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EVALUATION OF DIRECT AXIAL SAMPLE INTRODUCTION FOR ION MOBILITY DETECTION AFTER CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

An ion mobility detector has been designed and constructed for direct axial interfacing with capillary gas chromatography. The principle advantages of this detector were the following: (1) Direct concentric introduction of the capillary column into the ionization region, eliminating peak broadening in the transfer line and improving the efficiency with which neutral molecules were swept from the detector. (2) A variable capillary insertion distance, providing a sensitivity/resolution interplay that could be modified in response to the needs of the assay. (3) An inert gas flow external to the drift cylinder, preventing atmospheric impurities from infiltrating the ultratrace detector. Qualitative and quantitative capabilities of the detector were evaluated using standard preparations of *n*-hexyl ether.

INTRODUCTION

Ion mobility spectrometry (IMS), an atmospheric pressure technique for trace organic analysis, was first introduced in 1970 by Cohen and Karasek[1]. In IMS, organic molecules are ionized by any of several methods, including ^{63}Ni β ionization[1], photoionization[2,3], laser ionization[4], resonance enhanced two-photon ionization[5], coronaspray ionization[6], or via use of a high temperature ceramic alkali bead[7]. These ions are then driven by an electric field against a counterflowing neutral drift gas, achieving an average velocity dependent on the ion charge, mass, and collision cross sectional area. Ions can be thus distinguished by their arrival time at a downfield collector[8,9].

Due to the high sensitivity of the technique, particularly with ^{63}Ni β ionization, IMS has continued to be suggested as a tuneable selective detector for gas chromatography (GC). Several researchers have used GC–IMS[10–14], but its efficient utilization has only recently been realized. With the introduction of low bleed, bonded fused-silica capillary columns and a detector design which introduced a unidirectional gas flow, an enclosed drift tube, and a reduced ionization cell volume[15], IMS has become a reliable method of detection after high-resolution GC. The detector to be described within this paper, maintains the resolution enhancing characteristics of the previous detector, while introducing additional modifications directed towards improved chro-

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matographic efficiency and stability. General reviews of modes of operation and capabilities of ion mobility detection (IMD) for capillary GC have been published recently[16–18].

The purpose of this work was to design an ion mobility detector that could be interfaced directly to a capillary gas chromatograph. Initial experiments with the new design addressed spectral stability and detector residence times when measuring trace quantities of *n*-hexyl ether.

EXPERIMENTAL

Detector design and ancillary instrumentation

The ion mobility detector designed for direct interfacing to capillary GC is illustrated in Fig. 1. A stainless-steel detector base, with 1/16-in. stainless-steel tubing welded through its center and extending 1/16 in. above and 2.25 in. below the base, was connected to a 1 × 1 5/16″ × 3/4 in. heating block (not shown in schematic) by a swagelock fitting. The heating block temperature was controlled to within 1°C by the detector temperature controls of the HP 5890 GC system. The capillary column was inserted into 1/16-in. stainless-steel tubing, directing it through the heating block, detector base and macor insulator into the ionization region of the detector. This insertion distance was variable and the consequent trade-off between chromatographic peak areas and peak widths will be discussed in the results and discussion section.

The 1½-in. diameter by 7/16-in. round macor insulator electrically isolated the gas chromatograph from the high voltages applied to the drift tube. The ionizer was a 1½-in. diameter by ½-in. stainless-steel disc with a 1-cm diameter by 1-cm ionizing cell in its center (cell volume, 0.8 cm^3). Lining the ionizing cell was a 3.1 cm × 0.8 cm × 0.002 mm nickel foil electroplated on one side with 11.78 mCi/mg ^{63}Ni (E.I. du Pont de Nemours, Billerica, MA, U.S.A.). Total activity was 15 mCi β radiation with a

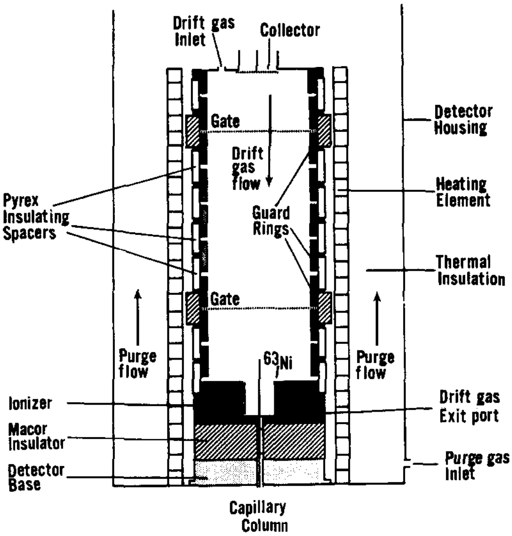

Fig. 1. Schematic of the ion mobility detector.

maximum beta energy of 67 keV. Four 1/16-in. openings at the base of the ionizer functioned as exit ports for the neutral drift gas and unionized chromatographic effluent molecules. The efficiency with which neutral molecules are swept through these ports determines the ultimate detector contribution to peak broadening.

The electric field was created and maintained by a high voltage applied directly to the ionizer block, from a ± 5000 V voltage supply (Bertan Assoc., Syosset, NY, U.S.A.). This voltage was then dropped to ground via a series of 1-MΩ resistors connected to successive guard rings. Guard rings were stainless-steel of 3.15 cm I.D. and 3.6 cm O.D. Their depth on the inner surface was 0.90 cm, a 0.1 × 0.1 cm ledge extended from the outer surface of the ring. The gates and insulating spacers were designed to fit over the ring and rest on the 0.1-cm outside ledge, providing a snug but not hermetically sealed fit. The electrical insulating spacers were pyrex rings of 3.7 cm I.D., 4.1 cm O.D., and 0.90 cm depth.

The gates were composed of parallel 0.003-in. nichrome wire (California Fine Wire, Grover City, CA, U.S.A.) separated by approximately 1 mm. The wires were sandwiched between two 3.7 cm I.D., 4.5 cm O.D., 0.45 cm depth macor rings with zirconia base 940 ceramic adhesive (Cotronics, Brooklyn, NY, U.S.A.). Alternate wires were biased + 25 V and − 25 V relative to the appropriate voltage based on the gates location in the electric field. With voltage applied to the wires, an approximately 500-V/cm field is generated orthogonal to the drift field (generally 150–350 V/cm). Drifting ions are thus neutralized on the gate wires.

The ion collector was a stainless-steel wire mesh spot welded into a 0.020 in. macor ring. Current was sent to a Keithley Model 427 current amplifier (Keithley Instruments, Cleveland, OH, U.S.A.) modified to provide a 2.1-s rise time for chromatography. The amplified signal proceeded to an HP 3392A integrator (Hewlett-Packard, Avondale, PA, U.S.A.) for chromatographic detection and integration or to an IBM XT personal computer for ion mobility spectral collection and processing by either signal averaging or fourier transform[19] methodology. Preceeding the collector was an aperture grid (not shown in schematic) also made of 0.003-in. parallel nichrome wires, separated from the collector by approximately 1 mm and biased at approximately 30 V. This grid capacitively decouples the collector from the approaching ion, providing improved resolution in signal averaging spectral collection.

Preheated drift gas entered through a 1/8-in. inlet in the top of the detector. The drift gas was preheated to the drift tube temperature by its entrance through 1/8-in. stainless-steel tubing that quadruply encircled the detector heating block and was then carried to the top of the drift tube within a insulating cylinder. Temperature control to the drift tube was provided by heavy insulated Samox heating tape, maximum temperature 760°C, (Thermolyne, Dubuque, IA, U.S.A.) wound around a 13 cm × 4.8 cm I.D., 5.1 cm O.D. Pyrex cylinder and held in place by high-temperature aluminum tape, maximum temperature 315°C (3M, St. Paul, MN, U.S.A.). The pyrex cylinder was insulated externally with moldable ceramic felt (Cotronics, Brooklyn, NY, U.S.A.) and held within an aluminum cylinder 19 × 9.5 I.D. The heating tape temperature was maintained with a Digisense Model 2168-70 temperature controller (Cole Parmer, Chicago, IL, U.S.A.), accurate to 0.4°C. The insulating cylinder was swept during operation with approximately 1 l/min of nitrogen gas to prevent infiltration of ambient impurities into the drift tube of the detector. Drift gas and external purifying gas were either prepure nitrogen or industrial grade compressed air (Liquid

Air, San Francisco, CA, U.S.A.), dried with 5Å molecular sieve (Linde Division, Union Carbide, South Plainfield, NJ, U.S.A.).

Capillary insertion distance studies

Injections of 2.0 μl of 68.0 ng/μl and 6.80 ng/μl standard solutions of tributylamine in hexane were made, producing 1.36 ng and 136 pg of tributylamine on column after the 100:1 split ratio. The average of duplicate measurements of each concentration at each insertion distance were used for graphical presentation. Peak areas and area/height measurements were made by an HP 3392A integrator. Deviation of duplicate points varied from 1 to 8% for peak areas, but was generally around 2%. The maximum deviation of duplicate peak width measurements was 6%, generally being <2%. Operational parameters are listed in Table I.

TABLE I

EXPERIMENTAL CONDITIONS OF THE INSERTION DISTANCE STUDY

Ion mobility detection	
Drift length	5.0 cm
Temperature	200°C
Drift gas flow-rate	1400 ml/min air
Electric field	285 V/cm
Gate voltage	± 25 V
Pressure	690 Torr
Chromatography	
Column	DB-5, 22 m × 0.25 mm I.D., 0.25 μm film
Split ratio	100:1
Flow-rate	0.9 ml/min helium
Injector temperature	200°C
Oven temperature	130°C
Drift times monitored	4.9–8.7 ms
Duty cycle (% of collection time entrance gate is open)	16%

Ether studies

Di-*n*-hexyl ether was first chromatographed under non-selective conditions[16], in which all product ion peaks were monitored. Retention time of the di-*n*-hexyl ether was determined to be 3.34 min using the chromatographic conditions listed in Table II. Spectral collection was triggered at 3.31 min, so as to capture the maximum intensity of the chromatographic peak.

From the spectra, the product ion drift time was determined to be 5.1 ms ($K_0 = 1.70 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$). A calibration curve was then obtained by selective monitoring of product ion drift times between 4.6 and 5.6 ms, with maximal collection centered at 5.1 ms. Spectral and chromatographic conditions for the ether studies are listed in Table II.

TABLE II

EXPERIMENTAL CONDITIONS OF THE ETHER STUDIES

Ion mobility detection	
Temperature	200°C
Drift gas flow-rate	1400 ml/min nitrogen
Electric field	310 V/cm
Entrance gate voltage	±32.5 V
Exit gate voltage	±15 V
Pressure	695 Torr
Chromatography	
Column	DB-5, 22 m × 0.25 mm I.D., 0.25 μm film
Flow-rate	0.7 ml/min helium
Split ratio	285:1
Injector temperature	250°C
Capillary insertion distance	1.3 cm
Oven temperature	150°C
Drift times monitored	4.6–5.6 ms
Duty cycle	5%
Spectroscopy, signal averaging	
Drift length	7.73 cm
Entrance pulse width	0.20 ms
Spectral collection time	25.6 ms
No. averaged	64
Total time	1.64 s
Spectroscopy, Fourier transform	
Drift length	6.0 cm
Frequency range	20–10 020 Hz
No averaged	1
Total time	2.05 s

RESULTS AND DISCUSSION

Design modifications

Salient modifications to earlier designs include firstly, the direct concentric introduction of the capillary column into the center of the ionizer. Our earlier design[15] introduced the chromatographic effluent laterally after traversing some 3 ft. of heated transfer line. The design reported in this paper eliminated the extracolumn addition to peak broadening while introducing the effluent in a more defined zone than is obtained with lateral introduction into a flowing drift gas. The resolution capabilities of the system are qualitatively demonstrated in Fig. 2, a gas chromatogram of light petroleum (90–110°C). Several additional chromatograms of complex samples are illustrated in a recent review of IMD[16].

A second unique characteristic of this detector was the ability to vary the distance that the column was inserted into the ionizer. The effect that varying this distance has on chromatographic peaks is illustrated in Fig. 3. It can be seen in the upper graph, that peak areas increased approximately 8 × when the insertion distance was varied from 0.4 to 1.8 cm. These areas were reasonably stable from 1.8 to 2.4 cm.

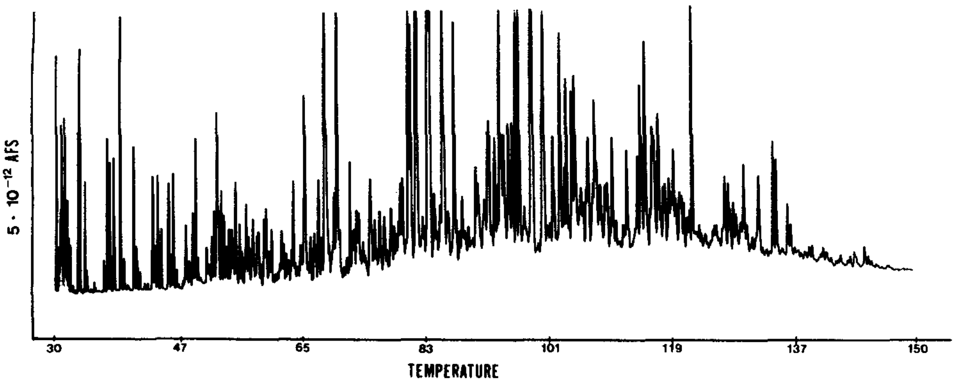

Fig. 2. Chromatogram of light petroleum using ion mobility detection. Column: DB-5, 22 m × 0.259 mm I.D., 0.25 μm film. Flow-rate, 1.3 ml/min hydrogen. Split ratio, 100:1. Injector temperature, 225°C. Temperature program: 30°C, 1 min; 0.6°C/min; 150°C, 5 min. Insertion distance, 1.9 cm. Detector temperature, 200°C. Drift gas flow-rate, 1400 ml/min air. Electric field, 340 V/cm. Gate voltage, 50 V. Drift length, 5.0 cm. Drift times monitored, 4.1–9.9 ms. Duty cycle, 5%.

The lower graph illustrates the effect on peak base widths of varying the insertion distance. Little peak broadening was observed as the insertion distance was increased. Insertion distance can thus be varied to maximize sensitivity without significantly sacrificing the resolving power of the chromatographic system.

The third major modification was the addition of a sheath of flowing gas between the drift tube and the insulating cylinder. This external flow functioned to eliminate infiltration of the detector by ambient impurities in the laboratory air. Impurities have been seen previously, in moderate cases as baseline instabilities or in extreme cases as complete depletion of the reactant ions[20]. With the design described here, no baseline instabilities were detected while exposing the detector to acetone vapors from a 250-ml beaker at a distance of approximately 4 in. Without the sheath gas flow, these acetone vapors completely depleted the reactant ions and produced a dominant acetone product ion.

Two additional modifications included firstly, the elimination of PTFE as an insulator in the detector which removed a previous limitation to high-temperature work. Secondly, the ionizing cell volume was reduced to 0.8 cm^3 from the previous 1.0 cm^3. No direct evidence links this cell reduction with the consequent increase in total ion current from 1.0 to 2.5 nA. However, based on these data, the increased speed with which a reduced cell volume can be swept, and the earlier work of Aue and Kapila[21] which proposes that the center of ionization occurs within 2 mm of a ^{63}Ni foil; the potential chromatographic benefits in resolution, sensitivity, and linear range from further cell size reductions deserves investigation.

Selective chromatographic detection of di-n-hexyl ether

In 1973, ion mobility spectrometry was evaluated as a separator/identifier and as a detector to be used in conjunction with chromatography[22]. Neat ethers were injected directly into the ionization region of a bidirectional flow ion mobility spectrometer. Ion mobility spectra revealed instabilities in product ion position and in-

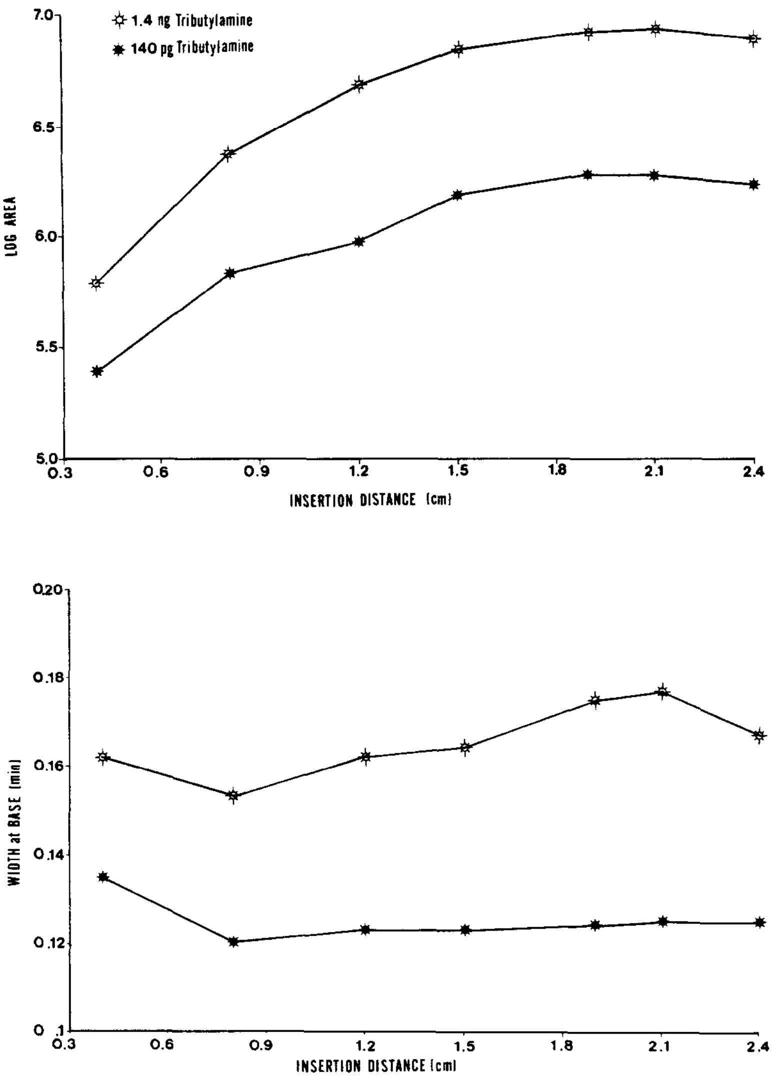

Fig. 3. (a) Chromatographic peak area *vs.* distance capillary column inserted into ionizer. 1 Area count = 6.25 · 10^{-19} C. (b) Chromatographic peak widths at base *vs.* distance capillary column inserted into ionizer. Conditions as in Table I.

tensity with detector clearance times exceeding 1.7 h. These instabilities were probably due to complex ion–molecule reactions occurring at high concentrations and the presence of trace contaminants in the ethers. The experiments discussed below were designed to evaluate spectral stability and detector clearance times when introducing trace quantities of chromatographically purified ethers into the unidirectional flow ion mobility detector described in this paper.

Fig. 4a shows the background reactant ions obtained with a signal averaged spectral collection method when only helium carrier gas was eluting from the capillary column. Fig. 4b is a signal averaged spectra collected as 27 ng of di-*n*-butyl ether was introduced. The product ion was seen as a shoulder on the second reactant ion. Comparison to the earlier work[22], revealed similarities between these spectra and those taken 1.7 h after the injection of more then 100 μg into an ion mobility spectrometer. This indicates that only after this time period were concentrations reduced to a level where stable product ion species were formed.

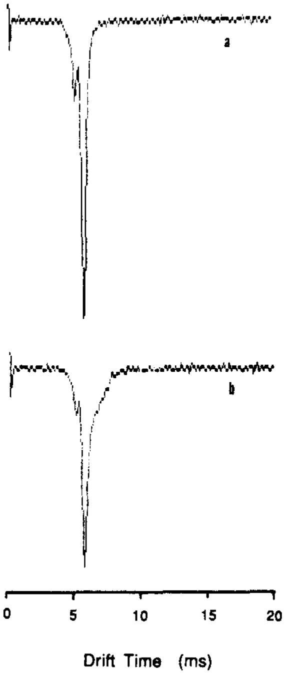

Fig. 4. (a) Background reactant ions, signal averaged spectral collection. (b) IMS Spectra of 27 ng di-*n*-butyl ether. Conditions as in Table II.

Using a Fourier transform method of spectral collection[19] and the slightly larger and thus slower drifting di-*n*-hexyl ether, we were able to baseline resolve the product ion from the reactant ions, as seen in Fig. 5. Fig. 5a displays the background reactant ions and Fig. 5b–d displays spectra obtained when increasing quantities of ether were injected into the GC system. Spectra varied as expected, reactant ions being depleted as product ions increase. The product ion drift time remains constant at 5.1 ms throughout, and no additional product ions were observed.

More sensitive and precise quantitative measurements can be obtained using the GC selective mobility monitoring mode[16]. By narrowing the entrance and exit gates, and using controlled timing, selective detection of ions drifting in 5.1 ms was obtained. Fig. 6 displays a calibration curve obtained under selective monitoring conditions. A well behaved response profile was evident from approximately 0.03 to 30.0 ng, indicating the stability of the product ions drift times in those ranges. Linear

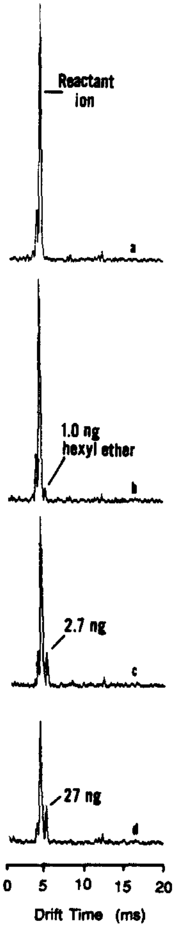

Fig. 5. (a) Background reactant ions, Fourier transform spectral collection. (b) 1 ng di-*n*-hexyl ether. (c) 2.7 ng di-*n*-hexyl ether. (d) 27 ng di-*n*-hexyl ether. Conditions as in Table II.

regression of the data points in Fig. 6 (excluding the point at 27 ng) produces a line of the following equation:

$$Y = 3.17 + 0.621X \quad \text{variance} = 5.15 \cdot 0^{-3}$$

Based on the calibration curve and examination of Fig. 5d and 4b of 27-ng samples, it can be stated that over three orders of magnitude extending from 28 pg to 27 ng, no spectral instabilities were observed.

Fig. 7a and b shows examples of two of the chromatograms used in the di-*n*-hexyl ether calibration curve. Peak base widths are on the order of 6 s, indicative of efficient clearance times from the ion mobility detector.

Based on these data, we conclude that the ion mobility detector herein described is suitable for sensitive and selective detection of ethers. With concentric.

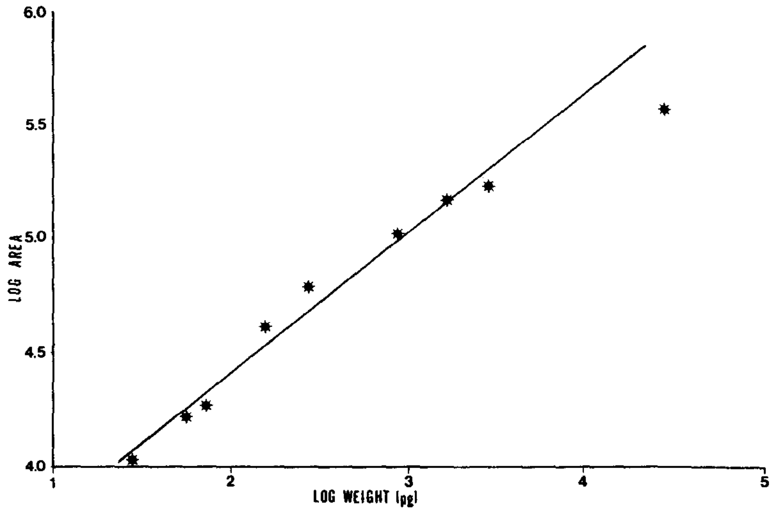

Fig. 6. Calibration curve of di-*n*-hexyl ether. Selective monitoring, 4.6–5.6 ms. Conditions as in Table II.

capillary introduction and unidirectional gas flow, clearance time of the detector ionization region is on the order of 1 s (the *entire* detector volume of 69.2 cm^3 being swept in 3 s by drift gas at a flow-rate of 1400 ml/min). With the introduction of chromatographically purified components at non-saturating concentrations, *i.e.*, reactant ions still visible in the spectra, only single product ion drift times were observ-

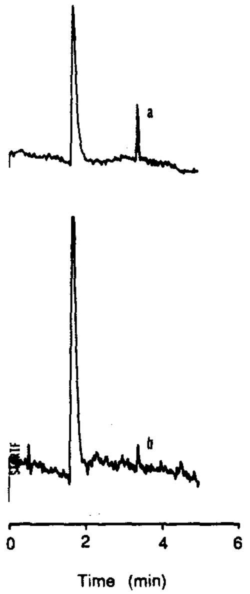

Fig. 7. Di-*n*-hexyl ether chromatograms. (a) 150 pg di-*n*-hexyl ether on column. (b) 28 pg di-*n*-hexyl ether on column. Conditions as in Table II.

ed. These drift times reflecting the charge, reduced mass and collision cross section of the product ion and consequently providing qualitatively useful information. While complex ion–molecule reactions at high concentrations restricts certain analytical applications of IMS, they do not diminish the usefullness of IMS as a chromatographic detection method for the determination of trace amounts of compounds.

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