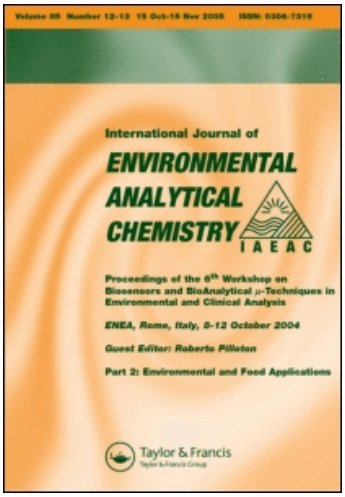

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Determination of Volatile Contaminants at the ng · l^{-1} Level in Water by Capillary Gas Chromatography with Electron Capture Detection

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An improved analytical headspace method is described for the quantiative determination of volatile contaminants in water. Detection limits at the 1.0 ng · l^{-1} level or better can be achieved for carbon tetrachloride using a suitable capillary column gas chromatograph and electron capture detector. The method is also applicable to the analyses of haloforms and associated halomethanes and haloethanes in drinking waters or quantitation of low ppt concentrations in ground or surface waters. This headspace technique is simple, inexpensive, easily applied to field conditions and well-suited for cryogenic capillary column chromatography.

KEY WORDS: Volatile, contaminants, water, analysis, gas chromatography.

INTRODUCTION

The determination of volatile contaminants, in particular haloforms in chlorine treated waters, is based on gas chromatography with a variety of extractive methods such as direct aqueous injection,[1] liquid/liquid extraction[2,3] and purge and trap procedures.[4] A more

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comprehensive method, also applicable to a larger variety of compounds is the closed loop stripping procedure developed by Grob and Zürcher[5] and with further adaptation for gas chromatographic-mass spectrometric analysis.[6] Although it has a high sensitivity, that method is difficult to use under field conditions and is based on carbon disulfide as the extraction solvent. Therefore, carbon disulfide and those compounds which elute before it cannot be determined with that method. Furthermore, its recovery efficiencies for highly volatile compounds were only 4 to 12 percent.[7] Overall, the low sensitivities of the above procedures and the analytical constraints of the closed loop technique limit their use in surface water studies of highly volatile compounds.

The principle of a solvent-free headspace method for the analysis of low-level volatile contaminants was described earlier by Kaiser and Oliver,[8] based on the equilibration of dissolved compounds in water with a small volume of gaseous headspace under reduced pressure at elevated temperature. They found the highest recovery of chloroform to occur at an equilibration temperature of 90°C after 30 minutes with a 2 ml headspace. The recoveries appeared linear for chloroform over a concentration range of 1 to 10 μg/l. This technique was applied to the determination of five volatile chloro- and chlorofluorocarbons in Lake Erie.[9] The samples were isolated in a similar manner using ampoules that were flame sealed. For analysis the gaseous content was quantitatively transferred into a centrifuge tube by a water displacement procedure. However, this technique was found to be limited to the range of compounds studied. In addition, sample losses were observed for carbon disulfide, methylene chloride and the chloro-ethanes/ethylenes when exposed to the atmosphere during filling of the syringe and for the brominated species when bubbled through the displacement water. These limitations were resolved and are now reported. As described earlier, the core element of this method is the transfer of the contaminants into an evacuated headspace resulting in their isolation as a small volume of gas. This matrix is highly suitable to cryogenic capillary column gas chromatography which provides an extended range of contaminant detection and allows greater flexibility in sample volume to be injected. As a result, a significant enhancement in sensitivity and chromatographic performance is achieved. Sample losses were minimized by removal of the water displacement step

and containment of the sample without exposure to the atmosphere at ambient temperatures prior to analysis.

Although this method is well suited to the analysis of haloforms in chlorine treated potable waters, its sensitivity is much better than that required for the levels commonly observed. Therefore, the major benefit of this technique is for the analysis of lower trace levels of contaminants in ground and surface waters as found beyond the immediate vicinity of point sources. Thus, hydraulic movements of ground and surface waters can possibly be detected on the basis of such trace contaminant analyses. Moreover, in combination with other volatile constituents, a fingerprint pattern can be developed that promises to be useful for the determination of sources and movements of water in natural groundwater aquifers or surface water systems. As an example, this paper describes the improved methodology and its application to a variety of lake, river and well water samples with various trace contaminant distributions and their possible differentiation on the basis of such contaminant levels. To date this procedure has been applied to the analyses of over 1200 samples under varying field conditions employing land vehicles, small craft and the research vessel CSS Limnos, and is easily handled by one person.

EXPERIMENTAL

Sampling

Samples were normally collected in the field and the headspace processed within one hour of collection. A field team obtained water samples in 300 ml precleaned glass bottles, which were filled to capacity. These samples were transported to a base area where the headspace sample was isolated. Equipment needs varied dependent upon the location and vehicles in use. Usually a 20 amp gasoline generator was used to supply power, although some vehicles had power takeoffs on their engines and the research vessel CSS Limnos required no additional electrical supply. The headspace isolation apparatus is shown in Figure 1. For our purposes, the heating bath was a one liter aluminium coffee pot on a 15 amp hot plate/stirrer. The vacuum pump had a free air displacement of 113 l/min with a capacity of 92 kPa (Fisher Scientific Limited).

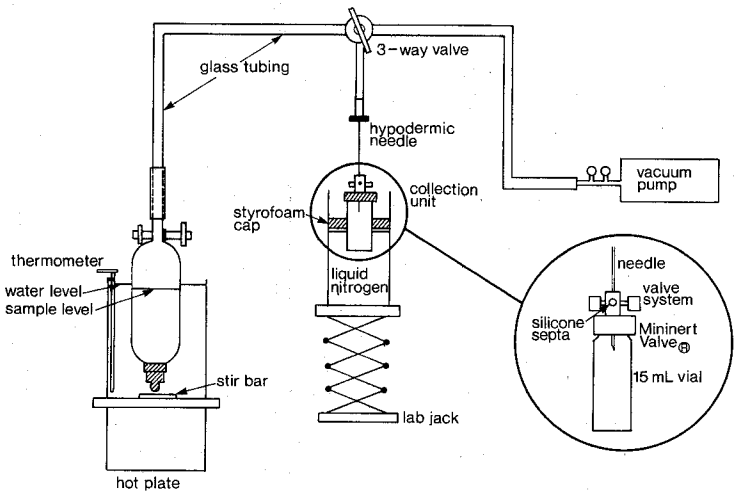

FIGURE 1 Apparatus for headspace analysis.

The collection unit was connected to the sample funnel and vacuum pump with glass tubing and separated from one another with a 3-way glass switching valve. For one day operations two 5 l dewars of liquid nitrogen were sufficient.

The samples for the results presented here were processed in the laboratory due to the close proximity of the stations. Samples were taken on October 29, 1981 from wells in the Burlington, Beamsville, Waterdown and Campbellville areas. Similar samples were obtained from a mineral spring in Ancaster and from Crawford Lake, Campbellville.

Headspace Collection

A 125 ml cylindrical separatory funnel was filled with a portion of the collected 300 ml sample. The funnel was drained to a volume of 100 ml, stoppered with a teflon-sleeved penny-head and attached to the experimental apparatus with a piece of tygon tubing. The headspace of the funnel was immediately evacuated with the vacuum pump through the funnel stopcock for two to three seconds. The stopcock was then closed and the funnel placed vertically into a heated water bath (90 to 95°C) with the sample level being slightly below that of the bath. While the sample was heating the collection

unit consisting of a 15 ml vial with a Mininert R valve (Chromatographic Specialties Ltd., Brockville, Ontario), and the sample lines were evacuated. The sample collection unit was then immersed approximately 0.5 cm in the liquid nitrogen by raising the plastic thermal container with a lab jack. After heating for five minutes, the stopcock was opened and the volatile portion of the sample transferred to the pre-evacuated collection unit by switching the 3-way glass valve. This transfer was promoted by raising the level of liquid nitrogen to one-half of the collection vial when the sample condensation layer reached the 3-way switching valve. The transfer was terminated by closing the stopcock when about 0.2 ml of the water vapor had condensed in the vial. The vial was then fully immersed for 10 seconds in the liquid nitrogen by raising the container on the lab jack. The liquid nitrogen was then withdrawn and the sample removed from the needle (22 gauge, stainless steel and 22° bevel) with a glove. The Mininert valve was moved to the closed position and the upper portion of the vial and cap inserted into the water bath for three to five seconds, removed and snuggly sealed by hand. The collection unit was then submerged in a beaker of distilled water and checked for leaks. With this equipment and technique, approximately 8 to 10 samples can be processed per hour. However, the processing rate can be increased up to threefold by heating several of the (headspace evacuated) samples simultaneously in a separate or larger water bath.

Essentially the headspace technique is a vacuum distillation with cryogenic trapping of the distillate. It was found that with the larger headspace volume and higher temperatures applied here, the headspace transfer gave sufficient sample for analysis with a shorter equilibration time than previously reported.[8] Also, the recovery levels obtained for chloroform were higher than before (90 percent as opposed to 73 percent) which is probably due to the larger headspace and minimization of sample loss at the collection point. For a comparison of the recovery rates of this headspace method with that of a liquid extraction method, 100 ml tap water samples were also extracted with 40 ml of pentane in separatory funnels. The pentane extracts were directly analyzed by gas chromatography and were compared with a standard solution of $CHCl_3$, $CHBrCl_2$ and $CHBr_2Cl$ in pentane. The same samples were also extracted by the headspace method.

Gas standards and recoveries

Each component was individually screened for purity by gas chromatography prior to use. Because of the high volatility of the compounds, we found that the most suitable procedure for the preparation of quantitative standards was to inject portions of each compound into a 15 ml vial filled with a predetermined amount of methanol and sealed with a Mininert valve. The individual compound concentrations were determined by weighing the vial before and after each injection. Thus, 150 μl injections of each of the compounds (see Table 1), 4, 5, 6, 7, 8, 12, and 14, and 50 μl injections

TABLE I

Recoveries and relative error for volatile analyses.

Compound	Number	Percent[a] recovery	Percent[b] RSD total	Detection[c] limits $ng \cdot l^{-1}$
Oxygen	1	—	—	—
Dichlorodifluoromethane	2	110	19	5.0
Trichlorofluoromethane	3	108	17	1.0
Vinyldene chloride	4	110	13	30.0
Carbon disulfide	5	85	15	30.0
Methylene chloride	6	102	18	30.0
1,2-dichloroethane	7	75	16	80.0
1,1-dichloroethane	8	84	19	80.0
Bromochloromethane	9	69	22	1.0
Chloroform	10	90	14	1.0
1,1,1-trichloroethane	11	94	15	0.9
1,2-dichloroethylene	12	104	18	40.0
Carbon tetrachloride	13	85	12	0.8
1,2-dichloropropane	14	81	19	30.0
Trichloroethylene	15	105	17	0.9
Dibromomethane	16	56	22	0.9
Dichlorobromomethane	17	58	20	1.0
Trichlorobromomethane	18	60	19	2.0
1,1,2-trichloroethane	19	54	25	20.0
Dibromochloromethane	20	54	22	1.0
Tetrachloroethylene	21	65	20	0.8
Bromoform	22	55	20	1.0
S-tetrachloroethane	23	48	27	1.0

[a]Adjusted for headspace losses.

[b]Percent RSD figures for splitless conditions outlined in total experimental section, reflects *total* experimental error for $n = 10$.

[c]Results for 100 μl injections, split/splitless mode of operation, five second hold time.

of each of the compounds 2, 3, 9, 10, 11, 13, 15 to 23 into a vial with 13.2 μl methanol resulted in stock solution A. The concentrations of the compounds in the standard (A) were also calculated from the volumes injected and their respective densities and were found to be identical with those determined from the weights. A secondary standard (B) was prepared by injecting 0.1 ml of solution (A) into another 15 ml sealed vial containing 14.9 ml methanol. A gaseous working standard (C) was then prepared by introducing 1 μl of standard (B) into a pre-evacuated 15 ml vial, sealed as before. The standard (C) was allowed to volatilize at room temperature for two to three minutes, after which a 100 μl injection of the gas phase was made on the gas chromatograph. This procedure resulted in concentrations of approximately 2 to 8 pg/μl in standard (C). For very low contaminant concentrations, another standard (D) was prepared by injecting 0.01 ml of (A) into a 15 ml vial filled with methanol and preparing a gaseous working standard (E) the same way as (C) from (B). A chromatogram, Figure 2, is given for a 100 μl injection of the working standard (C) using a 10:1 split ratio.

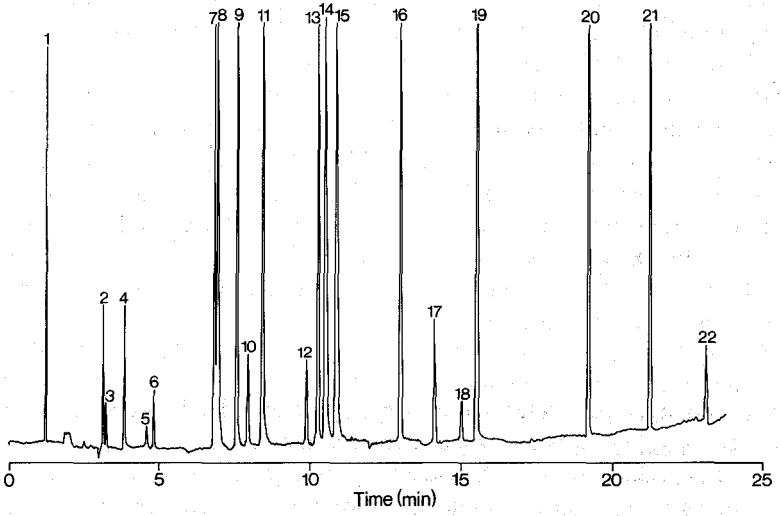

FIGURE 2 Gas chromatogram of working standard (C): see Table I for compound identification.

In order to avoid any carryover of contaminants in between samples, the headspace apparatus was cleaned between runs by

pumping hot air through the apparatus. This was done by attaching a piece of glass tubing over the hot plate and evacuating with the vacuum pump for at least 10 sec.

An alternate collection unit can be used if there is a requirement to shorten the collection time and an atmosphere essentially free of the contaminants. The needle can be substituted with a permanent cap fitted with 3 mm o.d. glass tubing. This requires exposing the frozen sample to air after the sample has been collected, since the vial must be removed from the permanent cap and sealed with a new one. This technique did not affect the recovery values but results in a three to five percent increase in the relative standard deviation. However, it allows for a more rapid processing of samples without introduction of a large error and was therefore the preferred technique for most of the samples.

Gas chromatography

A Hewlett–Packard Gas Chromatograph (Model 5700A) equipped with a ^{63}Ni electron capture detector (DANI) and cryogenic programming capability was used with a 25 m fused silica column (OV-101) and hydrogen (0.8 ml/min) as the carrier gas. The column was programmed from $-20°C$ to 80°C at 4°C/min with a two minute initial hold period. For analyses of drinking waters the instrument was operated with a 10:1 split ratio and 50 μl injections. For groundwater samples 100 μl injections were made using the splitless mode with the injector vented after a 5 sec hold time. The injector block was used without heating and had a temperature readout of 20°C. The detector was heated separately to 270°C with nitrogen as the cell gas.

Cryogenic temperatures were achieved with liquid nitrogen, supplied from a 165 l cylinder or a 30 l floor dewar system. The floor dewar appears preferable as we experienced back pressure problems on the solenoid valve when using the larger tanks.

For determation of the recovery rates of the entire process, it was necessary to produce a standard with known concentrations. It was found that immediately upon spiking of water, with small amounts of volatiles (1 μl of stock B), a significant portion of some volatiles escaped to the headpsace, due to equilibration between water and headspace. In order to determine the true concentration of the

volatiles in the water, the headspace volume had to be measured and the concentration of the individual components determined. After a three-hour equilibrium period, the loss to the headspace was measured by analysis of the volatiles concentrations in the headspace. The true volatiles concentration in the spiked water was then calculated by difference. We feel this procedure gave the best possible sample with a known concentration that was representative of a field sample and handled in a similar manner.

The recovery measurements were made by spiking, 100 ml of tripled-distilled, volatile-free water with 1 μl of stock solution B. Method blanks of the triple-distilled water and samples of laboratory air showed no measureable quantities of the contaminants under study.

RESULTS AND DISCUSSION

Recovery values are given in Table 1, for the compounds listed. These were determined on the samples previously described in the experimental section and are the mean values with associated error for ten separate measurements.

The total mean experimental error (percent RSD_{total}) for the recoveries was ± 18.6 percent using splitless injection with a five second hold time and 100 μl injections. This error was reduced to ± 14.3 percent when operated under the same experimental conditions but with a 10:1 split ratio and the necessary insert change-over. The mean instrumental error on ten duplicate injections was ± 12.6 percent for the splitless mode of operation.

This left a calculated net relative standard deviation for the headspace procedure of only ± 6.0 percent. It is therefore apparent that a major source of error for this method originates with the chromatography and, as partially implied from the percent RSD values, is a function of the injector reproducibility. For this particular injector these values are within reason. Hewlett–Packard estimates nominal reproducibility for this injection at 6 to 8 percent with the split mode of operation and 8 to 10 percent with splitless for this type of application (D. McIntyre, personal communication).

We found the split procedure more than adequate to the analyses of tap waters using 50 μl injections. For ground water samples the

splitless technique gave excellent results. With a five second hold time and a 100 μl injection, detection limits better than 0.75 ng·l^{-1} for carbon tetrachloride could be achieved at signal to noise ratios of three to one (Figure 3). The recovery range for this operation was 48 to 110 percent for the 22 compounds investigated (Table I) with a tendency to poorer recoveries for the less volatile components.

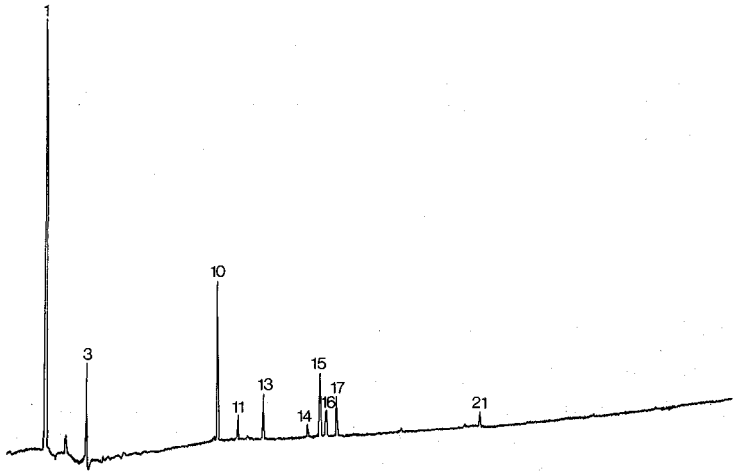

FIGURE 3 Gas chromatogram of volatile contaminants in a water sample from Crawford Lake. Compound numbers are given in Table I, the concentrations in Table II.

As mentioned previously, we feel that this level of analytical sensitivity and chromatographic separation can be useful in determining water flows and distributions. Results from our recent surveys[10,11] support this view as, for example, specific distinctions could be made between certain industrial and municipal outfalls in the Welland and Niagara River watersheds. Further examples for the application of this method to a variety of ground, surface and treated waters are given in Table 2. Among those tested was Crawford Lake, an isolated, meromictic water body located in an agricultural setting not exposed to any known source of industrial or municipal runoffs. Yet the lake contained small concentrations of many halogenated compounds of municipal and industrial origin (Figure 3, Table II). A reasonable explanation for their source would be from atmospheric transportation, a well established route of contamination of surface water.

TABLE II

Concentrations of volatiles in selected surface, well and treated waters in $ng \cdot l^{-1}$.

	Campbellville[a]	Crawford Lake	Waterdown[a]	Ancaster	Burlington[a]	Beamsville[a]	Burlington[b]	Niagara[b] Falls	Port[b] Robinson
Trichlorofluoromethane	ND	13	ND	ND	ND	ND	1,500	ND	ND
Chloroform	ND	58	41	ND	20	34	3,900	13,000	250,000
1,1,1-trichloroethane	ND	5.9	6.4	ND	2.6	13	75	15	10
Bromochloromethane	ND	ND	ND	ND	ND	ND	ND	ND	15
1,2-dichloropropane	T	T	ND	ND	T	ND	ND	ND	210
Carbon tetrachloride	8.5	3.8	3.2	1.1	1.3	17	54	100	900
Trichloroethylene	ND	32	ND	11	ND	10	ND	ND	45
Dibromomethane	4.9	10	ND	4.3	6.3	ND	ND	5	5
Dichlorobromomethane	3.7	20	27	6.1	16	25	3,800	11,000	160,000
Tetrachloroethylene	10	9.0	21	7.1	31	4.2	25	240	120
Dibromochloromethane	ND	ND	ND	ND	ND	ND	910	1,000	4,000
Bromoform	ND	ND	ND	ND	ND	ND	150	840	300
1,1,2-trichloroethane	ND	ND	ND	ND	ND	ND	ND	120	480

[a]Well water.
[b]Tap water.
ND—Not detected (less than detection limit, refer to Table I).
T—Trace amount (less than detection limit, greater than noise level).
+—Values not corrected for recovery values.

The wells from Waterdown, Burlington and Beamsville have higher than background levels of chloroform and dichlorobromomethane, which are normally the two most distinctive compounds in potable waters indicating some contact with chlorine-treated water. These three samples were the only ones with municipal treated water supplies in their area. The wells also showed varying degrees of trace contamination with industrial materials such as 1,2-dichloropropane, trichloroethylene, tetrachloroethylene and carbon terachloride. Although the differences, between various water sources appear minimal, they can be important in establishing water distributions and input sources of specific contaminants. As in the above examples, distinction between ground or surface water, municipal contamination and various industrial contaminants can be made on the basis of the composition of the volatiles.

Treated water supplies are quite different again as a result of the by-products of chlorination. High levels of chloroform, dichlorobromomethane, dibromochloromethane and to a lesser extent bromoform and 1,1,2-trichloroethane are typical for most potable waters. Also most raw water supplies still contain trace levels of the other volatile contaminants that contribute to the labelling effect and as such are often more distinct. Figure 4 shows a

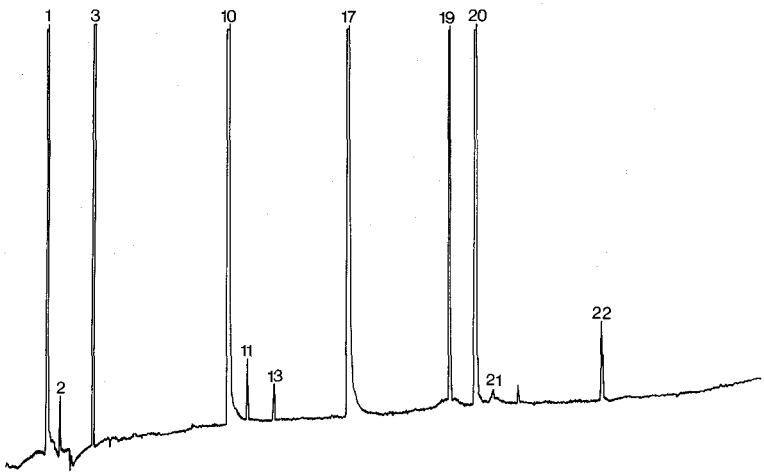

FIGURE 4 Gas chromatogram of a Burlington tap water sample. Compound numbers are given in Table 1, the concentrations in Table II.

chromatogram obtained for Burlington tap water with the concentrations given in Table II.

The effect of high concentrations of volatiles and other constituents on the recovery levels appears to have no effect based on the experimental data for tap water constituents. The results for treated water from Niagara Falls indicate that chloroform, dichlorobromomethane, dibromochloromethane and bromoform were within 50 percent of the values obtained in 1977 by different procedures. As to be seen from the data in Table III, the headspace method also compares well with the extraction of treated water by pentane. Both for chloroform and $CHBrCl_2$, the means for the two methods differ by less than 10 percent of the observed values.

TABLE III

Comparison of the headspace method with the pentane extraction method for haloforms in Burlington tap water. Data in $\mu g \cdot l^{-1}$, means and standard deviations for seven analyses each.

	Method of analyses	
Compound	Headspace	Pentane extraction
$CHCl_3$	4.3 ± 0.6	4.5 ± 1.2
$CHBrCl_2$	4.1 ± 0.9	4.4 ± 1.7
$CHBr_2Cl$	1.0 ± 0.2	2.3 ± 1.3

To our knowledge, this headpsace procedure presents the most sensitive technique available for the quantitative determination of highly volatile organics in water. Table IV lists a number of other routine analytical methods together with their detection limits. From the point of analytical sensitivity, only the closed-loop stripping procedure[5] appears competitive. However, that method is more suited to the analysis of contaminants with somewhat higher boiling points.[7] At present, the main source of error appears to be associated with our instrumentation, which can be reduced with better injector reproducibility. Sensitivity and accuracy of this method is expected to improve further with the introduction of an on-column injector and also be interfacing with GC/MS procedures

TABLE IV

Detection limits for volatile contaminants in water for various analytical techniques concentrations in $ng \cdot l^{-1}$.

Method	Reference	Sample size	Detector	Detection limits
Direct aqueous	1	10 μl	GC/EC	100[a]–2000
Injection	12	100 μl	GC/MS, fragmentography	100 –800[a]
Liquid/liquid	2	5 ml	GC/EC	1000 –or higher
extraction	3	10 ml	GC/EC	100 –or higher
	13	101	GC/MD	5 –50
	14	5 ml	GC/ED	40[a]–50,000
GROB, closed	6	1 l	GC/FID	1[b]–or higher
loop stripping	7, 13	41	GC/MIS	1[c]–10
Purge/trap	4	5 ml	GC/MCD	500 –or higher
	13	5 ml	GC/ECD	100 –50,000
Our method	—	100 ml	GC/EC	0.75[a]–80

[a]Detection limit for carbon tetrachloride.
[b]Detection limit for benzene.
[c]Detected 4 $ng \cdot l^{-1}$ carbon tetrachloride in drinking water influent.
GC—Gas chromatography, MS—mass spectrometry, EC—electron capture detector.
FID—Flame ionization detector, MCD—microcoulometric detector.
ECD—Electroconductivity detector, (Hall).

as no solvent is employed. The sensitivity of the method can be increased by using 7 ml collection vials and a 30 second hold time with up to 1000 μl injections in either split or splitless mode. However, we would recommend these conditions only to be applied when extreme sensitivity requirements are essential since the gas chromatographic parameters are more difficult to establish.

References

1. A. Nicholson, O. Meresz and H. Lemyk, *Anal. Chem.* **49,** 814 (1977).
2. J. P. Mieure, *J. Am. Water Works Assoc.* **49,** 60 (1977).
3. J. J. Richard and G. A. Junk, *J. Am. Water Works Assoc.* **49,** 62 (1977).
4. T. A. Bellar and J. J. Lichtenberg, *J. Am. Water Works Assoc.* **66,** 739 (1974).
5. K. Grob and F. Zürcher, *J. Chromatog.* **117,** 285 (1976).

6. F. Zürcher and W. Giger, *Vom Wasser* **47,** 37 (1976).
7. W. E. Coleman, R. G. Melton, R. W. Slater, F. C. Kopfler, S. J. Voto, W. K. Allen and T. A. Aurand, *J. Am. Water Works Assoc.* **73,** 119 (1981).
8. K. L. E. Kaiser and B. G. Oliver, *Anal. Chem.* **48,** 2207 (1976).
9. K. L. E. Kaiser and I. Valdmanis, *J. Great Lakes Res.* **5,** 160 (1979).
10. K. L. E. Kaiser and M. E. Comba, *J. Great Lakes Res.*, **9,** 274 (1983).
11. K. L. E. Kaiser, M. E. Comba and H. Huneault, *J. Great Lakes Res.*, **9,** 212 (1983).
12. Toshiro Fujii, *J. Chromatog.* **139,** 297 (1977).
13. R. G. Melton, W. E. Coleman, R. W. Slater, F. C. Kopfler, W. K. Allen, T. A. Aurand, D. E. Mitchell, S. J. Voto, S. V. Lucas and S. C. Watson, in: *Advances in Identification and Analysis of Organic Pollutants in Water, II* (L. H. Keith, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1982).
14. A. R. Trussell, J. L. Cormer, M. D. Umphres, P. E. Kell and J. G. Moncur, in: *Water Chlorination, Environmental Impact and Health Effects, III* (R. L. Jolley, W. A. Brungs, R. B. Cumming and V. A. Jacobs, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1979), p. 39.