

Simple device for permeation removal of water vapour from purge gases in the determination of volatile organic compounds in aqueous samples

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ABSTRACT

A commercially available Nafion tube (a perfluorinated ion-exchange resin membrane separator) inserted in a plastic container filled with 5A molecular sieve was tested on dry water-saturated gas streams containing common volatile pollutants of aqueous environmental samples after a purging cycle. The proposed device was shown to remove water vapour effectively from humidified gas streams (>90%) even under continuous operation for more than 10 days. The results showed that the system is compatible with the tested compounds (aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons and some sulphur compounds) because these compounds are practically unaffected on passing through the Nafion dryer tube. The losses of most compounds at the $\mu\text{g}/\text{kg}$ level are less than 5%. Therefore, the proposed device is suitable for the removal of water vapour from purging streams and can be used in the determination of these volatile organic compounds in aqueous samples using the purge-and-trap technique.

INTRODUCTION

Volatile organic compounds (VOCs) are an important class of water pollutants. The determination of trace amounts of VOCs in water is often carried out by gas chromatography (GC), usually after a preconcentration step [1–3]. Various methods are used for preconcentration, but the purge-and-trap (PT) technique is the most preferred, especially for the determination of purgeable priority pollutants listed by the US Environmental Protection Agency (EPA) [4–6].

In the first step of the PT technique, the analytes are stripped from the aqueous phase. In the next, the swept analytes can be either (1) adsorbed on a thermally desorbable sorbent bed (especially one containing Tenax) [7], (2) re-

tained in a cold trap (cryotrapping) [8], (3) cryofocused on the head of the column [9] or (4) transferred to a capillary column maintained at a cryogenic temperature (whole-column cryotrapping) [10,11]. Finally, the solutes trapped in different ways, after liberation, are separated on a column and detected.

The main disadvantage of the PT technique is the purging of significant amounts of water vapour along with the analytes. This ubiquitous presence of water can cause many problems, mainly during the focusing of the analytes and their chromatographic analysis. The same problem is encountered during the determination of trace amounts of VOCs in air samples, but the content of water is considerably lower.

The main problems caused by the presence of water in streams of gases in the mentioned procedures are as follows: decrease of the adsorption capacity of the sorbent used for the

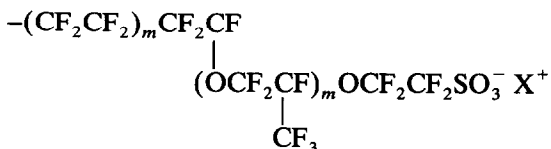
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concentration of VOCs owing to co-adsorption of water; condensation of water along with the analytes on the walls of the tubes connecting the purge device with the sorbent trap or GC injection port; plugging of traps and GC columns at sub-zero temperatures [10,12]; degradation of the performance of retention gaps or GC columns [13,14]; and variations of retention times and responses of the compounds that elute near water [15,16].

Several procedures have been used to avoid these adverse effects: using a hydrophobic sorbent [16]; heating the connection tubes [17]; the use of desiccants such as $\text{Mg}(\text{ClO}_4)_2$ [18–20], Ascarite [21], K_2CO_3 [22], CaSO_4 , $\text{Ba}(\text{ClO}_4)_2$ and Na_2SO_4 [23,24]; removal of water by reaction in a precolumn filled with triethyl orthoformate or 2,2-dimethoxypropane [25]; adsorptive removal of water by silica gel [26] or molecular sieves 3A, 4A and 5A [27]; removal of water by passing the moist streams through a short column of glass beads (condenser) at -10°C [8,9]; and permeation removal of water by using membrane tubes [27–31].

The last procedure, based on the use of perfluorosulphonic acid membranes made of Nafion tubes produced by DuPont, has two important advantages over conventional bed desiccants, namely a small dead volume and a small pressure drop.

A commercially available Nafion drier (a perfluorinated ion-exchange resin) has proved to be an efficient membrane separator. The exceptional performance of these membranes derives from the chemical, mechanical and thermal stabilities provided by a perfluorinated backbone and the ion-exchange properties supplied by the pendant sulphonate groups. In the salt form, Nafion has the following repeat structure [32]:



where m is small and X^+ is an exchangeable cation.

Some previous applications of Nafion tube dryers have helped to define the conditions

under which they can be used [27,30,33]. In most of these applications Nafion was used to remove water from ambient air samples. Coutant and Keigley [34] used Nafion in the direct injection of water samples of considerable volume. To our knowledge, no previous systematic investigations have been reported on drying of gases after purging volatiles from water samples containing typical environmental pollutants. In such cases the conditions are more drastic because saturation of the sample streams with water vapour occurs.

The purpose of this work was to test the compatibility of common volatile pollutants of water (aliphatic and aromatic hydrocarbons, organosulphur compounds and halogenated hydrocarbons) with Nafion to show its suitability for drying water-saturated gases in the PT–GC technique.

EXPERIMENTAL

Efficiency of the Nafion tube for drying of gas streams after the purging step

Nafion used in all experiments was obtained from Perma Pure Products (Toms River, NJ, USA) as tubing of 0.33 mm I.D. and 0.51 mm O.D., wall thickness 0.089 mm and internal volume $0.099 \text{ cm}^2 \text{ m}^{-1}$.

Initial studies to determine the water removal efficiency under approximately ambient conditions from gas streams in the PT technique were conducted in a system consisting of the following components: (1) an argon reservoir; (2) a 20-cm³ laboratory-made purge vessel with a medium pore size frit; (3) interchangeably, (a) a fused-silica capillary (system A), (b) a 1.2-m Nafion tube inserted in an empty clear plastic cylinder (system B) and (c) a 1.2-m Nafion tube inserted in the cylinder with molecular sieve type 5A (system C); and (4) a scrubber filled with magnesium perchlorate.

Argon was delivered to the purge vessel through a frit and was bubbled through 10 cm³ of water for 10 min at a flow-rate of $30 \text{ cm}^3 \text{ min}^{-1}$. It can be assumed that under these conditions the gas stream leaving the purge is saturated with water vapour (>90%). The efficiency of each system was determined from the mass increase of

the scrubber. The average mass increase in case 3a was 5.97 mg, which corresponds to complete saturation of gas with water vapour at ambient temperature ($18.7 \mu\text{g}$ of water in 1 cm^3 of gas) and is the expected value. In case 3b, this increase was 3.11 mg and in case 3c, in which the humidity outside the Nafion tube due to the presence of molecular sieve was close to 0%, the mass of the scrubber was virtually unchanged (0.1 mg).

Effect of the Nafion dryer on the recovery of the selected volatile organic compounds

Preparation of solutions. Stock standard solutions of trichloromethane, tetrachloromethane, dichlorobromomethane, chlorobenzene, *n*-propanethiol and *tert.*-butanethiol were prepared in methanol and those of 1,7-octadiene, 1-octene, thiophene, diethyl sulphide, styrene, benzene, toluene, nonane and decane in dimethyl sulphoxide (DMSO). The concentrations of the analytes ranged from *ca.* 0.1 to 1 g kg^{-1} . Model aqueous solutions at the $\mu\text{g kg}^{-1}$ level were prepared in measuring flasks (100 cm^3) by injecting 3–10 μl of stock solutions with a microsyringe. A 10-cm^3 volume of the model solution of each compound was taken for the recovery tests under different sampling procedures.

Purge-and-trap conditions. A general view of the laboratory-made PT system is shown in Fig. 1. The device consists of (1) a 20-cm^3 laboratory-made purge vessel; (2) optionally, a 1.2-m Nafion dryer inserted in the cylinder with molecular sieve type 5A (*ca.* 2–3-mm beads); (3) a six-port rotary valve; and (4) a trap with an appropriate sorbent.

For experiments with trichloromethane, tetrachloromethane and dichlorobromomethane the trap was filled with 30 mg of Carbosieve III S and 80 mg of Tenax TA. For all other compounds only 80 mg of Tenax TA were used. The purge gas, argon, was passed through the system (Fig. 1A) at a flow-rate of $30 \text{ cm}^3 \text{ min}^{-1}$ for 15 min for thiophene and diethyl sulphide, for 5 min for *n*-propanethiol and *tert.*-butanethiol and for 10 min for the remaining compounds. After that time, the flow was stopped and heating of the trap was started. When the trap reached a temperature of 170°C the carrier gas was di-

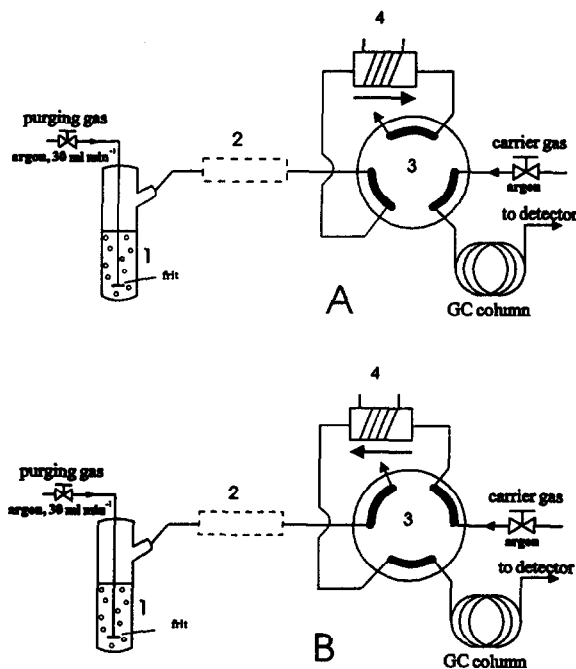


Fig. 1. Experimental apparatus assembly: 1 = purging vessel with frit; 2 = 1.2-m Nafion dryer embedded in 5A molecular sieve desiccant; 3 = six-port rotary valve; 4 = heated sorbent trap. (A) Purge and trap step; (B) desorption step.

rected to the trap (Fig. 1B) and desorbed analytes at 250°C [17] were passed to the chromatographic column.

Chromatographic conditions. Analyses for trichloromethane, tetrachloromethane and dichlorobenzene were performed using a Hewlett-Packard Model 5890 II gas chromatograph equipped with a 30-m DB-1 capillary column and an electron-capture detector. The temperature programme was initially 70°C for 4 min, increased at $10^\circ\text{C min}^{-1}$ to 110°C and held at the final temperature for 7 min.

The remaining compounds were measured using a Hewlett-Packard Model 5830 A gas chromatograph equipped with the packed columns and a flame ionization detector. Benzene, toluene, nonane, decane, thiophene and dimethyl sulphide were separated on $2 \text{ m} \times 0.3 \text{ mm}$ I.D. column packed with Dexil 300. The temperature programme was initially 80°C for 1 min, increased at 4°C min^{-1} to 120°C and held at the final temperature for 1 min. For the separation of the remaining compounds a $3 \text{ m} \times 0.3 \text{ mm}$

I.D. column packed with DC-550 was used. The column temperature was 50°C for propanethiol and *tert.*-butanethiol, 70°C for 1,7-octadiene, 80°C for chlorobenzene and 105°C for styrene.

RESULTS AND DISCUSSION

To prevent column plugging and chromatographic interference by water, the purge gas should be dried before reaching the column. The proposed systems should remove water vapour and not affect the analyte compounds.

Preliminary experiments showed that the proposed device, a Nafion tube inserted in a plastic container filled with 5A molecular sieve, effectively removes water from water-saturated gas streams after a purging step. Fig. 2 compares the water-removal efficiencies for the different systems used. The effectiveness of water removal with the tested systems was calculated on the basis of the mass increase of the scrubber containing magnesium perchlorate. A virtually unchanged mass of the scrubber (Table I) after passing the purge gas stream through the proposed system (A) indicates that water is nearly completely removed. From Fig. 3, it is clear that the effectiveness of the water removal remains almost constant for as long as 10 days of continuous operation.

In a second series of experiments, the effect of the system used on the recovery of common volatile pollutants of aqueous environmental samples after passing through the proposed de-

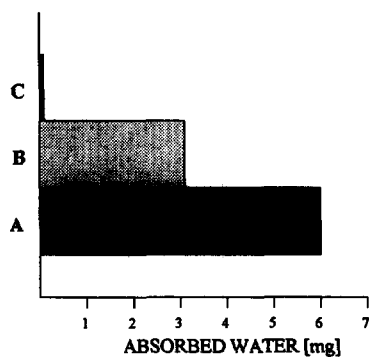


Fig. 2. Comparison of water-removal efficiencies of different drying systems: (A) without a Nafion tube; (B) with a Nafion tube; (C) with a Nafion tube inserted in 5A molecular sieve.

TABLE I
WATER REMOVAL FROM WATER-SATURATED GAS STREAM BY THE DIFFERENT SYSTEMS USED

System	Mass increase of scrubber (mg)	Standard deviation (mg) ($n = 3$)
(A) Without a Nafion tube	6.0	0.44
(B) With a 1.2-m Nafion dryer	3.1	0.13
(C) With a 1.2-m Nafion dryer inserted in 5A molecular sieve	0.1	0.16

vice was tested. Fig. 4 illustrates the recoveries of the tested compounds at the ppb level (expressed as the area of corresponding peaks) with and without the use of a Nafion tube. The tests were conducted for two different concentrations of the tested compounds and the results are averages of 5–11 measurements. Table II shows the differences in the recoveries of the investigated compounds with and without a Nafion tube. It can be seen that there is essentially no sample loss (generally <5%) when a Nafion tube containing molecular sieve was connected in-line. These results agree generally with data reported previously [27,30,33]. According to these reports, most inorganic gases, hydrocarbons, esters, chlorinated hydrocarbons and some sulphur compounds were unaffected when a Nafion tube was used for drying air samples. In our study, only the recoveries of octadienes and tetrachloromethane, especially at very low concentrations, are affected by the Nafion tube. The losses of these compounds are about 10%. This may be partially explained by the slightly polar character of some of these compounds. From previous reports it is known that Nafion removes polar compounds such as alcohols, amines, some ethers and esters [27,35]. It has also been reported that Nafion rearranged several monoterpenes and removed several oxygenated compounds [30]. However, this limitation may not be critical for polar compounds in the PT technique because this gas extraction technique is generally unsuitable for such compounds. If analyses for polar compounds are intended, more tests

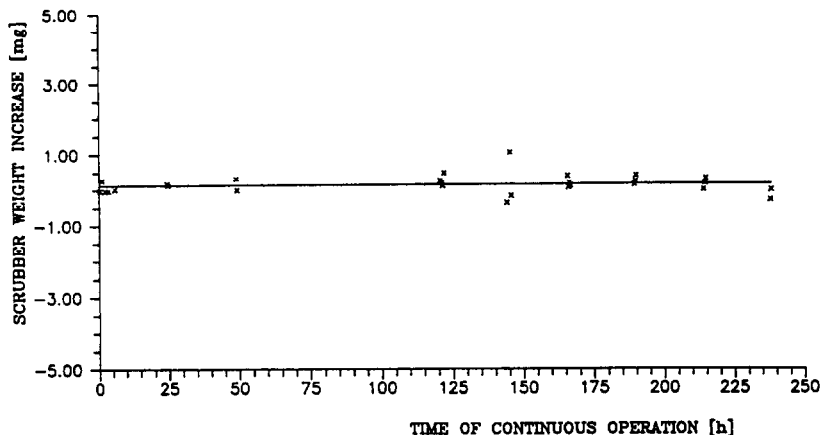


Fig. 3. Efficiency of water removal as a function of time.

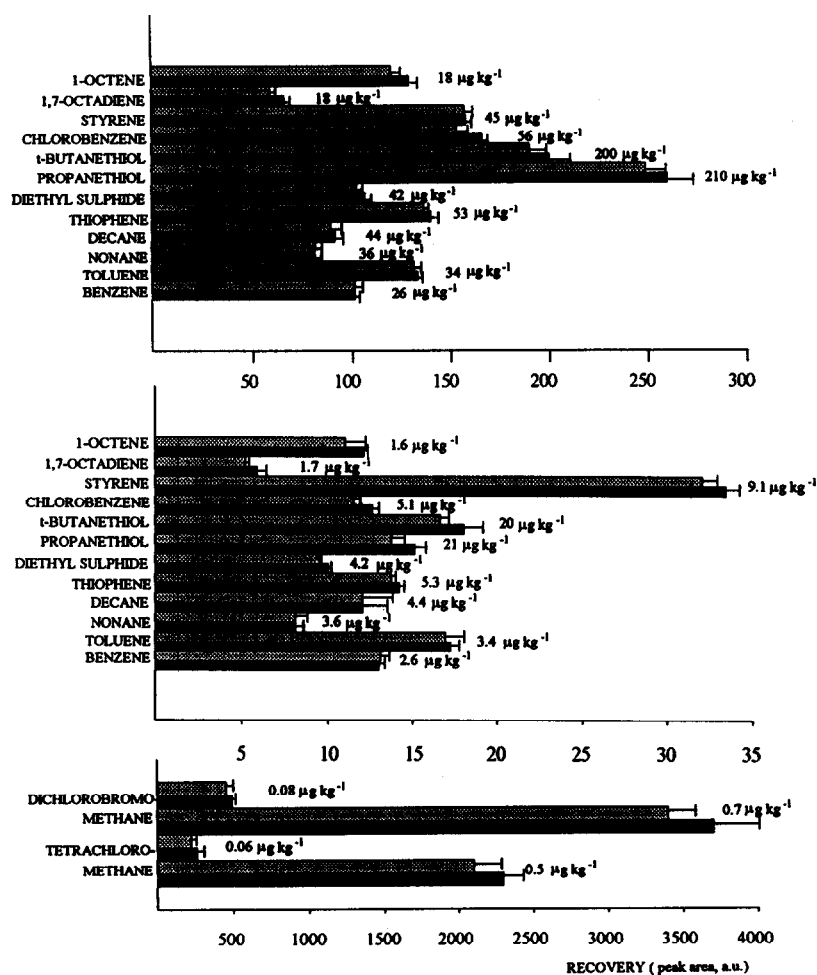


Fig. 4. Recovery of tested compounds with different sampling procedures. Black boxes, sampling directly after purging without a Nafion dryer; dotted boxes, sampling through Nafion dryer. \pm = Standard deviation. a.u. denotes arbitrary area units of integration.

TABLE II
RECOVERIES OF TESTED COMPOUNDS WITH AND WITHOUT A NAFION DRYER

Compound	Concentration ($\mu\text{g kg}^{-1}$)	Deviation ^a (%)	Compound	Concentration ($\mu\text{g kg}^{-1}$)	Deviation ^a (%)
Benzene	26	0.0	<i>tert.</i> -Butanethiol	200	-5.0
	2.6	0.8		20	-7.8
Toluene	34	-1.5	Chlorobenzene	56	-7.8
	3.4	-1.7		5.1	-8.7
Nonane	36	0.0	Styrene	45	-1.6
	3.6	0.0		9.1	-4.2
Decane	44	-2.2	1,7-Octadiene	18	-10.6
	4.4	0.0		1.7	-11.9
Thiophene	53	-2.9	1-Octene	18	-7.0
	5.3	-3.5		1.6	-9.1
Diethyl sulphide	42	-3.8	Tetrachloromethane	0.5	-8.7
	4.2	-5.0		0.06	-15.4
Propanethiol	210	-4.2	Dichlorobromomethane	0.7	-8.1
	21	-9.3		0.08	-8.2

^a Difference between recovery of purged compound with and without use of a Nafion dryer, expressed in %.

should be made to establish the suitability of a Nafion dryer.

CONCLUSIONS

It was found that a Nafion tube inserted in a plastic container with 5A molecular sieve is suitable for drying water-saturated gas streams leaving the purge vessel during analyses for many common volatile pollutants of water using the PT technique. Water is quantitatively removed from the humidified gas stream and the analyte compounds are virtually unaffected. The proposed device is much cheaper and technically simpler than commercially available equipment such as glass-bead dryers and permeation dryers with a countercurrent flow of dry gas.

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