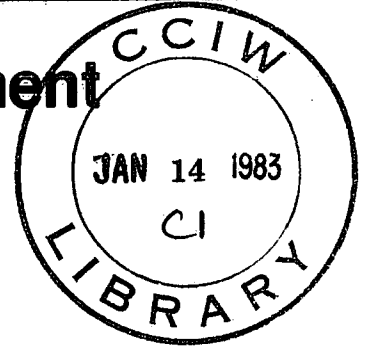**Environment Canada**

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water at the ng·L^{-1} level

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ABSTRACT

An improved analytical headspace method is described for the quantitative determination of volatile contaminants in water. Detection limits at the 1.0 $ng \cdot \ell^{-1}$ 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 adapted to field conditions and well-suited for cryogenic capillary column chromatography.

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 comprehensive method, also applicable to a larger variety of compounds is the closed loop stripping procedure developed by Grob and Zürcher (5) with further adaption for gas chromatographic-mass spectrometric analysis (6). Although of high sensitivity, this method is more difficult to use under field conditions and is based on carbon disulfide as the extraction solvent. Thus carbon disulfide and those contaminants which elute before it cannot therefore be determined in these samples. The low sensitivities of the aforementioned procedures and the physical restraints of the closed loop technique are limitations on their use in surface water studies.

The principle of a solvent-free headspace method for the analysis of low-level volatile contaminants was described earlier by Kaiser and Oliver (7), 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 chloro-fluorocarbons in Lake Erie (8). 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. Sample losses were observed for carbon disulfide, methylene chloride and the chloro-ethanes/ethylenes when exposed to atmosphere during the gas chromatographic step 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 signifi-cant enhancement in sensitivity and chromatgraphic performance is achieved. Sample losses were minimized by removal of the water displacement step and containment of the sample without exposure to the atmosphere prior to analysis.

Although this method is well suited to the analysis of halo-
forms in chlorine treated potable waters, its sensitivity is much
better than that required for the levels commonly observed. There-
fore, 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 move-
ments 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 head-space 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 aluminum 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).

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 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.

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 (7). 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.

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 only suitable procedure for the preparation of quantitative standards was to inject portions of each compound into a 15 mℓ vial filled with 13.2 mℓ methanol and sealed with a Mininert valve. The individual compound concentrations were determined by weighing the vial before and after each injection. Except for carbon disulfide and the dichloroethanes-methanes which were 150 μℓ injections, 50 μℓ injections of each compound were made to yield stock solution A. A secondary standard B was prepared by injecting 0.1 mℓ of solution A into a 15 mℓ vial sealed with a

Mininert valve and containing 14.9 ml of methanol. A working standard (C) was prepared by introducing 1 μl of solution B into a pre-evacuated 15 ml vial and 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 gave injection concentrations of approximately 2 to 8 pg/μl. A chromatogram, Figure 2, is given for a 100 μl injection of the working standard (C) using a 10:1 split ratio.

The headspace apparatus was cleaned between runs by introducing 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.

An alternate collection unit can be used if there is a requirement to shorten the collection time. The needle can be substituted with a permanent cap fitted with 3 mm o.d. glass tubing. This requires exposing the sample to atmosphere 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 any of the recovery values but gives a three to five percent increase in the relative standard deviation.

Gas Chromatography

A Hewlett-Packard Gas Chromatograph (Model 4700A) equipped with a [63]Ni electron capture detector (DANI) and cryogenic progamming capability was used with a 25 m fused silica column (SP-2100) and hydrogen (0.8 mℓ/min) as the carrier gas. The column was programmed from -20° 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 split/splitless mode with a residence time of five seconds. 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 determination of the recovery rates of the entire process, it was necessary to produce a standard with known concentrations. It was found that immediatley upon spiking of water, with small amounts of volatiles (1 µℓ of stock B), a significant portion of some volatiles escaped to the headspace, due to equilibration between

water and headspeace. 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 head-
space. 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 split/splitless injection with

a five second hold time and 100 μℓ injections. This value 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 split/splitless mode of operation.

This left a calculated net relative standard deviation for
the headspace procedure of only ±4.0 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 split/
splitless for this type of application (D. McIntyre, personal communi-
cation).

We found that the split procedure is more than adequate to
the analyses of tap waters using 50 μℓ injections. For ground water
samples the split/splitless technique gave excellent results. With a
five second hold time and a 100 μℓ injection, detection limits better
than 0.75 $ng \cdot \ell^{-1}$ for carbon tetrachloride could be achieved at signal
to noise ratios of three to one. The recovery range for this

operation was 48 to 110 percent for the 22 compounds investigated
(Table 1) with a tendency to poorer recoveries for the less volatile
components.

As mentioned previously, we feel that this level of analyti-
cal sensitivity and chromatographic separation can be useful in deter-
mining water flows and distributions. Results from our recent surveys
(9,10) 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. A reasonable explanation for
their source would be from atmospheric transportation, a well estab-
lished route of contamination of surface water.

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 con-
tamination with industrial materials such as 1,2-dichloropropane, tri-
chloroethylene, tetrachloroethylene and carbon tetrachloride.
Although the differences, between various water sources appear mini-
mal, they can be important in establishing water distributions and in-
put sources of specific contaminants. As in the above examples, dis-
tinction between ground or surface water, municipal contamination and
various industrial contaminants can be made on the basis of the compo-
sition 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.

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.

To our knowledge, this headspace procedure presents the most sensitive technique available for the quantitative determination of highly volatile organics in water. Table 3 lists a number of other routine analytical methods together with their detection limits. From the point of anaytical sensitivity, only the closed-loop stripping procedure (5) appears competitive. However, that method gives poor recovery efficiencies (4 to 12 percent) for most trihalomethanes (14) and is more suited to the analysis of contaminants with somewhat higher boiling points. 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 by interfacing with GC/MS procedures 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 200 μl split/splitless injections. 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.

LITERATURE CITED

1. Nicholson, A.; Meresz, O.; Lemyk, B. Anal. Chem., 1977, 49, 814.

2. Mieure, J.P. J. Am. Water Works Assoc., 1977, 49, 60.

3. Richard, J.J; Junk, G.A. J. Am. Water Works Assoc., 1977, 49, 62.

4. Bellar, T.A.; Lichtenberg, J.J. J. Am. Water Works Assoc., 1974, 66, 739.

5. Grob, K.; Zürcher, F. J. Chromatog., 1976, 117, 285.

6. Zürcher, F.; Giger, W. Vom Wasser, 1976, 47, 37.

7. Kaiser, K.L.E.; Oliver, B.G. Anal. Chem., 1976, 48, 2207.

8. Kaiser, K.L.E.; Valdmanis, I. J. Great Lakes Res., 1979, 5, 160.

9. Kaiser, K.L.E.; Comba, M.E. Volatile Contaminants in the Welland River Watershed, 1981, submitted to J. Great Lakes Res.

10. Kaiser, K.L.E.; Comba, M.E. Volatile Contaminants in the Lower Niagara River, 1981, submitted to J. Great Lakes Res.

11. Fujii, Toshiro. J. Chromatog., 1977, 139, 297.

12. Melton, R.G.; Coleman, W.E.; Slater, R.W.; Kopfler, F.C.;
    Allen, W.K.; Aurand, T.A.; Mitchell, D.E.; Voto, S.J.;
    Lucas, S.V.; Watson, S.C. Prepublication EPA 600/D-81-060, 1981,
    submitted to Ann Arbor Science Publishers, Inc., Ann Arbor,
    Michigan; Advances in Identification and Analysis of Organic
    Pollutants in Water, II, (L.H. Keith, ed.).

13. Trussell, A.R.; Cormer, J.L.; Umphres, M.D.; Kell, P.E.;
    Moncur, J.G. "Water Chlorination, Environmental Impact and
    Health Effects", (R.L. Jolley, W.A. Brungs, R.B. Cumming and
    V.A. Jacobs, eds.) Ann Arbor Science Publishers, Inc., Ann Arbor,
    Michigan, 1979, 3, 39.

14. Coleman, W.E.; Melton, R.G.; Slater, R.W.; Kopfler, F.C.;
    Voto, S.J.; Allen, W.K.; Aurand, T.A. (DWRD0010), presented at
    the Am. Water Works Assoc., Water Quality Technology Conf., VII,
    Philadelphia, Penn., Dec., (1979).

FIGURE CAPTIONS

Figure 1. Apparatus for headspace analysis.

Figure 2. Gas chromatogram of working standard (C): see Table 1 for
compound identification.

3-way valve
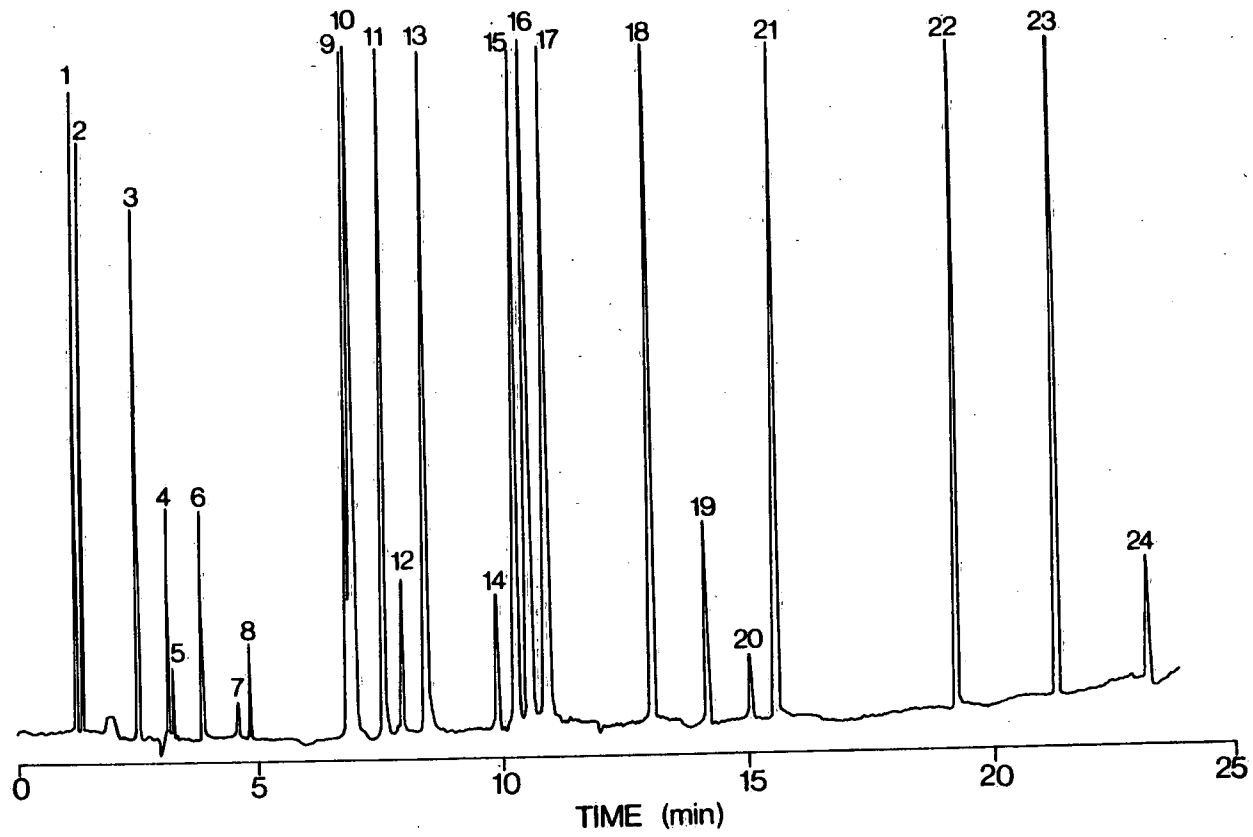
glass tubing

hypodermic
needle

collection
unit

styrofoam
cap

vacuum
pump

thermometer

water level
sample level

liquid
nitrogen

stir bar

lab jack

hot plate

needle

valve
system

silicone
septa

Mininert
Valve®

15 mL vial

TIME (min)
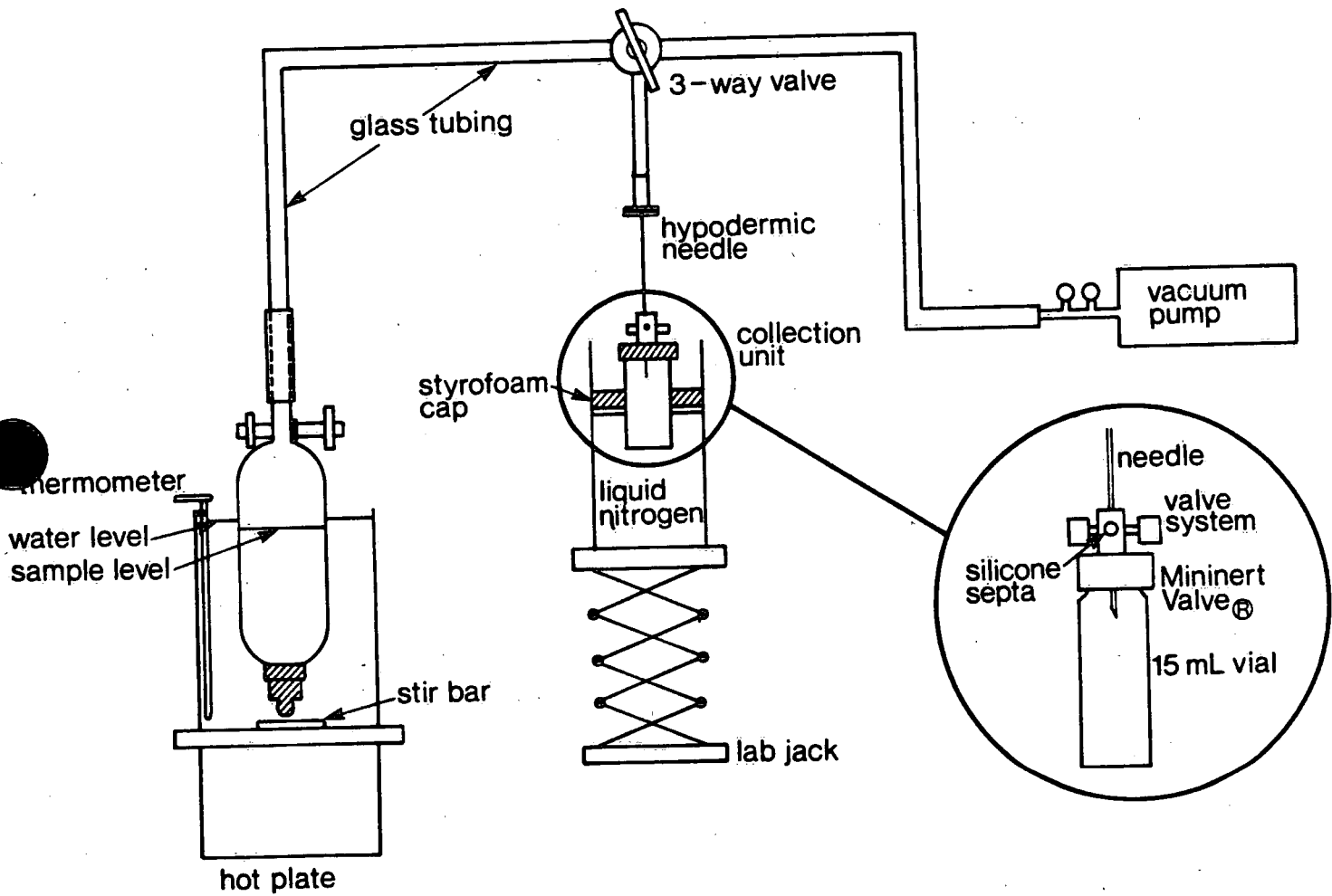
TABLE 1

Recoveries and Relative Error for Volatile Analyses

Compound	Number	Percent[a] Recovery	Percent[b] RSD Total	Detection[c] Limits $ng \cdot \ell^{-1}$
Oxygen	1	–	–	–
Dichlorodifluoromethane	2	110	19	5.
Trichlorofluoromethane	3	108	17	1.
Vinyldene chloride	4	110	13	30.
Carbon disulfide	5	85	15	30.
Methylene chloride	6	102	18	30.
1,2-dichloroethane	7	75	16	80.
1,1-dichloroethane	8	84	19	80.
Bromochloromethane	9	69	22	1.
Chloroform	10	90	14	1.
1,1,1-trichloroethane	11	94	15	0.9
1,2-dichloroethylene	12	104	18	40.
Carbon tetrachloride	13	85	12	0.8
1,2-dichloropropane	14	81	19	30.
Trichloroethylene	15	105	17	0.9
Dibromomethane	16	56	22	0.9
Dichlorobromomethane	17	58	20	1.
Trichlorobromomethane	18	60	19	2.
1,1,2-trichloroethane	19	54	25	20.
Dibromochloromethane	20	54	22	1.
Tetrachloroethylene	21	65	20	0.8
Bromoform	22	55	20	1.
S-tetrachloroethane	23	48	27	1.

a) Adjusted for headspace losses.
b) Percent RSD figures for splitless conditions outlined in total experimental section, reflects <u>total</u> experimental error for n = 10.
c) Results for 100 μℓ injections, split/splitless mode of operation, five second hold time.

TABLE 2

Concentrations of Volatiles in Selected Surface, Well and Treated Waters
$ng \cdot \ell^{-1}$

	Campbellville[a]	Crawford Lake	Waterdown[a]	Ancaster	Burlington[a]	Beamsville[a]	Burlington[b]	Niagara Falls[b]	Port Robinson[b]	Distilled Water[b]
Trichlorofluoromethane	ND	13	ND	ND	ND	ND	1,500	ND	ND	700
Chloroform	ND	58	41	ND	20	34	300	13,000	250,000	45
1,1,1-trichloroethane	ND	5.9	6.4	ND	2.6	13	7.5	15	10	6.0
Bromochloromethane	ND	ND	ND	ND	ND	ND	1,800	ND	15	550
1,2-dichloropropane	T	T	ND	ND	T	ND	ND	ND	210	T
Carbon tetrachloride	8.5	3.8	3.2	1.1	1.3	17	54	100	900	18
Trichloroethylene	ND	32	ND	11	ND	10	2.4	ND	45	ND
Dibromomethane	4.9	10	ND	4.3	6.3	ND	35	5	5	35
Dichlorobomomethane	3.7	20	27	6.1	16	25	21,000	11,000	160,000	4,000
Tetrachloroethylene	10	9.0	21	7.1	31	4.2	5	240	120	ND
Dibromochloromethane	ND	ND	ND	ND	ND	ND	22,000	1,000	4,000	6,000
Bromoform	ND	ND	ND	ND	ND	ND	15,000	840	300	4,000
1,1,2-trichloroethane	ND	ND	ND	ND	ND	ND	21,000	120	480	4,800

a) - Well water.
b) - Tap water.
ND - Not detected (less than detection limit, refer to Table 1).
T - Trace amount (less than detection limit, greater than noise level).

TABLE 3

Detection Limits for Volatile Contaminants in Water for Various Analytical Techniques
Concentrations in $ng \cdot \ell^{-1}$

Method	Reference	Sample Size	Detector	Detection Limits
Direct Aqueous	1	10 µℓ	GC/EC	100^a – 2000
Injection	11	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
	12	10 ℓ	GC/MD	5 – 50
	13	5 mℓ	GC/EC	40^a – 50,000
GROB, Closed	6	1 ℓ	GC/FID	1^b – or higher
Loop Stripping	12,14	4 ℓ	GC/MS	1^c – 10
Purge/Trap	4	5 mℓ	GC/MCD	500 – or higher
	12	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 $ng \cdot \ell^{-1}$ 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).

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