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The Plasma Chromatograph as a Separation–Identification Technique

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Abstract

The plasma chromatograph is evaluated as a separation and identification device using binary mixtures of ketones. Discrimination of components is not encouraging and the ion–molecule spectra of a mixture is not always the sum of the spectra of the individual components.

INTRODUCTION

Operating Principle

The Plasma Chromatograph, PC (Franklin GNO Corp., PO Box 3250, West Palm Beach, Florida, 33402) is an ion-molecule/ion-drift time of flight mass spectrometer. Its construction and operation has been described (*1–4*). In brief, a pure gas, e.g., nitrogen (Ultra Pure) or air (Zero Air) of low water content (2 to 10 ppm) (*4*), is passed over a ^{63}Ni source. The emitted β-electrons produce secondary electrons and counterions by inelastic collision and are soon slowed to thermal energies. The electrons are captured by electronegative species when present in the gas. Keller and Metro (*4*) reviewed the identity of these *primary reactant ions*. They are of the general type $(H_2O)_nH^+$ and $(H_2O)_nNO^+$ for positive ions and $(H_2O)_nO_2^-$ and $(H_2O)_n(CO_2)O_2^-$ for negative ions. Others have been suggested, e.g., CO_3^-. The degree of hydration, n, and the relative amounts of each species depends upon the composition of this gas, the *carrier* or

reactant gas, particularly the water content, and the temperature of the chamber in which this occurs, the *reaction chamber*. A constant but adjustable voltage exists across this region and the following drift region. This field may be reversed so either positive or negative ions flow down the axis of the tube. Because the process occurs at atmospheric pressure, constant ion velocities are soon produced, i.e., viscous flow. The reaction chamber terminates at an electronic gate which is pulsed to admit the mixture of ion-molecules to the *drift region*. Gas, the *drift gas*, nitrogen, flows counter to the ion beam. The intent is to prevent uncharged sample molecules from entering the drift region and participating in further charge exchange with the ion-molecules. Thus only ions enter the drift region. Keller and Metro (*4*) argue that this is differential migration from a narrow zone, the gated pulse, and hence the process is a form of chromatography. Each pulse of species is sensed by an electrode at the terminus of the drift tube.

Three read-out systems are available. Another gate, which is controlled to open at an increasing and regulated delay time after the first gate, is positioned in advance of the sensing electrode. Thus each admitted pulse is scanned for a signal at a particular but different delay time. These signals are sent to an x-y recorder and a curve of current intensity vs delay time read out. Two minutes is a reasonable time to scan 20 msec. This we have abbreviated as PC-mg (moving gate). Because of the excellent GNO high speed electronics, a single pulse may be scanned with the second gate open and the signal observed on an oscilloscope, PC-os. We use a storage scope and photograph the scans. This signal may also be sent to a signal averaging computer, stored, and then displayed on an oscilloscope or an x-y recorder, PC-sac. In terms of response, in order of superiority, PC-sac > PC-mg > PC-os.

When a sample is introduced into the reaction chamber, it interacts with the reactant ion-molecules by charge transfer to produce a new set of *product* ion-molecules which are admitted to the drift region for separation.

The overwhelming attraction of the PC is its calculated and experimentally demonstrated response to 10^{-12} mole fraction of some materials (*4*). This paper will examine experience with the instrument as a separation device.

Response

The β-source produces a constant stream of ionizing electrons. Each of these produces about 10^3 secondary electrons and counterions before

they reach thermal energies. The current established in the reaction chamber is about 1.5×10^{-9} A in a 1-cm diameter beam. If ${}_0n_R$ is the concentration of reactant ions in the reaction chamber then

$$ {}_0n_R = n_R + n_P \tag{1}$$

where, after the sample is introduced, n_R is the concentration of remaining reactant ion-molecules and n_P is the concentration of sample or product ion-molecules. This is a charge conservation condition and sets an upper limit on the response. We suggest that an *appropriate sample* is one less than or just equal to a size where $n_R = 0$. Any sample above this we have termed an *overload.* Overload will occur at different sample sizes of different substances. The nature of the product ion-molecules and their relative distribution will depend upon the competitive Lewis acid/base interactions which are both temperature and concentration dependent. Cram and Chesler (*5*) found some Freons different by as much as 280 in response factors.

Sampling

Pulse sampling is the injection of a finite amount of material over a short period of time into the carrier stream. The sample encounters a large pristine adsorptive surface. Karasek (*6*) found that he could record plasmagrams of the polychlorinated biphenyls for *several hours* as the sample slowly escaped from this surface. Cram and Chesler (*5*) strongly advise silylation of the grids and glass surfaces to reduce the clearing time of the sample and improve the response.

Most experience has been with overload pulse sampling. In time, as the sample concentration drops, the reactants reappear at the expense of the product ion-molecules. Because of the charge conservation, to a first approximation, the total area under all peaks on the plasmagram should remain constant. This is not strictly true because the constant admitting gate width will admit a larger number of high velocity ion-molecules. The faster ions will account for a proportionally larger admitted current. Thus the total peak area for a population of predominantly fast ion-molecules should be greater than the total area for a population of slow ion-molecules. Peak areas will be both concentration and velocity dependent. Other time-of-flight mass spectrometers approach this problem by placing a grid ahead of the admitting gate which is pulsed just prior to opening the admitting gate. This grid mixes the various "velocity" species. The admitted pulse of ions are velocity separated only after admission to the drift region.

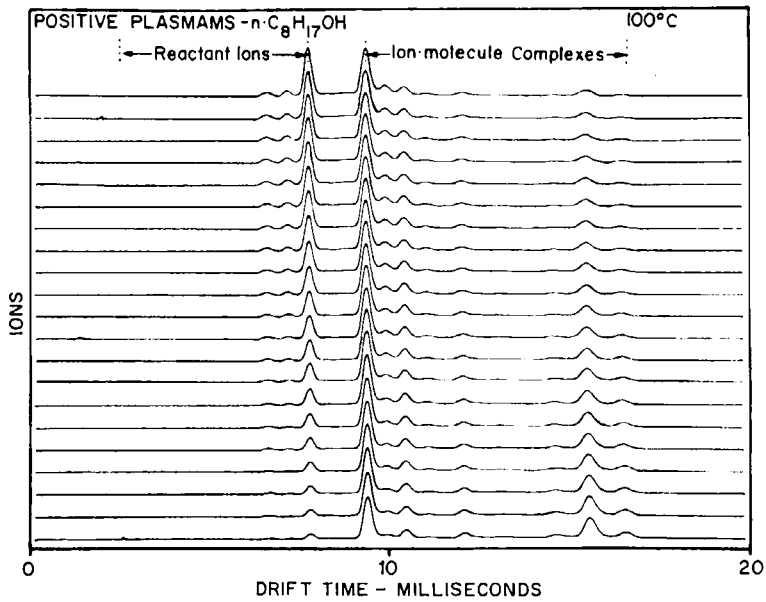

FIG. 1. Successive PC-mg scans of 1-octanol (*7*). (Courtesy of *Journal of Chromatographic Science.*)

It is advised that plasmagrams are reliable only after the reactants begin to reappear. Figure 1 is the plasmagram (PC-mg) of a 1-octanol pulse sampled at overload and recorded after reactants were apparent (*7*). It is a common and acceptable result. We note that as the reactants recover, the large drift time peak diminishes while the major peak remains fairly constant. It is important to note that peak position does not change. Figure 2 (*8*) is a PC-os scan of a severe overload pulse of di-*n*-butyl ether. The scan interval is the time (in seconds) between photographing the oscilloscope display. The instability is obvious. Results for diethyl and di-*n*-propyl ethers were similar. Reactant species reappeared after very different time periods for the three ethers, and the drift times for the product ions present at that instant showed no correlation with molecular weight. Speculating on the drifting "apparent" peak, Keller and Metro (*4*, *8*) suggested that because of the response of the PC, all samples must be considered as mixtures, and that primary component and impurities constantly change in concentration in the reaction chamber as they adsorb and desorb on the surface at different rates to give species of fixed drift

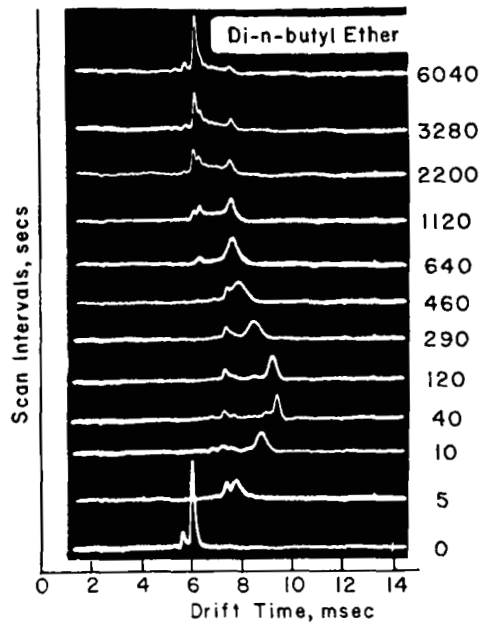

FIG. 2. PC-os scans of di-*n*-butyl ether (*8*). (Courtesy of *Journal of Chromatographic Science.*)

times but constantly changing intensities. The drifting peak could be an envelope of these poorly resolved species. There is also strong evidence (*4*) that even for reactant species the ion-molecule pulse does not contain a single species. Cram and Chesler (*5*) suggested that although neutral sample molecules are excluded from the drift region, ion-molecule reactions with materials in the drift gas could lead to continued reaction in this drift space. This could lead to further reaction, e.g., the following reactions suggested by Griffin et al. (*9*):

$$MH^+ + H_2O + N_2 \rightleftarrows M(H_2O)H^+ + N_2 \quad (2)$$

$$M_2H^+ + N_2 \rightarrow MH^+ + M + N_2 \quad (3)$$

when carrier and drift gas are identical. Metro and Keller (*8*) recalled the earlier work of Keller and Giddings (*10*) who showed that for A $\rightleftarrows$ B, where the elution times of A and B are presumed different, then if reaction rates are sufficiently fast that each molecule can undergo several transitions in the period of separation, A and B *cannot be separated* and a single zone

will elute with an elution time between those proposed for A and B. Since reaction rates are concentration dependent, overload would enhance this effect. The drifting "apparent" peak could also be due to such continued reaction.

The most clear-cut case of appropriate pulse sampling is the recent work of Cram and co-workers (*11*) with an exponential dilution flask. A heated 1 liter flask was arranged so that the carrier gas could sweep through it continuously at a temperature sufficiently high that the sample was in vapor form. The outlet was connected to a 3-way valve which could vent the sample or direct it into the PC. A quick turn of the valve sent a pulse sample to the PC. By waiting an appropriate period of time, the concentration of vapor could be reduced to the level of an appropriate sample. They used two of Metro and Keller's ether samples with a PC-sac. With overload pulse sampling they observed much the same thing as Metro and Keller; with appropriate pulse sampling they achieved stable ether spectra. Appropriate samples may simplify the plasmagrams by avoiding high molecular weight ion clusters which appear at high sample concentrations. Hopefully, a report of their work will appear soon.

An appropriate pulse sample seems superior to an overload pulse. The question of interacting species still remains but may be of reduced importance because of the low sample concentrations. There are some apprehensions about its use with mixtures. (a) The sampling flask must be at a sufficiently high temperature and adsorptive effects sufficiently moderated that the vapor composition is identical to that of the original sample and remains that way from the time of injection of the sample into the flask and the time of admitting a pulse to the PC. Because the vapor concentration is constantly reduced in the flask, it is doubtful if a reliable equilibrium period exists. (b) Although vapor/adsorbate equilibrium may exist in the dilution flask, the sample will still encounter a pristine surface in the interface between the flask and the PC injection port, injection tube, reaction chamber, and drift tube. A new equilibrium will be established which may affect the vapor composition. We fear that a highly adsorptive minor constituent can be so reduced in such a small sample that it is not seen by the PC. Elevated temperature coupled with surface deactivation, e.g., silylation, seems mandatory. (c) Cram (*11*) estimates sample sizes to be in the picog level. If the sample contains a relatively unresponsive minor constituent, it may remain undetected.

We have elected to do pulse sampling with overload with binary mixtures, where concentrations are not minor, to identify any promise as a separation-identification technique.

Steady-state or *continuous sampling* is introduction of the sample over a

sufficient period of time that equilibrium is established between adsorbate and vapor throughout the PC so the vapor composition is constant and is that of the sample. Steady-state sampling with overload has not been explored. Appropriate steady-state sampling has been approximated. Karasek and colleagues (*12*, *13*) drove alcohol vapors from a syringe slowly into the PC but seem to have terminated injection when the reactant ions vanished. Horning et al. (*14*) and Griffin et al. (*9*), using relatively nonvolatile samples, raised the temperature of the sample exposed to the carrier stream until the vapor concentration was such that reactant ions were on the point of vanishing. Unfortunately, they did not use the total PC system; only the reaction chamber as an ionization source to a vacuum mass spectrometer. Such sampling is unsuited for mixtures since the vapor composition is dependent upon the vapor pressure of the pure components and their concentration in the liquid mixture. Coffey (*15*) has perhaps come the closest. He introduced ammonia vapor at about 0.03 ppm and allowed his sample system to reach a steady state for at least 24 hr before taking data. Because of the high proton affinity of ammonia, species were exclusively $NH_4^+(H_2O)_n$.

Ideally, one requires a completely vaporized sample of very small amount and of unchanging concentration but of large total volume which can be steadily introduced over a relatively long period of time.

Product Ion Species

Unlike other chromatographic separations, a single molecular species will most likely yield more than one product ion-molecule. This is very undesirable to the separations chemist. If M is the sample species, it is possible to produce (*4*): (a) ion clusters $(M)_mH^+$, $(M)_m^-$, $(M)_mO^-$, and $(M)_mO_2^-$; (b) hydrated ion clusters $(M)_m(H_2O)_nH^+$ and $(M)_m(H_2O)_nO_2^-$; and (c) fragments, e.g., halides X^- from some halogenated aliphatics and aromatics and rupture at ether linkages with the Freons. Higher molecular weight clusters are apparent with large samples. The nature and relative distribution of the species are much dependent upon sample concentration and temperature. Add to this the strong possibility of continued reaction in the drift region, and the situation does not seem propitious. It is conceivable that mixtures (components M and N) could give mixed species $M_mN_nH^+$ and hydrates, and that fragments could recombine. Karasek and Kane (*13*) found: EtOH, 2 peaks; 1-BuOH, 5 peaks; 1-HexOH, 4 peaks; and 1-OctOH, 6 peaks. They remark that for identification purposes the temperature must be carefully selected, some indication of concentration should be available, and the samples should be a single component.

Mixtures

Unfortunately, there has been very little experience with deliberate mixtures, and mixtures are the subject of separations. Karasek (*16*) showed a relatively uncomplicated plasmagram of dimethylsulfoxide, malathion, and triethylphosphite. Carroll (*17*) reported good resolution of a 3-component mixture of chlorodibenzodioxins. Karasek and Keller (*18*) found the plasmagram of musk ambrette to be simple and independent of the solvent and of column bleed when a PC was interfaced with a gas chromatograph. Horning et al. (*14*) introduced samples as solutions, i.e., binary mixtures. The solvent, benzene or chloroform, present in excess, behaved as if it reacted directly with the source β-electrons to form a new set of reactant species to introduce a different series of Lewis acid/base interactions with the sample species. Cram and Chesler (*5*) investigated a binary mixture of Freons and concluded that a plasmagram of a binary system is very difficult to interpret by itself.

Identification

The hope that the masses of product ion-molecules could be determined from a general reduced mobility vs mass calibration curve, first established by interfacing a PC with a mass spectrometer, has proved chimerical. The very careful work of Griffin et al. (*9*) established that, for unknown compounds, the standard error in determining mass by such a curve is 20%. The situation is apparently better for members of a homologous series (2%). Masses can only be reliably determined by interfacing the PC with a mass spectrometer. It, too, is not problem-free, e.g., adiabatic expansion into a vacuum may alter species.

What remains seems to be a hope that each solute may have a relatively simple and unique plasmagram ["fingerprint" (*1*)] and that the plasmagram of a mixture is an additive sum of the plasmagrams of the components. This paper investigates that possibility using 2-butanone and 2-octanone both alone and together in deliberate mixtures to two different temperatures.

EXPERIMENTAL

Samples

The ketones were from the gas chromatographic reference compound kits prepared by Poly-Science Corp. (6366 Gross Point Road, Niles,

TABLE 1

Sample Composition

	2-Butanone		2-Octanone	
	Wt-%	Mole-%	Wt-%	Mole-%
Low temperature				
Mix 1	57.91	70.98	42.09	29.02
Mix 2	23.97	35.92	76.03	64.08
High temperature				
Mix 3	56.24	69.56	43.76	30.44
Mix 4	39.22	53.88	60.78	46.11

Illinois, 60648). Minimum purity of these references is 99.5%. Mixtures were prepared by weight in a septum-sealed sampling bottle. These were prepared and used immediately to minimize changes in composition on standing. Table 1 shows the composition.

Sampling

Samples were not introduced into the PC until the reactant ion spectrum was that associated with a clean tube. Thus at least 24 hr elapsed between experiments.

A Hamilton 1 μl syringe (7001 series) was flushed with the liquid sample 5 to 7 times, the last liquid expelled, the plunger drawn back to 0.5 μl, and the material remaining injected into the PC. This was still an overload. Presuming that the greater portion of the sample was vapor, it is highly probable that the vapor composition did not represent the solution composition. The syringe was cleaned between injections by drawing air through the heated needle for 5 min.

Data Collection

A PC-os and PC-mg scan was taken of the reactant ions. A PC-os scan was taken immediately after sample injection and this continued until the spectra showed promise of the reactant species. Thereafter PC-os and PC-mg scans were taken. We note from the PC-os scans that there was no drifting apparent peak as observed with severe overload pulse sampling of the ethers (*8*). Peak intensities changed but not drift times. Following the persistent advice that spectra are only meaningful when reactant species

begin to reappear, we considered only the PC-mg scans where reactants are apparent and show the PC-os scans immediately preceding and immediately following this PC-mg scan. The time interval from the instant of injection is shown in the figures. We report reduced mobilities (*4*) of persistent peaks. By this we mean: If a peak appears on several PC-os scans before and after the appearance of the reactant species, we report its reduced mobility even though it may appear as a minor peak on the PC-mg scan selected.

PC Conditions

Table 2 shows the PC conditions.

As with the ethers (*8*), the PC housing temperature was sensed with a Dymec Model 2081A quartz thermometer probe, insulated with glass wool, placed flush against the metal housing at the flange and bolt face.

RESULTS AND DISCUSSION

Figures 3 through 10 show the PC-mg scan where reactants just appear and the immediately preceding and following PC-os scan. The time the scans were made after sample injection are shown on the scans. The PC-mg scan times were 1.75 min. The peaks are labeled with raw drift times in milliseconds, i.e., not corrected for temperature. The advantage of the immediately following PC-os scan is that comparison of it with the PC-mg

TABLE 2

Operating Parameters for the Plasma Chromatograph

Flow rates:	
Drift gas:	Ultra pure grade nitrogen, 500 ml/min
Carrier gas:	Ultra pure grade nitrogen, 100 ml/min
Temperature:	
Carrier inlet:	138 °C
PC housing:	107–109 °C (low temperature)
	152 °C (high temperature)
Drift gas inlet:	129 °C
Voltage:	
3500 V, positive mode (collection of positive ions)	
Gates:	
PC-mg:	Admitting gate, 0.2 msec; exit gate, 0.2 msec
PC-os:	Admitting gate, 0.2 msec; exit gate, open

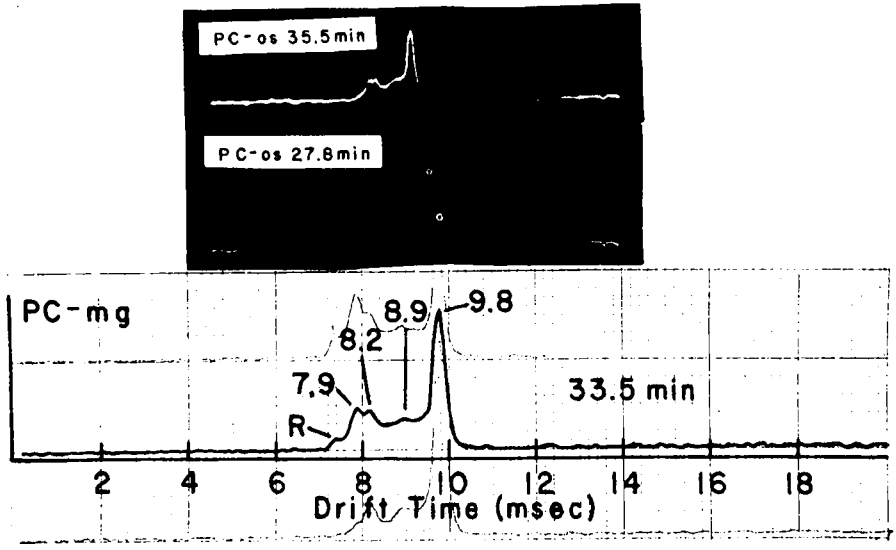

FIG. 3. PC-mg and PC-os scans of 2-butanone at low temperature (107.9°C).

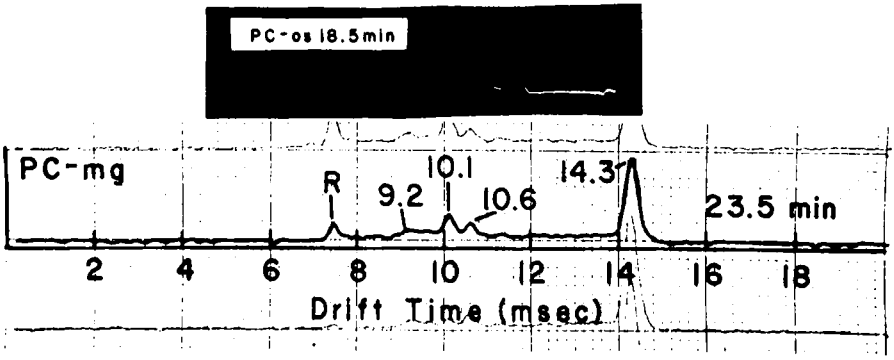

FIG. 4. PC-mg and PC-os scans of 2-octanone at low temperature (106.6°C). The PC-os scan following PC-mg is missing because of film failure.

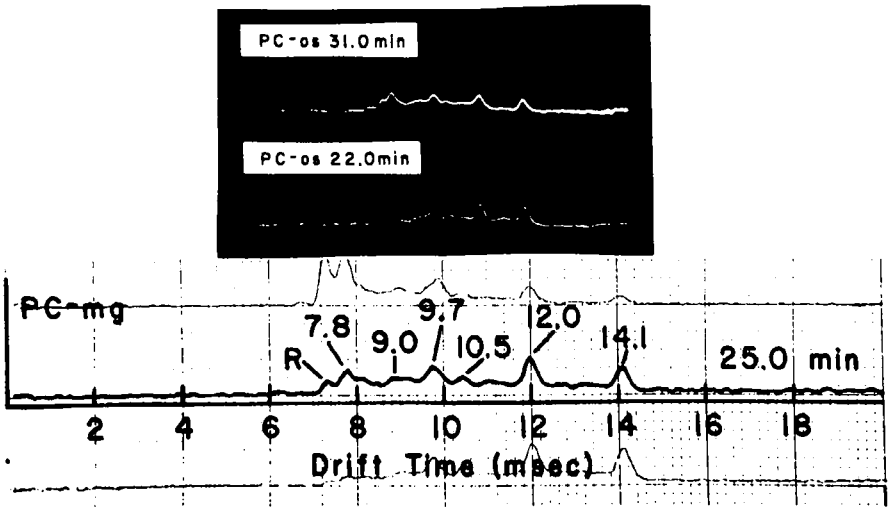

FIG. 5. PC-mg and PC-os scans of Mixture 1 (58/42 B/O) at low temperature (109.3 °C).

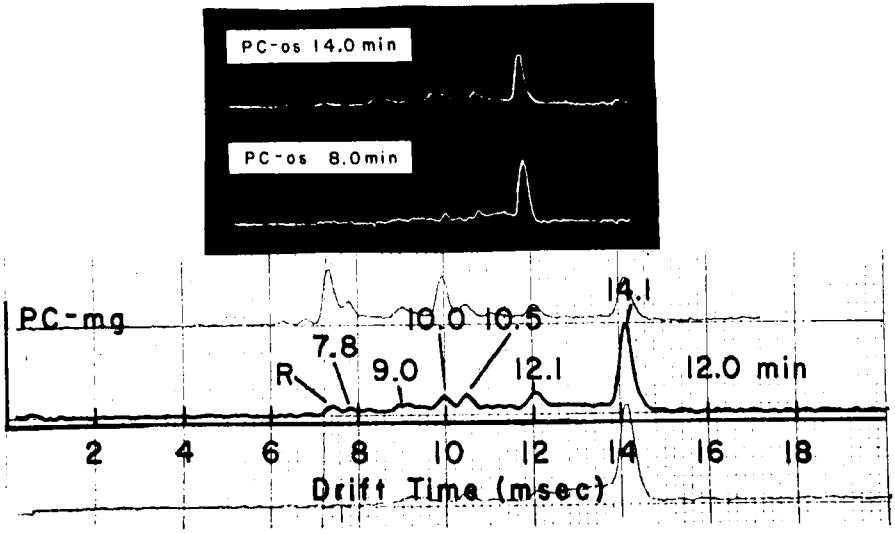

FIG. 6. PC-mg and PC-os scans of Mixture 2 (24/76 B/O) at low temperature (108.0 °C).

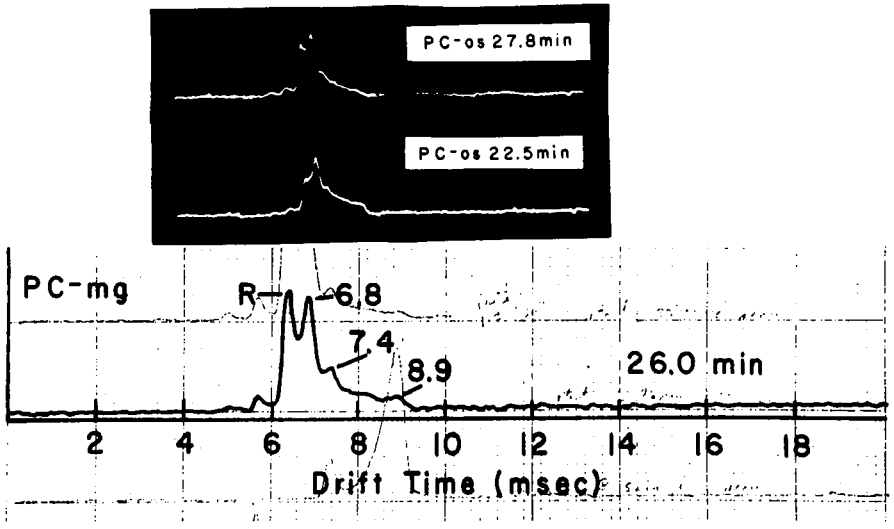

FIG. 7. PC-mg and PC-os scans of 2-butanone at high temperature (152.4°C).

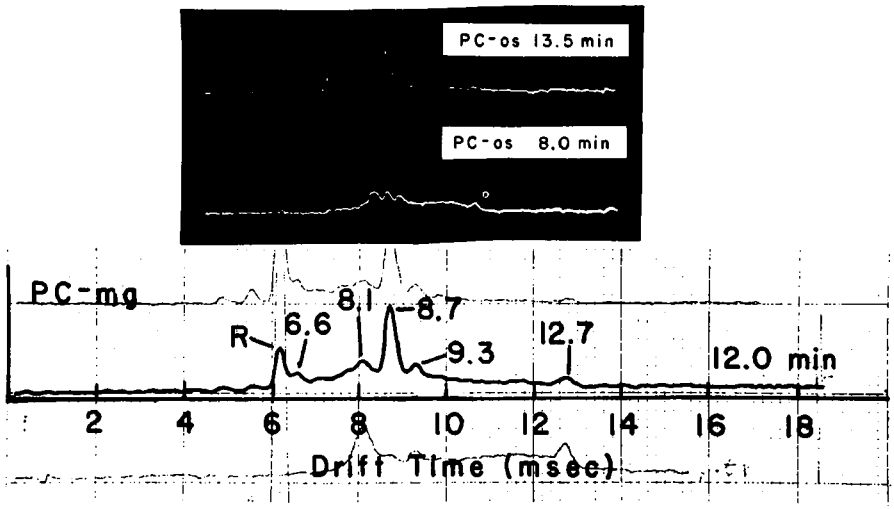

FIG. 8. PC-mg and PC-os scans of 2-octanone at high temperature (152.5°C).

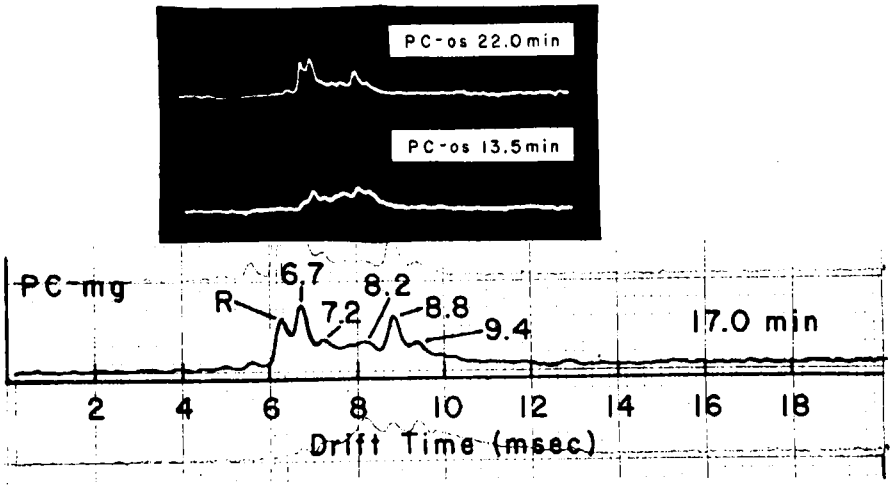

FIG. 9. PC-mg and PC-os scans of Mixture 3 (56/44 B/O) at high temperature (151.8°C).

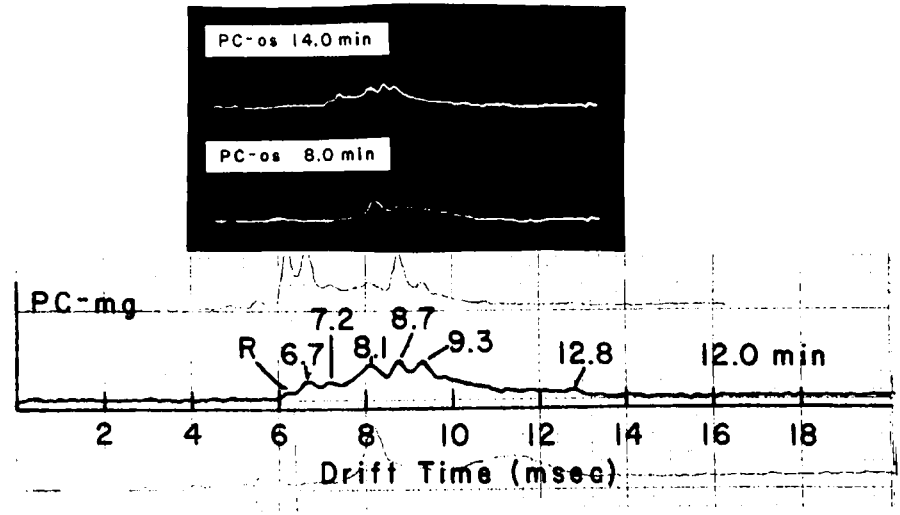

FIG. 10. PC-mg and PC-os scans of Mixture 4 (39/61 B/O) at high temperature (151.9°C).

scan detects any dramatic changes which might have taken place during the PC-mg scan time. Unlike the ethers, no such evolution occurred. In all cases the PC-mg scan is superior to the PC-os scan, which is to be expected.

Each calibration on the PC-mg scan corresponds to 0.2 msec. Because of some electronic noise, temperature difference, and slight peak shifts likely arising from the peak representing an envelope of poorly resolved species, we suggest that peaks not differing by more than 0.2 msec are due to the same component or are not definitive of the sample. Table 3 shows the raw drift times of the pure ketones and their mixtures at lower temperature. The table is arranged vertically in order of increasing drift time, and peaks of drift times within 0.2 msec are on the same horizontal line. Table 4 represents the results at the higher temperature.

TABLE 3

Low Temperature Raw Drift Times (msec)

2-Butanone, 107.9°C	2-Octanone, 106.6°C	Mix 1, 58/42 B/O, 109.3°C	Mix 2, 24/76 B/O, 108.0°C
7.9		7.8	7.8
8.2			
8.9		9.0	9.0
	9.2		
9.8		9.7	
	10.1		10.0
	10.6	10.5	10.5
		12.0	12.1
	14.3	14.1	14.1

TABLE 4

High Temperature Raw Drift Times (msec)

2-Butanone, 152.4°C	2-Octanone, 152.5°C	Mix 3, 56/44 B/O, 151.8°C	Mix 4, 39/61 B/O, 151.9°C
6.8	6.6	6.7	6.7
7.4		7.2	7.2
	8.1	8.2	8.1
8.9	8.7	8.8	8.7
	9.3	9.4	9.3
	12.7		12.8

We note in Table 3 that the 7.9 and 8.9 msec peaks for 2-butanone are definitive, i.e., they appear in both mixtures. The 9.8 msec peak is not; it appears only in the mixture where the butanone concentration is high. Likewise the 10.6 and 14.3 msec 2-octanone peaks are definitive since they appear in both mixtures. The 9.2 msec peak does not appear in either mixture, and the 10.1 msec peak appears only in the mixture of higher octanone content. Of particular interest is the 12.0 msec peak (Fig. 5 and 6) which appears in the mixture but never in either pure ketone. A careful examination of the PC-os and PC-mg scans of the pure ketones taken from the instant of injection up to and far beyond the reappearance of the reactants *show no evidence of a 12.0 msec peak for either ketone.* This peak is characteristic of the mixture and may be a mixed species as suggested earlier.

Table 4 shows that the only definitive peak for 2-butanone is the 7.4 msec peak. The 8.1 and 9.3 msec peaks are definitive for 2-octanone. The 12.7 msec peak appears only at the higher octanone concentration. There are no peaks present in the mixture which do not appear in the individual ketones. The 6.8 and 8.9 msec peaks are useless.

Our first conclusion is that "fingerprinting" is better at the lower temperature. We also conclude that the spectra of mixtures are largely the additive sum of the spectra of the components. The exception is the low temperature peak for the mixture which does not appear in the spectra of the pure components.

In order to compare results at different temperatures, we have calculated reduced mobilities, i.e., the speed of an ion in an electric field of 1 V/cm in a gas at standard conditions, by (*4*)

$$K_0 = (1/t)(D^2/V)(p/760)(273.2/T) \tag{4}$$

where t = observed transit time in seconds at p, T, and V
D = drift space distance, 5.96 cm
V = potential across the drift tube, 3500 V
p = pressure, 760 Torrs
T = drift space temperature, °K

Our results are shown in Table 5. The raw drift times are shown parantheti-cally to make it easier to compare Table 5 with Tables 3 and 4. We conclude:

1. The 0.96–0.99 cm/sec-V peaks are not useful. They appear for both ketones and two of the mixtures only at the higher temperature.
2. We feel that the 0.91–0.93 cm/sec-V peak for 2-butanone is definitive

TABLE 5

Reduced Mobilities ($\times$ 10)

2-Butanone		2-Octanone		Mix 1, 58/42 B/O, 109.3 °C	Mix 2, 24/76 B/O, 108.0 °C	Mix 3, 56/44 B/O, 151.8 °C	Mix 4, 39/61 B/O, 151.9 °C
107.9 °C	152.4 °C	106.6 °C	152.5 °C				
	9.6 (6.8)		9.9 (6.6)			9.7 (6.7)	9.7 (6.7)
9.2 (7.9)				9.3 (7.8)	9.3 (7.8)	9.1 (7.2)	9.1 (7.2)
8.9 (8.2)	8.8 (7.4)						
8.2 (8.9)				8.1 (9.0)	8.1 (9.0)		8.1 (8.1)
		7.9 (9.2)	8.0 (8.1)			8.0 (8.2)	
7.4 (9.8)	7.3 (8.9)		7.5 (8.7)	7.5 (9.7)			7.5 (8.7)
		7.2 (10.1)			7.3 (10.0)	7.4 (8.8)	
		6.9 (10.6)	7.0 (9.3)	6.9 (10.5)	6.9 (10.5)	6.9 (9.4)	7.0 (9.3)
				6.0 (12.0)	6.0 (12.1)		
		5.1 (14.3)	5.1 (12.7)	5.1 (14.1)	5.2 (14.1)		5.1 (12.8)

at both temperatures. We admit that it does not appear for the pure ketone (Fig. 7), but an examination of this figure demonstrates poor resolution at a raw drift time of 7.2 msec where the peak ought to appear.

3. The 0.88–0.89 cm/sec-V peak for 2-butanone is useless.
4. The 0.81–0.82 cm/sec-V for 2-butanone is promising. We understand why it is undetected for the pure ketone. An examination of Fig. 9 also indicates poor resolution. We note that there is a peak at 8.2 msec, but we have assigned it to 2-octanone in the next row of 0.79–0.80 cm/sec-V. We must admit that this next assignment is based more on wishful thinking and that the best conclusion is that the 0.81–0.82 cm/sec-V for 2-butanone is not sufficiently distinct from the 0.79–0.80 cm/sec-V for 2-octanone to be distinctive for either.
5. The 0.73–0.75 cm/sec-V peak is useless. It appears in both ketones and in only two mixtures. One may, in fact, conclude that the next row of 0.72–0.74 cm/sec-V ought to be combined with this one and both judged as not distinctive.
6. The 0.69–0.70 cm/sec-V peak is clearly distinctive for 2-octanone at both temperatures for all mixtures.
7. The 0.60 cm/sec-V is the proposed cross-product.
8. The 0.51–0.52 cm/sec-V peak for 2-octanone is nearly distinctive. It is absent from the 2-butanone-rich mixture at the higher temperature. This may be a sampling problem.

At best there is potentially one reduced mobility which is useful for the identification of 2-butanone and two reduced mobilities distinctive for 2-octanone. We must conclude that identification by fingerprinting binary mixtures is not very promising at our experimental conditions. Refinement of sampling may very well show improvement and needs to be investigated, but it is not obvious to us that this would be the case.

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