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MODIFIED STRIPPING TECHNIQUE FOR THE ANALYSIS OF TRACE ORGANICS IN WATER

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SUMMARY

A modification of closed loop stripping analysis that considerably reduces the problem of contamination of the standard system is reported. This modification also makes the system more flexible in regard to stripping temperature and flow-rate of the purging gas. This modification, designated the straight and open system, allows the stripping technique to be utilized without sacrificing sensitivity or capacity, but gives very few blank peaks in the subsequent high resolution gas chromatogram. A case study of trace organics in the Motala river is presented. This river is a raw water source for water works and is a recipient for industries and sewage plants.

INTRODUCTION

The closed loop stripping analysis (CLSA) developed by Grob and co-workers[1–4] is perhaps the most powerful technique for the rapid analysis of a large number of organic compounds in water. The method is ultrasensitive and is perfectly designed for capillary gas chromatography on methyl silicone liquid phases. However, the range of the compounds that can be measured by CLSA is somewhat limited. For example, the peaks of highly volatile compounds are hidden by the peak of the extraction solvent, and moderately or extremely polar organic species are either poorly purged or not recovered at all. The CLSA technique has most often been used for screening of large numbers of compounds; its outstanding concentration factor, without the need of an evaporation step, makes the system useful even when only a few compounds are of interest[5,6].

At the Department of Water in Environment and Society we have used this technique to study the problems which a water works in Norrköping has with the objectionable taste and odour in water supplied to approximately 100,000 inhabitants. During our investigation we focused on three problems related to CLSA: (1) statistical analysis of analytical data obtained from chromatograms, each containing more than 100 individual integrated peaks[7]; (2) improvement of the stripping procedure for maximum recovery of odour-causing compounds[8]; (3) modification of the stripping system in order to reduce the contamination problem and the related blanks in the conventional system. This article deals primarily with the recovery and contamination problems and a case study is presented.

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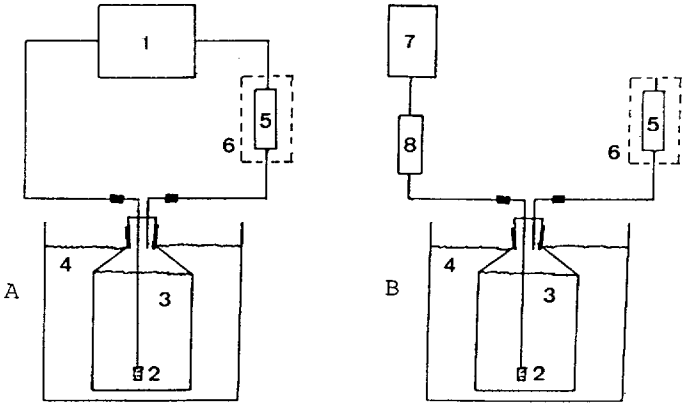

Fig. 1. Closed (A) and open (B) stripping systems. 1 = Pump; 2 = gas inlet; 3 = water sample; 4 = thermostatic water-bath; 5 = activated carbon adsorbent (analytical filter); 6 = oven; 7 = nitrogen gas cylinder; 8 = activated carbon adsorbent (gas cleaning filter).

CONTAMINATION OF THE CLSA SYSTEM

The performance of an analytical system is highly dependent on its blank level. When we first used conventional CLSA, chromatograms with few blank peaks were obtained. However, after 3 months of routine use many contaminant blank peaks appeared. Even after the insertion of an adsorbing analytical filter, prolonged recirculation in the empty system did not satisfactorily remove the contaminant peaks. An examination of the system (Fig. 1A) revealed five possible sources of contamination: (1) reversible adsorption in the stainless-steel tubings; (2) reversible adsorption in the pump; (3) reversible adsorption on the sintered glass of the gas inlet; (4) memory effects in the system caused by carbon particles from the analytical filter; (5) leakage in the closed loop system causing air from the laboratory to enter the system.

Passing 2 l of ambient air through the system and subsequently analysing it gave a very distinct "fingerprint" of the laboratory atmosphere (Fig. 2). Almost all peaks appeared between the standard compounds 1 and 3 (see standard procedure

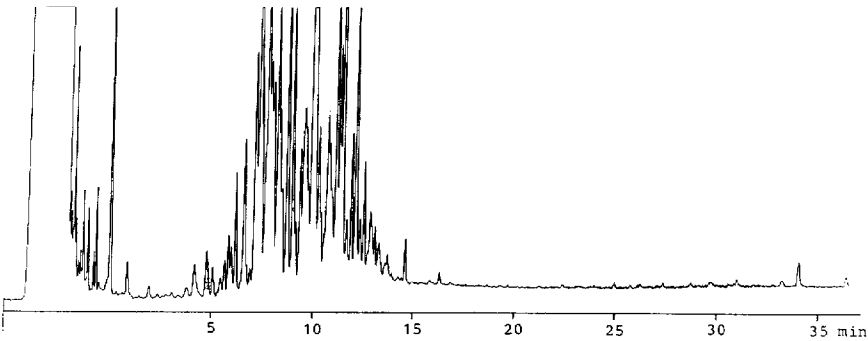

Fig. 2. Chromatogram of laboratory atmosphere: 2 l of ambient air passed through the open system. Column: 12 m × 0.2 mm, fused silica SP 2100. Temperature program in accordance with standard procedure.

below). Large leakages were unambiguously revealed but smaller ones were more troublesome. The contamination problem, however, could not usually be explained as being due to the air in the laboratory.

Shortening of the tubing resulted in a more rigid system with a slight improvement of the blank level. The inner surface of the opened stainless-steel tubing was very sensitive to water vapour, therefore this tubing was replaced by tubing made of PTFE. The glass frit of the inlet distributing gas in the water has a large surface area with many holes, only two or three of which are penetrated by the gas. To avoid contamination at this point the glass frit was replaced by a glass capillary tube when very impure water samples were analysed.

Problems with the blank of the closed system still remained. Since two of the possible sources of contamination (2 and 4 above) are connected with the closed loop of the system, an open system (Fig. 1B) was designed for comparison. One prerequisite for the success of the open system is the perfect performance of the analytical filter and its holder. In the closed loop system, compounds not adsorbed when passing the filter for the first time are believed to be adsorbed later. In the open system, almost all compounds have to be adsorbed immediately. The adsorption capacity of the filter was examined by placing two consecutive holders with adsorbent filters in the oven (Fig. 1B). Filter holders from different manufacturers were tested. The second filter showed almost no peaks when using holders from Bender & Hobein (Zurich, Switzerland).

A second prerequisite is extremely pure stripping gas. If nitrogen of ordinary quality is to be used as stripping gas it is necessary to remove the large number of organic compounds present in it, in order to avoid contamination of water samples.

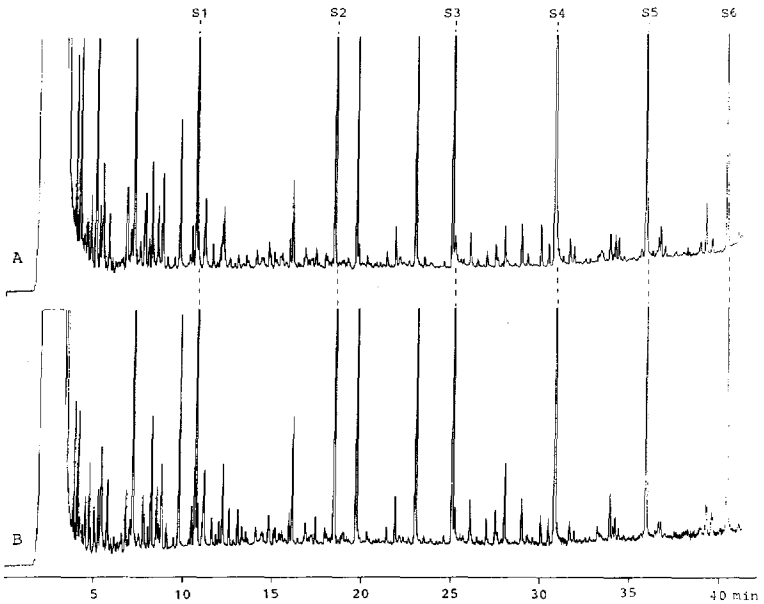

Fig. 3. Comparison of chromatograms of the same drinking water sample analysed by the closed loop system (A) and the open system (B). Chromatographic conditions in accordance with standard procedure. S1–S6 are internal standards.

We purified nitrogen of such quality by means of the same kind of activated carbon adsorbent as was used as an analytical filter. In this case the filter and filter holder were inserted between the nitrogen cylinder and the purging bottle. By using this procedure the problem of leakage of ambient air into the system is avoided because of the pressure created by the stripping gas. Chromatograms from the closed and open systems are shown in Fig. 3. The sensitivity of the open system (Fig. 3B) is generally speaking as good as that of the closed system (Fig. 3A).

STANDARD PROCEDURE

As standard procedure in the open system, 1 l of water is purged for 2 h at 30°C. The gas flow-rate is 1 l/min and the analytical filter is kept at 50°C in an oven. Extraction of the filter with dichloromethane (CH_2Cl_2 for spectroscopy, Merck) (9 + 6 + 5 μl) as solvent is carried out in the device shown in Fig. 4 (ref. 9). The solvent is applied to the carbon filter by an ordinary 10-μl syringe. Extraction is performed by moving the piston up and down 20 times. The piston is then pressed down completely and the system is shaken to transfer the solvent to the bottom of the vial. No septum is used during this procedure.

Ordinary quality nitrogen, purified by the cleaning filter (Fig. 1B), is used as stripping gas. Internal standards, C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16} and C_{18} 1-chloroalkanes, 5 μl solution (10 ng/μl) in propanone, are added to the water samples just before analysis. Both filters are cleaned with dichloromethane between each run. Filters and filter holders are manufactured by Bender & Hobein.

Gas chromatography: Hewlett-Packard 5880; flame ionization detector (FID) attenuation 2^0; column, fused silica, 50 m × 0.3 mm, OV-101; carrier gas He, flow-rate 40 cm/sec; split valve closed for 60 sec; injected volume 1.5 μl dichloromethane; program, 30°C for 5 min, then raised at 5°/min to 220°C, finally held at 220°C for 15 min.

VARIATION OF STRIPPING PARAMETERS

With the open system it is easy to vary the flow-rate, temperature and stripping time. In the closed loop system the flow-rate is determined by the pump. Leakage in the closed loop system is very common at higher temperatures, whereby ambient air can enter; temperatures of 25°C or 30°C are therefore most commonly used. The open system permits wider variation of temperature, since the constant overpressure keeps ambient air from entering. We have used temperatures in the range of 10–60°C.

During prolonged stripping the gas-cleaning filter has to be cleaned every 2 h when ordinary quality nitrogen is used.

An investigation of the stripping effeciency at different purging times and temperatures has been undertaken. In Fig. 5 the recovery at 30°C is shown at stripping

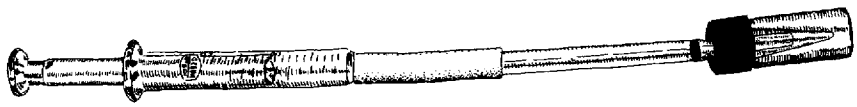

Fig. 4. The device used for extraction of the analytical carbon filter.

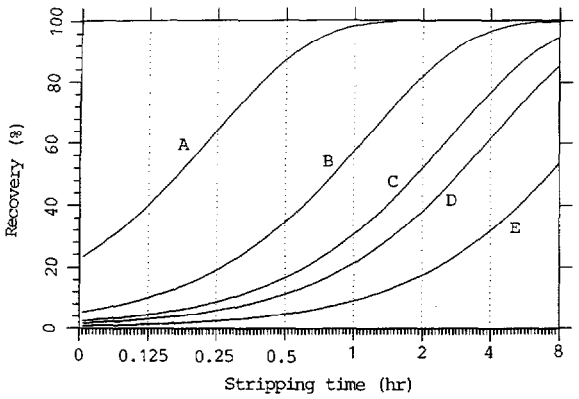

Fig. 5. Estimated effect of stripping time on the recovery of five different compounds. The curves are obtained from chromatograms corresponding to seven different stripping times. A = *p*-xylene; B = S5; C = cyclic ketone; D = methyl ketone; E = S6.

times varying from 7.5 min to 8 h. Extremely volatile and lipophilic compounds are completely stripped after approximately 15 min, but complete stripping of less volatile and more hydrophilic compounds (*e.g.*, ketones) is not attained after the standard 2 h. After very long stripping times (16 h or more) a decrease in recovery occurs.

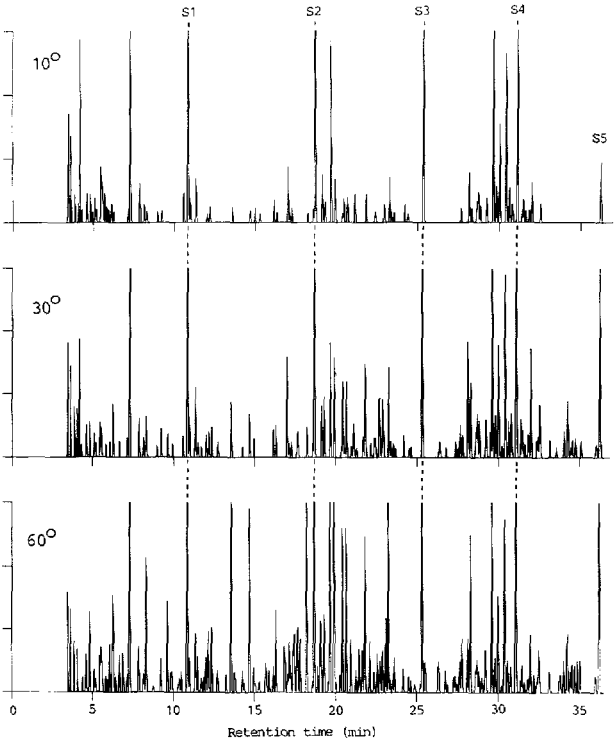

Fig. 6. Computer reconstructed chromatograms showing the effects of stripping temperature. Three identical raw water samples were stripped at 10°C, 30°C and 60°C respectively for 2 h.

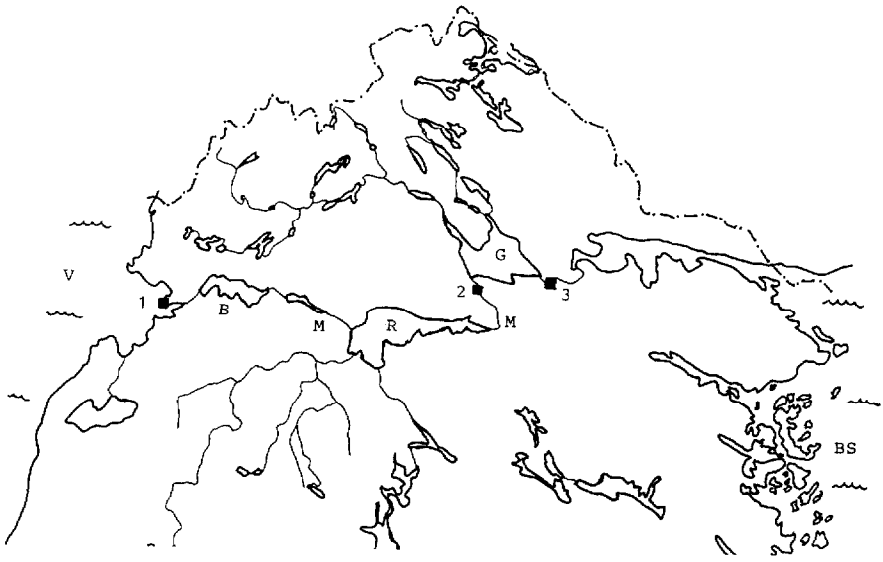

Fig. 7. The Motala river (M) from Lake Vättern (V) via Lake Boren (B), Lake Roxen (R) and Lake Glan (G) to the Baltic Sea (BS). 1 = Motala water works; 2 = Skärblacka water works, sewage plant and pulp mill; 3 = Norrköping water works.

This is due to desorption from the carbon filter, and might be thought to be a drawback of the open system since desorbed compounds in a closed system may be adsorbed again. Our experience of prolonged stripping times in a closed system is that they give, in this respect, the same results. This implies that compounds desorbed in the closed loop system are not recovered but instead only contaminate the system. In Fig. 6 three computer reconstructed chromatograms of the same water sample are shown. They are run at the standard stripping time (2 h) but at different temperatures. These chromatograms explicitly show that the standard stripping temperatures (25°C or 30°C) are far from optimum. The number of peaks as well as the peak areas are increased at 60°C compared to those obtained at 10°C or 30°C.

MOTALA RIVER, A CASE STUDY

The Motala river, running from Lake Vättern to the Baltic Sea (Fig. 7), is an example of an unfavourable combination of a large need for surface water by local water works and a great amount of pollution from several sources. The river flows through a highly agricultural district and many sewage plants use it as a recipient. There is also a large amount of discharge of industrial waste-water from a pulp mill and a few metal industries.

Fig. 8 illustrates chromatograms from four consecutive points along the river. Chromatogram A shows the raw water from the waterworks in Skärblacka (2 in Fig. 7). This raw water closely resembles that from Motala (1, chromatogram not shown). B shows waste-water from the municipal sewage plant in Skärblacka, situated downstream from the raw water intake. C is the chromatogram for the waste-water from the pulp mill in Skärblacka. Chromatograms B and C were obtained by diluting

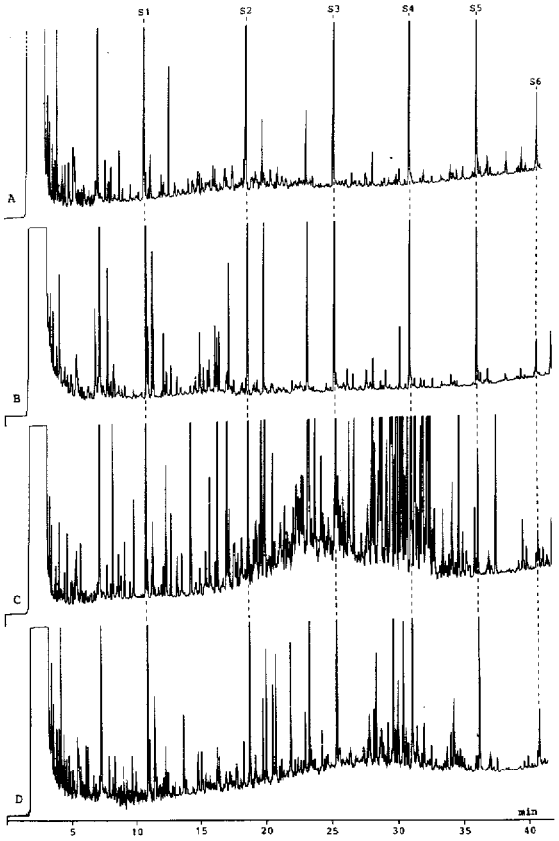

Fig. 8. Chromatograms of different sources along the Motala river. A = Raw water from Skärblacka water works; B = waste-water from the municipal sewage plant at Skärblacka; C = waste water from the pulp mill in Skärblacka; D = raw water from the water works in Norrköping. Samples B and C were diluted 200 times in "raw water A". Chromatographic conditions are in accordance with standard procedure.

200 times in "raw water A". The reasons for diluting are that the capacity of the stripping procedure would otherwise be exceeded and the dilution used corresponds to the actual amount of pulp mill waste-water in the river. For the corresponding amounts of sewage plant water occurring in the river the sample should be diluted another ten times. Chromatogram D shows the raw water for the water works in Norrköping. The contrast in quality with that from Skärblacka is striking. The major affluents to the Motala River have also been analysed and shown not to contribute significantly to the pollution of the river. All samples were collected during a period of approximately 2 weeks. It is remarkable that the permanganate numbers at the water works of Skärblacka and Norrköping were 29 and 30 mg/l respectively. These results show that the use of permanganate numbers is a very crude and uninformative measure of the organic content in water.

The drinking water in Norrköping has taste and odour problems that do not show any significant seasonal variation. Fig. 9 illustrates a comparison of the sesquiterpene part of the chromatograms of the waste-water from the pulp mill (A) and

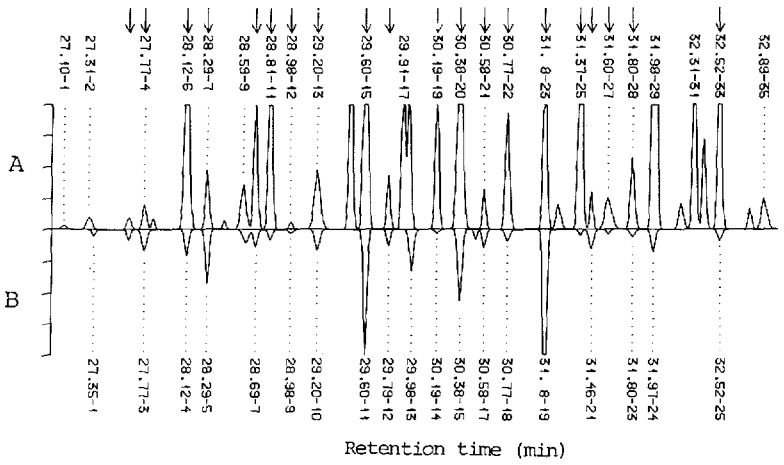

Fig. 9. Computer reconstructed chromatograms for comparison of the waste-water from the pulp mill at Skärblacka (A) and the raw water from the water works of Norrköping (B, inverted chromatogram). Peaks marked by arrows are in pairs given the same retention time by the computer.

the raw water of Norrköping (B, inverted). The procedure used for computerized statistical comparison is described elsewhere[7]. The comparison shows that almost all compounds present in the raw water from Norrköping are present in the waste-water from the pulp mill. This is probably the first time that compounds from the effluent of a pulp mill have been recognized in the raw water intake of a waterworks. These results have been obtained through the application of an extremely sensitive analytical technique with the lowest possible blank level.

REFERENCES

1 K. Grob, *J. Chromatogr.*, 84 (1973) 255.
2 K. Grob and G. Grob, *J. Chromatogr.*, 90 (1974) 303.
3 K. Grob, K. Grob, Jr. and G. Grob, *J. Chromatogr.*, 106 (1975) 299.
4 K. Grob and F. Zürcher, *J. Chromatogr.*, 117 (1976) 285.
5 S. W. Krasner, C. J. Hwang and M. J. McGuire, *Advances in the Identification and Analysis of Organic Pollutants in Water*, Vol. 2, Ann Arbor Sci. Publ., Ann Arbor, MI, 1981, p. 689.
6 M. J. McGuire, S. W. Krasner, C. J. Hwang and G. Izaguirre, *J. Amer. Water Works Ass.*, 73 (1981) 530.
7 A. Grimvall, R. Sävenhed and H. Borén, *Water Sci. Technol.*, 15 (1983) in press.
8 R. Sävenhed, H. Borén, A. Grimvall and A. Tjeder, *Water Sci. Technol.*, 15 (1983) in press.
9 H. Norin, National Institute of Environmental Medicine, Stockholm, personal communication.