

The Gas Phase Extraction and Analysis of Volatile Organic Pollutants in Water Using a Tenax G.C. Adsorption Tube

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A gas phase stripping technique is described for the concentration and subsequent measurement of trace quantities of volatile organic pollutants in water. The compounds are extracted on to a Tenax G.C. adsorption tube. The sample is transferred to a Tenax G.C. column by thermal desorption and analysed by temperature programmed G.C. or G.C./M.S. The factors governing the quantitative interpretation of the results are discussed and a sensitivity of 0.1 µg/litre is reported for the analysis of styrene in 250 ml of an aqueous sample.

The use of adsorbents for the extraction of organic pollutants from water, prior to analysis, has certain advantages over the techniques of liquid/liquid extraction since it permits a large concentration factor, without contamination, and at the same time it allows the concentration of volatile compounds, without significant loss.

The extraction may be carried out by:

- (a) gas phase stripping techniques¹⁻⁴ in which a gas is passed through the sample and carries the volatile species on to the adsorbent, or,
- (b) headspace analysis^{5,6,7} in which the headspace vapours of the water sample are drawn through the adsorbent, or,
- (c) direct passage of the aqueous sample through an adsorbent bed.⁵

The pollutants may then be removed from the tube by liquid extraction¹ or by thermal desorption.²⁻⁴

The principles involved in the operation of the gas phase stripping techniques are related to those for atmospheric sampling with adsorption tubes, and much of the groundwork involved in determining collection efficiencies and retention volumes is the same for both. It is a simple matter therefore, to extend the use of adsorption tubes, designed for air sampling, to include the extraction of organic pollutants from water. However, it is important to remember that gas phase stripping techniques introduce a new factor into the quantitative interpretation of the results of adsorption tube analyses. This is the efficiency with which the pollutants, particularly the less volatile pollutants, are removed from the aqueous sample.

The gas phase stripping technique described here uses the sample tube and analytical procedures described in the previous paper.⁸

Experimental

APPARATUS (see Figure 1)

The sample is contained in a Quickfit flask of appropriate size which is supported in a boiling water bath. Nitrogen is used as the stripping gas and it is cleaned by passage through a 30–60 mesh activated charcoal filter, before being bubbled through the sample via a porous glass frit. The gas and vapours pass through a double walled condenser and through the adsorption tube. There is the possibility that the less volatile components of the sample would be retained

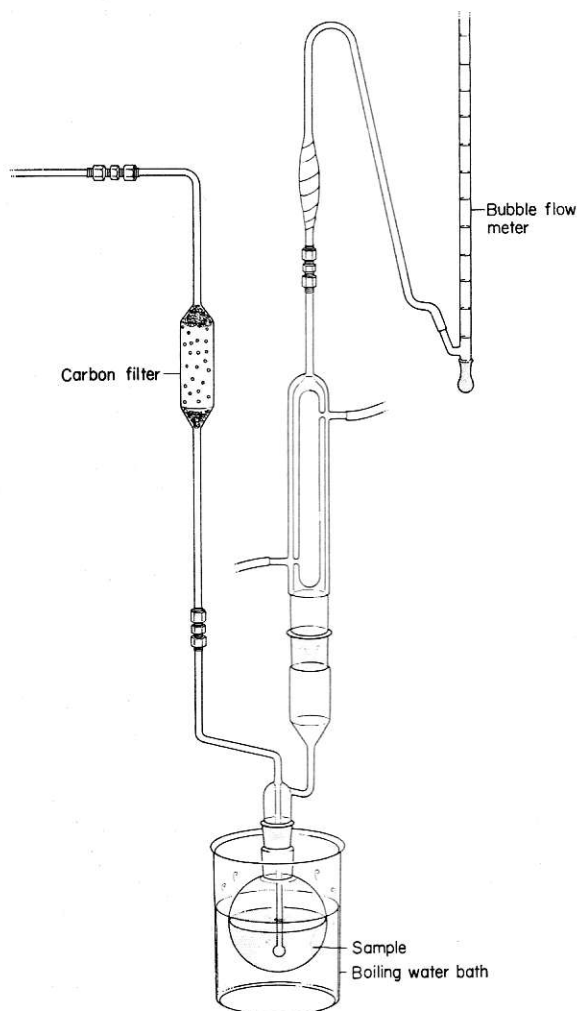


Fig. 1. The apparatus for the transfer of organic volatiles from the sample to the adsorption tube.

by the wall of the condenser and so it is advisable to clean the system between analyses by steaming as in the method described below. The use of rubber bungs and plastic or rubber tubing should be avoided in the construction of the

apparatus, but connections can be made with ground glass joints, Drallim couplings, or Swagelok couplings fitted with silicon rubber O-rings, as appropriate.

The adsorption tube and analytical techniques have already been described in detail.⁸ The adsorption tube contained 0.25 g of 60–80 mesh Tenax G.C. packed into a tube with an internal diameter of 7 mm. Analyses were carried out with a 2 metre $\times$ 2 mm, 60–80 mesh Tenax G.C. glass column fitted in a Pye Unicam series 104 G.C. oven. This was interfaced to a VG Micromass 16B mass spectrometer which could be used in the usual fast scanning mode, or as a selective ion detection system. During the analysis the column was temperature programmed from 50°C to 350°C at 10°C pm.

METHOD

Steaming out the equipment. Drain the condenser of its cooling water and half fill the sample flask with distilled water. Connect the flask to the apparatus and pass a slow stream (30 ml/min) of nitrogen. Boil the water in the flask for 10 minutes to steam out any organic contamination, and let the apparatus cool with the nitrogen still flowing.

Extraction technique. Empty the sample flask and put in a measured amount of the sample (10–250 ml, depending on the amount available and the expected level of contamination). Pass cooling water through the condenser, fit the adsorption tube to the apparatus, and attach the sample vessel. Increase the nitrogen flow rate to 2 ml/sec. (7.2 litre per hour) and raise a boiling water bath about the sample. After 1 hour, or less if the 75 per cent. retention volumes of the compounds of interest are likely to be exceeded, remove the tube and the water bath and turn off the nitrogen flow.

Analysis. Analyse the sample by one of the thermal desorption and G.C. methods described in the previous paper,⁸ and repeat the extraction and analysis using the purged sample and the same sample tube. If the repeat run is clean, this indicates that all of the contaminants were purged from the sample in the first run, and that the tube can be set aside ready for further use. If the repeat run still shows signs of contamination then, at the discretion of the operator, further extractions can be carried out—always finishing with a blank run from the purged sample, or, if necessary, from distilled water.

Results and Discussion

One of the frequent uses for this technique in the authors' laboratory has been the analysis of styrene in drinking water after the installation of a fibre glass tank. To illustrate the method, the results are given in Table I of two analyses of a drinking water supply in Glasgow, 250 ml samples of which were extracted on to adsorption tubes. The first sample, taken shortly after the installation of the tank, contained a significant amount of styrene, and its odour and taste could be detected in the water. There was a much smaller level of styrene in the second sample, taken 11 weeks after installation—the apparent increased level of the other constituents results from the use of the instrument in a more sensitive

mode. Most of the other compounds listed in Table I have also been reported in the literature as common components of drinking water from city supplies.³

The volume of stripping gas used in the extraction procedure, 7.2 litres, was well within the 75 per cent. retention volume⁸ of 60 litres for styrene on the adsorption tube, and so the collection efficiency was expected to be very high. However, it was necessary to check the efficiency with which the styrene was extracted from the sample. To do this a solution of 0.04 mg/litre styrene in water was prepared by injecting 25 μ l of 0.4 g/litre styrene in methanol, i.e. 10 μ g styrene, into 250 ml of distilled water. Two adsorption tubes were connected in series and the sample extracted by the normal procedure.

TABLE I
TWO ANALYSES OF A GLASGOW DRINKING WATER WHICH HAD BEEN
CONTAMINATED WITH STYRENE FROM A FIBRE GLASS TANK

Compound	Estimated concentration, μ g/litre†	
	1 week (approx.) after installation	11 weeks (approx.) after installation
Chloroform	—	2.0
Tetrahydrofuran	—	0.9
Bromo-dichloro-methane	—	0.9
Dibromo-chloro-methane	—	0.2
Styrene	200	<0.1
1,3-butanediol	2	—

† The styrene concentration was measured by calibration, the other compounds were quantified by assuming they had a similar calibration to that of styrene.

Analyses were carried out on the first and second tubes, and on a repeat extraction of the purged sample. Detector calibration was carried out with 25 μ l injections of the styrene in methanol solution using the same syringe as was used to prepare the aqueous sample. In this way the absolute error of the syringe calibration did not affect the efficiency calculations. The only important error was the reproducibility of the syringe, which was ± 3 per cent. The results are given in Table II.

TABLE II

	First tube	Second tube	Repeat extraction	Total
Styrene (μ g)	9.6	0.42	0.032	10.05

From this it can be seen that the efficiency of the analysis on the first tube was

$$9.6/10.05 \times 100 = 96 \text{ per cent.}$$

The efficiency of the vaporisation of the styrene in the first extraction was

$$(10.05 - 0.032)/10.05 \times 100 = 99.7 \text{ per cent.}$$

and the collection efficiency of the vaporised material on the first tube was

$$9.6/(9.6 + 0.42) \times 100 = 95.8 \text{ per cent.}$$

At 96 per cent. the overall efficiency of the first analysis was very high, and this is completely satisfactory for most purposes.

The results show that the main loss of styrene arose from the 95.8 per cent. collection efficiency, rather than the vaporisation efficiency, which was 99.7 per cent. It ought to be possible to improve this technique still further by reducing the volume of the purging gas. A small reduction should have little effect on the efficiency of vaporisation, but it could improve the collection efficiency by reducing the amount of styrene that elutes from the tube.

This work was carried out using the mass spectrometer in its fast scanning mode and the sensitivity for the 250 ml sample was estimated to be 0.1 $\mu\text{g/litre}$. A similar sensitivity would be expected with a flame ionisation detector. These techniques have also been used for the measurement of paint volatiles in drinking water and for the measurement of various forms of industrial contamination in sewer waters—including successful analyses for tetrahydrothiophene and for a tar based disinfectant.

Conclusion

The procedure described here provides a sensitive method of identifying and quantifying volatile pollutants for public health and pollution control investigations in situations where analyses by conventional methods would be tedious and unreliable.

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