Short Communication

HOLLOW-FIBRE MEMBRANE FOR SAMPLE INTRODUCTION IN A FLOW-INJECTION SYSTEM Determination of carbon disulphide in air

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Summary. A hollow-membrane fibre is used for the introduction of gaseous compounds into a flow-injection system. The sampling system consists of a certain length of asymmetric hollow-fibre membrane in which an acceptor stream is stopped for a fixed period of time. The analyte permeates from the surrounding environment through the membrane and is accumulated in the acceptor solution, then pumping is resumed. The method is tested for the determination of carbon disulphide in ambient air. The detection range of the method is from 3 to at least 30 mg l⁻¹.

When flow-injection systems are used for monitoring processes, reliability and maintenance-free operation are of major importance. Hence it is useful to study the possibility of avoiding moving parts, such as rotating injection valves. Audunsson [1] described a system in which the sample is introduced and concentrated by means of a liquid membrane. In his set-up, a liquid sample stream flows along the liquid membrane while the acceptor stream is stagnant for a certain period of time. Next, the acceptor stream, containing a plug of analyte, is pumped towards a detector. Hence the membrane module takes over the function of the injection valve.

In this communication, a similar flow-injection system is described for sampling compounds from gaseous samples such as ambient air. As an example, the determination of carbon disulphide was chosen. Carbon disulphide has a maximum permissible atmospheric concentration of 10 mg l⁻¹, above which it produces disturbances of the peripheral nerve function and vision and neuropsychiatric effects have also been reported [2]. Therefore, monitoring is necessary at locations where humans may be exposed to carbon disulphide.

The sampling system consists of a hollow-fibre membrane through which ethanol is pumped. The fibre is surrounded by air containing traces of carbon disulphide. The ethanol flow is stopped for a fixed period of time to collect sufficient carbon disulphide, then the flow is restored, the ethanol stream is mixed with a reagent stream and the reaction product is transported to the detector. The reagent consists of an ethanolic solution of diethylamine, trieth-

Fig. 1. Schematic diagram of the structure of the membrane fibre wall.

anolamine and copper acetate. The diethylamine, on reaction with carbon disulphide, forms a dithiocarbamate, and with copper(II) a yellow complex is formed. The triethanolamine is used for solubilization of both diethylamine and the complex [3].

The membrane fibre must have sufficient mechanical strength to withstand the pump pressure and must have a sufficiently high permeability to carbon disulphide. These requirements can be met by using so-called asymmetric membranes. This means that only a very thin layer on the outside has a dense structure, the remainder of the fibre wall having a considerably higher porosity (Fig. 1) [4].

Experimental

Chemicals. All chemicals were of analytical-reagent grade. The reagent was made dissolving $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (500.0 mg) in 5 ml of water. Diethylamine (10.0 ml) and triethanolamine (1.0 ml) and about 200 ml of ethanol were added. The mixture was placed in an ultrasonic bath until a clear solution was obtained and diluted to 500.0 ml with ethanol. Ethanol was used as the acceptor solution.

Apparatus. The manifold used is shown in Fig. 2. The peristaltic pump was a Gilson Minipuls II. Polyethylene tubing was used. The detector was a Zeiss PMQ III variable-wavelength photometer equipped with an 80- μl cell (Hellma).

Fig. 2. Manifold for the determination of carbon disulphide in ambient air.

Fig. 3. Arrangement for the preparation of the carbon disulphide-nitrogen-oxygen mixture.

An Apple II GS computer was used for controlling the experiments and for collecting the data. The signal data were collected at a sampling rate of 2 s^{-1} . The flow was checked with a flow meter as described by Caldwell and Myers [5]. The membrane module consisted of three fibres of a length of 200 mm. The outer diameter of the fibres, supplied by the Laboratory of Membrane Technology, University of Twente, was 0.65 mm and the inner diameter 0.30 mm.

The arrangement used for the preparation of the carbon disulphide-nitrogen-oxygen mixture is depicted in Fig. 3. Carbon disulphide vapour is led at a rate of 5 mg min^{-1} by a constant flow of nitrogen out of the diffusion tube to the dilution vessel, where it is mixed with oxygen. The carbon disulphide concentration can be varied by changing the oxygen flow-rate. The exact concentration of the carbon disulphide can be calculated by weighing the carbon disulphide vessel before and after the measurements. The nitrogen and oxygen flow-rates are adjusted by mass-flow controllers (Brooks 5850 TR series).

Procedure. The computerized measuring system consists of the following features: (1) control of the pump, e.g. 15 s off, 45 s on; (2) measurement of the detector signal at 500-ms intervals during the 45 s when the pump is on; (3) storage of the recorded data on disk; (4) graphical display of the measured data on the computer screen; and (5) measurement of the flow at 60-s intervals; if the flow is not correct, the procedure is aborted.

Results and discussion

Figure 4a shows the result of a typical measurement. It can be divided into three sections. Section III is the most important. The peak is obtained by stopping the pump for 15 s, then restoring the flow, mixing the acceptor stream with the reagent stream and pumping the product through the flow cell. Section I is the result of the following feature. During the pumping period a small amount of carbon disulphide is collected by the ethanol. In the next period

Fig. 4. (a) Result of the procedure with pump off 15 s, pump on 45 s. (b) Result of the procedure with pump off 15 s, pump on 55 s; the tube between the membrane fibre and T-piece is replaced with a tube that is four times longer. (c) Result of the procedure with pump off 20 s, pump on 55 s.

Fig. 5. Plot of peak heights after changing the carbon disulphide concentration several times.

(when the pump is off) this amount slowly forms more of the complex. This can be seen after restarting the pump, when the signals from the detector show a slight increase in absorption. The dip before the peak (section II) is caused by the carbon disulphide solution which is in the tube between the membrane module and the T-piece in the pump-off period. Contact between the carbon disulphide is shorter in section II than in section I. When this tube is replaced with a tube that is four times longer, the dip is more distinct (Fig. 4b).

By lengthening the pump-off period, it is possible to decrease the lowest detectable concentration, but of course at the expense of the total measurement time. An attendant advantage of working with lower concentrations and longer pump-off periods is the lowering of the level (section I), caused by the carbon disulphide during the pumping period, with regard to the peak (Fig. 4c).

By changing the procedure (from 15 s pump off and 45 s pump on to 20 s pump off and 55 s pump on), the lowest detectable concentration (8σ) is decreased from 3 to 1.5 mg l^{-1} . The standard deviation changed from 0.5 to 0.2 mg l^{-1} ($n=20$). The usable range (procedure with 15 s pump off and 45 s pump on) is from 3 to at least 30 mg l^{-1} . Calibration graphs measured at various instances showed slopes varying between 0.017 and 0.024 absorbance per mg

l^{-1} ; a typical calibration graph fitted to the line $y = ax + b$ showed the characteristic values $a = 0.024$ absorbance per $\text{mg } l^{-1}$, $b = 0.104$ absorbance, $r = 0.991$, $n = 9$.

By changing the oxygen flow in the device for the preparation of the carbon disulphide standards, it is possible to increase or decrease the carbon disulphide concentration. However, the alteration in concentration is not immediately reflected in the peak height. It takes a few measurements before the new level is reached (Fig. 5). As can be seen, the overall performance of the device is satisfactory.

In a first arrangement of the manifold, the reagent was pumped directly through the hollow-fibre membrane, so the carbon disulphide was concentrated directly in the reagent. A disadvantage of this method is the ca. 25 measurements necessary before the new level is reached after changing the carbon disulphide concentration. Probably an interaction takes place between the membrane and the reagent.

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REFERENCES

- 1 G. Audunsson, *Anal. Chem.*, 58 (1986) 2714.
- 2 J.E.F. Reynolds and A.B. Prasad, *Martindale: The Extra Pharmacopoeia*, 28th edn., Pharmaceutical Press, London, 1982.
- 3 K. Hayashi, Y. Sasaki, S. Tagashira and K. Hirata, *Anal. Chim. Acta*, 198 (1987) 271.
- 4 J.A. van't Hof and A.J. Reuvers, *Dutch Pat. Appl.*, 8 702 924, 1987.
- 5 K.D. Caldwell and M.N. Myers, *Anal. Chem.*, 58 (1986) 1583.