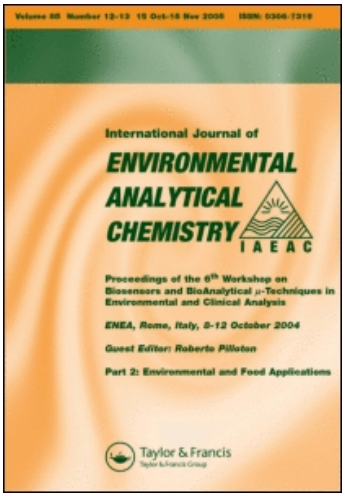

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USE OF DIFFUSION CONTROLLED PRECONCENTRATION SYSTEMS WITH CHEMICALLY IMMOBILIZED COATINGS FOR THE DETERMINATION OF ATMOSPHERIC NITRIC ACID

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A new coating procedure for different diffusion controlled preconcentration methods (tubular denuder, annular denuder, diffusion screen) is described for the determination of nitric acid in air. In this study, a silanization reaction is applied to obtain a chemically fixed coating with an end placed functional NH_2-group, which can be used as a sink to collect acidic compounds from air. This coating must be carried out only once and can be used for a long time. The denuders, coated with this procedures, were compared with conventionally coated NaF denuders.

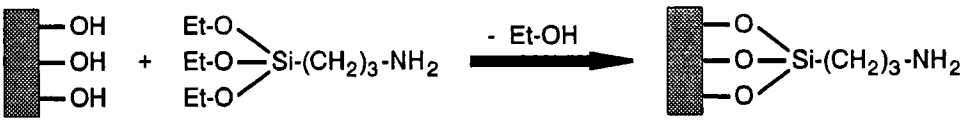
KEY WORDS: Immobilization, nitric acid, diffusion controlled sampling, atmosphere.

INTRODUCTION

Diffusion controlled preconcentration systems are versatile and reliable tools for the collection and determination of gaseous and particulate species in ambient air. Wellknown and often used for the collection of gases are tubular denuders[1-6] and, for higher flow rates annular denuders[7-9]. Another device for the preconcentration of gaseous compounds at elevated flow rates is a diffusion screen in a modified diffusion battery, which has been already used for the determination of carboxylic acids in air[10]. By using these systems, in most cases the adequate coating must be renewed before each sampling. This coating procedure results in time consuming work, not always reproducible conditions and higher fluctuating blanks.

Employing chemically immobilized reagents as wall coatings offers an attractive alter-

native to conventionally coated denuders. The coating reagent is fixed on the glass wall by a simple silanization reaction:



This coating procedure has to be carried out only once and a system carrying the immobilized reagent can be reused many times. Such diffusion controlled preconcentration systems, as

— **T**ubular **D**enuder with **I**mmobilized **C**oating (**TDIC**)
— **A**nnular **D**enuder with **I**mmobilized **C**oating (**ADIC**)
— **D**iffusion **S**creen with **I**mmobilized **C**oating (**SIC**)
— (not emphasized)

treated with 3-amino-propyl-triethoxy-silane (APTS), were evaluated for the determination of nitric acid in air.

EXPERIMENTAL

Denuder preparation

Tubular denuders were made from borosilicate glass tubes (500 mm length, 6 mm i.d.), annular denuders were made from Pyrex glass tubes (300 mm length, 9 mm i.d.) and inside from Pyrex glass rods (300 mm length, 6 mm o.d.) with a final annulus of 1,5 mm.[9] Prior to the coating the tubes were pretreated with a. 10% KOH/methanol, b. 40% HF, then rinsed with destilled water and finally dried at 80°C for 1 hour. An adequate amount (1 ml for tubular, 2 ml for annular denuders) of the coating reagent solution (10% 3-aminopropyltriethoxysilane (APTS, Fluka AG) in water, adjusted to pH 3.45 with 5 M HCl)[11], was filled into each tube, and then the tube was slowly rotated horizontally at 80°C during 2 hours in a specially designed apparatus. The coating process was repeated to make the coating of the activated glass surface as complete as possible. After immobilization the denuders were rinsed with destilled water, dried with clean dry air and capped at the ends in order to protect them from contaminations.

Just so after each air sampling and extraction for analysis, the denuder was also cleaned with destilled water, dried, closed and stored in a clean environment until the next sampling

Screen preparation

Prior to the immobilization, the fibers of the diffusion screens made of stainless steel

(diameter 44 mm, aperture: 34μm, fiberthickness: 23 μm) or PTFE (diameter 44 mm, apeture: μm, fiberthickness 80 μm) were first coated with SiO_2 by electron beam vaporization (Figure 1). The obtained SiO_2-layer thickness was measured to be nearly 0.5μm.

The screen was rinsed with 10% KOH/methanol solution, followed by destilled water and dried at 80°C for 1 hour. The screen was treated then 2 times with 2 ml APTS-solution (same as for denuder tubes) in a glass beaker for 2 hours at 80°C. Finally, the screen was rinsed with destilled water and dried with clean air. The prepared screens were kept in a closed glass vessel.

Analysis

After sampling each system was extracted with a carbonate solution ($NaHCO_3/Na_2CO_3$ 0.75/2 mM) (1 ml TDIC, SIC; 2 ml ADIC), and the extracts were measured by ion chromatography with suppressed conductivity detection. The conditions for IC were: column: HPIC AS-9 (Dionex); eluent: $NaHCO_3/Na_2CO_3$ 0.75/2 mM; flow rate: 1.5ml/min; suppressor: AMMS (Dionex); regenerant: H_2SO_4 0.01 M; flow rate: 2 ml/min;

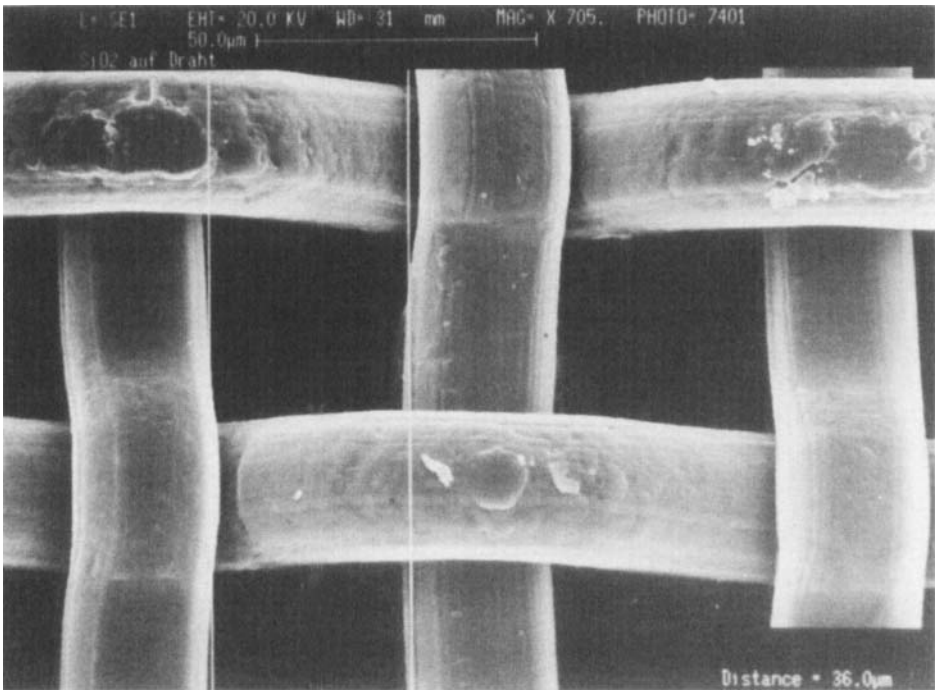


Figure 1 Diffusion screen, coated with SiO_2. (Stainless steel; aperture 34 μm, fiberthickness 23μm)

Table 1 Collection efficiency of Nitric acid in a TDIC(sampling time: 15 min, rel. hum.: 50%, flow rate: 0.7 l/min)

given amount [µg]	*amount collected in the TDIC [µg]*	*efficiency [%]*
6.3	6.6 ± 0.7	> 99
10.7	10.5 ± 0.9	98
40.6	15.3 ± 1.8	38

RESULTS AND DISCUSSION

The collection efficiencies of the systems were measured with standard test gases of nitric acid, generated by use of a permeation tube.

The results of the investigations with a TDIC are shown in Table 1. As can be seen, quantitative absorption efficiencies were obtained in normal concentration ranges, on the other hand the capacity of a TDIC will be overloaded with very high amounts of nitric acid. The annular denuder showed similar behaviour, the sorption efficiency of nitric acid in an ADIC with a flow rate of 7 l/min and a given amount up to 11.8 µg HNO_3 was > 98 %.

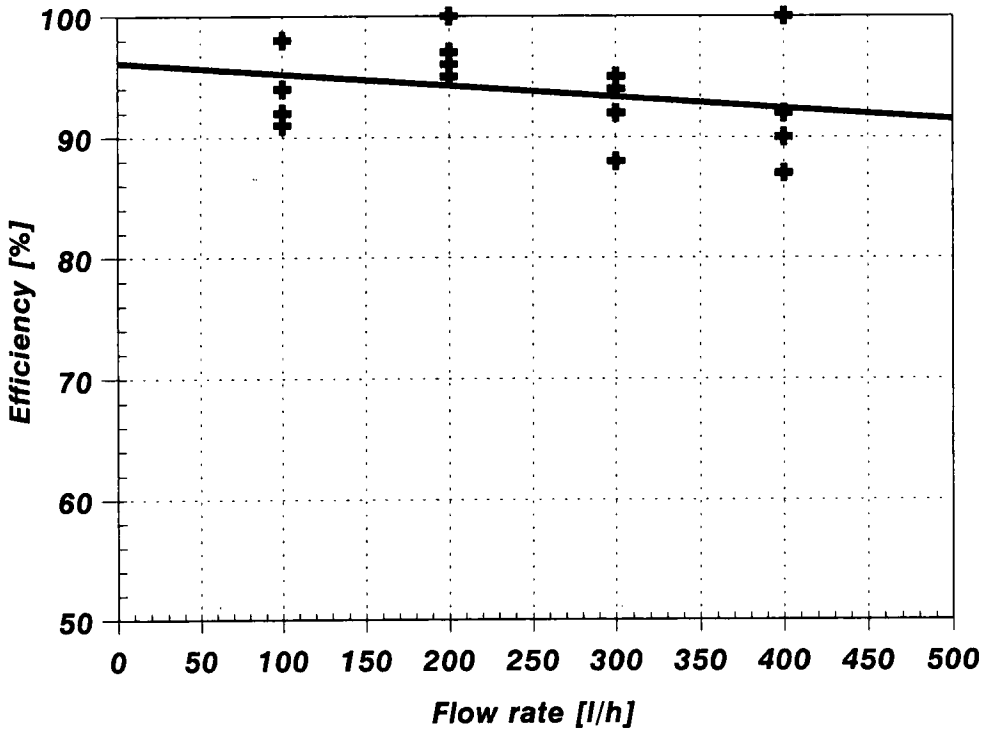


Figure 2 Collection efficiency of nitric acid on a SIC

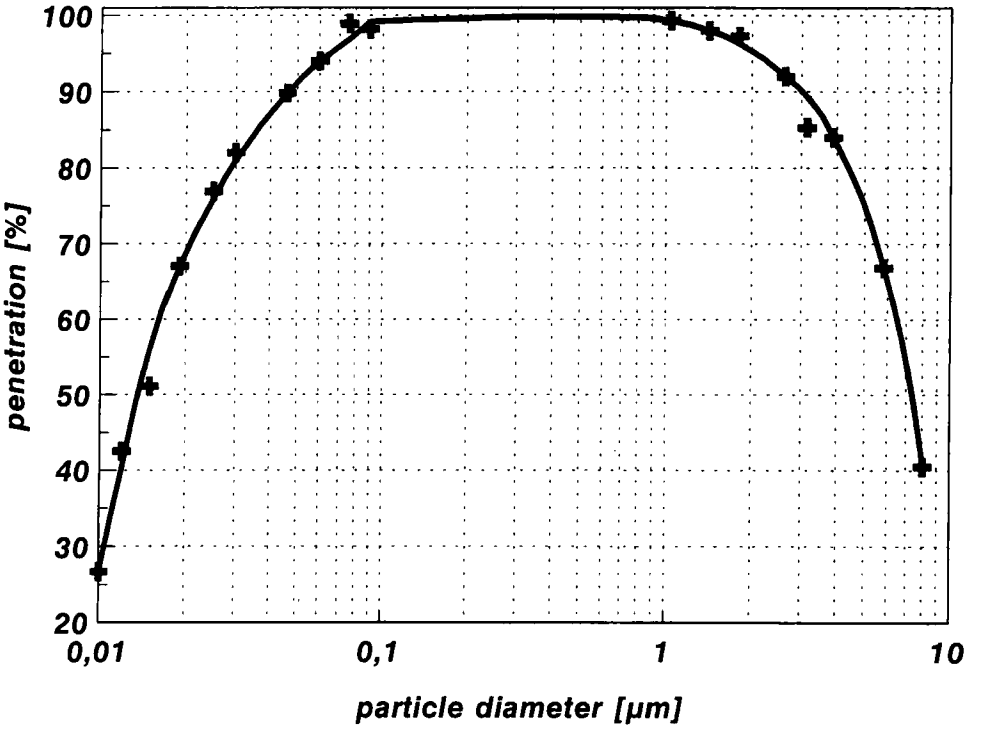


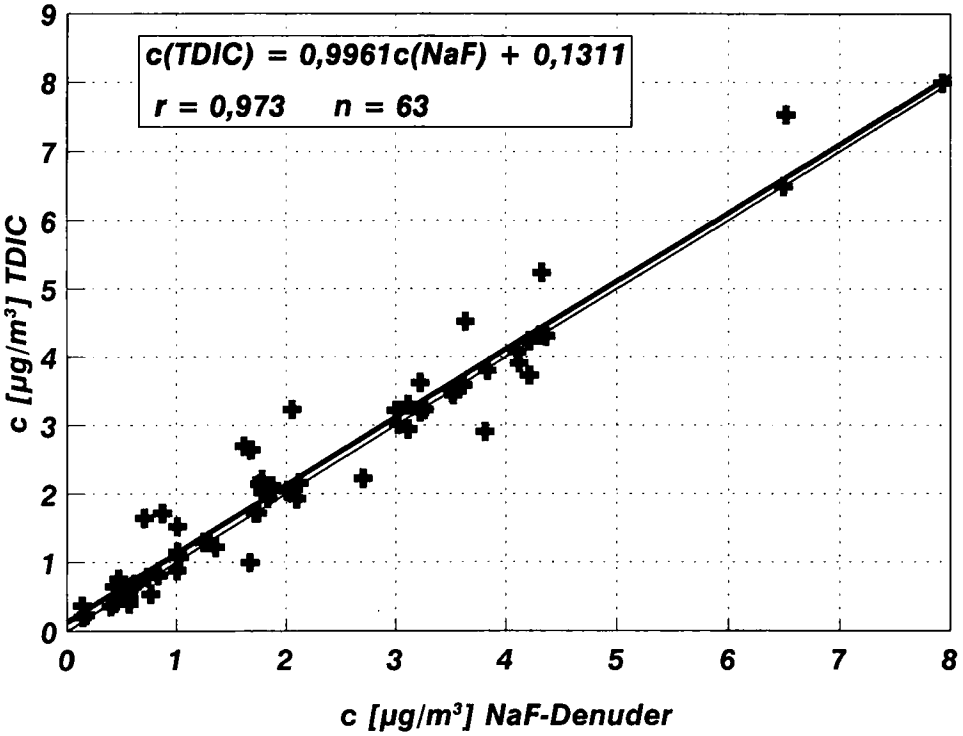
Figure 3 Penetration of particles through a SIC

Further experiments were performed to study the possible interferences of the relative humidity, and of SO_2 and NO_2, two important omnipresent gases in the atmosphere. The results showed, that the collection efficiency is not affected by the relative humidity and these gases mentioned above.

The average blank value for nitric acid in a TDIC were found to be 0.04 ± 0.02 µg per tube. With this value, a flow rate of 0.7 l/min through the denuder and a sampling time of 5 hours, a detection limit of to 0.19 ± 0.09 µg/m^3 HNO_3 was calculated.

The collection efficiency of nitric acid on a SIC in a modified diffusion battery is shown in Figure 2. At a flow rate of 6 l/min, a sorption efficiency of > 93% can be obtained. The separation ability of such a screen for particulates from gaseous compounds can be seen in Figure 3, where the penetration of particles is shown. Particles larger than 1 µm can interfere with the collection of gaseous compounds, because the probability of impaction increases with the particle size. Therefore they must be separated before the aerosol passes the screen. However, the used single stage plate impactor[12] showed some interferences for the collection of gaseous nitric acid, therefore, a newly designed impactor[13] would be necessary for a final estimation of this system.

Field experiments with the TDIC were performed in parallel with NaF-coated denuders at different sites. The sampling time were around 24 hours. The denuders were mounted vertically in order to avoid gravitational deposition of large particles. The inlet of the tube was connected to a conical PTFE device to enshure a laminar air flow in the denuder tube.



The comparison of both denuder methods for the determination of nitric acid in air is shown in Figure 4. As can be seen, the results of the TDIC is in good agreement with those obtained by NaF-denuders.

CONCLUSIONS

Diffusion controlled preconcentration systems with immobilized coatings described in this paper exhibit advantages as compared to conventional denuder tubes with coatings, which have to be renewed after each use:

— the coating procedure is required only once
— small blank values due to clean coating
— the stable, chemically fixed coating guarantees reproducible collection properties
— easy preparation of the preconcentration system before each use
— reusable for many times

Field measurements with tubular denuders showed, that the obtained results are comparable to those obtained with NaF-coated denuders

Acknowledgements

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