



ELSEVIER

Journal of Chromatography A, 704 (1995) 157–162

JOURNAL OF
CHROMATOGRAPHY A

Permeation tube approach to long-term use of automatic sampler retention index standards

Thomas J. Bruno

Thermophysics Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, CO 80303, USA

First received 29 December 1994; revised manuscript received 3 February 1995; accepted 9 February 1995

Abstract

A permeation tube that is sealed internally in a commercially-available automatic sampler vial provides a simple and convenient method of preparing, using, and storing standard retention index samples for long periods of time. The approach is especially suited to the handling of volatile organic compounds that are very important in fuels research, alternative refrigerant research and in many environmental analyses. It also provides the very desirable feature of dispensing sample that is at very low concentration or even at infinite dilution, since no commercial automatic sampler is currently capable of doing this for the analyst. The device is very simple, and can be constructed and prepared with a liquid sample in a few minutes. It requires the use of minimal quantities of sample, and substantially decreases the hazards associated with handling volatile organics in the laboratory.

1. Introduction

Automatic samplers are a vital tool for the chromatographic analysis of a wide variety of samples. They greatly reduce the time and labor required for analyses, and reduce the potential for operator exposure to potentially dangerous chemicals. The typical commercially available automatic sampler container, consisting of a glass vial and a crimped septum cap, performs only marginally when used with volatile organic compounds (VOCs), however. Leakage through the septum and around the seal is very common, and after the septum has been pierced by a syringe needle, leakage through the septum is inevitable and rapid. While this is of little consequence for VOCs that are sampled and analyzed quickly, it is a serious problem for sample vials that the analyst desires to retain and use on a

long-term basis. While it is possible to replace the crimped septum cap after each use, this approach is extremely inconvenient and time consuming. It also increases the risk of operator exposure to the sample, and the potential for accidental sample spillage. Moreover, leakage around the seal will persist even if the cap is replaced after each use.

Long-term samples include retention time and retention index standards and markers [1–5]. Such samples are used extensively in chromatographic qualitative analysis and peak assignment/identification. It is very desirable to package such samples in order to minimize material loss and handling, and to minimize the initial quantity of material that is required for their preparation. Moreover, retention index standards are usually used at very low concentrations (often approaching infinite dilution), or even as head-

space vapors. This is also true for samples used in physicochemical chromatographic measurements [6-8]. It is therefore helpful to package such standards in a way that facilitates drawing and delivering a very dilute aliquot.

In this paper, we present an approach to the application of automatic sampler vials to long-term retention index standards. The method is based on permeation tubes, well known devices that have been used for the preparation of gaseous mixtures for many years [9-12]. A permeation tube is a short length (usually between 5 and 20 cm) of a polymeric tubing through which a fluid may pass at a relatively slow, constant rate (at a given temperature). Numerous polymers have been used for the preparation of the tubes used for such permeation devices. These polymers include polyethylene, polyvinyl acetate, polyamide, polyester, silicones, polyvinylidene chloride and polyethylene terephthalate. The most common materials are fluorinated ethylene propylene (FEP Teflon¹) and tetrafluoroethylene (TFE Teflon). The most common use of permeation tubes is for the preparation of gas mixtures.

Such a permeation device is typically prepared by filling the inside of the tube (with one end plugged) with the desired fluid until approximately 80 percent of the tube volume is occupied with liquid. For more volatile fluids, this must be done in a pressurized manifold. Most permeation tube devices are two-phase (vapor + liquid) systems, however single-phase high-pressure gaseous tubes have been prepared occasionally. The tube is then "conditioned" at a constant suitable temperature to saturate the polymer with the fluid. At that point, the permeation rate of the fluid will be constant at a given temperature. If the temperature is changed, some time will be

required for the constant rate to be reestablished at the new temperature.

Permeation tubes are commonly used for the preparation of gas mixtures using dynamic techniques in which the tube containing the desired fluid is held in the slip stream of a flowing diluent gas. A knowledge of the diluent flow-rate and temperature allows the calculation of the concentration of the fluid in the diluent gas.

2. Theory

The operation of a polymeric permeation tube device is described fundamentally by Fick's law [9-11]:

$$q_d = (p_g A \Delta P) / L \quad (1)$$

$$p_g = D \cdot S \quad (2)$$

where q_d is the amount of sample material (fluid) that passes through the permeation material (in mass units per unit area per unit time), p_g is the fluid permeability constant, D is the diffusion coefficient (in area per unit time), S is the solubility constant of the fluid in the polymer (in concentration units divided by fugacity or pressure), A is the area of the material, ΔP is the pressure difference across the polymer, and L is the thickness of the polymer. The pressure difference ΔP is in practice usually taken as the difference between the vapor pressure of the permeating fluid and the pressure within the sampling area. As these equations demonstrate, the main factors that affect passage of a gaseous material through a polymeric permeation tube are (1) the vapor pressure of the permeating fluid and (2) the solubility of the permeating fluid in the polymer. At constant temperature, the solubility of the permeating fluid in the polymer is constant. In the great majority of permeation tube applications, the fluid is contained (usually under its head pressure) in the inside of a sealed tube made from the polymer, and the desired concentration of fluid is achieved by appropriate mixing with a diluent flowing outside the tube. The concentration of the fluid in the diluent can be approximated by:

¹ Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for that purpose.

$$[c] = \frac{(\nu \cdot 10^6)(T/273)(P/0.101325)q_D}{q_D M} \quad (3)$$

where $[c]$ is the concentration expressed in parts per million (that is, 0.0001 percent), T is the temperature of the permeation tube (in K), P is the pressure of the diluted gas stream (in MPa), q_D is the volumetric flow-rate of the diluent (in l/min), ν is the molar volume of the permeating fluid (in l) and M is the relative molecular mass of the permeating fluid. A common approximation is to replace ν with 22.4 l, the molar volume of an ideal gas. In the present case, with the permeation tube functioning in reverse, the diluted sample vapor is on the inside of the tube.

For purposes of Eq. (3), the flow-rate q_D for the current apparatus is taken as the sampling rate (in $\mu\text{l}/\text{min}$), done by syringe on an automatic sampler. This allows the approximate concentration of fluid inside of the permeation tube insert to be calculated.

3. Experimental

A standard wide-mouth commercial automatic sampler vial can be fitted with a permeation tube insert as shown in Fig. 1 to provide long-term sample storage and availability, and also to dispense the samples at low concentrations or in the infinite dilution range. The permeation tube insert consists of a short length of TFE (tetra-

fluoroethylene) or FEP (fluorinated ethylene propylene) Teflon permeation tubing (0.48 cm O.D., 0.32 cm I.D.). The typical length of exposed permeation tube is 1.9 cm. In general, the TFE material will provide a higher permeation rate for hydrocarbons than will the FEP material [13]. This rule of thumb appears not to hold for halogenated hydrocarbons, however. Branched hydrocarbons will have a much lower permeation rate than straight chain hydrocarbons. These considerations will affect the choice of permeation tube material.

The permeation tube is held in place in the neck of the vial by a collar made from a short length (0.48 cm) of flexible polyethylene tubing (0.64 cm O.D., 0.32 cm I.D.) that is press-fitted on the top end of the permeation tube. The relative sizes of the polyethylene ring (expanded with the permeation tube inserted) and the inside diameter of the neck of the vial (0.64 cm) provide an interference fit that allows for an excellent seal to the automatic sampler vial. An interference fit exists when the outside diameter of the insert exceeds the available inside diameter of the vial. The bottom of the permeation tube is securely plugged by a small disk of 25 percent glass-filled Teflon (PTFE-glass, 0.4 cm maximum diameter) machined to provide an interference fit with three points of contact.

To assemble the insert, the permeation tube, with one end plugged with the glass-filled Teflon disk, is fitted with the polyethylene collar. The liquid sample is then added to the vial, and the insert is press-fitted into the neck on a small laboratory hydraulic press or an arbor press. The collar and permeation tube are sized to be flush with the top of the vial, thus allowing a standard crimped septum cap to be fastened onto the vial. Before the septum cap is installed, a 30° chamfer is cut concentrically into the top surface of the collar and permeation tube, to help guide a syringe needle into the permeation tube. This is easily done with a hand-held carbide cutter that is commonly used to dress the ends of tubing used for packed chromatographic columns.

After the septum cap is crimped on the vial, the unit is placed in a laboratory oven and maintained between 50 and 100°C to allow

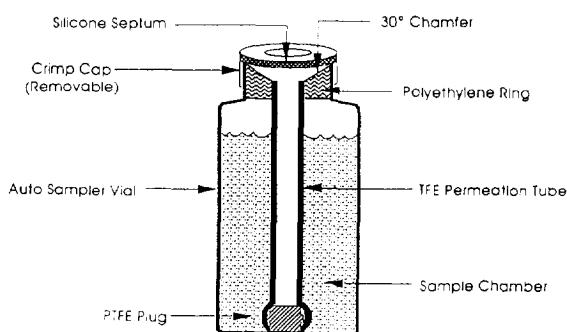


Fig. 1. Schematic diagram of an automatic sampler vial fitted with a permeation tube insert.

conditioning and induction of the permeation tube. The choice of the induction temperature depends on the boiling point of the fluid. The typical induction period for commercial permeation tubes is approximately 3 weeks to achieve a constant permeation rate [10]. We have found that for use as low concentration retention standards, a high level of concentration reproducibility is of secondary importance, and induction periods of 5-7 days are adequate.

4. Results and discussion

Automatic sampler vials containing a permeation tube insert have been prepared for a variety of VOC samples, and several of the more instructive examples will be described. The hydrocarbon samples have included *n*-hexane, *n*-octane, *n*-decane and 2,3-dimethyl pentane. Halocarbon samples have included fluorotrichloromethane (R-11), 1,1-dichloro-1-fluoroethane (R-141b) and 1,2-difluoroethane (R-152). The last compound is particularly illustrative of the advantages of this approach for sampling. R-152 is very toxic because its potential metabolic products include monofluoroacetic acid, even after exposure to moderate concentrations [14]. Moreover, the intermediate volatility (normal boiling temperature of 30.7°C) of this material makes it somewhat difficult to handle in a conventional automatic sampler vial.

A significant challenge associated with the preparation of permeation tubes has always been the prevention of leakage through the tube closure(s) [9,12]. For this reason, a number of experiments were done to verify the integrity of the plug at the bottom of the tube in the automatic sampler vial. Two sets of vials were prepared (with TFE permeation tubes) containing *n*-hexane, and were maintained at 70°C for 5 days after an initial induction period. One set of vials had crimped septum caps in place (the configuration shown in Fig. 1), and the other set was left uncapped. Although this temperature is slightly above the normal boiling temperature of *n*-hexane, there was no measurable decrease in the liquid levels of the vials. If leakage through the plug had occurred, some decrease in the

liquid level would have been noted. Similar observations were made with other hydrocarbons (straight chain and branched) that were maintained at relatively high temperatures.

Vials were also prepared with permeation tubes that were fitted with multiple plugs, some plugs having multiple barbs and some being simple cylindrical plugs. No change in tube performance was noted with any combination. As a final check, a vial was prepared in which a plug such as that shown in Fig. 1 was inserted, but the polyethylene tube used to form the collar extended throughout the length of the permeation tube. This sheath covered the entire active (that is, permeating) surface of the insert. This tube showed no permeation activity; no vapor could be detected inside the tube. We can therefore conclude that the material that enters the interior of the tube has in fact permeated from the liquid space, and has not leaked through a properly prepared and installed plug.

Because of differences in permeation rates of different fluids in the TFE and FEP materials, two different sampling modes (steady-state and dynamic) are noted for the performance of the vials. The steady-state mode is obtained when the sampling rate (removal of vapor sample) is balanced by the permeation rate (replenishment of fluid). This behavior is illustrated in Fig. 2a, with *n*-hexane as the sample drawn from a vial fitted with a TFE insert. This figure shows raw area counts from a flame ionization detector that were obtained from 7- μ l injections of the interior space of the permeation tube. These samples were injected into a polymethyl siloxane coated capillary column (1 μ m thickness, 50:1 split ratio). The concentration of sample is approximately constant (within approximately 6.5 percent) for a sampling rate of approximately once every 1.5 min. No attempt was made to control the temperature of the vial for these measurements. Temperature control would undoubtedly increase the reproducibility of the area measurements, but, as was noted earlier, this is a secondary concern for retention index samples. The dynamic mode occurs when the sampling rate exceeds the replenishment rate. This behavior is illustrated in Fig. 2b, with *n*-octane as the sample with an FEP insert. Here we note a

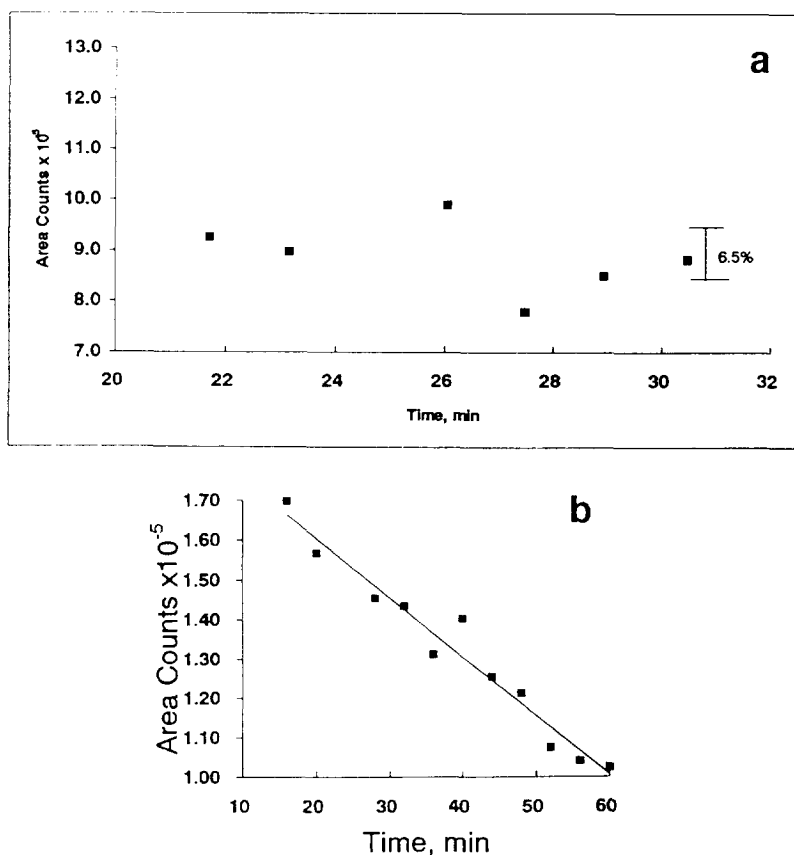


Fig. 2. (a) Plot of FID raw area counts against sampling time for *n*-hexane sampled through a TFE insert. (b) Plot of FID raw area counts against sampling time for *n*-octane sampled through a FEP insert.

steady decrease in the area counts for a sampling rate of once every 4 min.

Another potential use for automatic sampler vials equipped with permeation tubes is for the evaluation of permeation tubes themselves. One can use chromatographic instrumentation to sample the interior of the permeation tube at an increasing rate, rather than the uniform rate that was used here. One can then determine the transition from steady-state mode to dynamic mode. The permeation through the tube at this transition is characteristic for the sample for a given permeation tube material.

5. Conclusions

In this note, we have explored the application of permeation tube inserts to extend the utility of

automatic sampler vials, especially as applied to the measurement of retention index standards. The combination of these two components can provide a chromatographic sampling method that is safe, convenient and widely applicable. In addition, the approach is potentially useful as a method of characterizing the performance of permeation tube materials.

Acknowledgements

The financial support of the Gas Research Institute, Chicago Il. (Contract No. 5093-260-2720), and the United States Environmental Protection Agency, Stratospheric Ozone Protection Branch (Contract No. DW13935632-01-0), is gratefully acknowledged. The assistance of

T.G. Waldorf with some aspects of the fabrication is gratefully acknowledged.

References

- [1] E.sz. Kovats, *Helv. Chim.*, 41 (1958) 1915.
- [2] M.B. Evans, J.K. Haken, *J. Chromatogr.*, 472 (1989) 93–127.
- [3] T.J. Bruno, M. Caciari, *J. Chromatogr. A*, 672 (1994) 149–158.
- [4] T.J. Bruno, M. Caciari, *J. Chromatogr. A*, 679 (1994) 123–132.
- [5] T.J. Bruno, M. Caciari, *J. Chromatogr. A*, 686 (1994) 245–251.
- [6] J.R. Conder, C.L. Young, *Physicochemical Measurement by Gas Chromatography*, John Wiley and Sons (Wiley-Interscience), Chichester, 1979.
- [7] R.J. Laub, R.L. Pecsok, *Physicochemical Applications of Gas Chromatography*, John Wiley and Sons (Wiley-Interscience), New York, 1978.
- [8] T. Cserhati, K. Valko, *Chromatographic Determination of Molecular Interactions*, CRC Press, Boca Raton, FL, 1994.
- [9] G.O. Nelson, *Gas Mixtures: Preparation and Control*, Lewis Publishers, Boca Raton, FL, 1992.
- [10] J. Namiesnik, *J. Chromatogr., Chromatogr. Revs.*, 300 (1984) 79–108.
- [11] D.R. Paul, Y.P. Yampol'ski (Editors), *Polymeric Gas Separation Membranes*, CRC Press, Boca Raton, FL, 1994.
- [12] C.F. Cullis, J.G. Firth (Editors), *Detection and Measurement of Hazardous Gases*, Heinemann Educational Books, London, 1981.
- [13] D. Williams, VICI Metronics, personal communication, 1994.
- [14] T.J. Bruno (Editor), *Handbook for the Identification and Analysis of Alternative Refrigerants*, CRC Press, Boca Raton, FL, 1995.