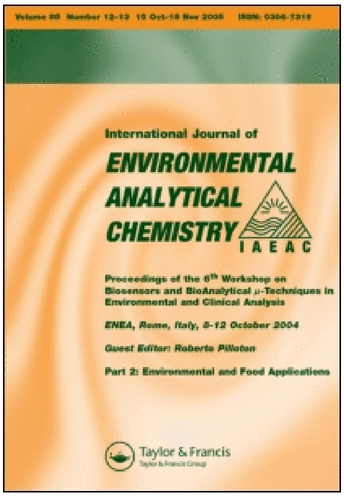

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A NEW METHOD FOR THE DETERMINATION OF THE GROUP PARAMETER "VOLATILE ORGANIC HALOGENS" IN GROUND WATERS

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A new method is presented for the determination of volatile organic halogens in ground water samples. The method comprises purge-and-trap by a modified CLSA technique and determination of organic halogens adsorbed on the activated carbon sorbent of the trap by means of a TOX analyzer. The method covers chlorinated solvents and trihalomethanes with recoveries of 70–90% within the range 0.5–100 μg Cl/l and with a relative standard deviation of 5.8% at the 8.6 μg Cl/l level. Inorganic interferences frequently encountered, when working with organic halogen group parameters, and likely to occur in ground waters do not bias the proposed analytical method in concentrations pertinent to most ground waters.

KEY WORDS: VOX, ground water.

INTRODUCTION

Chlorinated solvents and trihalomethanes belong to the most frequently occurring organic contaminants of ground waters.[1–4] The health risks of chlorinated solvents, including suspected carcinogenic effects of some compounds, have implied maximum allowable concentrations in drinking waters as low as 0.3–5 μg/l.[5–6] Consequently, the demand for analytical methods capable of determining the chlorinated C_1- and C_2-compounds at the low μg/l level has increased. Conventionally such compounds are determined in water sanmples by means of purge-and-trap methods, head-space techniques or solvent extraction in combination with gas chromatography.[7,8,9]

The determination of volatile organic halogens (VOX) as a group parameter has been used supplementary in investigations of ground water pollution,[10] in drinking water quality surveillances[11] and in ground water monitoring programmes.[12] Most commercially available, automated methods for the determination of VOX in water depend on stripping volatile organics from a small volume (10–100 ml) of sample on-line to combustion and coulometric detection of the evolved hydrogen halides.[13–15] Published limits of detection for these methods are 1–10 μg Cl/l,[13,14,16] but their practical application has demonstrated, that limits of

Table 1 Purge-and-trap conditions for the CLSA procedure

Sample size	1 l
Sample temperature	30 °C
Filterheater temperature	80 °C
Filter temperature	40 °C
Nitrogen flow	1.5 l/min
Purge time	1 hour
Filter	40 mg activated carbon

detection in real ground water samples are closer to 5–20 μg Cl/l.[10] In order to attain lower limits of detection it has been attempted to employ purge-and-trap techniques such as cryotrapping/thermal desorption[17] or Tenax-trapping/thermal desorption.[18] Another approach to improve the sensitivity of VOX methods has been to introduce on-line purge and combustion combined with trapping of the formed hydrogen halides and their discrete detection by coulometry[19] or ion chromatography.[20]

The interferences most commonly emphasized in method studies concerning organic halogen group parameters based on combustion/coulometric detection are nitrogen and sulphur compounds.[17,21–24] Nitrogen and sulphur oxides formed during the combustion may produce erratic responses from the detector.[22] Furthermore, the presence of inorganic halogenides in the water samples do constitute a serious risk of biasing the organic halogen analytical result,[13,21,25] especially, since the ratios of inorganic halogenide to organic halogen, IX/OX, of unpolluted ground waters are typically in the range of 10^3 to 10^5.

In spite of the efforts made to achieve a satisfactory method for the determination of VOX in ground water samples, no commercially available equipment exists, which meets the demands for precision (repeatability and reproducibility), accuracy and a low limit of detection. This paper describes a method developed for the determination of VOX in ground water samples at low levels. The basic principles of the method are stripping of the volatiles from the water sample to an activated carbon trap followed by transfer of the carbon with adsorbed compounds to combustion and coulometric detection. A combination of commercially available analytical equipment is the basis of the method.

EXPERIMENTAL

Apparatus

Purge-and-trap was performed using a closed loop stripping analysis equipment according to Grob,[26] purchased from Brechbühler (Zurich) and modified by replacing the pumped, recirculated strip gas with a flow of nitrogen purified by passage through an activated carbon filter.[27] Purge-and-trap conditions are summarized in Table 1.

Carbon filters were prepared from original (Bender and Hobein, Zürich) precision glass tubes of 5.0 mm outer diameter (o.d.) equipped with a constriction to approx. 2–3 mm o.d. in the outlet end. Granulated activated carbon (40 mg, 100–200 mesh, Dohrmann) was packed into the glass tubes by means of two small plugs of quartz wool (Cerafelt, Dohrmann).

A Dohrmann DX-20 TOX analyzer was used to analyse the halogen contents of the carbon adsorbent. The TOX analyzer was calibrated daily by analysing methanolic solutions (5–10 μl) of 2,4,6-trichlorophenol injected on a 40 mg carbon bed in the boat inlet of the analyzer.

Materials

Chemicals used were analytical grade or better. Solvents were of HPLC quality (Rathburn) or of p.a. quality (Merck). Solutions were prepared in low-TOC, deionized water (Milli-Q from Millipore). Membrane filters were 0.45 μm cellulose nitrate/acetate filters from Millipore. Standard solutions were prepared in methanol by dilution of a 10 g Cl/l stock solution of 1.856 g 2,4,6-trichlorophenol in 100 ml methanol. Soil humic acid was extracted from soil of a B podsol horizon by a modified IHSS procedure.[28]

Quality control

Each analytical series included a sample of low TOC water (blank) and a control sample prepared by the addition of 1 μl of a solution of 1,1,2-trichloroethane (8.6 g Cl/l, 75 μl 1,1,2-trichloroethane dissolved to 10 ml with acetone) into 1 l low TOC water. Analytical results for control samples were treated statistically by establishing X-charts and by performing run tests as suggested by the English Water Research Centre[29] in order to achieve an early warning of any malfunction of the analytical equipment or of deterioration of standard solutions.

Procedure

The ground water samples were tapped in 1 l glass stoppered flasks, 10 ml of a potassium nitrate solution (KNO_3, 5 % w/v aq.) were added, and the pH was adjusted to 8 with sodium hydroxide solution (NaOH, 10 M aq.) or with nitric acid (HNO_3, conc.). The flasks were each transferred to a water bath thermostatted at 30 °C and purged for 1 hour applying the purge-and-trap conditions specified in Table 1.

Upon completion of the purge-and-trap procedure, the carbon contents and quartz wool plugs of each filter were transferred to 10 ml screw capped glass vials. Acidified potassium nitrate solution (10 ml, KNO_3, 0.5 % W/V aq., acidified to pH 2.0 ± 0.2) was added, and the vials were shaken on a shaking tree (150 strokes per minute) for 10 min and centrifuged (3000 revolutions per minute) for 5 min. The carbon and quartz wool were filtered off (pressurized filtration on 0.45 μm membrane filters) and were transferred quantitatively to the boat inlet of the TOX analyzer. Combustion was performed applying standard conditions (vaporization at 250 °C, O_2/CO_2 carrier gas and combustion at 800 °C, O_2 carrier gas). The integrated signal was read from the instrument and converted to μg Cl from the obtained calibration curve.

RESULTS

Development

The initially used closed loop stripping procedure was replaced with an externally supplied nitrogen stripping procedure, as the pump of the CLSA equipment did not tolerate the increased back pressure of the 40 mg carbon filters substituting the standard 1.5–5 mg carbon filters.

The nitrate washing procedure was introduced in order to reduce the initially obtained high blind sample results, which were presumably caused by the transfer of inorganic chloride to the carbon filter as sample droplets in the strip gas. The risk of loosing volatiles adsorbed on the carbon by desorption during the nitrate wash procedure was tested in an experiment, in which 8.6 μg Cl as 1,1,2-trichloroethane were introduced into 10 ml vials containing 40 mg of activated carbon and an adequate amount of quartz wool. Performance of the nitrate wash procedure and subsequent determination of organic halogen contents of these samples and of pertinent blind samples revealed a 99% recovery of added 1,1,2-trichloroethane.

For the stripping conditions chosen, the stripping time needed to obtain maximum recovery of chlorinated volatiles was established with 1,1,2-trichloroethane as the model compound (Figure 1). From the results given in Figure 1 a strip of time of 1 hour was selected.

Performance characteristics

The performance characteristics of the method are summarized in Table 2, and the range of linear response with 1,1,2-trichloroethane as the model compound is pictured in Figure 2. The limit of detection (DL) given in Table 2 was calculated from the standard deviation (in this case: 0.074 μg Cl/l) of 6 determinations of VOX in blank samples (mean blank value, 0.56 μg Cl/l) in accordance with the suggestions of the Water Research Centre:[29]

$$DL = 2 \times S_B \times t_{m-1} \times (1 + 1/n)^{1/2} \qquad (1)$$

with S_B as the standard deviation of m blank results, t being the Student's t value at a 95% confidence level, and n being the number of blank determinations in each analytical series.

Recovery study

The recoveries of selected volatile halogenated organic compounds of environmental concern were determined analysing spiked low-TOC deionized water

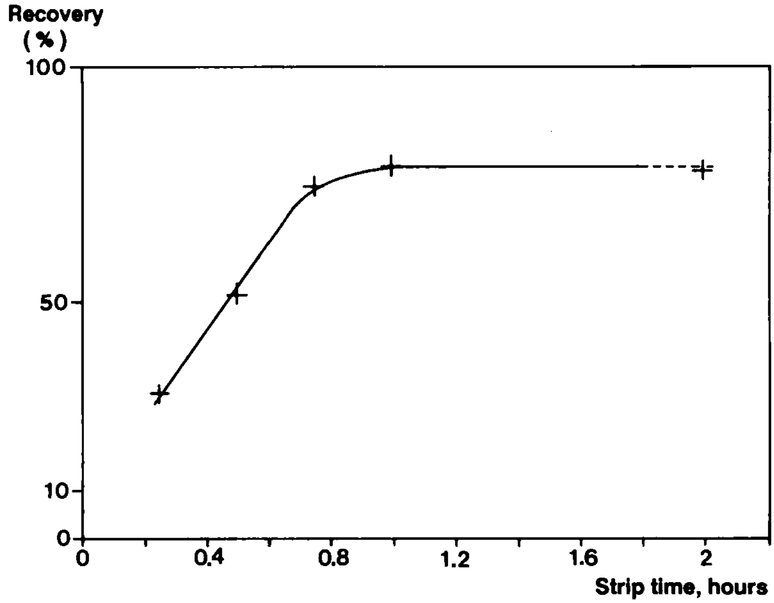

Figure 1 Recovery of 1,1,2-trichloroethane (8.6 μg Cl/l) from 1 l low-TOC deionized water versus strip time variation.

Table 2 Performance characteristics of the VOX method

Limit of detection	0.5 μg Cl/l
Relative standard deviation, 8.6 μg Cl/l	5.8 %
Recovery of 1,1,2-trichloroethane, 8.6 μg Cl/l	84 %–90 %
Dynamic range	0.5–100 μg Cl/l

samples. Duplicate samples, spiked to approx. 10 μg Cl/l, were prepared by the addition of 1–20 μl of stock solutions (approx. 1–10 g Cl/l) in acetone, in methanol or in 2-propanol. The results are presented in Table 3.

Interferences

The effect of ionic strength variations was investigated by analysing duplicate samples of water (ionic strength, approx. 0.01) with a composition resembling that of commonly occurring Danish ground waters (synthetic ground water). Recovery of added 1,1,2-trichloroethane (8.6 μg Cl/l) was 113 % compared to the recovery from low-TOC deionized water.

The interfering effects of some inorganics likely to occur in ground water samples were investigated by the analyses of duplicate samples of low-TOC deionized water, to which different concentrations of the potentially interfering components were added. The maximum concentrations analysed without measur-

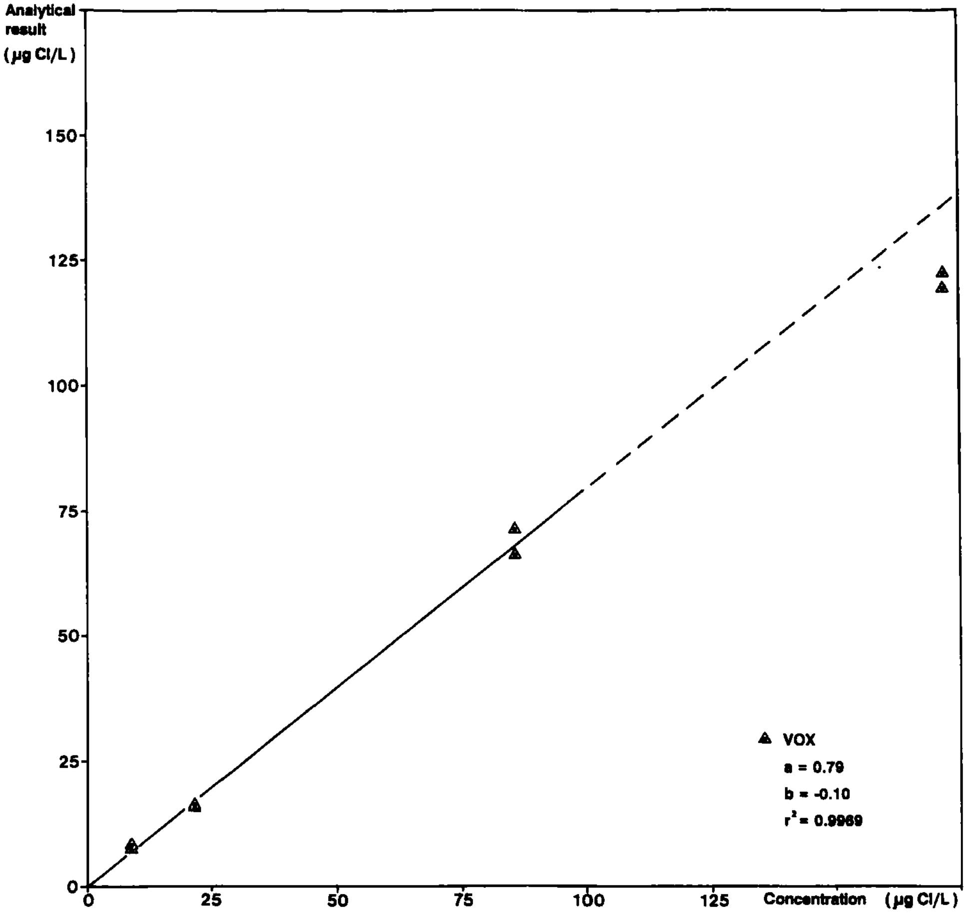

Figure 2 Range of linear response obtained with 1,1,2-trichloroethane as the model compound spiked into low-TOC deionized water.

able bias (Student's *t* test, 95% confidence level) are given in Table 4. It must be perceived at this point, that for several of the inorganics no bias was observed for the highest concentration tested.

The potential effects of non-halogenated organic compounds cooccurring with the VOX analytes in the ground water samples were investigated. Samples of low-TOC deionized water with 8.6 µg Cl/l as 1,1,2-trichloroethane added were spiked with 1,2-dimethylbenzene or acetone to 10 mg C/l. Furthermore, it was investigated whether humic acid added to low-TOC deionized water samples to 10 mg C/l affected the recovery of 1,1,2-trichloroethane (8.6 µg Cl/l). The results are given in Table 5.

DISCUSSION

The presented method for the determination of volatile organic halogens (VOX) in

Table 3 Recoveries of selected volatile halogenated compounds spiked into low-TOC deionized water (duplicate analyses)

Compound	*Added concentration (μg Cl/l)*	*Recovery (%)*
Dichloromethane	9.7	<5
Tetrachloromethane	9.2	87
Vinylchloride	12.6	<5
cis-1,2-Dichloroethylene	9.4	73
Trichloroethylene	11.9	87
1,1,1-Trichloroethane	10.7	77
1,1,2-Trichloroethane	8.6	84–90
1,1,2-Trifluorotrichloroethane	8.9	14
Chlorobenzene	8.7	86
Bromobenzene	11.4	46
2,4-Dichlorophenol	10.9	<5
2-(2,4-Dichlorophenoxy)propanoic acid	10.6	<5
γ-Hexachlorocyclohexane	11.4	9.9

Table 4 Maximum concentrations of inorganic potential interferents dissolved in low-TOC deionized water without measurable bias of the VOX result

Inorganic interferent	*Maximum allowable concentration (mg/l)*
Chlorine	2[a]
Chloride	2000
Bromide	97
Iodide	1
Iodate	1
Sulphide	10
Sulphate	>230[b]
Ammonia	10
Nitrate	>30[c]

[a] The maximum concentration of chlorine reduced fully to chloride by the standard addition of sulphite. Obtained from measurements of total chlorine and adsorbable organic halogens in low-TOC water samples with sodium hypochlorite and sodium sulphite solution added (AOX).[30]

[b] Inferred from the absence of interference on the AOX result in experiments with 500 ml samples of 460 mg SO_4^{2-}/l.[30]

[c] Inferred from the fact that 300 mg NO_3^-/l are added to the sample performing the VOX analysis.

ground water samples combines the modified CLSA preconcentration technique with the detection of a TOX analyzer employing commercially available instruments.

Table 5 Recoveries of 1,1,2-trichloroethane (8,6 μg Cl/l) from low-TOC deionized water after addition of 1,2-dimethylbenzene, acetone or humic acid to 10 mg C/l

Compound added	*Recovery of VOX*
None	1[a]
Acetone	1.03
1,2-Dimethylbenzene	0.72
Humic acid	1.03

[a] The VOX result obtained for 1,1,2-trichloroethane only added to the samples is arbitrarily assigned a value of 1.

The analytical limit of detection was 0.5 μg Cl/l and consequently satisfies the demand of being below 1/10 of the maximum allowable concentrations in drinking water for most halogenated organic volatiles of general occurrence (e.g., trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, trihalomethanes).[5,6] The dynamic range of the method spanned two orders of magnitude from 0.5 μg Cl/l to 100 μg Cl/l. The relative standard deviation at the 8.6 μg Cl/l level was 5.8 %.

Recoveries of the chlorinated volatile organic compounds of most frequent occurrence in ground waters[1-4] were 70–90 % from deionized water. It should be appreciated at this point that group parameter methods are optimized in order to obtain maximum recoveries of a broad group of compounds. Furthermore, the internal standardization procedures commonly used to compensate for poor recoveries of purge-and-trap methods for specific compounds[26] are inapplicable for group parameters. Recoveries might be slightly increased, when analysing real ground water samples of higher ionic strength. Compounds of poor adsorbability from air onto carbon (e.g. vinylchloride) and compounds of unfavourable carbon/water partitioning coefficients (e.g. dichloromethane) were not recovered. The shortcomings of the detection method were displayed by the low recoveries of the less combustible compound (Freon 113, 14 %) and of the brominated compound (bromobenzene, 46 %).

No bias was recorded of the method for inorganic halogenides, nitrogen compounds, sulphur compounds or humic acids at concentrations likely to occur in unpolluted ground waters. When analysing ground waters, which are heavily polluted with volatile aromatic compounds such as 1,2-dimethylbenzene, care should be exercised in the interpretation of the results, as a slightly decreased recovery was found at a concentration of 10 mg C/l. The investigated polar solvent (acetone) was without this effect at the level tested (10 mg C/l).

About 6 ground water samples can be analysed per day with one set of instruments, though the real time consumption equals 4 hours per 6 samples including quality control procedures. The total costs of the VOX method per sample may therefore be considerably less than the costs of traditional gas chromatographic analyses of chlorinated solvents and trihalomethanes.

The proposed VOX method has been included in the analytical programme of a nation-wide ground water monitoring programme sampling 145 wells[28] and has at present successfully been employed in several investigations on ground water pollution from chemical waste sites.[10]

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