A rapid extraction method for the gas chromatographic analysis of organic micropollutants in water

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Abstract

A simple, economical and dependable extraction procedure is described whereby groups of micropollutants can be analysed by detection methods such as GC, GC-MS, TLC and HPLC using a single sample. Samples were extracted in the same container with a mixture of organic solvents using a specially designed stirrer and modified micro Snyder evaporator. Recoveries of more than 70% were obtained for a wide variety of compounds. This method was found suitable for the rapid simultaneous screening of a number of samples for specific organic compounds which may have health implications.

Introduction

An estimated 70 000 different chemical compounds are currently in common use, a number which grows by about 1 000 each year (U.S. Environmental Protection Agency, 1979). Many of these chemicals may have direct, indirect or delayed toxic, mutagenic, carcinogenic or teratogenic effects, and indications are that chemicals in the environment may be responsible for 50 to 90% of human cancer cases (Commoner, 1977; U.S. Environmental Protection Agency, 1979). Since water plays an important role in exposing man to chemicals in the environment, research on the incidence of hazardous compounds in water, their health effects and methods for their removal, receives high priority in water research all over the world (Stander, 1979).

As a result of the complexity of organic compounds in water, numerous methods have been developed for their recovery for analytical purposes, including membrane adsorption procedures, headspace analysis, purge and trap methods, adsorption on resins such as XAD or Tenax, and various liquid-liquid extraction procedures (Rudling, 1970; Van Rensburg, 1977; Chapman et al., 1982; Peters, 1982; Van Rensburg and Hassett, 1982; Lopez-Avila et al., 1983; Poole and Schuette, 1983; Burchill et al., 1983). Each of these methods has its own advantages and disadvantages, and was to a large extent developed for a specific purpose.

This paper describes a rapid liquid-liquid extraction procedure adapted for the simultaneous recovery of a wide range of base/neutral and phenolic organic compounds. The percentage recovery was determined from waters 'spiked' with known concentrations of organic compounds.

Materials and methods

Extraction procedure

Collect the water sample in a suitable 4,5 ℓ glass jar with a teflon lined screw cap, properly cleaned with detergent, rinsed with distilled water and baked overnight at 200 °C. Commence processing preferably within 6 h of sampling. If this is not possible, the pH of the water must be reduced to 2 and the sample stored at 4 °C for not longer than a week. Dissolve 100 g of sodium sulphate (reagent grade, heated for 8 h at 650 °C and stored in a glass desiccator) in 4 ℓ of the water sample. Adjust the pH to 2

using concentrated sulphuric acid, and add 80 $\mu\ell$ of an internal standard mixture containing n-C_{12}, n-C_{14}, n-C_{20}, n-C_{28} and n-C_{32} saturated hydrocarbons (0,15 $\mu g/\mu\ell$ each) and 4-bromophenol (0,3 $\mu g/\mu\ell$) in benzene for quantification and retention index calculations. Close the jar and leave contents to stabilize at 4 °C for a minimum period of 24 h.

Add 100 mℓ of a 7:3 (by volume) mixture of dichloromethane and diethylether, both purified by fractional distillation using a 0,5 m × 50 mm glass column packed with glass helicals and a reflux ratio of about 10:1. Stir for 5 min with an 'uplift' stirrer (Fig. 1). The stirrer consists of a shallow stainless steel cylinder 25 mm high, 38 mm OD with a wall thickness of 1,6 mm. Inside the bottom of this cylinder four blades are positioned symmetrically and in the same plane at 15° from the horizontal. The blades are knife edged on the leading edges. A stainless steel rod, the length of which is determined by the depth of the sample vessel, is welded at the junction of the four apexes of the blades in the centre of the cylinder's diameter. The stirrer is placed off centre in the sample vessel with the blades approximately 1 cm above the solvent. At the optimum speed of 10 r/s the solvent is lifted from the bottom of the sample vessel and dispersed by the cylinder in a fountain-like action (Fig. 2).

Allow the phases to separate for at least 4 h at 4 °C, with the jar standing at an angle to permit easy recovery of the solvent.
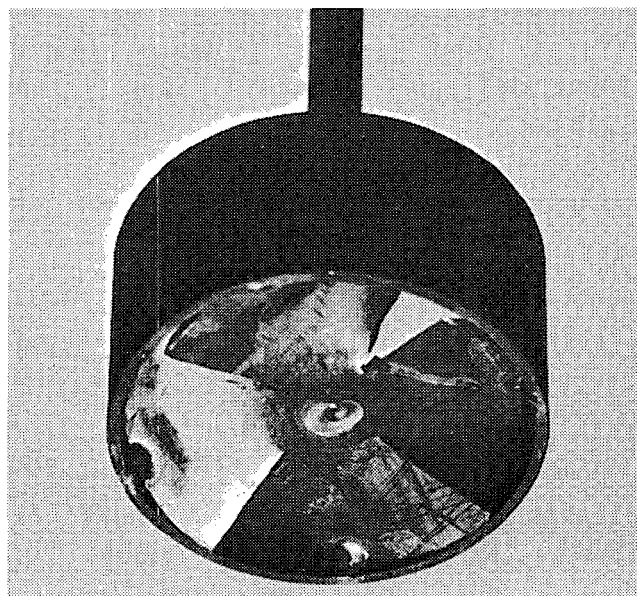

Figure 1
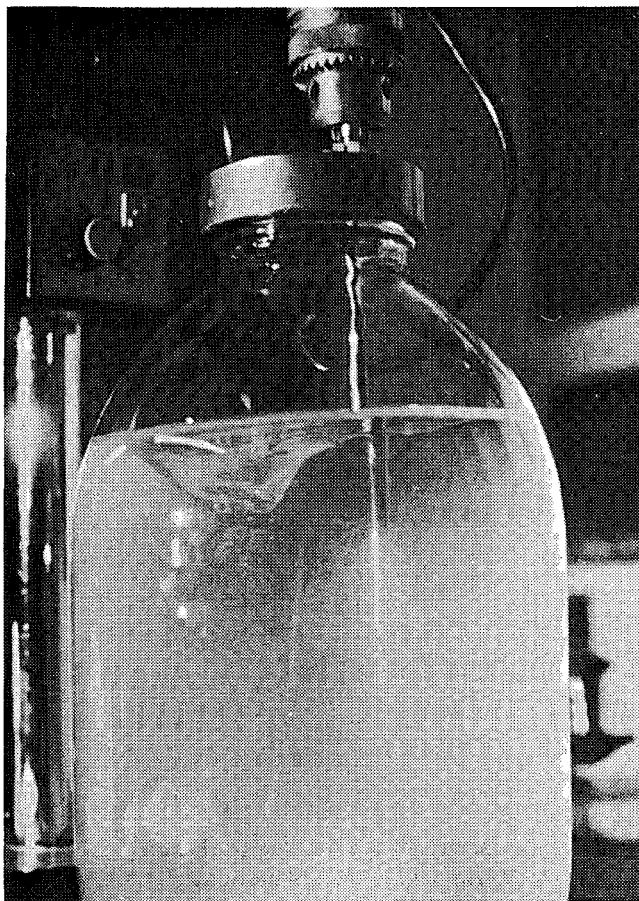*'Uplift' action stainless steel stirrer.*

Figure 2
Dispersion of solvent in the sample.

Remove the solvent phase using a pipette and dry through sodium sulphate into a condensator (Fig. 3(1)). Wash the sodium sulphate with 5 mℓ solvent mixture. Repeat the extraction, now allowing only 1 h for separation at room temperature, and pass the solvent phase through fresh sodium sulphate into the condensator with the first extract, and discard the water phase. Add boiling stones to the condensator and use a water bath at 42 °C for evaporation. When the volume of the extract is reduced to about 5 mℓ, remove the condensator from the waterbath, wash the sides down with 1 to 2 mℓ solvent, and transfer the extract to a micro Snyder condensator modified to permit side entry of nitrogen gas (Fig. 3(2)). Slowly bubble high purity nitrogen gas through the extract in the Snyder condensator held in the water bath (Fig. 4) until the volume is reduced to 400 μℓ. The volume can be reduced to 200 μℓ or less in a reactivial evaporator (Fig. 3(3)).

For the separation of base/neutral and phenolic compounds, transfer the extract into a 2 mℓ all glass syringe by means of a stainless steel needle fitted to the syringe. Remove the needle and add 1,0 mℓ of a 4 g/ℓ sodium hydroxide solution, containing 50 g/ℓ sodium sulphate, cap the syringe with a teflon stopper and shake gently for at least 1 min. Transfer the sodium hydroxide phase to a 10 mℓ glass syringe, repeat the extraction, and combine the sodium hydroxide phases which contain the phenolic compounds. Transfer the organic phase, which contains the base/neutral compounds, to a 1 mℓ serum vial and cap the vial (Fig. 5).

For derivatisation of the phenolic compounds, wash the combined sodium hydroxide extract by shaking for approximately 30 s with 0,5 mℓ n-hexane. Discard the hexane and add 15 μℓ of a saturated hydrocarbon mixture (0,3 μg/μℓ of each of n-C_{10}, n-C_{16}

and n-C_{20} in benzene), 400 μℓ n-hexane and 50 μℓ acetic anhydride. The hydrocarbon mixture serves as marker for retention index calculations. Cap the syringe with a teflon stopper and shake gently for at least 3 min. Transfer the hexane phase (Fig. 5), which contains the phenol acetates, to a 1 mℓ serum vial. Add sodium sulphate and cap the vial. The extraction procedures are schematically illustrated in Figure 6.

Analysis of extracts

The two extracts were analysed by 'direct' injection of 5 μℓ volumes into two flame ionisation detector (FID) gas chromatographs (GC) with injection ports similar to those developed by Van Rensburg (1977). The first was a Tracor Micro-Tek Model 550 gas chromatograph fitted with a 30 m × 0,32 mm, i.d., 1 μm film thickness, DB1 fused silica column (J. & W. Scientific, Inc. Rancho Cordova, California), used for base/neutral compounds. The instrument was programmed for an initial hold of 3 min at 60 °C followed by a temperature increase of 3 °C/min up to 300 °C with a final hold of 10 min at this temperature. In the second instance, the phenolic compounds were determined by means of a Varian Model 1400 gas chromatograph using a similar column to the one previously described and an initial hold of 90 s at 70 °C followed by a temperature increase of 3 °C/min up to 250 °C.

Results and discussion

In the evaluation of solvents for liquid-liquid extraction, hexane yielded poor recoveries when organic compounds were present in concentrations of less than 5 μg/ℓ. Dichloromethane yielded recoveries of more than 70% for all compounds listed in Table 1
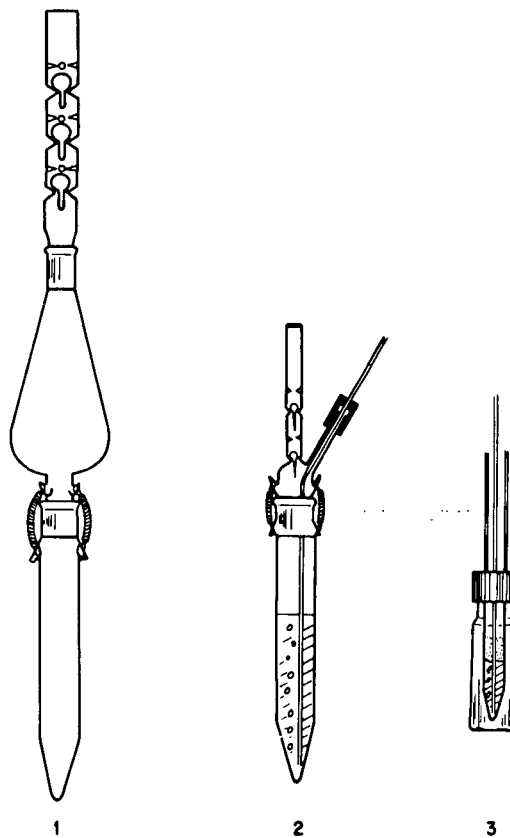

1   **2**   **3**
Figure 3
Condensator for extract concentration. 1. Snyder air condensator.
2. Modified micro Snyder condensator. 3. Reactivial evaporator.

TABLE 1
EFFICIENCY OF RECOVERY OF SELECTED COMPOUNDS FROM SPIKED WATER SAMPLES

Compound	Concentration in spiked samples ($\mu g/\ell$)	% Recoveries Mean value (n = 10)
PHENOLS:		
1. Phenol	0,5	95
2. 2-chlorophenol	0,5	89
3. 2,4-dichlorophenol	0,5	81
4. 4-chloro-3-methylphenol	2,5	76
5. 2,4-dimethylphenol	0,5	82
6. 2-nitrophenol	0,5	76
7. 2,4,6-trichlorophenol	1,5	72
8. 4-nitrophenol	2,5	78
9. 2,4-dinitrophenol	1,5	75
10. 2-methyl-4,6-dinitrophenol	2,5	75
11. Pentachlorophenol	2,5	76
BASE/NEUTRALS:		
1. 1,3-dichlorobenzene	1,0	74
2. 1,2-dichlorobenzene	1,0	72
3. bis(2-chloroethoxy)methane	1,0	77
4. Naphthalene	1,0	85
5. Hexachlorobutadiene	1,0	109
6. Acenaphthene	1,0	92
7. 2,4-dinitrotoluene	1,0	100
8. Diethylphthalate	1,0	98
9. Fluorene	1,0	89
10. Hexachlorobenzene	1,0	104
11. Anthracene	1,0	86
*12. Dibutylphthalate	—	—
13. Pyrene	0,5	77
14. Chrysene	0,5	78
15. Benzo(a)anthracene	0,5	81
16. Dibenzo(a,h)anthracene	0,5	73

*Already present in samples.

except for phenols, which yielded only about 40% recovery. The inclusion of diethyl ether considerably increased the recovery of phenols and a 7:3 (by volume) mixture of dichloromethane and ether was eventually found to yield the highest recovery. The distilled dichloromethane and ether must be of such a purity that the total solvent background contamination is less than 1 $\mu g/\ell$ after concentration by a factor of 10^4 and individual contaminants not exceeding 0,01 $\mu g/\ell$.

The average recovery of selected base/neutral and phenolic compounds from water by means of the dichloromethane-ether extraction procedure, varied between 72% and 109% (Table 1), which compares favourably with existing methods. In the method described, the detection limit was 0,01 $\mu g/\ell$ for each compound.

A typical GC/FID chromatogram of a raw water contaminated with hydrocarbons is illustrated in Figure 7.

This laboratory applies the extraction procedure on a routine basis on a variety of raw and treated drinking-water supplies. Details of surveys carried out on drinking- and surface water, using this method, have been described (Van Rensburg et al., 1982; Theron et al., 1983).

The described dichloromethane-ether extraction procedure has a high percentage of recovery of both base/neutral and phenolic compounds that cover a wide range of boiling points, water solubility and extractability.

Disadvantages of alternative methods for the recovery of organic micro-pollutants from water include the following: membrane filtration is time-consuming and not suitable for compounds adsorbed onto particulate matter, headspace analyses as well as purge and trap methods are primarily limited to volatile compounds, and column chromatography using XAD or Tenax resins is not suitable for highly polar compounds or compounds adsorbed onto suspended matter. Among alternative solvents for liquid-liquid extraction are ethyl acetate, not considered because of high solubility in water and a relatively high boiling point, while chloroform, benzene and tetrachloroethane are hazardous
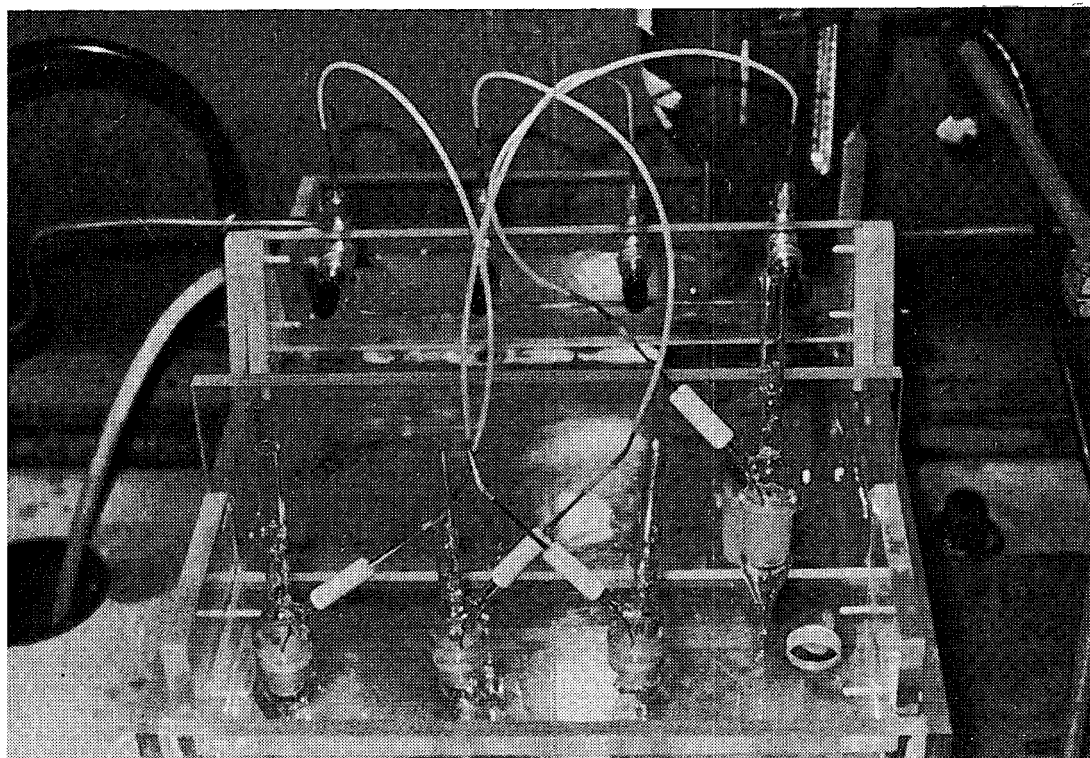

Figure 4
Water bath with modified micro Snyder condensator and nitrogen attachments.
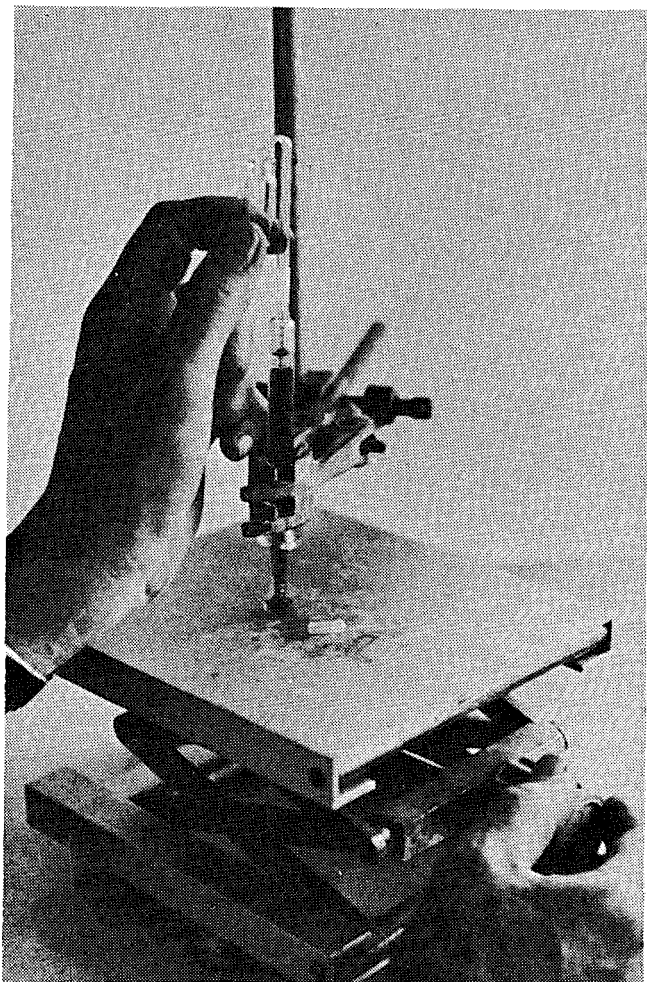
Figure 5
Laboratory jack and syringe system for the transfer of base/neutrals and phenolic extracts.

Figure 6
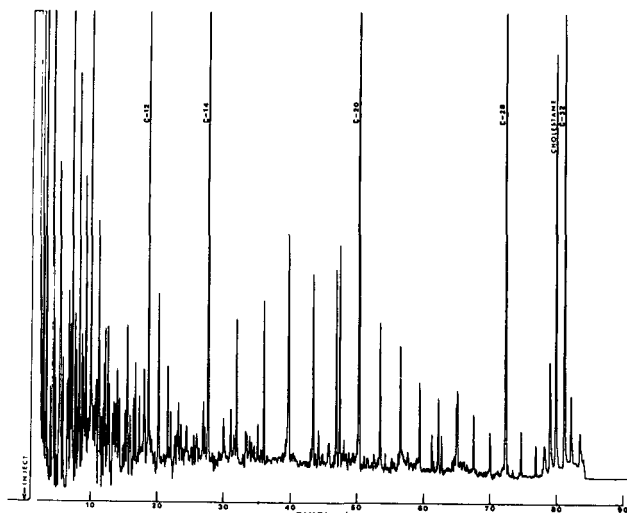*Schematic representation of extraction technique.*

Figure 7
Chromatogram of raw water contaminated with hydrocarbons.

to work with and have no particular advantages.

An important advantage of the extraction procedure described here is that test samples are collected and processed in the same container, thereby limiting losses as a result of adsorption onto sample containers or particulate material.

The recoveries of the compounds listed in Table 1 compare favourably with existing methods. Recoveries were calculated from samples of double glass distilled water, drinking-water, and surface water to which known quantities (0,5 to 2,5 $\mu g/\ell$) of analytical grade compounds selected from the list of Priority Pollutants (U.S. Environmental Protection Agency, 1980) (Table 1) were added. None of these compounds was detectable in the water prior to spiking. Gas chromatograms of the base/neutral and phenolic extracts were obtained from a spiked drinking water sample. (Figures 8 and 9).

In this kind of analysis it is essential to avoid plastic or rubber materials because they may adsorb organic compounds from the water sample or contaminate it with compounds such as plasticizers. Samples must also be protected from light and high temperatures which may induce chemical changes or biological decomposition of the compounds analyzed for.

Special attention should be given to the mixing of the extraction solvent with the sample. High speed mixing tends to form emulsions which have to be left overnight at 4 °C for phase separation and may even require centrifugation. With conventional propeller type stirrers the heavier-than-water solvent used in this study failed to disperse homogeneously. The specially designed 'uplift' stirrer solved this problem.

Sodium sulphate is added to the extraction mixture to lower the solubility of organic compounds and the pH is reduced to 2 to improve the recovery of phenols and limit biological activity.

The use of internal standards is known to be the most reliable way for quantification, and by comparing the ratio between the standard peaks, a close control can be kept on the extraction and concentration steps. If the sample under investigation is suspected of containing saturated hydrocarbons, the unsaturated hydrocarbons 1-dodecene, 1-tetradecene and 1-octadecene could be used to replace n-C_{12}, n-C_{14} and n-C_{20} in the internal standard mixture. Under the gas chromatographic conditions described good separation was obtained between the saturated and unsaturated hydrocarbons (at least 40 index units).
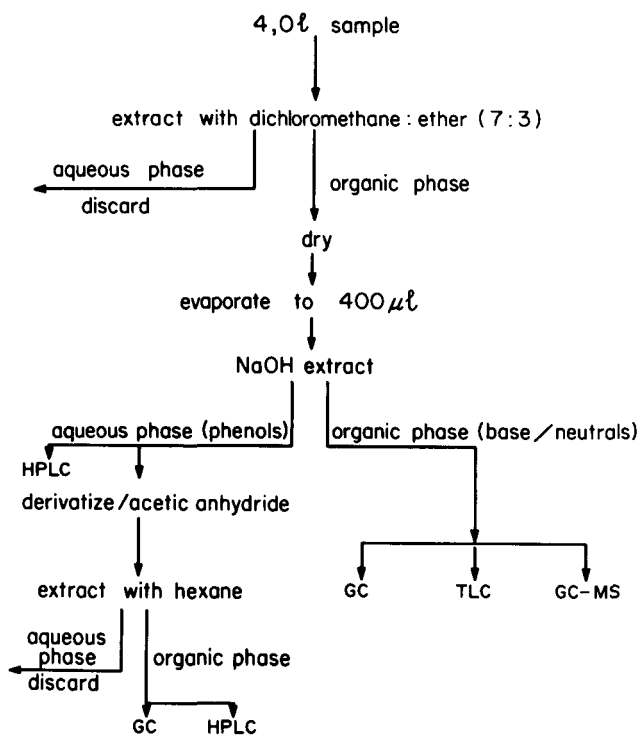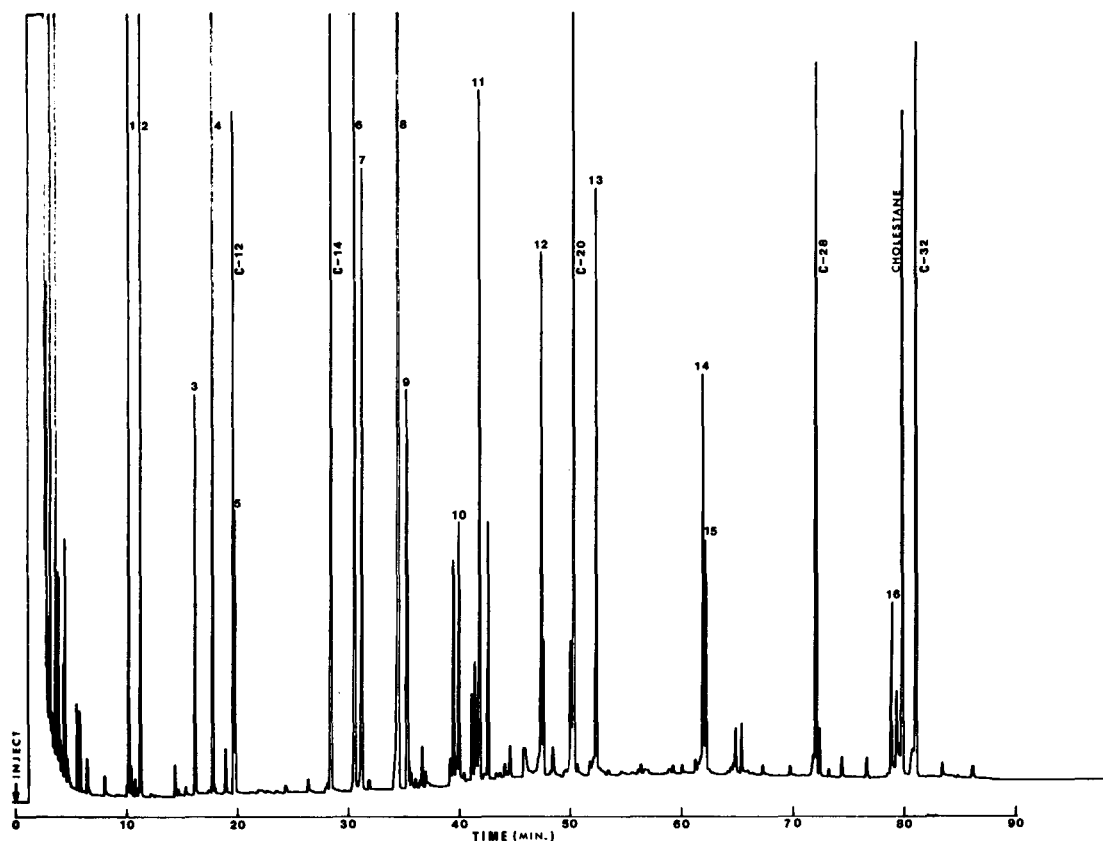
Figure 8
Chromatogram of drinking-water 'spiked' with base/neutral compounds
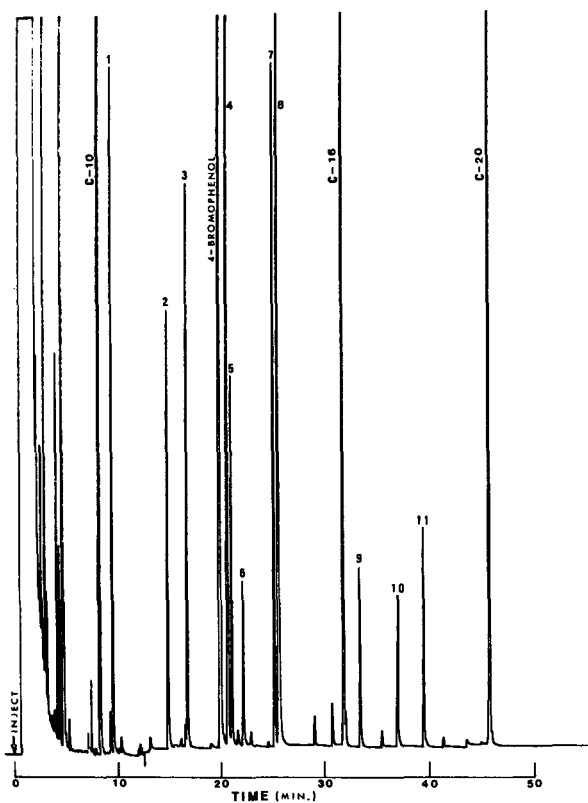*listed in Table 1.*

Conclusion

The extraction procedure proved simple, reliable and economical. The fact that samples are collected and processed in the same containers limits the possibility of losses and/or contamination by repeated transferring.

Added advantages of the method are a high efficiency of recovery of greater than 70%, detection limit of 0,01 $\mu g/\ell$ for a wide variety of compounds, and the suitability of the final products extracts for further analysis by gas chromatography, gas chromatography-mass spectrometry, thin-layer chromatography and high performance liquid chromatography.

Acknowledgements

Figure 9
Chromatogram of drinking-water 'spiked' with phenolic compounds
listed in Table 1.

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