HIGH-PRESSURE SAMPLING CONFERENCE REPORT

TECHNICAL REPORT
23 July 1965

Contract No. Nonr-3599(00)
ARPA Order No. 23-63, Amendment No. 38
Program Code No. 4910

MRI Project No. 2551-P

For

Director
Advanced Research Projects Agency
Washington, D.C.

MIDWEST RESEARCH INSTITUTE
425 VOLKER BOULEVARD/KANSAS CITY, MISSOURI 64110/AC 816 LO 1-0202

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by

Thomas A. Milne

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PREFACE

The following report on the high-pressure sampling conference held May 6 and 7 at Midwest Research Institute constitutes a special technical report prepared for the Advanced Research Projects Agency, under ONR Contract No. Nonr-3599(00), monitored by Mr. Roland Jackel and Dr. Ralph Roberts of the Power Branch, ONR. The report lists the program, attendees and abstracts of talks for this meeting. No publication of the proceedings will be made.

Approved for:

MIDWEST RESEARCH INSTITUTE

Sheldon L. Levy, Director
Mathematics and Physics Division

30 July 1965

HIGH-PRESSURE SAMPLING CONFERENCE

Jointly Sponsored

by

MIDWEST RESEARCH INSTITUTE
and
OFFICE OF NAVAL RESEARCH

May 6-7, 1965

Kansas City, Missouri, U.S.A.

MIDWEST RESEARCH INSTITUTE MRI

425 VOLKER BOULEVARD / KANSAS CITY, MISSOURI 64110 / AC 816 LO 1-0202

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HIGH-PRESSURE SAMPLING CONFERENCE

held May 6-7, 1965, at

Midwest Research Institute

This meeting, under the joint sponsorship of the Office of Naval Research through project SQUID and Midwest Research Institute, was held to bring together a small group with a variety of interests and experience bearing on the problems encountered in the direct sampling of systems at high pressures.

The purpose of this brief report is to list the program and attendees at this informal meeting. No publications of the proceedings of the meeting will be made. However, abstracts of the talks are included to indicate the range of topics covered. The list of attendees serves as a source of detailed information on particular aspects of sampling and related phenomena.

It is a pleasure to acknowledge the support of Dr. Sheldon L. Levy of MRI and Dr. Ralph Roberts of the Power Branch of ONR in the initiation and planning of this meeting. Dr. John Scott was very helpful in planning the scope, program, and arrangements of the meeting as were Mr. Gordon Gross and Dr. Frank Greene.

Thomas A. Milne

LIST OF ATTENDEES

Name	Organization
R. Andres	Princeton
J. Beachey	MRI
J. Brewer	MRI
H. Calcote	AeroChem
W. Chupka	Argonne National Laboratory
L. Daasch	Edgewood Arsenal
J. Deckers	University of Toronto
R. Diesen	Dow Chemical
P. Dimiduk	Air Force Materials Laboratory, WPAFB
J. Dove	University of Toronto
J. Fenn	Princeton
R. Fristrom	Applied Physics Laboratory
P. Ghosh	Rice University
F. Greene	MRI
G. Gross	MRI
K. Homann	Göttingen University
R. Jackel	Power Branch, ONR
P. Knewstubb	Cambridge University
E. Knuth	UCLA
S. Levy	MRI
G. Markstein	Cornell Aeronautical Laboratory
T. Miller	Georgia Institute of Technology
W. Miller	AeroChem
T. Milne	MRI
H. Morton, Jr.	University of Virginia
C. Nutt	Birmingham University
G. O'Halloran	Bendix
J. Scott, Jr.	University of Virginia
F. Sherman	Berkeley
N. Spokes	SRI
R. Stearman	MRI
G. Stein	Yale
H. Wagner	Göttingen University
A. Westenberg	Applied Physics Laboratory
W. Wilson	Applied Physics Laboratory

PROGRAM

THURSDAY MORNING, May 6, 1965

8:30 - Registration

9:00 - Introductory Remarks and Welcome - S. Levy

9:15 - Fluid Mechanics in Sampling - Chairman, E. Knuth

F.S. Sherman - University of California at Berkeley
J. Fenn - Princeton University

Coffee Break

J.E. Scott, Jr. - University of Virginia
J.M. Deckers - University of Toronto

THURSDAY AFTERNOON, May 6, 1965

2:00 - Special Effects in Sampling and Detection - Chairman, W.Wilson

C.W. Nutt - Birmingham University
R. Fristrom - Applied Physics Laboratory

Coffee Break

A.A. Westenberg - Applied Physics Laboratory
W. Chupka - Argonne National Laboratory

FRIDAY MORNING, May 7, 1965

9:00 - Sampling of Neutral Species - Chairman, J. Dove

R. Diesen - Dow Chemical Company
F. Greene - Midwest Research Institute

Coffee Break

H. Homann - University of Göttingen

11:30 - Free Time - Visits to Linda Hall Library, Midwest Research Institute

PROGRAM (Concluded)

FRIDAY AFTERNOON, May 7, 1965

2:00 - Sampling of Ions - Chairman, H. Calcote

G.N. Spokes - Stanford Research Institute
P. Knewstubb - Cambridge University

Coffee Break

W. Miller - AeroChem Research Laboratories
G.J. O'Halloran - The Bendix Corporation

ABSTRACTS OF TALKS
PRESENTED AT THE MEETING

CONTINUUM FLOW PROBLEMS IN DIRECT SAMPLING

by

F.S. Sherman
University of California, Berkeley

The basic fluid dynamical problem in direct sampling is the threat to the chemical integrity of the sample which is presented by rapid expansion over a large temperature range, which may permit gas phase reaction; by boundary layer growth, which may deprive the sample of wall-reactive species or introduce wall-originated contaminants; and by diffusive separation of the sample in regions of highly curved or highly rarefied flow.

Typical sampling situations appear to fall roughly into two classes:

1. In the first, downstream of the sampling orifice, there exists a free-jet expansion into a low pressure chamber, with the sample being skimmed from the supersonic region of the jet, or if background pressure permits, from a nearly collisionless flow which evolves out of an originally collision-dominated hydrodynamic flow. For such cases it is possible to deduce that, providing the Reynolds number of the orifice exceeds 500 (based on orifice diameter, sample sound speed, density and viscosity in the nearly stagnant state upstream of the orifice), boundary layer problems and diffusive separation problems are not serious threats to chemical integrity of the flow near the jet axis, providing (a) that the sample is "skimmed" out of the jet at a point upstream of the region of collisionless flow, in which region the sort of diffusive separation discussed by Fenn takes place, and into which background gas molecules may penetrate; (b) that the skimmer is designed and positioned so as to avoid a detached shock wave and assoicated "flow spillage" around the skimmer. Diffusive separation in such a skimmer-induced flow field can be very serious.

There is almost unavoidably a design conflict between criteria (a) and (b), in typical sampling systems in which the sampled mass flow is small. In such cases criterion (a) must be relaxed, and this lends importance to efforts to understand the mechanisms of the evolution from continuum to collisionless flow.

2. In the second class of sampling systems, the passage downstream of the sampling orifice is a more or less slender and extended cone, making the internal flow quite similar to that in a contoured or conical convergent-divergent nozzle for a low-density wind tunnel. It has been thoroughly established,both theoretically and experimentally, that boundary layer effects

on such flows become extreme for nozzle Reynolds numbers and geometrics similar to those of sampling probes, so that at the exit from such a nozzle it must be assumed that the entire cross section of the flow has felt the influence of the temperature and chemical nature of the walls. For a given probe orifice Reynolds number, these effects are minimized by increasing the internal cone angle and keeping the cone as short as possible. However, this design solution conflicts with the necessity to keep the probe slender on the outside, so that a thick external boundary layer does not grow and get sucked into the sampling orifice. Again there does not seem to be an ideal probe design which avoids the need to understand the mechanics of rarefied gas flow in the nozzle, and the chemistry of surface reactions on the inner walls.

Both free jet and conical nozzle flows, when one ignores boundary layer growth in the latter, bear a considerable similarity to simple point-source flows. This has been exploited in numerous theoretical studies of the "freezing" of chemical reactions, molecular internal energy exchanges, and even translational energy exchanges. These analyses would be helpful mostly in free jet sampling systems, to assess any changes in chemical composition due to the expansion, or any residues of electronic excitation or vibrational energy, which might influence the ionization efficiency of the mass spectrometer. For nozzle sampling systems, the thermodynamic history of the sample is under the strong influence of the temperature and drag of the nozzle wall, and source-flow analogies would be at most qualitatively suggestive.

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III. On Rotational, Vibrational and Chemical Relaxation Effects in Source or Nozzle Flows

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NONEQUILIBRIUM EFFECTS IN FREELY EXPANDING JETS

by

John E. Scott, Jr.
University of Virginia

Consideration is given to a dilute, high-temperature, single component, neutral gas whose molecules have no internal degrees of freedom, i.e., an essentially ideal monatomic gas. Emphasis is placed on the nonequipartition of energy among the three translational degrees of freedom. A velocity distribution function is used to describe the behavior of the gas. It is shown that if the distribution function is an even function of velocity there can be no shear stresses and heat conduction in the gas, and if the distribution function is also isotropic, the gas pressure must be the same in all directions. The Maxwell-Boltzmann velocity distribution function satisfies these criteria and thus represents the statistical behavior of a gas in equilibrium. However, if spatial gradients in the macroscopic variables (e.g., streaming velocity, pressure, temperature) exist, the velocity distribution function cannot be Maxwellian or isotropic. Steep gradients of the macroscopic variables are produced during expansion of a gas through a nozzle or orifice into a vacuum (a typical sampling process). The results of some calculations by Professor Harold S. Morton, Jr., are described for a typical sampling system which show that the density, temperature, pressure, streaming velocity, and Mach Number changes with axial distance downstream of the orifice are appreciably different from those changes which occur in a reversible adiabatic (equilibrium) expansion. The gradients are such that one should expect a temperature anisotropy of the order of 10 per cent. Experimental observations of the distribution of speeds in molecular beams produced with a nozzle source demonstrate these effects in a qualitative manner and indicate that the conditions for equilibrium do not hold in the region where the flow is making the transition from collision-dominated (hydrodynamic) to collisionless (free molecular) flow. It is concluded that the results of the application of equilibrium, continuum gasdynamics to the free expansion process taking place in most high pressure sampling systems are, at best, misleading and are quite incorrect in many practical sampling devices.

MASS BIAS IN VACUUM SAMPLING FROM HIGH PRESSURE

by

J.B. Fenn
Princeton University

Mass spectrometers usually operate at pressure levels of the order of 10^{-4} Torr or less. Frequently the source of gas to be analyzed is at a pressure which is a substantial fraction of an atmosphere. Under these conditions the sampling orifice becomes a sonic nozzle which gives rise to a supersonic jet. The consequences of the resulting high mean mass motion on what the spectrometer "sees" can be very significant if there are large differences in molecular weight of the components of the sampled gas.

First to be noted is that because the nozzle flow is convective all species enter the first stage chamber at the same velocity. Because the exit flow is usually effusive each species leaves at a velocity determined by its molecular weight. Therefore, in the first stage chamber the number density ratio of a heavy to a light species will be higher than in the source by the factor $(M_h/M_l)^{\frac{1}{2}}$ where M_h is the molecular weight of the heavy species and M_l is the molecular weight of the light species. This bias in favor of heavy species will be maintained in all subsequent stages or chambers as long as the nature of the flow (usually effusive) is the same at both inlet and outlet.

If the inlet to the second stage (i.e., exit from the first stage) is on the axis of the jet from the original sampling orifice, the entrance velocity to the second stage chamber will also be the same for both species, even though the flow will not be convective in the ordinary sense. In this case the average composition of gas in the second chamber will show the same $(M_h/M_l)^{\frac{1}{2}}$ bias in favor of the heavy species as in the first stage chamber. However, if the ions for the mass spectrometer are formed from molecules on the axis of the beam defined by the entrance slit to the second stage chamber, the bias in favor of the heavy species will be the molecular weight ratio, M_h/M_l, directly and to the first power. This is because the radial component of velocity away from the beam axis, which is due to thermal energy, will be higher for the light than for the heavy species. Therefore, the heavy molecules are preferentially "focused" on the beam axis.

If, on the other hand, the ion source is in a third chamber whose entrance is coaxial with the source orifice and the entrance to the second chamber, and if the entering beam is randomized in this chamber before being ionized, the bias in favor of heavy species will be $(M_h/M_l)^{3/2}$ relative to the original source gas. In other words, the radial velocity effect and the "convection-in-effusion-out" effect will supplement each other.

In addition to these fairly well describable mass discriminations there are further complicating factors which can contribute substantially to mass bias. Condensation-polymerization may occur during the jet expansion and result in effective mass ratios much greater than the molecular weight ratios. Selective scattering of one species from the beam may occur all along its trajectory if background pressures are high enough. Finally, if the inlet to the second stage (i.e., "skimmer") is close enough to the sampling orifice so that a shock wave can occur, there can be separation effects over and above those already mentioned. In general, all of these factors contribute to bias in favor of heavy species.

THE INFLUENCE OF SELF COLLISIONS IN SUPERSONIC MOLECULAR BEAMS

by

J.M. Deckers
University of Toronto

The influence of self collisions in a molecular beam isolated from the exhaust of a small supersonic nozzle permits the accounting for observed intensity variations of the molecular beam at the detector as a function of the stagnation conditions, the nozzle-skimmer distance and the geometric arrangement of the beam defining elements. These self collisions are due to the residual velocity distribution, the temperature of the nozzle exhaust not being zero. When the temperature of the sampled gas is being decreased the number of self collisions decreases faster than the number density and hence, the beam intensity at the detector station passes through a maximum. The residual velocity distribution results in a larger transverse velocity component for the lighter molecules and thus explains the "mass separation." An increase in the stream velocity is due to the "asymmetric cooling" because the faster molecules spend less time in the beam than the slower molecules, and have thus a smaller probability of being thrown out of the beam after a collision.

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COLLISIONS IN MOLECULAR BEAM COLLIMATING CHAMBERS

by

C.W. Nutt and M.S. Rifai
University of Birmingham

When a molecular beam is used to transfer sample molecules from a reaction vessel to a mass spectrometer ion source for analysis, the molecules which are ionized should ideally have experienced a collision-free transit, and may be termed "main-beam" molecules. However, the mass spectrum may also contain contributions from sample molecules which have reached the ion source after suffering one or more wall collisions. Molecules which emerge from the first aperture with velocity vectors directed off the molecular beam axis can collide with the walls of the collimating chambers and thereby form background gas there. If such a molecule collides with another background molecule at a point along the axis, one may effuse into the ion source. Alternatively, at high beam intensities, background molecules may suffer collision with main beam molecules or be knocked on into the mass spectrometer. Furthermore, molecules which have crossed the ionization region once may suffer wall collisions and recross the region before being pumped away. Their contribution may be reduced by introduction of an exit slit downstream of the ion source, into a separately pumped compartment.

The contribution to the mass-spectrum made by background gas in a chamber can be determined by adding more background gas into the chamber via an auxiliary inlet, off the beam axis. Then extrapolation to zero pressure, of a plot of peak height versus background gas pressure, gives the main beam peak height (plus background from other compartments) and the difference between this and the peak height under normal operating conditions gives the background contribution under these conditions. Alternatively by reducing the pumping speed and plotting the peak height versus pressure, a similar graph is obtained which can be interpreted similarly. Strictly, these procedures require measurement of the partial pressure of the sample. Therefore, for the ion source compartment, or chambers near it, where the partial pressure of residual gas cannot be ignored, a different gas may be introduced via an auxiliary inlet and its peak height used to monitor the sample background pressure as the pumping speed is reduced stepwise. The results are interpreted as before.

These procedures have been employed for the analysis of the behavior of a four-aperture beam system, having a path length of 5.25 in. from gas source to ionization point. Background contributions were largest from the first and ion source compartments. The results also showed that with some of the aperture systems tested, some scattering from the molecular beam occurred in the first and second chambers.

COMMENTS ON THE DISTURBANCES BY SONIC SAMPLING PROBES IN FLAMES AND OTHER SYSTEMS*

by

R.M. Fristrom
Applied Physics Laboratory
The Johns Hopkins University
Silver Spring, Maryland

INTRODUCTION

The insertion of any probe into a system would be expected to disturb it (the system) to a greater or lesser degree. The sonic sampling probes used in flame studies (Ref. 1) are no exception to this generality. A typical probe is shown in Fig. 1. It consists of a small (compared with flame front thickness) orifice in a quartz probe connected to a pumping system and analytical instrument. The pressure drop is large ($\approx 10^3$ in a typical case and never less than 10). The orifice diameter is chosen to be in the continuum flow regime ($d > 5\lambda$ at the lowest density point in the flame), but small compared with the flame front thickness. Minimal flame disturbance dictates a small probe angle while rapid quenching dictates a large probe angle. Probe angle is normally chosen to be that at which separation would be expected to occur in the internal flow (30°).

This paper summarizes observations and conclusions concerning the effect of such probes on flame systems. Isothermal systems are simpler than flames which are complicated by steep temperature and concentration gradients and strongly coupled by thermal conduction and diffusion. Therefore, a probe satisfactory for flame studies will also be satisfactory for a similar isothermal system. Probe effects can be classified as aerodynamic, thermal, and chemical. These will be discussed in order.

AERODYNAMIC EFFECTS

Aerodynamic disturbances stem from two factors: (1) the wake due to the insertion of a solid object in the flow field, and (2) disturbance of the flow due to sample withdrawal. Wake can be a serious problem in a flow system

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* This work supported by Bureau of Naval Weapons, Department of the Navy, under Contract NOw 62-0604-c.

(Fig. 2). The problems are usually not severe because the probes are small and the factors of wake and sample withdrawal oppose one another. A well designed quartz probe enters a flame with no visible disturbance of the luminous region and the principal disturbance of flow lines is confined to a region about 5-10 diameters around the orifice. Rosen (Ref. 2) has calculated the flow disturbance of a sonic disc sink assuming incompressible inviscid flow and concludes that the velocity disturbance will be less than 5 per cent diameter upstream of an orifice. Flow stream tubes passing into a typical probe have been visualized using a combined hot wire schlieren technique (Ref. 3) (Fig. 1b).

The calculated near field ($z < r$) disturbance of the orifice where flow is compressible is unimportant aerodynamically outside 1 diameter radius. However, related changes which could effect the chemistry will be mentioned under concentration disturbances.

THERMAL DISTURBANCE

The thermal disturbance of a probe does not affect the sample since in a correctly designed system the stagnation stream line will lie in such a position that none of the probe boundary layer (Fig. 1) is captured. The probe can affect the flow, however,by introducing an enthalpy loss in an otherwise approximately adiabatic (over-all) system. This loss will be reflected in the sample through the coupling produced by the processes of diffusion and thermal conduction. If the heat loss to the probe is small compared with the enthalpy flux through the flame, the effect can be ignored. Fluxes through a typical flame are of the order of 0.5 cal/cm^2/sec (1 atm., CH_4 - 0.078, O_2 flame, V_o = 70 cm/sec) (Ref. 2). With a water-cooled or metal probe this loss could be serious and each individual case should be considered. In the case of the quartz probe conduction losses are negligible and radiation losses are small enough so that in a typical case the probe at 1500°K lies within 100° of the gas temperature and the enthalpy loss of the gas itself is negligible.

CONCENTRATION EFFECTS

The effects which a probe has on the concentration of a flame sample are due to the effects of the sonic orifice as a sink and to the effects of the probe.

The most serious problem is presented by the sink itself. This has several aspects: (1) a physical changing of the sample composition due to diffusion, and (2) a chemical change in the sampled gas due to aerodynamic changes induced in the approach gas by the sonic orifice. The physical aspects of the sink have been investigated by Westenberg, Fristrom, and Raezer (Ref. 5), both experimentally and theoretically with the conclusion that the physical effects of diffusion on concentration measurements in a concentration gradient were small (≈ 1 per cent) providing the gas velocities and diffusion velocity are small compared with the sonic velocity at the throat of the probe.

$$V_i = \frac{D_o}{X} \frac{dX}{dZ} \tag{1}$$

$$V_s = \left(\frac{2\gamma}{\gamma+1} \frac{RT}{M} \right)^{\frac{1}{2}} \tag{2}$$

Since $V_o + V_i \approx 100$ and $V_s \approx 10^5$

$$\frac{V_o + V_i}{V_s} < 10^{-2} \tag{3}$$

In these equations, V_i is the diffusion velocity (cm/sec), D is the diffusion velocity of species i at the point (function of temperature and composition) (cm^2/sec), X is the concentration in mole fraction, and Z is distance (cm). V_s is the sonic velocity (cm/sec), R is the molar gas constant (8.3×10^7 er deg^{-1} °K mole^{-1}), T is the temperature (°K), and M is the molecular weight (g/molar mass).

The effect of the probe itself on the sample is probably minor since <u>clean</u> quartz is a poor surface for catalysis. The principal action is probably a net recombination of radicals on the surface since it is cooler than the gas and radical concentrations lie above thermal equilibrium. The effect can only be transmitted into the sample by diffusional coupling since as mentioned previously, the stagnation point precludes a boundary layer contribution to the sample. Since the probe represents a smaller disturbance than the sonic sink discussed, this effect should be smaller than that of the sink.

The disturbance of sample concentration due to compressibility effects adjacent to the orifice stems from changes in sample temperature and pressure with finite residence times before quenching. If residence time is short compared with reaction half life, then no effect would be expected.

On the other hand, if the temperature drop is rapid enough to freeze the sample in this region, then no effect would be expected either. In the intermediate case, the effect could be appreciable for radicals (as much as a factor of two-three, but less than an order of magnitude), but minor for the stable species (a per cent or less).

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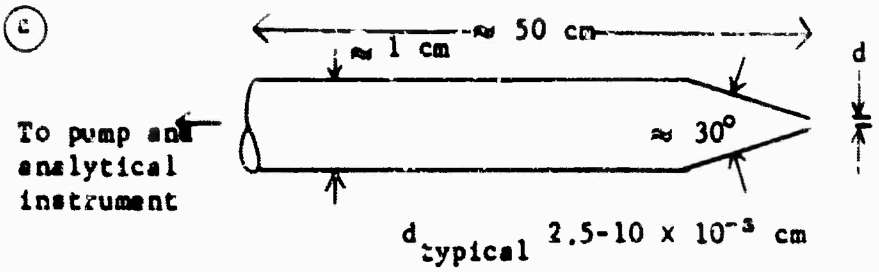


Figure 1. Sampling Probe.
a. Overall View
b. Orifice details

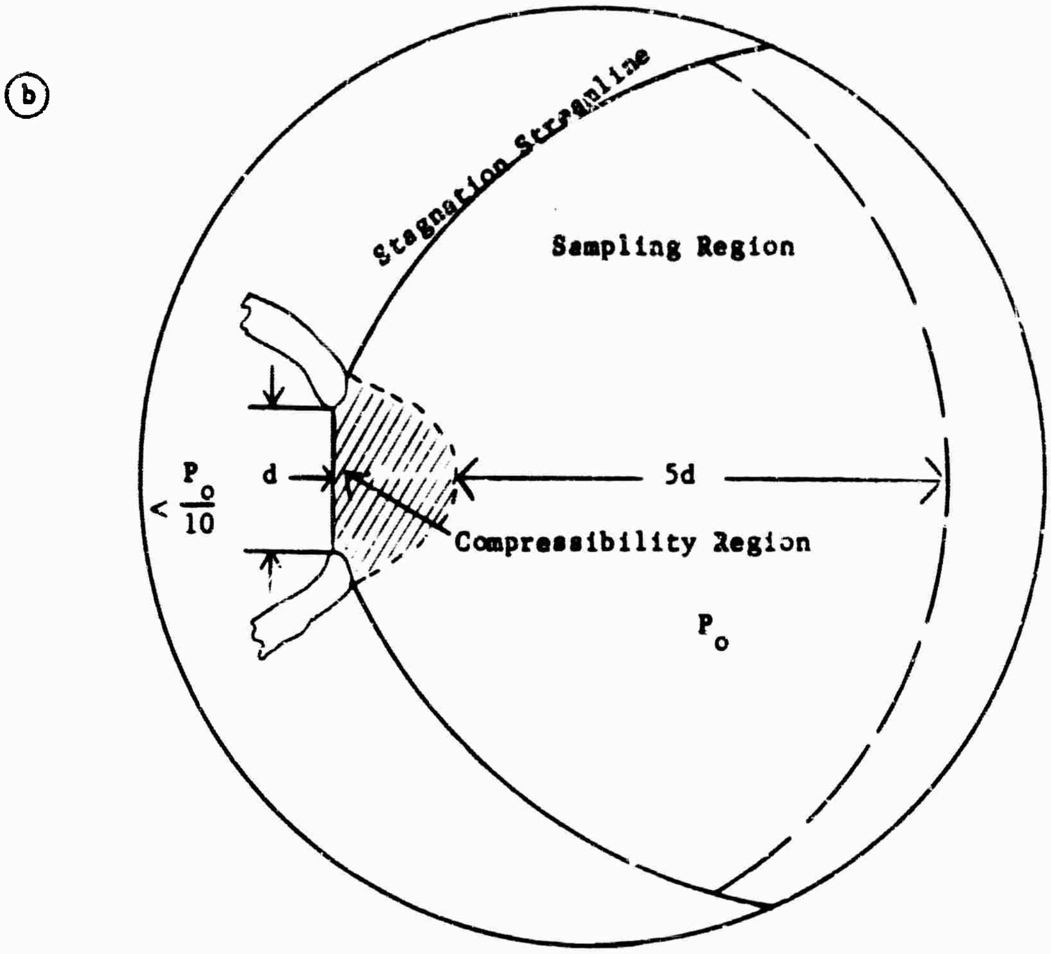
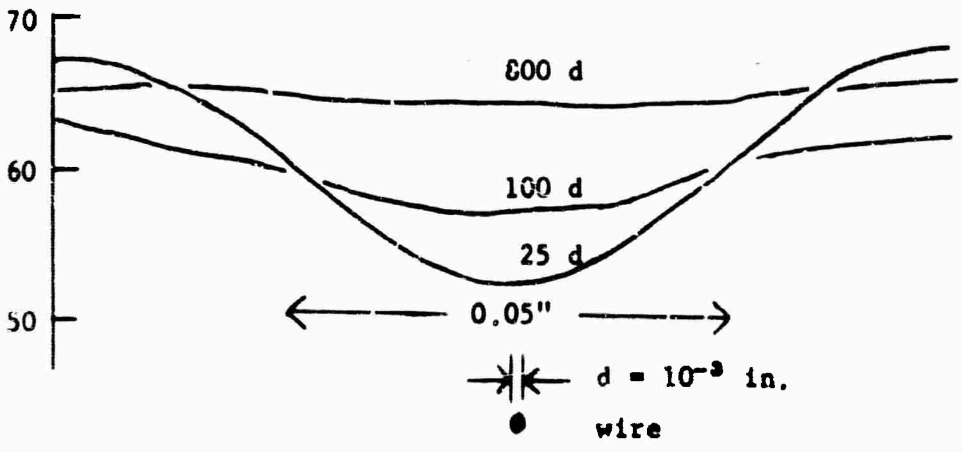


Figure 2. Velocity Wake Behind a Wire Determined by Hot Wire Anemometry (R. E. Walker, APL/JHU).



FREE RADICAL SAMPLING FROM NONEQUILIBRIUM SYSTEMS

by

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The Johns Hopkins University
Silver Spring, Maryland

Several experimental and theoretical observations have been made on the practicality of sampling radical-containing gases through a fine quartz probe and passing them through the detecting cavity of an electron spin resonance (ESR) spectrometer, with continuum flow throughout. The ESR analysis has been established as an absolute method for simple atom (and OH) concentration measurements in other work (Refs. 1,2). Three experimental checks on the validity of such a sampling technique have been made.

1. Using O-O_2 mixtures at room temperature from an electric discharge, the atom concentration upstream and downstream of a "probe" was measured with ESR and was shown to be the same. This indicates that there is no appreciable loss of atoms on the walls of such a probe under these conditions.

2. A comparison of the O atom concentration in a C_2H_6-O_2 flame at 0.1 atm.determined by sampling ESR and that calculated independently from the rate of NO generation (measured by mass spectrometry) by the known reaction $O + N_2O \rightarrow 2NO$ agree very well, i.e., 0.52 and 0.57 mole per cent, respectively.

3. A similar comparison was made on H atoms from a rich H_2-O_2 flame using the tracer reaction $H + D_2 \rightarrow HD + D$. This gave 1-2 mole per cent, while the direct sampling-ESR value was 1.2 mole per cent.

Theoretical computer calculations were also carried out on the flow of initially nonequilibrium gas with complex chemistry through a small (0.1 mm throat diameter) supersonic nozzle taken to represent a sampling probe. The main result of the calculations was that if the inlet gas is in a state of near "partial" equilibrium (equilibration of the bimolecular reaction steps) no significant composition changes occur in the probe. If this partial equilibrium state is not met initially, some composition change ought to occur in the first few microseconds of passage through the converging section. After that the residence time available in the probe is so small that no further composition changes occur either upstream or downstream of the throat.

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SOME PROBLEMS OF MASS SPECTROMETRIC DIRECT SAMPLING*

by

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Argonne, Illinois

A major problem of mass spectrometric direct sampling is the determination of the identity and concentration of neutral molecular species in the sample gas from the observed ion intensities. The solution of this problem requires knowledge of the ionization cross section and fragmentation pattern of each important molecular species as a function of temperature.

Electron impact ionization cross sections can be calculated theoretically in principle. However, only for the simplest atoms has this been done with any accuracy. Simple and crude approximations, such as that of Otvos and Stevenson give only slightly better than order-of-magnitude accuracy and the postulate of additivity of ionization cross sections for molecules is of the same accuracy. The probable error involved in the use of such estimated values is roughly a factor of 2 to 3 in typical cases. For related atoms and molecules, the error can often be much less. Total ionization cross section is essentially independent of temperature.

The fragmentation pattern and its temperature dependence are likewise difficult to estimate. For larger molecules, the statistical theory of mass spectra may be used to provide such estimates. Both the amount of fragmentation and the temperature coefficients increase with molecular size. The parent ion always has a negative temperature coefficient which can be estimated crudely but quickly by the equation

$$\frac{d \ln I^+(p)}{dT} = - \frac{C_V}{A.P.(1)-I.P.}$$

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

where $I^+(p)$ is the intensity of parent ion, C_v the contribution of internal degrees of freedom to the heat capacity of the molecule, I.P. the ionization potential of the molecule and A.P.(1) the fragmentation appearance potential of lowest energy. For diatomic and small polyatomic molecules, a statistical treatment is less valid.

Vibrational energy affects the shape of ionization efficiency curves for parent and especially fragment ions. These effects are most pronounced for photoionization. Photoionization coupled with mass spectrometry can lead to more reliable identification of molecular species and even to measurement of vibrational temperatures.

DIRECT SAMPLING FROM A SHOCK TUBE*

by

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The use of a mass spectrometer for the purpose of analyzing the chemical composition of reactive species formed in a shock tube necessitates direct sampling and a large pressure difference between the shock tube (~ 10^2 mm) and the mass spectrometer (~ 10^{-6} mm). This is accomplished by means of a small orifice (~ 3 mil) located concentrically in the end plate of the shock tube and a large ballast volume, the transient pressure pump, around the ion source of the spectrometer.

The basic premise governing this application is that the boundary layer at the end of the shock tube has a negligible influence on the kinetic history of the sampled gas. Once established all other factors in sampling can be corrected, at least in principle, by direct calibration. A crude estimate of the boundary layer effect can be calculated from the time required for the laminar temperature profile to match the flow radius, giving test times of the order of milliseconds.

Possible boundary layer effects have been investigated experimentally and have not been observed in terms of chemical kinetics. However, under some conditions the boundary layer is observed in terms of temperature-dependent flow parameters, a necessary but not sufficient precursor to a kinetic effect. With neon as a diluent in the shock tube at relatively low pressures (Knudsen numbers of > 0.04) the density is observed to increase a function of time indicating a temperature decrease in the general vicinity of one orifice diameter. Even here the chemical kinetics are observed to be unaffected in the few cases investigated. It is concluded that boundary layer effects are of minor concern with possible exceptions at long test times or for a gas with a high thermal diffusivity such as helium.

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The density decrease on expansion was checked experimentally by following the chemiionization reaction

$$Ar^* + Ar \longrightarrow Ar_2^+ + e$$

where Ar^* is an excited state produced along with primary ionization, Ar^+, on electron impact. The known pressure dependence of this reaction enables the calculation of the effective pressure (density) in the electron beam. The results are adequately described in terms of the inverse square of the distance to the electron beam in terms of orifice diameters.

Some evidence is available indicating that the axial velocity from expansion along with the beam's translational temperature are focusing parameters of the spectrometer. Also the quenched vibrational energy, particularly for large molecules, presents a practical problem in terms of interpretation of the spectra. This point merits careful consideration in any application of this kind.

BEAM FORMATION AND SAMPLING OF NEUTRALS FROM ONE ATMOSPHERE FLAMES

by

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Studies at MRI on the mass spectrometric sampling of high pressure-high temperature systems have been primarily directed toward flame sources. The use of flames as media for the study of high temperature equilibria has the advantage of avoiding the "container problem." On the other hand, this approach can introduce additional problems in sampling as the result of the interaction of the probe with the flame.

The expansion history, as calculated for our aerodynamic molecular beam sampling device using inviscid flow theory, appears very promising for the quenching of reactive species.[1/] For a monatomic gas at 2000° and 1 atmosphere expanding through a 0.125 mm orifice, the pressure drops to 10^{-5} atmosphere and the temperature to less than 100°K within 1.5 microseconds after the first significant pressure-temperature changes. Gases at lower temperatures or having greater complexity will expand more slowly.

Empirical tests of our sampling system have been carried out. It has been possible to quantitatively sample stable products, H, O, OH, HBO_2 and Cl from 2000-3000°K, H_2-O_2 and CO-O_2 flames to within experimental error. Since the reactions of the free radicals are very rapid, it appears that most chemical species, with the exceptions noted below, can be faithfully sampled.

Reactions with negative temperature coefficients, such as condensation, will not always be quenched, since the drop in temperature during the expansion will increase the reaction rate, and the equilibria will be frozen only by the drop in collision frequency. For example, pure argon sampled from a few atmospheres gives a myriad of clusters caused by nucleation during the expansion. There are, however, several possible methods which could be used to correct for "polymers" created by the expansion process. One method involves determining the concentration of a polymer in the beam as a function of orifice diameter and extrapolating to zero orifice diameter. Since the number of collisions which occur during the expansion is roughly proportional to the orifice diameter, this procedure should give the equilibrium concentration. When this was done for argon beams formed from 1 atmosphere, the equilibrium dimer concentration was in good agreement with that calculated from the virial coefficients.[2/] It appears that this procedure may give a simple method for correcting for both nucleation and shifts in equilibrium during the expansion.

In addition to the finite rate of expansion and the related nucleation, there are two phenomena which can complicate high pressure sampling. One is the mass separation effect which we have previously shown to be proportional to the first power of the molecular weight. The second arises from the fact that a mass spectrometer is a density detector, and is therefore sensitive to the velocities of molecules in the beam. Since, in a typical sampling situation, one could be dealing simultaneously with molecules having molecular weights differing by several hundred mass units, this could be of importance. However, we have recently measured the most probable velocities in 1 atmosphere He-Ar and N_2-Ar mixtures, using a phase shift method. Significant velocity differences appeared only in He-Ar mixtures rich in He. In these cases, the Ar velocities lagged those of He by as much as 10 per cent. Since this is an extreme case, velocity differences should not normally be a significant source of error in high pressure sampling.

In general, it now appears that even species which undergo very fast reactions can be directly sampled from 1-atmosphere sources. It is still uncertain to what extent refractory condensible species, which may nucleate excessively during the initial expansion, can be sampled. Nucleation phenomena will probably provide the practical limit as to the systems (and pressures) which can be studied.

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A SAMPLING SYSTEM FOR NEUTRAL PARTICLES

by

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The properties of a molecular beam sampling system for flames and isothermal flow reactors are described. It consists of a cone-shaped quartz probe (cone angle about 50°, cone length 7 cm, nozzle diameter up to 0.3 mm) and two differentially pumped chambers separated by a slit. The ion source of a mass spectrometer which is situated in the second pumping chamber serves as detector. The pressure in front of the nozzle is limited to about 50 Torr in order to keep the pressure behind the probe low enough (10^{-3} to 10^{-4} Torr). The background pressure in the ion source is 10^{-6} Torr. After passing the ionization region the beam runs into a wide pumping line to reduce back diffusion of particles which have hit the walls. The sampling system is meant to analyze free radicals, atoms and other highly reactive particles which can be detected by a mass spectrometer but are sensitive to wall collisions. The efficiency of the arrangement for determination of free radicals and atoms was tested by sampling from flames and electrodeless discharges. Unstable molecules such as polyacetylenes up to $C_{12}H_2$ which are present in carbon forming flames could be analyzed as well. The shape of the probe assures that by far the most of the molecules which enter the nozzle have not hit the wall of the probe near the orifice. This holds even more so when sampling from rapid flow isothermal systems. The quartz probe's influence on the temperature of a low pressure flame has been studied. A mass separation effect with this beam arrangement has been studied with H_2-N_2 mixtures. It has been observed that the separation, expressed as the ratio of the mole fractions before the nozzle and in the ion source, is not independent of the composition of the sampled gas mixture. Polymer formation has not been observed under our sampling conditions.

The mass spectra of hydrocarbons sampled from flame gases at 1600°K by the beam did not show any difference as compared to those taken at room temperature from a conventional inlet system. This suggests considerable cooling of the gases during expansion. The mass separation and the cooling might be evidence for a supersonic flow of the gases behind the nozzle before it turns into molecular flow.

It is concluded that this kind of sampling system is very well suited to following reactions in fast flowing isothermal systems and also in flames. When sampling from the reaction zone of a low pressure flame, however, a slight distortion of the flame must be taken into account.

ION SAMPLING FROM GASEOUS PLASMAS

by

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Studies of ion sampling from a nitrogen afterglow at a pressure of a few Torr indicate that the ion-sampling process depends strongly on the local electric fields at the sampling apertures. Gas dynamic effects also play a role in the sampling process.

Ions sampled from a nitrogen afterglow were primarily N_2^+, N_3^+, and N_4^+. At constant pressure, the balance between N_2^+, N_3^+, and N_4^+ is almost independent of the nature of the material from which the sampling electrode is constructed and of the potentials used for ion extraction. When using pure gold electrode material and with uncontaminated gases, the ion sampling behavior for the ions N_2^+, N_3^+, and N_4^+ accorded with simple theory. K^+ and Na^+ impurity ions behaved differently.

Dielectric coatings on electrode surfaces lead to very long duration ($\sim$ 30 sec) time effects in the ion-sampling process. These effects are explained in terms of a theory of surface charging. The surface charge has a very strong influence on the ion-sampling process.

Under conditions of air addition to active nitrogen, long-term time dependencies of ion currents were experienced when using a system with gold electrodes. These effects can be explained in terms of a changed surface condition associated with the air addition.

Experiments with a sandwich sampling electrode (very thin mylar with aluminum deposits on the upper and lower surfaces) proved the great importance of local electric fields at the sampling aperture.

Ions were sampled from a low-pressure atomic oxygen-acetylene diffusion flame. Ion currents were much higher when a "pusher" electrode was given a negative potential than when given a positive potential. An explanation is given.

ION SAMPLING FROM A FLOWING GAS STREAM

by

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a. Negative ions in flames: Firstly, a brief description was given of some experiments on the sampling of negative ions from premixed acetylene flames at atmospheric pressure. It is possible to state with some certainty that the concentration of heavy negative ions present in the burnt gases is very small, and much less than the positive ion concentration. The mass spectrometer did show large negative ion currents when sampling in and before the reaction zone, but only when a relatively large diameter sampling orifice was used. The interpretation of the results is still not clear.

b. Photoionization in a rapid gas flow: A new apparatus was described which attempts a direct measurement of the rates of ion-molecule reactions, chiefly of the three-body attachment type. The ions are generated at one position in a rapidly flowing gas stream, by a high energy light pulse. A short time later the ion cloud passes over a sampling nozzle, and the results shown encourage belief that the ion cloud expands by (ambipolar) diffusion processes, and that the nozzle takes a representative sample, showing quite closely the correct profile for the simple case of argon. It is noteworthy that the diffusion coefficient used to achieve a fit is approximately 400 cm^2/sec at 1 mm., which is much greater than the value of 69 given by Biondi.

When more than one ion is present, the individual ion profiles may be measured, as the ion sample is analyzed by a quadrupole mass filter. The change in ion ratios with time gives the rate constant of the ions involved. Approximate preliminary results are:

$$N_2^+ + 2N_2 \longrightarrow N_4^+ + N_2 \qquad k \sim 4 \times 10^{-28}\ cm^6\ molecule^{-1}\ sec^{-1}$$

$$Ar^+ + 2Ar \longrightarrow Ar_2^+ + Ar \qquad k < 10^{-30}\ cm^6\ molecule^{-1}\ sec^{-1}$$

The system may be developed in due course to test the possibilities of isokinetic sampling.

ION SAMPLING FROM HYDROCARBON COMBUSTION PLASMAS

by

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A program of research on chemi-ionization has been in progress at AeroChem for several years. The technique, briefly, involves the mass spectrometric sampling of ions formed in low-pressure flames and interpretation of the resulting data in terms of flame ion chemistry. Thus far the results have been of only a semi-quantitative nature but have, nevertheless, constituted a significant contribution to our understanding of chemi-ionization. A description of the apparatus and some recent results of the experimental program can be found in Refs. 1 and 2, respectively.

We are now endeavoring to put a firm quantitative foundation under the study by calibrating our instrument in terms of absolute ion concentrations. Obviously, then, a more detailed knowledge of the sampling system and its idiosyncrasies are of immediate necessity. A series of experiments have recently been undertaken, therefore, in an attempt to illuminate our particular sampling problem. Some of our results demonstrative of possible pitfalls and phenomena peculiar to ion sampling are presented below.

The first set of experiments was designed to test the effect of orifice length on relative ion currents. Three ions, H_3O^+, $C_3H_3^+$, and $H_5O_2^+$, were examined using a sampling orifice of 0.010 cm diameter and two different lengths -- 0.010 and 0.018 cm. The only significant effect of the longer orifice was a reduction in ion currents. After normalizing the currents by multiplying the lower numbers by a factor of 6.6, the profiles fall very nearly on top of one another. Further thinning of the plate in which the orifice is drilled increased the currents only slightly. Reactions which may occur in the boundary layers around the input system are apparently not enhanced by lengthening the orifice -- at least at the low pressure (2 Torr) employed in this program. Boundary layer effects, however, are important in certain configurations.

Enlarging the area surrounding the orifice immersed in the flame has a profound effect on the apparent location of ion current maxima. All ions, with the exception of $H_5O_2^+$, appear to maximize further downstream of the flame front when the solid surface surrounding the orifice is increased. This effect is most dramatic, reasonably enough, when the sampling orifice is drilled in a flat plate. Placing the orifice in a cone tip and making the face of the cone as small as 4 mm in diameter alleviates this problem. The area about the orifice also affects the apparent relative abundance of $H_5O_2^+$; larger areas strongly favor its formation. Green and Sugden[3] have concluded that this ion is not a "flame" ion but an "input system" ion. Our results reinforce this conclusion. Moreover, the appearance of large quantities of this ion indicates poor sampling system performance.

We have also examined the effect of imposing a potential across the flame front between burner top and sampling cone or plate. In normal operation the burner and cone are at the same potential: +200 volts for positive ion sampling. A negative potential would therefore be expected to have a retarding effect on positive ions. If the ions are all influenced to the same extent by an electrostatic field, primary ions should be inhibited in their path to the sampling orifice and the result should be a longer reaction time and an enhancement of secondary ions. The effect, if operative, is too small to be seen. The converse -- preferential sampling of primary ions at positive (accelerating) burner potentials -- is observed. At least the ion most commonly cited as the primary ion, CHO^+, undergoes the largest increase upon imposing a positive potential. Most of the other curves are anomalous with respect to this interpretation, however. The same experiment when performed using a flat plate resulted in much smaller departures from normal response.

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