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Plasma Chromatography

Roy A. Keller[a]; Michael M. Metro[a]
[a] Department of Chemistry, State University of New York, College at Fredonia, Fredonia, New York

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PLASMA CHROMATOGRAPHY

Roy A. Keller and Michael M. Metro
Department of Chemistry
State University of New York, College at Fredonia
Fredonia, New York 14063

INTRODUCTION

In its brief history the PLASMA CHROMATOGRAPH, PC, (Franklin GNO Corporation, PO Box 3250, West Palm Beach, Florida, 33402) has been used as a mass spectrometer, a pre-separator attached to a quadrupole mass spectrometer, an interface between a gas chromatograph and a mass spectrometer, and as a detector for a gas chromatograph. We intend to examine its potential as a separation device. The PC is an ion-molecule/ion-drift time of flight mass spectrometer and is a separation method to the extent that a time of flight mass spectrometer is a separator. Both qualify as differential migration separation methods, i.e., the driving force, the electric field, causes the different species to migrate at different velocities so they appear at different times, the *drift times*, at the terminus to the migration path. The PC has several features which set it apart from the conventional mass spectrometer. Firstly, it operates at atmospheric pressure. Secondly, its electric field may be reversed so that either positive or negative ions may be collected. Karasek[1] justifies the term "chromatograph" on the basis of the similarity of the data presentation to that of a gas chromatograph and that "...like a chromatograph, the peaks can be used in a qualitative

and quantitative manner". This early preliminary report leaves this last claim unsubstantiated. Later Cohen and Karasek[2] justified it being a chromatograph because of "...the sequential generation of individual peaks from each chemical species of the sample". From the number of challenges made to the name at various presentations, the semantics of the title seem important to some. Nearly two decades ago H.H. Strain defined chromatography as differential migration from a narrow initial zone. As we shall discuss, a "pulse" (the narrow initial zone) of the *melange* of ion-molecules formed in the reaction chamber is electronically gated into the migration medium, the drift tube, where differential migration occurs. Strain pointed out that a selective resistive force, one which opposes the driving force, is often operative but not mandatory in a chromatographic system. Such a resistive force is provided in the PC by drift gas flowing counter to ion flow. There is some indication that this force is selective. Carroll and Mason[3] showed that the ion-molecule mobility should be a function of ionic radius rather than mass alone. This introduces the possibility of selective viscous flow. This does not seem a first order effect at this time and does not seem exploitable to enhance separations with gas at atmospheric pressure in the drift tube. We know of no published results of experiments at higher pressures but the idea seems worthy of theoretical and experimental exploration. An early paper by Cohen and Karasek[2] suggested that pressures of 0.1 to 10 atm are feasible. We feel that this argument justifies the generic term chromatograph and the method belongs to the subset electrophoresis or electrochromatography. Besides, PLASMA CHROMATOGRAPHY is a registered trade mark.

INSTRUMENTATION

A complete description of the instrument and its important operating parameters will be given by Metro and Keller[4]. Only the most important features will be reviewed here.

Figure 1 is a photograph of one modification of the instrument.

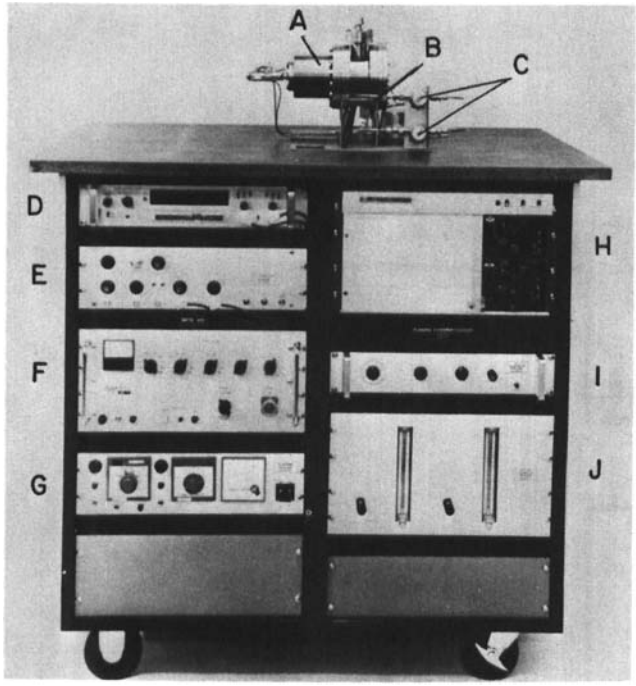

FIGURE 1

Model Beta/VII Plasma Chromatograph
(Courtesy of Franklin GNO Corporation,
West Palm Beach, Florida)

A SIFAD Tube, sample inlet on left. The entire unit is encased in heating mantles
B Solid state preamplifier
C Carrier and drift gas shut-off valves
D Hewlett Packard Model 5325A Universal Counter
E GNO PC Controller
F Fluke Model 408B High Voltage Power Supply
G GNO Temperature Controller and Sensor
H Hewlett Packard 7035B x-y Recorder
I GNO PC Electrometer
J GNO PC Flow Controller. The rotameters shown here are replaced by Hastings Mass Flowmeters.

Figure 2 is a schematic of the "separate ion formation and drift tube" (SIFAD). *Carrier* (also called the *reactant*) *gas*, nitrogen or air, with a very low water content continuously sweeps

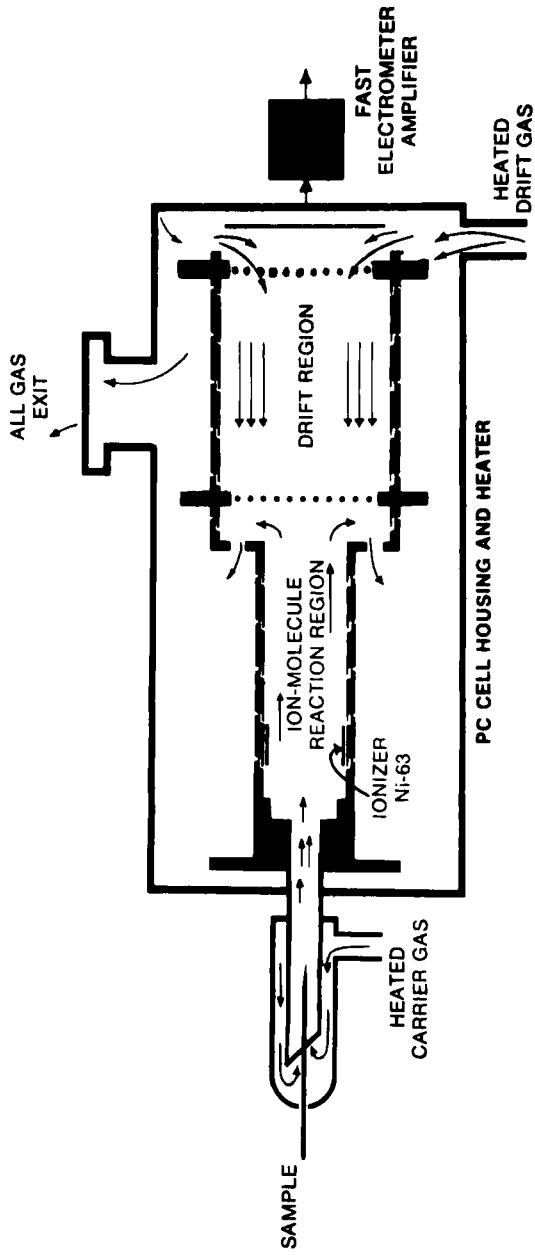

FIGURE 2

Schematic of the SIFAD Drift Tube and Sample Injection (Courtest of Franklin GNO Corporation, West Palm Beach, Florida)

through the sample injector and passes over a ^{63}Ni source where *reactant* (also called *primary*) *ions*, positive and negative, are produced from carrier gas components in the *reaction region*. These enter an electric field, which may be reversed, and positive or negative ions move toward the *drift region*. An admitting gate is electronically pulsed to sample the ion-molecule mixture in the reaction region. This feature introduces the narrow initial zone. *Drift gas*, generally nitrogen, flows counter to the ion-molecule flow in the drift region and it is here where differential migration occurs. A second gate is positioned at the end of the drift region and it admits the separated ion-molecule species to a sensing electrode. The second gate may be set to open at regulated and increasing delay times after the first gate pulses. Thus each admitted pulse is sampled once by the second gate each at a different delay time. The signal is sent to an electrometer and its intensity recorded on an x-y recorder. We find that a 2 min scan of a 20 msec drift time range is about the fastest one can operate without serious distortion of the spectrum by the recorder. We refer to this mode of operation as PC-mg (moving gate). The preamplifier and high speed electrometer of the Beta/VII makes it possible to open the second gate and scan the separated ion-molecule species in a single pulse. This signal may be read-out directly on an oscilloscope, PC-os. We use a storage scope and photograph the scans. The signal may also be sent to a signal averaging computer, stored, and read-out on an oscilloscope or printed out with an x-y recorder, PC-sac.

Carrier gas and drift gas meet ahead of the admitting gate and are vented to the atmosphere. Sample, reaction, and drift tube regions are enclosed in heating mantles.

REACTANT ION FORMATION

The *reactant ions* are those ion-molecules formed from the carrier gas.

Our experience has been with Airco Ultra Pure nitrogen (typical analysis: 1 ppm O_2, 2 ppm Ar, < 0.5 ppm CO and CO_2, < 0.5 ppm hydrocarbons, dew point = - 100°F or 1.53 ppm water) as carrier gas and as drift gas and Airco Zero Air (typical analysis: 0.8 ppm hydrocarbons, dew point = - 98.5°F or 1.74 ppm water) as the carrier gas only. Drift and carrier gases each pass through 2.25 l stainless steel cartridges containing Linde Molecular Sieve 13X and through a micron filter. Franklin GNO[5] advises the use of air or some other electron attaching gas in any study of negative ions and nitrogen or air in any study of positive ions. Water contents in the carrier gas have been reported to be ∿ 1 ppm[2], 10 ppm[6,7,8], 100 ppm[9,10], and 10 to 100 ppm[11,12]. Horning *et al*[13] state that the sieves reduce the partial pressure of water to 10^{-5} torr. These values seem to be estimates because none of the references cite experimental techniques for their determination. Several papers claim that the nature and relative abundance of the reactant species depend upon the water content[1,2,6,8,10,14] as well as the temperature[4,6,8,10]. Adding our own speculative opinion, the water content may not be easily controlled, even if a desirable one is ever identified, because it is very likely that the efficiency of the molecular sieve depends upon the flowrate of the gas through it. We do guess that by the time the carrier and drift gases pass through the sieve, plumbing, and flow controllers and meters that the water content is something other than the specifications on the source cylinders.

The entrance to the reaction region (Figure 2) is immediately followed by a repeller electrode which collects ions of charge opposite in sign to the charge of the ion-molecules of interest. The repeller electrode is followed by the ^{63}Ni source. The emitted β-particles have energies as high as 60 keV[5]. Our source, a standard electron capture detector source, is rated at 11.28 mCi. Franklin GNO literature and other references describe the process. The source generates about 6×10^8 high energy parent electrons per sec in all directions. Half of these are in the direction of

source mounting and another fraction is lost by source self-absorption. About 10 per cent of the total high energy electrons are available for ionization[5]. The electrons from the β-source randomly collide inelastically with neutral carrier gas molecules. Each collision yields an ion and a low energy electron. The parent electron loses about 30 eV per collision. Finally about 2000 thermal ion pairs are produced per parent source electron. The thermal electrons attach to electronegative species in the carrier gas to form negative reactant species. Taking air as an example, there are 5×10^{18} O_2 molecules/cm^3 at 1 atm pressure. At these conditions the collision frequency is of millions/sec and so there is a very high probability that a thermal electron will encounter an O_2 molecule and undergo a stabilizing collision with a third body.

$$e + O_2 + M \rightarrow O_2^- + M \qquad (1)$$

In air the energy for this reaction is 0.05 eV[5]. Approximately one O_2 in every 10^{11} is ionized and all thermal electrons are captured. The production of these reactant ions is claimed to occur within a fraction of a msec and within a mm of the β-source[1,2,6,7]. The current in the reaction chamber is reported as $\sim 1.5 \times 10^{-9}$ amp in a 1 cm diameter beam. Most of this current terminates at the closed shutter grid[2,5,7].

A good deal of discussion has been devoted to identifying the reactant ions. Whether dealing with reactant species or sample species, the least ambiguous identification requires that the PC be interfaced with a mass spectrometer to determine the mass number of the species in each resolved pulse of ion-molecules which appears as a "peak" on the plasmagram. As will be demonstrated, these pulses may contain more than one species. Also, the mass spectrometer will not distinguish between different chemical species with the same mass numbers. The second method attempts to establish a general mass number vs drift time calibration curve based on mass spectrometric results and this is often used to identify the mass when a mass spectrometer is not available. This

has not proved reliable which is very unfortunate because it cripples plasma chromatography as an identification method; one cannot reliably identify what has been separated. This will be discussed in greater detail under "samples" and is mentioned here only to alert the reader to the problem. In what follows we will mention the method of identification when the original paper specifically states the technique. Species identified without such a statement are ambiguous.

In his first report on plasma chromatography, Karasek[1] identifies the positive reactant species as $(H_2O)_nH^+$ and the negative species as $(H_2O)_nO_2^-$ as formed in moist air. The degree of hydration, n, is said to be dependent upon the moisture content. Mass spectral results (experimental details omitted) identify $(H_2O)H^+$ and $(H_2O)_2H^+$. Cohen and Karasek[2] make the generalization that the negative species formed in moist air at 200°C is $(H_2O)_nO_2^-$ with n = 0,1,2. In the positive mode, the initially formed N_2^+ and O_2^+ eventually produce $(H_2O)_nH^+$ with n = 0,1,2 at 25° to 200°C. They justify this by reference to other authorities who employed conventional vacuum conditions. Using a quadrupole mass spectrometer interfaced with the PC they specifically identify $(H_2O)H^+$ and $(H_2O)_2H^+$ as formed in dry air at 760 torr and 150°C (the monohydrate predominates) and O_2^-, $(H_2O)O_2^-$, CO_3^-, and CO_4^- in dry air at 760 torr and 200°C on the basis of mass numbers. Really hard data is lacking in this report. Karasek, Kilpatrick, and Cohen[6] refer to $(H_2O)_2O_2^-$ in the negative mode and $(H_2O)_2H^+$ and $(H_2O)_3H^+$ in the positive mode. Mass assignment of sample species were made by reference to a mass vs drift time curve. Their experimental curve stops at mass 50 and it is not clear how the hydrated proton species were established. Reference is made to results of workers in conventional mass spectrometry. Karasek and Tatone[7] mention $(H_2O)_nO_2^-$, $(H_2O)_nH^+$, and $(H_2O)_nNO^+$ in general and specifically refer to $(H_2O)_2H^+$, $(H_2O)_2NO^+$, and $(H_2O)_4H^+$ with the tetrahydrate as the most dominant species in the reactant ion-molecule species. Their reactant ion-molecule spectrum most

closely corresponds to our own. The mass-drift time correlation curve is used. One of their remarks is of considerable importance: *"Mass spectral data indicate there may be more than one ionic species in each plasmagram peak of the positive reactant ions."* The species assignments indicate only the most abundant species considered present. We will refer to this statement again. Karasek and Kane[8] again refer to $(H_2O)_nO_2^-$, n = 0 to 3, and $(H_2O)_nH^+$. No data on identification is given. They state that at 125°C, 90 per cent of the electrons are converted to $(H_2O)_nO_2^-$ while at 190°C, 20 per cent of the electrons are converted to this species. This gives a quantitative appreciation of the effect of temperature. Karasek[9] lists $(H_2O)_4H^+$, $(H_2O)_2O_2^-$, and $(CO_2)O_2^-$. He refers to the mass vs drift time curve and mentions the difficulty in using it for identification for masses less than 100 mass units because of its flatness. The species listed have masses less than or equal to 76. Karasek and Kane[10] list $(H_2O)_nO_2^-$ and $(H_2O)_nH^+$ and refer to a mass-mobility curve. They also remark that reactant ion-molecule peaks may not be homogeneous and suggest traces of $(H_2O)_nNO^+$. Karasek[11] and Karasek, Tatone, and Kane[12] repeat $(H_2O)_nH^+$ and $(H_2O)_nO_2^-$. No direct use of a mass spectrometer was made in these studies. Karasek, Cohen, and Carroll[14] add $(H_2O)_n(CO_2)O_2^-$ to the list. A coupled mass spectrometer was used in this case as specific mention is made of $(H_2O)_2H^+$, $(H_2O)_3H^+$, $(H_2O)NO^+$ (small amount), $(CO_2)O_2^-$, and CO_3^-. Karasek[15] reports $(H_2O)H^+$ and $(H_2O)_2H^+$ without reference to experiment. Horning, Horning, Carroll, Dzidic, and Stillwell[13] refer to the work of Good, Durden, and Kebarle[16] for a reaction scheme of electron impact, first with dry nitrogen

$$N_2 + e \rightarrow N_2^+ + 2e \qquad (2)$$

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2 \qquad (3)$$

and then further reaction in moist nitrogen

$$N_4^+ + H_2O \rightarrow H_2O^+ + 2N_2 \qquad (4)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \qquad (5)$$

$$H_3O^+ + H_2O + N_2 \rightarrow (H_2O)_2H^+ + N_2 \quad (6)$$

$$(H_2O)_{n-1}H^+ + H_2O + N_2 \rightarrow (H_2O)_nH^+ + N_2 \quad (7)$$

They state that the value of n and the relative distribution of clusters depends upon the water content and the temperature. This group used the reaction chamber of the PC as an ionization source for a modified but largely conventional vacuum quadrupole mass spectrometer. They assign masses to sample species but not to reactant species. Griffin, Dzidic, Carroll, Stillwell, and Horning[17] quote Good's scheme and add the following reactions:

$$N^+ + 2N_2 \rightarrow N_3^+ + N_2 \quad (8)$$

$$N_3^+ + O_2 \rightarrow NO^+ + O + N_2 \quad (9)$$

$$NO^+ + H_2O + N_2 \rightarrow (H_2O)NO^+ + N_2 \quad (10)$$

$$(H_2O)NO^+ + H_2O + N_2 \rightarrow (H_2O)_2NO^+ + N_2 \quad (11)$$

They refer to a "steady-state" concentration of reactant ions without amplification of this remark. They used a quadrupole mass spectrometer to directly study the species produced and report observation of masses corresponding to $(H_2O)H^+$, $(H_2O)_2H^+$, NO^+, $(H_2O)NO^+$, and $(H_2O)_2NO^+$. Coffey[18] identified $(H_2O)_2H^+$ and $(H_2O)_3H^+$ in ultra-pure nitrogen (2 ppm water) at 21°C in the drift tube. At 500 ppm water vapor, the following species were identified (relative abundance is given in parentheses): $(H_2O)_3H^+$(1), $(H_2O)_4H^+$(28), $(H_2O)_5H^+$(30), $(H_2O)_6H^+$(4), and $(H_2O)_7H^+$(3), again at 21°C. A mass spectrometer was interfaced with the drift tube and a duPont 501 Moisture Analyzer established water content. Cram and Chesler[19] repeat Good's scheme and add

$$N_2^+ + H_2O \rightarrow H_2O^+ + N_2 \quad (12)$$

Rate constant data are also quoted. Without referral to direct mass spectrometric data they suggest $(H_2O)_2H^+$, O_2^-, N_2O^-, and CO_2^-. They make the provocative statement: "However, it should be recognized that any or all of these peaks could represent several species *in equilibrium* (our italics). They speculate that one of

their peaks (7.1 msec) could contain $(H_2O)H^+$, $(H_2O)_2H^+$, and $(H_2O)_3H^+$.

GNO promotional literature states that the counterflowing drift gas quenches further ion-molecule reactions in the drift space. Several papers refer to stable sample ion-molecules and a non-reactive drift gas[1,6,7,8,10,14]. "The principal purpose of this drift gas...is to spatially limit the reaction region..."[2]. "The drift region is purged of *sample* (our italics) material by a large counter-current flow of nitrogen gas which prevents ion-molecule reactions from continuing during the drift time measurement period"[17]. Coffey[18] states that the major difficulty with drift tubes is that ion-molecule reaction may not stabilize or reach completion so that ion species may change their identity one or more times during transit. This is said to give broadened mobility peaks with reduced resolution. The counterflowing drift gas is claimed to minimize this effect by only allowing ions to enter the drift region. All ion-molecule reactions are essentially terminated and the ions are not expected to change species and mobility during transit. We presume that what is meant here is that no neutral sample molecules enter the drift region and they are excluded from further reaction. This is a far cry from saying there is no further reaction. GNO[5] also refer to further ion-molecule interaction in the drift region which can occur at any point within it. The resulting ions will not be "spatially coherent and will not give unique peaks". It is not wholly clear if this particular discussion excludes neutral sample molecules. Cram and Chesler[19], excluding the presence of uncharged sample molecules, state that a variety of reactions of the ion-molecules admitted to the drift chamber can occur with the drift gas and its impurities to produce unexpected new species. They state that it is impossible to identify the ions at the terminus of the drift tube without a mass spectrometer and that a given peak may be due to ions which "...*spent a significant fraction of their drift time as another species*" (our italics). Thus any reaction in Good's

scheme which involves an ion-molecule and a neutral nitrogen or water molecule is potentially reversible [e.g., eqns (6,7,10,11, 12)]. Reaction between ion-molecules of the same charge seems unlikely because of repulsive forces. The authors give some rate constant data. In general, ion-molecule reaction rates are very fast and ion intensities are pressure dependent. Metro and Keller[20] pointed out the significance of this by referring to the theoretical work of Keller and Giddings[21] where it was shown that in the chromatography of two reversibly interacting species of different R_f-value or elution times, 1, 2, or 3 solute zones can be produced depending upon the value of the rate constants as compared to the time of chromatography. Of particular interest here is when $A \rightleftarrows B$ and interconversion is sufficiently swift that nearly every molecule will make several A-B transitions. Then A cannot be separated from B and a single zone will result with a concentration profile maximum between where A and B would fall in the absence of such reversible interaction. This would mean that not only is peak broadening and resolution very bad but a *drift time measured from the peak position would not correspond to any real ion-molecule species.*

We have introduced this problem in the discussion of reactant ion species for several reasons. Firstly, mass spectrometric data clearly indicates that reactant ion peaks are mixtures. One reference[19] speculates that one peak might contain $(H_2O)H^+$, $(H_2O)_2H^+$, and $(H_2O)_3H^+$ which fit into Good's mechanistic scheme. Secondly, a reasonable mechanism has been suggested and rate constant data exist. If this situation exists for reactant species then it is likely to exist for sample species also. In these cases, mechanisms and rate data are currently lacking and each solute could become a separate kinetic problem. All we can do is state the problem and suggest that it deserves consideration.

Whenever identification is made by an empirical mass vs drift time curve, reference is almost universally made to Carroll and Mason[3] and Kilpatrick[22]. To this should now be added the paper by

Griffin *et al*[17] and the comment by Karasek and Kane[10] that uncertainties exist whenever a mass spectrometer is used for mass identification which arise from the interface of the SIFAD tube at atmospheric pressure and the vacuum mass spectrometer "because of phenomena associated with condensation, energetics, and ion-molecule reactions". No elaboration is volunteered.

In summary, the following reactant species have been suggested and in some cases identified (mass numbers are given paranthetically):

Positive reactant ions

General: $(H_2O)_nH^+$, $(H_2O)_nNO^+$

Specific: $(H_2O)H^+(19)$; $(H_2O)_2H^+(37)$; $(H_2O)_3H^+(55)$; $(H_2O)_4H^+(73)$, $NO^+(30)$; $(H_2O)NO^+(48)$; $(H_2O)_2NO^+(66)$*

Negative ions

General: $(H_2O)_nO_2^-$, $(H_2O)_n(CO_2)O_2^-$

Specific: $O_2^-(32)$; $(H_2O)O_2^-(50)$; $(H_2O)_2O_2^-(68)$, $CO_2^-(44)$, $(CO_2)O_2^-(76)$; $CO_3^-(60)$; $N_2O^-(44)$

*Verified by an interfaced quadrupole mass spectrometer.

All mass numbers are less than 100, the point where the mass vs drift time curve becomes unreliable.

The identity and relative abundance of these species will depend upon the nature of the carrier gas and its purity and upon the temperature. All too often the purity of the gas used is not stated.

Figure 3 is a plasmagram of reactant ions. It is similar but not identical to other published reactant ion plasmagrams[4,6,7,9,10,14,20,23].

When operating in the negative mode with a carrier gas containing no electronegative species, e.g., pure dry nitrogen, the ion beam consists of the uncaptured thermal electrons. Because

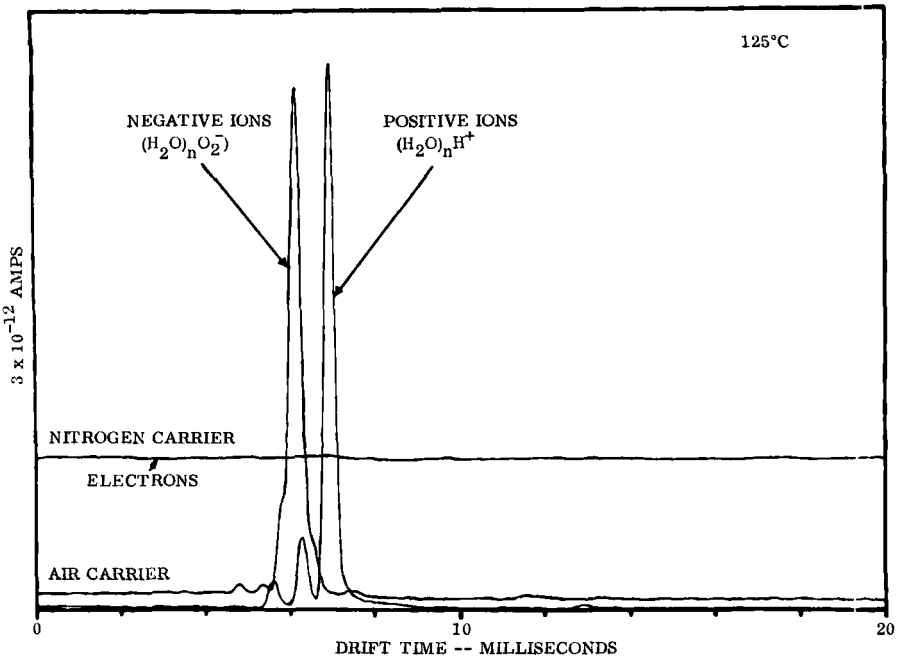

FIGURE 3

Plasmagram of Positive and Negative Reactant Ions[8]
(Courtesy of *Analytical Chemistry*)

the shutter grids do not close perfectly for such small, high speed particles, the electrons appear as a continuum across the scan of Figure 3. If the grids could exclude electrons, the scan would show a single peak at 0.01 msec with a magnitude 15 times that of the continuum[8]. If an electronegative sample species is introduced, this continuum initially vanishes, begins to regain and approach the continuum value and near this value shows the peaks of the negative sample ion-molecules. Then the trace returns to the continuum value[7]. When an electron capturing species is in the carrier, negative reactant ions consume all of the thermal electrons and give the trace labeled "air carrier" and "negative ions" in Figure 3.

SAMPLE BEHAVIOR

When injected into the carrier gas stream the neutral sample molecules interact with the reactant (primary) ions to produce product (secondary) ions in the ion-molecule reaction region (Figure 2) and these are gated into the drift region.

Secondary Ion Formation:

The primary ions collide with neutral molecules with a frequency of 10^{10} collisions/sec[5]. The majority of these are not with the solute but with carrier gas components. This frequency is based on molecule/molecule collision rates and the rate for ion-molecule/molecule collisions may be greater. In the presence of a sample, a fraction of these collisions will be with the solute. In 10 msec 10^8 collisions occur and this is presumed sufficient for completion of the very fast charge transfer reaction[1,5,14]. The mean free path is stated to be 1000 Å[15]. An ion-molecule can gain 0.001 V of energy between collisions which is small compared to thermal energy of 0.050 V. Energy gains are mostly lost on collision[15]. Reaction of the primary ions with sample molecules is presumed to be electron transfer to a more electronegative molecule or proton transfer both of which are very fast. Negative secondary ions are expected of all species showing a response to the electron capture detector, e.g., molecules containing C=O, NO_2, S, P, and halogens. Formation of positive secondary ions involve proton transfer and solvation and is expected of species containing O, S, and P. Hydrocarbons are not expected to respond much in either mode. Such charge transfer reactions involve energies less than 0.1 eV[2]. It seems we must expect a variety of responses and response factors. Cram and Chesler[19] found some Freons to differ in response by a factor of 280. Indeed, a solute will generally show a response superior in one mode compared to that in the other[6].

GNO promotional literature describes electron transfer. The O_2^- induces a field in a neutral but electronegative molecule and establishes an attractive force. The primary ion exchanges the

electron with the neutral sample molecule over a relatively large distance so the sample has a relatively large collision cross section. This seems to us to be a superior alternate to saying that ion-molecule/molecule collisions are more frequent than molecule/molecule collisions at the same pressure and temperature.

Threshold Amount and Lower Limit of Detection:

We take the term *response* to include all of the following: The *lower limit of detection* is the smallest amount or concentration of a solute which can be detected by the total analytical system. The *threshold amount* is that amount or concentration at which the signal for the presence of the sample material can be distinguished from the signal when no material is present, i.e., when the signal is distinguishable from the baseline. These two quantities are not necessarily identical. The first asks if there is any signal at all; the second asks at what point the signal begins. *Sensitivity* is the rate of change of signal intensity with respect to the amount or concentration of the sample.

Lower limits of detection have generally been reported as approximate values and are quite impressive but to us seem to imply "we've seen as little as this but we really don't know how little we could see at optimum conditions because we don't know what these conditions are". An early GNO suggestion was that sample ion-molecule response be stated in terms of the fraction of the total current carried by the ion-molecules. It is not stated if this is the current in the reaction chamber or in the drift tube which would be important if this fraction is itself a function of the total current. The current seen by the sensing electrode is that in the drift tube and this depends upon the width of the admitting gate. It seems reasonable that this gate could be reduced to a point where a peak carrying *all* of the ion-molecules or the total current could barely be seen. Responses ought to depend upon the gate width. Intuitively the current in the drift tube can be increased by increasing the gate width. This, however, would broaden the narrow initial zone desired in chromatography and impair resolution. Responses will also depend upon the read-out

system. For the same gate width the PC-os combination is inferior to the PC-mg which, in turn, is inferior to the PC-sac[1,23].

Cohen and Karasek[2] give a "first" calculation of threshold amounts. They assume a bimolecular reaction between R^-, the charged reactant ion, and P, the uncharged neutral sample molecule, to produce the uncharged reactant, R, and the charged sample ion-molecule, P^-.

$$R^- + P \rightarrow R + P^- \tag{13}$$

Letting

n_P = concentration of charged P^-

n_R = concentration of charged R^-

N = concentration of uncharged P

they write

$$dn_P/dt = -(dn_R/dt) = KNn_R \tag{14}$$

where K is the bimolecular reaction rate constant. They evidently assume that $N >> n_R$ because their subsequent equations can only come from psuedo first order kinetics. Their integrals are

$$n_R = {}_on_Re^{-KNt} \tag{15}$$

and

$$n_P = {}_on_R[1 - e^{-KNt}] \tag{16}$$

${}_on_R = n_R$ at t = 0, the reactant ion concentration before sample injection. This is a threshold calculation because a lower limit of detection calculation would assume that $n_R >> N$. They expand the exponential of eqn (16) and ignore higher order terms for small t where $n_P \leq 0.1\ {}_on_R$, i.e., product ions are formed very swiftly. This seems valid. Then

$$n_P = {}_on_RKNt \tag{17}$$

They assume that the reaction chamber or beam is 5 cm in length and 1 cm^2 in cross section and that N is uniform throughout this region. This is valid if N is large. They write

$${}_on_R = j/ev \tag{18}$$

where j = current density taken as 10^{-9} amp/cm^2. Since this is the number quoted for the current in the reaction chamber it has little

to do with what is sensed at the terminus of the drift tube. The electronic charge is e and v is the ion velocity taken as 10^3 cm/sec as representative of the fields used. This incidently gives them a time of flight of 0.005 sec across the reaction chamber. Thus ${}_on_R \sim 10^7$ ions/cm^3. They take the reaction rate constant to be 10^{-9} cm^3/molecule-sec as typical of charge transfer and represents a charge transfer occurring every other collision of the ion and the proper molecule. They assume that a reasonable minimum threshold signal is $n_p/{}_on_R = 0.01$ which we take as equivalent to saying that the sample molecules carry 0.01 of the total current. A more optimistic estimate is that a detectable signal is generated if 0.1 per cent of the total current is carried by the product ion-molecules[5]. From this they calculate that $N \sim 10^9$ molecules/cm^3 which corresponds to 10^{-10} mole fraction; 10^{-12} gm/cm^3 and a total of 10^{-11} gm in a volume of 5 cm^3 for a molecular weight of 100 at 100°C for a *threshold* signal.

The numerical results are impressive but their foundation is not. The drift tube is the detector, not the reaction tube. A threshold signal is calculated, not the lower limit of detection, for an irreversible pseudo first order (large sample) reaction which rapidly produces a single secondary ion species. The favorable reaction rate constant contains the activation energy and hence part of the response factor. A reaction rate where charge exchange happens every second collision in a tube where 10^8 collisions[5] occur is bound to yield impressive results. More sophisticated calculations are required.

A variety of numbers (all in mole parts) are in the literature. In general, GNO brochures claim 10^{-11} and 20 x the response of the electron capture detector for electronegative compounds. On the basis of our experience, the PC-sac is very much superior to the flame ionization detector[19,23]. Karasek[1] states < 0.1 ppb. Dimethylsulfoxide[5] is detectable at 10^{-11} and at 2 x 10^{-12} if the signal is integrated[1]. In the negative mode 1,3,6,8-tetrachloro-dibenzo-p-dioxin is detected in a 1 µl solution of benzene containing 1.5 x 10^{-14} moles[24]. Detection of compounds containing

$-NO_2$ and $-NO_3$ is claimed[5] at 10^{-11}. GNO literature claims 5 x 10^{-11} for nitrobenzene, 10^{-11} for trinitrotoluene, 2 x 10^{-11} for celestolide and carbon tetrachloride, and 4 x 10^{-11} for Aldrin, all in the negative mode.

Horning *et al*[13] state some interesting numbers which we will not quote because they used the reaction chamber as an ionization chamber for a more conventional mass spectrometer and did not do plasma chromatography.

The Plasmagram:

We will discuss the read-out prior to sampling techniques because the latter requires an appreciation of the former.

Figure 4 is an ideal but real result taken from GNO promotional literature. It is a composite of results based on experiments performed by GNO laboratories and by Karasek and Keller[23]. The initial four scans in the foreground are of the reactant ions. When the sample is introduced (fifth scan) product ions begin to form and reactant ions are depleted. This continues even to the point where reactant ions vanish. As the sample is depleted in the

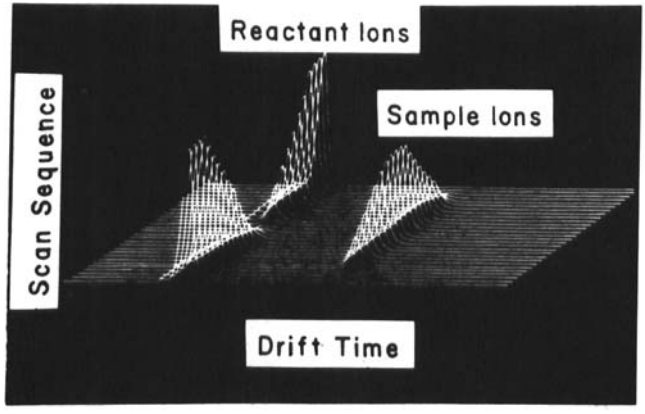

FIGURE 4

Composite of Successive Plasmagrams of Musk Ambrette
(Courtesy of Franklin GNO Corporation,
West Palm Beach, Florida)

injection and reaction chambers, product ions decrease and reactant ions reappear. Finally the reactant ions are completely recovered and product ions vanish. Carroll[24] expressed this change as

$$A_P = {}_oA_R(1 - e^{-Kc}) \tag{19}$$

where

A_P = product ion peak area

${}_oA_R$ = original reactant ion peak area

K = calibration constant

c = sample concentration

When $Kc > 2$, the response is saturated.

Several points must be kept in mind when considering these results.

In all of the PC results examined in this paper, sample purity has never been examined by an independent method of established superior response. We may, in fact, be dealing with one of the best ultratrace detectors available. A sample judged pure by the best gas chromatographic technique with flame ionization may still be impure by PC standards. *It is best assumed that all "single component" samples are contaminated, i.e., that they are mixtures.* As is the case in all trace analysis, the preparation and calibration of trace standards is a major problem.

It is an axiom of analytical chemistry that the sample analyzed must represent the source. In terms of the PC this means that the ion pulses reaching the sensing electrode should represent the qualitative and quantitative composition of the sample taken from its container for analysis. Such assurance cannot be given at this time. Ideally this condition is best met by sampling a uniform mixture of gases from a wall-less container and performing the analyses in a wall-less PC. The reader may judge how divergent practice is from this ideal. As a rule in trace analysis where adsorptive surfaces contact the sample, the integrity of the sampling decreases as the surface to sample size ratio increases.

With the PC the surface is at least the sum of the surfaces of the injection device, the inlet tube, and the reaction chamber.

Secondary sample ion-molecules are produced by interaction with primary reactant ions. Very often samples are inadvertently taken which are sufficiently large to consume all of the primary ions and they vanish from the spectrum. The ionizing source produces a fixed concentration of primary ions, ${}_{o}n_{R}$. On sample introduction this fixed amount of charge is distributed between unused primary ions of concentration n_R and sample ion-molecules of concentration n_p. Conditions require[2]

$$ {}_{o}n_{R} = n_{R} + n_{p} \tag{20} $$

When reactant ions just vanish and beyond

$$ {}_{o}n_{R} = n_{p} \tag{21} $$

and since ${}_{o}n_{p}$ is fixed, n_p is fixed *regardless of increasing sample size*. This sets a severe limitation on quantitative work and there must be consideration of an upper limit to sample size. A consequence of this charge conservation is that the total area under all peaks of a plasmagram should be fixed. It has been common practice to inject an overly large sample and observe the reactant ions vanish. It is, in fact, nearly impossible to avoid this particularly on the first injection of a new material. Varying degress of instability are observed[9,10]. Karasek and Kane[10] noted this initial instability and did not record scans until the reactant ions began to reappear. They strongly urge that only spectra taken under such conditions are reliable. Figure 5[10] is a series of scans of the PC-mg of 1-octanol. Injection of this sample is discussed later. The bottom scan shows the first reappearance of reactant ions and at least five sample peaks. We note that the reactant peak is regained largely at the expense of the large drift time peak while the major small drift time peak remains relatively constant (see product ion-molecule species). It is also very important to note that peak heights and areas change in time but *not in position*. Such a plasmagram is fairly common and acceptable, i.e., one can live with it. We confess

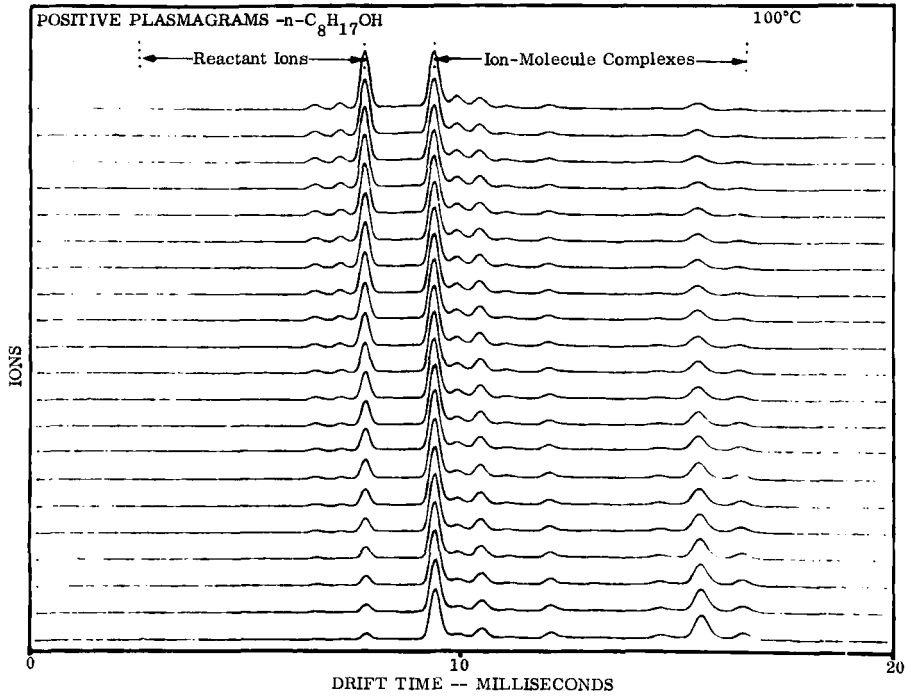

FIGURE 5

Successive PC-mg Scans of 1-Octanol[10]
(Courtesy of *Journal of Chromatographic Science*)

that our own work[20] with diethyl ether, di-n-propyl ether, and di-n-butyl ether has confused the situation. Figure 6[20] is a PC-os series of scans of di-n-propyl ether using a 0.2 µl sample which now seems a bit much. First one notes 1 peak at 5 sec, 2 peaks at 10 sec, 3 peaks at 15 sec, 2 peaks at 310 sec, 1 peak at 760 sec, and 1 peak at 1060 sec where reactant species begin to reappear. A 2 min PC-mg scan would yield something similar to the scan at 20 and 230 sec. The apparent peak drift was given several possible explanations. The peaks may be envelopes of unresolved species with fixed drift times but changing intensities so the resultant envelope changes in position. These multiple peaks

which contribute to the envelope may be due to impurities which are discernable because of the large sample size and which desorb from surfaces at different rates. The drifting peaks might also represent reversible interacting ion-molecule species in the drift tube so some peaks are the resultant of fast transitions. The authors note that for the same sample size the reactant species reappear at vastly different times: 10 sec for diethyl ether, 17.7 min for

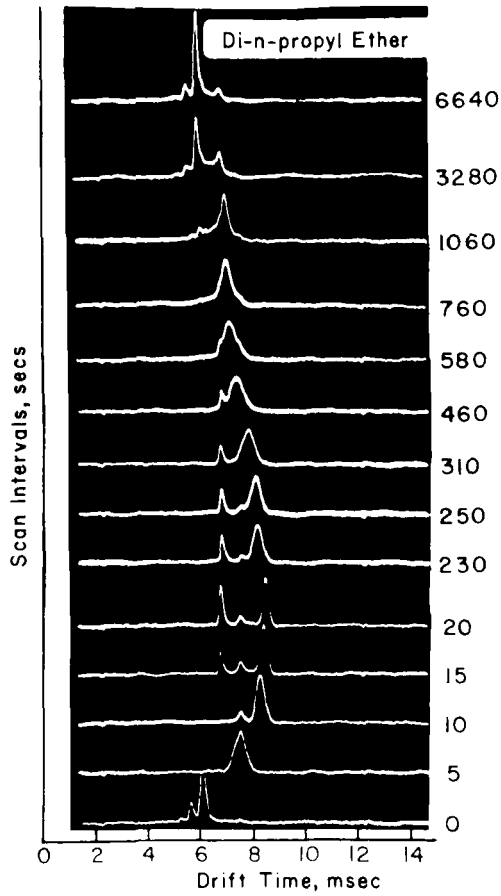

FIGURE 6

Successive PC-os Scans of Di-n-Propyl Ether[20]
(Courtesy of *Journal of Chromatographic Science*)

di-n-propyl ether, and 36.7 min for di-n-butyl ether. When this occurs the remaining major peak shows little correlation of the molecular weight of the ether used and the drift time: in order, 7.9 msec, 6.9 msec, and 7.7 msec. Cram[25] in a very recent investigation using two of the same ether samples of Metro and Keller and a different PC-sac of GNO laboratories verified the results of Metro and Keller for large samples but achieved stable ether spectra by a sampling technique which injected a sample sufficiently small that reactant ion-molecule species never vanished. The problem of sampling must be clarified.

Sampling:

GNO[5] advises that the sample should be introduced into the carrier or into diluent gas and then into the carrier in such a manner that its concentration does not exceed 1 ppm and for most materials should remain below 1 ppb. This will yield the highest resolution and avoid "clustered" ion-molecules (see sample species). High sample concentrations give broadened peaks, tails, and multiple peaks. Direct liquid sampling gives overloading. At low concentrations, wall effects become serious[13]. The sample will act as a low resolution gas chromatograph in the reaction chamber. The solute concentration in the tube will show a slow rise-time pulse and be eluted from the chamber as a tailing concentration profile. Wall effects are reduced by heating the SIFAD tube to several hundred C°. This increases the solute vapor pressure and reduces wall effects by several orders of magnitude. Cram and Chesler[19] feel that it is essential that all grids and surfaces be silylated to decrease sample clearing time and reduce the lower limit of detection. They did this by repeated injections of 1 µl of hexamethyldisilizane followed by several hours of baking out. This decreased the clearing time of dimethylformamide from 10 to 3 sec and of chlorinated alkanes from 40 to 5 sec. The response to dimethylsulfoxide was improved by a factor of 50. Horning, *et al*[13] found it difficult to remove traces of pyridine and the silylating reagent from the reaction chamber. Even then it required 10 to 20 sec for nonadsorptive 2,6-dimethyl-γ-pyrone to clear the

reaction chamber. Subsequent solvent injections gave responses thought to be due to flushing the pyrone from prior samples from the walls of the assembly. Some fear of disproportionation reactions with the alkyl umbrella of the silylated tube have been expressed[20].

Most PC results have dealt with single components. Separations deal with mixtures and with them we must fear selective adsorption of the components by the surface to give a vapor concentration in the reaction tube different from the sample composition, e.g., the different clearing times of the ethers. The vapor composition and the rate of release from the surface will depend upon sample composition, adsorption coefficients, and the temperature. This will also apply to impure "single" components.

When walls are contaminated, bake-out procedures are advised. GNO[5] advises bake-out at 350°C at 10^{-6} torr with a liquid nitrogen trapped diffusion pump or at 10^{-3} torr with a molecular sieve trapped roughing pump for 8 to 12 hr. Horning *et al*[13] and Griffin *et al*[17] could get consistent and reproducible background spectra by baking out the reaction chamber at 300°C with carrier gas flowing overnight. Persistent samples required 300°C at 10^{-7} torr. Cram and Chesler[19] reproduced reactant spectra by heating at 100°C above the operating temperature for 3 or more days. Karasek, Cohen, and Carroll[14] employed an overnight bake-out at 290°C at 10^{-6} torr.

GNO suggests cleaning a wire by flaming to red heat in ambient air and cooling to near room temperature but while still warm placing it in the vapor above the sample (head space sampling) and allowing it to cool there. The wire is then inserted in the hot sample inlet of the PC. This seems unsuitable for mixtures. The vapor composition above a liquid mixture will depend upon its composition and the vapor pressure of the components. The amount condensed or adsorbed on the wire will depend upon the vapor composition and the adsorption coefficients of the components on the wire. Desorption or vaporization from the wire will depend upon the same factors. This hardly seems a responsible way of sampling mixtures. Another method is to use a solution of the

sample in nanograde benzene and using a syringe to extrude 1 μl onto the beveled tip of a wire in a stream of warm air. This manipulation is done with the aid of a 10X binocular microscope. A solvent blank is necessary. Quantitation is claimed by using sample solutions of increasing concentration of picog/μl. Such sampling was used in some of the studies of Cram and Chesler[19] and Karasek and Keller[23].

Karasek[9] placed a small crystal (< 0.1 mg) of his individual polychlorinated biphenyls in a glass sample tube which was simply a closed end tube with no needle orifice over the inlet tube and heated it slowly until there was a response. The sample tube was quickly removed and replaced with a clean empty tube. Samples had to be < 1 ppm to avoid saturating the instrument. Plasmagrams stabilized after about 30 min and *several hours of data taking were possible* (our italics). Maximum sampling temperatures ranged from 25 to 120°C depending upon the biphenyl dealt with. The authors presumed that during data taking the major source of sample was from desorption of the biphenyl from the inlet surfaces. Concentrations were estimated at 1 ppb during data accumulation. This procedure was used by Karasek, Kilpatrick, and Cohen[6] for benzoic acid and naphthalene.

Horning *et al*[13] and Griffin *et al*[17] placed a 1/8 in Swagelock elbow at the carrier gas inlet so arranged that sample could be injected into the elbow by a syringe through a septum. The elbow was heated by an aluminum block and a 100 W cartridge heater. The stainless steel carrier line between the elbow and the inlet was heated with a tape to a temperature higher than the drift tube to avoid condensation. Microgram samples of liquid or solid were placed in the elbow and heated until there was a substantial reduction in background ion spectra. A relative constant level of sample was maintained in the carrier by the stable block temperature. Quantitative evaluation of the response was not possible. This system has some distinct advantages. Firstly, the reactant species do not initially vanish to reappear at some much later time. Secondly, the sample is not introduced as a pulse but

at a steady state level. Steady state injection deserves more study.

Karasek, Kilpatrick, and Cohen[6] injected very dilute water solutions of acetophenone, phenethyl alcohol, and salicylaldehyde by a μl syringe. Data could be taken for several hours. For moderately volatile liquids, a glass rod wet with the liquid and inserted into the sample inlet tube for 3 to 5 sec was sufficient.

Another common method is to fill a 1 μl syringe with liquid, expell the sample, pull the syringe plunger back, and inject the vapor remaining. Karasek and Tatone[7] used about 0.1 μl of vapor of the monohalogenated benzenes. The sample, estimated at 1 ppm to less than 1 ppb, was sufficient for 15 to 30 min of data taking. Using ∿ 0.8 μl of vapors of n-alkyl alcohols, Karasek and Kane[10] collected PC data for well over an hour. Karasek, Cohen, and Carroll[14] working with 1-octanol and 1-nonanol wet the barrel of a 5 cc gas tight syringe, back filled it several times with dry nitrogen, allowed the syringe to come to equilibrium, and drove the vapor into the inlet by a syringe pump at 10 μl/min. This probably approximated steady state injection.

Cram and co-workers[25] used a heated 1 l flask through which carrier gas was continuously passed. A sample of 1 μl of each ether was injected into the flask and a pulse of vapor admitted to the sample tube by turning a 3-way valve. By waiting some minutes before injection the ether vapor concentration could be reduced so the reactant species were still present in the first scan.

With the exception of the group at Baylor[13,17] and Cram[25], samples were sufficiently large to saturate the instrument and some time elapsed before reactants reappeared[6,10], whereupon spectra were taken. The extreme case was the study of Metro and Keller[20] who injected 0.2 μl of liquid.

Cohen and Karasek[2] did some preliminary calculations of the potential of interfacing the PC with a gas chromatograph. First treating a conventional packed column, they assumed a 1 μl sample of a solution of 10 components of 10^{-5} g each at a flowrate of

40 ml/min to give a 10 min chromatogram and a solute peak width of 30 sec. For a molecular weight of 100, there would be 10^{-7} moles of solute in each 10 ml (10^{-3} moles) peak volume of nitrogen carrier or a mole fraction of 10^{-4} of solute. For a PC response of 10^{-8} to 10^{-12} mole fraction, a reduction of 10^{-4} of the solute concentration in the effluent would be required. They suggested two cascaded 100:1 splitters with dry carrier at 100 ml/min added between them to provide adequate gas flow. At the exit of the second splitter each peak would contain 10^{-9} g of solute in 1 ml/min of carrier. Carrier at 200 ml/min is added to sweep material into the PC. The concentration would now be 10^{-11} g/cm^3 or 5 x 10^{-10} moles. They then consider a conventional open tubular column and a 100 component sample of 10^{-6} g each. A 100:1 inlet splitter would admit 10^{-8} g to the column. At a flowrate of 5 ml/min and 100 min for the 100 peaks, each would elute in 30 sec bands in 2.5 ml of gas. Gas is added at 100 ml/min and into another 100:1 splitter to give 10^{-10} g in 1 ml/min for injection into the PC. More gas at 100 ml/min is added to give a sample of 2 x 10^{-10} mole fraction. Feasibility of interfacing seems acceptable. No experiments were performed which is too bad because the rapidity of solute appearance in the effluent must be matched with solute clearing time from the PC. This seems to be the critical experience needed.

Cram and Chesler[19] and Karasek and Keller[23] interfaced a gas chromatograph with a conventional packed column with a flame ionization detector, FID, and a PC-sac. The effluent from the column was split to the FID and PC. The stream to the PC was led through 18 in of 1/8 in OD clean and silylated stainless steel tube terminating with a 2 in No 25 hypodermic syringe needle in the sample orifice of the PC. This tube volume was 5 cm^3. The PC response appeared 10 sec after the FID response. Karasek and Keller used a 2:1 FID/PC split with 0.1 µl samples of a benzene solution of 100 nanog of musk ambrette per µl. The FID response was neary the 2:1 signal to noise ratio while the PC response was vastly larger and no where near such a limit. Cram and Chesler

used a 3:2 split with 0.1 µl samples of the Freons. Clearing time was not a serious problem.

We distinguish two sampling modes at two levels. *Pulse sampling* is the rapid injection of a limited amount of material into the PC where the sample encounters pristine surface. Components of a mixture will adsorb and desorb from the surface which in our viewpoint will lead to a constantly changing vapor composition in the reaction chamber. *Continuous* or *steady state sampling* is the slow injection of the sample over an extended period of time so the surfaces reach an equilibrium with the vapor mixture.

Overload involves sample sizes which completely depletes the reactant ions. For lack of a better term, an *appropriate sample* is one which never depletes the reactants.

Pulse sampling with overload, as done by Metro and Keller, seems bad. Most sampling has been done this way to one degree or another but very few times with deliberate mixtures. Cram performed pulse sampling with an appropriate sample using a pure substance. Adsorption could well alter the vapor composition of a vapor mixture so that a minor component is lost. Continuous sampling with an overload has not been performed with a substance or a mixture. Continuous sampling with an appropriate sample has been done by the Baylor group but not extensively with deliberate mixtures and in one case, not with a PC. We currently vote for this last method.

Product Ion Species:

The charged species in the reaction chamber consists of reactant and secondary ions, or in case of too large a sample, of product ions only. This mixture is what is admitted to the drift region[5]. As either the concentration or reactivity of the sample species increases, higher molecular weight secondary ion-molecule complexes containing the trace molecules will appear[6,7]. A similar effect is found in chemical ionization mass spectrometry[6]. The plasmagram reflects the relative reactivity between the reactant ions and the sample[6]. Karasek and Kane[10] state: "Since the plasmagram patterns are quite dependent upon temperature and concentration, when this technique is used for identification

the temperature must be carefully selected, some indication of concentration should be available, and *the sample should be a single component* (our italics)". We here examine the import of this problem because it will largely determine the future of the method as a separation-identification technique.

Griffin *et al*[17] write the following suggestions for reaction of a sample, M, with reactant ions. Which occurs and to what extent will depend upon Lewis acid/base strengths.

$$(H_2O)H^+ + M \rightarrow MH^+ + H_2O \quad (22)$$

$$(H_2O)NO^+ + M \rightarrow MH^+ + HNO_2 \quad (23)$$

$$(H_2O)H^+ + M + N_2 \rightarrow M(H_2O)H^+ + N_2 \quad (24)$$

$$MH^+ + H_2O + N_2 \rightarrow M(H_2O)H^+ + N_2 \quad (25)$$

$$MH^+ + M + N_2 \rightarrow M_2H^+ + N_2 \quad (26)$$

Working with dimethylsulfoxide, DMSO, and using a coupled mass spectrometer Karasek[1] and Cohen and Karasek[2] report reactants $(H_2O)H^+$ and $(H_2O)_2H^+$ only at 10^{-12} parts DMSO; both reactants and $(DMSO)H^+$ at 10^{-10} parts; both reactants and $(DMSO)H^+$ and $(DMSO)_2H^+$ at 10^{-8} parts; and no reactants and $(DMSO)_2H^+$ only at 10^{-6} parts. This was in air at 760 torr and 150°C. In the negative mode at 200°C, reactants O_2^-, $(H_2O)O_2^-$, CO_3^-, and CO_4^- only at 10^{-12} parts DMSO; and CO_3^-, CO_4^-, $(DMSO)O^-$ and $(DMSO)O_2^-$ at 10^{-7} parts DMSO.

Karasek, Kilpatrick, and Cohen[6] worked with a series of functionally different compounds and identified secondary ions from a mass-drift time calibration. In general they found a strong reactant peak and a single product peak at low concentrations. In summary:

Benzoic acid: $(H_2O)_2H^+$, $C_7H_6O_2(H_2O)H^+$, and an unidentified low broad peak; two major peaks, $C_7H_6O_2^-$ and $C_7H_6O_2(H_2O)_3O_2^-$ plus 5 minor peaks at low concentration; two major peaks, $C_7H_6O_2^-$ and $(C_7H_6O_2)_2(H_2O)O_2^-$ plus 4 minor peaks at high concentration.

Salicylaldehyde: $(H_2O)_2H^+$, $C_7H_6O_2(H_2O)_2H^+$ plus 2 unidentified minor peaks; $C_7H_6O_2^-$, $C_7H_6O_2(H_2O)O_2^-$ plus minor peaks.

Naphthalene: no reactants, $C_{10}H_8(H_2O)_2H^+$ plus an unidentified minor peak; $(H_2O)O_2^-$ plus three unidentified minor peaks.
Acetophenone: $(H_2O)_2H^+$ and $C_8H_8O(H_2O)_3H^+$ at low concentration; $(C_8H_8O)_2(H_2O)H^+$ and $(C_8H_8O)_4(H_2O)H^+$ at high concentration.
Phenethyl alcohol: $(H_2O)_3H^+$, $C_8H_{10}O(H_2O)_3H^+$ and $(C_8H_{10}O)H^+$ at low concentrations; $C_8H_{10}O(H_2O)_3H^+$, $(C_8H_{10}O)_2H^+$, and $(C_8H_{10}O)_3(H_2O)H^+$ at high concentrations.
The authors suggest that benzoic acid forms complexes with $(H_2O)H^+$, salicylaldehyde and naphthalene with $(H_2O)_2H^+$, and acetophenone and phenethyl alcohol with $(H_2O)_3H^+$. Some species gave stronger responses in one mode than in the other.

In the positive mode 1-octanol and 1-nonanol each gave 8 distinct peaks[14]. Only the major peaks were examined with the mass spectrometer. The negative species were identified as clusters with oxygen. A subsequent publication[10] dealing with ethanol, 1-butanol, 1-hexanol, and 1-octanol in the positive mode with nitrogen and in the negative mode with air at 22, 55, and 100°C identified the clusters as $(ROH)_m(H_2O)_nH^+$ and $(ROH)_nO_2^-$. At high concentrations the multiple alcohol clusters were more abundant (see Figure 5). The positive mode spectra were complex: EtOH, 2 peaks; 1-BuOH, 5 peaks; 1-HexOH, 4 peaks plus minors and shoulders; 1-OctOH, 6 peaks.

Karasek[15] reports the following for aluminum trihexafluoroacetylacetone as found by Cram (unpublished): $[Al(HFA)_3]H^+$, $[Al(HFA)_3]_2H^+$, and $[Al(HFA)_3]_4H^+$.

Karasek[9] found that the polychlorinated biphenyls gave relatively simple spectra and did not form clusters. A mass-drift time curve was used. With low chlorine content the positive mode gave superior response; with high chlorine content, the negative mode was superior. This correlated well with electron capture detector responses.
4-Chlorobiphenyl: $(C_{12}H_9Cl)(H_2O)H^+$, no negative species.
4,4'-Dichlorobiphenyl: $(C_{12}H_8Cl_2)H^+$, no negative species.
2,3,4,5-Tetrachlorobiphenyl: no positive species, $(C_{12}H_6Cl_4)^-$.

2,2',4,4',6,6'-Hexachlorobiphenyl: no positive species, $(C_{12}H_4Cl_6)^-$.
2,2',3,3',4,4',6,6'-Octachlorobiphenyl: $(C_{12}H_2Cl_8)(H_2O)H^+$, $(C_{12}H_2Cl_8)^-$.
Decachlorobiphenyl: $(C_{12}Cl_{10})(H_2O)_2H^+$, $(C_{12}Cl_{10})O_2^-$.

Carroll[24] seems to have been the first to report *fragments* as another product. Working with the chlorodibenzo-p-dioxins, three different compounds gave a characteristic peak of ions of about one-half the mass of the sample molecule as well as an ion-molecule peak of about the same mass as the sample. This was not observed with dibenzofuran, chlorinated pesticides and chlorinated biphenyls. The negative mode was more responsive.

The halogenated benzenes except the fluorides also show fragmentation[7]. The appearance potential of F^- is 3.9 to 20 eV which is well above thermal energies. Appearance potential for the other halogens range from 0 to 0.1 eV.
Fluoride: $(C_6H_5F)H^+$, $(C_6H_5F)_2H^+$.
Chloride: $(C_6H_5Cl)H^+$, $(C_6H_5Cl)_2H^+$, Cl^-.
Bromide: $(C_6H_5Br)H^+$, $(C_6H_5Br)_2H^+$, Br^-.
Iodide: $(C_6H_5I)H^+$, $(C_6H_5I)_2H^+$, I^-.
Carbon tetrachloride yields Cl^-; n-butyl chloride yields Cl^- and $C_4H_9Cl^-$. A mass-drift curve was used.

Dihalogenated benzenes[12] show dissociation in the order I > Br > Cl, e.g., o-Cl,Br-benzene yields Br^-, etc. Chlorinated toluene and two biphenyls are reported to give Cl^-. Nitrobenzene is reported to show non-dissociative electron capture below 0.03 eV and dissociation to NO_2^- above 1.0 eV. Nitrobenzene gave $C_6H_5NO_2^-$ and $(C_6H_5NO_2)H^+$. Chloronitrobenzene gave Cl^-, $C_6H_4NO_2^-$ and $C_6H_4ClNO_2^-$.

Cram and Chesler[19] found Cl^- to be split off without detection of the positive fragment. Karasek also reports no corresponding positive fragment. They indicated that the Freons underwent cleavage at the ether linkage and suggested fragmentation and recombination could occur as well as solvation.

MIXTURES

Separations deal with mixtures. Unfortunately there is little experience with deliberate mixtures. If this paper serves any purpose it will be a warning not to equate the "chromatograph" part of the name with the famous separation power associated with chromatography.

Karasek[1] showed a plasmagram of a mixture of DMSO (2 peaks), malathion (2 peaks) and triethylphosphite (2 peaks), and a mixed peak all at concentrations less than 10^{-10} parts each. The peaks are moderately well resolved and the spectrum is simple by most standards. Insufficient data were presented to determine if the PC of the mixture was a simple composite of the individual components. Carroll[24] reported good resolution and detection of a ternary mixture of the chlorodibenzodioxins at the nanog level. The promise of separation and detection at such trace levels certainly warrents further investigation and evaluation. Karasek and Keller[23] found the plasmagram of musk ambrette and background column bleed to be independent of each other. The complexity of the plasmagrams of the alcohols and the advice that they be run only as pure individuals[10] is not promising. Cram and Chesler[19] investigated a binary mixture of Freons. In view of the fragmentation, recombination, and dimerization they suspect, they feel that the result is a complex equilibrium distribution of species which is strongly dependent upon the ratio of components. To this we add temperature. They conclude that *the plasmagram of a binary system is very difficult to interpret by itself.* We're certain that all chromatographers would consider binary mixtures as elementary. Horning *et al*[13] used benzene solutions of their solutes which we will view as mixtures. The solvent, present in the greatest proportion, reacts with the reactant ions to consume them completely and form a new set of reactant ions with the source electrons, $C_6H_6^+$ and $C_{12}H_{12}^+$. These now react with the solute

$$C_6H_6^+ + A \rightarrow A^+ + C_6H_6 \qquad (27)$$

$$C_6H_6^+ + B \rightarrow BH^+ + C_6H_5 \qquad (28)$$

The second equation was verified by using deuterated benzene. A chloroform solvent yields reactant species Cl^-, $(CHCl_3)Cl^-$, and $(CHCl_3)_2Cl^-$. The extent of interaction of components of a mixture with simple reactant species, e.g., hydrated protons, and with one another will depend upon Lewis acid/base strengths. Thus we think that the plasmagram *will not* be the sum of those of the pure components because response factors of the components in a mixture will not be the same as for the pure components. Lewis acid/base competitions between components may prove to be unique for each mixture. Mixed clusters are conceivable, e.g., $(R_1OH)_m(R_2OH)_n(H_2O)_p$. Add to this reversibly interacting species in the drift tube and admit that all of this is concentration and temperature dependent and it becomes mild to say that the situation seems grim. Much more work with mixtures is required.

IDENTIFICATION

The drift velocity is determined by the millions of collisions between the secondary ion-molecules and the neutral drift gas molecules. A steady state velocity is reached very swiftly. Drift times or mobilities are best reported in terms of the *reduced mobility*, K_o, the speed of an ion in an electric field of 1 V/cm in a gas at 273°C and 760 torr[2,5,14].

$$K_o = (1/t)(D^2/V)(p/760)(273/T) \qquad (29)$$

where

t = observed transit time at p, T, and V; sec

D = drift space distance, cm

V = potential across the drift tube, volts

p = pressure, torr

T = drift space temperature, °K

Most of the prior experience with drift times dealt with ion masses less than 50[2].

Early GNO literature promised an empirical mobility-mass correlation whereby a mass could be obtained to ± 10 per cent for an unknown species and ± 2 per cent for a homologous seris for

masses as great as 10,000. A more modest estimate of mass range was 120 to 2600 with the promise that the drift times could be replaced by a mass scale[15]. The relationship was found to be non-linear but seemed to follow the Langevin mobility equation[6,14,15] which was originally developed for simple atomic ions in gases at low pressure[6].

$$K = H(1 + M_g/M_i)^{1/2} \qquad (30)$$

where

K = mobility

M_g = mass of the gas molecule

M_i = mass of the charged particle

H = polarization factor

It quickly became apparent from data analysis that this was only true for small masses[6,14]. The Langevin equation shows a polarization mobility limit at about 100 amu whereafter there is little change in mobility with further mass increase. PC results were far more mass sensitive. Empirical curves were developed. The polychlorinated biphenyls[9] gave an excellent curve down to a mass of 100 whereupon the curve flattened so the drift time vs mass was a poor function (a mass of 50 gave a drift time of 6 msec). Correlations of 5 per cent were claimed[6]. Good correlations were noted for the monohalogenated benzenes as long as the species were of similar compositon and structure but different curves were observed for positive and negative species[7]. It finally was recognized that for an unknown molecule, the error in mass could be 20 per cent at the 1 σ confidence limit and 2 per cent for homologues[24]. No unique and general curve exists[10]. Griffin *et al*[17] put an end to the situation by pointing out that 6 different mobility curves have been published, only one of which was based on a PC interfaced with a mass spectrometer. Their careful statistical study supports a standard error of ± 18 to 20 per cent for unknown compounds and ± 2.0 per cent for polynuclear aromatics for which they used a mass spectrometer.

Ion mobility is size and mass dependent[17], i.e.,

$$K = (3e/16N)[(1/m) + (1/M)]^{1/2}(2\pi/kT)^{1/2}(1/\Omega_D) \qquad (23)$$

where

K = ion mobility

N = neutral gas molecule density, molecules/cm^3

e = charge on the ion

M = neutral molecule mass

m = ion mass

Ω_D = average collision cross section

Mass dependence appears only in M and m. The evaluation of Ω_D depends upon the nature of assumed interaction forces between the ion-molecule and neutral atoms. Cram and Chesler[19] also discuss this equation and review some points about Ω_D as it depends upon the interaction forces.

Lighter ions have K_o values which are slightly temperature dependent[10].

Thus, even if plasmagram peaks are unique, mass identification from reduced mobility is highly doubtful.

We agree with others[19], the plasma chromatograph is superior when sensitivity is desired but presently the gas chromatograph/mass spectrometer is more desirable for separation-identification problems.

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