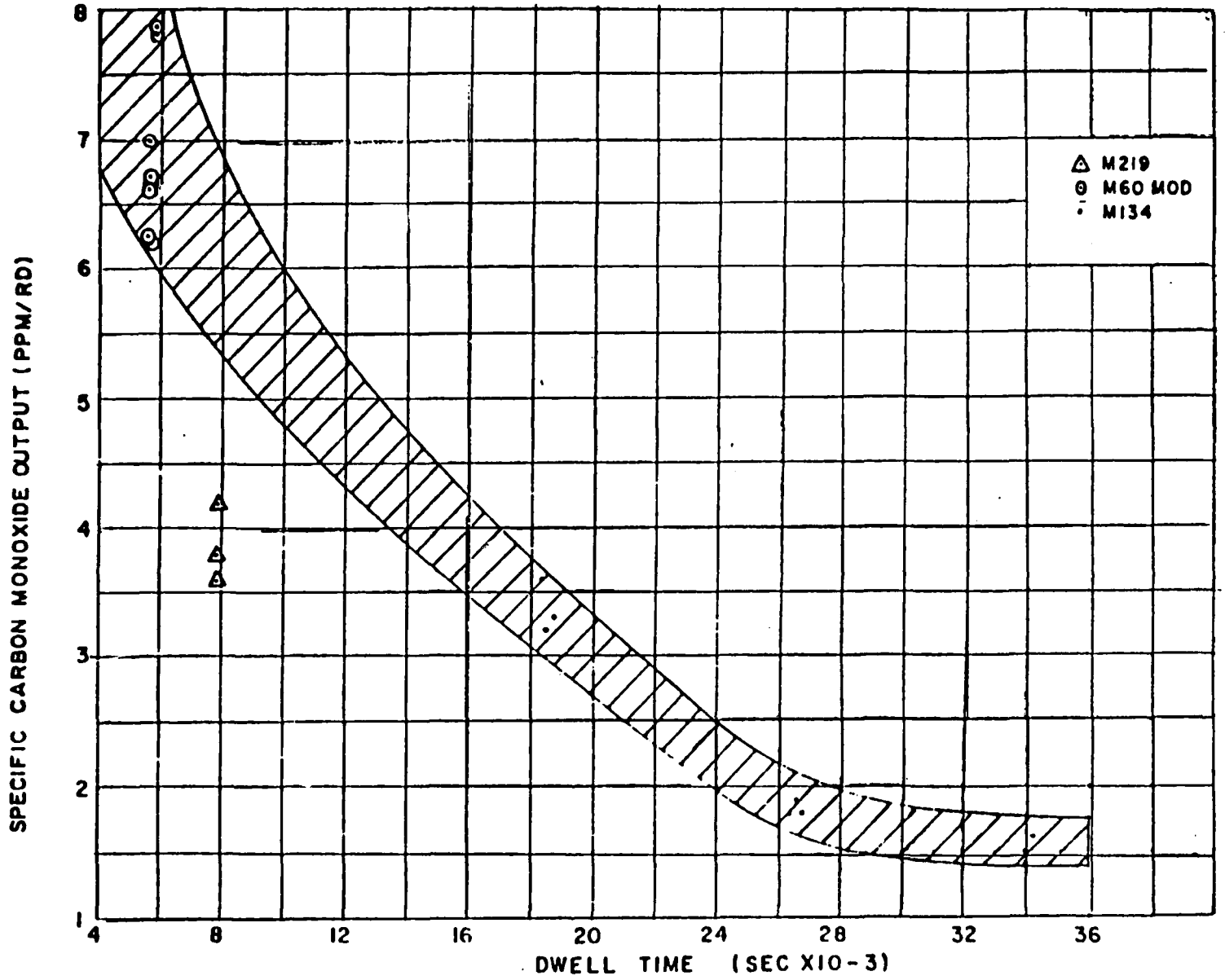

Figure A-1. Specific gas contamination vs dwell time, optimum sealing, 50 RD bursts

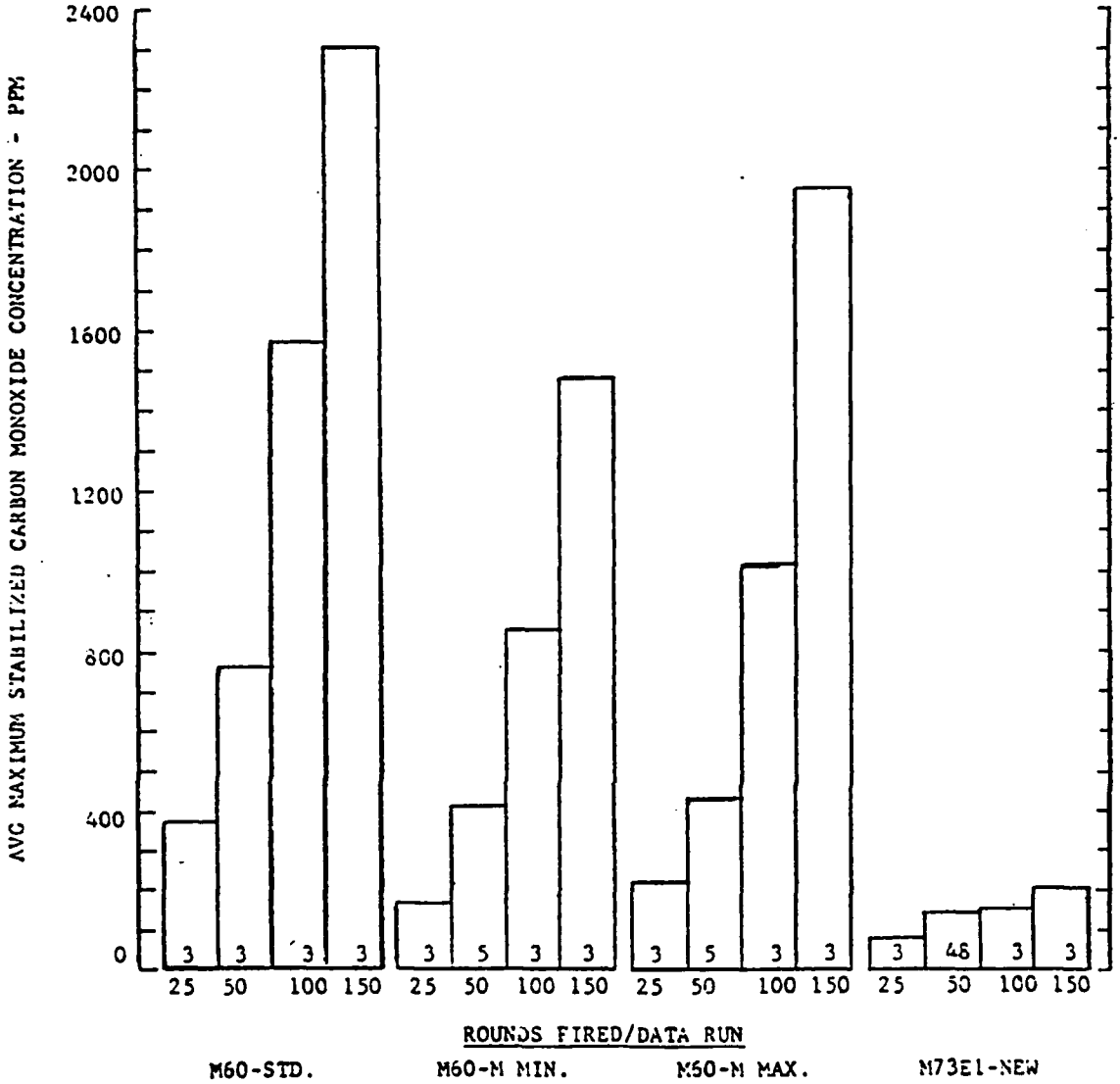

Figure A-2. Comparison of stabilized CO concentrations resulting from firing a continuous burst with optimum weapon sealing conditions.

Notes: 1. Numbers in bar graphs denote number of data runs averaged.
2. The M73E1 50-round burst data were obtained on the dates that the comparison weapons were fired.

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APPENDIX B: TABULAR DATA SUMMARIES

AD-A191 290 PROBLEM DEFINITION STUDY ON TECHNIQUES AND METHODOLOGIES FOR EVALUATING T..(U) OAK RIDGE NATIONAL LAB TN R H ROSS ET AL. MAR 88 ORNL-6334-VOL-1 4/4

UNCLASSIFIED F/G 21/2 NL

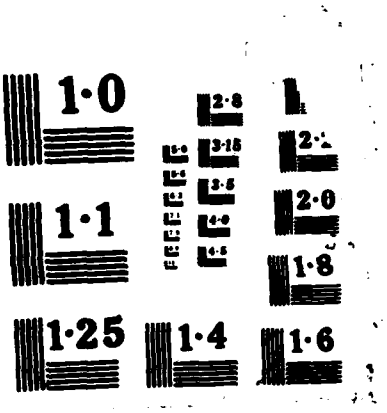
1·0
1·1
1·25
1·4
1·6
1·8
2·0
2·8
3·15
3·5
4·0
4·5

TABLE B-1. CHARACTERIZATION OF THE TOXICOLOGICAL TESTING OF DIESEL EMISSIONS

Species	Test type/endpoint	Protocol[a]	Reference
I. MUTAGENICITY AND CARCINOGENIC POTENCY OF DIESEL EXTRACTS			
Salmonella typhimurium	Mutagenicity	Strains TA98, TA100, TA1535, TA98-FRI; with and without S-9	Claxton 1980
Saccharomyces cerevesaie D3	Mitotic recombination	Tested with and without S-9	Mitchell et al. 1980
L5178Y mouse lymphoma cells	Mutagenicity	Tested with and without S-9	Mitchell et al. 1980
Chinese hamster ovary cells	Sister chromatid exchange/DNA damage	Tested with and without S-9	Mitchell et al. 1980
Mouse BALB/c 3T3 cells	Transformation and mutagenicity	With and without S-9	Curren et al. 1980
Mouse (SENCAR)	Skin tumor carcinogenicity test	Skin carcinogenic, co-carcinogenic, and and tumor initiating and promoting activities determined	Slaga et al. 1980
Hamster V79 cells	Mutagenicity	With and without S-9	Rudd 1980
Human lymphoblasts	Mutagenicity	With and without S-9	Liber et al. 1980
Normal human fibroblasts	DNA damage	-[b]	McCormick et al. 1980
Escherichia coli	DNA damage	Strains WP2 trp, WP2$_s$ trp uvrA, WP10 trp recA, and WP100 trp uvrA recA	Doudney et al. 1980

TABLE B-1. (Continued)

Species	Test type/endpoint	Protocol	Reference
	II. MUTAGENICITY TESTING OF WHOLE DIESEL EMISSIONS		
Drosophila melanogaster	Sex-linked recessive lethal assay	8 hr exposures	Schuler and Niemeier 1980
Mouse	Urinary mutagenicity assay using *Salmonella typhimurium*, micronuclei assay, and metaphase analysis	8 hr/day, 5 days/week for 1, 3, or 7 weeks	Pereria et al. 1980a
Hamster	Sperm morphology, micronucleus, sister chromatid exchange, and chromosomal abnormality bioassays	8 hr/day for 6 months	Pereria et al. 1980b
Mice	Sperm morphology	8 hr/day for 31 or 39 weeks	Pereria et al. 1980c
Dog	Micronuclei or sister chromatid exchanges in periperal lymphocytes	13-week continuous exposure	Benz and Beltz 1980
Tradescantia clone #4430	Micronucleus	0, 20, 40, 60, 80, or 100 min exposure	Ma et al. 1983

TABLE B-1. (Continued)

Species	Test type/endpoint	Protocol	Reference
III. BIOCHEMICAL AND METABOLIC EFFECTS TESTING OF DIESEL EMISSIONS[c]			
Rat	Lung biochemistry	20 hr/day, 5 1/2 days/week for 36 weeks; interim sacrifice	Misiorowski et al. 1980
Rat microsomal fractions	DNA binding	Particulate extracts	Pederson 1980
Rat, guinea pig	Pulmonary prostaglandin dehydrogenase	Animals exposed to various regimens	Chaudhari et al. 1980
Rat, guinea pig	Adenylate and guanylate cyclase activity of liver and lung	24 week exposures; interim sacrifice	Schneider and Felt 1980

TABLE B-1. (Continued)

Species	Test type/endpoint	Protocol	Reference
IV. NON-ONCOGENIC TOXICOLOGICAL TESTING OF INHALED DIESEL EMISSIONS			
Rat	Pulmonary function	20 hr/day, 5 1/2 days/week for 267 days	Gross 1980
Rat, guinea pig	Lung structural physiology and pulmonary function	2-week and 1-year studies	Barnhardt et al. 1980
Rat	Behavioral alterations	8 hr/day, 7 days/week for 16 weeks	Laurie et al. 1980
Rat	Neurophysiological alterations	8 hr/day, 7 days/week to neonatal animals	Laurie and Boyes 1980
Hamster	Pulmonary function	8 hr/day, 7 days/ week for 6 months	Pepelko et al. 1980a
Cat	Pulmonary function	8 hr/day, 7 days/ week for 1 year	Pepelko et al. 1980b
Mice	Pulmonary function and morphology	3-month exposure	O'Neil et al. 1980
Mice	Enhanced susceptibility to infection	8 hr/day for various durations	Campbell et al. 1980

TABLE B-1. (Continued)

Species	Test type/endpoint	Protocol	Reference
	V. ONCOGENIC EFFECTS TESTING OF DIESEL EMISSIONS		
Hamster	Intratracheal instillation	15-week instillation of diesel exhaust particles, particulate extracts, and condensates	Shefner et al. 1980
Hamster	Lifetime bioassay	7-8 hr/day, 5 days/week[d]	Heinrich et al. 1980
Mice (Strain "A")	Inhalation of exhaust or intraperitoneal injection (i.p.) of particulates	7 week exposure to exhaust, then placed in central chamber for 26 weeks or i.p. injections 3 x per week for 8 weeks then sacrificed at same time as inhalation group	Orthoefer et al. 1980
	VI. REPRODUCTIVE AND TERATOGENICITY TESTING OF DIESEL EMISSIONS		
Mouse	Multigeneration	-[b]	Pepelko 1980
Rat, rabbit	Teratology	Gestational exposure	Pepelko 1980

a. Original article should be consulted for further details.

b. Not provided in brief experimental description

c. If exposure was to particulate extracts, it will be so stated under protocol.

d. Protocol assumed from subchronic exposure protocols.

TABLE B-2. CHARACTERIZATION OF THE TOXICOLOGICAL TESTING OF TOBACCO SMOKE

Species	Test type/endpoint	Protocol[a]	Reference
I. GENOTOXICITY TESTING OF CIGARETTE SMOKE CONDENSATE (CSC)			
Allium cepa	Chromosomal aberrations	Aqueous emulsion that had been extracted with ether from root tip of *A. cepa*	Venema 1959
Rat	Chromosomal aberrations	In vivo exposure	Rees et al. 1973
Salmonella typhimurium	Mutagenicity	Strain TA 1538, with and without metabolic activation	Hutton and Hackne 1975
Salmonella typhimurium	Mutagenicity	Strain TA 98, with and without metabolic activation	Yoshida and Matsu 1980
Neurospora crassa	Mutagenicity	With and without metabolic activation	DeMarini 1981
Drosophila melanogaster	Sex-linked recessive lethal	Larval males fed CSC equivalent to 6/100ths of one cigarette per mL of food	Pescitelli 1979
Mouse lymphoma L5178Y/TK$^{+/-}$ cells	Mutagenicity	With metabolic activation	Clive et al. 1979
Chinese hamster ovary cells	Sister chromatid exchange	With and without metabolic activation	DeRaat 1979
Human lymphocytes	Sister chromatid exchange	With and without metabolic activation	Hopkin and Evans 1979
Human lymphocytes	DNA repair	Neutral fraction of CSC tested	Gaudin et al. 1972
Hamster tracheal epithelial cells	DNA repair	Tracheal epithelium in organ culture exposed to 1 or 10 μg/mL	Schiff et al. 1983
Hamster lung fibroblasts	Cell transformation	In vitro exposure for 3 hr	Inui and Takayama 1971

TABLE B-2. (Continued)

Species	Test type/endpoint	Protocol[a]	Reference
	II. GENOTOXICITY TESTING OF CIGARETTE SMOKE		
Hamster	Chromosomal aberrations	In vivo exposure, bone marrow cell examined	Korte et al. 1981
Human	Chromosomal aberrations	Chromosomes of smokers and nonsmokers examined	Nordenson et al. 1978
Saccharomyces cerevisiae	Mutagenicity	Exposure to fresh cigarette smoke	Gairola 1982
Drosophila melanogaster	Sex-linked recessive lethal	Male larvae exposed to 2-3 puffs/day for 7 days	Pescitelli 1979
Human	Sister chromatid exchange	Lymphocytes of smokers and nonsmokers examined	Hollander et al. 1978
Human	Sister chromatid exchange	Lymphocytes of smoking and nonsmoking pregnant women	Ardito et al. 1980
Human	Sister chromatid exchange	Urine from smokers and nonsmokers tested in Diploid (WI-38) cells	Guerrero et al. 1979
Hamster	Sister chromatid exchange	Exposure for 1 hr/day for 12 weeks	Korte et al. 1981
Human	Mutagenicity	Urine concentrates of smokers and non-smokers tested in Salmonella with and without activation	Yamasaki and Ames 1977
Dog	Mutagenicity	Urine concentrates tested in Salmonella with and without activation	Ramey et al. 1979
Mouse	DNA repair	DNA repair quantified in excised lung from chronically exposed animals	Rasmussen et al. 1981
Human	Sperm morphology	Sperm from smokers	Viczian 1969

TABLE B-2. (Continued)

Species	Test type/endpoint	Protocol[a]	Reference
III. ACUTE, SUBCHRONIC, AND CHRONIC TOXICOLOGICAL TESTING OF INHALED CIGARETTE SMOKE			
Rabbit	Effect on alveolar permeability	5, 10, 20 and 30 tidal volume breaths delivered with 20 minutes between each subset	Witten et al. 1985
Dog	Subchronic toxicity	Animals exposed to equivalent of smoke from 4 cigarettes daily for 9 months	Huy et al. 1975
Rat	Effect on metabolism and function of alveolar macrophages	Exposure for 6 months	Drath et al. 1979
Hamster	Oncogenicity	Exposure for 59-80 weeks	Bernfeld et al. 1979
Rat	Oncogenicity	Lifetime exposure, seven cigarettes per day	Dalbey et al. 1980
IV. DEVELOPMENTAL TOXICITY OF INHALED CIGARETTE SMOKE			
Mouse	Fetotoxicity	Inhalation exposure equivalent to 1-1/2 cigarettes per day on gestation days 6-17	Peterson et al. 1981
Mouse	Teratology	Exposure on day 10 of gestation	Goeringer and Fazel 1983
Human	Epidemiological study	Outcome of 5200 pregnancies examined in relation to cigarette smoking	Mau and Netter 1974

a. Original article should be consulted for further details.

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LIST OF ABBREVIATIONS

ALA	Aminolevulinic acid
ALAS	ALA synthetase
ASTM	American Society of Testing Materials
BZ	Personal breathing zone sample
CBI	Clean-burning igniter
CHO	Chinese hamster ovary
CI	Cascade impactor
CS	Cigarette smoke
CSC	Cigarette smoke condensate
CEB	Controlled expansion bullet
DF	Diesel fuel
DNPH	2,4-dinitrophenylhydrazine
ETS	Environmental tobacco smoke
FFAR	Folding fin aircraft rockets
FIA	Flame ionization analysis
FID	Flame ionization detector
FPD	Flame photometric detection
GC-FID	Gas chromotographic-flame ionization detection
HMX	Cyclotetramethylenetetranitramine
HPLC	High-performance liquid chromatography
IR	Infrared spectroscopy
ITC	Interagency Testing Committee
LC	Liquid chromatography
LDV	Laser Doppler velocimeter
LOVA	Low vulnerability ammunition
MBTH	3-methyl-2-benzothiazolone hydrazone
MLRS	Multiple launch rocket system
MS	Mainstream (smoke)
MSA	Mine safety appliance
MVE	Motor vehicle exhaust
NDIR	Nondispersive infrared (analyzer)
NIOSH	National Institute of Occupational Safety and Health
OPC	Optical particle counter
ORNL	Oak Ridge National Laboratory
PEL	Permissible exposure level
PETN	Pentaerythryte tetranitrate
RDX	Cyclotrimethylenetrinitramine
SCE	Sister chromatid exchange
SPART	Single-particle aerodynamic relaxation time
STEL	Short term exposure limit
TCD	Thermal conductivity detector
TEA	Thermal energy analyzer
TLV	Threshold limit value
TNT	2,4,6-trinitrotoluene
TPM	Total particulate matter
TSNA	Tobacco-specific nitrosamine
USAEHA	U.S. Army Environmental Hygiene Agency
USDHEW	U.S. Department of Health, Education and Welfare
USDOE	U.S. Department of Energy
USEPA	U.S. Environmental Protection Agency
VNA	Volatile nitrosamines
ZPP	Zinc protoporphyrin

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