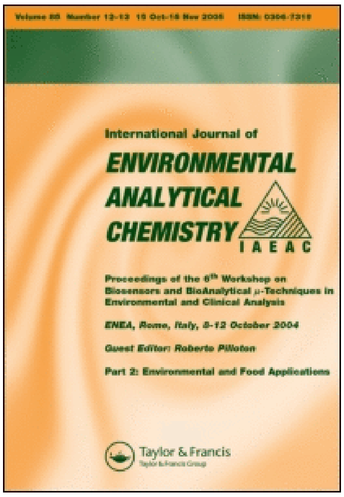


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Optimisation of a Gas Stripping Concentration Technique for Trace Organic Water Pollutants

B. A. Colenutt[a]; S. Thorburn[a]
[a] School of Chemistry Brunel University, Uxbridge, Middlesex, U.K.

To cite this Article Colenutt, B. A. and Thorburn, S.(1980) 'Optimisation of a Gas Stripping Concentration Technique for Trace Organic Water Pollutants', International Journal of Environmental Analytical Chemistry, 7: 3, 231 — 244
To link to this Article: DOI: 10.1080/03067318008071870
URL: http://dx.doi.org/10.1080/03067318008071870

Intern. J. Environ. Anal. Chem., 1980, Vol. 7, pp. 231–244
0306-7319/80/0703-0231 $4.50/0

Optimisation of a Gas Stripping Concentration Technique for Trace Organic Water Pollutants

B. A. COLENUTT and S. THORBURN

School of Chemistry, Brunel University, Uxbridge, Middlesex, U.K.

(*Received June 10, 1979 in final form August 15, 1979*)

The application of gas stripping for the concentration prior to analysis of organic water pollutants at the parts per million and parts per billion level has been studied. Solutes are stripped from solution by a stream of inert gas and subsequently adsorbed onto active carbon from which surface they are taken up in a solvent for analysis.

The method is shown to be applicable to the analysis of a wide range of compounds including pesticides and polychlorinated biphenyls. The effect of gas flowrate, the time of stripping, adsorbent particle size, and desorbing solvent on the percentage recovery of a range of organic compounds has been measured.

Problems of contamination of aqueous solutions by absorption of atmospheric vapours prior to analysis are considered, and the analysis of a typical water sample is demonstrated.

KEY WORDS: Gas chromatography, gas stripping, organic water pollutants.

INTRODUCTION

Analysts have devoted much effort to the determination of low concentrations of organic compounds in aqueous systems. The essence of the vast majority of studies is an initial concentration step followed by an instrumental analytical technique.

Solvent extraction has most frequently been employed as the concentration method[1-4] and a study to determine the best general purpose solvent has been reported.[5] Another technique involves concentration by adsorption onto a suitable adsorbent surface. Charcoal[6,7] has been often used as the adsorbent. A thorough examination of the influence of particle diameter, contact time, temperature, pH, and other relevant factors has been reported.[6]

A third technique involves evaporation of the organic content of aqueous solutions prior to analysis. Summerton and co-workers[8–10] were the first to report that volatile substances present in aqueous samples could be evaporated, or stripped, from the water by a stream of inert gas. The technique was later extended to include solutes such as benzene and toluene,[11] and subsequently substances with a boiling point up to 140°C.[12] Later Grob[13] reported a sophisticated apparatus capable of detecting a wide range of hydrocarbons up to a chain length of twenty four at concentrations down to 1 in 10.[13]

The first work[8] involved evaporating the organic compounds and trapping them cryogenically. The compounds so trapped were then transferred to the analytical system by rapid heating of the freezing trap. An improvement of the recovery was achieved when Grob[13] used an adsorbent trap. The adsorbate could then be recovered in solution by washing the adsorbent with a suitable solvent. As the molecular weight of the compounds being analysed increases and the vapour pressure decreases, so the volume of gas required to liberate them increases. The relatively large volumes of gas required for compounds even with an intermediate boiling point results in a loss of efficiency with cryogenic traps, but presents few problems with a suitable adsorption trap.

In almost all of the reported studies the adsorbent selected has been active carbon. This material is unique in its ability to adsorb a very wide range of organic compounds from a gas stream as has been demonstrated by its wide application in air pollution and other studies.[14,15] The presence of large amounts of moisture in the gas stream seem to have little effect on active carbon's adsorption properties. Indeed Grob[13] has shown that in many cases steam is a suitable inert gas for the evaporation of organic components of aqueous solutions, demonstrating that a totally wet gas stream is no barrier to adsorption.

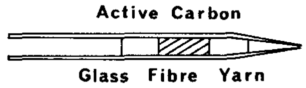
Previous work[8–13] has suggested that there are limitations on the general application of the stripping technique, and the present work was undertaken to establish the practical limits of the system, both in standard mixtures and real water samples. The object was also to study the various factors affecting the efficiency of the method and to optimise them.

When the concentration stage has been achieved the analyst has still to choose a suitable analytical technique. In this work gas chromatography has been used to monitor the efficiency of the stripping technique.

EXPERIMENTAL AND RESULTS

Stripping apparatus

The system used is illustrated diagrammatically in Figure 1. Nitrogen from a gas cylinder was purified by passing through an active carbon trap and then a flow controller. The gas was then bubbled through the aqueous sample which was contained in a flat bottomed flask. The gas outlet into the sample was through a coarse frit, and in all cases the volume of the flask was selected to be as near to the sample volume as possible, so reducing any contamination by laboratory air entering the system. After passing through the water the gas was passed through a splash trap to remove any drops of water and then through the active carbon trap.



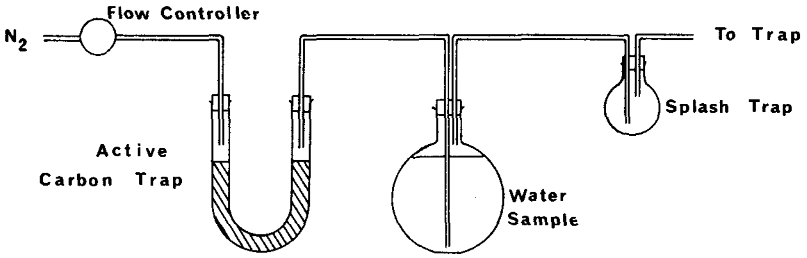


FIGURE 1 Diagram of the stripping apparatus.

The active carbon trap was formed from a piece of $\frac{1}{4}$ in. outer diameter glass tube. This was drawn to a fine jet at one end and had an overall length of 8 cm. Active carbon (between 5 and 25 mg) was held in the tube by two pieces of glass fibre yarn. The combined length of the plugs of glass fibre yarn and the active carbon was about 5 cm, leaving an empty portion of tube at the wider end. Flow of gas through the trap was always from the wider end to the narrower end, eliminating any possibility of the adsorbent being blown out of the trap by the gas. The flow control valve ensured constant flow throughout a particular experiment. A soap bubble flowmeter was connected to the outlet end of the trap in order to measure the gas flow at the start and end of each stripping operation.

All the glass joints in the system were lined with PTFE sleeves. Connections between glass tubing were made with Swagelok stainless steel fittings incorporating combined PTFE ferrules.

Desorption from the adsorbent was carried out in the following manner. A 5-cm length of PTFE tube was connected to the wider end of the trap.

The solvent was then dropped onto the adsorbent by means of a dropping pipette. The active carbon provided a restriction to the flow of the solvent so that when a dropping pipette with a rubber teat was connected to the trap by means of the PTFE tube it was possible either to force the solvent through the adsorbent or suck the solvent up through the solid. Thus by careful manipulation of the pipette bulb the solvent was drawn back and forth over the adsorbent several times before the solvent eventually reached the drawn end of the trap and was collected in a calibrated tube. The volume of solvent used for desorption was variable but was routinely between 50 μl and 1 ml.

Efficiency of recovery from the traps

Initially the active carbon traps were spiked with known amounts of selected compounds using a microlitre syringe. The percentage recovery of the adsorbate from the adsorbent was measured. Desorption was carried out with a range of solvents in the manner described above. The solutions were then made up to standard volume and analysed by gas chromatography. All the analyses were carried out on a Perkin Elmer Model F11 gas chromatograph fitted with a flame ionisation detector (FID) and an electron capture detector (ECD). Column effluent was split in a 1:1 ratio between the two detectors. The columns used for the analysis were either 2 m long, $\frac{1}{4}$ in. outer diameter glass column packed with 5% OV17 coated on acid washed Chromosorb W (80/100 mesh) or a 2 m long, $\frac{1}{4}$ in. outer diameter glass column packed with 5% Carbowax 20 M coated on silianised acid washed Chromosorb W. The oven temperature used varied depending upon the compound being analysed. Nitrogen was the carrier gas at a flowrate of 25 ml . min.$^{-1}$.

For each compound in each solvent the size of the peak on the chromatogram was compared with the peak obtained by injection of a solution of known comparable concentration under the same conditions. It was thus possible to calculate the percentage of the adsorbate recovered. Typical recoveries of compounds from 100/200 mesh active carbon achieved with particular solvents are listed in Table I. Recoveries obtained from different particle size adsorbent with carbon disulphide are given in Table II. A similar pattern of results was obtained using *n*-hexane solvent.

Efficiency of the traps

Subsequently the trapping efficiency of the adsorbent was determined. Mixtures of the selected compounds were made in known concentration.

TABLE I

Recovery of compounds from 100/120 mesh active carbon traps with various solvents

Adsorbate	Solvent				
	n-hexane	Toluene	Carbon disulphide	Diethyl ether	Carbon tetrachloride
n-octane	99	97	99	97	96
n-decane	98	97	99	95	96
Toluene	97	—	100	97	96
Ethyl benzene	98	99	100	98	96
1,2-dichlorobenzene	96	96	100	95	98
Ethanol	90	90	95	92	88
n-butanol	91	88	96	91	92
Phenol	94	91	96	92	90
Methyl ethyl ketone	91	90	94	93	91
Ethyl benzoate	92	91	92	92	90
Acetic acid	90	90	95	95	88

TABLE II

Effect of adsorbent particle size on recovery efficiency (percentage of adsorbate recovered after extraction with carbon disulphide)

Adsorbate	Mesh range and corresponding particle size				
	44/60 0.251–0.353 mm	60/85 0.178–0.251 mm	85/100 0.150–0.178 mm	100/120 0.124–0.150 mm	120/200 0.076–0.124 mm
n-octane	92	95	98	99	99
n-decane	92	96	98	99	99
Toluene	91	95	99	100	100
Ethyl benzene	92	97	99	100	100
1,2-dichlorobenzene	94	96	99	100	100
Ethanol	86	90	93	95	96
n-butanol	86	91	92	96	97
Phenol	90	93	95	96	97
Methyl ethyl ketone	86	90	92	94	94
Ethyl benzoate	83	86	90	92	93
Acetic acid	86	90	93	95	95

Aliquots of the mixtures were then added to measured volumes of distilled water using a microlitre syringe. The addition was arranged to give solutions of the organic solute in a concentration between 1 and 10 ppm. To ensure that the solutions were homogeneous after preparation they were sealed and stirred using a magnetic stirrer for one hour. The solutions so prepared were transferred to the stripper and the operation started. A gas flowrate of 1 l.min^{-1} was used. The time period required for complete stripping of all the organic solute was determined by carrying out repeated stripping operations for increasing times. Figure 2 illustrates the increase in percentage recovery of these compounds as a function of time.

Subsequently the procedures were repeated using solutions with organic concentrations within the range of 1 to 10 parts per billion (p.p.b., 1 part in 10^9) and the data are shown in Table III. The possibility of contamination from external sources at these exceedingly low concentrations was high. The solutions were prepared in freshly distilled water which had itself been stripped by a flow of nitrogen for 2 h immediately prior to the preparation of the solution. The particle size of the active carbon used in the traps for this work was 100/200 mesh.

To ensure that none of the compounds was passing through the traps and failing to be adsorbed in some experiments a second identical trap was connected in series with the first trap. This was analysed at the end of the stripping procedures in the same way as the first trap. In no case were there breakthrough of sufficient quantities to be detected in the chromatographic analysis.

Blank analyses were performed in two ways. If a sample having once been stripped was subjected to a second stripping operation a zero blank was obtained, with the chromatogram showing no peaks. However, if distilled water from the laboratory stock was stripped in the same manner the resulting chromatogram frequently showed traces of some compounds, as Figure 3 illustrates. This was suspected to be as a result of contamination by these compounds present in the laboratory atmosphere. This was confirmed when it was found that distilled water samples left standing in the laboratory overnight showed higher concentrations of trace pollutants than a sample of freshly distilled water. Problems could arise if water samples with very low concentrations of organic solutes were left exposed in the laboratory since adsorption of further traces of organic compounds could occur. For this reason prior to analysis all samples were kept in securely sealed bottles filled to capacity.

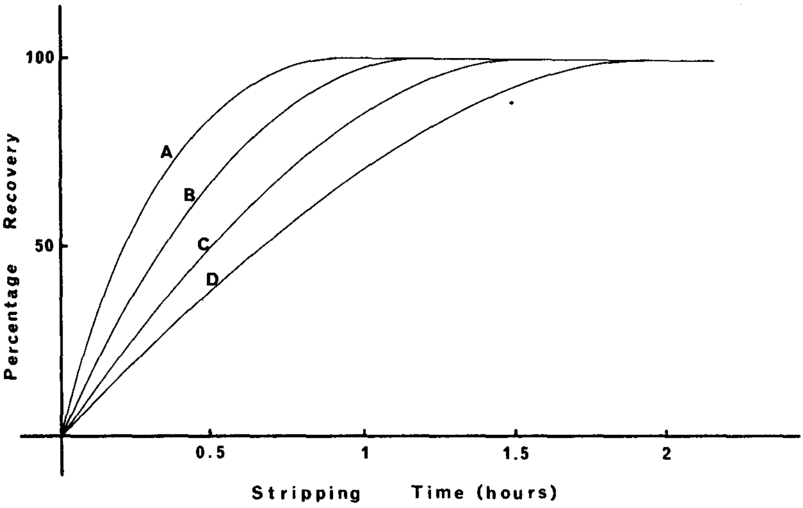


FIGURE 2 Percentage recovery of stripped compounds with increasing stripping time. A *n*-hexane, B *n*-octane, C *n*-decane, D *n*-dodecane.

Analysis of chlorinated compounds

Experiments were carried out to determine the possibility of analysing a range of compounds not previously examined by the stripping technique. The test compounds used were various chlorinated pesticides and poly-

TABLE III

Percentage recovery of solutes in aqueous solution using time stripping technique (Each solute present in the range 1 t

Solute	Solvent			
	n-pentane	Toluene	Carbon disulphide	Diethyl ether
n-octane	88	90	92	88
n-decane	90	92	94	90
Toluene	94	—	96	89
Ethyl benzene	95	95	96	93
1,2-dichlorobenzene	90	90	92	90
Ethanol	82	80	85	82
n-butanol	88	87	92	88
Phenol	90	88	92	85
Methyl ethyl ketone	80	80	82	80
Ethyl benzoate	83	83	88	83
Acetic acid	80	80	81	80

chlorinated biphenyls (PCB's). The solubility of the pesticides in water was exceedingly low, and to ensure a more nearly homogeneous solution the pesticides were first dissolved in *n*-hexane. A calculated volume of the *n*-hexane solution was then added to a known volume of water to give solutions in the sub-ppm range. The percentage recovery of the pesticides by the stripping technique was calculated by comparison of the peaks obtained from solutions of pesticides. Detection in these cases was by the ECD which gave much better response than the FID. A similar procedure was adopted with the PCB's. However, these commercially available compounds are mixtures of a large number of similar compounds. In order to calculate the recovery the total of all the peak areas due to the PCB mixture were totalled and compared with standards. Thus the recovery quoted in Table IV is an average figure although provided a sufficiently long stripping time is used there is no significant difference in the rates of recovery for individual components of the mixture.

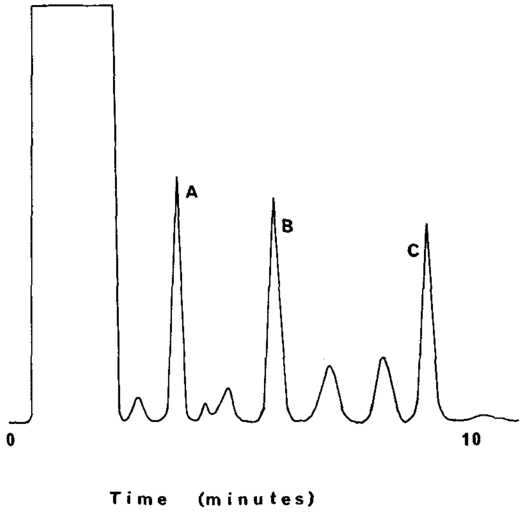


FIGURE 3 Chromatogram of sample stripped from distilled water. A *n*-octane, B benzene, C toluene.

Analysis of water samples

Water samples were taken from the River Pinn which runs through the Brunel University campus. The samples were collected in Winchester quart bottles which were filled to capacity and securely stoppered.

TABLE IV

Recovery of pesticides and polychlorinated biphenyls by stripping

Solute	*n*-pentane	Carbon disulphide	Carbon tetrachloride	Diethyl ether
Aldrin	95	96	96	88
Dieldrin	92	94	95	85
Lindane	94	94	95	80
*p,p'*DDT	95	92	95	85
Endrin	90	92	95	85
Heptachlor	92	94	98	90
Methoxychlor	92	90	94	88
Aroclor 1221	94	92	92	90
Arolor 1248	96	95	94	89
Aroclor 1254	96	98	96	92

Wherever possible the samples were subjected to stripping immediately upon return to the laboratory. Two l of the water was used and stripping was carried out for 4 h at a gas flowrate of 1 l.min^{-1}. The adsorbate trapped on the surface of the active adsorbent was desorbed either with carbon disulphide or *n*-pentane. Solutions were made up to a standard volume and subjected to gas chromatography. The standard analysis involved using a 2 m long $\frac{1}{4}$ in. outer diameter column packed with 5% OV17 on acid washed Chromosorb W. Nitrogen carrier gas was used at a flowrate of 25 ml.min^{-1}. The oven temperature was programmed from 50°C to 250°C at 4° min^{-1}. The column effluent was equally split between a FID and an ECD. A typical chromatogram is illustrated in Figure 4. The identification of some of the peaks was tentatively possible from a comparison of retention times with those of the standard analyses. Confirmation was achieved by a mass spectrometry of the separated components using a Hitachi Perkin Elmer RMS4 mass spectrometer. Those compounds identified in this manner are listed in Table V together with the concentration measured.

DISCUSSION

Gas stripping has been demonstrated to be a useful tool in analysis of a range of organic compounds present in trace amounts in aqueous solution. Important variables are the flowrate of stripping gas, the time period for which stripping is carried out, the particle size of the adsorbent, and the choice of solvent used for desorption.

For a particular compound the use of a higher flowrate would decrease

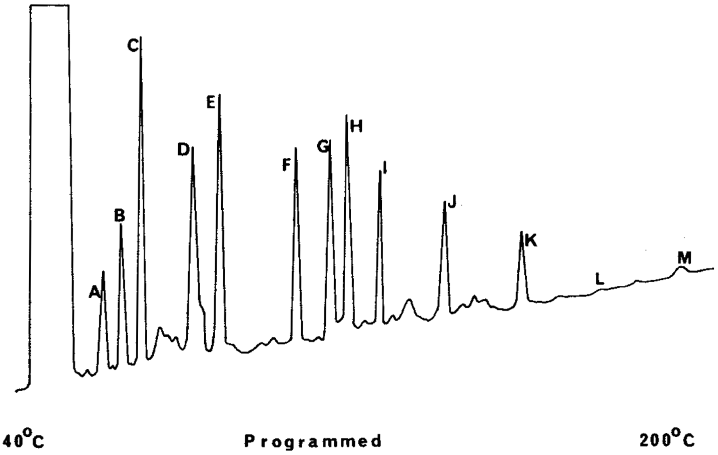


FIGURE 4 Chromatogram of sample stripped from River Pinn water. A *n*-octane, B *n*-nonane, C benzene, D *n*-decane, E toluene, F *n*-undecane, G ethyl benzene, M xylenes, I *n*-dodecane, J *n*-tridecane, K *n*-tetradecane, L *n*-pentadecane, M *n*-hexadecane.

TABLE V

Typical analysis of River Pinn water sample

	Concentration in ppb	
	A	B
n-octane	48.9	3.2
n-nonane	8.6	4.1
n-decane	41.2	2.2
n-undecane	39.7	2.1
n-dodecane	22.5	3.0
n-tridecane	20.1	1.1
n-tetradecane	6.8	2.4
n-pentadecane	18.7	2.6
n-hexadecane	5.4	2.8
Benzene	120.0	7.1
Toluene	87.2	3.8
Ethylbenzene	31.1	1.1

A is an occasion when a thin film of oily material was observed on the water surface.
B is an occasion when there was not obvious pollution.

the time required for complete stripping. Figure 5 shows how the length of time for stripping increases with decrease of gas flowrate for selected compounds. For a homologous series of compounds the stripping time increases with increasing molecular weight and decreasing vapour pressure. Although there is broad relationship between diminishing vapour pressure and increasing stripping time at constant flowrate there may be other more subtle influences also at work which a more thorough study of the precise time required might demonstrate.

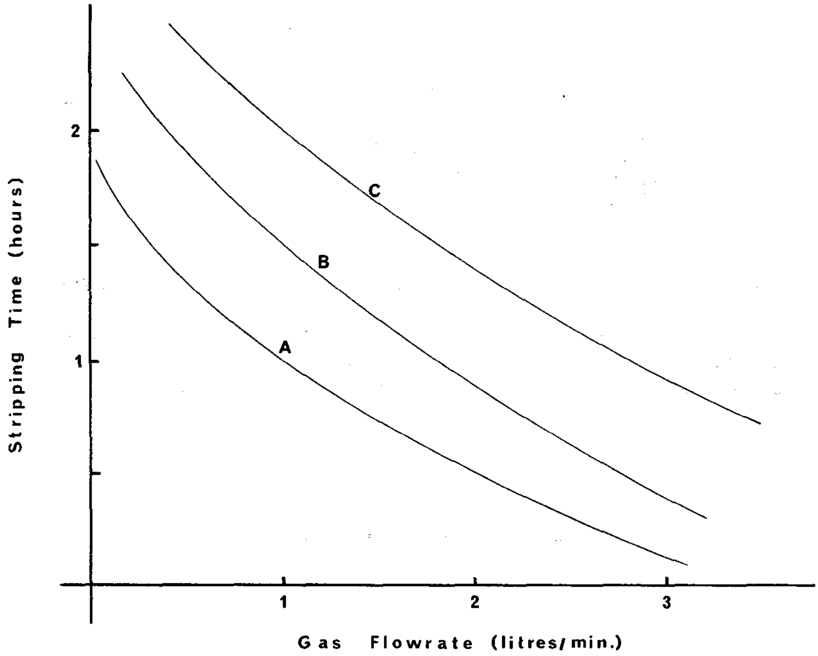


FIGURE 5 Variation of stripping time required for maximum sample recovery with gas flowrate. A *n*-hexane, B-decane, C *n*-dodecane.

Increasing the flowrate reduces the stripping time, but the particle size of the adsorbent limits the flowrate which can be achieved. If very small particles are used the maximum flowrate for a particular applied pressure is decreased. The date in Table II show that greater recovery of adsorbed compounds is achieved with smaller particles. The particle size does not significantly affect the surface area since this is internal surface rather than the outer surface. However, with smaller particles the desorbing solvent has less distance to travel to reach the innermost pores. This results in a greater desorption efficiency with smaller particles, as has been observed. The particle size used here was generally 100/120 mesh. The data in Table II show that there is an increase in the amount of adsorbate recovered as the particle size decreases, but there is relatively little difference between the 100/120 mesh range and the 120/200 mesh range. The increased stripping time or gas flowrate called for in using the smaller adsorbent particles results in the 100/120 mesh range being preferred.

The percentage recovery of adsorbate in any particular case may be different for different solvents and although a number of solvents may be suitable factors other than the overall recovery may be important in making the final selection.

For the whole range of test compounds the recovery was normally over 90% although the hydrocarbon solvents *n*-pentane, *n*-hexane and toluene and carbon disulphide were superior to the others tested. Carbon disulphide was the best solvent overall and for general use must be recommended. This is especially so if the solution is to be examined using gas chromatography with a FID since the detector response is very much less to this solvent and the lack of a large solvent peak makes interpretation of the chromatogram easier.

Whichever solvent is chosen, the stripping technique when applied to synthetic aqueous solutions of organic compounds at the ppm level showed satisfactory recoveries. The percentage recovery in most cases was over 90% and often more than 95%, figures which are considered acceptable at these levels. Providing that sufficient stripping time is allowed the recovery of even relatively high molecular weight compounds is possible. Thus even the pesticides and PCB's in solution could be analysed.

The percentage recoveries achieved with solutions of concentrations in the ppb range were lower than for higher concentrations but still satisfactory when considering the minute quantities to be manipulated. With carbon disulphide as solvent, greater than 90% recovery was possible with many compounds.

In practice for solutions with concentrations in the ppb range a problem more serious than low recovery is the possibility of contamination. The possibility of organic solutes evaporating from aqueous solution is apparent, but the uptake of vapours by a relatively "clean" solution is less so. The present work shows that water samples may become contaminated by organic compounds if they are left exposed to the laboratory atmosphere for a period of time. Thus it was impossible to obtain a zero blank even with freshly distilled water, although it was possible when a stripped sample was subjected to a second stripping operation. Contamination can be an important factor and may have an adverse effect on the results obtained. The greatest precautions must be taken to avoid contamination of samples in the laboratory prior to analysis. However, major problems of contamination only occur when dealing with solutions in the sub-ppm range.

The results of analysis of water samples from the River Pinn show that the method can be applied to real samples. Although the typical analysis of the water, Table V, shows the organic concentrations are at the ppb level it is gratifying that the chromatogram (Figure 4) is markedly different from that produced by laboratory contamination, showing that the pollutants are actually present in the water rather than having been introduced prior to analysis. It was possible to identify some of the components present on the FID trace, but the ECD trace showed no correlation with any of the standard compounds. This is not unexpected since there are many thousands of possible contaminants and a very limited range of standard compounds was used. However, the analysis of the synthetic and real samples do serve to show that the technique is widely applicable.

References

1. L. H. Keith, *Sci. Total Environ.* **3,** 87 (1974).
2. A. L. Brodie, J. Bos and S. Herzberg, *J. Inst. Pet.* **59,** 263 (1973).
3. A. V. Holden and K. Marsden, *J. Proc. Inst. Sew. Purif.* **3,** 295 (1966).
4. M. Ochiai and T. Hanya, *Environ. Poll.* **11,** 161 (1976).
5. R. G. Webb, *Int. Jour. Environ. Anal. Chem.* **5,** 239 (1978).
6. P. M. Hertjes and A. P. Meijers, *Wasser Abwasser,* **111,** 61 (1970).
7. R. D. Kleopfer and B. J. Fairless, *Environ. Sci. Technol.* **6,** 1036 (1972).
8. J. W. Swinnerton, V. J. Linnenbom and C. H. Cheek, *Anal. Chem.* **34,** 483 (1962).
9. J. W. Swinnerton, V. J. Linnenbom and C. H. Cheek, *Anal. Chem.* **34,** 1509 (1962).
10. J. W. Swinnerton and V. J. Linnenbom, *J. Gas Chromatogr.* **5,** 570 (1967).
11. E. Desbaumes and C. Imhoff, *Water Research,* **6,** 885 (1972).
12. J. Novak, J. Zluticky, V. Kubelka and J. Mostecky, *J. Chromatogr.* **76,** 45 (1973).
13. K. Grob, *J. Chromatogr.* **84,** 255 (1973).
14. M. Rollet and M. Moisson, *Poll. Atomos.* **57,** 33 (1973).
15. F. K. Mueller and J. A. Miller, *Amer. Lab.* **6,** 49 (1974).