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Continuous measurement of volatile organic chemicals in natural waters

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ABSTRACT

The use of membrane inlet mass spectrometry for the continuous monitoring of volatile organic chemicals at the low μg/l concentrations in natural waters is described. The results of four field surveys undertaken between 1985 and 1988 are presented as examples of the type of information this novel instrumentation can generate on the distribution of organic chemicals in natural waters. The applicability of the method for this type of analysis is also discussed with reference to the key parameters.

Key words: membrane inlet; mass spectrometry; volatile organic chemicals; environmental; continuous monitoring

INTRODUCTION

The measurement of certain organic chemicals in waste and receiving waters is becoming of increasing importance in view of recent legislation aimed at restricting their levels in the aquatic environment. Such legislation requires that appropriate methods of measurement are available to ensure that the regulatory standards are not infringed. Conventionally, this can be accomplished by discrete sampling of the water body followed by analysis back at the laboratory using methods such as gas chromatography and gas chromatography-mass spectrometry after appropriate work up of the samples. However, informative as this process is, it is not generally applicable to rapid analysis because of the finite time required for each determination. Additionally, it is difficult to use this type of method in the field. Consequently, there would appear to be a need for a field method that will allow rapid determination of the compounds of interest. Preferably this would enable continuous monitoring to provide much greater information on distribution in the water column. Membrane inlet mass spectrometry (MIMS) has the capability for the direct measurement of a number of volatile organic substances in water. Since 1963 (Hoch and Kok), it has been used by a number of workers in the biological field for the measurement of dissolved gases and organic components in aqueous systems (Lloyd and Scott, 1983; Cox et al., 1984). Its use in analytical chemistry dates from 1974 (Westover et al.), since when it has been employed in a number of areas, particularly reaction monitoring (Kallos and Tou, 1977; Calvo et al., 1981; Brodbelt and Cooks, 1984; Savickas et al., 1989). Recently, it has been suggested by the USEPA as a potential field method (Budde, 1990), but to date there seems to be little in the literature on this particular application.

This laboratory, in conjunction with VG Gas Analysis Systems Ltd. (Middlewich, Cheshire, UK), has conducted four separate field surveys on waste and receiving waters with this method. Examples of the type of information produced by this work are described in this paper together with the apparatus used. Additionally, the advantages and disadvantages of membrane inlet mass spectrometry as a field technique are discussed.

PRINCIPLE OF THE METHOD

The membrane inlet system acts both as a sample enrichment and sample introduction device for the mass spectrometer. In conventional systems (see Fig. 1), a flat supported membrane sheet is stretched across the inlet port of the source of a mass spectrometer and the aqueous sample is flowed past its external surface. Volatile organic chemicals together with water permeate through the membrane into the mass spectrometer source where they are detected, the resultant spectrum being a composite of the spectra of all the components in the pervaporate (the material transferred through the membrane). Quantitative measurements are normally made using selected ion monitoring.

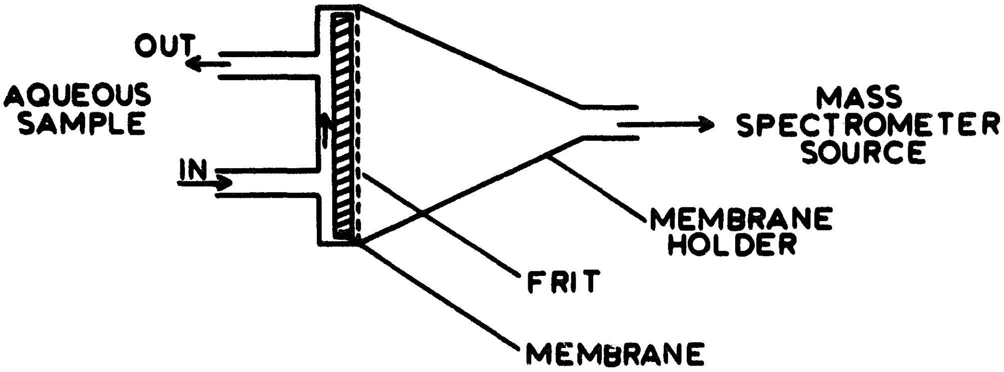

Fig. 1. Schematic diagram of membrane inlet system.

The most significant property of membrane inlet systems is their capacity for sample enrichment. By choice of a suitable membrane material (e.g. silicone rubber), the relative concentration of certain organic chemicals to water in the original aqueous sample can be greatly increased (i.e. enriched) in the pervaporate. Enrichment factors of several thousand have been measured for some volatile hydrophobic compounds, e.g. toluene, chlorobenzene, etc. (Eustache and Histi, 1981; Harland et al., 1987; LaPack et al., 1990). This feature allows µg/l sensitivity to be achieved for such substances rather than the mg/l levels which would be obtained with a simple leak inlet system to the mass spectrometer source.

Although the flat supported membrane attached directly to the source is probably the most common form of membrane inlet system, other variants have been used. Silicone rubber hollow fibres, either of the 'flow through type' developed by Cooks and his coworkers (Bier and Cooks, 1987) or the 'flow over' type (Westover et al., 1974) have found increasing application. The relative performance of these two hollow fibre systems has been evaluated by LaPack et al., 1990. Although most membrane inlets are attached directly to the source, some workers have used an intermediate reservoir connected to the source via a capillary leak (Eustache and Histi, 1981; Harland et al., 1987). However, these systems have slow response times and are unsuitable for use in field monitoring.

The theory of membrane inlet systems has been explored (Lee, 1975; LaPack et al., 1990) although the fundamental understanding of which compounds transfer most readily is still not good. Our laboratory obtained a correlation between the aqueous volatility of a compound and its enrichment factor (Harland et al., 1987) although other workers have put forward an alternative hypothesis (Watson et al., 1987) Further work of a fundamental nature is needed. It would appear that those compounds which are most readily measured by this technique are those of a volatile and hydrophobic nature, whilst the more aqueously soluble or less volatile compounds show a reduced sensitivity.

EXPERIMENTAL

Location of work

The field survey work was undertaken at three separate locations. The first two surveys, 10–12 September 1985 and 16–18 June 1987, were carried out on the estuary of the River Tees in Northern England. In both these surveys, the mass spectrometer was located on the banks of the estuary at selected positions. The later surveys, 13–15 and 18–19 July 1988, involved the use of the instrumentation from a boat. The first was carried out on the Manchester

Ship Canal, a narrow waterway in Northern England and the second on the estuary of the River Forth in Scotland.

Apparatus

(a) Mass spectrometer

The mass spectrometer used for all of the survey work was the AquaPetra (VG Gas Analysis Systems Ltd., Middlewich, UK) which went through several modifications after its initial conception in 1984.

Initially, for the first survey in 1985, it was based on simple modification of a small quadrupole mass spectrometer which was designed for atmospheric monitoring. This instrument, the Petra, had an electron impact source, a mass range of 200 a.m.u. and an electron multiplier detector. It was fitted with a silicone rubber membrane inlet and for aquatic monitoring work the greater part of atmospheric flow/calibration system was disconnected and replaced with an aqueous flow system which was linked directly to the membrane. The flow system was constructed from nylon and PTFE tubing (o.d. 6 mm) and the sample was pumped around the system by a high speed pump (Micropump) which was placed downstream of the membrane. This was able to operate at flow rates of up to 4 l/min. The vacuum system for the Petra was an ion pump, but for survey work this was supplemented by a 50-l/s turbomolecular pump (Balzers) backed by a rotary vacuum pump (Edwards E2M2).

The instrument was boxed in two parts, an electronics control system of dimensions 500 mm × 800 mm × 570 mm and a vacuum analyser unit of dimensions 220 mm × 800 mm × 570 mm. The data system was an Apple II microcomputer with single disc drive and 48 K memory.

For the second survey in 1987, some modifications were made to the apparatus. The flow system was changed to include a cartridge heater which could heat the sample to 60°C. This higher water temperature reduced boundary layer effects at the membrane surface and thus allowed the use of a lower flow rate (140 ml/min) than the original 4 l/min. The pump for this flow system was of the magnetically coupled type and was fitted with Ryton gears (Michael Smith Engineers). The analyzer box was also repackaged to include the turbomolecular pump which previously had been externally mounted; this increased its dimensions to 250 mm × 600 mm × 900 mm. For the 3rd and 4th surveys, the only major modifications made to the apparatus used for the second survey were the replacement of the Apple II data system with one based on an IBM PC and the incorporation of a shut off device between the membrane and the source. This was set to trigger if the pressure was raised excessively, i.e. hole in the membrane.

(b) Power supply

The apparatus required approximately 3 kWh (50 Hz, 240 V) electric power and this was supplied either by portable generator or by an inboard generator for the boat surveys.

(c) Sampling system for waste and natural waters

A sampling system (see Fig. 2) was utilised on all surveys since it was impossible to get closer than a few metres to the natural waters, even with a transportable mass spectrometer. This system was constructed from 10–20 m of wide bore hosepipe tubing (12.5 mm i.d.). To pump the sample up to the vicinity of the mass spectrometer, a gas operated diaphragm pump (P&G Pageboy SFD 15) was attached to a fish-shaped baseplate at the inlet end of the tubing. This was able to maintain a sample flow rate of approximately 1 l/min. Nitrogen (oxygen free) gas was used to operate the pump and this was supplied from a gas cylinder (size K, BOC Ltd., UK) via 6 mm o.d. nylon tubing. The outlet end of the hosepipe line was connected to the bottom of an interceptor vessel which was placed in close proximity to the mass spec-

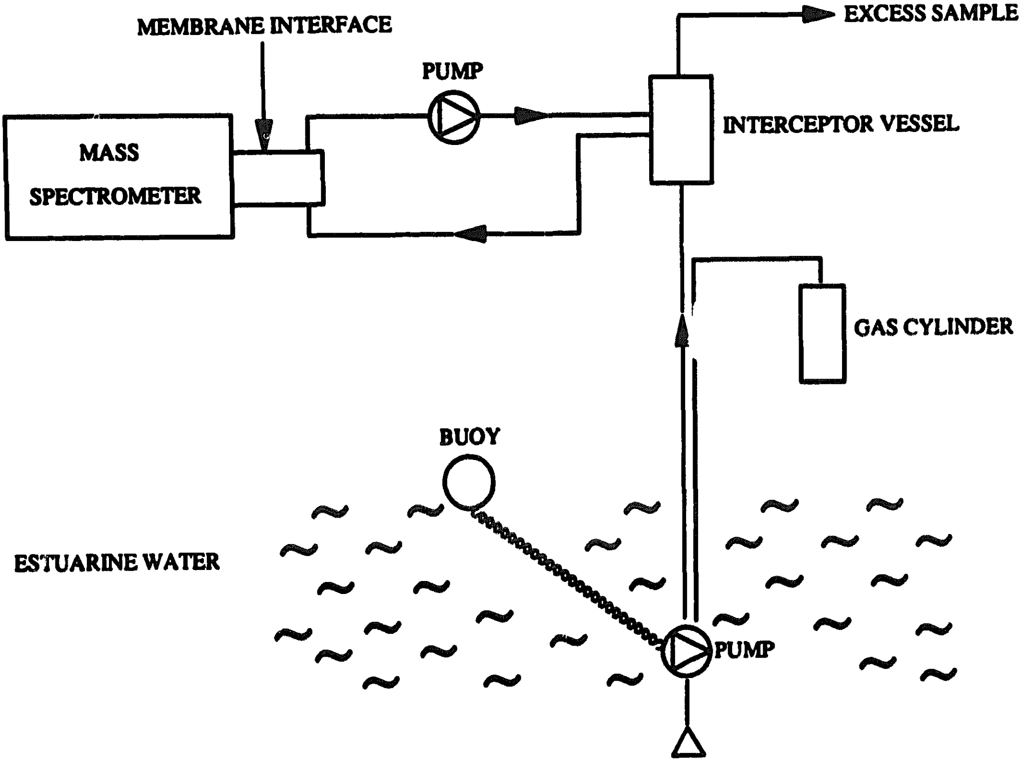

Fig. 2. Block diagram illustrating the connection of the sampling system to the membrane inlet of the mass spectometer (1st survey).

trometer. This was sampled on a return basis by the flow system of the mass spectrometer. All connections from the interceptor to the mass spectrometer flow system were made with 6 mm o.d. PTFE or nylon tubing. Excess water was allowed to drain from the top of the interceptor. Use of the interceptor for the first survey was essential because of the much higher sample flow rate of the mass spectrometer flow system, 4 l/min, than the sampling system. However, even on the later surveys when the mass spectrometer flow system was reduced to 140 ml/min, the interceptor was still retained since it damped the pulsing of the diaphragm pump.

The inlet part of the sampling system was suspended in the water sample either from a buoy or from a convenient fixed point, e.g. scaffold pole on land, or hydraulic hoist on boat, etc. The fixed point suspension was the preferred arrangement since it enabled depth profiling to be carried out much more quickly than was possible with the buoy system.

(d) Sampling platform

A mobile van was used for transportation of the apparatus on the first two surveys. This was fitted out as a mobile laboratory by the insertion of a small amount of benching.

For the last two surveys, the apparatus was mounted in a boat. The first boat used was an 80-foot fishing boat, 'Branding' (Carmet Marine), which had been converted as a survey vessel. The second boat was a 70-foot motor vessel, 'Conserver' (Forth Ports Authority) which was normally used for buoy maintenance work, etc.

Mass spectrometer operation

Two basic modes of operation of the mass spectrometer were used during the survey, histogram and ion table.

The histogram mode displays a mass spectrum of the sample over a predefined mass range up to 100 mass units wide. While this mode is useful for identification purposes, it is not very sensitive and was therefore used infrequently. Instead, nearly all of the survey work was carried out using the ion table mode of operation which gave better quantitative results. This allowed the intensity of 16 selected ions to be monitored at frequencies of from a few seconds to several minutes for a complete cycle of the 16 ions. Where possible, two to three ions were selected for each compound that was to be determined, although for some compounds this was impracticable. Additionally, the ions selected had to be free from interference from other constituents that might be present in the sample. Using the ion table mode of operation, low μg/l sensitivity for many volatile organic compounds was achieved. For both histogram and ion table modes, the data could be as hardcopy output. For the third and fourth surveys, disk storage of the data was also practicable.

Calibration of system

The system was calibrated by running standard solutions of aqueous standards of the target chemicals through the flow system of the mass spectrometer. The standards were made up in large graduated flasks (1 or 5 l) in deionised water and were prepared immediately before each calibration run. All chemicals used were either of Analar or General Purpose grade. The response of the mass spectrometer to these standards was determined by monitoring appropriate selected (major) ions in their spectrum.

Intercomparison apparatus

Some work, independent of the field surveys, was carried out to assess the comparability of membrane inlet mass spectrometry data to that from more conventional analytical methods. The apparatus used in the methods employed in this exercise is briefly described below:

Method 1 (Membrane inlet mass spectrometry)
A laboratory based membrane inlet mass spectrometer was used for this analysis. It was essentially similar to the smaller versions used in the field surveys apart from having larger quadrupole rods which gave it increased sensitivity.

Method 2 (Purge & Trap GC-FID)
Samples were analysed using a purge and trap injector (Chrompack PTI) which was coupled to a gas chromatograph fitted with flame ionisation detector.

Method 3 (Purge & Trap GC-MS)
Samples were analysed using the Chrompack PTI coupled to a GC-MS system, a Varian 3400 gas chromatograph linked to a Finnigan TSQ-70 tandem mass spectrometer (used in the single analyser mode).

RESULTS AND DISCUSSION

Examples of the information generated by the surveys

Some examples of the results generated during the four separate field surveys are presented below to show the type of information that can be generated on the distribution of volatile organic chemicals in natural waters with this type of instrumentation.

(i) Identification of substances in waste water

During the first survey, the apparatus was placed adjacent to what was essentially a neat waste liquid effluent discharge. The histogram from the effluent sample is shown in Fig. 3 and the corresponding background sample (deionised water) is shown, at ten times greater sensitivity, in Fig. 4. Study of the higher mass part of the two spectra shows the appearance in the effluent spectrum of major ions at *m/z* 77, 78, 79, 91, 92, 105 and 106; the first four of which are saturated. Part of this pattern was interpreted as corresponding to the presence of benzene (*m/z* 78), toluene (*m/z* 91 and 92) and C2-benzenes (*m/z* 91, 105 and 106), i.e. ethyl benzene and xylenes, in the sample. This interpretation was in agreement with the known composition of the discharge since these substances are present at low mg/l concentrations. However, interpretation of such composite spectra is generally extremely difficult. An experienced mass spectroscopist could probably hope to identify at least the top two to three components appearing in the spectrum of an un-

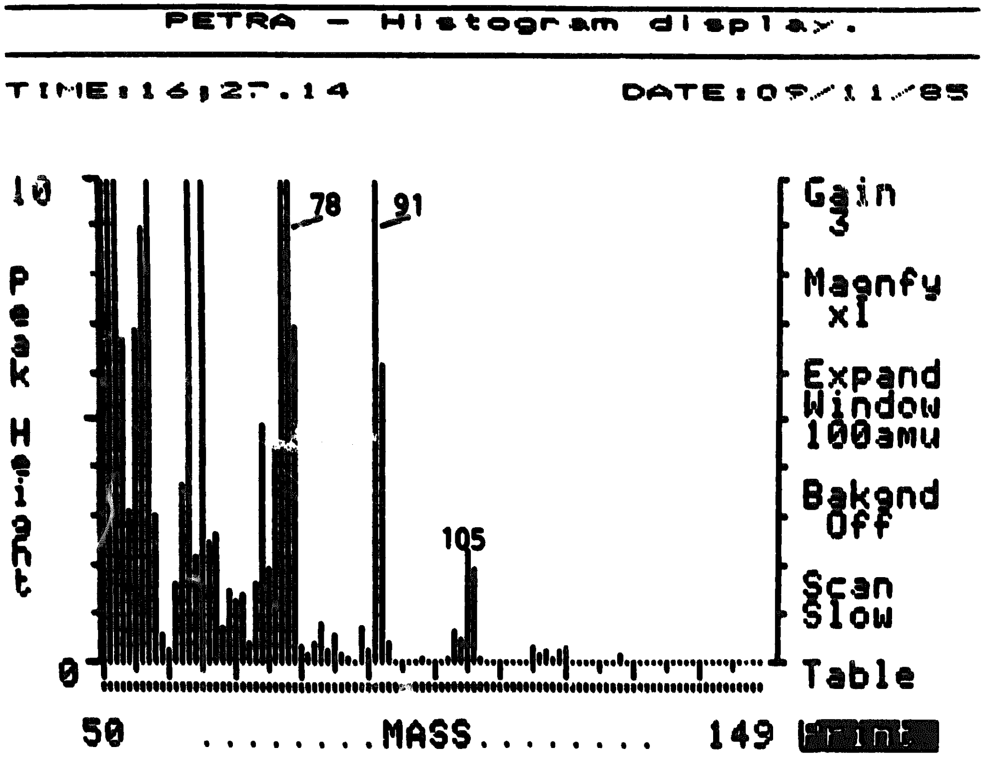

Fig. 3. Mass spectrum (histogram) of a waste water sample taken over the range *m/z* 50–150 with a gain setting of 3.

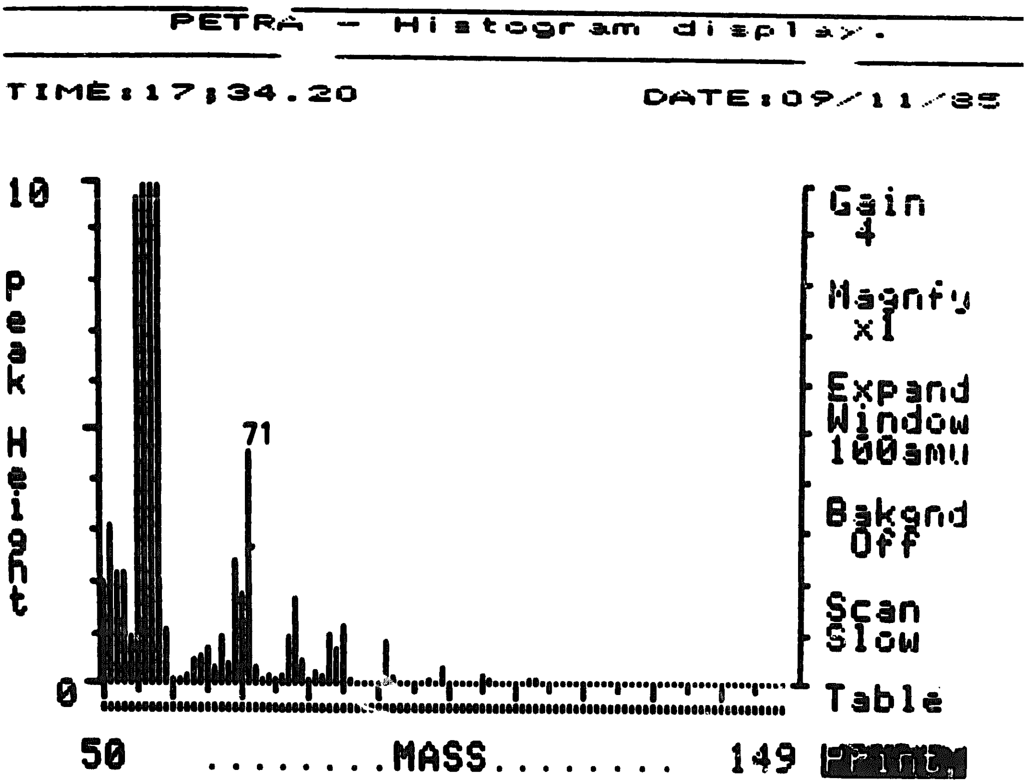

Fig. 4. Mass spectrum (histogram) of a background (deionised) water sample taken over the range m/z 50–150 with a more sensitive gain setting (4) than used in Fig. 3.

known waste water sample, providing their major fragment ions are clearly visible and are not overlapped to any great degree. This identification process would be greatly assisted by use of a spectral deconvolution procedure. Nevertheless, the complexity of the composite spectrum means that there is always the possibility of making false assignments and, for unknown discharges, the use of a complimentary method, e.g. GC-MS, to obtain confirmation of identity would be recommended.

(ii) Quantification of substances in water

The greater part of the work conducted in all four surveys was concerned with the quantification of a number of substances in the waste and natural waters sampled. A particular example of this process, taken from the second survey on the Tees estuary, is shown in Fig. 5. On this occasion, the apparatus was monitoring estuarine water at a point several metres from an effluent discharge. Before monitoring the estuarine water, the system was first calibrated, according to the procedure described above, for a number of compounds including benzene and toluene. The calibration range was between 10 μg/l and 1000 μg/l as illustrated in Fig. 5.

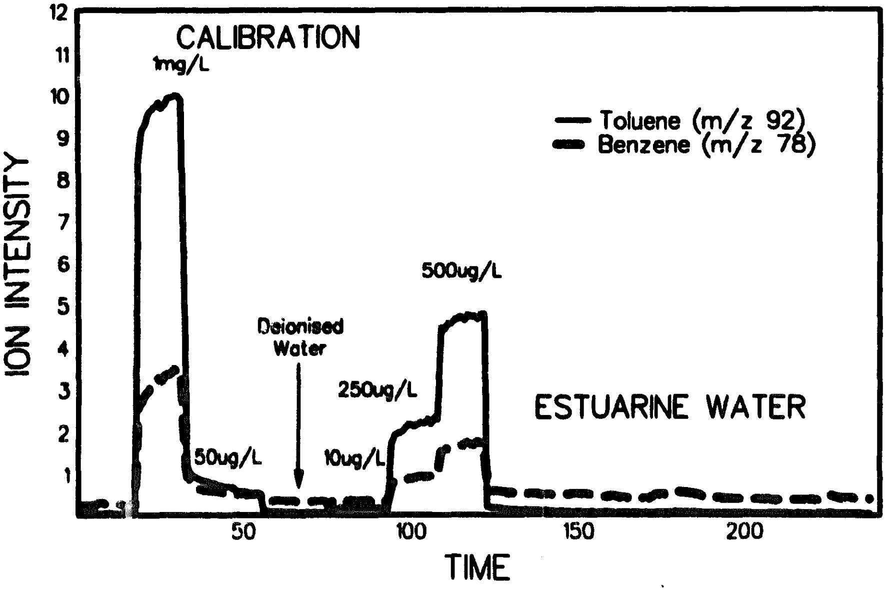

Fig. 5. Calibration of AquaPetra for benzene and toluene (10 μg/l–1 mg/l range) followed by monitoring of the estuarine water of the River Tees. Duration of calibration and monitoring is 71 min.

Inspection of the results shows that the toluene response, as given by the *m/z* 92 ion shows good linearity over the whole calibration range. Benzene also shows good linearity at the higher concentrations but there are problems at the low end of the calibration where some deviation is experienced and indeed the 10 μg/l standard is not discernible from the background. The reason for this is believed to be a memory effect with the membrane for this compound, possibly related to previous use of the instrument. The instrumentation was hired for all surveys, and no pre-evaluation by the Laboratory was possible. (That good linearity for benzene can be obtained was illustrated by experience on the fourth survey when the 10 μg/l standard was clearly discernable and was found to be linear in response to a 100-μg/l standard.)

After calibration of the system, the estuarine water was monitored at 0.5 m depth for approximately 2 h. Measurements of the benzene response indicate an estuarine concentration of between 10–100 μg/l, while the concentration of toluene observed was below the determination level, i.e. less than 10 μg/l.

(iii) Mobile field use of the technique

The final two examples are taken from two boat based surveys which were carried out in 1988. Boat based use of the instrumentation was introduced to allow the distribution of the components in the water to be investigated over a much larger area.

The first of these examples, which is taken from the work on the Manchester Ship Canal, shows in Fig. 6 the results from profiling a 16-km stretch for benzene (*m/z* 78) on a narrow waterway. Initially, a longitudinal profile was undertaken over a 16-km stretch at nominal 2 m depth, although the actual depth of sampling was probably between 1–1.5 m because of the motion of the boat. The benzene concentration was found to decrease gradually over the first few kilometres as can be seen from the figure. However, at a distance of 8 km, two distinct peaks in the profile were observed and these were immediately followed by a third peak, which was much broader and weaker. These three peaks occur in the most industrialised part of the waterway and represent benzene discharges from petrochemical complexes, etc. At the 16-km point, the boat was moored and some depth profiling was conducted at this location. Generally, there was a small increase in benzene concentration with depth although there was some inversion in the bottom water.

The second example is taken from the other boat survey, on the Forth estuary and is concerned with the profiling of toluene using the *m/z* 92 ion. The results are shown in Fig. 7. Initially, a calibration for toluene was carried out at the 100 μg/l level and this was then followed by monitoring the estuarine water at fixed location at 1 m depth where toluene concentrations of the order of 5–10 μg/l were observed. Next, a 4-km upstream longitudinal

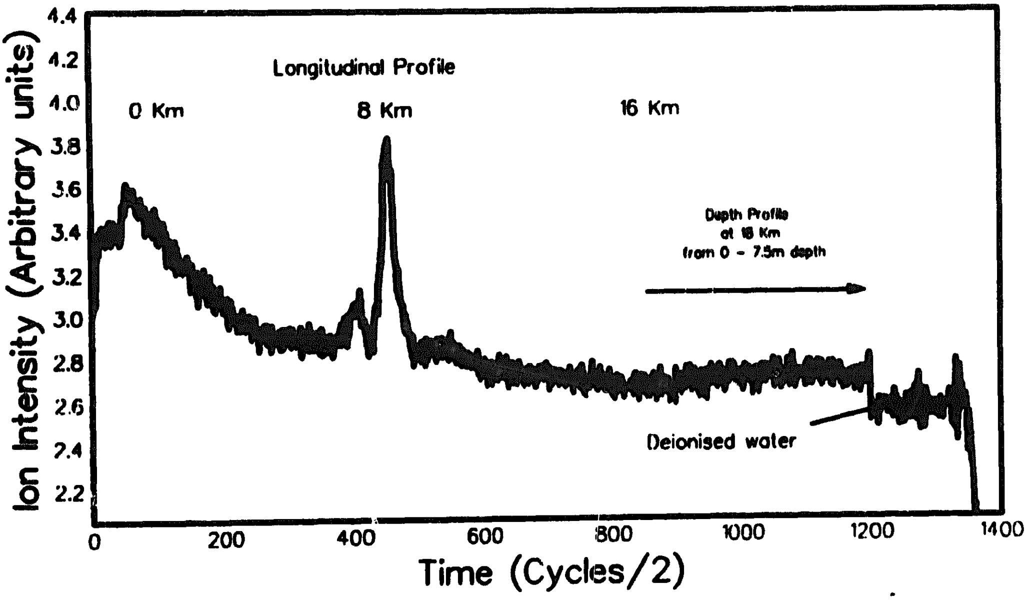

Fig. 6. Profile of benzene (*m/z* 78) in the Manchester Ship Canal from a boat based survey. Initially a longitudinal profile of the water was carried out over a 16-km stretch. This was followed by depth profiling at the end location from sub-surface to bottom (7.5 m depth). Finally the baseline for the system was established by running deionised water. This figure covers a time period of 263 min.

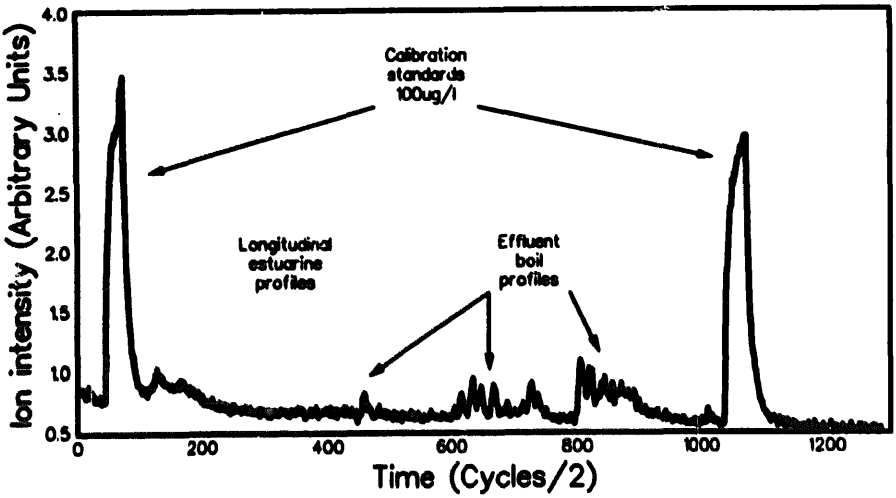

Fig. 7. Profile of toluene (m/z 92) in the estuary of the River Forth. The figure shows two 100 μg/l calibrations at start and end and estuarine and effluent profiling between as indicated; the figure covers a time period of 236 min.

profile of the estuary was undertaken followed by a return (downstream) profile of 3.2 km. These profiles which were carried out at depths of between sub-surface and 1 m showed no evidence of toluene until the submerged discharge of a large chemical works was crossed. (This pipe was not monitored on the upstream profile because the clearance was too low.) The sharp distinct peak observed above the pipeline represents a toluene concentration of approximately 7 μg/l. Attempts were then made to profile this discharge but this was hindered by the inability to anchor, because of potential damage to the pipeline. Nevertheless, further profiling was achieved on occasions as is illustrated by Fig. 7 and a maximum concentration of 20 μg/l toluene was observed at 3 m depth. The work was completed by another calibration standard for toluene at the 100 μg/l level.

The four examples above illustrate the large amount of data that can be generated by membrane inlet mass spectrometry in the field, especially when it is considered that only selected examples have been given from each of the surveys. Each of the profiles presented shows only one of the 16 ions that were monitored in that particular run and a number of separate runs were undertaken on each of the four surveys.

Suitability of membrane inlet mass spectrometry as a field method

Although, only results from work on benzene, toluene and C_2-benzenes have been presented above, the laboratory has monitored a number of other compounds during the surveys including: 1,2-dichloroethane, chloroform, carbon tetrachloride, chlorobenzene and a number of other chlorinated hydrocarbons, both aliphatic and aromatic. This experience allows some general conclusions to be drawn about the strengths and weaknesses of membrane inlet mass spectrometry as a field method for their continuous monitoring. These are outlined below with particular reference to the key parameters, viz. sensitivity, response characteristics, specificity and reliability. Additionally, a comparison is made between the data generated by this technique and that from more conventional methods.

Sensitivity

The most sensitive of the compounds monitored during the surveys were 1,2-dichloroethane and toluene which could be detected at the 5 μg/l level. The detection level for benzene is likely to be similar although this data is not yet available. Chlorobenzene and chloroform were slightly less sensitive with detection levels of around 10 μg/l while the corresponding value for carbon tetrachloride was 20 μg/l. These values are close to, although slightly higher, than those found for four of the five compounds by LaPack et al. (1990) and are lower than those quoted by Cooks et al. (1991) for three of the compounds. Better stability would be expected from a laboratory based instrument since there is no requirement for it to be switched off overnight. Additionally, it may also possess greater sensitivity for other reasons, e.g. larger quadrupole rods, as was the case with the instrument used for the intercomparison work (vide infra).

Some problems were experienced in the field surveys in the determination of certain substances that were expected to be reasonably sensitive to membrane inlet mass spectrometry, viz. tri- and tetra-chloroethenes and di- and tri-chlorobenzenes, when using ions above 130 a.m.u. This was believed to be because of the poor sensitivity of the AquaPetra in this higher mass range. To counteract this problem, a small amount of work was undertaken using ions below 120 a.m.u. for their determination and this indicated that the detection levels for trichlorobenzene was around 50 μg/l and those for the other three substances were in the 20–50 μg/l range. Certain less volatile and/or more soluble substances have also been assessed on survey, but their sensitivity was very much less as would be expected.

For compounds of a hydrophobic and volatile nature, as noted above, the sensitivity is normally in the low μg/l range and this is adequate for many applications in natural waters where these substances are present in significant concentration, e.g. benzene and toluene profiles in Figs. 6 and 7. However, the UK regulatory standards for many of these chemicals now approach or are lower than the current field detection limits of the system, and there is a clear need for greater sensitivity if it is to be used to assess compliance. Recent work has indicated that this might be achieved by using a membrane inlet of the flow over hollow fibre type which is purged on the inside by a helium gas stream (Slivon et al., 1991). The detection levels claimed for this system are several times lower than those previously quoted in the literature for the same compounds.

Response time

Besides sensitivity, the response time of the system is also an important factor. This is a measure of the time taken to achieve maximum signal response to a sample of fixed concentration, i.e. to achieve a steady state composition. For a membrane inlet system, the signal response approaches the asymptotic and consequently determination of the true response time is extremely difficult. Nevertheless, an attempt has been made in this work to estimate these for some of the compounds used. Of these, 1,2-dichloroethane again shows the best performance with a response time of 1 min, followed by benzene with 1.5 min. The corresponding figures for the other compounds are 3 min for chloroform and carbon tetrachloride, 4 min for toluene and greater than 6 min for monochlorobenzene. The values for the higher chlorinated compounds have not yet been assessed but are believed to be equivalent to or worse than that for chlorobenzene. All of the above values are from the third and fourth surveys where the sample temperature was 50°C. Increase in temperature is known to decrease the response times (Harland et al., 1987). The finite time of response of the membrane system might seem a disadvantage but effectively it would appear to be sufficient to adequately determine the variation of the chemical concentrations in natural waters.

Reliability of equipment

During all of the surveys which lasted for a combined total of 11 days, only once was a problem encountered which necessitated abandonment of the work. This occurred at the end of the final day of the first survey when the mass spectrometer filament failed. Otherwise a high operational capacity was maintained on all surveys.

Specificity of analysis

It is apparent that the specificity of the method must be less than that of techniques such as GC-MS where some separation of the compounds is obtained before they are presented to the mass spectrometer. Some compensation for this can be achieved by monitoring several ions for the same compound, but this, as stated earlier, is not always practical. Consequently, when using this system, either knowledge is required of the substances which are being monitored or a backup method has to be applied to confirm the accuracy of the information being generated. The use of tandem mass spectrometry with a membrane inlet system greatly increases the degree of specificity over that of a conventional mass spectrometer (i.e. single analyser), but although this has been used in the laboratory (Lauritsen et al., 1990), it is unlikely to be available in a field instrument in the near future.

Comparison with other methods

In only one of the field surveys was an attempt made to compare the results generated by the AquaPetra to those from a more conventional method, but this was unsuccessful because of apparatus failure at the participating laboratory. However, in November 1991 in conjunction with a sister laboratory, an intercomparison exercise was conducted on the measurement of six volatile halogenated hydrocarbons in environmental water samples. Duplicate samples were taken at five separate locations in the Mersey Catchment area in Northwest England and the contents of one of the sampling containers were split to provide subsamples for the principal methods used by the two laboratories for these compounds, purge and trap analysis with either GC-FID or GC-MS determination. The other, duplicate, sample was analysed by membrane inlet mass spectrometry using a laboratory based instrument which was similar to the AquaPetra taken on the field surveys and was operated in the same manner, i.e. ion monitoring mode for quantitative determinations.

In the analysis of the samples, a problem was experienced in the determination of one of the substances, chloroform, in two samples (numbers 4 and 5) by the purge and trap GC-FID method. This was caused by the contamination of two of the sampling containers with hexane which interfered with this determination.

The results from the intercomparability exercise, which was primarily designed to compare the purge and trap methods used by the two laboratories, are shown in Table 1. Generally, agreement between the two purge and trap methods is very good for all compounds except perchloroethylene where the results of one laboratory are approximately twice as high as the other for unknown reasons. However, the results produced by membrane inlet mass spectrometry are also in very good agreement with both of these methods for the other compounds and compare well with one of the methods for the sixth, i.e. perchloroethylene. This data indicates that membrane inlet mass spectrometry is capable of producing results which are comparable to those

TABLE 1

Summary of intercomparison data (all values in μg/l)

Substance	Method[a]	Sample number				
		1	2	3	4	5
Chloroform	MIMS	<1.5	2.2	2.2	56	69
	P&T/GC-FID	2	2.9	3.5	[b]	[b]
	P&T/GC-MS	1.8	3.6	3.9	49	62
1,2-Dichloroethane	MIMS	2	7.1	1	49	67
	P&T/GC-FID	2.2	4.1	0.5	37	90
	P&T/GC-MS	2.1	4.9	0.5	36	65
1,1,1-Trichlorethane	MIMS	<1.5	<1.5	<1.5	3.5	3.1
	P&T/GC-FID	0.3	0.4	0.3	1.6	2
	P&T/GC-MS	<0.5	0.8	<0.5	1.6	2.3
Carbon tetrachloride	MIMS	<1	1.7	14	58	71
	P&T/GC-FID	1	0.7	12	49	60
	P&T/GC-MS	0.8	1.1	13	47	56
Trichloroethylene	MIMS	<1	1.6	<1	7.9	12
	P&T/GC-FID	1.2	1.5	0.1	6.5	9.4
	P&T/GC-MS	1.2	1.8	<0.2	8.7	9.8
Perchloroethylene	MIMS	<1	2.8	<1	30	36
	P&T/GC-FID	2	4.6	0.1	54	65
	P&T/GC-MS	1.3	2.4	<0.1	32	34

[a] Analytical methods: MIMS, membrane inlet mass spectrometry; P&T/GC-FID, purge and trap GC-FID (information supplied by Miss D. Baker, ICI C&P Ltd, Runcorn); P&T/GC-MS, purge and trap GC-MS (information supplied by M.J. Hetheridge, ICI Group Environmental Laboratory, Brixham).

[b] Sample container contaminated, no values available.

from more conventional analytical methods for these substances. Obtaining good agreement with conventional methods when used by different laboratories is in itself difficult as is illustrated by some recent work (Report No. FR/D 0001).

CONCLUSION

The work carried out by this laboratory has demonstrated the potential of membrane inlet mass spectrometry for the continuous monitoring of volatile organic chemicals in natural and waste waters. This can provide a considerable amount of information on their distribution in the water column which is not currently obtainable by any other method. Additionally, use of the instrumentation on a boat greatly extends the radius over which these measurements can be made.

However, the current instrumentation can only measure a relatively restricted range of compounds. Further, the detection levels for several of the more sensitive compounds are not sufficiently low to assess compliance with current UK regulatory standards for natural waters. Improvement of instrument performance in both of these areas is required if the method is to gain wide usage in the future.

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