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Evidence for selectivity of absorption of volatile organic compounds by a polydimethylsiloxane solid-phase microextraction fibre

Stefan Niedziella[1], Susan Rudkin, Michael Cooke*

The Toxic Gases Research Group, Centre for Chemical Sciences, Royal Holloway University of London, Egham, Surrey TW20 0EX, UK

Abstract

Solid-phase microextraction using a 30 μm polydimethylsiloxane fibre has been used to sample the volatile organic compounds from standard mixtures and from mixtures produced by the decomposition of organic compounds. This method of sampling has been compared with the direct injection of an aliquot of headspace gas and shows an enrichment factor of approximately 100 over a 1 ml gas injection for organosulphur gases such as dimethyldisulphide. The performance of the fibre has been evaluated with respect to accuracy and precision at several concentrations in representing the composition of multicomponent mixtures. It was found that the presence of a second component in a gas sample reduced the capacity of the fibre to absorb the primary component. The selectivity of the fibre for various volatile compounds with differing functionality was also studied. It was found that the non-polar polydimethylsiloxane fibre preferentially absorbed the non-polar components of a mixture, e.g nonane and, correspondingly, under reported the more polar components, e.g. ethanol. Hence, the fibre discriminates in favour of non-polar and against polar components in a mixture in comparison with direct analysis of a headspace sample. Thus, quantitation of a component in a multi-component mixture is liable to error from competitive interference from other components. A major advantage of the technique, however, is that it does not absorb, and therefore introduce, water into the analytical system.

Keywords: Solid-phase microextraction; Selectivity; Polydimethylsiloxane fibres; Volatile organic compounds

1. Introduction

The determination of low concentrations of organic compounds in the gas phase in air remains a challenge for the analytical chemist. Low concentration and large volume means that introduction into a capillary gas chromatograph is a complex procedure [1]. Traditional packed columns made the process simpler with the use of a gas loop of fixed volume in line with the carrier gas to deliver a known volume of gaseous sample into the carrier gas flow immediately ahead of the column [2]. Providing the gas volume was small in comparison with the carrier gas flow then chromatographic performance was not seriously degraded. However, the ability to pre-concentrate samples is limited by this method. When a capillary column is used then one of several procedures has been adopted. Firstly, the gas sample

*Corresponding author. Tel.: +44-178-444-3414; fax: +44-178-444-3386.

E-mail address: m.cooke@rhbnc.ac.uk (M. Cooke)

[1]Present address: Europa Fachhochschule Fresenius, Limburger Strasse 2, D-65510 Idstein, Germany.

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(typically of the order of 1 ml) is introduced into the injector in the split mode. In this case the majority of the sample exits via the split valve and sensitivity is thus restricted by the volume of sample introduced onto the column [3]. In an effort to reduce this loss micro-valve systems introducing small (ca. 20 μl) of sample directly into the capillary column have been developed [4], but they are of limited value because of the small initial volumes used.

To overcome this problem techniques such as purge and trap and cryofocussing have been developed to concentrate gaseous compounds at the head of the capillary column or in the injection port [5–7]. Whilst the desired increase in sensitivity is achieved these techniques are complex and are not well suited to certain types of sample. Specifically when the gas sample to be analysed is contained in the headspace above an aqueous sample then the major component of the headspace (apart from oxygen and/or nitrogen) is water vapour. Trapping or cryofocussing water either harms the column and disrupts detection or necessitates the use of a desiccant in the injection port area [7] which further complicates the analysis procedure.

Our research group interest in the biomobilisation of elements [8,9] is centred on the study of organic compounds present in the headspace above microbiological cultures but extends to the study of landfill gas [10] where biomobilisation of a range of elements is suspected. Such samples are usually saturated with water vapour. Some compounds we wish to study are only produced under anaerobic conditions [8,9], are thermally labile and/or are reactive with oxygen. Minimal sample manipulation is thus desirable.

Solid-phase microextraction (SPME) is a simple technique which has been developed to extract low concentrations of organic compounds such as pesticides from water [11–13], and has been extensively used for food aroma analysis [14–18]. Examples of medical applications are few but examples of its use include urine headspace sampling and blood and drugs analysis [19–21]. The use of a hydrophobic polymer as the extracting phase means that the sample introduced is effectively water free. A sampling method which pre-concentrates organic compounds in situ in the sample but which rejects the major component (water), and also does not introduce either oxygen or nitrogen into the chromatograph, is well suited to headspace sampling when water vapour is present at high concentrations.

The aims of this study were (a) to evaluate the SPME system for the pre-concentration of organosulphur and similar compounds from the headspace gases generated by biocultures without interference from air or water, (b) to attempt quantitation of specific organosulphur compounds, (c) to trap phosphine present in the headspace, and (d) to evaluate the ability of the fibre to accurately reflect the composition of a complex mixture of volatile organic compounds.

2. Experimental

Chromatographic analysis of bioculture headspace samples was performed on a Finnegan ITS-40 gas chromatograph–mass spectrometer fitted with an Optic 1 injection system (ATAS, Cambridge, UK) and equipped with a DB 1701 capillary column (30 m×0.32 mm I.D., d_f 1.0 μm), carrier gas; helium at 1.0 ml/min. Gas injections were made with a 1 ml gas-tight syringe (SGE, Milton Keynes, UK).

Standard gas samples were contained in suitable glass containers, (unsilanized), fitted with small surface area septa (teflon coated) to minimise loss of volatile components to the septum or contamination of the sample by the septum. The injector programme was: trapping temperature 30°C; desorption temperature 240°C; rate of increase 16°/s; splitless time, 1.0 min. The SPME system (Supelco, Bellefonte, PA, USA) was fitted with 30 μm polydimethylsiloxane fibres.

Solvent samples were chromatographed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with electronic pressure control, split/splitless injector, flame ionisation detector and a capillary column (Rtx-1, Thames Restek, Maidenhead, UK) 30 m×0.32 mm I.D., d_f, 0.5 μm), nitrogen carrier at 1.0 ml/min. Dimethyldisulphide and di-isopropyl sulphide and other volatile organic compounds were supplied by Aldrich (Gillingham, UK).

3. Results and discussion

Our interests in the biomobilisation of elements

such as sulphur, arsenic, phosphorus and antimony has led us to develop analytical techniques suitable for the introduction and separation of volatile compounds containing these heteroatoms. For simplicity we have developed a method which uses a 1 ml gas sample introduced directly into the injection port of the GC–MS system with the split shut. At 1 ml/min the transfer time onto the column is of the order of 1 min and most of the volatile components are trapped at the front of the column which is held at 30°C. Any introduced oxygen and nitrogen together with more volatile components such as phosphine and dimethylsulphide are not retained. Information on the presence of these compounds is thus lost as they elute in the delay time before the detector is switched on. By using a relatively thick film column (1.0 μm) and a relatively polar phase (DB 1701, 50% phenyl/50% methyl) we have been able to obtain retention of dimethyldisulphide and later eluting species. This approach has been used to study a variety of samples, usually anaerobic biodegradation reactions, where a range of volatile compounds including organosulphides, short chain organic acids (C_3–C_7) and alcohols are present. However, because of the introduction of both water vapour and air components chromatographic quality in the early part of the chromatogram is poor and column attrition is fairly rapid. Nonetheless a range of compounds can be detected including organosulphur compounds, organo-oxygen compounds and saturated and unsaturated hydrocarbons.

Although solid-phase micro-fibre extraction has been extensively used for headspace sampling of flavours and aromas in food science its application has been more limited as a headspace sampling method for environmental studies. Polydimethylsiloxane fibres are non-polar and are thus hydrophobic because of the nature of the polymer and thus offer the potential of not absorbing water from high humidity headspace samples such as exists over a bioculture. To evaluate the fibres for sampling water saturated headspace above a culture various cultures were set up containing either cooked meat medium (CMM), Schaedler Anaerobe Broth (SAB) or Tryptone Soya Broth (TSB). Inorganic phosphate was added to each in an attempt to stimulate phosphine generation, and an anaerobic mud was used as inoculant. These were incubated for several days and the headspace gases sampled both directly as a 1 ml injection (splitless) and via the fibre with a 60 min exposure time (splitless).

After sampling for 60 min the fibre was thermally desorbed in the injection port of the GC–MS system using an Optic 1 injection system equipped with an open liner. Typically for a 1 ml gas injection only three major components were observed (dimethyldisulphide, dimethyltrisulphide and, tentatively, methoxyethanol: t_R 9.21 min) but for the fibre injection a complex series of components was observed with several major components being identified (Table 1). Although peak shape for the carboxylic acids was satisfactory on this relatively polar column the possibility of derivatisation was briefly investigated. In situ derivatisation of formaldehyde in the fibre has been reported previously using a dinitrophenylhydrazine impregnated fibre [22]. Exposure of the fibre impregnated with organic acids to hexamethyldisilazane in the vapour phase for 30 min followed by thermal desorption and study by GC–MS indicated that trimethylsilyl esters had been produced. Full details of this methodology will be reported elsewhere.

Comparison of the peak intensities of the two sulphur-containing compounds common to both chromatograms suggests that the fibre yielded approximately a 100-fold increase in response over the 1 ml injection. Thus, the fibre produced a response equal to approximately 100 ml of headspace. In view of the range of polymers available in fibre form and the range of polarities thus available it should be possible to optimise the polymer character to produce a maximum efficiency concentration step for a particular compound. Thus, the polydimethylsilox-

Table 1
Identification of the typical major components of a culture headspace sampled by SPME

Retention time (min)	Compound
9.21	Unknown
11.13	Dimethyldisulphide
15.12	*l*-Threonine
17.11	1-Methoxyethanol
18.25	Butylpropanoate
20.16	3-Methylbutylpropanoate
20.67	2-Methylhexanoic acid
21.09	Dimethyltrisulphide
24.06	An aminobutylcarboxylic acid
26.01	Undecanal or dodecanal

ane polymer used has proved to be capable of trapping a wide range of compounds including organosulphur compounds and there are indications that it is also suitable for use with medium chain fatty acids.

Profiling of saturated headspaces over biocultures was thus shown to be simple and free from the introduction of oxygen and nitrogen into the GC–MS system. Water vapour was not trapped by the fibre and so did not interfere with the mass spectrometry nor damage the column. Attempts to trap phosphine on the fibre proved unsuccessful and pre-concentration of phosphine prior to analysis remains an objective.

Quantitation of the organosulphur compounds was attempted through generation of a samples containing known concentrations of dimethyldisulphide and then exposing the fibre to them for different periods of time from 1 to 60 min.

Standard mixtures of dimethyldisulphide (DMDS) in nitrogen were made by filling a 1 l conical flask, fitted with a small rubber seal, with nitrogen and then introducing a known volume of DMDS using a microlitre syringe. From a knowledge of the density of DMDS, the concentration in μg/ml was calculated. By serial dilution, using a gas-tight syringe [9], more dilute standards were made giving a range of standards from 1900 to 2.7 μg/ml. Standards were allowed to equilibrate at room temperature overnight and the glass vessels used were not deactivated. Hence, it was assumed that some of the DMDS would adsorb to the glass and that an equilibrium concentration would be established in the gas phase. Thus, all concentrations quoted are nominal and are not corrected for possible losses through adsorption. A total of six standards was thus made (Table 2).

From Table 2 the following conclusions can be drawn. Firstly the amount of DMDS delivered by the fibre is independent of the time of exposure. This is reflected in both the RSDs with respect to time sampled, which are essentially constant at approximately 10%, and the constancy of the regression coefficients *R* for each plot of area vs. concentration at various times. These results differ somewhat from those of Ai [23] who found a concentration–exposure time relationship. Two factors may explain the dissimilarity. Firstly Ai used 1-octanol with a non-polar fibre (100% dimethylsiloxane) and it is possible that the larger molecule with a polar end group is slower to reach equilibrium in the non-polar fibre. Secondly we used a 30 μm polymer thickness whereas Ai used 100 μm giving some 15 times more volume of polymer (assuming constant fibre length and silica core diameter). Thus, our reduced phase volume (and thus reduced sample capacity) will facilitate rapid saturation of the phase. Hence a headspace concentration vs. fibre concentration relationship which is independent of exposure time is observed at these relatively high concentrations. Clearly in our experiments an equilibrium concentration in the fibre was rapidly attained. An incidental observation was that, over a sequence of measurements, particularly at higher concentrations the capacity of the fibre decreased slightly. After a

Table 2
Peak area measurement against variation of time and concentration for dimethyldisulphide

Concentration of DMDS (μg/ml)		1900	900	270	27[a]	22[a]	2.7[a]	R[a]
Order of measuring		1	6	2	3	5	4	
Peak area for *t* (min)								
	t=1	118 500	24 800	22 700	4450	1070	215	0.958
	t=2	127 400	25 300	21 300	4360	1060	280	0.957
	t=5	117 600	26 700	19 500	3520	870	160	0.966
	t=10	110 000	26 400	19 100	4150	970	250	0.968
	t=30	116 900	32 900	17 500	3410	1200	290	0.973
	t=60	93 400	32 900	17 500	3410	1200	230	0.990
	Total	683 800	169 000	117 600	23 300	6370	1425	
Average area counts, *n*=6		113 400	28 100	19 600	3880	1060	238	
Standard deviation		10 500	2850	1730	410	130	43	
Relative standard deviation (%)		9.25	10.1	8.98	10.6	12.3	18.6	

[a] By serial dilution. *R*=correlation coefficient for time *t*.

period of non-use capacity recovered. It would appear that repeated heating of the fibre during a working day causes some temporary loss of capacity which is reversible. A longer term, progressive loss of capacity over a duration of this study was also observed (see below).

The rapid attainment of equilibrium mass of dimethyldisulphide in the polymer highlighted the fact that the amount of polymer available is fixed and so its capacity to absorb/desorb analytes must also be limited. By implication therefore, in a two (or more) component mixture each substance must compete with the other component(s) for space in the fibre. To test this hypothesis three standard gas mixtures were prepared in nitrogen. These were 1850 μg/ml of DMDS, 868 μg/ml of di-isopropylsulphide (DIPS) and a mixed standard of 1850 μg/ml of DMDS and 868 μg/ml of DIPS. Each standard was sampled for 1, 5, 10, 30 and 60 min and the areas of the resultant peaks recorded. Plots of area against time for all three standards were constructed (Fig. 1). For DMDS alone line A was plotted, for DIPS alone line B resulted. For the mixed standard DMDS produced line C and DIPS

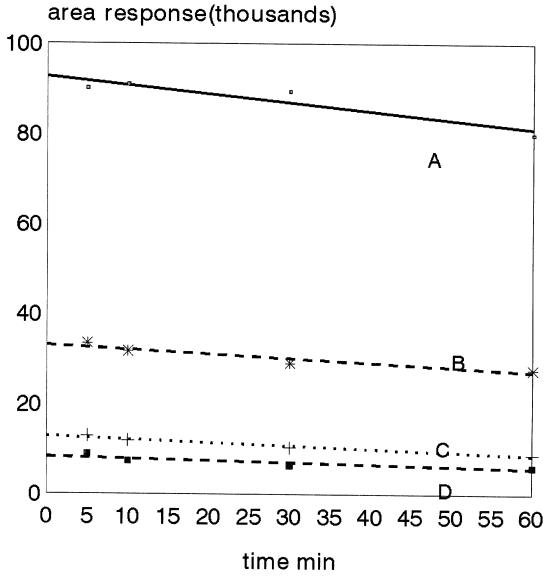

Fig. 1. Response vs. time plots for (A) dimethyl disulphide (DMDS) only at 1850 μg/ml, (B) di-isopropylsulphide (DIPS) only at 868 μg/ml, (C) for DMDS at 1850 μg/ml when both compounds are present and (D) for DIPS at 868 μg/ml when both components are present in the same headspace.

gave line D. Clearly there is a competitive effect for the fibre when the two components are present. This results in a reduction in the equilibrium amounts of each in the fibre even though the concentration in the gas phase remains the same. Thus, for a single component mixture the total mass in the fibre will be proportional to the concentration in the headspace. However, for a multi-component mixture the total mass of analytes in the fibre is made up of the equilibrium concentrations of the individual components moderated by the competitive effects of the other analytes. In other words the fibre is no longer polydimethylsiloxane (PDMS) but PDMS modified by absorbed analytes which change its properties. We suggest a further complication in that the relative affinity of each analyte for the polymer will also influence the equilibrium mass achieved as occurs between analytes and stationary phase in a gas chromatography capillary column with the difference being that in a capillary column they are present sequentially in the phase whereas in the fibre they are present simultaneously. Clearly this must make quantitation difficult because the mass of analyte which partitions into the fibre will depend not only on the partial pressure of that analyte in the sample matrix but also the chemical character of the other components and their relative concentrations. In any multi-component sample, therefore, there must exist a degree of mutual interference. Thus, standard addition would appear to be the most promising quantitative procedure but even then the addition of a known amount of target compound to a fixed volume gas sample will necessarily change the relative concentrations of the other components present. Hence, the relationship between mass of analyte in the fibre and the concentration of the analyte in the sample matrix is complex. Goreki et al. [24] has recently reported a similar conclusion for the extraction of a two component mixture from water.

To test the influence of analyte structure and polarity on relative fibre concentration a mixture of eight solvents (ethanol, propan-1-ol, methyl isobutyl ketone (MIBK), butan-1-ol, cyclohexane, toluene, nonane and α-pinene) was prepared in a 2 l flask by addition of 10 μl of each to the flask and then allowing the mixture to equilibrate overnight. The concentration range achieved was thus of the order of 5 ng/l. Aliquots of the mixed standard were then

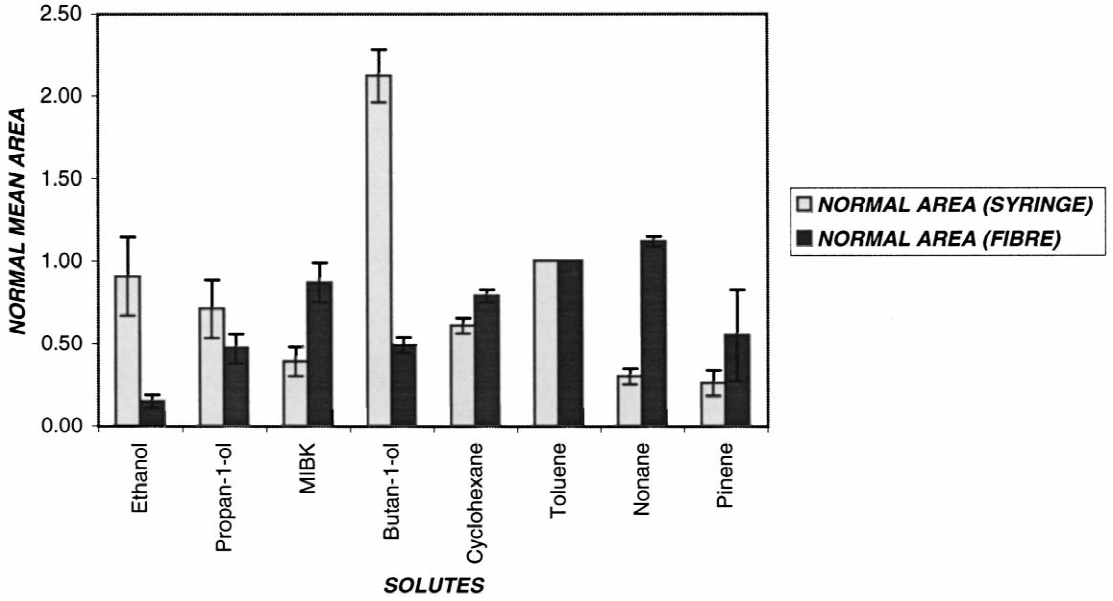

Fig. 2. Comparison of normalised area responses for an eight-component mixture sampled by gas-tight syringe and SPME.

removed either by gas-tight syringe (approximately 50 μl per injection split 20:1) or by fibre (15 s absorption time, 15 s desorption time at 200°C, split ratio 20:1). Samples were chromatographed in random order, i.e. fibre injections interspersed with those made with a gas-tight syringe. Peak area data was collected and processed as follows. Following calculation of the means for each compound response for the six injections the mean area for a component was divided by the area for toluene to give a ratio of areas. This was done to eliminate the need for accurate volume injections and because the relative responses for fibre vs. syringe were required. Thus we derived seven ratios by syringe and seven by fibre and toluene which was 1.0. If the fibre injection method was equivalent to the gas syringe method, which takes a whole sample of the gas phase, then the two sets of ratios should match for the respective components. If the fibre method discriminates within the sample because of factors such as relative solubility in the stationary polymer phase then dissimilar ratios would result. The results are shown in Fig. 2. The data is given in Table 3.

Clearly the ratios are dissimilar. Moreover the

Table 3
Data for syringe and fibre injections normalised to toluene

Compound	Mean peak area (syringe)	Normal area (syringe)	SD	Mean peak area (fibre)	Normal area (fibre)	SD
Ethanol	1942	0.91	0.24	4290	0.15	0.04
Propan-1-ol	1514	0.71	0.18	13 173	0.47	0.09
MIBK	782	0.39	0.09	25 002	0.87	0.12
Butan-1-ol	4293	2.12	0.16	13 754	0.49	0.05
Cyclohexane	1231	0.61	0.05	23 550	0.79	0.04
Toluene	2050	1.00	0.00	30 204	1.00	0.00
Nonane	586	0.30	0.05	27 306	1.12	0.03
Pinene	495	0.26	0.08	10 403	0.55	0.28

polar compounds such as ethanol and propan-1-ol are discriminated against by the non-polar polymer whereas the apolar compounds such as nonane and cyclohexane are preferentially absorbed. The degree of discrimination can be large. For ethanol the fibre under-states the true, i.e. headspace concentration by a factor of approximately 80% whereas for nonane it over-states the true value by a factor of some 300%. This experiment was repeated 7 days later with a similar compositional mixture of the same components and produced a similar profile of results. Note, however, the low RSDs for the fibre method of sampling compared with those for direct headspace gas analysis.

The components studied can be sub-divided into two categories (Fig. 3), with components lying either side of the normalised toluene ratio. Components with an affinity for the non-polar phase, nonane for example, lie above the line whereas low phase affinity components, for example butan-1-ol, ethanol and propan-1-ol all lie below the line. This correlates well with capillary column phase selection where a non-polar phase would not be a usual choice for separating short chain alcohols because of their low solubility in the phase which would cause phase saturation at relatively low concentrations.

After some 3 months of use in which approximately 130 thermal desorption cycles were performed the fibre suddenly lost all capacity. Microscopic inspection revealed an uneven surface and the sample was subjected to examination by scanning electron microscopy. Fig. 4 depicts the fibre when it has ceased to trap organic compounds. The darker background is bare silica and the polymer coating has degraded and broken up leaving shreds and flakes of material adhering to the silica. This has resulted in the loss of fibre capacity observed. The observed slow loss of capacity over the study period probably equates to a slow loss of polymer mass by thermal degradation and abrasion with abrasion dominating and accelerating towards the end of the working lifetime. This process can be considered analogous to the slow loss of liquid phase from a capillary column over its working lifetime leading to a slow reduction in retention times as the phase volume is reduced. There may also be an element of oxidative degra-

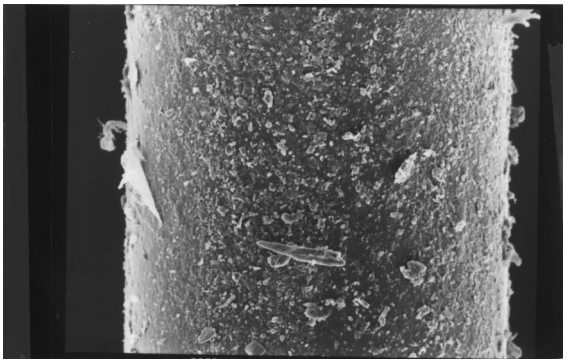

Fig. 4. Electron micrograph of fibre at the end of the working lifetime showing the breakdown of the polymer coating (light grey) and the underlying silica showing through (dark grey).

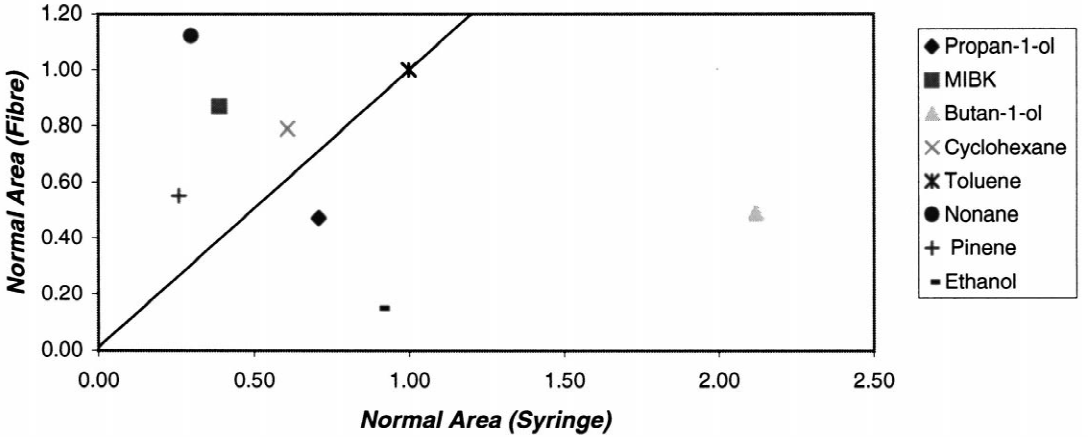

Fig. 3. Correlation plot of syringe area vs. fibre area ratioed against toluene.

dation of the polymethylsiloxane as the microfibre system is exposed far more often to oxygen (in air) than is a capillary column phase.

4. Conclusions

The fibre injection technique provides a simple method of concentrating a headspace sample and of performing an injection without introduction of either air or water. However, the adsorption process suffers from two disadvantages. Firstly in any multi-component system the amount of a single component which can be taken in is influenced by the concentration of the other components present. This is shown in the experiments with DMDS and DIPS. Secondly, the structure of a component influences its affinity for the polymer phase leading to discrimination in the absorption process. Thus, a sample is presented to the chromatograph which does not truly reflect the composition in the original gas sample. Clearly both these factors make accurate quantitation with the micro-fibre an extremely complex process. Extension of the study to the 100 μm fibre indicates similar, thought less marked, discrimination. Finally the fibre slowly loses capacity, and hence performance, during its working lifetime which, again, makes long term quantitative use unreliable.

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