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Ion mobility detection of polydimethylsilicone oligomers following supercritical fluid chromatographic separation

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SUMMARY

A mixture of polydimethylsilicones (Dow Corning 200), average molecular weight 2000 a.m.u., was separated by simultaneous density and temperature-programmed supercritical fluid chromatography and detected by ion mobility detection. Ion mobility spectra were captured by Fourier transform ion mobility spectrometry. Using information from these spectra it was possible to selectively detect a single compound in the complex mixture. A detector temperature investigation demonstrated that, for the efficient transfer of high-molecular-weight compounds from the column to the detector, the interface to the detector must be heated. Using a 50 μm I.D. column, a Guthrie-type restrictor and a detection temperature of 250°C, as many as 70 oligomers were separated and detected.

INTRODUCTION

The potential for developing a detector for supercritical fluid chromatography (SFC) based on the principles of ion mobility spectrometry (IMS) has been previously demonstrated[1–4]. Advantages of the ion mobility detection (IMD) system for SFC include: (1) sensitivity to a wide variety of compounds, such as those that do not contain a large molar absorptivity, (2) selectivity based on size and shape rather than hetero-atom content, (3) compatability with many flame-ionizable supercritical mobile phases and (4) ruggedness of detector due to ambient pressure operation.

In one study’, the SFC separation of Triton X-100 surfactant demonstrated successful detection of the polymer in several of the IMD system’s operational modes. More importantly, drift spectra were captured for individual oligomers. which provided qualitative information about the size of each oligomer. Selective detection was demonstrated for several single oligomers in the mixture using drift time data. The highest-molecular-weight compound detected was a Triton X oligomer of ca. 1000 a.m.u.

In early attempts to interface IMD to SFC, a decrease in SFC resolution was encountered. This was most likely due to inefficient transfer of the analytes from the chromatograph to the detector resulting from operation of the IMD system at a

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relatively low temperature and a long viscous restrictor serving as the interface between SFC and IMD. The importance of temperature in the transfer of solutes from a supercritical fluid has been well documented[5,6]. It has also been found that a long viscous restrictor does not transfer solutes out of the supercritical fluid as well as either a tapered restrictor or a frit restrictor’.

In this work the effect of the IMD temperature on the separation of high-molecular-weight polymers was studied. Ion mobility spectra were collected for individual oligomers of the polymer mixture and, using the information from the ion mobility spectra, selective detection of a contaminant in the polymer was demonstrated.

EXPERIMENTAL

The SFC system used in this work was constructed using a high-pressure syringe pump (Alpine West Labs, Provo, UT, U.S.A.) and a GC oven (Model 5830; Hewlett-Packard, Avondale, PA. U.S.A.). The components of the chromatograph have been described in more detail in an earlier publication’. The SFC system was operated in two different configurations. The first configuration had a 100 μm I.D. column with a splitless injection system and a viscous restrictor. The second configuration had a 50 μm I.D. column, a split injection and a Guthrie-type restrictor.

The 100 μm I.D. column was 20 m long and coated with a DB-1 stationary phase, 0.4 μm film thickness (J & W Scientific, Folsom, CA, U.S.A.). The flow restrictor was a 10 cm × 10 μm I.D. uncoated fused-silica capillary attached to the column with a butt connector (Supelco, Bellefonte, PA, U.S.A.). A double-ended ferrule, which had been cut to ca. 3/4 of its original length, was used to connect the column directly to the injector. The O.D. of the column was large enough so that the column could not pass through the injector body and damage the sample rotor. Compression of the ferrule kept the column centered and eliminated any dead volume in the injector. A 60-nl sample volume was injected directly onto the column.

The 50 μm I.D. column was 20 m long and was coated with an SB-Methyl- 100 stationary phase, 0.25 μm film (Lee Scientific, Salt Lake City, UT, U.S.A.). The injection volume was 60 nl, split ca. 20: 1. The flow restrictor was 12 cm × 50 μm I.D. fused-silica which had been tapered at one end in the manner described by Guthrie and Schwartz*. The restrictor was calibrated to provide a linear velocity of about 3 cm/s at a constant temperature of 100°C and constant pressure of 100 atm and was attached to the end of the column with a butt connector, 0.4 mm I.D. (Scientific Glass Engineering, Houston, TX, U.S.A.). Inside the butt connector the end of the column and the non-tapered end of the restrictor were inserted into a length of 200 μm I.D. fused silica. This ensured end-to-end alignment of the column and restrictor.

The IMD system used for this work was similar to earlier designs[9,10]. A schematic of the drift tube is shown in Fig. 1. One modification in this design was that the collector was completely surrounded by a grounded drift ring to reduce background noise. Also, a new method of ion-gate construction produced gates which were less prone to failure at high temperatures. Although there are several methods of gathering drift spectra[10],Fourier transfrom ion mobility spectrometry (FT-IMS) was used in this study[11].Chromatographic detection was accomplished by continuous mobility monitoring (CMM)[12].

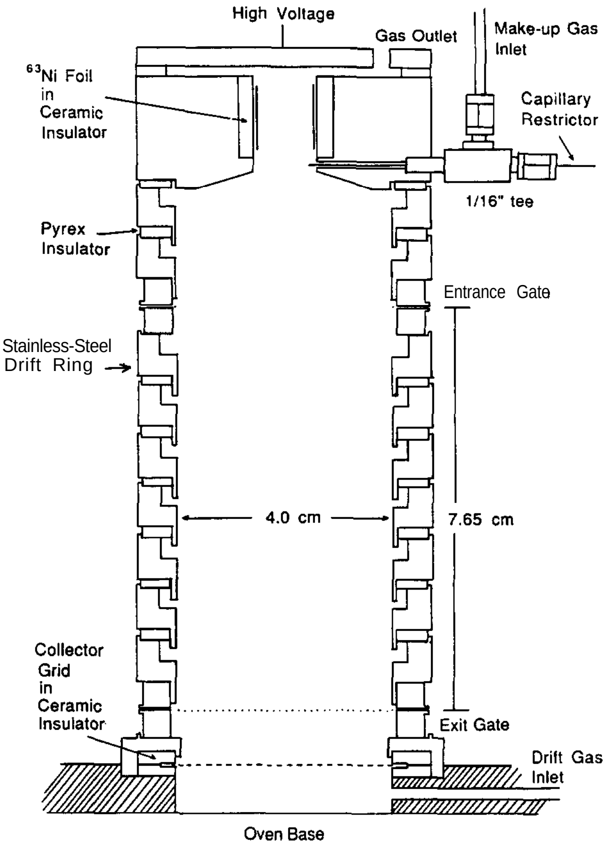

Fig. 1. Schematic of the ion mobility detector drift tube.

Electronics

Schematics of control electronics are shown in Fig. 2. The components of the system were an IBM microcomputer, a high-voltage source and gate controller (WSU Technical Services), a scanning square wave generator (SSQW) (WSU Technical Services), a Keithley 417 picoammeter (Keithley Electronics, Cleveland, OH, U.S.A.), an interface box and a chart recorder and integrator. The signal source for the CMM mode of operation and the data collection system for the FT-IMS mode were both built into the IBM microcomputer equipped with a multi-input/output expansion card, a memory expansion card, a math coprocessor and a PCI-2000 intelligent instrumentation system (Burr-Brown, Tucson, AZ, U.S.A.).

The timer module generated the logic for the opening and closing of the gates in the CMM mode of operation. Two timer element outputs were used as the pulses for the opening and closing of the entrance and exit gates. A combination of compiled basic and assembly language programs were used to control the timing of the gates.

In the FT-IMS mode both gates were opened and closed simultaneously while the opening and closing of the gates were scanned through a frequency range. The SSQW acted as the signal source for gate control in the FT-IMS mode of operation.

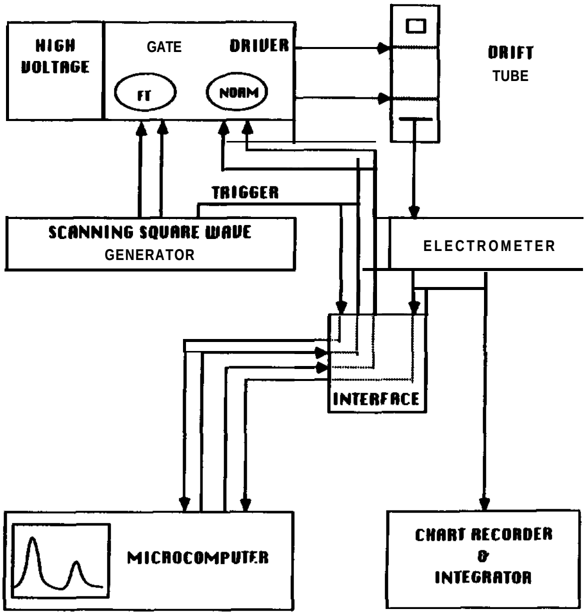

Fig. 2. Schematic of the electronics for the ion mobility detector.

As ions drifting through the drift region came in and out of phase with the frequency of the gates, they created an interference pattern at the collector. This interference pattern was collected by the computer as a mobility interferogram and converted to a time-domain drift spectrum via a fast-FT algorithm.

The IMD controller converted the logic signals from the signal sources to the proper voltages to open and close the ion gates. The devices for the gate control were contained on two custom PC cards (Redmond's Circuits, Redmond, WA, U.S.A.), one for each gate.

The chart recorder and integrator was a Hewlett-Packard 188 17A GC terminal. The output of the picoammeter was routed through a voltage divider to an auxiliary analog/digital (A/D) board of the chromatograph.

The interface box was designed and built in-house. It performed several functions. In the CMM mode of operation the interface box configured the timer elements of the timer module so that the drift window was created, configured the system to an internal trigger signal set in the computer software and inverted the logic signals from the timer module so that they were compatible with the transistor-transistor logic (TTL) of the IMD controller. In the FT-IMS mode the interface box routed the output of the picoammeter to the A/D module of the computer, configured the system to an external trigger signal from the SSQW, and set the full-scale input voltage of the A/D module. This last function was used as an additional gain switch.

Operating conditions

Pure carbon dioxide (instrument grade, Liquid Air, Tacoma, WA, U.S.A.) was used as the mobile phase for all separations. Later *et al.*[13] showed that much higher

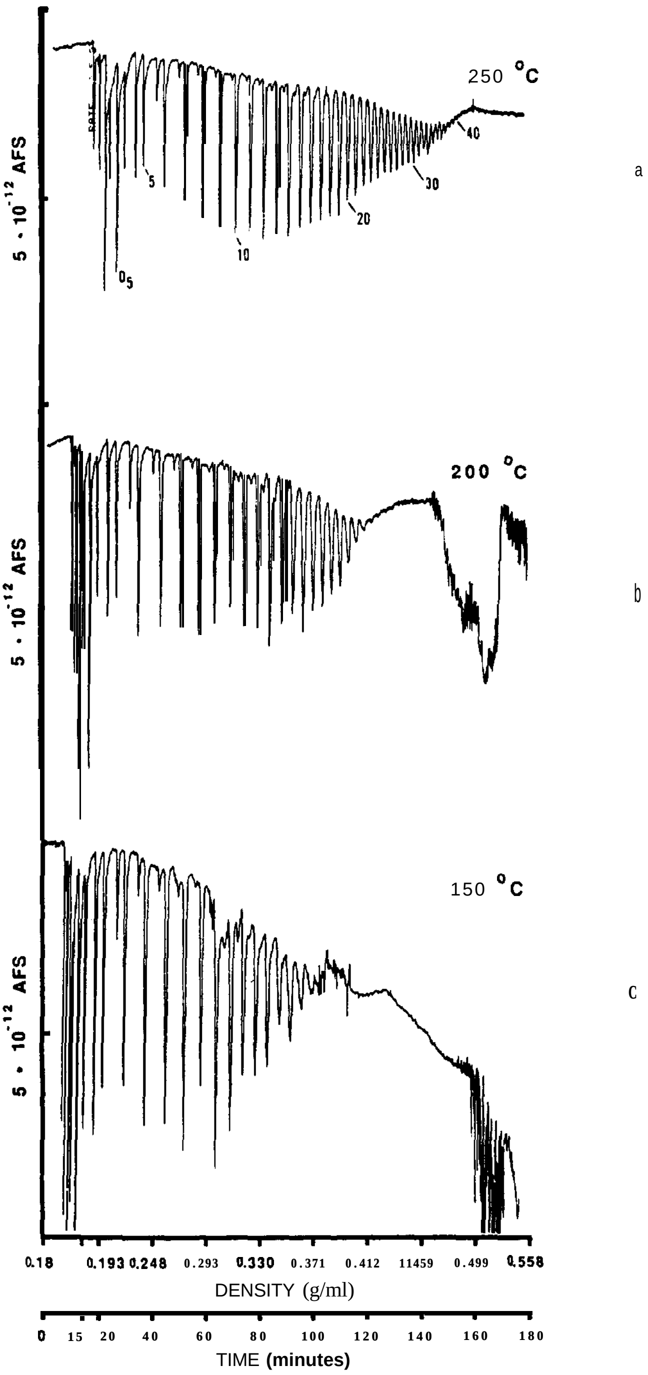

Fig. 3. SFC-IMD separation of Dow Corning 200. J & W Scientific column, 20 m × 100 μm I.D., DB-I stationary phase, 0.4 μm film. Detector temperature: (a) 250°C, (b) 200°C, (c) 150°C.

efficiency separation of polydimethylsilicones could be achieved by simultaneous density and temperature programming than by either density or temperature programming alone. Unfortunately, the SFC system used for this work was capable of linear density programming at a constant temperature, but was incapable of compensating for the change in temperature as the chromatographic run progressed. Therefore, temperature and density were programmed independently, ***i.e.,*** the temperature was programmed from 100°C to 140°C, but density was programmed at an ***assumed*** constant temperature of 100°C. The density line shown along the bottom of the chromatograms has been corrected for temperature programming.

RESULTS AND DISCUSSION

Temperature effect

Fig. 3 shows the separation of Dow Corning 200 at IMD temperatures of 150, 200 and 250°C. In each case the detector had been tuned to monitor the depletion of the reactant ions (those ions present in the spectrometer when the sample is not in the spectrometer). This reactant ion monitoring mode is a non-selective method of detection[1–8]. Other pertinent detector conditions are given in Table I. All three separations were carried out on the 100 μm I.D. column with splitless injection and a viscous restrictor. In each case the sample concentration was ca. 1 mg/ml of the polydimethylsilicone polymer, Dow Corning 200. Temperature and density programs are given in the figure.

There are several important features in Fig. 3 that should be noted. First, in Fig. 3c the IMD operating temperature of 150°C is the same operating temperature used in the earlier Triton X-100 separation’. Only, cu. eighteen peaks can be seen in this chromatogram, far short of the number of oligomers expected in the sample. Also, at the end of the chromatogram was a large unresolved peak. This was most likely due

TABLE I

DETECTOR CONDITIONS

IMD	
Nitrogen drift gas	400 ml/min
Nitrogen make-up gas	100 ml/min
Temperature	250°C[a]
Electric field	+ 316 V/cm
Ion drift length	7.6 cm
Ambient pressure	698 mmHg
FT-IMS	
Scan range	20–10 020 Hz
Scan time	10.24 s
Gate voltage	+/− 20 v
Continuous mobility monitoring	
Drift time base	24 ms
Gate voltage	+/− 40 v
Drift times monitored	noted in figures

[a] Except where indicated.

to samples which had precipitated in the restrictor and then, as the mobile phase density increased, was eventually eluted, but poorly separated.

The effect of increasing the detector temperature to 200°C can be seen in Fig. 3b where the number of peaks increased to around 25. Although this was an improvement, fewer peaks were eluted than expected and unresolved peaks were found between 160 and 180 min.

Fig. 3a shows the same separation at an IMD temperature of 250°C. In this chromatogram the number of peaks suggests the separation of 50 compounds in the polymer mixture. The numbers over individual peaks represent the number of monomers believed to be in the peak. The identification relied on the comparison of this separation to previous separations with assigned monomer numbers[13]. Note that this chromatogram lacked the poorly resolved group of peaks near the end that were prominent in the two chromatograms at lower detector temperatures.

Ion mobility spectra

Using the FT capabilities of the detector, spectra were obtained for individual

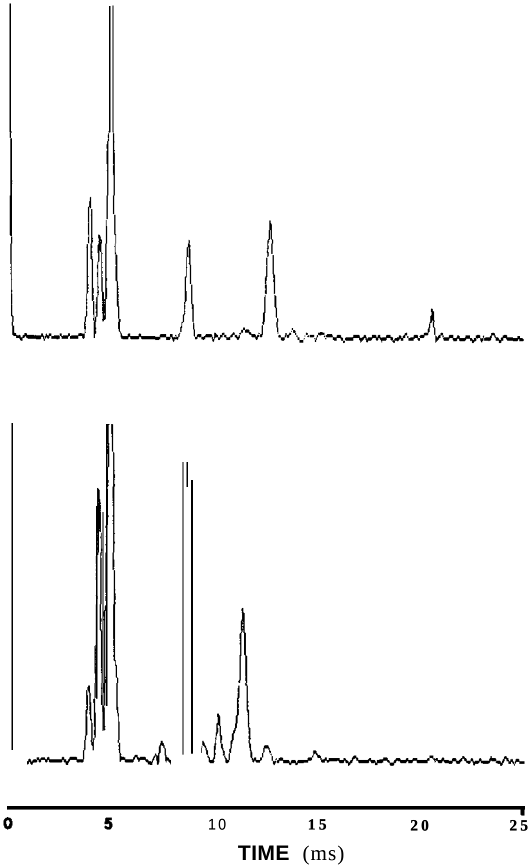

Fig. 4. Drift spectra of Dow Corning 200 oligomers. (a) Drift spectrum captured at 27 min, (b) drift spectrum captured at 64 min.

peaks of the Dow Corning 200. Twenty-eight spectra were collected during a single chromatographic run over a time period of 120 min. Fig. 4 shows the spectra collected for peaks which eluted at 27 and 64 min. (Chromatographic conditions are given in Fig. 3, detector conditions given in Table I). The spectrum shown in Fig. 4b for the peak which eluted at 64 min is representative of most of the spectra collected. All of the spectra contained more than one product ion and the majority showed two major product ion peaks at drift times of 8.8 and 11.4 ms.

Spectra were collected during a single chromatographic run. During the run it was possible to observe the major product ions increasing and decreasing in intensity as the chromatographic peaks passed through the detector. Early in the chromatogram it was possible to observe the absence of any product ion peaks, which would correspond to the valleys in the chromatogram. Later in the chromatography. after cu. 70 min, the presence of some of the compounds in the detector was almost continuous and it was not possible to capture a spectrum without the major product ions.

Minor peaks varied in number and drift time. The drift times of the minor peaks shown in Fig. 4b are 7.5, 9.5, 10.2 and 12.5 ms. The peak at cu. 14 ms is a noise artifact.

Of the twenty-eight spectra collected during chromatography only the peak at 27 min showed a unique drift spectrum. The spectrum for this compound can be seen in Fig. 4a. The drift spectrum had two major product ion peaks at 8.8 and 12.7 ms. The product ion at 12.7 ms was the largest product ion of major intensity in the Dow Corning 200. The unique features of this peak suggest that this compound is a contaminant in the polymer mixture. The drift times of the reactant ions and product ions in Fig. 4 are summarized in Table II.

Chromatography

Using the information from the drift spectra it was possible to selectively detect the peak at 27 min. The IMD system was tuned to monitor only ions with drift times between 12.2 and 13.2 ms. Selective detection can be seen in Fig. 5a. From the reten-

TABLE II

DRIFT TIMES AND REDUCED MOBILITIES

Compound	*Drift time (ms)*	*Reduced mobility ($cm^2/V \cdot s$)*
Reactant ions	4.0	2.88
	4.5	2.56
	5.0	2.31
Peak at 27 min	8.8	1.31
	12.7	0.91
Peak at 64 min	1.5	1.54
	8.7	1.33
	9.5	1.21
	10.2	1.13
	11.4	1.01
	12.7	0.92

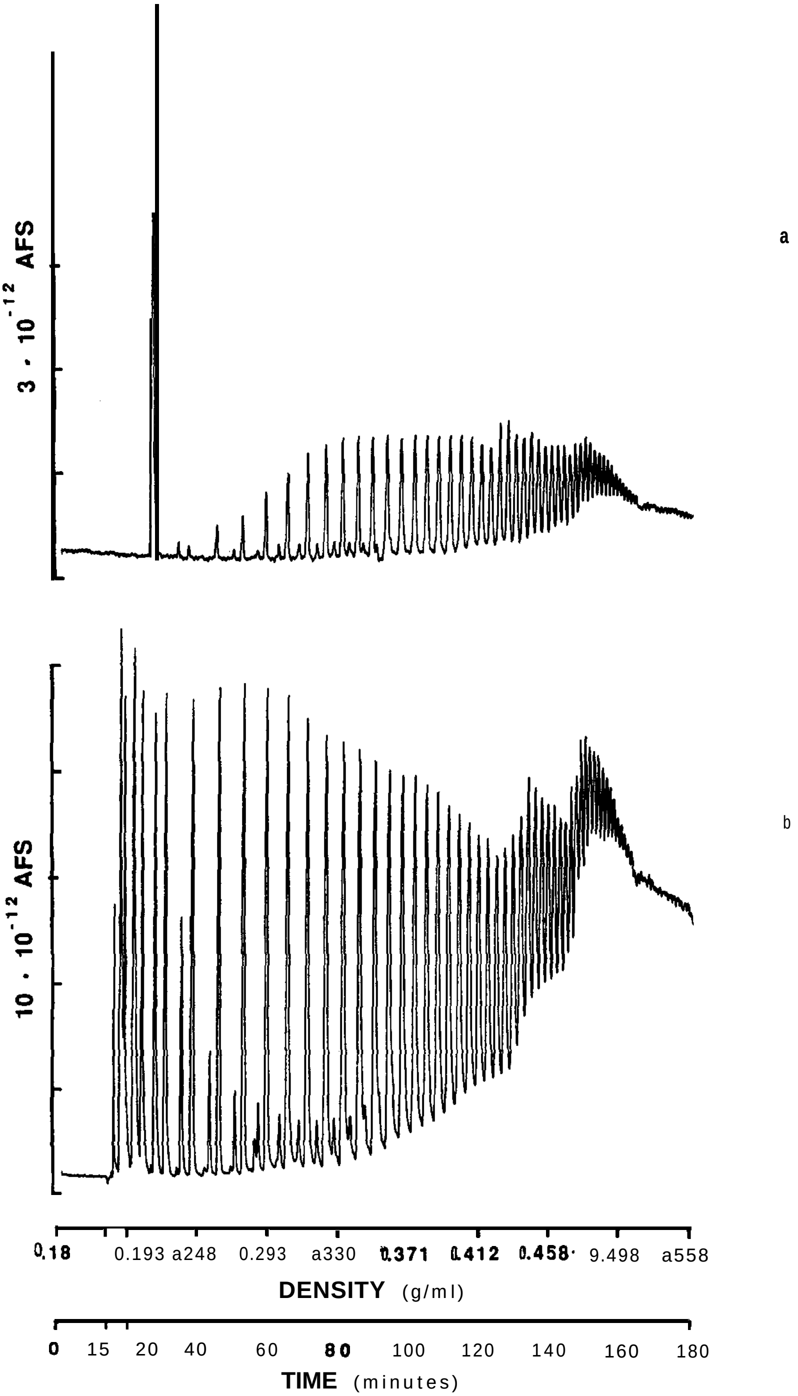

Fig. 5. Selective detection of polydimethylsilicone oligomers. (a) Drift window 12.2 to 13.2 ms, (b) drift window 7 to 15 ms.

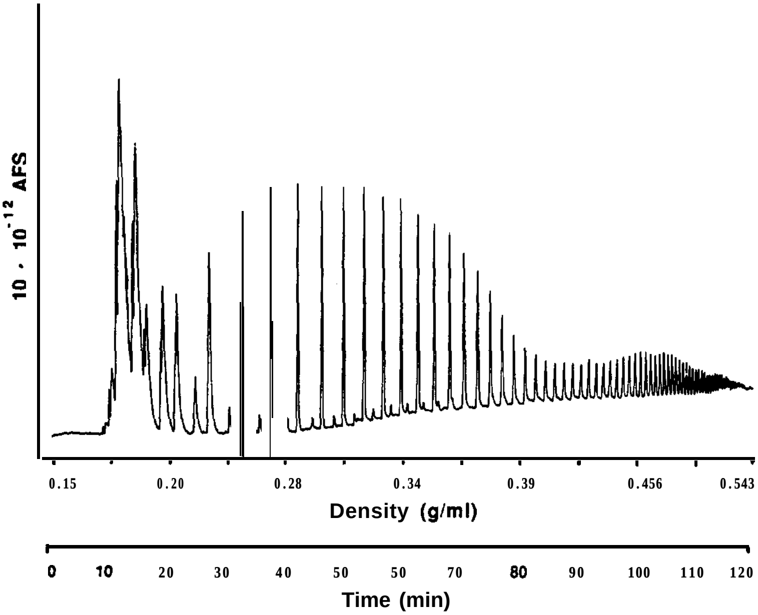

Fig. 6. SFC-IMD separation of Dow Corning 200. Lee Scientific column, 20 m × 50 μm I.D. column, SB-Methyl-100 stationary phase, 0.25 μm film. IMD temperature 250°C.

tion time data in Fig. 5 and matching the chromatographic profiles of the figure to the chromatograms obtained by Later *et al.*[13], it appears that the selectively detected peak is a compound which elutes before the fifth oligomer. For comparison, drift times between 7 and 15 ms were monitored to provide non-selective detection of the Dow Corning 200, shown in Fig. 5b. From Fig. 5b it appears that the Dow Corning 200 mixture was composed of two series of peaks: a major series and a minor series. Without mass spectral data for the product ions produced by these peaks it is difficult to determine the identity of the ions.

Finally, Fig. 6 shows the separation of the Dow Corning 200 using the 50 μm I.D. column with a split injection and Guthrie restrictor. The Dow Corning 200 sample was prepared at a concentration of 5% in hexane. The detector was programmed to monitor drift times between 7 and 15 ms. As can be seen in the figure, the efficiency of the separation and the number of peaks observed have been increased. It is estimated that compounds corresponding to oligomers of 70 monomer units were detected. Furthermore, the use of a higher-efficiency column has shortened the analysis time by an hour. With higher-efficiency columns and superior restrictors the performance of the IMD was roughly equivalent to separations using flame ionization detection[13]. The unique advantages of selective detection and qualitative information from the drift spectra are not affected by the improvement in the chromatography. It is likely that if the temperature of the IMD could be raised to match normal operating temperatures of the flame ionization detection, the performance of the IMD could be improved beyond what is shown here.

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