troduction of sufficiently small quantities of compounds such that only simple uncomplicated spectra were observed by the ion mobility spectrometer. Microprocessor-controlled operation of the ion gates in the drift tube permitted both selective and nonselective detection of chromatographic effluent [2] and the Fourier transform method of operation enabled spectra from rapidly eluting capillary chromatographic peaks to be captured "on the fly" [3]. It was also found that the linear range of the detector could be extended by the use of a photoionization source [4]. As a GC detector the IMD has been compared to the FID and the ECD for contamination effects [5] and has been applied to the detection of 2,4-D in soils [6] and for the determination of barbiturates [7].

Current Goals

More recently, our work has led to investigation of the mobility of ions produced from organic compounds with molecular weights higher than those that can be conveniently eluted from a gas chromatograph. One approach to achieve this goal has been to use supercritical fluid chromatography as the introduction method for IMS [8,9]. Besides the detection of medium range (500–5000 amu) molecular weight compounds, advantages of ion mobility detection after SFC include sensitive detection of compounds which do not contain chromophores, universal detection mode of operation, tunable selective detection, Fourier transform spectra of SFC separated compounds, and compatibility with a wide range of mobile phases.

Future Challenges

Now that interfaces and operational modes for the ion mobility detector have been developed for both gas and supercritical fluid chromatography, the methodology is being investigated for application to real samples. The real challenge for ion mobility spectrometry as a chromatographic detector, however, lies in the detection of compounds separated by liquid chromatography. A significant step toward achieving this goal is the recent development of an electrospray ion source for IMS. By introducing the effluent from a liquid stream into the spectrometer via an electrically charged capillary, we have been able to capture ion mobility spectra from nonvolatile compounds dissolved in the mobile phase. The practical utility of this method of ionization is currently under investigation.

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Quantitative Aspects of Glow Discharge Mass Spectrometry

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The problems of quantitation that arise in the direct analysis of solid samples are well known. Amongst them are the preparation and certification of homogeneous standards, and the transfer of calibration factors from standards to similar or dissimilar matrices. These problems have been more aggravated as a result of the increased need for trace analysis at sub-ppm (microgram/gram) levels. Laboratory based instruments traditionally used in this area suffer from poor precision or large matrix effects.

The glow discharge mass spectrometer (GDMS) offers some attractive possibilities in this regard. The glow discharge source delivers a stable, high intensity, ion beam enabling good precision to be achieved from the electrical detection system. The method of ion formation in the source involves sputtering neutral atoms from the sample and then ionizing them in the plasma. This two-step process is expected to considerably reduce dependence on matrix effects, giving relative ion yields that are not very sensitive to the material or chemical compositions of the sample. Finally, the application of high resolution mass spectrometry removes spectral interferences which in many cases would cause problems for elemental signals at ppm or lower. Results have been obtained by a number of laboratories operating GDMS (VG 9000—manufactured by VG Elemental), which show the above features. Table 1 is a compilation [1] of relative ion yields obtained from a range of standards of different materials. They have been normalized to the value for iron, and it can be seen that the relative yields vary by less than 30% for these dissimilar matrices.

The relative ion yields in table 1 can be used to construct a table of average relative sensitivity factors which can then be applied to matrices for which no convenient standard exists. The expectation is that, in general, this should provide quantitative analysis to within 30%, which is often sufficient at trace levels. Table 2 shows a test of this using a molybdenum sample [2]. After correction with average factors the results are well within 30% of the certified values. Other examples have been obtained. Quantitation can be further improved by using appropriate standards under controlled conditions. In these cases accuracies of 1–2% have been achieved.

Table 1. Relative ion yields for various matrices with the VG 9000 GDMS

Element	Ga	Al	Fe	Cu	Mean RIY	Max deviation %
B		1	1	1.2	1.1	9
Na	1	0.5	0.66		0.72	38
Mg	1	.77	.91		.89	13
Al	0.85	1	.63	1	.87	27
Si	.63	0.91	.5	1	.76	31
S	.5			0.34	.42	19
Cr	.5	.5	.5	.8	.6	33
F	1	1	1	1	1	
Cu	0.34	0.25	0.25	0.30	0.29	17
Ga	.5	.4			.45	11
Zn	.15	.2		.15	.16	25
Se	.3			.33	.34	3
Ge	.63		.5		.56	12
Cd	.18	.17		.17	.17	6
Sn	.34	.4	.42	.43	.42	2
Te	.34			.36	.35	3
Pb	.36	.34	.34	.38	.36	5

Table 2. Analysis of molybdenum sample following calibration with average sensitivity factors

Element	VG 9000 result using average sensitivity factors (ppm wt)	Quoted conc. (ppm wt)
Co	24	21
Cr	51	45
Cu	33	28
Fe	2125	1880
Mn	19	18
Ni	29	28
Si	151	133
V	1.4	1
W	5075	4700
Zr	99	120

Good internal and external precisions are inherent in achieving good quantitation. However, such measurements inextricably link sample homogeneity and instrumental reproducibility. Table 3 shows precisions [2] measured using a VG 9000 on 10 separate samples taken from a block of aluminum. Internal/external precisions of a few percent at the ppm level and 10–20% at the tens of ppb level show *both* good sample homogeneity and instrumental reproducibility. This exercise was in fact undertaken to assess the homogeneity of the material prior to a round-robin exercise.

Table 3. VG 9000 analysis of BCR high purity aluminum

Element	Conc. ppm (ion beam ratio)	RSD %
Mg	0.800 [a]	10
	.792 [b]	8.5
Si	.755	6.3
	.766	2.5
Ca	.126	19
	.149	15.4
Ti	.272	11.8
	.243	14.4
V	.048	6.3
	.047	6.4
Cr	.010	20
	.011	20
Mn	.036	8.3
	.038	7.8
Fe	.497	10
	.519	5.6
Ni	.042	26
	.054	14.8
Cu	.130	42
	.128	27.3
Zn	.017	23.5
	.019	10.5
Pb	.017	11.8
	.017	11.8
Th	.007	14.2
	.006	14.6
U	.005	20
	.005	20

[a] Upper level figures are internal measurements (same sample).
[b] Lower level figures are external measurements (different samples).

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Studies of Limit of Detection on 2,4,6-Trinitrotoluene (TNT) by Mass Spectrometry

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Various ionization methods including positive chemical ionization (PCI), negative chemical ionization (NCI) and electron impact (EI) were used to study the mass spectra of TNT. Methane, isobutane and ammonia were used as the CI reagent gases. The mass spectrometric quantitation in this study was performed by selected ion monitoring (SIM), with sample introduction via a short capillary column and a solids probe. The best TNT detection limit (ca. 0.020 ng) was obtained with the NCI-SIM technique with isobutane as a reagent gas.

Introduction

The trace analysis of explosives is of importance in forensic science and analytical problems encountered in this field involve the detection of nanogram quantities of explosives in extracts obtained from post-explosion residues [1]. The identification of an explosive residue usually involves extracting the debris with acetone or methanol, then separating the extract by chromatographic methods coupled with a detection technique. Single ion monitoring (SIM) by combined gas chromatography-mass spectrometry is the most promising technique to determine a trace amount of an explosive in an unknown mixture.

The mass spectra of a series of explosives have been reported [2–3]. This report describes the investigation of the limit of detection (LOD) of TNT by gas chromatography-mass spectrometry.

Experimental

All mass spectra were generated with a Finnigan Model 4023 combined gas chromatograph/mass spectrometer (GC/MS) equipped with a dual