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Short communication

# Investigation of membrane dryers and evaluation of a new ozone scrubbing material for the sampling of organosulphur compounds in air

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## Abstract

The applicability of two different types of Nafion membrane dryers (based on counter-current flow and desiccant drying) and of a new ozone scrubbing material, polyphenylene sulphide wool (noXon-S), to adsorptive sampling of selected volatile sulphur compounds (methanethiol, dimethyl sulphide, isopropanethiol and isobutanethiol) is investigated at the low ppb (v/v) level (1–5 ppb). No analyte losses occur with either type of dryer at relative humidities (RH) of  $\leq 50\%$ , while at higher RH values particularly the thiols tend to be lost (between 6 and 32%) even after conditioning. The actual losses depend more on the state of the individual permeation membrane rather than on the type of dryer. NoXon-S is a highly suitable ozone scrubber material for sulphur compounds since it efficiently removes ozone without retainment of the analytes and without the formation of blanks or artefacts from the scrubber material. The combined use of a Nafion membrane dryer and a noXon-S ozone scrubber is thus recommended for artifact-free sampling of sulphur compounds. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Membrane dryers; Ozone scrubbing material; Air analysis; Polyphenylene sulfide; NoXon-S; Sulfur compounds

## 1. Introduction

In recent years the interest in the development of analytical techniques for the determination of volatile organosulphur compounds has increased [1] and references therein. Organosulphur compounds naturally occur in the atmosphere at very low concentration levels [2,3] and references therein. Sampling of these compounds is commonly done by preconcentrating sampling techniques, mainly sampling onto solid adsorbents or cryogenic freeze-out

[1] and references therein. Separation and detection is done by gas chromatography and sulphur selective detectors, which allow the selective detection of organosulphur compounds even in the presence of large amounts of hydrocarbons [4,5] and references therein. During sampling as well as during separation and detection the presence of oxidants and water can cause severe problems. Oxidants like ozone and nitrogen oxides are known to oxidise labile compounds like terpenes and organosulphur compounds sampled on adsorption tubes or in cryogenic traps [6] and references therein. Water significantly lowers the capacity of adsorbents and clogs cryogenic traps but can also cause baseline perturbations and retention

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time shifts in chromatography and can interfere with detection. Therefore methods for the efficient removal of water and oxidants prior to sampling are needed. The main problems in connection with drying and ozone scrubbing techniques are losses of the analytes and the formation of artifacts. Organosulphur compounds like sulphides, disulphides and thiols are prone to artifact formation due to oxidation, and are known for their high affinity towards metal surfaces, which leads to losses due to irreversible adsorption by chemisorption [7] and references therein. This reactivity is particularly pronounced for thiols.

Among the drying techniques currently in use for the sampling of volatile organic compounds only permeation drying with Nafion membranes [8–12] and drying of the sample stream in direct contact with  $\text{CaCl}_2$  [13,14] are known not to cause significant losses of dimethyl sulphide, dimethyl disulphide and methanethiol. Other techniques are only suitable for dimethyl sulphide and either cause losses of thiols or have not been investigated for this compound class [15–18]. Permeation drying with Nafion membranes is advantageous due to the low and constant pressure drop of the permeation dryers, the high capacity of the dryer, the low maintenance needs and the fact, that the analytes do not come into direct contact with the desiccant. Nevertheless differences in the performance of Nafion dryers for organosulphur sampling are reported and Hofman et al. [11] speculate that these differences may be explained by the different types and the different use of the Nafion dryers, for example counter-current versus desiccant mode.

Several methods are currently in use for ozone scrubbing for sampling of dimethyl sulphide:  $\text{Na}_2\text{CO}_3$  coated onto Chromosorb W AW, filters or Anakrom [19–23], KOH or NaOH impregnated filters [18,24,25], phosphate buffered neutral KI solutions [26], KI–glycerol–Vitex on glass fiber filters [27], KI [17], KI–NaOH solution [28], silicone rubber [29] and cotton wadding [10,11]. Most of these methods have not been tested for thiols or are known to cause severe losses for this compound class [11]. No method is currently known, which does not cause losses of thiols. Rieger et al. [30] introduced noXon-S (polyphenylene sulphide) as ozone scrubbing material for the use in ozone

analysers. Calogirou et al. [31] successfully used this material for ozone scrubbing in the sampling of terpenes and their oxidation products. NoXon-S is an efficient ozone scrubbing material [30,31], seems to have a low adsorption capacity for organic compounds [31] and is easy to handle.

Due to the attractive properties of noXon-S (polyphenylene sulphide wool) this material was investigated in the present communication for the sampling of organosulphur compounds. Since there is no general agreement concerning the choice of Nafion dryers for organosulphur sampling, dryers operating both on a dry counter current and on dry molecular sieve as desiccant were examined in more detail.

## 2. Experimental

### 2.1. Preparation of standards

A schematic of the apparatus used for dynamic generation of gaseous standard mixtures is given in Fig. 1. Certified permeation tubes (VICI Metronics, Santa Clara, CA, USA) filled with methanethiol (MeSH), dimethyl sulphide (DMS), isopropanethiol (i-PrSH) and isobutanethiol (i-BuSH) were placed in the thermostated oven ( $30 \pm 0.1^\circ\text{C}$ ) of the permeation apparatus (VICI). Compound data are given in Table 1. The standards were prepared in ambient air, which was supplied by an oil-free compressor and further purified from water and organic compounds by the use of silica gel and activated charcoal. The standard compounds were released at constant permeation rate into the chamber flow of the permeation apparatus, which could further be diluted by a dilution gas flow of variable relative humidity (concentration ranges of the compounds of interest are given in Table 1). After the homogenisation of the standard gas atmosphere in a mixing chamber a flow of 100 ml/min was pumped through a dryer and/or the ozone scrubber and a glass mixing chamber with a volume of approximately 300 ml (sampling chamber). For the determination of the reference values the sample was pumped directly into the sampling chamber by bypassing the dryer and the ozone scrubber. For sampling the PTFE-coated septum of the sampling chamber was pierced with a manual device for solid-phase microextraction (see Section 2.2).

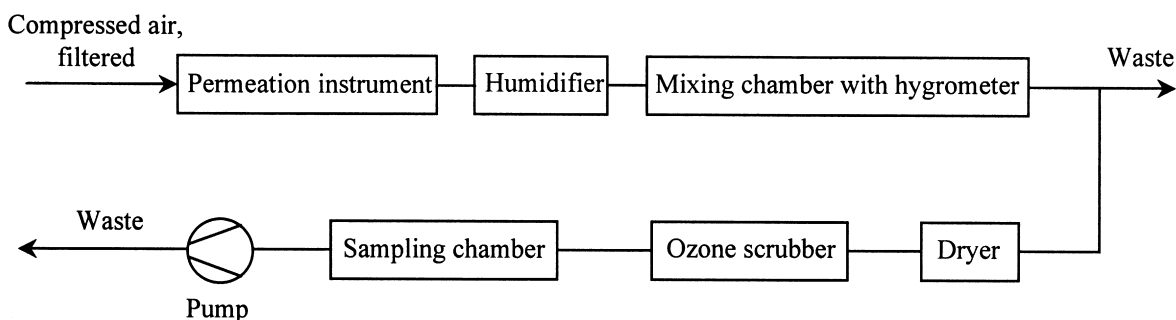


Fig. 1. Apparatus for the generation of gaseous standard mixtures.

## 2.2. Sampling, separation and detection

Samples of the spiked air samples were collected by solid-phase microextraction (SPME). SPME was carried out manually with the appropriate SPME holder and 75  $\mu\text{m}$  Carboxen–polydimethylsiloxane-coated fused-silica fibers (all obtained from Supelco, Bellefonte, PA, USA).

The analytes were extracted by piercing the septum of the mixing chamber port with the protecting needle and exposing the fiber to the continuously supplied standard mixture for 15 min. Before retracting the SPME fiber holder the fiber was withdrawn into the protecting needle. The needle was immediately introduced into the split/splitless injector of the gas chromatograph, which was equipped with a dedicated SPME liner (0.75 mm I.D., Supelco, Bellefonte, PA, USA). By exposing the fiber to the carrier gas stream the analytes were thermally desorbed and transferred onto the GC column (parameters are given in Table 2). The needle with the exposed fiber was left in the heated split/splitless injector (250°C) for at least 4 min in order to avoid memory effects. All experiments were carried out at a temperature of 21°C.

GC–atomic emission detection (AED) analysis was carried out with an HP 5890 gas chromatograph coupled to an HP 5921A atomic emission detector (AED, Hewlett-Packard, Palo Alto, CA, USA). The parameters for sampling and desorption as well as the separation and detection parameters of the GC–AED system are given in Table 2.

## 2.3. Materials

NoXon-S was obtained from Hoechst (Frankfurt/Main, Germany). Silanised pyrex tubes (18 cm  $\times$  6 mm O.D., 4 mm I.D.) were loosely packed with either 70 or 140 mg of the scrubbing material (packing density of 40 and 80 mg/ml, respectively).

The permeation dryer MD-250-12S (Perma Pure Products, Toms River, NJ, USA) was operated with a counter current of dry nitrogen (purity >99.999%) on the outside of the Nafion membrane (27.2 cm  $\times$  2.5 mm I.D.). The second type of dryer investigated was purchased from International Science Consultants (Type DP-3S, Ringwood, Hants, UK) and is based on a Nafion membrane (1 m  $\times$  1.1 mm I.D., 1.36 mm O.D.) which is embedded in a dry molecular sieve (MS 5A). Two different membranes which

Table 1  
Compound data and concentration ranges of sulphur compounds of interest in the generated gaseous standard mixtures

Compound analysed	Molecular mass	Boiling point (°C)	Range of analyte concentrations	
			ppb (v/v)	ng S l <sup>-1</sup>
Methanethiol	48.11	6	0.89–48.04	1.17–63.23
Dimethyl sulphide	62.13	38	1.16–62.99	1.53–82.91
Isopropanethiol	76.16	57–60	0.33–17.94	0.44–23.61
Isobutanethiol	90.19	87–89	0.38–20.32	0.50–27.02

Table 2  
Parameters for sampling by SPME, injection (sample desorption) and separation and detection by GC–AED

Sampling time	15 min
Sampling flow	100 ml/min
Injection port	Split/splitless, SPME-liner 0.75 mm I.D. (Supelco)
Injector temperature	250°C for the Carboxen–PDMS fiber
Location of the fiber	4.4 cm from the top of the injector
Desorption time (=purge delay time)	100 s
Analytical column	HP 1, 60 m×0.32 mm I.D., 1 µm film thickness
Column flow	2.5 ml/min He, purity>99.9996%
Temperature program	–20°C for 2 min, with 15°C min <sup>–1</sup> to 120°C, with 25°C min <sup>–1</sup> to 180°C, with 40°C min <sup>–1</sup> to 280°C, 2 min hold
AED total He flow	20 ml min <sup>–1</sup>
AED reagent gases	2.1 bar O <sub>2</sub> , 0.7 bar H <sub>2</sub>
Detection wavelengths	181 nm (sulphur), 193 nm (carbon)
Data acquisition rate	5 Hz
Cavity temperature	300°C
Transfer line temperature	290°C

have both been in use previously for low-level volatile organic compound (VOC) sampling were investigated for the latter dryer. The drying efficiency of the dryers under sampling conditions (100 ml/min sampling flow) and at variable relative humidity (RH) was determined by infrared spectroscopy using an IFS88 Fourier transform (FT) IR instrument (Bruker, Karlsruhe, Germany) with a 10-cm pathlength gas cell.

### 3. Results

#### 3.1. Sampling

The SPME procedure for sampling of organosulphur compounds has been described in detail [32]. The figures of merit published by Haberhauer-Troyer et al. [32] are valid for stopped flow conditions and a sampling time of 20 min only. Due to the fact that for the present investigation of the ozone scrubber and the Nafion dryers sampling was carried out with a flow of 100 ml/min through the sampling chamber and a sampling time of 15 min calibration graphs had to be re-evaluated. Measurements in continuous flow result in an increase in sensitivity for all of the investigated compounds except MeSH due to the fact that gas phase diffusion is the rate limiting step for DMS, i-PrSH and i-BuSH. Only the lowest part of

the concentration range accessible with the permeation instrument was investigated (0.9 to 4 ppb (v/v) for MeSH, 1.2 to 5 ppb for DMS, 0.3 to 1.4 ppb for i-PrSH, 0.4 to 1.6 ppb for i-BuSH) because higher concentrations are not environmentally relevant. Also, the expected effects can be considered to be more pronounced at lower concentrations. In the investigated concentration range calibration graphs were found to be linear.

#### 3.2. Drying

Both dryer models were compared in terms of drying efficiency, conditioning time and losses of organosulphur compounds in the dryer. In Table 3 drying efficiencies are given at variable relative humidity. Drying efficiency is higher for the DP-3S. This might be due to the higher inner surface area of the Nafion membrane in the DP-3S in comparison with the MD-250-12S, but might as well be caused by differences in the membrane properties. An increase of the counter-current drying gas flow from 200 to 400 ml/min did not result in any significant increase of the drying efficiency of the MD-250-12S, which is in accordance with the manufacturer's recommendation (counter-current flow should be at least 1.5 times the flow of the humid gas stream). No significant losses of the organosulphur compounds investigated occur at relative humidities up to 50% in

Table 3

Operating principle, membrane surface and drying efficiency for the Perma Pure MD-250-12S and the International Science Consultants DP-3S dryer

	Perma pure MD-250-12S	International Science Consultants DP-3S
Desiccant	N <sub>2</sub> (purity >99.999%), Counter current (200 ml/min)	Dry molecular sieve 5A
Residence time	0.84 s	0.57 s
Inner membrane surface	2140 mm <sup>2</sup>	3460 mm <sup>2</sup>
Drying efficiency (%) at:		
16% RH	62±5	90±2
50% RH	81±3	91±2
85% RH	90±2	94±2

both dryers after a conditioning time of at least 50 min. On the contrary constant losses of thiols do occur at higher relative humidities even after a conditioning period of 50 min (Table 4). No losses of DMS occur even at high relative humidities, which is in accordance with the fact that thiols exhibit a much higher reactivity than sulphides. The extent of the losses does not only differ between the two dryer models investigated, but also between the two membranes used with the same model (DP-3S, Table 4). The extent of the losses seems not to be determined by the operation principle (dry counter current versus molecular sieve 5A as desiccant) or the inner surface area of the membrane but rather by the condition of the individual membrane used. This is reflected by the strong differences in the extent of the losses when the two different membranes investigated for the DP-3S are compared. Neither membrane showed any visible damage.

### 3.3. Ozone scrubbing

The capacity of the NoXon-S ozone scrubber was investigated in detail by Calogirou et al. [31] and

was therefore not further examined. NoXon-S as an ozone scrubbing material was only investigated for losses or blanks of organosulphur compounds. After conditioning the scrubber for 5 min no significant losses of the organosulphur compounds could be detected at a packing density of 40 mg/ml and concentration levels of 3.8 ppb MeSH, 4.9 ppb DMS, 1.4 ppb i-PrSH and 1.6 ppb i-BuSH. On the contrary, losses of up to 10% of i-BuSH occurred at a packing density of 80 mg/ml but could easily be avoided by extending the conditioning time to 10 min. A packing density of 80 mg/ml is favourable due to increased capacity (4 h at 170 ppb ozone and a sampling flow of 112 ml/min, [31]). A conditioning time of 10 min is not a significant practical limitation since the equilibration time of the investigated dryers is much higher and thus the limiting step. The recoveries of the organosulphur compounds investigated are given in Fig. 2 for the noXon-S scrubber at 8% RH and for the MD-250-12S and the noXon-S-scrubber in series at 8 and 93% RH. The losses at 93% RH are solely caused by the dryer. No blanks of organosulphur compounds were observed. This is in accordance with the finding that the polymer chains

Table 4

Recoveries of MeSH, DMS, i-PrSH and i-BuSH at relative humidities >70% and a conditioning period of 50 min

Recoveries (%) <sup>a</sup>	MeSH (3.9 ppb)	DMS (4.9 ppb)	i-PrSH (1.4 ppb)	i-BuSH (1.6 ppb)
MD-250-12S (72% RH)	90±7	100±3	92±2	94±3
DP-3S (membrane 1, 92% RH)	68±8	99±2	77±3	71±6
DP-3S (membrane 2, 90% RH)	97±8	98±2	102±3	100±3

<sup>a</sup> Reference values are measurements at 5% RH without dryer, standard deviations were obtained based on the law of the propagation of errors.

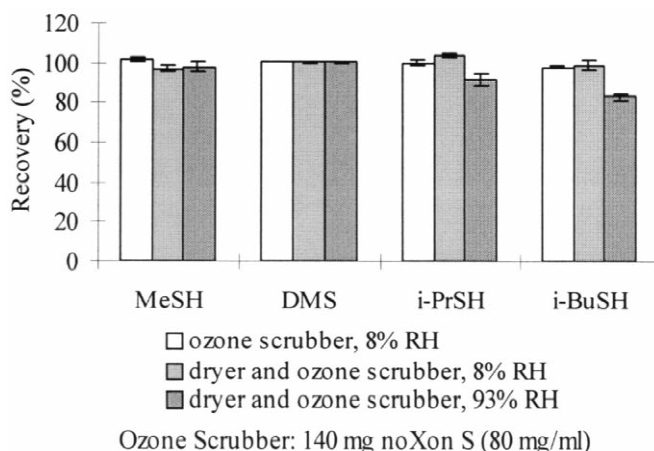


Fig. 2. Recoveries using the noXon-S ozone scrubber (8% RH) and the MD-250-12S dryer and the noXon-S ozone scrubber in series at 8 and 93% RH.

of polyphenylene sulphide are not cleaved by ozone [31].

#### 4. Conclusion

Nafion dryers operating both with a dry counter current or a solid desiccant can be regarded to be well suited for the sampling of organosulphur compounds at relative humidities up to 50%. Nevertheless losses of MeSH, i-PrSH and i-BuSH at the ppb level occur at higher relative humidities, the extent of which strongly depends on the condition of the membrane in use while DMS remains basically unaffected. Consequently, different results regarding losses of organosulphur compounds in Nafion dryers should not be attributed to their operation principle (dry counter current versus solid desiccants like molecular sieve) and recommendations for certain dryer models cannot be given. Instead each Nafion membrane has to be tested before and during use.

NoXon-S as ozone scrubber causes no significant losses of the compounds investigated. Ozone scrubbing with noXon-S therefore is the first technique which is known not to cause any losses of C<sub>1</sub> to C<sub>4</sub> thiols. Though noXon-S is not reusable and the method discontinuous it is characterised by its ease of use, especially if compared to the ozone scrubbing techniques currently applied for the sampling of organosulphur compounds.

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