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COMPUTER RESOLUTION OF PLASMA CHROMATOGRAPHIC PEAKS

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SUMMARY

Used as a gas chromatographic detector, the plasma chromatograph produces low resolution positive and negative mobility spectra to identify chromatographed components. The negative plasma chromatographic mobility spectra obtained for chlorobenzene, bromobenzene, and iodobenzene give only Cl^-, Br^-, and I^- ionic species. Application of a deconvolution technique to the halide ion peaks gives resolution of the same number of components as isotopes present: two for the Cl^- and Br^-; one for the I^-. The areas of the Cl^- and Br^- deconvoluted components were approximately equal to the isotope abundances of these elements. Enhanced resolution by this technique increases qualitative data obtainable with the plasma chromatograph.

INTRODUCTION

The plasma chromatograph functions as a new and very sensitive quantitative as well as qualitative detection system for gas chromatography (GC)[1–8]. The instrument combines an ion–molecule reactor with an ion-drift spectrometer, both operating at atmospheric pressure. Reactant ions are created in the plasma chromatograph by a ^{63}Ni radioactive source from partially-dried nitrogen gas. The plasma of positive ions and electrons reacts with sample molecules from a GC effluent, or from samples injected directly into the plasma chromatograph, to form stable ion–molecule pairs. These are then injected by a pulsed grid into the drift spectrometer where they are separated to give mobility spectra characteristic of the sample components. Although an individual mobility spectrum occurs in a 20-msec time span, electronic gating techniques permit recording of a spectrum in seconds to minutes time spans. The instrument may be operated to give either positive or negative mobility spectra, and is sensitive to picogram amounts or less of sample. Compounds studied to date include dimethyl sulfoxide, *n*-alkyl alcohols[2,3], naphthalene, phenethyl alcohol, acetophenone, salicylaldehyde, and benzoic acid[4], polychlorinated biphenyls[5], monohalogenated benzenes[6], substituted aromatics[7], *n*-alkyl halides[8], *n*-alkanes[9], and *n*-alkyl esters and ketones[10].

The drift spectrometer produces mobility spectra with low resolution which is

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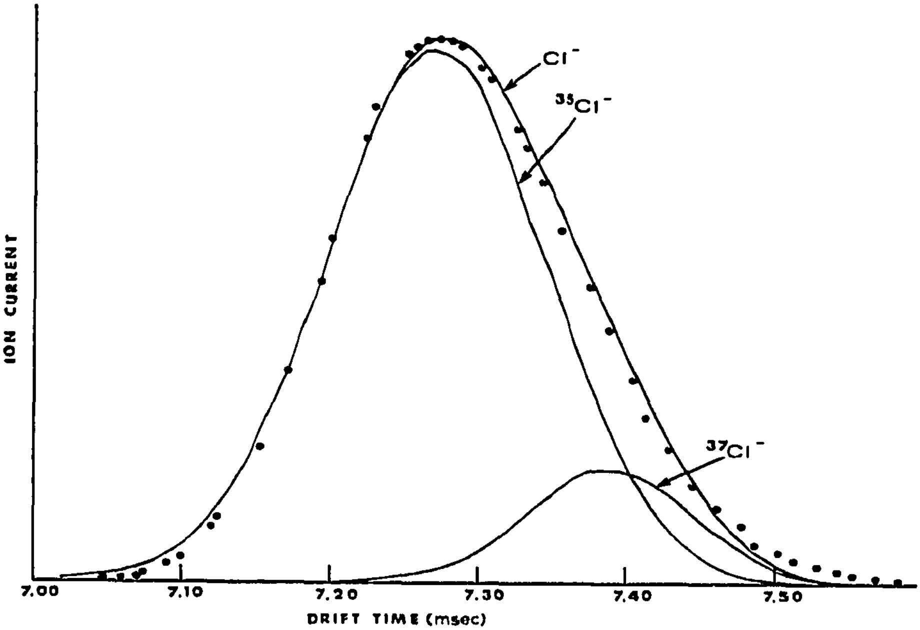

Fig. 1. Computer plot of the Cl$^-$ data showing the experimental points, the best-fit curve to the points, and the deconvoluted components of the best fit curve. Plasma chromatograph conditions: reactant gas flow, 100 ml/min dry nitrogen; drift gas flow, 450 ml/min dry nitrogen; ion–molecule reaction space, 6.0 cm; ion-drift space, 6.0 cm; electric field, 178.57 V/cm; injection pulse, 0.1 msec; gating pulse, 0.1 msec; recording time, 2 min; sampling temperature, 136 °C. The average error of the curve fit to the data points is 2.9%.

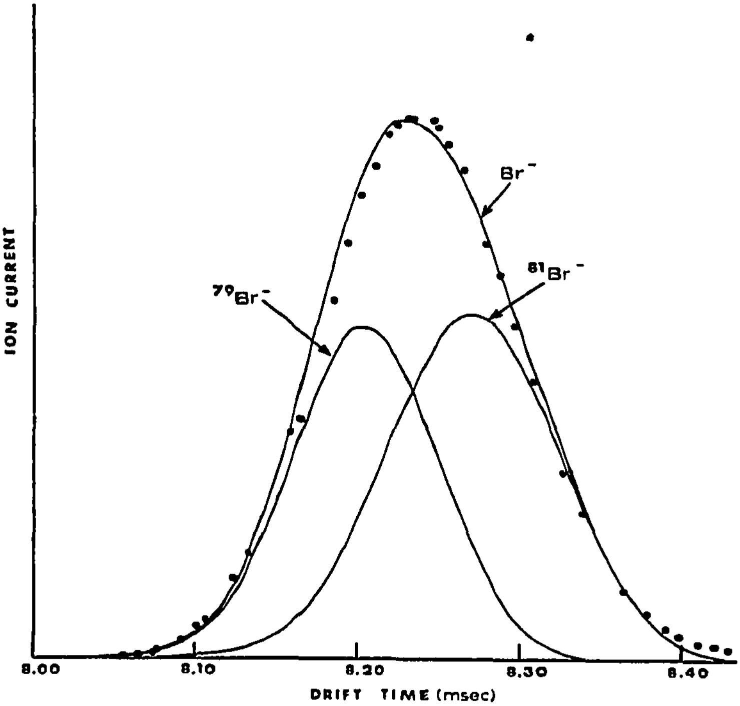

Fig. 2. Computer plot of the Br$^-$ data showing the experimental points, best-fit curve, and the deconvoluted curve components. Conditions are as in Fig. 1; the curve fit error is 5.5%.

a function primarily of the pulse width of ions injected into the spectrometer. The resolution is theoretically limited by diffusion broadening of the separated peaks, and practically by the response characteristics of the detector system. Thus, peaks can be differentiated only if there is an appreciable difference in molecular weight or size separating two species. The use of high-speed instrument-dedicated computers, however, presents the possibility of significant improvement in resolution by the deconvolution of overlapping peaks. This work was undertaken to explore the use of such computer techniques, and examines the resolution of chloride and bromide isotopes.

EXPERIMENTAL

Instrumentation

A Beta-VI Model plasma chromatograph was used (Franklin GNO Corp., West Palm Beach, Fla., U.S.A.). A detailed discussion of the instrument is provided elsewhere[5,6]. The curve resolving apparatus has previously been described[11].

Procedure

Both positive and negative mobility spectra were obtained for chloro-, bromo-, and iodobenzene. These compounds were CP reagent grade of greater than 99.9% purity. A 2.5-μl Hamilton student syringe was used to introduce compounds into the instrument. The syringe was rinsed with sample, the excess ejected, and the remaining material (less than 0.005 μl) injected as vapor into the instrument. This procedure produced mobility spectra for as long as 10 min.

The negative ion mobility spectra were used for the deconvolution studies. The peaks were manually digitalized onto cards and read into the PDP-11/20 curve-resolving system. A pure Gaussian function was used to obtain a best fit to the experimental points.

RESULTS AND DISCUSSION

Karasek and Tatone[6] have previously described the positive and negative mobility spectra of monohalogenated benzene in some detail. The negative ion mobility spectra give only a single ion peak for the negative halogen ions Cl^-, Br^- and I^-. Fluorobenzene does not give F^- because of the high appearance potential of the ion in fluorinated compounds[12]. The negative ions from the halogenated benzenes were re-examined for this work: the expanded-scale spectra show peak asymmetry for Cl^- and Br^-, while the I^- peak is Gaussian.

To identify the source of the asymmetry, the Cl^- and Br^- peaks were manually digitalized and deconvoluted, using the method of Davis and co-workers[11], which employs a Gaussian function to obtain a best fit to the experimental data. The experimental peak points, curves, and deconvoluted components are given in Fig. 1 (Cl^-) and Fig. 2 (Br^-). Fig. 3 gives the experimental curve for I^-. The experimental and calculated drift times, reduced mobilities (K_0), peak areas, and errors of the fits are presented in Table I.

Data in the figures can be compared to those from isotopic mass spectra. The relative peak areas shown in Fig. 1 are not in complete agreement with the $^{35}Cl/^{37}Cl$

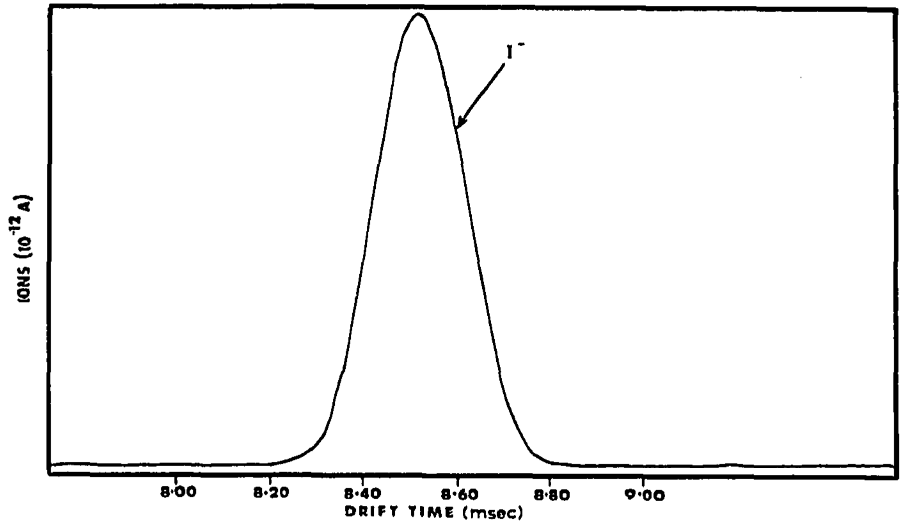

Fig. 3. Experimental negative mobility spectrum of iodobenzene showing I^-. Plasma chromatograph conditions are the same as Fig. 1 except for the electric field of 285 V/cm, the time base of 2 msec, which were altered to enlarge the experimental curve. I^- gives a single Gaussian peak component to within 5.3% error when attempts are made to deconvolute the data in the same manner as for Cl^- and Br^-.

relative abundances of 75/25 given by mass spectra[13]. Our data in Fig. 1 give the relative areas (height·width at half-height) as 87/13. The Br^- data give closer agreement. The mass spectral relative abundances for $^{79}Br/^{81}Br$ are 51/49, while our deconvoluted values in Fig. 2 give a relative area of 55/45. The lone isotope of iodide gives $^{127}I^-$ as a single Gaussian peak shown in Fig. 3, which could only be fitted by one component to a low error of value 5.3%; attempting to fit with more than one component gave an error in excess of 10%.

Although drift time differences are on the order of only 0.1 msec, Figs. 1 and 2 indicate that a clear distinction can be made between isotopes using computer de-

TABLE I

EXPERIMENTAL AND CALCULATED ISOTOPE DRIFT DATA

Ion	*Drift time (msec)*		*K_0* ($cm^2 \cdot V^{-1} \cdot sec^{-1}$)*	*Curve fit error (%)*
	Experimental	*Calculated*		
Cl^-	7.28	—	2.90	2.9
$^{35}Cl^-$	—	7.26	2.91	
$^{37}Cl^-$	—	7.39	2.86	
Br^-	8.23	—	2.59	5.5
$^{79}Br^-$	—	8.19	2.60	
$^{81}Br^-$	—	8.28	2.58	
$^{127}I^-$	8.53	—	2.50	5.3

* $K_0 = \frac{d}{\tau \cdot E} \cdot \frac{P}{760} \cdot \frac{273}{T}$; where d = drift distance (cm); E = field strength (V/cm); τ = drift time (sec); T = temperature (°K); P = pressure (torr).

convolution techniques, these methods being well-known in IR, Raman, UV, and NMR spectroscopy, mass spectrometry and GC. Direct digitation and automatic computer data reduction will therefore undoubtedly lead to higher resolution in plasma chromatography. For example, the resolution (drift time/peak width at half-height) for the experimental Cl^- and Br^- curves is 36 and 55, respectively. Resolution for the deconvoluted isotopes is 40 ($^{35}Cl^-$), 57 ($^{37}Cl^-$), 74 ($^{79}Br^-$), and 65 ($^{81}Br^-$), respectively.

Increased resolution in plasma chromatography mobility spectra is desirable in order to develop a more satisfactory qualitative detection system for gas chromatography. Resolution can be improved by shortening the gate grid pulse, but sensitivity decreases in a fashion analogous to narrowing slit widths in spectroscopy. Fig. 4 shows detector response *vs.* resolution for reactant ions[14]. All instrument parameters were held constant except the time duration of the gate grid. Resolution of approximately 45 appears to be the upper limit attainable for the reactant ions by shortening the gate pulse, but sensitivity is severely curtailed. A gate time width of 0.5 msec gives sensitivity which is 15 times as great, but at a cost of reducing resolution to one fifth. The use of computer deconvolution techniques, however, allows a gate pulse width in the high sensitivity range of 0.2 to 0.5 msec to be employed, while at the same time realizing an increase in resolution. For example, at the gate time width of 0.1 msec used for this study, an increase in resolution of 20 was provided by deconvolution.

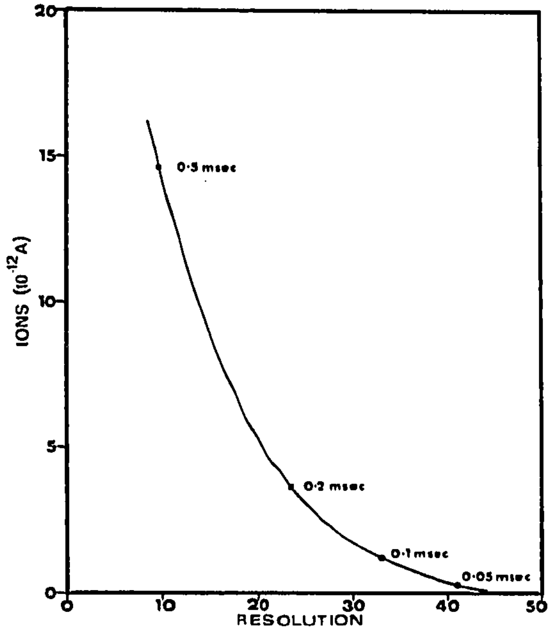

Fig. 4. Ion current *vs.* resolution for the $(H_2O)_3H^+$ reactant ion is shown. The mass spectral definition of resolution of $M/\Delta M_{\frac{1}{2}}$ is used, where drift time values are substituted for M and ΔM.

Work is now in progress to interface the plasma chromatograph instrument in this laboratory with the appropriate computer hardware in order to increase resolution while maintaining high sensitivity. An experimental verification of the data reported here can be made using monoisotopic compounds; this work is also now in progress.

ACKNOWLEDGEMENTS

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