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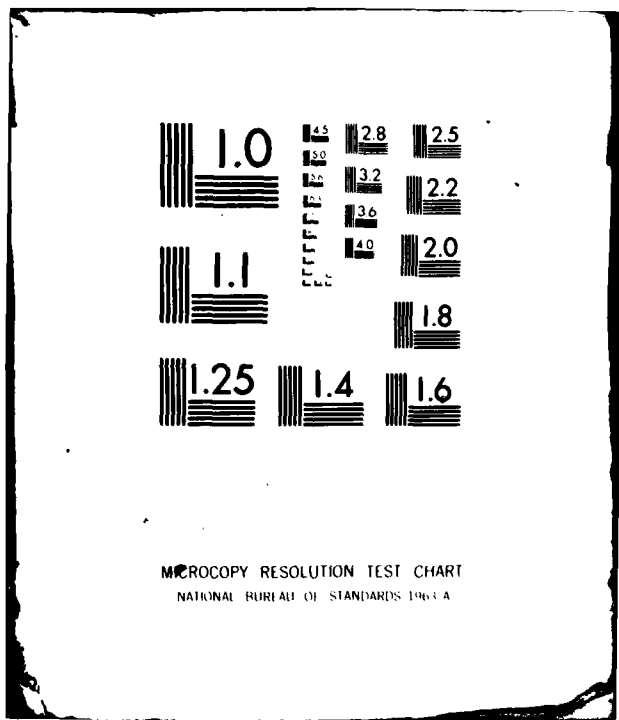
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COMPOSITIONAL, ATOMIC AND MOLECULAR ANALYSIS IN SUPPORT
OF MATERIALS NEEDS OF THE U.S. AIR FORCE

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May 1980

TECHNICAL REPORT AFWAL-TR-80-4064
Final Report for Period May 1977 through February 1980

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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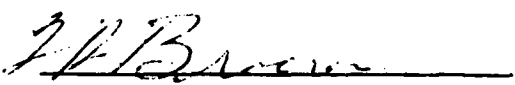
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This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


James H. Muntz
Project Engineer

FOR THE COMMANDER


Q.R. BROEREN, LCol, USAF, Chief
Materials Technical Services Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Work performed during the period May 1977-February 1980 in support of various Air Force programs is summarized. The work covers method development, support programs, service functions, materials characterization and development and application of analytical chemical techniques of various kinds. In addition, research in the areas of molecular structure determination and materials characterization was performed.		

20. Major areas of effort include inorganic analyses, micro-analysis, mass spectrometry and molecular spectroscopy. A brief discussion of the effort in each of these areas is given along with the number of samples analyzed by various techniques during the period of contract performances.

FOREWORD

This report was prepared by the Department of Chemistry, Miami University, Oxford, Ohio under Air Force Project No. 7360, "Chemical, Thermal and Dynamic Properties of Materials," Task No. 736005, "Compositional, Atomic and Molecular Analysis." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Contract #F33615-77-C-5058. Captain Duane Dinwiddie and Mr. James Muntz served as Project Engineers.

The work was performed at Miami University and at the Materials Laboratory, Wright-Patterson AFB during the period 12 May 1977 through 10 February 1980. The report was submitted by the author in March 1980.



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SECTION I
INTRODUCTION

This report was prepared by the Department of Chemistry, Miami University, Oxford, Ohio and is the final report of USAF Contract F33615-77-C-5058. It covers the period 12 May 1977 - 10 February 1980. The work was performed at Miami University and at the Materials Laboratory, Wright-Patterson Air Force Base, Ohio. The major participants were Messrs. J. R. Kerns, T. E. Kerschner, T. H. Stout, J. H. Ossege, Mrs. Anne Papania and Drs. Tung-Yang Yu, Chi K. Yu and J. E. Katon. Dr. J. E. Katon served as Project Leader. The contract involved method development, support programs, service functions, material characterization and development and application of analytical techniques of various kinds in support of Air Force programs. It also involved research in the areas of molecular structure determination and materials characterization.

The rapid development of aerospace science in the last thirty years has resulted in the synthesis and development of many new materials possessing unusual chemical and physical properties. This rapid development of new and exotic materials has required that a good deal of effort be expended in the development of new techniques to analyze and characterize them. Seldom are the classical methods applicable to these new compounds and therefore a good deal of research and method modification is necessary to develop new techniques. Once such techniques are developed, they must be applied to the analysis of such new experimental methods.

In addition to the analysis and characterization of experimental materials, the need often arises for accurate and expeditious analysis of samples arising from practical problems encountered by the Air Force in one of its many widespread areas of operation. This is most generally typified by accident investigations or equipment malfunctions.

Because of the sometimes rapidly changing requirements of the Air Force, the effort on the contract has varied at times with regard to the particular areas of emphasis. For instance, there was a large need in the area of inorganic analyses in the early part of the effort which had been greatly reduced by the later part of the contract period. The effort in infrared spectroscopy has been variable over the three-year period and was high at the end of the period although there was a time period of about six months in which little effort was expended in this area. The areas of micro-chemistry and chemical ionization mass spectrometry involved

a continuous, nearly constant level of effort over the period of the contract.

A significant amount of the service work has been subcontracted to other organizations during the performance of this work. This involves primarily specialized service and support functions which can be provided by organizations which have particular capabilities in the required fields. The rate of subcontracted effort decreased drastically as the contract effort progressed, however, due to the development of in-house capabilities to perform these specialized functions when there existed a continuing need. In-house performance of these functions is desirable since it results in a large time-saving, in general.

The succeeding sections of this report summarize the effort expended and the results obtained in the various areas during the performance of contract F33615-77-C-5058.

SECTION II

INORGANIC ANALYSES

During the time period of the contract there occurred a large reduction in the demand for inorganic analyses. This reduction occurred after about two years. As a result, the final year of the contract involved mostly routine determinations of various kinds and very little method development.

During the first two years of the contract a rather large amount of effort was expended in developing methods and putting new equipment into operation so that analyses that were formerly subcontracted could be performed in-house. There were three basic areas in which this work was performed. (1) The Leco induction furnace was modified and repaired and new accessories purchased so that metal samples could be analyzed for sulfur and phosphorus. At the beginning of the contract only carbon analyses could be performed on metals (especially steels), and the development of these two analyses resulted in reduction of 2-3 weeks in turnaround time per analysis on the various samples submitted. (2) A flameless atomic absorption spectrometer was purchased (IL 152) because of the development of various analytical procedures of great value to the Air Force requiring such an instrument. This has resulted in the capability of performing analyses that were previously impossible or a significant increase in the accuracy obtainable for certain analyses. (3) A polarographic analyzer was purchased and put into operation for the determination of various metals in liquid phases.

In the areas of method development, new methods were developed for various analyses. These consist of: (1) tellurium (both as the metal and as organotellurium compounds) in film samples; (2) a flameless atomic absorption method for lead in oil samples; (3) a new method for the determination of phosphorus in steels; (4) a method for trace levels of copper and cadmium in aircraft fuels; (5) equipment was designed and constructed and a method for catalytic micro-hydrogenation developed; and (6) various specialized methods for the analysis of particular samples which were received.

The number of analyses of various kinds performed in a primarily routine nature (sometimes after method development) are given below.

Carbon Determinations	218
Samples for Semi-quantitative Emission Spectrometric Analysis	83

Samples for Quantitative Emission Spectrometric Analysis	8
Samples for Flame Atomic Absorption Analysis	41
Samples for Flameless Atomic Absorption Analysis	110
Sulfur Determinations	28
Phosphorus Determinations	10
Alkali Metals Determinations in Graphite Fibers	6
Miscellaneous Gravimetric Analysis	11
Microscopic Analysis	<u>21</u>
Total	536

SECTION III
MICROANALYSIS

A relatively large effort in microanalysis was required throughout the contract period on a continuing basis. The largest number of samples received for analysis were those requiring microanalytical procedures of some type.

Within the area of microanalysis, carbon and hydrogen determinations are by far the most requested single analysis. These are normally performed on the Perkin-Elmer Model 240 C,H,N analyzer. This instrument is now rather old and is obsolete in the sense that newer models require considerably less operator time per analysis. During the period of the contract rather severe downtime problems were encountered from time to time. Each of these was corrected, but such behavior is expected to continue and perhaps increase due to the age of the instrument. During instrument downtime periods the C, H analyses must be run by the Pregl method. This is considerably more time consuming. In addition this method is not suitable for nitrogen determination.

Included in the microanalysis area are many other quantitative determinations of other elements present in samples as well as certain physical properties. Also included are molecular weight determinations by vapor pressure osmometry and determination of unsaturation by hydrogenation.

Occasionally, microanalyses are subcontracted. These are usually because the sample submitter requests that the work be done by a particular laboratory since they are particularly qualified or because of particular time constraints with individual samples.

The number of microanalyses of various kinds performed during this contract are summarized below.

Type of Analysis	Determinations	
	In-house	Subcontracted
1. Carbon and Hydrogen	602	43
2. Nitrogen	250	10
3. Chlorine	71	15
4. Bromine	122	1
5. Iodine	11	5

6. Oxygen	2	6
7. Sulfur	58	43
8. Silicon	52	27
9. Phosphorus	24	0
10. Ash	26	1
11. Melting Point	10	0
12. Molecular Weight	35	24
13. Microhydrogenation	3	6
14. pH	19	0
15. Iron	8	0
16. Fluorine	3	4
17. Density	<u>17</u>	<u>0</u>
Totals	1313	185

SECTION IV

MASS SPECTROMETRY

The mass spectrometer which has been used in this work is a DuPont 21-490 Chemical Ionization Mass Spectrometer. The instrument is a prototype model which has been modified several times and is now getting rather old. As a result, a good bit of down time is experienced with the instrument and successful operation can only be accomplished by a trained mass spectrometrists. On the preceding contract a Hewlett-Packard 5700A Gas Chromatograph utilizing a packed column was interfaced with this instrument so that gas chromatograph-chemical ionization mass spectra could be obtained (GC/CIMS).

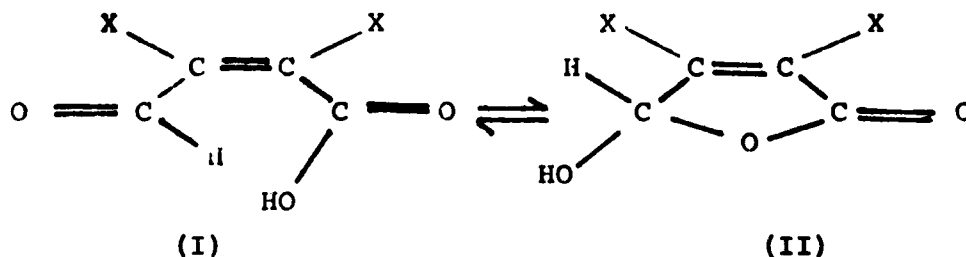
The work on this contract can be divided into four different areas: (1) instrument modification and improvement, (2) development of new methods, (3) molecular structure studies, and (4) service analytical work. Effort in each of these areas will be summarized.

In the area of instrument modification and improvement, the GC/MS interface has been completed for the situation in which glass capillary columns are used in the GC. The resolution is much better than when using packed columns. The GC is directly coupled to the MS and a separator is unnecessary. A computer has been interfaced with the mass spectrometer and necessary software created such that the computer can control the scan of the MS, read and process the data, write the data on a disk and repeat the process. After the completion of the run the computer will print out all mass spectra on a teletype. In addition, the computer can monitor mass numbers while at the same time adjusting ion accelerating voltages through the digital to analog converter. In this way the mass spectrometer can be "locked" to a particular mass number while concurrently reading the pulse counter. This results in about a 10-fold increase in sensitivity and quantitative accuracy. Finally, the computer can be used with the GC system as well. A program has been written and put into operation which will result in a printout of retention time, peak area and their ratio for each peak in the chromatogram. In addition, the instrument has been modified with regard to the ion accelerating voltage. If one is to determine molecular weights over 1000, one must operate the instrument in the 1-2000 mass range. Originally mass spectra obtained under these conditions suffered poor resolution and sensitivity because the ion accelerating voltage was limited to 700V. This has been corrected such that the ion accelerating voltage is now adjustable from 700V to 1400V and the mass range continuously increased from 1000 to 2000. Performance of the instrument in this higher mass

range is greatly improved by this modification and compounds with molecular weight over 1000 can now be determined rapidly.

With regard to method development, one of the problems generally encountered is difficulty in obtaining good mass spectra from materials which are normally solids, or have very low vapor pressures. Mixtures of such materials cannot be readily separated using GC and, although liquid chromatography is many times successful in separation, there is great difficulty in transferring the samples to the mass spectrometer in such a way that a mass spectrum can be easily obtained. As a result, a good bit of effort was expended in developing methods utilizing thin-layer chromatography (TLC) in conjunction with mass spectrometry for analysis of mixtures of solids. The pure solid can then be introduced directly into the mass spectrometer through the heated probe or introduced directly into the source. Although the latter method is not generally used, it has been found that mass spectra can often be obtained, although they are often weak, for samples which do not give any signal when introduced through the probe because of low volatility. There are problems associated with the TLC/MS procedure, however. The major problems encountered are: (1) only a small amount of sample can be separated; sometimes not enough material is obtained to yield a good mass spectrum; (2) TLC does not always give a complete separation of all compounds, leading to difficultly interpretable mass spectra of mixtures; (3) at high probe temperatures the binder in the TLC substrate gives a high background; and (4) certain compounds decompose during the development of the TLC. Programmed multiple development of the TLC is useful for problem (2) and is sometimes helpful for problems (1) and (3).

The only molecular structure study carried out during this period was the investigation of the mass spectra of mucochloric and mucobromic acid. Until recently, the structures of mucochloric and mucobromic acids had not been unambiguously determined. Previously the mucohalic acids had been reported to exist in two tautomeric configurations. The tautomeric isomers predicted are the 2,3-dihalo-4-oxo-2-butenoic acid (I) and 2,3-dihalo-4-hydroxybut-2-enelactone (II). A vibrational spectral study of mucochloric and mucobromic acids indicated that they exist as the hydroxylactone structure in both solid and liquid phases.



In order to investigate the gas phase ion chemistry, the chemical ionization and electron impact mass spectra of mucochloric and mucobromic acids were examined utilizing the DuPont 21-490 Mass Spectrometer. In addition to these compounds, the mass spectra of several structurally similar molecules were recorded for comparison. The structurally related molecules are: crotonaldehyde; crotonic acid; cis-3-chlorocrotonic acid; 2,3-dichloroacrylic acid; 4-butyrolactone; 2,3-dichloromaleic anhydride; and 2,3-dibromomaleic acid. The chemical ionization spectra, obtained using methane, isobutane and helium as reagent gases, were compared with electron impact spectra of each compound recorded at various primary electron beam energies.

The fragmentation patterns of the structurally related compounds were compared with those of mucochloric and mucobromic acid. The results of this comparison are consistent with the hydroxylactone structure previously reported for these acids, but inconsistent with the open chain structure.

Data on an ion with $m/e = 39$ ($C_3H_3^+$) have been obtained from the spectra of cis-3-chlorocrotonic acid, crotonic acid and crotonaldehyde. The relative abundance of this ion suggests the probability that it has an aromatic cyclic structure in agreement with that previously postulated.

The samples analyzed on a service basis over the period of this contract are listed below.

GC/MS	-	380
MS only	-	382
GC only	-	11
LC/MS	-	<u>2</u>
Total		775

SECTION V

MOLECULAR SPECTROSCOPY

The effort in the area of molecular spectroscopy is almost exclusively limited to infrared and Raman spectroscopy. Occasionally there is a demand for ultraviolet-visible spectroscopy or nuclear magnetic resonance spectroscopy. These latter two areas are very small, however. The infrared and Raman spectroscopy effort is divided into two main areas - service, and research and method development. The service work is further divided into that performed at W-PAFB and that performed at Miami University. All routine infrared work in the 4000-400 cm^{-1} region is performed at W-PAFB. However, the Air Force does not possess the required instrumentation for either Raman spectrometry or unusual types of infrared spectroscopy. As a result, all of the latter two areas is covered at Miami University. In the area of unusual infrared spectroscopy requirements the most widely demanded data is far infrared data and low temperature infrared data.

The total number of service samples analyzed during the contract period was 854 at W-PAFB and 19 samples (infrared) and 15 samples (Raman) at Miami University. It should be noted that many of these samples require the recording of several spectra for complete analysis. In general, the number of actual spectral observations is about twice the number of samples for those analyzed at W-PAFB. Since the samples received at Miami are normally unusual and difficult, normally each sample requires about five spectra recorded to obtain clear and definitive results.

The research and method development in the areas of vibrational spectroscopy carried out during the period of the contract falls into four main areas: (1) the use of vibrational spectroscopy to elucidate the detailed molecular structures of several series of compounds; (2) the use of polarized infrared spectroscopy to characterize the crystal structure of several compounds; (3) the investigation of possible correlations between a wide variety of spectroscopic data and the pK_a 's and Taft sigma constants of a series of substituted acetic acids; and (4) modification of the sampling configuration of the Cary Model 81 Raman spectrometer in an effort to improve its performance and flexibility. The results of each of these areas of studies will be summarized in turn.

The mucohalic acids are a group of organic compounds whose structures and dynamical properties had been investigated superficially by a number of workers. The

results were conflicting and no detailed information concerning the physicochemical properties of these molecules was available, despite their reported usefulness as fungicides, herbicides and insecticides. A detailed study of the structures of some of the simpler members of the class was therefore undertaken. The results of a mass spectrometric study has been summarized earlier (Section IV). The infrared spectra of mucochloric acid (2,3-dichloro-4-oxo-2-butenoic acid), mucochloric acid-d₁, and mucobromic acid were recorded in the solid and liquid phases in the 4000-50 cm⁻¹ region. The solid phase Raman spectra of the mucochloric and mucobromic acids was also recorded. In addition, partial spectra of a number of model compounds were also recorded for comparison purposes. Analysis of the complete spectral data indicates that the compounds exist in the solid and liquid phases as the hydroxylactones (2,3-halo-4-hydroxybut-2-enelactone) rather than the chain configurations indicated by the names. These results have been confirmed by a study of the C¹³ nuclear magnetic resonance spectra of these compounds. However, the H¹ NMR spectra of the compounds in a solution of acetone-d₆ show that in dilute solution, both tautomers of the compounds exist, although in concentrated solution only the hydroxylactone structure is detectable.

One of the interesting classes of organic compounds from the point of view of studying conjugation effects is the α -dicarbonyl class. Certain examples of this class have had their structures elucidated by x-ray diffraction and shown to possess the trans carbonyl structure. Conformational isomerism in the fluid phases has been proposed and the vibrational spectra of some of these compounds has been studied. In an attempt to learn more about the structures, conformations and vibrational coupling, or conjugation effects, of this class, a number of representatives have been chosen and their vibrational spectra studied in detail. As representatives of the oxalate series, dimethyl oxalate, oxanilide, oxamic acid, sodium oxamate, oxalyl hydrazide and semioxamazine were chosen. As representatives of the pyruvate series, pyruvic acid, pyruvoyl chloride and sodium pyruvate were chosen. The studies in the pyruvate series are not as yet complete, although significant progress has been made. Conformational equilibria have been characterized in both dimethyl oxalate and pyruvoyl chloride. The more stable structures of all of the molecules are the trans carbonyl structure and there appears to be little, or no, coupling between the carbonyl groups.

The determination of crystal structures utilizing polarized infrared spectra and oriented polycrystalline films has been discussed in the final report of the previous contract (which is listed in Section VIII). Previous work was

concentrated on hydrogen bond structures of organic acids. One such study was also completed during this contract. The polarized infrared spectra of one polymorph of bromoacetic acid was studied. The results indicate a hydrogen bond polymer structure. This is in contrast to the other two polymorphs of bromoacetic acid, both of which have been reported to have hydrogen bond dimer structures.

The crystal structure of p-chloroaniline has been reported by three different groups of workers by x-ray diffraction. Although these workers agreed on the crystal space group, they disagreed on the molecular structure in the crystal. Our studies with polarized infrared show that the molecule is nonplanar in the crystal, in agreement with one of the x-ray studies.

A study was made of the polarized infrared spectra of crystalline dimethyl oxalate. Up until this time our studies had been limited to orthorhombic crystals. Dimethyl oxalate forms a monoclinic crystal and it was desirable to test our procedures and techniques on such a crystal to determine their generality. The results obtained are quite consistent with x-ray data and so the method appears to be general with other crystal systems. As always, further information is gained with regard to vibrational assignments of molecules in crystals.

Finally, a short study was made on crystals of methyl formate. It was discovered that methyl formate crystallizes in two different polymorphic forms. The crystal structures were not elucidated, but the two forms have distinctly different spectroscopic properties.

A good deal of effort has been expended in the past in an attempt to derive correlations between the chemical and spectroscopic properties of various organic compounds. The availability of a number of substituted acetic acids has led to the investigation of possible correlations between a wide range of spectroscopic properties of these molecules and two properties related to their chemical nature, their pKa values and their Taft sigma constants. Various spectroscopic data from the infrared, near infrared, ultraviolet, Raman and nuclear magnetic resonance spectra were collected for acetic acid and seven monosubstituted acetic acids and were plotted against pKa and Taft sigma constants and correlation coefficients calculated. Correlation coefficients ranging from |0.066| to |0.984| were obtained. The frequency values of the ν_{CH_2} combination modes in the near infrared (approximately 8370 and 8550 cm^{-1}) had excellent correlation coefficients with both pKa and Taft sigma values (>0.98). Ultraviolet spectral absorption frequencies in aqueous solution also had

good correlation frequencies with the two parameters and other spectral data gave correlations ranging from fair to poor.

The instrument with which we obtain Raman spectra is a Cary Model 81 Raman Spectrometer modified for laser excitation. This is a rather old instrument and one of its greatest drawbacks is a very small sample compartment which does not allow for very much flexibility. In addition, the optical path followed by the Raman radiation is rather long and complex before it reaches the monochromator slits. This latter fact is due to the fact that the instrument was originally designed for Toronto arc excitation. Some years ago, Dr. Ira Levin of the National Institutes of Health modified his Cary 81 to circumvent these difficulties and produce a more sensitive and flexible system. We have essentially followed the same path and developed a similar system. This requires the construction of a suitable optical bench behind the instrument. The bench has an open sampling area and suitable focussing lenses, reflecting mirrors, etc. such that the Raman radiation is introduced through an entrance cut in the back of the instrument and then reflected by a corner mirror directly onto the monochromator entrance slits. At present, the system operates with about a five-fold increase in sensitivity and greatly increased flexibility. Further minor improvements could probably be made in the quality of the optical components, but the next step to significantly increased sensitivity is the replacement of the old photomultiplier tube detection system with a new photon counting detection system.

SECTION VI
GENERAL ANALYTICAL SUPPORT

During the initial phases of this contract nearly all of the analyses required were of some specific type. The more general problems were, at that time, handled primarily by Air Force personnel. Because of personnel and responsibility changes within the Air Force organization, however, there has been a large increase in the number of requests involving analytical problem solving. This has caused the devotion of about one-man year level of effort in this area over the last twelve months of the contract period. The problems encountered are extremely varied but usually involve some malfunction of Air Force equipment or failure of such equipment to meet specifications. Such practical problems involve a good deal of chemical expertise and detective work and may well involve several different analytical chemical or physical testing procedures. Often some separation technique must be applied prior to the actual analytical methods.

A particularly large amount of effort has been expended in the area of high performance liquid chromatography (HPLC). In some cases the separation characteristics themselves are sufficient to give the answer desired, but often fractions must be collected and then subjected to other analytical methods such as infrared spectroscopy or mass spectrometry. Over the last 12-16 months of the contract we have averaged about 10-15 samples per month which required the use of HPLC, either as a characterization method, or as a preliminary separation method to be followed by identification of components by other methods. Typical types of samples received are: used and new compressor oils, general lubricant samples, adhesives, glycol-water coolants, dyes, coatings, fabrics and fabric coatings, polyols used to prepare polyurethane helmet liners, etc.

A significant amount of effort was also expended in the area of x-ray diffraction analyses of powders. This method is often very useful for the identification of precipitates and corrosion products of various kinds from a wide variety of sources. We normally receive 5-10 samples per month which require x-ray diffraction studies. Early in the effort a computer program was developed which allowed automatic calculations, comparisons with file data and proper formatting of data for x-ray diffraction studies. This program is now routinely used.

Various other methods and techniques have been developed as demanded. Expertise has been developed to

identify various materials by microscopic examination. Identification of fiber samples and the differentiation of asbestos and "Rock Wool" are examples of areas where this procedure has been successfully applied. A polarographic method for the determination of copper in JP-4, a sensitive micro method for the quantitative estimation of mercaptans, a titrimetric microanalysis of iron and several other methods have been developed for the analysis of particular samples for which a need has arisen.

In addition, there is a requirement of about 1/5 man-year effort for consultation with various Air Force personnel on other projects, particularly various SPO's. This type of service has been in particularly high demand over the past 12 months.

Certain very specialized types of analyses are occasionally subcontracted in this area. Examples are spark source mass spectrometry, GC/MS studies of high molecular weight compounds using electron impact mass spectrometry, magnetic studies of magnet materials, neutron activation analyses, and F¹⁹ nuclear magnetic resonance spectra.

Many of the samples received are practical samples which require the use of several methods of analysis and the fitting together of the results to solve given problems. Such problems require not only the actual obtaining of the data, but detailed interpretation of the data by knowledgeable chemists in conjunction with the sample submitters. These projects became group projects in which there is a great deal of interaction between various contractor and Air Force personnel.

SECTION VII

SUBCONTRACTED ANALYSES

A number of analyses are routinely subcontracted to various laboratories. This arises because (1) these laboratories are particularly skilled in the analysis; (2) they have specialized expensive equipment necessary for the analysis; (3) the number of analyses of this kind do not justify setting up in-house procedures; or (4) the in-house equipment is undergoing maintenance or repairs and it is important that results be obtained quickly. A summary of the analyses subcontracted during this contract is given below. This does not include microchemical analyses subcontracted (see Section III).

I. Nonmetallic Elemental Analyses

Sample Type	C	H	O	N	Si	P	S
1. Titanium	64	90	100	61	1	-	-
2. Steel	2	5	-	5	-	6	5
3. Silicon Carbide	1	-	-	-	1	-	-
4. Titanium Carbide	2	-	-	-	-	-	-
5. Aluminum	4	11	25	-	10	-	-
6. Alloys	2	9	2	-	3	-	4
7. Silicon	-	-	1	-	-	-	-
8. Copper	-	2	6	-	-	-	-
9. Miscellaneous	-	-	-	1	-	-	5
TOTALS	75	117	134	67	15	6	14

Total Nonmetallic Elemental Analyses - 428

II. Metallic Elemental Analyses and Chemical Analyses of Metal Samples

Sample Type	Analysis Type	
	Metals	Chem. Anal.
1. Alloys	31	-
2. Aluminum	-	6
3. Inorganic Compounds	-	2

	Metals	Chem. Anal.
4. Water	21	-
5. Glass	<u>-</u>	<u>1</u>
TOTALS	52	9

Total Metallic Elemental Analyses and Chemical Analyses of Metal Samples - 61

III. Anion Analyses

Sample Type	Anion					
	Sulfate	Chloride	Nitrate	Nitrite	Phosphate	Misc.
1. Water	3	8	8	-	-	-
2. Residues	1	-	-	-	-	-
3. Liquids	<u>-</u>	<u>-</u>	<u>1</u>	<u>1</u>	<u>1</u>	<u>3</u>
TOTALS	4	8	9	1	1	3

Total Anion Analyses - 26

IV. Miscellaneous Analyses

1. X-ray diffraction - 5
2. Karl Fischer titrations - 5 silanol, 11 water - Total 16
3. Water analyses - 8 hardness, 3 alkalinity, 3 residual chlorine, 5 conductivity - Total 19
4. Cesium oxide - 5
5. Organic Samples - 6 hydroxyl number, 19 mass spectrometric analyses, 13 gas chromatograph - mass spectrometric analyses - Total 38

Total Miscellaneous Analyses - 83

Total Subcontracted Analyses - 598

BIBLIOGRAPHY

During the time period covered by this report, the following papers, articles and reports based in whole, or in part, on work performed under this contract were published. In most cases, a significant portion of the work was also supported by Miami University. The coauthors of the various publications were/are students at Miami University, according to the following.

- P. F. Krause, Postdoctoral Research Associate, 1973-5
R. W. Mason, B.S., Miami University, 1973
S. -L. Lin, M.S., Miami University, 1976
R. D. Moore, Ph.D., Miami University, 1978
N. L. Ranieri, B.S., Miami University, 1973
G.N.R. Tripathi, Postdoctoral Research Associate, 1977-8
W. J. Ray, Ph.D., Miami University, 1980
D. T. Covington, M.S., Miami University, 1979
K. K. Smith, B.S., Miami University, 1975
J. M. Rogers, B. S., Miami University, 1974
1. J. E. Katon, P. F. Krause, K. K. Smith and J. M. Rogers, "Polarized Infrared Spectral Studies of Crystalline, Hydrogen-Bonded Organic Acids," Tech. Rept. AFML-TR-77-89, May 1977.
 2. P. F. Krause, J. E. Katon and R. W. Mason, "The Polarized Infrared Spectra and Crystal Structure of Bromoacetic Acid," Paper MH8, Thirty-second Symposium on Molecular Spectroscopy, Columbus, Ohio, June 1977.
 3. P. F. Krause, J. E. Katon and R. W. Mason, "Polarized Infrared Spectra and Crystal Structure of Bromoacetic Acid," 33rd Southwest Regional Meeting, American Chemical Society, Little Rock, Arkansas, September 1977.
 4. J. E. Katon, "Crystal Structure Information from Infrared Spectroscopic Data," Seminar, Indiana University - Purdue University at Indianapolis, Indianapolis, Indiana, October 1977.
 5. J. E. Katon, "Spectroscopic Studies of Hydrogen Bond Structures of Crystalline Carboxylic Acids," Invited Paper, No. 54, IVth Annual Meeting, Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, Michigan, November 1977.
 6. R. D. Moore and J. E. Katon, "The Vibrational Spectra and

- Structure of Mucochloric and Mucobromic Acids," Appl. Spectrosc. 32, 145 (1978).
7. P. F. Krause, J. E. Katon and R. W. Mason, "The Polarized Infrared Spectra and Structure of Crystalline Bromoacetic Acid," J. Phys. Chem. 82, 690 (1978).
 8. R. D. Moore, J. E. Katon and T. Y. Yu, "Comparative Chemical Ionization and Electron Impact Mass Spectrometric Studies of Mucohalic Acids and Related Molecules," Paper 599, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1978.
 9. J. E. Katon and Nancy Ranieri, "The Infrared Spectrum of Crystalline Methyl Formate," Spectrosc. Lett. 11, 367 (1978).
 10. G.N.R. Tripathi and J. E. Katon, "The Vibrational Spectra of Crystalline Oxamic Acid and Sodium Oxamate," Paper FD7, Thirty-third Symposium on Molecular Spectroscopy, Columbus, Ohio, June 1978.
 11. J. E. Katon and S. L. Lin, "The Vibrational Spectra and Conformational Properties of Liquid Dimethyl Oxalate," J. Mol. Struct. 48, 335 (1978).
 12. J. E. Katon, "The Vibrational Spectra and Conformational Behavior of Molecules of the Oxalate Series," 14th Midwest Regional Meeting, American Chemical Society, Fayetteville, Arkansas, October 1978.
 13. J. E. Katon, "Crystal Structure Information from Infrared Spectroscopic Data," Seminar, University of New Mexico, Albuquerque, New Mexico, October 1978.
 14. J. E. Katon, G.N.R. Tripathi and S. L. Lin, "The Vibrational Spectra of Oxalic Acid and Several of Its Derivatives," Vth Annual Meeting, Federation of Analytical Chemistry and Spectroscopy Societies, Boston, Massachusetts, November 1978.
 15. J. E. Katon, "Polarized Infrared Spectra of Organic Crystals," Seminar, Old Dominion University, Norfolk, Virginia, December 1978.
 16. G.N.R. Tripathi and J. E. Katon, "The Vibrational Spectra and Structure of Crystalline Oxanilide," Appl. Spectrosc. 33, 32 (1979).

17. J. E. Katon, "Polarized Infrared Spectra of Organic Crystals," Cincinnati Section, American Chemical Society, Cincinnati, Ohio, February 1979.
18. G.N.R. Tripathi and J. E. Katon, "The Infrared Spectrum of Crystalline p-chloroaniline at Low Temperatures," J. Chem. Phys. 70 1383 (1979).
19. G.N.R. Tripathi and J. E. Katon, "Vibrational Spectra and Structure of Crystalline Oxamic Acid and Sodium Oxamate," Spectrochim. Acta 35A, 401 (1979).
20. W. J. Ray, J. E. Katon and P. F. Krause, "Spectroscopic Investigations of Monosubstituted Acetic Acids," Paper 541, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1979.
21. G.N.R. Tripathi and J. E. Katon, "The Vibrational Spectra and Structure of Crystalline Oxalyl Hydrazide and Semi-oxamide," J. Mol. Struct. 54, 19 (1979).
22. W. J. Ray, J. E. Katon and P. F. Krause, "Spectroscopic Investigations of Monosubstituted Acetic Acids," Appl. Spectrosc. 33, 492 (1979).
23. J. E. Katon and W. J. Ray, "Conformational Isomerism in α -Dicarbonyl Compounds - Temperature Dependent Infrared Spectral Investigation of Pyruvoyl Chloride," J. Mol. Struct. 57, 309 (1979).
24. G.N.R. Tripathi and J. E. Katon, "The Polarized Infrared Spectrum of Crystalline Dimethyl Oxalate," Chem. Phys. 45, 141 (1980).
25. J. E. Katon and Donna T. Covington, "The Vibrational Spectra of Crystalline Sodium Pyruvate," Spectrosc. Lett. 12, 761 (1979).
26. J. E. Katon, W. J. Ray and D. T. Covington, "Vibrational Spectra and Conformational Properties of Pyruvoyl Chloride," Paper 383, Vith Annual Meeting, Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, Pennsylvania, September 1979.