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Journal of Chromatography A, 903 (2000) 155–172

JOURNAL OF CHROMATOGRAPHY A

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SnifProbe: new method and device for vapor and gas sampling

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Received 3 May 2000; received in revised form 21 August 2000; accepted 21 August 2000

Abstract

SnifProbe is based on the use of 15 mm short pieces of standard 0.53 mm I.D. capillary or porous layer open tubular columns for sampling airborne, headspace, aroma or air pollution samples. A miniaturized frit-bottomed packed vial named MicroSPE was also prepared which served for the sampling of solvent vapors and gases as well as liquid water. The short (15 mm) trapping column is inserted into the SnifProbe easy-insertion-port and the SnifProbe is located or aimed at the sample environment. A miniature pump is operated for pumping 10–60 ml/min of the air sample through the short piece of column to collect the sample. After a few seconds up to a few minutes of pumping, the short column is removed from the SnifProbe with tweezers (or gloved hands) and placed inside a glass vial of a direct sample introduction device (ChromatoProbe) having a 0.5 mm hole at its bottom. The ChromatoProbe sample holder with its glass vial and sample in the short column are introduced into the GC injector as usual. The sample is then quickly and efficiently desorbed from the short sample column and is transferred into the analytical column for conventional GC and/or GC–MS analysis. We have explored the various characteristics of SnifProbe and demonstrated its applicability and effectiveness in many applications. These applications include: the analysis of benzene, toluene and *o*-xylene in air, SO_2 in air, perfume aroma on hand, beer headspace, wine aroma, coffee aroma, cigarette smoke, trace chemical warfare agent simulants, explosives vapors, ethanol in human breath and odorants in domestic cooking gas. SnifProbe can be operated in the field or at a chemical process. The sample columns can be plugged and stored in a small union storage device, placed in a small plastic bag, marked and brought to the laboratory for analysis with the full power of GC and/or GC–MS. Accordingly, we feel that the major and most significant feature of SnifProbe is that it brings the field and process to the laboratory. Thus, SnifProbe can extend the ''arm'' of the GC and GC–MS laboratory and enable high-quality field and process analysis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: SnifProbe; Vapor sampling; Gas sampling; Direct sample introduction device; Sampling methods

1. Introduction

Gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) are central analytical techniques for the analysis of a broad range of compounds that can be vaporized. Currently, most analyses are performed in the laboratory whereby samples are brought from the field or other origins into the laboratory for further sample preparation and final chromatographic analysis. Since most samples originate outside the laboratory, the area of field portable GC and GC–MS has been a perpetual need [1,2]. However, field portable instrumentation usually performs worse than its laboratory-based equiva-

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PII: S0021-9673(00)00877-3

lent. Accordingly, there is a continued and growing need to find better methods and devices that will enable fast sampling in the field combined with easy transportation for effective analysis in the laboratory.

Airborne samples originate from a variety of sources including: air pollution, food and beverage aromas, perfumes and cosmetics, solvent, chemical processes, gas leaks, cigarette smoke, off gases of processed materials, odorants, hidden explosives or drugs of abuse and chemical warfare agents.

Currently these airborne samples are sometimes collected in air bags and brought to the laboratory for analysis [3]. One of the problems with this approach is that semi-volatile compounds may irreversibly adsorb onto the bag walls. It is also costly and bulky. Alternatively, solid-phase extraction (SPE) cartridges are brought to the field for air sampling followed by thermal desorption into the GC inlet performed in the laboratory [4,5]. This approach can be very effective and enables low detection limits due to the large sample volumes, but it is limited in its applicability to semi-volatile compounds that may not be effectively desorbed. Furthermore, analyte degradation, memory and matrix effects can also pose some problems. In addition, it requires expensive thermal desorption instrumentation that is external to the GC system. The adsorption sample containers are also not as small as desirable for certain applications.

Solid-phase microextraction (SPME) [6–8] is another approach that finds growing use recently, and was adopted for field sampling [9,10]. However, the SPME sample collection kit is not inexpensive and the samples suffer losses during transportation if not cooled. In addition, SPME sampling can be time consuming and may suffer from limited sensitivity.

Recently, we have developed a new GC sample introduction device termed Direct/dirty sample introduction device (DSI) [11,12]. A DSI device is available from Varian called ChromatoProbe. Sampling with the DSI device is based on sample introduction in a micro-vial that is directly inserted into the GC injector. Thus, a micro-vial replaces the standard syringe-based injections of liquids or gases. Previously, this device has been shown to be useful for two different major applications, each with several advantages listed as follows:

(A) Sample introduction for mass spectrometry – a cost effective probe. The DSI device, followed by a short (2 m×0.1 mm I.D.) capillary column, effectively transforms a conventional GC injector into a cost-effective alternative to the standard direct insertion probe. As a sample introduction device for MS and MS–MS studies the DSI is characterized by low cost as well as fast and easy operation and DSI to GC–MS interchange. Furthermore, it is inherently immune against leaks and thus can be operated by untrained personnel.

(B) Extract-free dirty sample introduction for GC and GC–MS analysis. In this approach, sampling is performed in a small disposable vial that retains the contaminating non-volatile matrix residue of real world samples and thus eliminates the need for further sample clean-up. Each analysis begins with gentle solvent vaporization, followed by brief heating of the injector to the desired temperature required for achieving intra-injector thermal extraction and sample compound vaporization. The semi-volatile compounds from the sample are cryo-focused on the early portion of the column and analyzed as usual. The DSI is a low-cost device that can reduce the analysis time and cost by reducing sample preparation, and it enables analysis of complex small solids or sludge samples. It also enables efficient thermal extraction combined with excellent GC integrity and may provide higher sensitivity through large-volume injection of concentrated extract. The dirty sample analysis capability of the DSI was demonstrated in the analysis of drugs in raw urine [11,12], cocaine and heroin in a single hair [13] and pesticides in mixed/blended fruit and vegetables [14–16]. Recently, Lehotay explored the quantitative aspects of pesticide analysis in agricultural products with the DSI [16].

In this paper we describe a third usage of the DSI device, in the sampling and analysis of airborne vapor and gas with a separate device named SnifProbe.

SnifProbe is based on the use of a short piece (15 mm) of a standard 0.53 mm I.D. capillary or porous layer open tubular (PLOT) column for sampling airborne samples. A miniature pump samples the air through the short trapping column. The sample column is then removed, placed inside the DSI/ChromatoProbe glass vial and introduced into the GC injector for thermal desorption followed by GC and/or GC–MS analysis. The major goal for de-

veloping SnifProbe is to provide an important tool for bringing samples from the field to the laboratory. The compact sample columns can be plugged, marked and brought to the laboratory for analysis with the full power of GC and/or GC–MS.

The idea of air sampling and sample trapping with GC capillary columns is not new. In 1970 Cronin [17] described the use of glass PLOT columns for quantitative sample trapping. In 1985 Grob and Habich [18] described the use of open tubular traps for headspace analysis by capillary GC. A year later, Burger and Munro [19] described the use of fused-silica capillary traps in combination with stainless steel tubes for fast thermal desorption by direct current heating. Lovkvist and Jonsson [20] discussed the theory of such sampling and pre-concentration columns. Bicchi et al. [21] described field sampling of plant volatiles with long (up to 3 m) capillary traps and the use of dual GC for the analysis (one GC for trap thermal desorption and one for the analysis). On-line sample treatment for capillary GC analysis is reviewed by Goosens et al. [22]. Recently, Tuan and co-workers [23,24] described the use of capillary traps in combination with a portable micro GC system.

The SnifProbe method and device that is described in this paper, although similarly uses capillary columns for sampling, represents a different approach of bringing samples from the field to the laboratory. The sampling capillary or tube is being used in the field for sampling while the analysis is performed in the laboratory with the full power of laboratory GC or GC–MS instrumentation.

2. The SnifProbe device and instrumentation

The SnifProbe vapor and gas sampling device is shown in Fig. 1 together with enlarged sections of its major components. SnifProbe sampling uses 15-mm long standard 0.53 mm I.D. capillary columns. The use of commercially available GC columns enables low-cost sampling units with a wide range of adsorption materials and film thickness, from thin dimethylsiloxane to various PLOT columns. The 0.53 mm I.D. was chosen because its column O.D. (about 0.7 mm) is compatible with the smallest size (No. 1) Viton o-ring that is used to seal it during sampling. The "megabore" diameter capillary also has the highest gas pumping conductivity for fast sampling as well as effective intra-injector vaporization. The trapping columns were cut from standard analytical columns and placed inside a heated injector for a few minutes for final cleaning. The 15 mm piece of column was inserted into a Wilson seal type of connector shown at the middle right side "SnifProbe Head". The sampling column can be protected from the external environment by a removable brass shield. The clamped and sealed column is connected to a small pump (ASA 3003 G) followed by a metal frit flow restrictor [Mott 250 ml/min at 30 p.s.i. ($2\cdot10^5$ Pa)]. This frit element enables a steady flow-rate of 45 ml/min under the pump-produced reduced pressure. A pump time selector determines the air pumping time in the range of 1–2048 s. The hand portable SnifProbe unit is powered by three standard AA 1.5 V batteries, has dimensions of 220×95×45 mm and a weight of 450 g.

After air sampling, the trapping column was removed either with tweezers or by gloved hands and placed inside a DSI/ChromatoProbe micro-vial. We made special such vials with 10 mm×1.9 mm I.D.× 2.5 mm O.D. having a 0.5 mm hole at their bottom. The vial was kept inside the DSI/ChromatoProbe vial holder during the insertion of the trapping column. For injection, the ChromatoProbe/DSI was inserted into the GC injector for intra-injector thermal desorption. The GC injector can be of any type including a standard split–splitless injector that is not temperature programmable. Its temperature was 150–300°C in our experiments depending on the application. Note that if the vial holder was just taken out of the hot injector, we had to wait about 3 min for cooling to prevent external pre-vaporization in the next analysis. This does not cause a delay if two ChromatoProbe vial holders (provided by Varian) are utilized alternately. Additionally, during the sampling time, while the injector with the ChromatoProbe is open, the helium purge flow keeps out most of the room air. It is even safer to have the column at a relatively low temperature of 100°C or below during this time for further protection. The vial holder is built with a small diameter tolerance to the glass liner I.D. (3.4 mm) and thus the carrier gas partially flows through the trapping column for

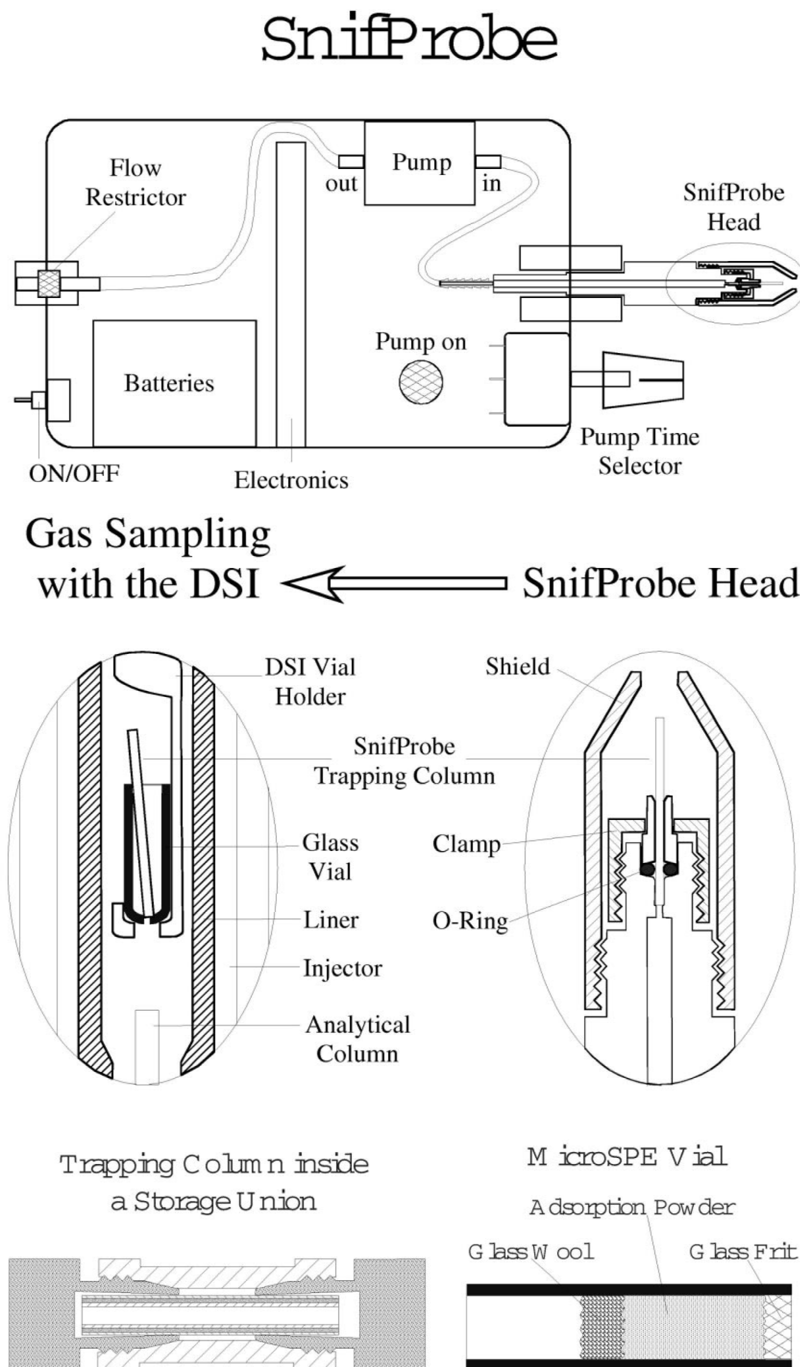

Fig. 1. SnifProbe vapor and gas sampling device, including the SnifProbe sampling unit shown in the upper part. An expanded view of the SnifProbe sampling head with the trapping column at its center is shown in the middle right side while the final position of the trapping column inside the GC injector after insertion with the ChromatoProbe is shown in the middle left side. At the bottom left side a standard trapping column is shown inside our modified LC Union-based storage device. At the lower right side a MicroSPE tube is shown based on a standard ChromatoProbe vial, modified with a fritted glass bottom and packed with adsorption powder and glass wool. The various parts are not drawn to scale.

improved sample vaporization. Furthermore, the volume between the bottom of the vial holder and the analytical column is small (separated by less than 5 mm) and thus a fast splitless injection response time is obtained.

For field applications a simple storage and transportation device was designed for these trapping columns (shown at the bottom left side of Fig. 1). It is based on a standard polyether ether ketone (PEEK) plastic union for 1/16 in. tube connections available as zero dead volume unions for liquid chromatography (PEEK ZDV Union P/N P-714 from Upchurch Scientific) (1 in.=2.54 cm). In this union, the central hole diameter was increased to 1 mm and a hole with 7 mm depth and 0.75 mm diameter was drilled in the plugs. The trapping column piece was inserted into the hole in the plug, and by closing the union with the second such plug, the trapping column was sealed with minimal added surface area. In this way, the union with its trapping column could be transported or mailed to the laboratory in a standard bag with the sample details written on it.

As will be described, the capillary column-based sampling columns serve effectively for the analysis of semi-volatile vapors while with solvents their efficiency is reduced and with permanent gases it cannot be used. For this reason we have also developed a miniaturized trapping tube, similar to a packed capillary column, that can be loaded in the DSI/ChromatoProbe and inserted inside the GC injector for thermal desorption. We call this trapping unit MicroSPE (micro solid-phase extraction) tube and it is shown schematically at the lower right side of Fig. 1. The MicroSPE tube was prepared in the following way. A standard 15 mm×1.9 mm I.D., ChromatoProbe micro-vial was loaded with 5 mm of crushed glass frit (Duran, Pore size 160–250 μm). The vial was gently heated in a flame until the crushed glass frit started to melt. The vial was then treated with a glass disc saw while water flowed around and its bottom was gradually removed until water penetrated into the vial. This was our indication that the solid glass was removed and only a permeable frit bottom remained. The frit-bottomed vial was washed and loaded with 3–6 mm of standard GC packing material, so that the volume of the adsorption material was between 8.5 and 17 μl. We used HayeSep Q (based on divinylbenzene) as the adsorption powder. A piece of glass wool was further added above the adsorption material to keep it in place. Then, the vial was placed inside a heated injector for a few minutes for final cleaning. The MicroSPE tube required a modified SnifProbe head that had a different clamp and o-ring size, but the rest was the same. After sampling, the MicroSPE vial was loaded into the ChromatoProbe vial holder as is (naturally it fitted since it is based on a ChromatoProbe vial) and thermally desorbed as usual.

The experimental apparatus included a Varian 3600 GC system with a 1078 split–splitless temperature programmable injector, a flame ionization detection (FID) system and our laboratory-made pulsed flame photometric detection (PFPD) system [25,26]. The 1078 injector was equipped with a laboratory-made ChromatoProbe sampling device [11,12,14]. Helium was used as the carrier gas at flow-rates given in the text.

3. SnifProbe vapor and gas sampling method and features

The SnifProbe sampling method (see Fig. 1) is based on pumping 10–60 ml/min of air sample through the short piece of sample collection column. After a few seconds to a few minutes of pumping, the short column is removed from the SnifProbe head and placed inside a ChromatoProbe glass vial (with a 0.5 mm hole at its bottom). The ChromatoProbe with the sample is then introduced into the GC injector for intra-injector sample thermal vaporization followed by conventional GC and/or GC–MS chromatographic analysis.

The SnifProbe vapor sampling method is based on the selective adsorption of the sample compounds while the gas or air medium is not retained. The general theory of GC can be used for the explanation of SnifProbe trapping. In contrast to SPME [6–8], SnifProbe is based on dynamic gas pumping and its motion inside the trapping column. For a 0.53 mm I.D. column, the optimal carrier gas flow velocity is 16 cm/s for nitrogen (or air). Under such optimal conditions, this column has about 1800 theoretical plates per meter and thus one can assume a plate

height of about 0.53 mm. When the sampled air flow-rate is 45 ml/min, its velocity is 340 cm/s and the plate height should be about 11 mm. Accordingly, at 45 ml/min air sampling rate the sample compounds find their way to the walls of the trapping column in about 11 mm. Thus, for semi volatile compounds, adsorption can be quantitative, while the other volatile air ingredients are adsorbed but are quickly desorbed and are not retained. This simple description also suggests that about 60 ml/min is the upper flow-rate limit above which no gain in sensitivity will be achieved for a 15 mm long trapping column. In addition, after a given time that depends on the compound, temperature and trapping column type, a steady state will be achieved and the trapped compound amount will saturate so that on each trapped compound amount an equivalent amount is being desorbed. Before that time the trapped compound amount is expected to linearly increase with the air pumping time. We note that this saturation level depends on the ambient temperature and thus, temperature variations can lead into sampling irreproducibility in the quantitative analysis of compounds that are in steady state adsorption conditions. As a result, for the precise analysis of these compounds calibration at the same temperature might be needed. On the other hand, compounds that are fully adsorbed are much less affected by the trapping column temperature variations. In Fig. 2 we demonstrate the existence and some features of SnifProbe in the analysis of benzene, toluene and *o*-xylene (BTX) in air. Benzene, toluene and *o*-xylene were dissolved in dioctylphthalate (DOP) at concentrations of 80 ppm (v/v), 270 ppm (v/v) and 1000 ppm (v/v), respectively, to provide about equal headspace concentration of 10 ppm (v/v) each. The headspace above the DOP solution was pumped through a 15 mm long PoraBOND trapping column (all the PLOT trapping columns were kindly donated by Jaap de Zeeuw of Varian Chrompack) for 5 s at 15 ml/min pumping flow-rate. The chromatogram achieved with a 4 m×0.25 mm I.D., DB1 column (isothermal separation at 60°C) is shown at the upper left side. In the lower right side the same headspace is analyzed with a standard 0.5-ml gas-tight syringe injection for comparison. From the obtained results shown in Fig. 2 we conclude that: (a) the SnifProbe vapor sampling method and device works; (b) the

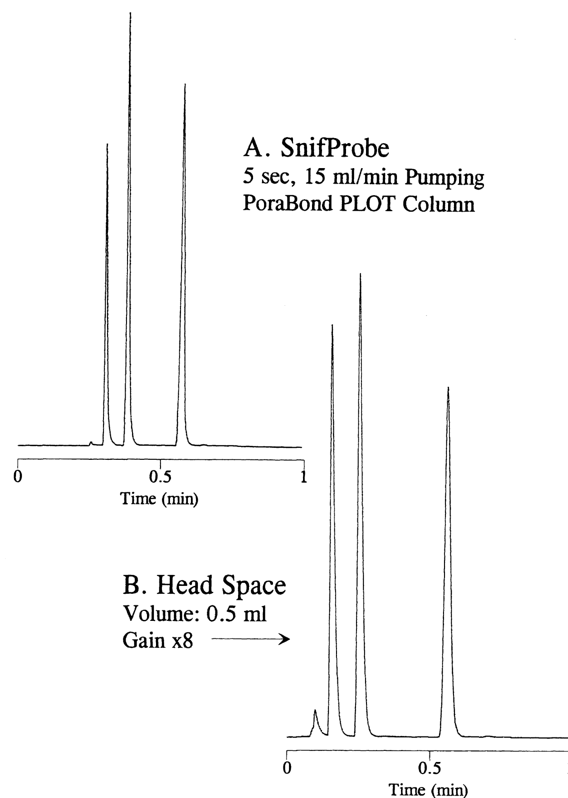

Fig. 2. Benzene, toluene and *o*-xylene (in order of their elution) in air analysis with (A) SnifProbe and (B) 0.5-ml gas-tight syringe sampling. PoraBOND was used with SnifProbe as the trapping column, with 5 s pumping at 15 ml/min air flow-rate. The injector temperature was 300°C and the analytical column was 4 m×0.25 mm I.D., with 0.25 μm DB1 film and 2 ml/min He carrier gas flow-rate with 5:1 split injections. A FID system was used as the detector. The BTX concentration in air was about 10 ppm, prepared by dissolving 80 ppm benzene, 270 ppm toluene and 1000 ppm *o*-xylene in dioctylphthalate.

SnifProbe injection is faster than standard syringe injection as manifested by the sharper GC peaks obtained. As an example, the peak width at half height of toluene was measured as 0.38 s and 0.86 s for SnifProbe and headspace injections, respectively. Fast GC analysis of 1 min was obtained with a split ratio of only 5:1. This is easily explained in view of the considerably smaller effective liner volume. In separate measurements we found that with splitless

injections at 2 ml/min column flow-rate the sample introduction time constant was only about 3 s; (c) the GC–FID signal height is about 6–7-times higher with SnifProbe than with the standard syringe sampling. In part, this is due to the sharper GC peaks with SnifProbe but in addition, the peak areas are also about four-times higher. This is since with SnifProbe, 1.2 ml headspace air was passed through the trapping column. Since the liner volume enabled no more than 0.3 ml gas sample size, the SnifProbe sample is four-times larger; (d) some discrimination against the more volatile benzene is observed, but it is relatively small with the PoraBOND PLOT column and 1.2 ml sample size.

In Fig. 3, we show the SnifProbe sampling response obtained with nitrobenzene using a PoraBOND PLOT column for trapping. Clearly, linear dependence on the trapping time is observed, and in this case 15 ml sample volume was easily achieved. Even though the 15 ml sample volume was achieved in only 1 min, it was much larger than what can be obtained with SPME sampling [27]. On the other hand, this is a smaller sample size in comparison with the standard packed column cartridge type sampling tubes.

We studied the response reproducibility of nitrobenzene trapped with the PoraBOND trapping column. Variability of 4.3% RSD was measured. This relatively low RSD value is attributed mostly to the use of an automated sampling time. The achievement of this reproducibility requires a little practice and reproducible vial holder insertion into the GC system.

In Fig. 4 we show the retaining power of PoraBOND and CarboBOND trapping columns with benzene, toluene and *o*-xylene. In these experiments pure air was pumped through these trapping columns after sample collection. Since we did not see any change in the residual amount of *o*-xylene (within

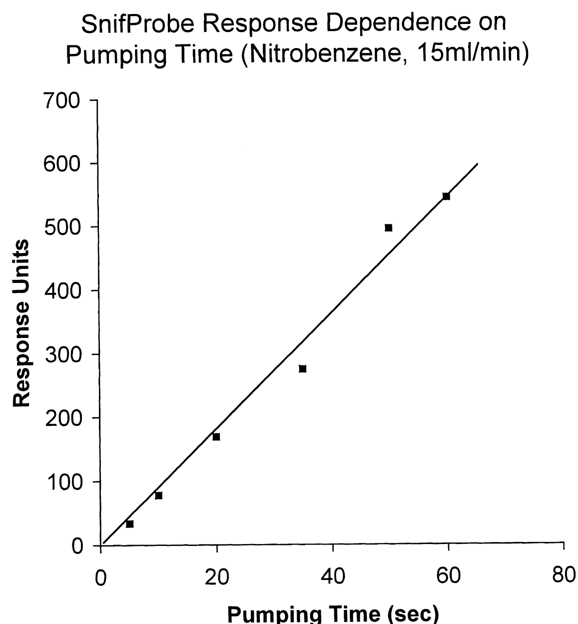

Fig. 3. SnifProbe response dependence on the sampled air pumping time. Nitrobenzene headspace was studied with PoraBOND trapping column at 15 ml/min sampled air flow-rate. The injection and detection conditions are the same as in Fig. 2.

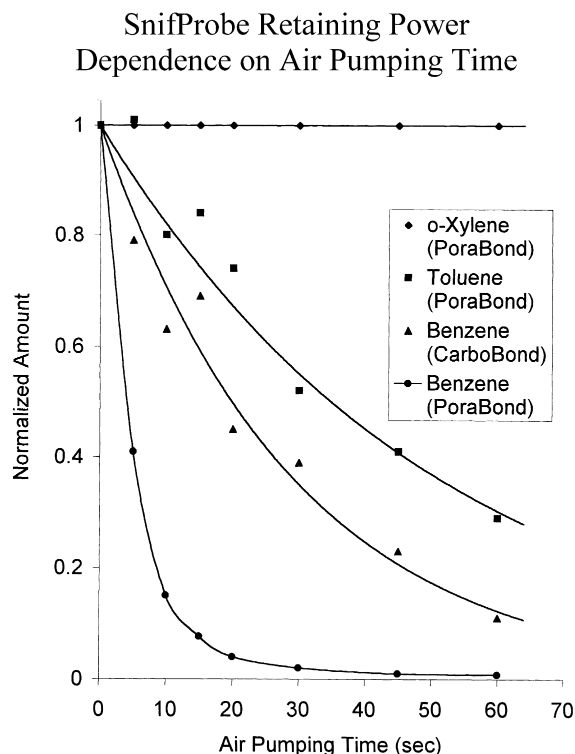

Fig. 4. Sample compound holding capability of the SnifProbe trapping column versus the time of additional clean air pumping. BTX sample was taken as in Fig. 2, followed by additional clean air pumping through the PoraBOND or CarboBOND trapping columns for the indicated time period. No change in the *o*-xylene signal was observed and thus it was used as an internal standard.

our experimental uncertainty), its signal was used for internal calibration. From the results, we concluded that the equilibration time was 5 s for benzene, about 45 s for toluene and it is in the several minutes range for xylene. This type of experiment can serve as an easy way for SnifProbe method development and choice of the optimal trapping column and sampling time. From this experiment we also conclude that if the relative ratio of BTX compounds need to be conserved, the allowable sampling time should be less than 5 s. For optimal toluene sensitivity a 1-min sampling time can be used, while for *o*-xylene the detection sensitivity will increase for several minutes with increasing the sampling time. Additionally, the allowable sampling time depends on the trapping column and it is longer for CarboBOND than for PoraBOND. In an independent study we found that all of these compounds, including nitrobenzene were quantitatively desorbed in a few seconds in the injector at 250°C.

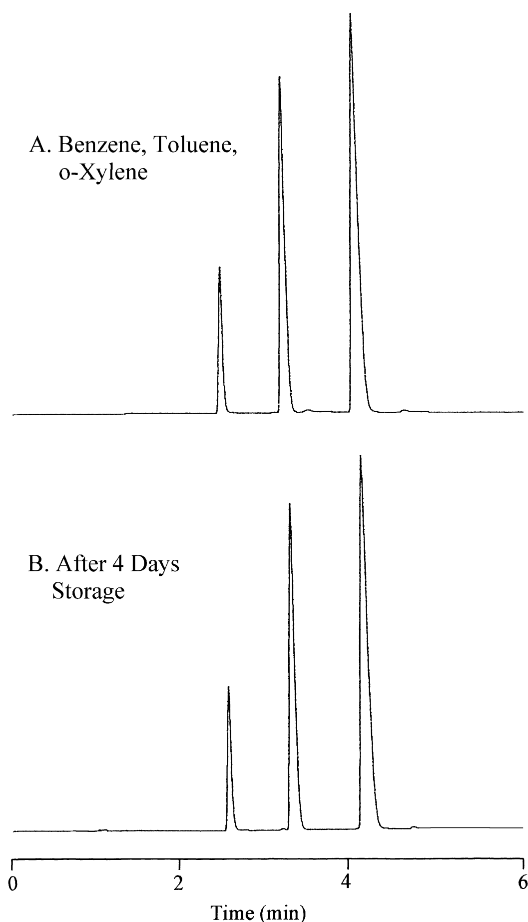

Fig. 5. A demonstration of the storage efficiency of SnifProbe trapped compounds. The BTX sampling procedure was similar to that used in Fig. 2 but with 45 ml/min sampling flow-rate for 5.2 s. The upper trace (A) shows the chromatogram obtained in less than 1 min after sampling while the lower trace (B) show the results after the trapping column was stored inside a modified PEEK union storage unit for a full 4 days at room temperature. The results are practically identical. The time-integrated peaks are the same within the 4% reproducibility of the method and also the relative peak ratios are the same within the experimental uncertainty.

Perhaps the most important aspect of the SnifProbe method is its use for field or process sampling with sample transportation for laboratory analysis. In Fig. 5 we demonstrate the use of a SnifProbe trapping column union device that was previously described (see Fig. 1) based on a modified zero dead volume LC 1/16 in. tube union. As shown, no losses, even of the more volatile benzene were observed after 4 days of storage at room temperature. The obtained chromatograms, both with and without storage, are practically identical. We feel that the easy sample transportation from its true origin to the laboratory for accurate GC and or GC–MS analysis is the single most important feature of SnifProbe.

4. SnifProbe applications

SnifProbe can be used for a very broad range of applications in the analysis of airborne, headspace, process environment, food aroma or air pollution samples. In order to better explore the features and capabilities of SnifProbe we tested it in several applications. In this section we demonstrate and describe our results and briefly discuss their implications.

4.1. Coffee aroma analysis of sulfur compounds.

Sulfur compounds play a major role in coffee aroma (and taste), and thus its monitoring is important for the coffee industry [28]. In Fig. 6 we show our results of SnifProbe analysis of coffee

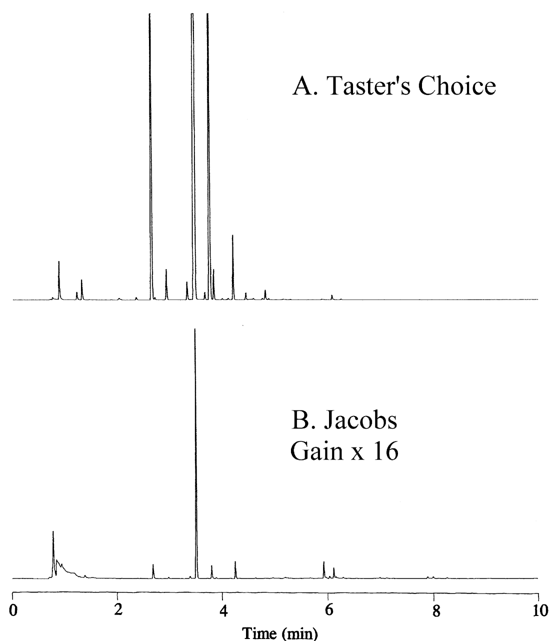

Fig. 6. SnifProbe analysis of coffee aroma. Taster's Choice and Jacobs regular instant coffee were used. PoraBOND was used as the trapping column with 15 s sampling time at 12 ml/min air flow-rate. The analytical column was 15 m×0.25 mm I.D. with 1 μm Rtx-5 film (Restek). A PFPD system was used as the sulfur-selective detector, thus the chromatograms indicate only sulfur compounds with infinite selectivity.

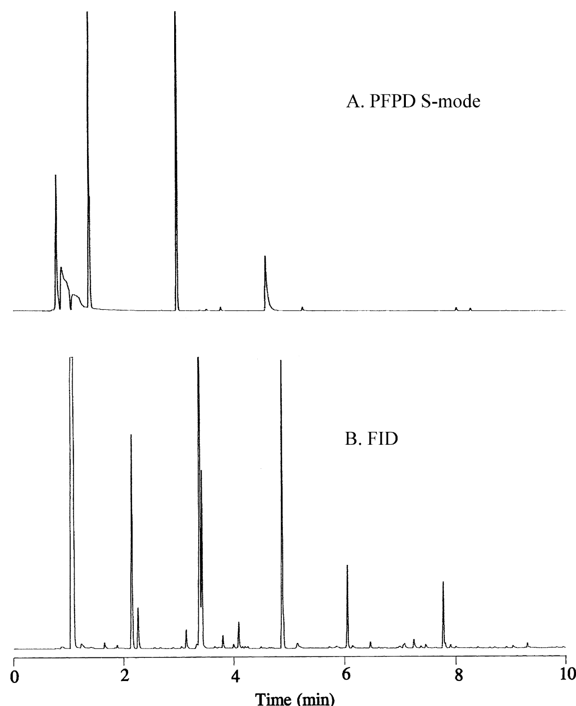

Fig. 7. SnifProbe analysis of beer headspace. Beck's beer was used at room temperature. Both PoraBOND and CarboBOND trapping columns were used and inserted together with the ChromatoProbe for analysis. A 30-s pumping time with each trapping column was employed with 12 ml/min sampled air flow-rate. The analytical column was 15 m×0.25 mm I.D. with 1 μm Rtx-5 film (Restek). Both PFPD (upper trace A) and FID systems (lower trace B) were used for the GC detection.

aroma of both Taster's Choice regular instant coffee and Jacobs instant coffee. PFPD was used for sensitive sulfur-selective detection. A large number of sulfur compounds was observed, especially in the Taster's Choice trace (after magnification). Note that the Taster's Choice coffee brand contains many more and much more sulfur compounds in its aroma and this fact is easily confirmed by its smell. In this application we used a PoraBOND trapping column for a broad range of semi-volatile sulfur compounds. We also found not surprisingly, that in time, especially if the coffee container is left open, the aroma intensity decreased.

4.2. Beer headspace analysis

In Fig. 7, we show the SnifProbe analysis of beer headspace. Beck's beer was analyzed for the presence of trace level sulfur compounds in its aroma with PFPD as well as for general organic analysis with FID. The SnifProbe PFPD results are comparable with those obtained by Hill and co-workers using SPME–GC–PFPD combination [29,30]. However, we feel that the major advantage of SnifProbe is that it can be used at the beer brewing process for sampling followed by laboratory GC analysis.

4.3. Wine aroma analysis

In Fig. 8 we show the results obtained with SnifProbe sampling of wine headspace. FID was

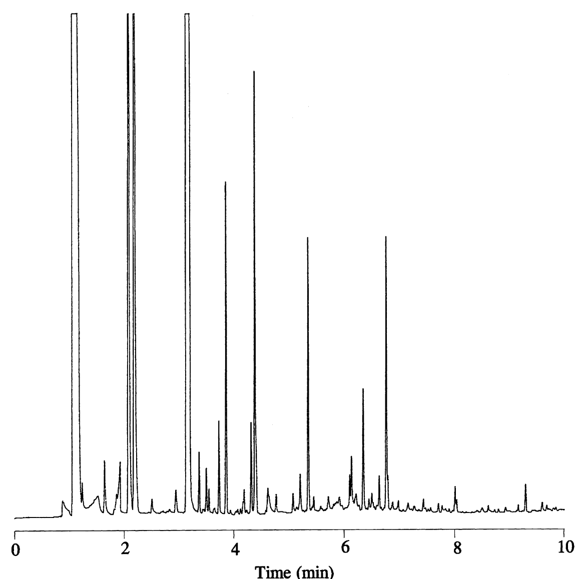

Fig. 8. SnifProbe analysis of wine headspace. Cabernet Sauvignon at room temperature was used. PoraBOND was used as the trapping column with 1 min sampling at 12 ml/min air flow-rate. The analytical column was 15 m×0.25 mm I.D. with 1 μm Rtx-5 film (Restek) and an FID system was used as the detector.

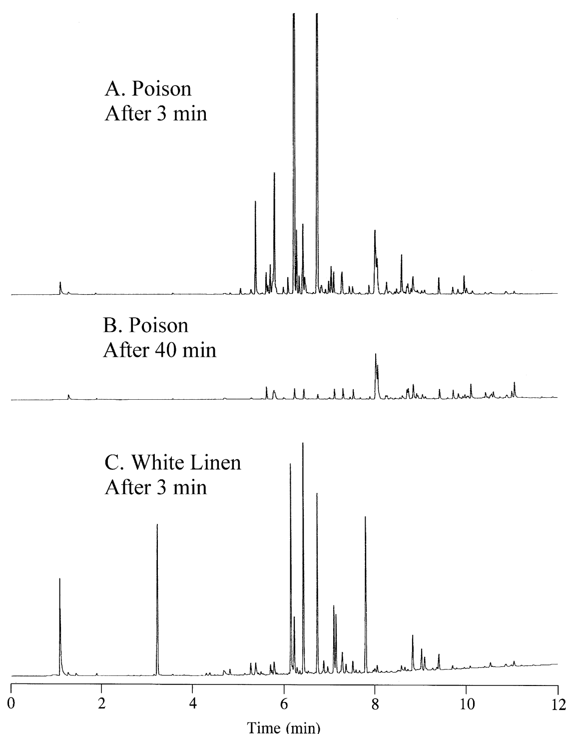

Fig. 9. SnifProbe analysis of perfumes. Poison (Christian Dior) and White Linen (Estee Lauder) perfumes were sprayed on a hand of a male subject and the resulting perfumed air at the hair volume of the hand was explored. PoraBOND was used as the trapping column with 1 min sampling at 12 ml/min air flow-rate. The analytical column was 15 m×0.25 mm I.D. with 1 μm Rtx-5 film (Restek) and an FID system was used as the detector. Sampling was initiated at the indicated time after the perfume was sprayed on the hand.

used for GC detection. A rather complex chromatogram is obtained but it is wine specific and can be used for qualitative purposes.

4.4. Perfume analysis

SnifProbe can also be used for perfume evaluation and identification (FID). Perfume was sprayed in the usual way on the hand of a male subject and its vapor was collected in a PoraBOND trapping column while the SnifProbe head was placed at the hair of the hand. The SnifProbe cover protected the trapping column from breakage in this type of operation. In Fig. 9 we show the SnifProbe sampling results with two perfume brands of Poison and White Linen. It was clearly observed that each perfume is easily differentiated from the other perfume and that in time the more volatile components evaporate. We also note that some new organic components are possibly created by the Poison perfume.

4.5. Odorants analysis in cooking gas

Another easy application was the analysis of mercaptan odorants in domestic cooking gas that is mostly a mixture of butane and propane. The mercaptans are much less volatile than the cooking gas main components and thus they are easily collected by the PoraBOND trapping column for fast (under 1 min) analysis with GC–PFPD, as shown in Fig. 10.

4.6. Breath analysis

A somewhat more challenging application was the analysis of ethanol in human breath after beer

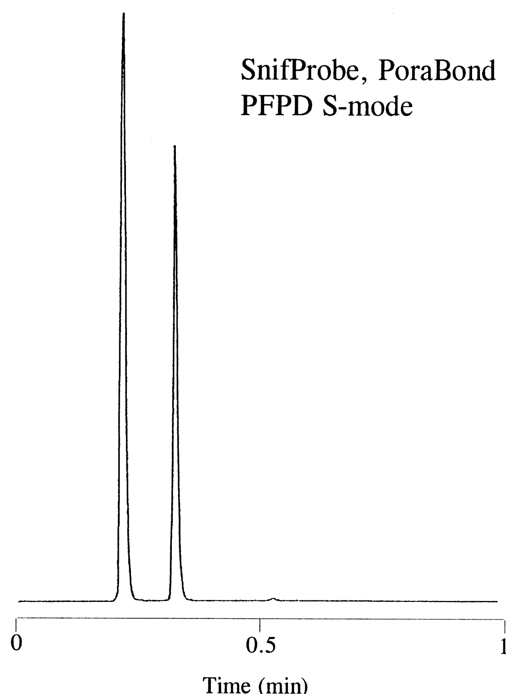

Fig. 10. Mercaptan odorants analysis in domestic cooking gas. PoraBOND was used as the trapping column with 3 s sampling time at 25 ml/min sampled gas flow-rate. The injector temperature was 300°C and the analytical column was 4 m×0.25 mm I.D. with 0.25 μm DB1 film. The column He carrier gas flow-rate was 1.5 ml/min and the injection was with split ratio of 100:1 at 60°C isothermal GC oven analysis conditions. A PFPD system was used for the sulfur-selective detection.

drinking as demonstrated in Fig. 11. A male subject was chosen (one of the authors) and his breath was analyzed for the presence of ethanol after the consumption of one 250 ml bottle of local Carlsberg beer (4.5%, v/v, ethanol). The ethanol is easily detectable in the breath after 3 min from the beer consumption and its level is gradually reduced in time but it can clearly be detected even after 1 h. The actual breath sample collection is fast and easy with only 5 s of breath sampling. Sampling was performed with CarboBOND trapping column and the analyte was detected by FID. In comparison with a similar SPME analysis [31] we note that with SnifProbe, the analysis is faster, the observed sensitivity is superior and the transportation of the sample to the laboratory is easier. After ethanol calibration, we found that the SnifProbe method measured ethanol in the 1–50 ppm range and that the detection limit can be in the low ppb (v/v) range with FID.

4.7. Chemical warfare agent simulants analysis

Each trapping column has an optimal boiling point range of analyzed compounds. For example, PoraBOND seems ideal for the boiling point range of 100–280°C, and its use can be extended to the range of 60–320°C. For the less volatile compounds, a standard dimethyl silicone coated trapping column should be employed, while for more volatile compounds the CarboBOND is preferable or a MicroSPE tube should be used. In some cases there can be a need to analyze a mixture with a broad range of compound volatility. An important group of compounds relevant to this situation are the chemical warfare agents (CWAs) which have a boiling point range from about 150°C for sarin (GB) to 300°C for VX. In Fig. 12 we demonstrate the SnifProbe analysis of CWA simulants with a GC–PFPD combination. The PFPD system was used in the sulfur plus phosphorus mode for the simultaneous detection of both mustard and nerve agent simulants. The lower trace (C) shows the results obtained with the use of PoraBOND as the trapping column. All the CWA simulants are observed but one may suspect that the detection sensitivity of the tributylphosphate (TBP) (VX simulant) is reduced due to non-quantitative intra-injector desorption. This problem may be more pronounced with the real VX agent that is usually not amenable for such method development experiments. Thus, in the middle trace B, an Mxt-5 column was used for easier intra-injector thermal desorption. Indeed the TBP signal was increased but the signals of the more volatile thioxane and DMMP (dimethylmethylphosphonate) were greatly reduced. The SnifProbe solution for this problem was simple, and in the upper chromatogram A we show the results obtained with the simultaneous analysis of two different trapping columns. We used the ability to place as many as four trapping columns in a single DSI/ChromatoProbe vial, and thus we employed SnifProbe sampling with PoraBOND followed by sampling with the Mxt-5 column and both were

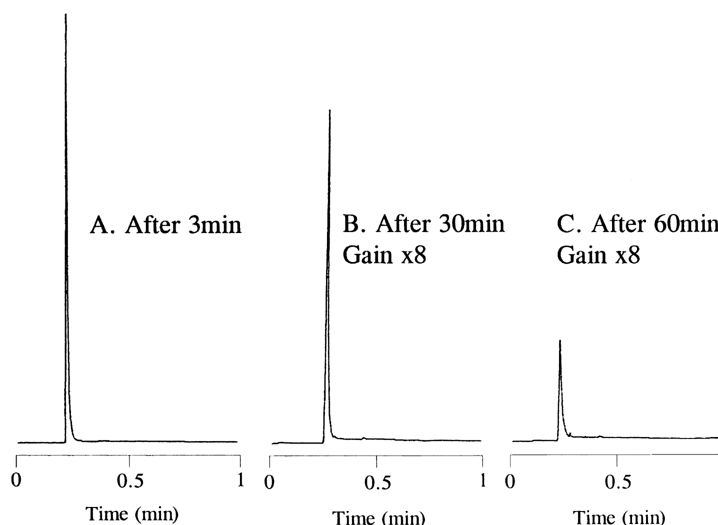

Fig. 11. SnifProbe analysis of alcohol in human breath after beer drinking. One bottle of Carlsberg beer was consumed (250 ml, 4.5% ethanol) and a male subject breath was sampled at the indicated time after consumption. CarboBOND was used as the trapping column with 5 s sampling at 15 ml/min sampled air flow-rate. The injector temperature was 300°C and the analytical column was 4 m×0.25 mm I.D. with 0.25 μm DB1 film. The column He carrier gas flow-rate was 2 ml/min and the injection was with a split ratio of 2:1 at 50°C isothermal GC oven analysis conditions. An FID system was used for the GC detection.

analyzed in a single ChromatoProbe sampling into the injector. The obtained upper chromatogram is well balanced and provides the analysis of a mixture with a broad range of compound volatility.

An additional important feature of the SnifProbe sampling is its high sensitivity. The CWA simulants used were at a concentration level of 500 $\mu g/m^3$. The observed signal-to-noise ratio is about 5000. Thus, with a simple SnifProbe sampling of 1 min, sub-$\mu g/m^3$ detection limits can be achieved with PFPD in about a 5-min laboratory analysis time.

4.8. Explosive and drug analysis

Oftentimes the sample is a solid or a powder. In these cases, GC analysis requires solvation of the sample and frequently sample clean up is needed to avoid column and liner degradation. If the headspace of that sample could be analyzed, sample clean up can be eliminated. An important example in the area of forensic analysis is the determination of a given powder content for the presence of drugs of abuse or explosives. SnifProbe enables fast and clean sampling of an unknown powder that is slightly heated on a heated plate at 70–100°C for increased sample vapor pressure. This use of a heated plate was employed in our SnifProbe studies only for this application, but it might be used for broader range of applications. In Fig. 13 we show the SnifProbe analysis of a mixture of TNT, PETN and RDX solid explosives. SnifProbe sampling was performed at about 4 cm above the heated powder. PFPD was used in its nitrogen-selective mode [25,26] for the explosive detection. The three explosives were clearly observed with a few additional unidentified peaks. Note that two of these explosives are thermally labile and that their GC analysis requires a low injector temperature of 200°C and a short, 4 m×0.25 mm I.D., 0.25 μm DB1 film thickness analytical column with relatively high carrier gas flow-rate of 4 ml/min. The injection was splitless for 0.12 min at 60°C GC oven temperature, followed by temperature programming of 15°C/min to 200°C. The GC method development was performed initially with pure

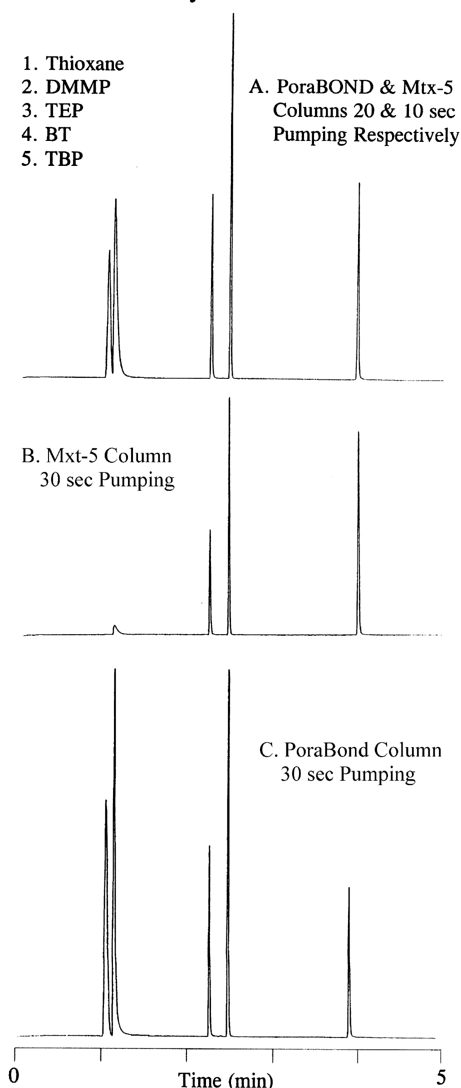

Fig. 12. SnifProbe analysis of chemical warfare agent simulants. Thioxane, dimethylmethylphosphonate (DMMP), triethylphosphate (TEP), benzothiophene (BT) and tributylphosphate (TBP) were used in their order of elution. PoraBOND was used as the trapping column in the lower trace C while Mxt-5 (Restek) was used for the middle chromatogram B. The upper trace was obtained by the insertion of both trapping columns simultaneously with the ChromatoProbe into the GC injector. Sampling rate was 15 ml/min at the indicated sampling time. The injector temperature was 300°C and the analytical column was 4 m×0.25 mm I.D. with 0.25 μm DB1 film. The column He carrier gas flow-rate was 1.5 ml/min (at 40°C) and the injection was splitless for 0.12 min at 40°C isothermal GC oven analysis conditions, followed by 40°C/min temperature programming to 200°C. A PFPD system was used in the S+P mode for detection.

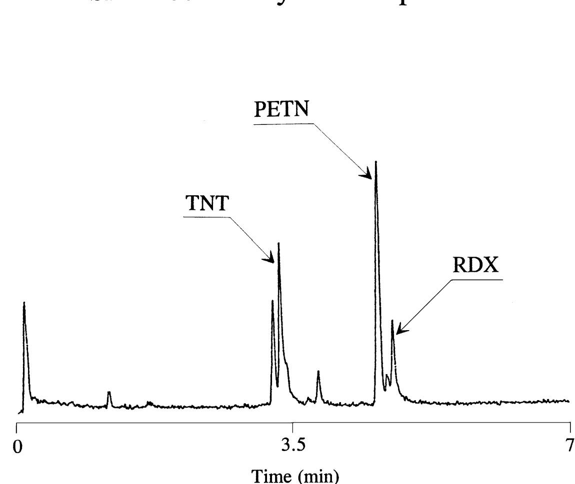

Fig. 13. SnifProbe analysis of explosives. A mixture of technical grade TNT, PETN and RDX was used, placed on a hot plate at 100°C inside a beaker. An uncoated transfer line 0.53 mm I.D. column was used as the trapping column with 3 min pumping at 12 ml/min sampled air flow-rate. A PFPD system in its nitrogen-selective mode was used for detection.

explosives. In this analysis, we used a piece of deactivated capillary column as the trapping column for easier intra-injector desorption at lower temperatures.

5. SnifProbe sampling with a MicroSPE tube

In the previous section several SnifProbe analyses of semi-volatile organic compounds were described. Here, we extend the range of SnifProbe applications to include the more volatile range of solvents and permanent gases. For these applications the adsorption power of even the PLOT trapping columns is insufficient and packed column materials need to be used. In the lower right side of Fig. 1 and in Section 3, the MicroSPE tube is described. In essence this is a miniaturized version of the standard "Tenax" purge-and-trap cartridge tubes. However, the MicroSPE tube is designed to be amenable for intra-GC injector insertion with the ChromatoProbe for its intra-injector thermal desorption. We used the MicroSPE vial with HayeSep Q adsorption material but the full range of other adsorption materials is available for use as well. The MicroSPE tube can be used

for trace level solvent sample collection and analysis including the applications listed below.

5.1. BTX in water headspace

In Fig. 14 we show the use of the MicroSPE tube with SnifProbe sampling of water headspace. The water headspace contained about 1 ppb (v/v) each of benzene, toluene and *o*-xylene. Since the MicroSPE tube with HeyeSep Q adsorbs benzene much better than PoraBOND, a 1-min sampling time was employed which corresponds to 45 ml headspace sampled volume. All three BTX compounds were clearly observed as the dominant three peaks using FID. The 256-times magnified noise suggests that a 1 ppt detection limit of BTX in water could be realized if chemical noise from other organic compounds would be eliminated or if a more selective detector such as a mass spectrometer was used.

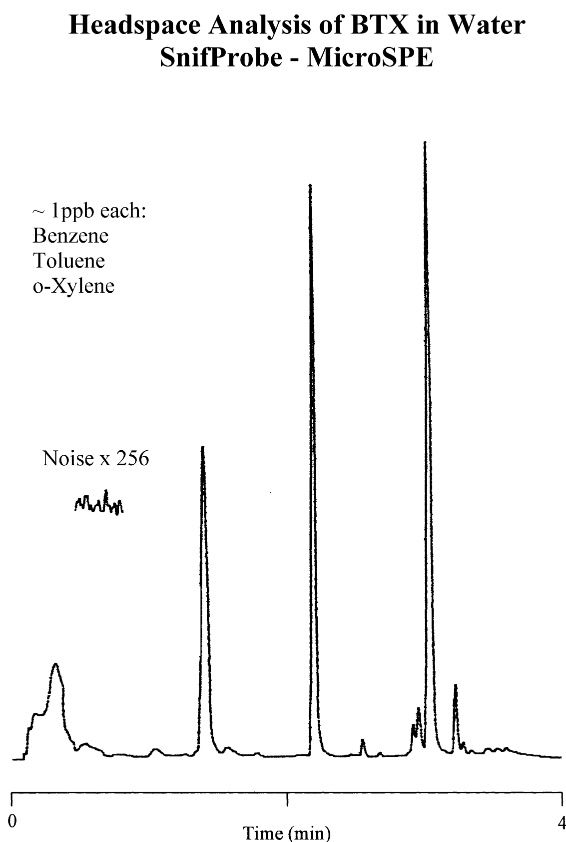

Fig. 14. Headspace analysis of BTX in water by SnifProbe with a MicroSPE sampling tube. The water contained 10 ppb benzene, 30 ppb toluene and 100 ppb *o*-xylene resulting in about 1 ppb each component in the water headspace. The MicroSPE tube pumping through rate was 45 ml/min for 1 min. The injector temperature was 300°C and the analytical column was 4 m×0.32 mm I.D. with 10 μm PoraBOND layer (PLOT column). The column flow-rate was 2.6 ml/min and the injection was splitless for 0.3 min at 100°C GC oven temperature followed by temperature programming rate of 30°C/min to 200°C. An FID system was used as the GC detector.

5.2. Solvent vapor analysis

In Fig. 15 the SnifProbe MicroSPE analysis of nine solvents is demonstrated (FID) each at about 0.5 ppm concentration in air. This chromatogram shows that SnifProbe with MicroSPE can be used for a full range of solvents, regardless of their volatility and with detection limits that are limited by chemical noise.

5.3. Analysis of SO_2 in air analysis

In Fig. 16 we show the analysis of SO_2 in air. A certified gas mixture of 540 ppm SO_2 in nitrogen was mixed at a ratio of 5000:1 with air and sampled with SnifProbe using the MicroSPE vial. At this level, SO_2 is easily analyzed using a 4 m×0.32 mm I.D. PoraBOND column as the analytical column with 2.6 ml/min helium carrier gas flow-rate and PFPD in the sulfur mode as the GC detector. We also measured the level of SO_2 in the ambient air of Tel Aviv University outside the laboratory and found that it contained 40 ppb SO_2. The emerging chromatogram with 40 ppb SO_2 in air looks the same as that in Fig. 16, with pen limited noise and a 6.2-times lower signal. We note that the air of northern Tel Aviv contains relatively high levels of SO_2 due to its proximity to the Reading electrical power station and it depends on the wind direction and fuel that is used.

5.4. Beer headspace analysis

In Fig. 17 we show the SnifProbe analysis of beer headspace for the presence of sulfur aroma compounds. In this case MicroSPE was used and in comparison with the results shown in Fig. 7 achieved with PoraBOND trapping column, the observed

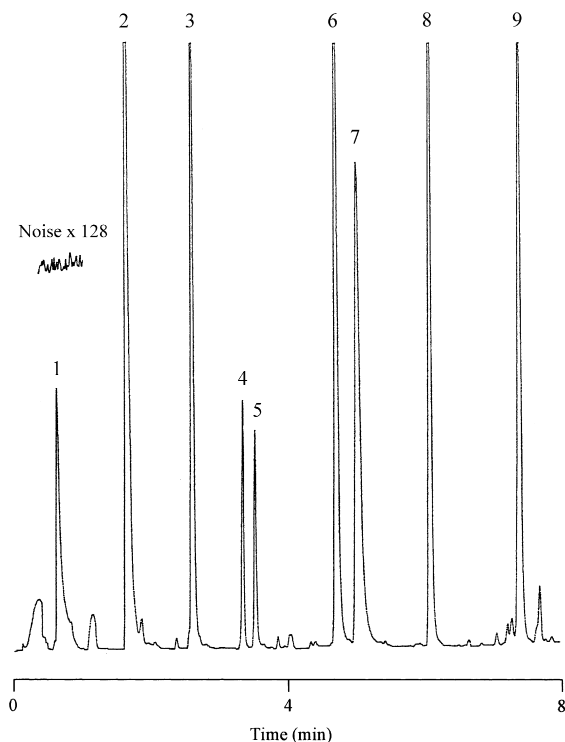

Fig. 15. SnifProbe MicroSPE analysis of solvent vapors in air. The nine indicated solvent compounds were dissolved at concentrations in the 1–50 ppm range in trioctyltrimellitate to provide headspace concentrations of about 0.5 ppm for each compound. The column and GC conditions are as in Fig. 14 above except that the initial GC oven temperature was 40°C.

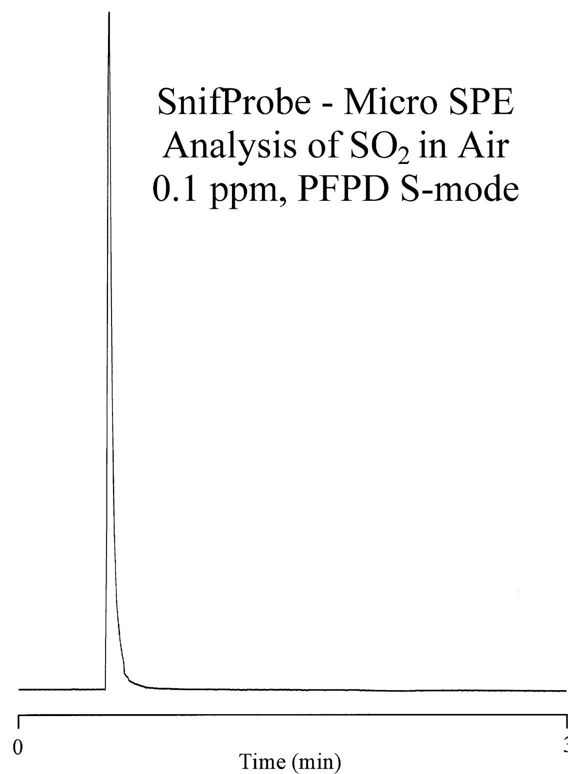

Fig. 16. SnifProbe-MicroSPE analysis of SO_2 in air. Micro tube with HayeSep Q powder was used for trapping with 45 ml/min pumping flow-rate for 1 min.

sensitivity is now considerably improved since a larger headspace volume could be probed.

5.5. BTX in water analysis

Finally, the MicroSPE can also be used for liquid sampling in addition to air sampling. In Fig. 18 we show the results of BTX analysis obtained by direct pumping of water through the MicroSPE vial. In this experiment, 12 ml water was pumped at a rate of 2 ml/min for 6 min followed by a few seconds of drying by further air pumping. The air pumping was found to have no adverse effect on the quantitative results. The three BTX compounds were easily observed as the dominant three peaks even at 1 ppb concentration. The signal-to-noise ratio was over 1000, suggesting a possible chemical noise limited detection limit below 1 ppt. The subject of water and liquid sampling with the MicroSPE tube and/or other SnifProbe trapping columns requires further description that is beyond the scope of this paper and thus the results shown in Fig. 18 are described only as a demonstration of this additional capability.

6. Discussion and conclusions

SnifProbe is a major new capability and device for the current ChromatoProbe sample introduction device. It extends the DSI/ChromatoProbe range of samples to also include gas phase samples.

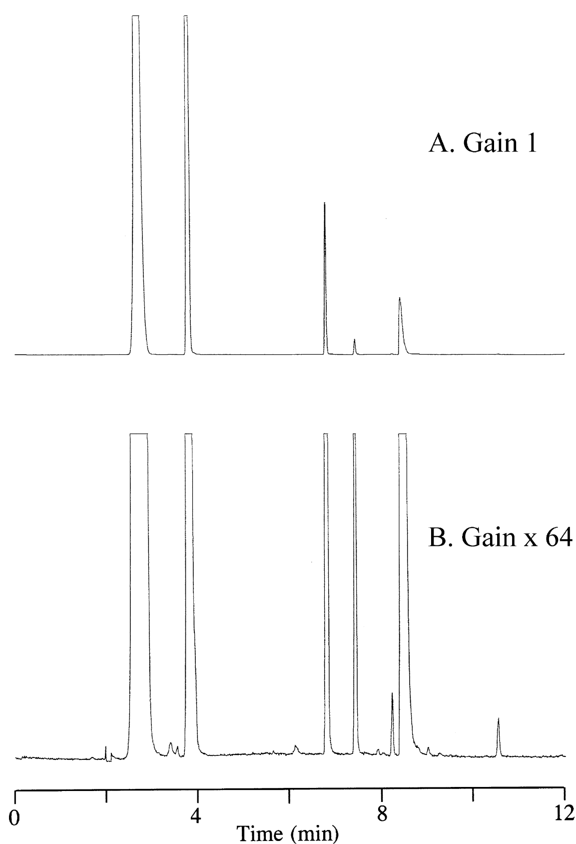

Fig. 17. SnifProbe-MicroSPE analysis of sulfur compounds in beer headspace. Beck's beer headspace was sampled at room temperature for 1 min at 45 ml/min sampling flow-rate (three×20 s with 30 s breaks for equilibration). The analytical column was 4 m×0.32 mm I.D. with 10 μm PoraBOND layer (PLOT column), with He column flow-rate of 2.6 ml/min. The injection was at 40°C GC oven temperature for 1 min (0.3 min splitless time) followed by 15°C/min temperature programming rate to 280°C. The bottom trace B is trace A magnified 64 times. A PFPD system was used as the sulfur-selective GC detector.

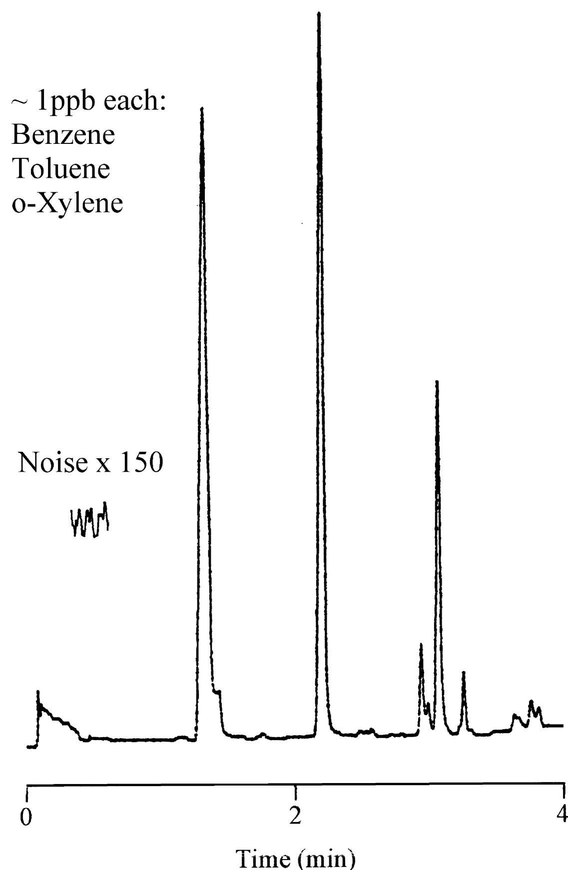

Fig. 18. MicroSPE analysis of benzene, toluene and *o*-xylene in water at 1 ppb concentration level. HayeSep Q powder was used in the MicroSPE vial. The GC analysis conditions are as in Fig. 14.

The SnifProbe approach is based on the use of the SnifProbe pumping and sample collection unit followed by GC sample introduction of the SnifProbe trapping column or MicroSPE vial with the DSI/ChromatoProbe. Unlike with ChromatoProbe sampling that requires a temperature programmable injector, the SnifProbe method can be employed with any standard split–splitless injector that can be easily converted to accept a DSI device. In comparison with the variety of available thermal desorption units we note that SnifProbe uses the available GC injector for intra-injector thermal desorption and thus it is inherently less complex and should cost less. In addition, it enables the analysis of less volatile and more labile compounds that might be irreversibly adsorbed on the standard packed column type adsorption tubes. Similarly, SnifProbe extends the range of compounds amenable for analysis with air bags to the semi volatile groups that can be sampled

with SnifProbe. In this paper we have shown that SnifProbe can be employed in a wide variety of applications and for a broad range of sample volatility. SnifProbe offers air analysis capability practically anyplace, most importantly in the field or chemical process where it is needed. The storage apparatus enables easy transportation to the laboratory for chromatographic analysis. Since it is based on air pumping it can be fast and enables high sensitivity analysis of trace level airborne impurities. Thus, the major attribute of SnifProbe is that it extends the ''arms'' of the GC and GC–MS laboratory to the field and process where it is needed.

In summary, SnifProbe unique features and advantages includes:

1. SnifProbe brings the field and process to the laboratory. SnifProbe can be operated in the field or at the process. The sample columns can be plugged, placed in a small plastic bag, marked and brought to the laboratory for analysis with the full power of GC/GC–MS. This is in our opinion the most significant feature of SnifProbe.
2. SnifProbe has a small size and its miniature sample containers are easy to transport.
3. Thermally labile and semi-volatile compounds such as explosives and CWA can be collected since the trapping column is easier to desorb than Tenax tubes.
4. Fast sampling and GC analysis can be obtained. A large sample volume is quickly probed and fast GC analysis (under 1 min) is enabled with only a small split ratio.
5. A uniform response can be achieved. The narrow column diameter ensures that all molecules are adsorbed. If the sampling time is limited, all the sample compounds are retained.
6. Built-in external protection. Since the adsorption layer is internal, the short sample column can be introduced into difficult locations while lightly touching the matrix. The sniffing column can also be fully covered except its opening with a brass shield.
7. High sensitivity can be provided through the pumping of a large sample volume. Compound and trap type dependent breakthrough volume restricts the sensitivity.
8. Dirty/reactive sample analysis capability is enabled. Since the sample short column costs very little it can be employed for dirty or reactive sample analysis and be disposed of after the analysis (cigarette smoke for example).
9. A broad range of sample column adsorption materials is available for sample collection optimization. From thin dimethyl silicone to thick PLOT column films and including the variety of packing materials with the MicroSPE tubes.
10. Cost effective. SnifProbe is an added capability to the ChromatoProbe that can serve for extract-free dirty sample introduction or as an MS probe.

Acknowledgements

The authors thank Mr. Gad Frishman for his help with the experiments and sample preparation. The help of Mr. Peter Hill with beer samples, advice and his available SPME–GC–PFPD results is greatly appreciated. This research was supported in part by grants from the Israel Ministry of the Environment and the James Franck Center for Laser Matter Interaction Research.

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