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# DETERMINATION OF HIGHLY VOLATILE ORGANIC CONTAMINANTS IN WATER BY THE CLOSED-LOOP GASEOUS STRIPPING TECHNIQUE FOLLOWED BY THERMAL DESORPTION OF THE ACTIVATED CARBON FILTERS

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## SUMMARY

Very volatile organic contaminants in water were determined by using closed-loop gaseous stripping combined with thermal desorption from the activated carbon filter into a high-resolution gas chromatograph. The operating parameters for quantitative applications were evaluated. The solvent-free thermal desorption procedure permits the determination of compounds that normally elute under the gas chromatographic solvent peak (*e.g.*, dichloromethane and Freons). Sixteen volatile compounds with boiling points in the range −30 to 120°C were determined with an overall recovery of 12–52%. Qualitative determinations of volatiles from a secondary sewage effluent were in good agreement with the results found by two more established methods.

## INTRODUCTION

Since its introduction in 1973[1], closed-loop stripping analysis (CLSA) has been successfully applied to the determination of a broad range of highly volatile organic compounds from a wide variety of aqueous samples[2]. The attributes of this method include a large enrichment factor, minimal contamination problems and closed-circuit recycling of substances that break through the carbon filter. One of its limitations is its inability to determine compounds that elute under the gas chromatographic (GC) peak of the solvent (usually carbon disulphide). The most obvious remedy for this problem is the use of a solventless thermal desorption technique. We have introduced thermal desorption CLSA in our laboratory and present here our observations concerning its potential and its limitations.

Thermal desorption has been used in the past for a variety of adsorbents for both air and water analysis. Its main advantage is that, given sufficient recovery, the

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entire amount of material is placed on the analytical column. Although thermal desorption of activated carbon has been reported[3–6], by far the most widely used adsorbent for the recovery of volatile compounds purged from water is the porous polymer Tenax[7–11].

Tenax is employed in the popular "purge and trap" technique according to Bellar and Lichtenberg[7]. It is used to adsorb organic compounds purged from a water sample by a helium stream and, subsequently, thermally desorbed on to a GC column. In recent publications, the limited adsorption capacity of Tenax for highly volatile compounds has been recognized and has led to the development of mixed traps employing silica gel[9] or activated carbon[2,10] in addition to Tenax.

Given the attractive features of activated carbon (high specific surface area, high temperature limit, lack of bleeding), it is surprising that it has not been employed as a single adsorbent for such purge and trap techniques. Its successful use in the determination of vinyl chloride and other industrial air contaminants is well documented[12]. Thermal desorption of activated carbon has been applied to the analysis of tobacco headspace[3] and acetone vapour in air[4], but it does not seem to have been applied to water analysis.

Our aim was to combine the advantages of CLSA using activated carbon filters with those of thermal desorption. In this paper we describe the major factors that must be considered for this purpose.

## EXPERIMENTAL

### *Closed-loop stripping apparatus*

Closed-loop stripping was performed in a commercially available apparatus (Brechbühler, Schlieren, Switzerland). This apparatus differs very little from the original instrument designed by Grob and Zürcher[13] but incorporates a very helpful temperature probe situated in the gas stream after the adsorption filter. An additional modification was made for the determination of filter breakthrough volumes. For these experiments, two filters each containing 8 mg charcoal were used in series and a special dual filter holder was constructed to accommodate both.

### *Activated carbon filters*

Adsorption filters containing 8 mg of 140–160-mesh Pica activated carbon with a bed diameter of 2.5 mm and a bed thickness of 3.5 mm were used. The filters were flushed before each use with 0.5 ml of redistilled carbon disulphide followed by 0.5 ml of *n*-pentane (Merck, p.a. grade).

After 10 min under the vacuum of an aspirator pump, the filters were heated in the injection port of a gas chromatograph at 250°C twice for 10 min with a helium flow-rate of 10–20 ml/min. This regimen gave satisfactory filter blanks, but varying amounts of carbon disulphide, sulphur dioxide and *n*-pentane remained as contaminants.

### *High-resolution gas chromatography–mass spectrometry (HRGC–MS)*

A Carlo Erba 4160 gas chromatograph interfaced to a Finnigan 4021C mass spectrometer with an INCOS 2000 data system was employed. To facilitate the recondensation of materials desorbed from the carbon filters, a glass capillary cold trap

immersed in liquid nitrogen was placed between the injector and the analytical GC column. The cold trap consisted of a single U-loop (15 cm), in which a 2-cm section was filled with silylated Chromosorb. The cold trap was attached to the column by a sliding PTFE shrink-tubing connection.

The analytical column was a 40 m × 0.32 mm I.D. glass capillary coated with a 2.3-$\mu$m film of immobilized SE-54. The GC column was interfaced directly to the ion source by a fused-silica capillary. The mass spectrometer was operated in the electron impact–positive ion mode with an ion source temperature of 250°C, a multiplier voltage of −1400 V, a dynode voltage of −3000 V, an emission current of −0.3 mA and an electron energy of 70 eV. The data system was programmed to scan the analyser from $m/z$ 33 to 300 in 1 sec.

*Materials*

The reference mixture used to evaluate the method contained the 17 compounds listed in Table I. It was prepared at individual compound concentrations of 100 ng/$\mu$l in methanol (Mallinkrodt, Nanograde) with the exception of components 1–5, which were purchased from Supelco at concentrations of 200 ng/$\mu$l in methanol. In addition, 1-chlorobutane served as an internal standard for quantification, using concentrations varying from 0.5 to 20 $\mu$g/l in the water samples.

For the optimization of the method the reference mixture was spiked into purified water that had been prepared by stripping tap water at 30°C for 1 h with a 5-mg CLSA filter. This gave sufficiently clean water when checked by the *n*-pentane extraction GC/electron-capture detection method of Henderson *et al.*[14]. The one exception was chloroform, which remained present at a concentration of approximately 2 $\mu$g/l.

Field samples were collected in 1-l or 150-ml flasks with ground-glass stoppers and stored at 4°C until taken for analysis.

*Closed-loop stripping procedure*

The stripping procedure of Grob and Zürcher[13] was used with slight modification. Volumes of 100 ml of pre-stripped tap water were spiked with 1 $\mu$g/l each of the reference mixture and internal standard. The stripping was carried out using a 150-ml gas wash-bottle. A sample temperature of 25°C was maintained throughout the stripping period. An optimal filter temperature of 35–37°C could be obtained after 2–3 min of stripping with the heating unit at 90°C. For very short stripping times (less than 5 min) or for the larger dual filter assembly, auxiliary heat from a hair dryer was required in order to attain the desired temperature.

The air flow-rate through the circuit with one 8-mg filter was 350 ml/min, and using the dual filter configuration it was 160 ml/min. A glass capillary restrictor was placed in line between the pump and the stripping flask in order to reduce the stripping flow-rate to 160 ml/min during normal operation with one 8-mg filter.

*Desorption procedure*

Activated carbon filters were desorbed by direct insertion into the unmodified injection port of the gas chromatograph. The initial conditions were injector temperature 225°C, inlet pressure 1.0 atm helium, column temperature 25°C, split flow 20 ml/min and septum sweep 2 ml/min.

For the results presented in Table II and in the application section, the following desorption procedure was applied:

(1) Place the cold trapping loop into a Dewar flask containing liquid nitrogen.

(2) Disconnect the cold trap from the column by the sliding PTFE connection. Plug the open inlet of the column with a short section of sealed capillary.

(3) Lower inlet pressure to *ca.* 0.1 atm.

(4) Open the septum cap and insert filter (carbon end up) after a 10-sec period of flushing with helium.

(5) Close the septum cap, split valve and sweep valve (time: 0.00 min).

(6) Allow the inlet pressure to remain at 0.1 atm for 1 min, then increase it slowly (during 30 sec) to 0.8 atm.

(7) Continue desorption for 6 min and 45 sec (time: 6.45 min).

(8) At 6.45 min, open the split flow and septum sweep valves.

(9) At 7.00 min, reduce the inlet pressure to *ca.* 0.1 atm.

(10) At 7.15 min, open the septum cap and remove the filter. Close the septum cap.

(11) At 7.45 min, reconnect the cold trap to the capillary column.

(12) At 8.00 min, remove the liquid nitrogen and replace it with a beaker of hot water.

(13) At 8.15 min, increase the inlet pressure to 1.0 atm and start the temperature programmer.

The column remained at 25°C for 3 min and was then programmed at 4°C/min to 160°C and held there for 2 min.

*Quantitation*

A single characteristic ion from the mass spectrum of each compound was chosen to serve as a quantitation ion (see Table I). GC–MS response factors were determined by five replicate injections (2 $\mu$l) of a methanolic standard solution containing 100 ng each of components 1–5 and 50 ng each of components 6–17. The areas of the mass spectrometric peaks were automatically integrated and compared with the peak area of the internal standard, 1-chlorobutane, monitored by its quantitation ion of $m/z$ 56.

Overall recoveries (Table II) were determined by comparison of single ion current peak areas obtained from a directly injected aliquot of the standard solution with the corresponding peak areas resulting from spiking the same amount of standard mixture to 100 ml of water followed by thermal desorption CLSA. Calibration factors (Table III) were established by spiking pre-stripped water at 1 $\mu$g/l concentrations.

## RESULTS AND DISCUSSION

*GC separation*

A total ion chromatogram obtained after thermal desorption-CLSA of a reference water sample is shown in Fig. 1 and demonstrates the excellent resolving power of the thick-film SE-54 column when used with an efficient cold trap. The particularly difficult separation of compounds 1–5 is depicted in Fig. 2 by the partial reconstructed mass chromatograms monitoring the respective quantitation ions.

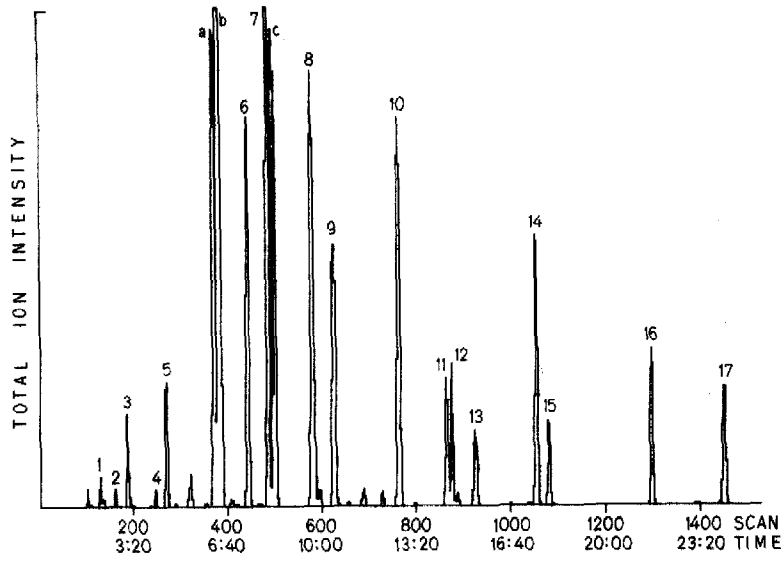


Fig. 1. Reconstructed total ion chromatogram of a thermal desorption closed-loop stripping analysis. Reference mixtures added to a water sample at 1 μg/l concentrations. Numbers refer to Table I. (a) Acetone; (b) *n*-pentane; (c) carbon disulphide. For experimental details, see text. Stripping and desorption conditions optimized for methylene chloride.

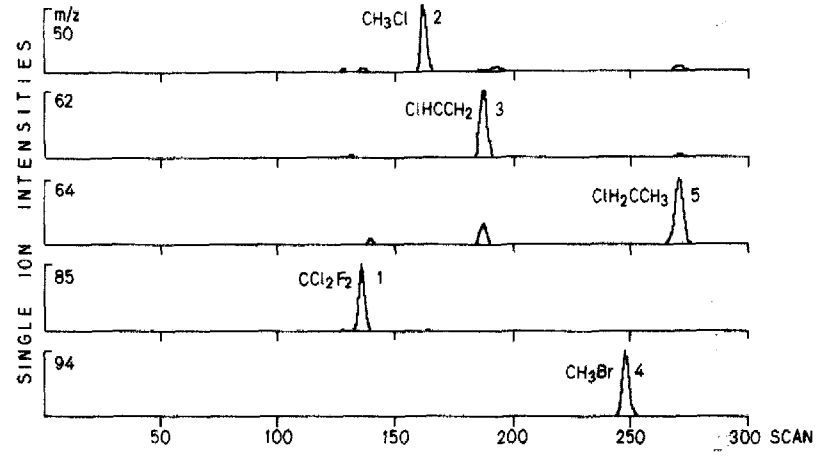


Fig. 2. Partial reconstructed mass chromatograms of a thermal desorption closed-loop stripping analysis. Same analysis as in Fig. 1.

Table I gives results from five replicate injections of the methanolic reference mixture. The GC–MS response factors for 12 of the 17 compounds could be measured with good precision. Only five compounds gave coefficients of variation above 10%. Of these five, three were the most volatile components of the mixture and the other two, methylene chloride and chloroform, suffered from severe peak broadening in the analyses of methanolic solutions.

TABLE I

GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC CHARACTERIZATION OF THE STANDARD MIXTURE USED FOR THE EVALUATION OF THE THERMAL DESORPTION CLOSED-LOOP STRIPPING ANALYSIS

| *Compound* | | | *Molecular ion (m/z)* | *Quantitation ion (m/z)* | *Retention time (min. sec)* | *GC–MS response factor, $\bar{x} \pm s$ (n=5)* |
|---|---|---|---|---|---|---|
| *No.* | *Formula* | *Name* | | | | |
| 1 | $CCl_2F_2$ | Dichlorodifluoromethane | 120 | 85 | 1.45 | 0.131 ± 0.05 |
| 2 | $CH_3Cl$ | Chloromethane (methyl chloride) | 50 | 50 | 2.12 | 0.268 ± 0.05 |
| 3 | $ClHCCH_2$ | Chloroethene (vinyl chloride) | 62 | 62 | 2.36 | 0.308 ± 0.05 |
| 4 | $CH_3Br$ | Bromomethane (methyl bromide) | 94 | 94 | 3.35 | 0.060 ± 0.004 |
| 5 | $ClH_2CCH_3$ | Chloroethane (ethyl chloride) | 64 | 64 | 4.25 | 0.044 ± 0.004 |
| 6 | $Cl_2CCH_2$ | 1,1-Dichloroethene (vinylidine chloride) | 96 | 96 | 7.20 | 0.030 ± 0.002 |
| 7 | $Cl_2CH_2$ | Dichloromethane (methylene chloride) | 84 | 84 | 8.00 | 0.333 ± 0.09 |
| 8 | ClHCCHCl | *trans*-1,2-Dichloroethene (ethylidene chloride) | 96 | 96 | 9.35 | 0.427 ± 0.006 |
| 9 | $Cl_2HCCH_3$ | 1,1-Dichloroethane | 98 | 63 | 10.23 | 0.773 ± 0.03 |
| 10 | $CHCl_3$ | Trichloromethane (chloroform) | 118 | 83 | 12.40 | 0.198 ± 0.05 |
| 11 | $Cl_3CCH_3$ | 1,1,1-Trichloroethane (methylchloroform) | 132 | 97 | 14.20 | 0.393 ± 0.018 |
| 12 | $ClC_4H_9$ | 1-Chlorobutane | 92 | 56 | 14.35 | 1.000 |
| 13 | $CCl_4$ | Tetrachloromethane (carbon tetrachloride) | 152 | 117 | 15.20 | 0.322 ± 0.007 |
| 14 | $C_2HCl_3$ | Trichloroethene (trichloroethylene) | 130 | 130 | 17.30 | 0.415 ± 0.018 |
| 15 | $CHBrCl_2$ | Bromodichloromethane | 162 | 83 | 18.02 | 0.496 ± 0.006 |
| 16 | $C_6H_5CH_3$ | Toluene | 92 | 92 | 21.40 | 1.061 ± 0.03 |
| 17 | $C_2Cl_4$ | Tetrachloroethene (tetrachloroethylene) | 164 | 164 | 24.10 | 0.390 ± 0.01 |

*Quantitative evaluation of the method*

For successful quantitative use of the thermal desorption CLSA, several steps of the procedure have to be optimized:

(1) the transfer of volatile organic compounds from aqueous solution into the gas phase (stripping) combined with simultaneous enrichment of volatiles from the gas phase on to activated carbon (adsorption);

(2) thermal displacement of volatile compounds from the carbon filters (desorption) and subsequent concentration in the chromatographic column (cold trapping);

(3) separation and determination of individual volatile compounds using GC–MS (separation and quantification).

*Stripping*

The circulation of inert gas through the water sample (100 ml) with flow-rates of 3–6 ml/sec results in a well mixed water–gas bubble system. During passage through the water column the gas bubbles reach saturation with volatiles. Under these conditions, the stripping efficiency depends mainly on the stripping ratio. This ratio is defined as the volume of inert gas ($V_G$ = gas flow-rate × stripping time) divided by the volume of water sample ($V_W$). For constant gas flow-rates at a given sample volume, the stripping ratio is proportional to the purge time.

Fig. 3 shows the results of stripping experiments. The stripping efficiencies of

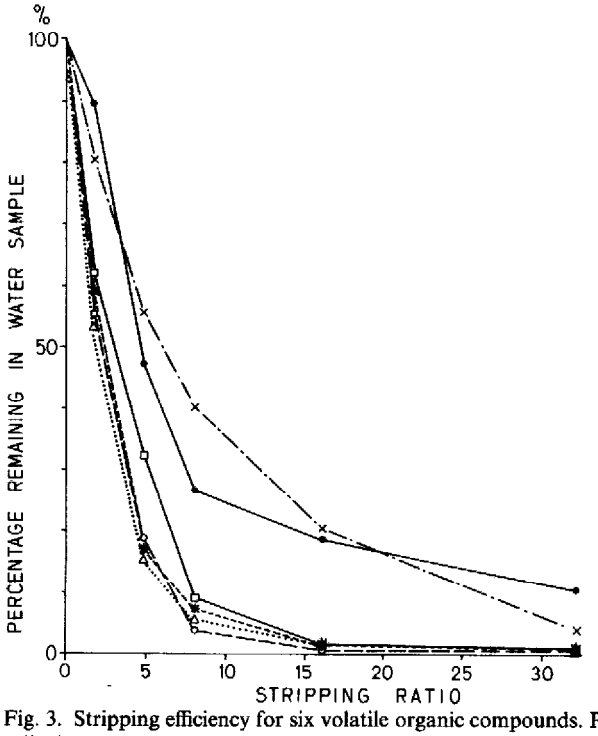


Fig. 3. Stripping efficiency for six volatile organic compounds. Percentage of compound remaining in the spiked water sample (initial concentrations: 5.0 μg/l) as a function of the stripping ratio. Aqueous concentrations were determined by pentane extraction followed by capillary GC with electron-capture detection. Compounds (see Table I): ●, 10; ○, 11; △, 13; □, 14; ×, 15; ✱, 17.

six selected volatile compounds are plotted as a function of the stripping ratio. Compounds 11, 13, 14 and 17 are stripped with more than 90% efficiency with a purge ratio of about 8, which, in our system, is equivalent to a purge time of 2.5 min. To ensure a sufficient stripping efficiency for chloroform and bromodichloromethane (compounds 10 and 15), a much higher purge ratio would be needed. This behaviour can be explained by their lower distribution coefficient between the aqueous and gaseous phases. Such coefficients, known as Henry's law constants ($H_c$), can be applied to predict stripping behaviour and are estimated from individual vapour pressure and aqueous solubilities (see Table II and the references cited therein). For the range of compounds tested, 1–17, dichloromethane showed the lowest stripping tendency ($H_c$ = 0.002 atm $m^3$ $mol^{-1}$) and dichlorodifluoromethane (Freon 12) the highest ($H_c$ = 2.9 atm $m^3$ $mol^{-1}$).

$H_c$ values are temperature dependent and may differ with water composition, *e.g.*, the solubility of volatiles may change with content of solubilizing water constituents.

*Adsorption*

During stripping, volatile organics are continuously transferred to the carbon filter. The gas volume passing through the filter is identical with the gas volume used for stripping. The efficiency of the carbon filter in retaining volatiles is governed by the volume and humidity of the transport gas, the concentrations and carbon affinities of the components of the mixture and the temperature of the filter bed.

Increased humidity of transport gas and elevated filter temperature reduce the capacity of the carbon filter. A compromise had to be made between the optimal temperature of the carbon bed for adsorption and the temperature required to reduce the relative humidity.

To limit water adsorption during enrichment of volatiles the stripping gas was heated upstream of the carbon filter so as to reduce the relative humidity to below 40%[13].

The breakthrough volumes listed in Table II reflect the capacity of the carbon filter to retain volatile organic chemicals. Individual adsorption capacities for the small halogenated molecules tested are related to their vapour pressure (boiling point) and can be divided into three groups; low capacity (1–4), intermediate capacity (5–7) and high capacity (8–17) compounds. The capacity for compounds of interest may be reduced by the adsorption of polar or heavier volatile compounds through displacement effects.

*Desorption*

Volatiles enriched on the carbon filter are separated from it by thermal desorption into a stream of heated inert gas. The efficiency of thermal desorption depends on the temperature of the carbon filter during desorption and the volume of desorbing gas (flow-rate × desorption time).

The desorption temperature must remain below the threshold for pyrolytic decomposition, which we observed at injector temperatures higher than 275°C. Using a flow direction opposite to the adsorption flow, the desorption volume has to be related to the adsorption volume (stripping volume) to complete desorption. Owing to practical limitations, the desorption volume was roughly 10% of the adsorption volume (see Table II).

*Cold trapping*

In the course of developing thermal desorption CLSA, we observed significant breakthroughs of highly volatile compounds from a simple capillary cold trap immersed in liquid nitrogen. This behaviour was discovered while GC–MS data were acquired during the desorption process. A detailed documentation and discussion of this breakthrough phenomenon has been presented separately[15]. In summary, it could be shown that quantitative trapping of highly volatile organic compounds (boiling point < 70°C) cannot be assumed even at the temperature of liquid nitrogen (−196°C). This problem was solved by incorporating a 2-cm section of silanized chromosorb (120–140 mesh) filled into the 15-cm trapping loop. The increased surface area gave essentially 100% recondensation for all of the compounds in our standard mixture.

The overall recoveries given in Table II show what we were able to achieve during initial experiments in our laboratory. These values are disappointingly low and vary drastically within the reference mixture. It can be concluded that the volatility range of our reference mixture (b.p. −30 to 130°C) was too large to be covered by the operating conditions of thermal desorption CLSA.

TABLE II

METHOD EVALUATION RESULTS FOR SIXTEEN VOLATILE ORGANIC COMPOUNDS DETERMINED BY THERMAL DESORPTION CLOSED-LOOP STRIPPING ANALYSIS

Stripping conditions: 8-mg dual filter; sample size, 100 ml; concentration, 1 μg/l each; sample temperature, 25°C; filter temperature, 36°C; stripping flow, 160 ml/min; stripping time, 5 min. Breakthrough volumes determined at various stripping times (1–20 min). Desorption conditions: injector temperature, 225°C; desorption flow, 13 ml/min; desorption time, 7 min. Adsorption/desorption ratio = $\frac{160 \text{ ml/min} \times 5 \text{ min}}{13 \text{ ml/min} \times 7 \text{ min}} = 8.8$.

| *Compound* | *Boiling point (°C)*[17] | *Solubility in water (g/1000 g $H_2O$)*[18] | *Henry's law constant ($H_c$) × $10^{-3}$ (atm $m^3$ $mol^{-1}$)*[19] | *Breakthrough volume (ml)* | *Overall recovery (%)* |
|---|---|---|---|---|---|
| 1 | −30 | 0.3 | 2980 | < 160 | 26 |
| 2 | −24 | 6.3 | 40 | | 12 |
| 3 | −13 | 2.7 | 81 | | 21 |
| 4 | 4 | 8.4 | | | |
| 5 | 12 | 5.7[21] | 148 | 200 | |
| 6 | 37 | 4.2 | 190 | 1500 | ND* |
| 7 | 40 | 13.7 | 2.0 | 500 | |
| 8 | 48 | 6.3[21] | 67 | | 47 |
| 9 | 57 | 4.8 | 4.6 | | 46 |
| 10 | 62 | 8.2 | 2.9 | | 32 |
| 11 | 74 | 1.6 | 30 | | 43 |
| 12 | 78 | | | | 30 |
| 13 | 77 | 0.80[21] | 23 | > 3200 | 34 |
| 14 | 87 | 1.6 | 9.1 | | 52 |
| 15 | 90 | 5.2[19] | 2.4 | | 39 |
| 16 | 111 | 0.52[20] | 6.6 | | 27 |
| 17 | 121 | 0.15 | 15.3 | | 33 |

* Not determined because the solvent peak (methanol) precluded the determination of the recovery of these compounds.

To achieve optimum performance it is necessary to focus on a narrow range of compounds, adjust the gas volume (mobile phase) during adsorption and desorption and optimize the temperature of the carbon filter (stationary phase).

Practical recommendations for the described CLSA thermal desorption procedure are as follows. First, optimize the stripping gas volume for the selected range of compounds. (Except for chloromethane and dichloromethane, the gas volume required for sufficient stripping is smaller than the measured breakthrough volume.) Then, adjust the desorption volume (desorption time) to transfer all volatiles from the carbon on to the cold trap. (Maximize the desorption volume.)

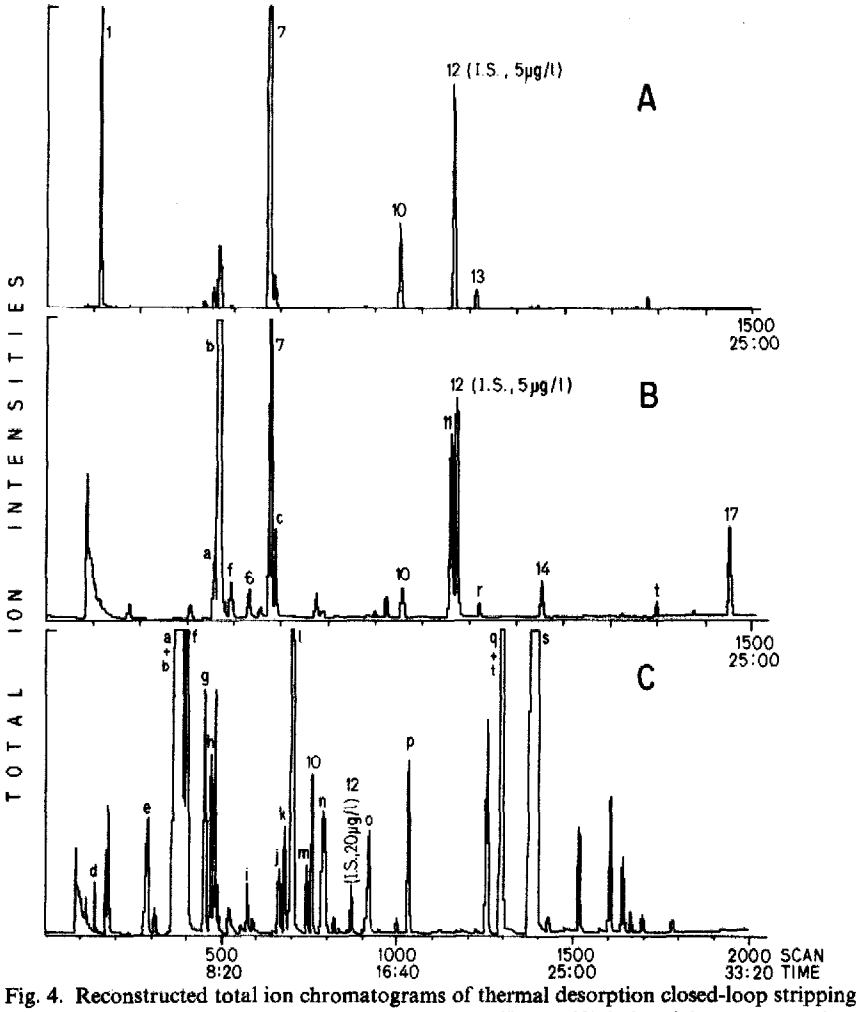


Fig. 4. Reconstructed total ion chromatograms of thermal desorption closed-loop stripping analysis. (A) Contaminated groundwater; (B) secondary sewage effluent; (C) industrial wastewater. Sample volumes, 100 ml (sample C diluted 20-fold); filter size, 8 mg; stripping time, 5 min; flow-rate, 160 ml/min. For desorption procedure and GC–MS conditions, see text. Peak numbers refer to Table I. Internal standard: 1-chlorobutane (peak 12). System contaminants: (a) acetone, (b) *n*-pentane and (c) carbon disulphide. Tentative peak assignments: (d) dimethyl ether, (e) ethanol, (f) diethyl ether, (g) methoxypropene, (h) methyl acetate, (i) cyclopentane, (j) butanol, (k) 2-butanone, (l) dipropyl ether, (m) ethyl acetate, (n) isopropanol, (o) 1-butanol, (p) pentenal, (q) butyl acetate, (r) benzene, (s) cyclopentanone, (t) toluene.

*Applications*

The method described was successfully applied to a number of samples of different types, including pure drinking and natural waters and heavily contaminated wastewaters. Although most analyses were performed on a qualitative basis, it was also possible to achieve semi-quantitative determinations for a number of compounds. A few selected examples are presented in this section. Fig. 4 shows the reconstructed total ion chromatograms obtained by thermal desorption CLSA of these typical samples.

Only three major compounds could be detected in a groundwater that had been used in a heat-exchange pump (Fig. 4A). The quantitative results were 35 μg/l of dichlorodifluoromethane (Freon R-12), 10 μg/l of dichloromethane and 6.2 μg/l of chloroform. The widely used Freon R-12 could be determined with a detection limit of approximately 1 μg/l. The increasing popularity of heat pumps using groundwaters and Freons as heat-transfer media will probably bring a growing demand for analytical methods that permit quantitative determinations of highly volatile organics such as the Freons.

Quantitative analyses were performed on a secondary effluent from a mechanical–biological sewage treatment plant in Zürich. The sample was also analysed by two established methods: (i) carbon disulphide elution CLSA[13] and (ii) sealed pentane extraction followed by glass capillary GC with electron-capture detection[14]. The results of these analyses, presented in Table III, showed excellent agreement for those compounds which could be determined by more than one method.

Fig. 4C shows a total ion chromatogram that was obtained by thermal desorption CLSA of a raw wastewater from a chemical plant. A series of low-boiling oxygenated compounds was tentatively identified by their mass spectra. This example demonstrates that the method presented in this paper is also applicable to highly

TABLE III

VOLATILE ORGANIC MICROPOLLUTANTS IN A SECONDARY SEWAGE EFFLUENT DETERMINED BY THREE DIFFERENT METHODS

(A) Thermal desorption–CLSA (this work); (B) $CS_2$ elution–CLSA with flame ionization detection[13]; (C) Sealed pentane extraction followed by glass capillary GC with electron-capture detection[14].

| *Compound* | *Concentrations (μg/l)* | | | *Calibration factor** |
|---|---|---|---|---|
| | *A* | *B* | *C* | |
| Dichlorodifluoromethane (Freon R-12) | 1.2 | ND** | ND | 0.009 |
| Dichloromethane | 1.6 | ND | ND | 2.8 |
| Chloroform | 0.46 | ND | 0.42 | 1.5 |
| Carbon tetrachloride | 0.06 | ND | 0.04 | 0.11 |
| 1,1,1-Trichloroethane | 9.8 | ND | 8.3 | 0.41 |
| Trichloroethylene | 0.70 | 0.36 | 0.65 | 0.47 |
| Tetrachloroethylene | 5.0 | 7.5 | 6.4 | 0.16 |
| Toluene | 0.44 | 0.43 | ND | 0.38 |

* Calibration factors are overall factors expressing GC–MS response and recovery efficiency relative to the internal standard.

** Not determined.

contaminated wastewaters. In this application, care must be taken to ensure that the adsorbent is not overloaded. This can be avoided by either diluting the sample with pre-stripped doubly distilled water or by reducing the stripping time. Quantitative work becomes especially critical when determining a very broad a spectrum of compounds because of the displacing effect of the heavier materials on the lighter ones.

## CONCLUSIONS

The thermal desorption procedure widens the applicability of CLSA to those compounds which interfere with the solvent peak during HRGC. In summary, thermal desorption can serve to determine trace amounts of compounds with boiling points below 60°C. The method is easily established in laboratories already familiar with the closed-loop stripping technique.

It is apparent from our results that the operating parameters must be balanced and optimized in order to obtain satisfactory quantitative results.

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## REFERENCES

1 K. Grob, *J. Chromatogr.*, 84 (1973) 255.
2 R. G. Melton, W. E. Coleman, R. W. Slater, F. C. Kopfler, W. K. Allen, T. A. Aurand, D. E. Mitchell, S. Y. Voto, S. V. Lucas and S. C. Watson, in L. H. Keith (Editor), *Advances in the Identification and Analysis of Organic Pollutants in Water*, Vol. 2, Ann Arbor Sci. Publ., Ann Arbor, MI, 1981, p. 597.
3 K. Grob and G. Grob, in *Proceedings of the Vth International Tobacco Scientific Congress, Hamburg*, Beckers Publishers, 1971, p. 235.
4 J. E. Scott, *Analyst (London)*, 102 (1977) 614.
5 K. Alben, *Anal. Chem.*, 52 (1980) 1821.
6 B. A. Colenutt and S. Thorburn, *Chromatographia*, 12 (1979) 519.
7 T. A. Bellar and J. J. Lichtenberg, *J. Am. Water Works Ass.*, 66 (1974) 739.
8 R. H. Brown and C. J. Purnell, *J. Chromatogr.*, 178 (1979) 79.
9 A. R. Trussel, F.-Y. Lieu and J. G. Moncur, in L. H. Keith (Editor), *Advances in the Identification and Analysis of Organic Pollutants in Water*, Ann Arbor Sci. Publ., Ann Arbor, MI, 1981, p. 171.
10 P. A. Boland, B. A. Kingsley, D. F. Stivers and I. H. Pomerant, in L. H. Keith (Editor), *Advances in the Identification and Analysis of Organic Pollutants in Water*, Vol. 2, Ann Arbor Sci. Publ., Ann Arbor, MI, 1981, p. 831.
11 E. D. Pellizzari and L. Little, *Collection and Analysis of Purgable Organics Emitted from Wastewater Treatment Plants*, EPA-600/2-80-017, 1980.
12 J. E. Cuddeback, W. R. Burg and S. R. Birch, *Environ. Sci. Technol.*, 9 (1975) 1168.
13 K. Grob and F. Zürcher, *J. Chromatogr.*, 117 (1976) 285.
14 J. E. Henderson, G. R. Peyton and W. H. Glaze, in L. H. Keith (Editor), *Identification and Analysis of Organic Pollutants in Water*, Ann Arbor Sci. Publ., Ann Arbor, MI, 1976, pp. 105–112.
15 J. W. Graydon and K. Grob, *J. Chromatogr.*, 254 (1983) 265.
16 E. Molnar, J. W. Graydon and W. Giger, unpublished results.
17 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, CRC Press, Cleveland, OH, 53rd ed., 1972–73.
18 A. L. Horvath, *Halogenated Hydrocarbons, Solubility–Miscibility with Water*, Marcel Dekker, New York, 1982.
19 W. R. Maybe, J. H. Smith, R. T. Podoll, H. L. Johnson, T. Mill, T. W. Chou, J. Gates, I. W. Partridge, H. Jaber and D. Vandenberg, *Aquatic Fate Process Data for Organic Priority Pollutants*, SRI International, EPA Report No. 440/4-81-014, Washington, DC, 1982.
20 C. McAuliffe, *J. Phys. Chem.*, 70 (1966) 1267.
21 W. L. Dilling, *Environ. Sci. Technol.*, 2 (1977) 405.