INT. J. BIOL. BIOTECH., 2 (3): 629-639, 2005.

DETECTION AND ANALYSIS OF HALOGENIC COMPOUNDS IN GROUND WATER

M. Jamal Haider[1], Atif Dawar[2], Rukhsana Talat[1] and Saadat Ali[2]

[1]Department of Zoology, Federal Urdu University of Arts, Sciences and Technology, Gulshan-e-Iqbal, Karachi-75300, Pakistan
[2]Department of Physics, Federal Urdu University of Arts, Science and Technology, Gulshan-e-Iqbal, Karachi-75300, Pakistan

ABSTARCT

For the determination of organic halogens in ground water, AOX, EOX and VOX parameters are used. This method can be used in the range of 1-100 µg Cl/L with a coefficient of variation of 5-10%. The methods are unbiased by interference from many common constituents in ground water, but high concentrations of iodide and sulphide may bias the AOX determination. Highly humic waters and waters heavily polluted with volatile, non-halogenated organics might exhibit reduced recoveries at EOX and VOX, respectively. Each method provided information on the nature of the organic halogens with respect to volatility and polarity of selected test compounds.

Key-words: Organic halogens, AOX, EOX, VOX parameters, ground water, Karachi

INTRODUCTION

The aim of present investigation was to determine the amount of organic halogens compounds from the ground water. Usually organic pollution of the under ground water is the group of halogenated organics, chlorinated C^{1-} and C^{2-} compounds, chlorobenzenes and halogenated pesticides are frequently found in ground waters at significant levels (Hanson, 1985; Page, 1981; Fielding *et al.*, 1981; Montiel *et al.*, 1985; Veenendaal *et al.*, 1986; Pionke *et al.*, 1988; Oki and Giambelluca, 1987; Wilson *et al.*, 1987; Junk *et al.*, 1989; Peoples *et al.*, 1980; Richard *et al.*, 1975; Lahav and Kahanovitch, 1974; Brodie *et al.*, 1984). Maximum contents of the halogenated organics limited in potable waters range from sub-ppb levels to ppm level reported by EPA (1985), EPA (1977), WHO (1984). Hence the presence of the haloorganic pollution in the ground water is carefully observed. The nationwide ground water monitoring programmes have urged on development of analytical programmes, yielding the broadcast coverage at the lowest costs. Hence, the demand for adequate analytical methods has been rising. In order to meet the request for cost efficient, broadly covering analytical methods, efforts have been made to adapt group parameter methods, previously developed for the determination of organic halogens in waste water and in chlorinated drinking waters to ground water investigation purposes.

Chronic halogenic poisoning as occurs after long terms exposure through drinking water is very different to acute poisoning. Immediate symptoms on an acute poisoning typically include vomiting, oesophageal and abdominal paint and bloody rice water diarrhea. Chelationthreapy may be effective in acute poisoning but should not be used against long terms poisoning. The symptoms and signs resulting from halogenic causes, appear to differ between individuals, population groups and geographic areas. Thus there is no universal definition of the disease caused by halogen. This complicates the assessment of the burden on health of halogen. Similarly, there is no method to identify those cases of internal cancer of the skin, lungs, urinary bladder and kidney, as well as other skin changes such as Pigmentation changes and thickening (hyperkeratosis). Increased risk of lung and bladder cancer and of halogenic associated skin lesions have been observed at drinking water halogenic concentrations of less than 2PPL.

The performance characteristics of the developed organic halogen methods have been reviewed (Dressman *et al.*, 1979; Wegman, 1981; Wegman, 1982; Cooper and Young, 1984; Gron, 1988), and standard methods or standard method drafts have been developed for the determination of adsorbable organic halogens (AOX) (Joyce, 1981; EPA, 1982; Din, 1985; Standard, 1985; ISO/DIS, 1988), of volatile organic halogens (VOX) (Method, 1982; NEN, 1986; and of extractable organic halogens (EOX) (Din, 1984; Nen, 1986), in water samples. Analytical principles and typical performance characteristics of some commonly used organic halogen methods are summarized in Table1.

Among the interferents recognized chlorine and chlorinating agents are known to bias the results of the commonly used organic halogens group parameters positively. This interference is marked by the addition of a dechlorinating agent such as sulphite, 0.04 – 10 moles per L sample (Standard, 1985; ISO/ DIS, 1988). Inorganic halides, of which chloride has received most attention, are also known to bias the AOX methods positively, Maximum allowable concentrations of chloride are suggested in the range 100 – 1000 mg/ L in order to provide a limit of detection of 5µg Cl/ L (DIN, 1985; NEN, 1986; Oake and Anderson, 1984; Takahashi *et al.*, 1981). In an extensive batch washing procedure for more efficient removal of the inorganic halides from spent carbon prior to combustion has been introduced (Martinsen *et al.*, 1988). The suggested maximum allowable concentrations for bromide are 1-250 mg/L (Oake and Anderson, 1984; Takahashi *et al.*, 1981; Kussmaul *et al.*, 1988). Whereas 100 µg/L of iodide have been shown to cause positive bias of the AOX method (Kussmaul *et al.*, 1988). Also studies of retaiment of inorganic chloride from apolar organic solvents during extraction of water samples have been conducted (Schmitt and Zweig, 1962; Lunde, 1973; Lunde *et al.*, 1975). The presence of organic compounds, such as humics, other than haloorganics is expected to influence the efficiency of the carbon adsorption in the AOX method Snoeyink *et al.*, 1977; Kuhn, 1983), and the extraction step of the EOX method (Chiou *et al.*, 1986; Fish *et al.*, 1989). The maximum allowable concentrations of organic matter suggested for the AOX method are in the range 1-10 mg Cl/L as non-purgeable organic carbon per 10 mg of activated carbon (DIN, 1985; ISO/DIS, 1988; Oake and Anderson, 1984). From the presentation given above it is clear, that there ia a need for development and subsequent avaluation of analytical methods aiming at the determination of organic halogen group parameters in ground waters. In the investigation presented here, a known method for the determination of AOX (Takahashi *et al.*, 1981), was adopted for the use in ground water investigations primarily along the lines suggested by Martinsen *et al.*, 1988, increasing the sample volume and including a batch washing procedure. An EOX method widely used in Holland (NEN, 1986), was adjusted to include the ionic strength uniforming sodium sulphate addition of the German Standard method (DIN, 1984). Furthermore, a new VOX method was developed combining the modified closed loop stripping analysis (CLSA) (Grob *et al.*, 1976; Boren *et al.*, 1982) with the total organic halogen (TOX) analyzer (Gron, 1990).

The methods are described and their performances are evaluated. Hence to overcome any ground water pollution incidents a nationwide ground water monitoring programmes must be initiated. The presence of the haloorganic pollution in the ground water was carefully observed. The demand for adequate analytical methods has been rising. The conventional approach includes chromatographic methods such as gas chromatography, (GC) and high performance liquid chromatography (HPLC). Concentration techniques and possibly, derivatizations are used with suitable detection techniques. Each of such method allows the specific determination of a comparatively small subgroup of the halogenated organics likely to occur in ground water samples. In order to meet the request for cost efficient, broadly covering analytical methods. Some efforts have been made to adapt group parameter methods, previously developed for the determination of organic halogens in waste waters and in chlorinated drinking waters to ground water investigation purposes. However, a comprehensive survey of the importance of bias caused by inorganic and organic nitrogen and sulphur compounds likely to occur in ground waters, has not been presented.

MATERIALS AND METHODS

Equipment

The adsorption step of the AOX method was performed on an AD-2 adsorption module from *Dohrmann.* Combustion and coulometric detection was carried through on a DX-20 ToX analyzer from *Dohrmann.* combustion and coulometric detection of the EOX method was done on an Euroglass microcoulometeric equipped with an auto injector. CLSA was performed by means of equipment purchased from ICT Japan employing filters of 40 mg of granulated activated carbon pached with a small amount of quartz wool into original (wood brothers USA) precision glass tubes of 5.0 mm outer diameter (0.d) and constricted to 2-3 mm 0.d in the outlet end. The quantification of the halides of the carbon trap was done on a DX-20 ToX Analyzer from *Dohrmann.*

Chemicals

All chemicals and solvents used were of analytical grade (Merck p.a). acetone for stock solutions and pentane for EOX extractions were of HPLC quality (Rathburn). Sodium sulphate was pretreated by heating to 450°C over night. Granulated activated carbon (GAC, 100/200 mesh) and quartz wool (cerafelt) were purchased from Wood Brothers. Membrane filters were 0.45 μm cellulose nitrate/acetate abtained from Millipore. Reagents grade water was obtained from a Millipore system (Milli-Q), and low TOC water was prepared by additional activated carbon treatment of reagent grade water.

AOX procedure

The pH of the sample was adjusted to 2$\pm$0.2 by the addition of nitric acid (approximately 2ml HNO_3, Conc., per L sample). Sulphite (2ml/l 0.1 M Na_2SO_3 aq.) and sodium nitrate (10 ml/L 5% KNO_3 aq.) were added. After pretreatment, 500 ml of sample, in portions of 100ml, were passed through two columns in series each containing 40 mg GAC applying a nitrogen pressure of 1.6 bar and with a resultant flow of approximately 3ml/minute. After completion of the adsorption, the carbon of each column was separately transferred to 10ml glass vials with teflon lined screw caps, and 10 ml of acidified potassium nitrate solution (0.5% KNO_3 acidified with concentrated nitric acid to pH= 2±0.2) were added. The vials were shaken for 10 minutes on a shaking tree (150 strokes per minute, rpm) and the carbon was sedimented by centrifugation (3000 revolutions per minute, rpm) for 5 minutes. The supernatant was discarded, and the washing procedure was repeated twice. The carbon of each column was transferred separately by means of a few ml of fresh nitrate solution to a pressurized (N_2-gas) filtering device (Stainless steel) equipment with a 0.45μm membrance filter. Subsequently, the carbon of each filter was scraped from the filter into the boat inlet of the DX-20 TOX Analyzer. Combustion was performed under standard conditions (Vaporization at 250°C, O_2CO_2 and combustion at 800°C or carrier gas). The integrated signal of the coulometric detector was read as μg Cl from the display and was converted into a calibrated signal. The standard curve was obtained by injection of 5-10μl of methanolic solutions of 2, 4, 6 trichlorophenol onto 40mg GAC in the DX-20 boat inlet and subsequent combustion and quantification. The results were expressed as μg Cl/L.

EOX Procedure

To 900-950ml sample in a 1000ml measuring flask was added sulphite solution (2ml/L 0.1 M Na_2SO_3 aq.) and 20g of Na_2SO_4. Then pH was adjusted to 2±0.2 by the addition of nitric acid (Conc.). The extraction was performed with 25 ml of pentene by stirring (1100 rpm) on a magnetic stirrer for 30 minutes followed by separation of the organic phase.

At this stage, the pH of the sample was adjusted to 9±0.2 with sodium hydroxide (9.1 M aq.), and the extraction was repeated with an additional 25ml portion of pentane. The combined organic phases were dried with 5.0 g of Na_2So_4 (Sic.) applying magnetic stirring, and the sodium sulphate was washed with 3 x 5 ml of fresh pentane. The combined organic phases were reduced to a volume of 10 ml on a rotavapor at atmospheric pressure and 10°c with a gentle stream of nitrogen. The reduced extract was transferred to a tapered flask

With microvolumetric calibration equipped with an air cooled vulster, and 0.05ml. of hexadecane was added. The final extract volume of 0.50ml was obtained by blowing down the volume with nitrogen at ambient temperature. The halogen content in the reduced extract was determined by automatic injection (0.5μl.sec.) of 0.1ml into the Euro glass microcoulometer, applying standard combustion conditions (injector temperature; 500°C, combustion temp; 50°C, absorber temperature: 200°C, carrier gas: O_2/Ar). The integrated signal was read as ml from the recorder and was converted into a calibrated signal. The standard curve was established by injection of 0.1ml of standard solutions of aldrin in pentane/ hexadecane. 9:1 into the equipment. The results were expressed as μg Cl/L.

VOX Procedure

To 1 L of sample in a glass stoppard flask was added potassium nitrate (10ml, 5% aq.), and the pH was adjusted to approximately 8 (pH paper) by the addition of nitric acid (Conc.) or sodium hydroxide (9.1M aq.) as approximate. The sample was placed in a water bath thermostated to 30°C and was stripped with nitrogen, 1.5L/minute, for one hour. The strip gas containing the volatile organics was heated to 80°C before entering the 40 mg carbon trap, which resulted in a trap outlet temperature of 40°C, the carbon and packing aid (quartz wool) were transferred to 10ml screw capped glass vials and were washed once with acidified nitrate solution as described in the AOX procedure. Combustion, detection and quantification were as described for the AOX method. Results were expressed as μg Cl/l.

Performance Study

The limits of detection were evaluated by analyses of reagent grade water blanks, whereas precisions and dynamic ranges were investigated through analyses of reagent water samples spiked with 2, 4, 6- trichloraphenol (AOX), aldrin (EOX) or 1, 1, 2- trichloroethylene or acetone. However, the precision expressed for the EOX method was conducted by spiking reagent water samples with a pesticide mixture of equal amounts by weight of aldrin, DDT, DDD, DDE and heptachlor in acetone.

Recovery studies concerning combustion/ detection were performed by analyses of solutions of fluorinated, Chlorinated, brominated and iodated methanes, benzenes and phenols in pentane/ hexadecane/ acetone, 9:1:1. The solutions were injected on a 40mg bed of granular activated carbon in the boat ion let of the Dohrmann DX – 20ToX analyzer or directly into the oven of the euroglas microcoulometer by means of the automatic injector. Recovery studies including the full analytical methods were done by analyses of reagent water samples spiked with 1-40μL of stock solutions in acetone, methanol or toluene of halogenated organics representing compounds likely to occur in ground waters. The effects of the major inorganic components in ground waters were investigated analyzing samples of artificial ground water. The composition (Na^+, Ca^{++}, Mg^{++}, Fe^{++}, Cl^-, NO_3^-, SO_4^{--}, inorganic carbon) and ionic strength (≈ 0.01 Mg resemble fresh ground water of intermediate hardness, without $NaHCo_3$content, as commonly found in Denmark (Odum and Christensen, 1936). Interference studies were performed by analyses of pure solutions of the potential interferent in reagent water, unspiked or spiked with the previously employed test compounds. The potential maximum effects of organic sulphur and nitrogen were investigated by injecting methanolic solutions of methyle phenyl sulphide and N-methylani line into the combustion/ detection units of the Dohermann and Euro glass equipments as outlined for the recovery studies. Humic acid was prepared by an aqueous hydroxide extraction, in analogy with the standard extraction procedure (Malcolm, 1976) from soil of the B pod sol horizon of skirled in central Jylland, Denmark. The standard procedure was modified in order to diminish organochlorine artifacts produced durng the extraction and purification (Gron, 1990).

Quality assurance

Each analytical series included at least one blank (reagent grade water)and one control sample (AOX: 5μg Cl/L as 2, 4-dichlorophenol, EOX: 1μg Cl/L as aldrin, VOX: 8, 7 μg Cl/L as 1,1,2-trichloroehtane) prepared from reagent water stastical treatment of quality control results included control charts of the R-type and the X-type, recovery evaluation and retests. The statistical procedures have been described previously (Duncan, 1974; cheese man and Wilson, 1978) and were used in a PC version (Jensen *et al.*, 1984; Farr, 1984) with the purpose of obtaining an early warning of analytical errors caused by equipment malfunction or deterioration of standards, solvents or reagents etc.

Table 1. Analytical principles and pefromance characteristics of some commonly used organic halogen methods.

Analytical parameter	Principle	limit of detection	Typical precision	Recoveries of selected compounds	References
AOX	Adsorption of organics on activated carbon in microcolumn or in batch combustion of Carbon and Coulometric detection of evolved hydrogen halides	2.5-5 μg Cl/L	5-15% relative standard daviation at the 10-100 μg Cl/L level	Dichloromethane 7% Trichloromethane 94% Terachlorometane 97% 1,3-Dichloroethane 107% 1,2,4-Trichloroprophenol 106% Aidrin 80%	Oake and Anderson, 1984; Takahashi *et al.*, 1981; Christmann and Erzmann, 1983
EOX	Extraction with apolar solvent, combustion of the reduced extract coulo-metric detection of evolved Hydrogen halides	0.1-10 μg Cl/L	2-10% relative standard deviation at the 2-300 μg Cl/L level	Tetrachloroethane : <5% 1,2-Dichlorobenzene: 45% Hexachlorobenzene: 72% 2,4-Dichlorophenol: 74%	Wegman and Greve, 1977; Stachel *et al.*, 1984; Fritschi *et al.*, 1978
VOX	Stripping of volatites on line to combustion and coulimetric detection of evolved Hydrogen halides	1-10 μg Cl/L	7% relative standard deviation at the 100μg Cl/L level	Dichloromethane: 87-101% Trichloromethane: 79-81% Tetrachloroethane: 76-86% 1,2-Dichlorobenzene: 61%	*et al.*, 1984; Jekel and Roberts,1980
	Stripping of volatiles trap and release from the trap to combustion and coulimetric detection of evolved Hydrogen halides	0.1-0.5 μg Cl/L	-	Dichloromethane: 91% Trichloroethane: 90% Tetrachloroethane: 74% 1,2-Dichlorobenzene: 32%	Wegman, 1982

Statistical methods

The limits of detection (DL) of the methods were obtained as described by the English water research centre (WRC) (Chees man and Wilson, 1978) from the standard deviation obtained for blind sample analyses (S_B of n blank results):

$DL = 2 - S_{B} - t_{n} - 1^{-}(1 + 1/m)^{\frac{1}{2}}$

Here, + is the student's 't' – value on a 95% confidence level, and m is the number of blank determinations in each analytical series. Means were, when appropriate with respect to the number of determinations performed, compared by a two sided student's t–test on a 95% confidence level followed by a two–sided F–test (95% confidence level) of equality of variances (DIS/ISO, 1980).

RESULTS AND DISCUSSION

The limits of detection, precisions and recoveries of the test compounds are presented in Table 3. Dynamic ranges are pictured in Fig. **1** and noted in Table 3. The performance data of the analytical methods was given with the main purpose of approach to give an impression of the abilities of the methods during laboratory routines. This point was kept in mind, when we were examining the performance data given. The limits of detection of the AOX, EOX and VOX methods (Table 3) were low as compared to data previously presented (Table 1).

Table 2. Results of the 1988 inter laboratory comparison on AOX and EOX conducted by KIWA, the Netherlands {EOX and AOX (Report, 1988}.

	1[a]	2[a]	3[a]	4[b]	5[b]	6[b]	7[c]
Inter Lboratory Comparison of AOX, (μmol/L)							
VK/d result	0.09	0.29	0.40	0.84	0.77	0.76	-e
Mean result	0.01	0.33	0.34	0.81	0.69	0.70	
Standard deviation	0.06	0.24	0.08	0.17	0.07	0.26	
Intrer laboratory Comparison of EOX, (μmol/L)							
VKI result	<0.005	0.030	0.045	0.006	0.066	0.090	70
Mean result	0.007	0.041	0.052	0.016	0.075	0.11	65
Standard deviation	0.016	0.020	0.015	0.006	0.025	0.030	11

a:drinking water samples; b: river water samples; c: concentrate in pentane/octane; d: water quality in institute;
E: not amenable to AOX analysis.

Table 3. Limits of detections precisions, recoveries of test compounds and dynamic ranges of the investigated methods.

Analytical method	AOX	EOX	VOX
Limit of detection	1μg Cl/L	0.1 μg Cl/L	0.5 μg Cl/L
Relative standard Deviation	9.3%	11%	5.8%
True value	5.0 μg Cl/L	6.7 μg Cl/L	8.6 μg Cl/L
Recovery	102%	80%	84%
Dynamic range	1-100 μg Cl/L	0.1-500 μg Cl/L	0.5-100 μg Cl/L
Test compound	2,4,6-Trichiorophenol	Pesticide mixture aldrin	1,1,2-Trichioroetane

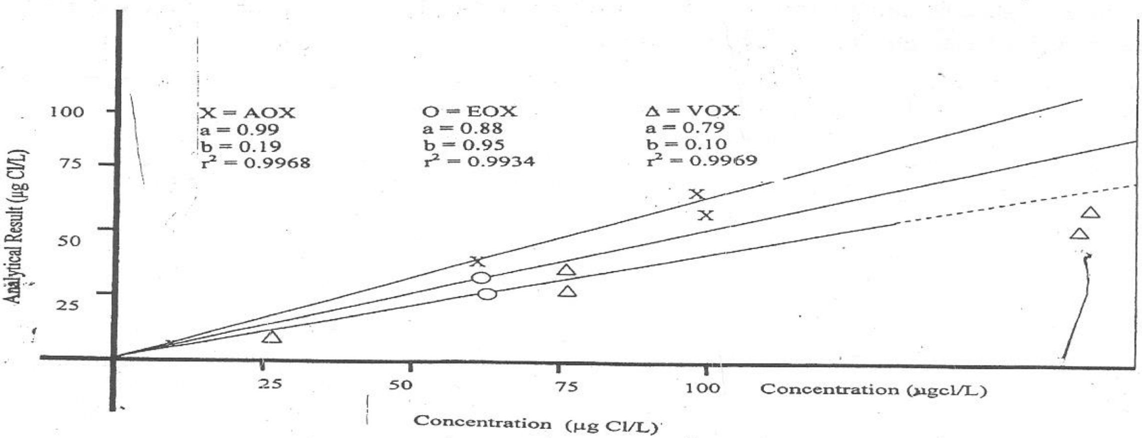

Fig.1. Dynamic ranges of the investigated methods.

Table 5. Recoveries of haloorganic compounds, when applying the full analytical procedures.

Compounds	AOX	EOX	VOX
	a	a	a
	%	%	%
Dichloromethane	14	<2	<5
Tetrachloromethane	67	5.0	87
c-1,2-Dichloroethane	65	<2	73
Vinylchloride	<5	<2	<5
1,1,1-Trichloroethane	54	3.8	77
1,1,2-Trichloroethane	77	-b	84-90
1,1,2-Trifluorotrichloroethane	<5	<2	14
Trichloroethane	64	6.7	87
Chlorobenzene	86	32	86
Bromobenzene	35	-	46
1,2,4-Trichlorobenzene	-	72	-
Hexachlorobenzene	50	61	-
2,4-Dichlorophenol	100	32	<5
2,4,6-Trichlorophenol	102	-	-
Pentachlorophenol	73	86	-
2-Chloroaniline	102	3.2	-
Lindane	87	109	9.9
Aldrin	-	80-98	-
DDT	-	73	-
Heptachloro c	-	73	-
Atrazine	96	10	-
Dichloroprop d	88	<2	<5
Dalapon e	59	<2	-
PCB f	76	75	-

a: recovery as % of theoretical value; b: not analysed; c: 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanolndene; d: 2-(2,4-Dichlorophenoxy) propanoic acid; e: 2,2-Dichloropropanoic acid; f: Arochi or 1242 mixture.

The very low limit of detection of the EOX method (0.1µg cl/l) obtained in the with in series experiment (Table 3) does not reflect the actual DL during sampling and analyses of ground waters. Results in the range 0.1–0.5 µg cl/L were not reproducible to a satisfying degree (Gron 1989). In accordance with other investigators (Veenendaal *et al.*, 1986) the practical limit of detection is consequently set to 0.5µg cl/L for the EOX method.

The methods cover linearly arrange of two to three orders of magnitude with 5–10% relative standard deviation at the 5–10µg cl/L level. Thus, the methods can be used with out modification on slightly as well as on severally polluted ground water samples.

Table 6. Effect of standard sulphite addition to low TOC water samples with sodium hypochlorite added, expressed as total chlorine and apparent AOX.

Total Chlorine added (mg Cl_2/L)	Total chlorine found after suphite addition (µg Cl/L)	AOX a,b found after sulphite addition (µg Cl/L)
0	<0.03[c]	n.d[d]
1	<0.03	n.d
5	<0.03	n.d
10	0.6	n.d
16	2.3	9.1
23	8.6	51

a: apparent AOX detected; b: 100 mL sample analysed; c: limit of detection; 0.03 mg Cl2/L; d: result indistinguishable from reagent grade water blanks.

Results of the combustion/detection performance test are presented in table4, and the recoveries obtained, when applying the full analytical procedures to spiked reagent water samples, are given in Table 5. The combustion/detection evaluation demonstrates, that chlorinated organics are quantifiable with 8–1–94% recoveries fluororganic compounds are, as expected, not detected by any of the instrumental setup's. bromoorganics are partly detected only (23–39%, slightly higher for the Dohrmann procedure), and organic iodine compounds are detected with the Dohrmann instrument only, and here to a limited extent (21–26%).

The AOX method recovers fully (73–102%) chlorinated polar compounds such as chlorophenols and to some degree (54–77%) most of the volatile chlorinated C_1 and C_2 compounds chlorinated pesticides are recovered by 76–96%, except for the strongly acidic (PKa=1.74–1.84)and consequently poorly adsorb able Dalapon. The reasons for the slightly unsatisfactory recovery data for the volatile compounds remain obscure. Experiments have demonstrated, that it is neither caused by evaporation from the samples, nor by break through on the carbon columns (Gron, 1989). The poor recoveries of dichloromethane, vinyl chloride and Freon 113 can tentatively be explained by poor adsorb ability from water onto activated carbon, by extremely high volatility (H= 81+10–3 atm m^3/mole) and by poor combustibility, respectively. A polar compound such as lindane, aldrin, DDT, PCB, and pentachlorophenol are recovered with 73–109% by the EOX method. The recoveries are reduced with increasing polarity and with increasing volatility.

The VOX method recovered most of the volatile haloorganics tested with 73–90%. Vinylchloride is recovered with less than 5%, presumably due to its poor adsorb ability from air onto carbon ($0.26+10^{-3}$ mg/mg carbon [Guenier and Muller, 1981]). Dichloromethane and the Freon compound are pooly recovered, possibly as a consequence of desorption during the nitrate wash procedure caused by the poor adsobability from water onto carbon and of poor combustibility, respectively. It should be recognized, when evaluating the recovery data, that an analytical group parameter must be optimized for the recoveries of several groups of organics of widely differing properties, rather than selectively for a signal, well defined group of compounds of uniforms properties. Further more, it is not possible to apply internal standardization procedures, commonly employed for compensation of initial poor recoveries.

The masking capacity of the standard sulphite addition of 0.2 moles/L sample has been investigated by the determination of total chlorine and of AOX (100ml sample) in hypochlorinated and sulphite treated 10w Toc water samples (table 6). It can be inferred from the results, that the method in the 500 ml version tolerates at least a content of total chlorine of 2mg cl_2/L. the AOX method is therefore applicable to most chlorinated drinking waters.
The EOX and VOX methods are considered less susceptible to bias from chlorine, than the AOX method, due to their less efficient transfer of the potential interferent to combustion.

Table 7 shows the maximum concentrations of inorganic potential interferents, which did not procedure any biasing of the methods of this investigation. The maximum allowable concentrations of organic sulphur and organic nitrogen are further more displayed in table 7. Inorganic chloride, bromide, ammonia, hydrogen sulphide and sulphate do not bias any of the methods at concentrations likely to occur in unpolluted ground waters. However, care should be taken to ensure chloride contents below 750mg Cl–/L and hydrogen sulphide concentrations below 5mg/L, when performing the AOX analyses./ iodide and iodate do bias the AOX method severely at concentrations above 0.06 and 0.08mg/L respectively. As inorganic iodine is ubiquitous in ground water and is frequently found at levels affecting the AOX methods, the possibility of iodide or iodate bias should be investigated whenever elevated AOX contents of ground water samples are detected. The maximum amounts of organic sulphur and nitrogen tolerated by the detector systems correspond to 0.2–1.5mg S/L and 0.3–1.5mg N/L. assuming a typical maximum sulphur and nitrogen content of 5% in the humic compounds (Steelink, 1985). Constituting the bulk mass of naturally occurring ground water organics, the permissible humic content is <4mgc/l. the sensitivity of the methods towards humic nitrogen and sulphur may be averestimated considerably by this approach. It has recently been demonstrated by the use of element specific neutron activation analyses as a supplementary detection technique in AOX analyses on humic ground water samples (Gron, 1990), that no S/N interference could be seen for samples of humic content as high as 30mg C/L.

The effects of the main components of ground waters are shown in Table 8. The inorganic anions (Cl^-, NO^-_3, SO^-_4, inorganic carbon)and cat ions (Na^+, Ca^{++}, Mg^{++}, Fe^{++}) of the artificial ground water do not affect the analytical results of the tested methods significantly. A slight increase of the recovery by VOX due to the well known "salting out" effect of the increased ionic strength is implied though, by the results obtained. An increase of the chloride contents of the artificial ground water samples by a factor 10(AOX) to 100(EOX and VOX)does not give rise to elevated blank values. It is there by disproved, that ion pairs of chloride and the common inorganic cations should bias any of the methods.

Table 7. Maximum concentrations of potential interferents without biasing effects.

	AOX	EOX	VOX
Cl_2, mg/L	2	2	2
Cl^-, mg/L	750	2000^{a}	2000^{a}
Br-, mg/L	97^{a}	97^{a}	97^{a}
I^-, mg/L	0.06	1^{a}	1^{a}
1O$_{-3}$, mg 1/L	0.08	1^{a}	1^{a}
NH+4, mg N/L	10^{a}	10^{a}	10^{a}
H_2S, mg S/L	5	10^{a}	10^{a}
SO_4, mg S/L	150^{a}	450^{b}	75^{c}
Organic sulphur, mg S/L	0.4^{d}	1.5^{d}	0.2^{d}
Organic nitrogen, mg N/L	0.6^{a}	1.5^{d}	0.3^{a}

a: no bias detected; b: value estimated from details of the method; c: Value estimated from the value for AOX; d: bias less than the standard deviation on results in the range tested.

Table 8. Effcet of major inorganic ground water components or blanks and recoveries.

Sample type	True value (ug Cl/L)	Analytical Result		
		AOX	EOX (%)	VOX (%) (%)
Spiked reagent water	5-11	100 a,d	100 b,d	100 c,d
Artificial ground water	"0"	n.d. e	n.d.	n.d.
Artificial ground water With 200 mg Cl/L added	"0"	n.d.	n.d.	
Artificial ground water with 2000 mg Cl-/L added	"0"			n.d.
Spiked artificial ground water	5-11	94+	89f	113f
Artificila ground water diluted X10 and spiked	5		89f	

A: 2,4,6-trichlorophenol; b: aldrin, c: 1,1,2-trichloroethane; d: recovery from spiked reagent water samples arbitrarily assigned 100% recovery; e: result indistinguishable from reagent grade water blank; f: relative to; Recovery from spiked reagent water samples.

Selected non–halogenated organic compounds have been tested for effects on recoveries of the halogenated model compounds. The sensitivity of the AOX method to occurring non–halogenated organics is less than reported previously (DIN, 1985; Standard methods, 1985;ISO/DIS, 1988; Oake and Anderson, 1984) as 100mg C/L as phenol and at least 16mg C/L as humic acid are tolerated without reduction in the recovery of 2, 4, 6–trichlorophenol. The presence of humic acid at the 10mg C/L level reduces the recovery by EOX of a polar compound, such as aldrin, by 41%. This is in accordance with the reports on reduced extractabilities of a polar organics from aqueous solutions of humic compounds (Chiou *et al.*, 1986; Fish, 1989). The humic contents of most unpolluted ground waters are below 5mgC/L, but the EOX results obtained for humic or severely polluted ground waters might underestimate the actual impact of a polar haloorganics. Humic acid at the 10mg c/L level does not reduce the recovery of 1, 1, 2–trichloroethane by the VOX analysis. Also, the VOX method is undisturbed by 10mg/L of acetone, but the recovery of 1, 1, 2,–trichloroethane is reduced by 28% in the presence of 10mg/L of 1, 2–dimethane benzene. The results obtained with the VOX method should consequently be interpreted with some care. Whenever the samples analyzed are heavily contaminated with non–halogenated, volatile organics. The resulted quoted from the participation of this laboratory in an interlaboratory comparison with the tested methods indicate, that the results obtained for drinking water and river water samples are statistically indistingwishable from the mean results of the comparison. The time of analyses for the organic halogen group parameters can for the full program be estimated to 4 days per6 samples, including general trouble shooting during the analyses, maintenance of the equipment, as well as quality assurance and reporting of the results.

CONCLUSIONS

A set of analytical methods for the determination of organic halogens has been developed and tested with respect to limit of detection, precision, potential interferents and recoveries of test compounds. The methods can be applied linearly over at least 2 orders of magnitude from 0.5–1μgCl/L with a relative standard deviation of 5–10%.

Where as the AOX method covers most organic halogen compounds of common occurrence as a ground water pollutants, the EOX results express the contents of a polar compounds such as several chloropesticides and PCB's, and the VOX method includes a volatile haloorganics such as frequently used chlorinated solvents. Each method suffers from drawbacks. The recoveries of volatile compounds by AOX are slightly low, and the susceptibility to bias by iodide and iodate urges for caution in interpretating elevated AOX values. The EOX method is sensitive to co occurrence of humic organic matter, which cause reduced recoveries of a polar haloorganics. The recoveries of volatile haloorganics by the VOX method are slightly decreased, If non–halogenated volatile organics such as 1, 2–dimethylbenzene are present at the 10mg/L level.

Used in combination the three organic halogen group parameters constitute a useful and cost effective tool for the evaluation of ground water pollution with halogenated organics.

Table 9. Bias from cooccurring non-halogenated organics.

Analytical method	Compound tested	Concentration tested	Recovery relative to Recovery from reagent water
AOX	Phenol	100 mg C/L as NPOC [a]	96% [c]
AOX	Humic acid [b]	16 mg C/L as NPOC	98% [c]
	Humic acid	10 mg C/L as NPOC	59% [d]
VOX	1,2, dimethylbenzene	10 mg /L	72% [e]
	Acetone	10 mg /L	103% [e]
	Humic acid	10 mg C/L as NPOC	103% [e]

a: non-purgeable organic carbon; b: performed as standard ddition experiment as the employed humic acid itself containes AOX; c: 2,4,6-trichlorophenol as the model compound. D: aldrin as the model compound. E: 1,1,2-trichloroethane as the model compound.

REFERENCES

Boren, H., A. Grimval and R. Savenhed (1982). Helogenic contaminated underground Water. *J. Chromatogr, Sci.* 125: 91 – 99.

Brodie, J.S., W.S. Hicks, J. Richard and F.G. Thoms (1984). The underground polluted water. *Environ Pollu.* 35: 125 – 130.

Cheese man, R.V and A. L. Willon (1978). A manual on analytical quality control for the water industry. *J. Water.* Res. 37: 110 – 121.

Chiou, C.T., R.L. Malcolm and T.I. Brinton (1986). Organic contamination in drinking ground Water. *Environ. Sci. Technol.* 20: 502 0 526.

Christmann, W and M. Erzmann (1983). Analytical ground water Chemitpy. *Lufthyg. Pub.* PP. 394.

Cooper, W.J. and J.C. Young (1984). Water analysis. *Pub. Acad. Press.* PP. 600.

DIS/ISO [Denmark International standard/International standar organization] (1980). Statistical Interpretation of data, techniques of estimation and tests relating to means and variances. *Proc. Dansk.* Stat. 15: 20 – 32.

DIN [Denmark International/Network] (1984). Summarishe wirkungs – und stoffkenn grossen Eox (Grouppe H). *Bestimmung der.* 11:615– 630.

DIN [Denmark International Network] (1985). Summarische wirkungs – und stoffkenngrossen AOX (Grouppe H) *Bestimmung der.* 12:225 – 245.

Dressman, R.C., Najar, B.A. and Redzik P (1979). The organic pollution in underground water. *Tech. Conf. Am. Water work. Assoc.* pp 69-92.

Duncan, A.J (1974). *Quality control and industrial statistics.* Wiley. Pub. PP 600.

EPA [Environmental Protecting Agency] (1982).Test methods for evaluating solid waste. *Fed. Reg.* 45:1300 – 6000.

EPA [Environmental Protecting Agency] (1985). Organic Polluted Water. *Fed. Reg.* 7021– 46880.

Farr. J. A (1984). Microcomputer System for Internal quality control in water laboratories. Proc. Water. Cont. *Quilt. Inst.* 40:102 – 130.

Fielding, M., T.M. Gibson and H. James (1981). Pollution in underground water. *Environ. Lett.* 20:55 – 65.

Fish, C.L., M.S. Driscoll and J.P. Hasset (1989). In: Aquatic humic substances. *Proc. Am. Chem.* Soc. 90:152 – 160.

Fritschi, U., G. Frithschi and H. Kussmaul (1978) Organic contamination in ground water. *Proc. Hydrol. Sci.* 73:957 – 969.

Grob, K., and Zucher, J. (1976). Organic Intensity in ground water*Chromatogr*. 52:300 – 318.

Gron, C (1988). Organic Pollution in water. Vatten. 44:12 – 25.

Gron, C (1989). Organic helogensin Denish ground waters. *Proc. Den. Acad.* 90:175 –290. (Ph.D thesis, technical Uni. Denmark].

Gron, C. (1990). Studies on Contaminated underground water, *In. J. Environ. Chens.* 55:375 – 389.

Guenier, J. P and J. Muller (1981). Humic contamination in ground water. *Dan. J. Sci.* 70:445 – 461.

ISO/DIS [International standard organization / Denmark International Standard] (1988). water quality – determination of adsorbable organic helogens. *Pub ISO/DIS* PP 130.

Jager, W., H. Hagenmaier and A. Wasser (1980). Organic compounds in ground water. *Forsch.* 13:9 – 16.

Jenson, VIB., M. Reuss and C. Gron (1984). Ahand book in Internal quality control in water Laboratories. Pub. Water. *Quli. Inst.* PP 212.

Jekel, M.R and P.V. Roberts (1980). Organic pollution in ground water. *Proc. Environ. Chem.* 77:326 – 338.

Joyce, R. J (1981). Proposed method of test for organic halides in water by carbon Adsorbtion. *Proc. Rnviron. Sci.* 55:81 – 99.

Junk, G.A., R.F. Spalding and J.J. Richard (1989). The humic contents in ground water. *Environ. Quality.* 55:50 – 65.

Kuhn, W. (1983). Contamination of ground water. Atlantic work shop. *Proc. Euviron. Soc.* 6:245 – 259.

Kussmaul, H., H. Simon and M. Sietz (1988). Studies on organic compound in ground water *J. Hydrol.* 35:367 – 380.

Lahav, N and Y. Kahanovitch (1974). Air and Soil Pollution. *Pestic. Monit* 45:20 – 32.

Lunde, G. (1973). Organic Pollution in underground water. Biochem. Biophys. *Act.* 18:67 – 80.

Lunde, G., J. Gether and B. Josefsson (1975). Examination of Helogenic underground water. *Bull. Environ. Contam.* 13:25 – 39.

Malcolm, R. L. (1976). Organic Pollution in underground water. *J. Geo. Res.* 35:59 – 65.

Martinsen, A., K. Kringstad and I. Carberg (1988). Helogen in Ground water. *Water. Sci.* 20:45 – 56.

Method, S. (1982). Purgeable organic halides. *Proc. Hydrol.* 90:322 – 340.

Montiel, A., S. Rauzy and D. Tricard (1985). Organic aquatic Pollution. *Water. Suppl.* 3:64-90.

NEN [Netherland Environmental Network] (1986). Water – Bepaling ven het halogengehlfe. *Afkomsting.* 95:47 – 60.

Oake, R. J and I.M. Anderson (1984). The determination of carbon Adsorbable organohalide in waters. *WR.C. Tec. Rep.* T.R.217.

Odum, H and W. Christensen (1936). Danish ground water types and their geological occurrences. *Reitzel.* 12:6 – 20.

Oki, D.S and T.W. Giambelluca (1987). Study on ground water pollution. *Ground water.* 25:693 – 702.

Page, G.W (1981). Water pollution. *Environ. Sci.* Tec. 15:81 – 147.

Peoples, S.A., K.T. Maddy and T. Cusick (1984). Organic pollution in ground water. *Environ. Contain.* 20:55 – 70.

Pionke, H., A. Glotfelby and J.B. Lucas (1988). Organic pollution in underground water. *Environ. Qual.* 17:60 – 70.

Report, C. (1988). EOX and AOX inter laboratory comparative study. *Neth. J. Environ.* 30:417-435.

Richard, J.J., G.A. Junk and M.J. Avery (1975). Organic Pollution in water. *J. Geochem.* 11:135 – 143.

Stachel, B., V. Lahl and B. Zeschmar (1984). Helogenic compounds in under ground waters. *J. Water.* Sci. 53:120 – 127.

Standard, M. (1985). Examination of Water and wastewater. *Am. Pub.* Halt. 19:60 – 80.

Schmitt, R.A and Z. G. Weig (1962). Halogen in groundwater. *J. Agr. Sci.* 50:93 – 105.

Steelink, C (1985). *Humic Substances is soil, Sediment and water.* Willey. Pub. PP. 400.

Snoeyink, V.L., J. Mccreary and C. Muri (1977). Organic Pollution in water. *Proc. Chem. Sci.* 70:40 – 47.

Slingerland, P., G.J. Piet and J. Zuider (1982). Helogenated organic compound and Phenols. Work shop Dubendorf (switzerland) *Proc. Envirn. Soc.* 2:45 – 50.

Takahashi, T., R.T. Moore and R.J. Joyce (1981). Chemistry in water. *Revtt.* 29:47 – 59.

Van Steenderen, R. A (1980). Analysis of drinking underground water. *Lab. Prac.* 29:170 – 185.

Veenendaal, G., E.M. Van Beek and R. Wood (1986). Organische stoffen in ground water.*KIWA mededeling nr.* 97:131 – 138.

Wegman R.CC and P.A. Greve (1977). Analytical study on organic Polluted groundwater. *Sci. Total. Environ.* 7:30 – 38.

Wegman R.C.C (1981). Analysis of organic micropollutants in water. *Proc. Europe. Sympos.* 2:148 – 160.

Wegman, R.C.C (1982). Helogenated organic compounds and Phenols. *Proc. WorkshopDubendorf* (Switzerland). May 18 – 19. PP 500.

WHO [World Helth Organization] (1984). Guidelines for drinking water quality. *Bull. WHO.* 101:87 – 122.

Wilson, M.P., E.P. Savage and D.D. Adrian (1987). Helogen in under ground water. *Bull. Environ*. 39:14 – 20.

(*Accepted for publication May 2005*)