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STRIPPING OF TRACE ORGANIC SUBSTANCES FROM WATER

EQUIPMENT AND PROCEDURE

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SUMMARY

While our previous papers on the stripping method for the detection and determination of organic substances in water were primarily concerned with principles, comparisons and examples, and provided little information for laboratories wishing to introduce the method, in this paper is given a detailed description of the equipment and practical procedures for routine application. Several modifications and improvements resulting from experience gained in routine use are included.

INTRODUCTION

The closed-loop stripping procedure that we developed 3 years ago[1–3] is now in routine use in a considerable number of water research laboratories. We find this surprising as the procedure is based on equipment that is not readily available and involves a difficult technique[4]. With the aim of offering a simpler and more rapid alternative, we developed the so-called micropentane extraction[5]. In spite of this, stripping has gained more acceptance, presumably because the procedure has a high reproducibility as all steps can be accurately standardized; it is less influenced by special conditions of the water samples, *e.g.*, a high content of organic or inorganic particulate matter; there is no alternative procedure with such a wide range of sensitivity; extracts obtained by stripping are ideally suited for subsequent gas chromatographic (GC) analysis, and recovery rates for polar substances are similar to or better than those obtained by extraction with solvents or with solid adsorbents.

An important limitation is the volatility range, which includes low- and medium-molecular-weight organic compounds up to about eicosane in the *n*-alkane series. Another limitation is that the most volatile substances, *i.e.*, the substances that are eluted with the solvent used for extraction from the charcoal, cannot be determined. It is feasible to analyze these substances by direct transfer of adsorbed material from the charcoal on to the GC column, and we shall describe the corresponding technique in a subsequent paper.

Routine application of the procedure, especially at EAWAG, has produced

additional practical experience, and has led to some technical modifications. In this paper we give a complete and detailed description, with the aim of assisting laboratories who wish to introduce the procedure into their routine work.

STANDARDIZATION OF PARAMETERS

The stripping procedure is based on a set of interdependent parameters. Changing a single parameter commonly necessitates corresponding modifications throughout the entire set, and may eventually require modified equipment. The parameters recommended below are the result of studies with a wide range of experimental conditions.

Water sample: volume, 0.5–2.0 l; temperature, 30°; internal standards, C_6, C_{10}, C_{14} and C_{18} 1-chloroalkanes, 5.0 μl of solutions in acetone of concentration 1:100,000–1:20,000.

Adsorbent filter: pure wood charcoal, heat activated; particle size, 0.05–0.1 mm; amount, 1.5 mg for relatively pure samples and 5.0 mg for moderately contaminated samples: disc geometry, diameter 2.7 mm and thickness 0.7 mm for 1.5-mg amount, and diameter 3.6 mm and thickness 1.5 mm for 5.0-mg amount.

Stripping: flow-rate, 1.0–2.5 l/min; duration, 1–3 h (normally 2 h); temperature of gas entering filter, 40° (ref. 5).

Extraction of 1.5-mg filter: for very pure water, 5–15 μl of carbon disulphide (analytical-reagent grade), purified and re-distilled; for contaminated water, 10–100 μl of methylene chloride (chemical grade), re-distilled; no further concentration of extracts.

SOURCES OF FAILURE

Both the stripping equipment and procedure must be designed so as to eliminate errors and uncertainty. The failures most often encountered and their causes are as follows:

Cause	Effect
Leakage in the closed-loop system.	Sample contaminated with constituents of ambient air; losses of water constituents.
Adsorptive material (charcoal dust, plastic material) in the pumping circuit.	Losses of water constituents; memory effects (high background).
Carbon particles irregularly distributed in the filter disc.	Reduced filter capacity; extraction of filter rendered more difficult.
Water droplets from bubbling carried on to the filter disc.	Plugging of filter by non-volatile water constituents (e.g., salts).
Condensation of water in the pores of filter particles.	Drastic reduction of filter activity and capacity.

APPARATUS

The stripping apparatus is shown schematically in Fig. 1. The MB-21-E pump[*] functions with stainless-steel bellows. The reed valves are placed between two PTFE discs which close the open end of the bellows. During routine use for several months, we have experienced no difficulties with this system in the analysis of surface waters, although this may not apply to very pure water. Special attention must be paid to the possible accumulation of suspended matter under the reed valves, which causes memory effects and a reduction in pump performance.

The sample flask (1 l) is stoppered with a ground-glass joint. Both glass tubes that leave the cap are terminated with Sovirel–Rotulex[**]. These male joints of 5 mm I.D. allow a gas-tight, easy demountable connection to the stainless-steel part of the circuit to be made (see Fig .5).
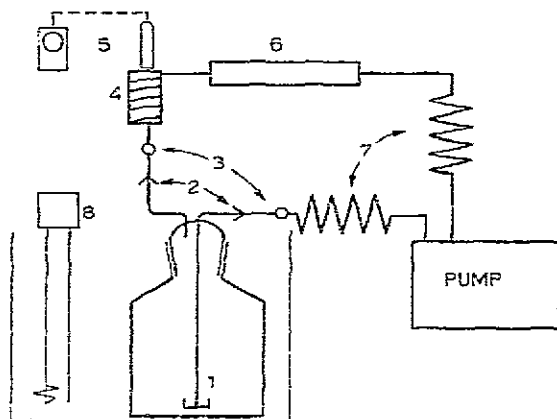

Fig. 1. Closed circuit for stripping with inert gas. 1, Glass frit of porosity 0; 2, Rotulex bowl joints with PTFE seal (Sovirel); 3, fused glass–metal connections; 4, aluminium heating cylinder; 5, soldering iron (15 W) with time relay; 6, filter holder; 7, stainless-steel tubing, 1 m × 3.2 mm O.D., 2.0 mm I.D.; 8, thermostatic water-bath.

As shown in Figs. 1 and 2, the gas enters the bottle horizontally, passes through the sintered glass disc (porosity 0) and leaves vertically through an elbow that acts as a barrier for water droplets. The bottle is dipped in a thermostated water-bath to the depth of the grinding in order to control the stripping temperature and prevent air contamination. The influence of varying the stripping temperature is shown in Fig. 3, which gives recovery rates for spiked homologous 1-chloroalkanes. The stainless-steel tube is warmed near the filter holder so as to minimize the possible condensation of water from the moist inert gas leaving the sample. The heating element is constructed from an aluminium cylinder with threads for the tube and a 15-W soldering iron in the centre, as shown in Figs. 4 and 5. The individual temperature,

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[*] Metal Bellows Corp., Sharon, Mass., U.S.A.; distributor in Europe, Zurn-Industries GmbH, Metal Bellows, D-75 Karlsruhe 51, G.F.R.
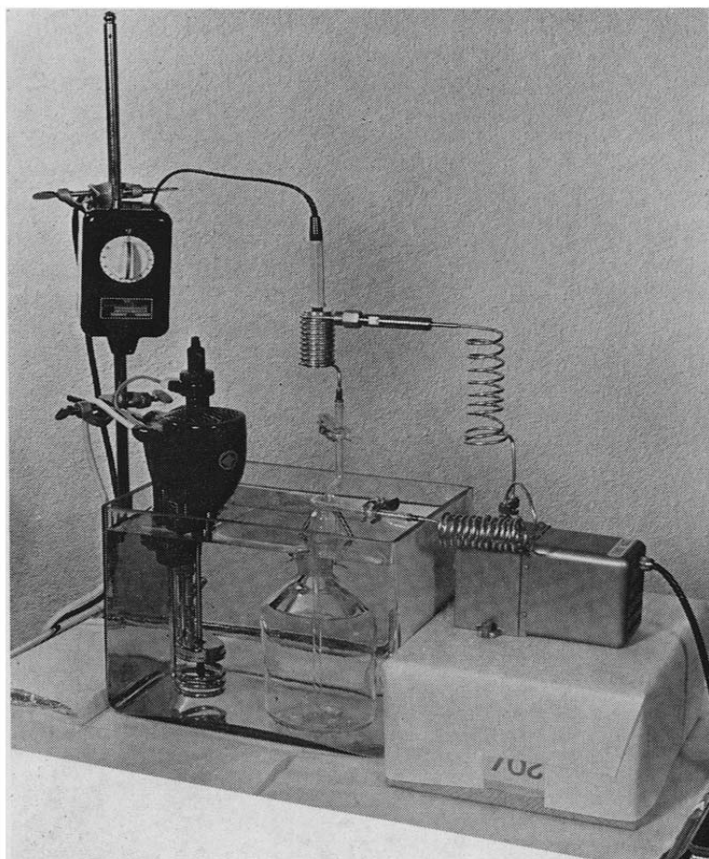[**] Rotulex unpolished spherical joint, sealed with PTFE covered silicone rubber O-ring.

Fig. 2. Equipment for routine application of stripping method. Left: 1-l sample flask, dipped in a thermostated water-bath and attached to the circuit with Rotulex joints and fused glass–metal connections. The metallic filter holder attached to the heating cylinder is shown above. Right: Model MB-21-E pump (Metal Bellows, Sharon, Mass., U.S.A.).
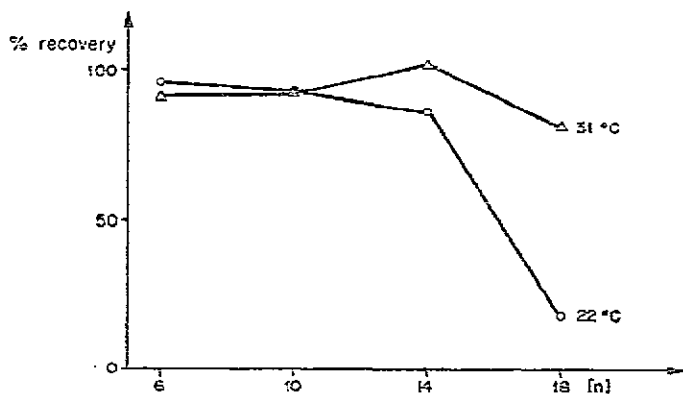

Fig. 3. Recovery rates for 1-chloroalkanes ($C_nH_{2n+1}Cl$) obtained by stripping from tap water spiked with 50 ppt of each; mean values of two measurements (100% values extrapolated from finally added homologues).
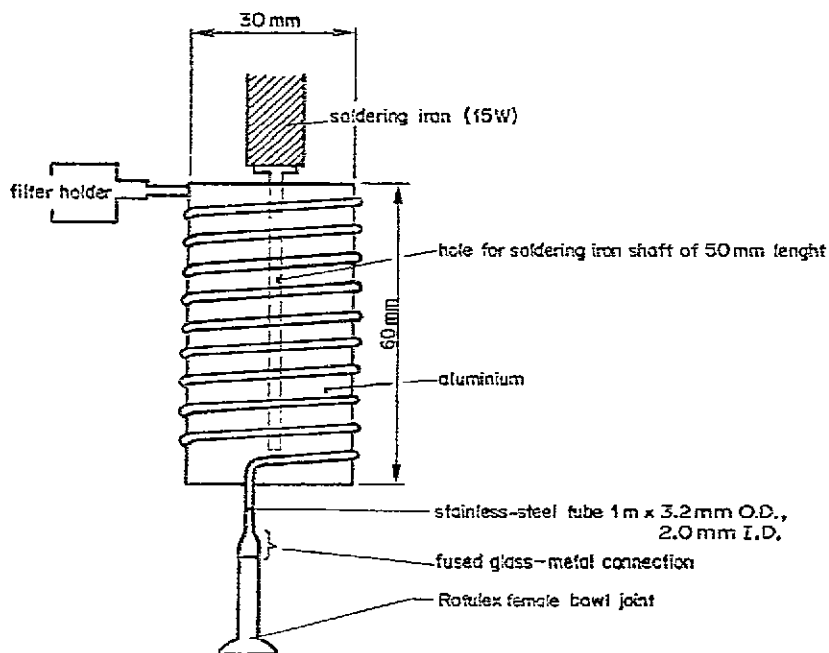
Fig. 4. Aluminium heating element with stainless-steel tube wound through threads, and soldering iron.

depending on the sample temperature selected, ranges from 60° to 80° and is controlled with a simple laboratory relay.

The filter holder described earlier[1] is still in use, with one modification: the conical joint can now be sealed easily by hand (Fig. 5). The preparation of adsorbent filters (Fig. 6) has been described previously[1*].

The stainless-steel tube between the different parts of the stripping circuit are each 1 m long, with I.D. 2 mm and O.D. 3.2 mm. The tubes are spirally rolled so as to dampen the vibration from the pump and to protect the glass–steel connections. The flow-rate within the closed system, measured with a nozzle flow meter, was approximately 1.2 l/min.

In order to transfer the adsorbed organic substances from the carbon filter into a solvent suitable for GC, the equipment shown in Fig. 6 is used. For elution, the carbon filter is attached to the eluate container with a small piece of PTFE shrinking tubing with an original diameter of 7 mm. The elastic tube is doubled over in the middle with a PTFE ring so that the fixing is stronger.

The sample tube, of O.D. 5 mm, consists of a 25-mm long eluate container and a handle that is *ca.* 75 mm in length. It is prepared from a thick-walled Pyrex glass tube (5 mm O.D.) by melting a small area of the glass until the tube becomes closed, as shown in Fig. 6. The outer and inner borders of the plane polished container head that comes into contact with PTFE tubes are cautiously smoothed in a flame.

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* Filter and filter holder are available from Bender–Holbein AG, Riedlistr. 15, 8006 Zürich, Switzerland.
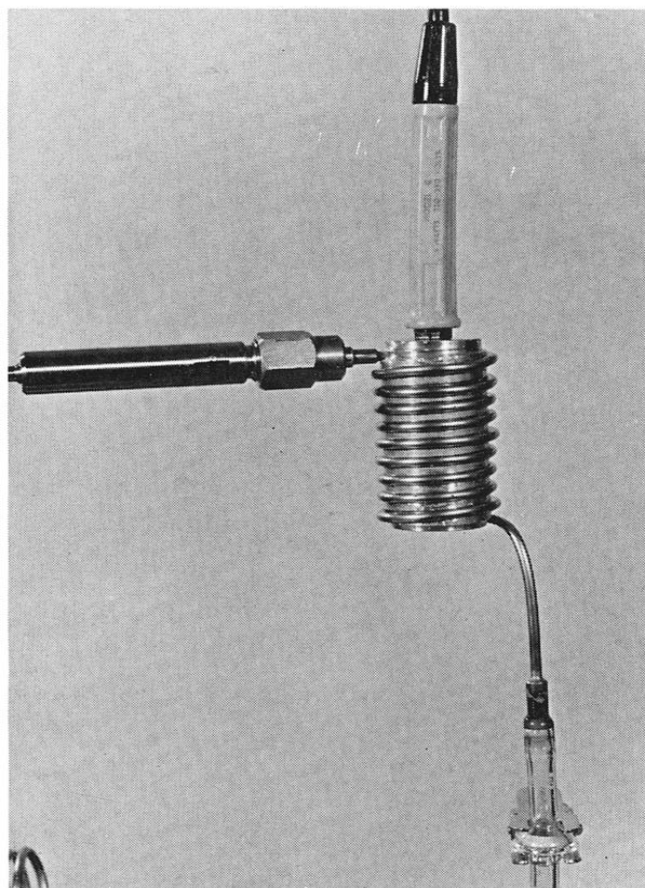
Fig. 5. Stainless-steel tube wound through threads of the heating cylinder next to the filter holder (left). Above: 15-W soldering iron. Below: Rotulex bowl joint with PTFE seal and fused glass–metal connection.

Because of evaporation of the solvent during storage, a glass stopper that minimizes the free volume is used. The slightly conical piece of glass is partly covered with PTFE shrinking tubing, as indicated in Fig. 6. It has been found that eluates (15 μl) can be stored for several months in the above equipment without significant loss of solvent. The sample tubes are usually cleaned by heating them in a flame and the PTFE parts are stored in methylene chloride.

We found that it was necessary to purify the solvents prior to use. For methylene chloride of chemical grade, fractional distillation (5 theoretical plates) resulted in an acceptable GC quality. A more complex procedure outlined by Obach[6] was required in order to remove odorous sulphur compounds from the carbon disulphide.

PROCEDURE

Water sample

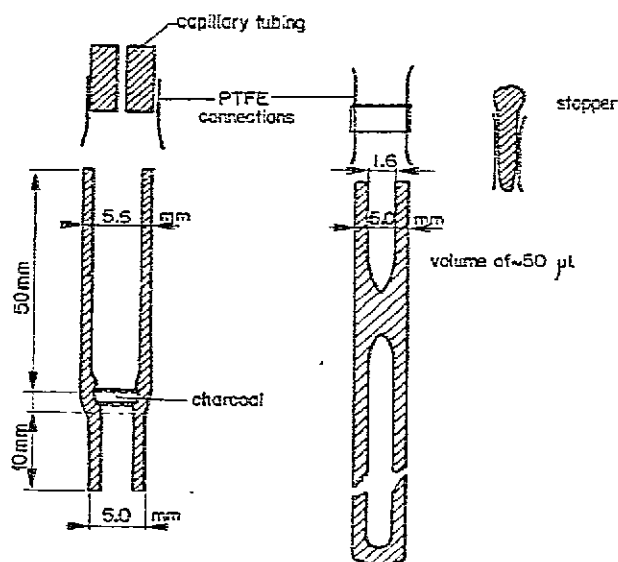The sample flask should be used for no other purpose than water analysis.

Fig. 6. Left: charcoal filter tube with cap. Right: sample tube in which the batches of carbon disulphide eluates are collected, with PTFE double tubing providing a tight connection to the filter tube, and glass PTFE stopper for storage.

Before filling, it is advisable to rinse it thoroughly with tap water. Cleaning with organic solvents or inorganic reagents is not recommended, but if they are unavoidable for particularly adherent impurities, then subsequent prolonged rinsing with tap water should be carried out.

The optimum volume of water depends on the degree of pollution and the sensitivity required; it is best selected experimentally. The internal standard is added from a syringe with its needle immersed in the rotating water. The flask can then be stoppered using the wet ground-glass joint, and placed in the water-bath.

Pre-conditioning of the adsorbent filter

It is advisable to recondition the filter immediately after use, *i.e.*, when it is still wetted by the extracting solvent. The glass tube is filled with methylene chloride at least three times and the solvent is allowed to flow through the filter disc. This procedure is then repeated with pure *n*-pentane as a solvent. During rinsing, the flow-rate of the solvent should be observed in order to check the resistance of the filter disc. A high resistance, normally caused by salt deposits, can be remedied by immersing the filter in 1 M nitric acid and evacuating three to five times so that the acid penetrates the carbon completely. This treatment normally re-establishes the original flow conditions. After washing with acid, the filter is rinsed with distilled water for at least 10 min and then with acetone, methylene chloride and *n*-pentane for 2 min each. In order to eliminate the remaining solvent, the rinsed filter should be kept under vacuum for about 2 min in a glass-stoppered tube; it is then ready for use. For stored filters, a short rinse and evacuation immediately before use is recommended.

The filter disc should not be touched as carbon dust from broken carbon particles would be produced. Carbon dust is best eliminated by connecting the filter

directly to the water pump and immersing the open end repeatedly in water that contains a detergent. During this operation, the direction of flow is reversed several times by connecting the filter to the vacuum the opposite way.

Treatment to activate or reactivate the charcoal is not recommended. The filter can be used for an almost unlimited number of runs provided that no treatment other than appropriate rinsing is used.

Stripping

The sample flask is fitted into the closed loop, making all connections abso-lutely air tight. The pump is turned on only when the metal tubing between the flask and filter holder has attained a temperature of 40°.

The standard stripping time is 2 h, but can be considerably reduced if only low-molecular-weight substances are of interest, *e.g.*, to 15 min if no subtances heavier than xylenes are to be determined. Prolonged stripping can be used in order to collect heavier substances, but one must be certain that the substances of interest are not affected by biological degradation.

Extracting the filter

One of the parameters that govern the extraction step is the amount of moisture on the charcoal[5]. For several reasons, non-polar or weakly polar solvents with low miscibility in water have to be used and moist particles are poorly wetted by such sol-vents. For this reason, we introduced a drying step prior to addition of the solvent. Recent observations, however, have indicated that no wettability problems occur, even with completely non-polar solvents, when the filter temperature is kept at least 10° above the water temperature (30°). This temperature difference reduces the rel-ative humidity of the gas passing the filter to about 40 %. Extraction can then be start-ed without prior drying and with any solvent.

The higher the extraction efficiency of the solvent, the smaller is the volume of solvent needed for satisfactory extraction. High efficiencies are especially important with relatively pure water samples, because all available concentration procedures cause severe losses of extracted substances, not just of the most volatile substances. The most efficient solvent, carbon disulphide, unfortunately presents problems with purification. If a larger volume can be tolerated, methylene chloride, which is easier to purify, is recommended. Table I gives extraction efficiencies for both solvents

TABLE I

EFFICIENCY OF EXTRACTION FROM CHARCOAL

1.0 l of tap water was spiked with 0.5 ppb ($5 \cdot 10^{-7}$ g/l) of the substances indicated. Stripping was carried out for 20 min at 30° on to 1.5 mg of charcoal (for extraction technique, see text).

Substance extracted	Extraction (%)		
	15 µl CH₂Cl₂	30 µl CH₂Cl₂	15 µl CS₂
n-Octane	78	84	75
n-Nonane	93	95	92
Toluene	80	98	90
Ethylbenzene	96	99.4	99.3
m-Xylene	92	99.0	99.4

under conditions that we routinely use. The figures show the well known, although at first surprising, fact that extraction of the most volatile substances is extremely difficult.

The following extraction procedure is suitable for most water samples. For relatively pure samples, a reduced volume of carbon disulphide, instead of methylene chloride, may be preferable. Values are given for a 1.5-mg filter.

Calibrate the sample tube (Fig. 4) with a mark indicating a volume of 20 μl. Use the sample tube with attached PTFE connection for extracting the filter from the filter holder and fasten the connection so as to leave no dead volume between the glass parts. Cover the filter tube with the capillary cap (Fig. 4) and add 5–7 μl of methylene chloride to the filter disc. Using a small piece of ice or a cotton-wool plug wetted with cold water, cool the closed volume in the sample tube, which causes the solvent to accumulate on the lower side of the filter disc. Push the solvent back to the upper side by warming the closed volume between two fingers. After this procedure has been repeated four times, cool the tube and transfer the liquid down to the bottom of the sample tube by swinging it gently in the hand. Add 3–5 μl of solvent and repeat the above procedure. Continue rinsing (four or five times) until about 20 μl of combined extract have been collected in the sample tube. Mix the liquid with the syringe needle and inject an aliquot for GC analysis.

Quantitative determination

The determination of the extracted organic compounds is influenced by the following parameters: the efficiency of stripping from the water sample, the efficiency of adsorption on the filter, the efficiency of extraction from the filter, the fraction of the total extract transferred on to the GC column and the sensitivity of the GC detector for an individual substance. These parameters may be unknown or poorly reproducible. Further, they vary greatly with the type of substances involved and their molecular weights. These uncertainties can be overcome by the following procedure based on the use of internal standards.

Standard substances that do not occur in the water sample are added so as to give concentrations comparable with those of the substances to be determined. A direct comparison of the peak areas of the sample constituents and the internal standards gives a rough estimation of the concentration of the former substances, provided that the two behave similarly with respect to stripping from water, extraction from charcoal and detector response. For more exact results and in the case of widely different behaviours, the peak comparison must be calibrated as follows. A very pure water sample that does not contain the substances of interest, or a water sample from which these substances have been completely removed, is spiked with known amounts of both the substances to be determined and internal standards. The analysis then produces the basis for an exact comparison of peak areas.

We found acetone to be the best carrier for spiking water with any kind of substance. If the amounts added are not greater than a few microlitres per litre, acetone is soluble enough in water not to interfere in the stripping process.

We chose the 1-chloroalkanes as standard substances for the following reasons. Firstly, they are rarely found in the environment. Secondly, chloroalkanes are representative of a wide variety of organic substances with respect to their behaviour in stripping and extraction. Thirdly, the 1-chloroalkanes are commercially available as

a homologous series and can be evenly distributed over a chromatogram so as to be representative of compounds with various volatilities. Further, it is desirable to have the standards as a homologous series as the distance between their GC peaks can be pre-determined, which greatly facilitates the identification of standard peaks in complex chromatograms.

ACKNOWLEDGEMENTS

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