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Organic halogens: Determination in marine media of  
adsorbable, volatile, or extractable compound totals

C. GRØN

Department of Geology and Geotechnical Engineering  
Technical University of Denmark  
DK-2800 Lyngby  
Denmark

INTERNATIONAL COUNCIL FOR THE EXPLORATION OF THE SEA  
CONSEIL INTERNATIONAL POUR L'EXPLORATION DE LA MER

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## ORGANIC HALOGENS: DETERMINATION IN MARINE MEDIA OF ADSORBABLE, VOLATILE, OR EXTRACTABLE COMPOUND TOTALS

### 1 INTRODUCTION

The environmental impact of the release of halogenated organic compounds to the sea has become of increasing interest during recent decades. Most compounds in this group are xenobiotic of origin and, consequently, of potential environmental hazard. The characterization of domestic and industrial discharges with respect to their contribution of halo-organic compounds to the sea, as well as monitoring to determine the occurrence and levels of halo-organic compounds in the marine environment, have been major topics. This leaflet reviews frequently employed methods for the determination of organic halogens as group parameters in water samples. The methods are evaluated with respect to their applicability in waste water characterization and marine monitoring. Results from the analysis of organic halogens in samples of marine water, sediments, and biological organisms are summarized. It appears that determinations of extractable organic halogens (EOX) in marine samples are the methods of prime interest.

The nature and concentrations of halogenated organic compounds in waste waters are largely dependent on the source of the waste water, and only general statements can be made on this subject. The results of numerous investigations on the characterization of halo-organics in waste waters have been published, but the compilation of these data is beyond the scope of this leaflet. It can be stated, however, that half of the chemical substances considered 'priority pollutants' are halogenated organics (Keith and Teillard, 1979) and that halogenated organic compounds belong to the chemical substances (List 1) whose use in the European Economic Community should be minimized to the lowest possible level (Keune, 1976).

Investigations of marine contamination have revealed a 'background' level in sea water of 0.1-10 ng/l for individual halogenated organic compounds, such as halogenated C<sub>1</sub>-C<sub>2</sub>-aliphatics, chlorophenols (CPs), polychlorinated biphenyls (PCBs), DDTs, and chlorinated benzenes (Fogelquist, 1984; Folke *et al.*, 1983; Giger, 1977; Lunde and Gether, 1976; Øresund Commission, 1984).

In marine sediments and organisms, the baseline levels of chlorophenols, PCBs, DDTs, and chlorinated benzenes are generally within the range 1-100 ng/g wet weight. Some species of marine organisms and some biological tissues particularly capable of bioaccumulation can show levels as high as 10 µg/g wet weight, even in the absence of an actual emission zone (Brevik *et al.*, 1978; Folke *et al.*, 1983; Granby, 1987; Greig and Sennefelder, 1987; Knutzen *et al.*, 1984; Schults *et al.*, 1987; Tanabe and Tatsukawa, 1987; Young and Gosset, 1980).

It is to be expected that many xenobiotics, which are not easily detected by the commonly applied analytical methods such as gas chroma-

tography (GC) and high performance liquid chromatography (HPLC), will occur in the marine environment in addition to the types of compounds mentioned above. Furthermore, a contribution to the total load of halo-organics in the marine environment is anticipated from the degradation products of major halogenated organic contaminants, from minor contaminants, and from naturally occurring halogenated organics, such as algal metabolites.

Consequently, there is a need for analytical methods capable of determining the total amount of organic halogens in sea water, marine sediments, and tissues of marine organisms.

## 2 GROUP PARAMETERS FOR THE DETERMINATION OF ORGANIC HALOGENS IN WATER SAMPLES

A number of methods for the determination of organic halogens have been developed since 1973 with special reference to the analysis of waste waters and drinking waters. The applicable methods and their performance characteristics have been reviewed occasionally (Cooper and Young, 1984; Dressman *et al.*, 1979; Stevens *et al.*, 1984; Wegman, 1982a, 1982b). Standard methods or drafts of standard methods have been developed for the determination in water samples of adsorbable organic halogens (AOX) (Anon., 1985; DIN, 1985; ISO, 1986; Joyce, 1981; U.S.EPA, 1982a), of volatile organic halogens (VOX) (NEN, 1986a; U.S.EPA, 1982b), and of extractable organic halogens (EOX) (DIN, 1984; NEN, 1986b). To the knowledge of the author, no standard methods are available for the determination of organic halogens as group parameters in other matrices.

Generally, methods for the determination of organic halogens comprise three steps: (1) enrichment, (2) mineralization of organic halogens to halogenides, and (3) detection of halogenides.

Enrichment techniques employed include the adsorption of organics onto a solid sorbent, the extraction of lipophilic organics with an organic solvent, and the purging of volatile organics from the sample.

Mineralization techniques employed are: (a) combustion in an  $O_2/CO_2$ -atmosphere, (b) combustion in an  $O_2$ - or  $O_2/Ar$ -atmosphere, (c) combustion in an  $O_2/H_2$ -flame, and (d) saponification with sodium and photolysis under UV-irradiation. Methods using detection by neutron activation analysis (NAA) or particle-induced X-ray emission analysis (PIXE) do not demand a mineralization step.

Detection is achieved by means of microcoulometry, ion-chromatography, titrimetry, ion-selective electrodes, neutron activation analysis, or particle-induced X-ray emission analysis.

### 2.1 Enrichment steps

For the determination of AOX, granular activated carbon (GAC) is usually the sorbent of choice. The organics of the sample are adsorbed by passing the acidified (pH 2) and dechlorinated sample through two columns in series, each containing 40 mg of GAC (Takahashi *et al.*,

1981). Subsequently, inorganic chloride is removed by on-column washing with a few millilitres of acidified  $\text{KNO}_3$  solution. Alternatively, the adsorption is carried through batchwise, followed by filtering off the sorbent and removing the chloride by washing the GAC on the filter with nitrate solution. When there is a high concentration of inorganic chloride ( $>1$  g/l), it is advisable to resuspend the filtercake in a few millilitres of nitrate solution (DIN, 1985).

Sorbents such as XADs (polystyrene-divinylbenzene and polyacrylic ester resins) and Tenax (vinylacetate polymer) have been suggested as alternatives (Glaze *et al.*, 1977; Sekerka and Lechner, 1982). Method studies have shown that higher AOX values are obtained for chlorinated drinking waters and for waste waters from the pulp industry using GAC adsorption compared to the XAD sorbents. This is presumably caused by the loss of polar and/or high molecular weight compounds from the XAD resin (Glaze *et al.*, 1979; Sjöström *et al.*, 1985). Only thermally desorbable compounds can be determined using the Tenax enrichment.

For the determination of EOX, the use of several solvents in liquid-liquid extraction has been attempted. The solvents of choice in the standard methods available are apolar solvents or solvent mixtures, such as pentane, hexane, or low-boiling petrolether (DIN, 1984; NEN, 1986b). In order to improve the recovery of polar compounds, a second extraction step employing a more polar solvent, such as diisopropyl-ether, can be incorporated into the method. A comparison of extraction efficiencies shows that a somewhat lower recovery is to be expected using an apolar solvent only, when analysing, for example, polluted river water. This is caused by the low recovery of polar compounds, such as chlorinated phenols (Fritschi *et al.*, 1978) and trichloroacetic acid (Jäger and Hagenmaier, 1980). Using an apolar solvent only, the recovery of most chlorinated xenobiotic compounds of interest has been found to be greater than 80% (Wegman and Greve, 1977). Reversed-phase high pressure liquid chromatography (HPLC) has been suggested as a versatile, alternative method for the preconcentration of lipophilic organic compounds (Maierski *et al.*, 1982).

The analysis for VOX is, strictly speaking, a determination of purgeable organic halogens under purging conditions specified with respect to purge temperature, purge-gas-volume/water-sample-volume ratio, and the selectivity of preconcentration steps (Wegman, 1982b). Generally, compounds with a water solubility below 1%, a boiling point below  $180^\circ\text{C}$ , and a Henry's law constant larger than 0.05 should be recovered satisfactorily (Wegman, 1982b).

Purge temperatures ranging from  $20^\circ\text{C}$  to  $95^\circ\text{C}$  and purge-gas-volume/sample-volume ratios from 5 to 150 have been reported (NEN, 1986a; Wegman, 1982a; Wegman, 1982b).

Purging directly to the mineralization unit is applied in a number of methods (Jekel and Roberts, 1980; Maierski *et al.*, 1982; Takahashi *et al.*, 1981; U.S.EPA, 1982b; Zuercher, 1982). In order to lower the analytical limit of detection, a preconcentration step can be included. Among the preconcentration methods employed are cryotrapping (Slingerland, 1983; Slingerland *et al.*, 1982) or trapping on Tenax

(NEN, 1986a; Wegman and Piet, 1982), followed by thermal desorption to the mineralization unit. Trapping on GAC by means of a modified closed-loop stripping method (CLSA), followed by transfer of the GAC to the mineralization unit has also been suggested (Grøn, 1990).

## 2.2 Mineralization steps

The mineralization technique generally used is combustion in a controlled atmosphere. The composition of the combustion gas and the temperature of combustion are the main features controlling the recovery of individual halogenated compounds.

Combustion gasses consisting of oxygen, oxygen/hydrogen, oxygen/inert gas, or oxygen/carbon dioxide have been used. Larger recoveries of bromine compounds and of some chlorinated compounds are obtained with the  $O_2/CO_2$ -combustion than with the  $O_2$ - or  $O_2$ /inert-gas methods (Stachel et al., 1982; Takahashi et al., 1987). For the AOX determination, this effect is insignificant (Oake and Anderson, 1984). From other comparisons of methods, it is also suggested that oxygen combustion is more efficient than the Wickbold combustion ( $O_2/H_2$ ) and than saponification with sodium (Bauer, 1983; Stachel et al., 1984a, 1984b).

Combustion temperatures are selected between 800 °C and 2100 °C in order to prevent incomplete combustion (coking).

No comparative evaluations are available with regard to the mineralization efficiencies of the Schöniger combustion (Pictrogrande et al., 1985) or of UV-photolysis (McCahill et al., 1980).

## 2.3 Detection steps

Automated coulometric titration is the most common detection technique. This detection method allows the quantification of the total amount of chloride, bromide, and iodide evolved during mineralization.

New ion chromatographic methods have been developed that permit the separate quantification of fluoride, chloride, bromide, and iodide (Brandt and Kettrup, 1987a,b,c; Henschel et al., 1983; Zuercher, 1982).

Ion-selective electrodes and potentiometric titration can be employed allowing the separate quantification of chloride and bromide (Glaze et al., 1979; Pictrogrande et al., 1985).

Methods without the need for a mineralization step, such as PIXE and NAA, have been used for the determination of chloride or of chloride, bromide, and iodide (Ahnoff et al., 1979; Häsänen and Manninen, 1987; Hemming and Holmbom, 1984; Lunde et al., 1975; Watanabe et al., 1987). A simplified gas chromatographic method has also been suggested (Nulton et al., 1984).

## 2.4 Interferences

The major interference when determining the AOX of a water sample on GAC is inorganic halide. Ratios of inorganic chloride/organic halide (ICl/OX) of the order 2000 - 50,000 have been suggested as the maximum acceptable ratios in order to avoid interference (Joyce, 1981; Takahashi *et al.*, 1981). These figures refer to the standard procedures, as outlined above, and to the interference of chloride. Modification of the standard procedure (Kringstad, pers. comm.) allows a ratio ICl/OX of 300,000 (Grøn, unpubl.). It has been shown that concentrations of bromide and iodide below 1 mg/l do not cause interference (Oake and Anderson, 1984). Inorganic as well as organic halogens in suspended solids contribute to the AOX of the sample (DIN, 1985).

Glaze *et al.* (1979) showed that no significant interference occurred from 350 mg/l chloride with the XAD AOX method.

For all methods, chlorine and related chlorinating agents must be masked by the addition of a reducing agent such as sulfite or thio-sulfate.

In order to avoid competitive adsorption by the GAC AOX methods, an organic carbon concentration of less than 10 mg C/l must be aimed at (DIN, 1985).

Nitrogen and sulfur compounds can cause interference in methods based on combustion/coulometry (Glaze *et al.*, 1979; Jäger and Hagenmaier, 1980; Oake and Anderson, 1984). The significance of this interference has not been agreed upon. However, it has been stated that, for equipment with a washing flask containing concentrated sulfuric acid between the furnace and the coulometric cell, combustion of approximately 0.5 mg each of organic sulfur or nitrogen can occur without interference (Oake and Anderson, 1984).

## 2.5 Evaluation of methods applied to water samples

Some generally accepted and widely applied methods for the determination of organic halogens in water samples are listed in Table 1.

Data on the recoveries of selected halogenated organic compounds of major environmental concern are compiled in Table 2. These data are sorted according to the type of enrichment step, and comments are given on mineralization and detection steps.

A few interlaboratory comparisons have been conducted to evaluate the overall analytical performance of the methods for organohalogen determination (ASTM, unpubl.; KIWA, 1988; U.S.EPA, 1986). Table 3 summarizes selected statistical estimates from two recent interlaboratory comparison exercises.

It can be concluded from the method performance data given above (see Sections 2.1 - 2.5) that methods are available for the reliable determination of AOX, EOX, and VOX in waste waters and in freshwater recipients. Each parameter provides important information on the nature and properties of the organohalogens in question. However, when

Table 1. Methods generally applied for the determination of organic halogens.

PRECONCENTRATION	MINERALISATION	DETECTION	ANALYTICAL LIMIT OF DETECTION	REFERENCES
Adsorption, GAC	Combustion, $O_2/CO_2$ , $800^{\circ}C$	Coulometric titration	2.5-5 $\mu g$ Cl/l	2, 31, 52, 59, 61
Adsorption, GAC	Combustion, $O_2/Ar$ , $950-1000^{\circ}C$	Coulometric titration	5-10 $\mu g/Cl/l$	12, 28, 45
Adsorption, GAC	Combustion, $O_2$ , $1050^{\circ}C$	Ion chromatography	65 $\mu g$ Cl/l 20 $\mu g$ Br/l	7
Adsorption, GAC	None	NAA	5 $\mu g$ Cl/l 0.5 $\mu g$ Br/l	25
Adsorption, XAD	Combustion, $O_2$ , $800^{\circ}C$	Coulometric titration	2 $\mu g$ Cl/l	19
Adsorption, XAD	None	PIXE	10 $\mu g$ Cl/l	26
Extraction, petrolether	Combustion, $O_2/Ar$ , $850^{\circ}C$	Coulometric titration	0.1-1 $\mu g$ Cl/l	43, 67
Extraction, pentane	Combustion, $O_2/H_2$ , $2100^{\circ}C$	Coulometric titration	20 $\mu g$ Cl/l	11
Extraction, cyclohexane	None	NAA	0.05 $\mu g$ Cl/l	1
Purge, $45-60^{\circ}C$ , on line	Combustion, $O_2/CO_2$ , $800^{\circ}C$	Coulometric or potentiometric titration	1-5 $\mu g$ Cl/l	59, 62, 71
Purge, $60-95^{\circ}C$ , Tenax-trapping	Combustion, $O_2$ , $850^{\circ}C$	Coulometric titration	0.05-0.5 $\mu g$ Cl/l	42, 68
Purge, $60^{\circ}C$ , cryotrapping	Combustion, $O_2/He$ , $900^{\circ}C$	Coulometric titration	0.1 $\mu g$ Cl/l	53, 54, 69
Purge, $30^{\circ}C$ , GAC-trapping	Combustion, $O_2/CO_2$ , $800^{\circ}C$	Coulometric titration	0.5 $\mu g$ Cl/l	22



Table 2. Recovery data for methods to determine organic halogens for some compounds of environmental concern.

COMPOUND	AOX % <sup>a</sup>	EOX %	VOX %
Dichloromethane	7 <sup>b</sup> , 98 <sup>c</sup>	58 <sup>i</sup>	87-101 <sup>l</sup> , 91 <sup>m</sup>
Trichloromethane	91 <sup>c</sup> , 73 <sup>d</sup> , 94 <sup>e</sup>	34 <sup>i</sup>	79-81 <sup>l</sup> , 90 <sup>m</sup>
Tribromomethane	101 <sup>e</sup> , 63 <sup>f</sup>	-	64 <sup>l</sup>
Trichloroethene	97 <sup>b</sup>	-	76 <sup>l</sup> , 98 <sup>m</sup>
Tetrachloroethene	98 <sup>b</sup> , 48 <sup>c</sup>	35 <sup>i</sup> , 0 <sup>j</sup>	76-86 <sup>l</sup> , 74 <sup>m</sup>
Dichlorobenzenes	41 <sup>c</sup> , 107 <sup>e</sup>	90 <sup>j</sup>	51-65 <sup>l</sup> , 32 <sup>m</sup>
Chlorophenols	91 <sup>c</sup> , 104 <sup>d</sup>	67 <sup>k</sup>	0-5 <sup>l</sup>
Trichlorophenols	106 <sup>e</sup> , 70 <sup>g</sup>	72 <sup>k</sup>	-
Aldrin	80 <sup>f</sup>	92 <sup>j</sup>	-
Lindane	83 <sup>f</sup>	84 <sup>j</sup>	-
PCBs	75 <sup>h</sup>	79-82 <sup>j</sup>	-

<sup>a</sup> Relative to the theoretical value.

<sup>b</sup> GAC-adsorption, O<sub>2</sub>/CO<sub>2</sub>-combustion, coulometric detection, ref. 9

<sup>c</sup> GAC-adsorption, O<sub>2</sub>-combustion, ion chromatographic detection, ref. 7

<sup>d</sup> XAD-adsorption, O<sub>2</sub>-combustion, coulometric detection, ref. 19

<sup>e</sup> GAC-adsorption, O<sub>2</sub>/CO<sub>2</sub>-combustion, coulometric detection, ref. 59

<sup>f</sup> GAC-adsorption, O<sub>2</sub>-combustion, coulometric detection, ref. 45

<sup>g</sup> XAD-adsorption, PIXE detection, ref. 26

<sup>h</sup> GAC-adsorption, O<sub>2</sub>/CO<sub>2</sub>-combustion, coulometric detection, ref. 23

<sup>i</sup> Pentane- and diisopropylether-extraction, O<sub>2</sub>/H<sub>2</sub>-combustion, coulometric detection, ref. 9

<sup>j</sup> Petrolether-extraction, concentration of extract, O<sub>2</sub>/Ar-combustion, coulometric detection, ref. 67

<sup>k</sup> Diisopropylether-extraction, concentration of extract, O<sub>2</sub>/CO<sub>2</sub>-combustion, coulometric detection, ref. 16

<sup>l</sup> Purge at 45<sup>o</sup>C on line to O<sub>2</sub>/CO<sub>2</sub>-combustion, coulometric detection, ref. 16, 49

<sup>m</sup> Purge at 60<sup>o</sup>C to Tenax, thermal desorption and O<sub>2</sub>/He-combustion, coulometric detection, ref. 68

dealing with unpolluted natural waters, the limit of detection of some methods might be higher than the actual concentrations.

The determination of AOX by means of GAC-adsorption cannot be considered appropriate for the purpose of sea water analysis. Chloride interferences are negligible only for the analysis of waters of low salinity (brackish waters), and the detection limits attainable are above the expected concentrations of organohalogens outside areas of discharge.

The data available on chloride interferences in the conduct of AOX analysis by means of XAD-adsorption are insufficient to judge the applicability of this method for sea water analysis. The detection limits reported for this method are also high.

EOX analysis by means of extraction, concentration, combustion, and coulometric detection, and by means of extraction and NAA detection, is applicable down to levels of 5 to 10 times the background concentrations recorded for individual halogenated organic compounds in sea water. Chloride interferences have not been thoroughly investigated, but are not expected to present major difficulties. These methods can be considered potentially useful for monitoring sea water quality with regard to organohalogen compounds. It must be emphasized, however, that the NAA technique cannot be characterized as a routine method.

With respect to limits of detection and potential chloride interferences, the VOX methods with a trapping step can be regarded as potentially useful for sea water monitoring, based on the considerations stated above for EOX determinations. It should be noted that specific analysis using the GC technique permits the determination of individual halogenated volatile organic compounds at the ng/l level at a cost level comparable to that of VOX analyses.

Table 3. Results of recently conducted interlaboratory comparisons on AOX and EOX determinations, expressed as statistical estimates.

ANALYTICAL METHOD	SAMPLE TYPE	MEAN VALUE	RECOVERY OF ADDED STANDARD %	COEFFICIENT OF VARIATION %
EOX	Drinking water <sup>a</sup>	2 µg Cl/l	69	29
	Fresh surface water <sup>a</sup>	5 µg Cl/l	67	27
AOX	Drinking water <sup>a</sup>	12 µg Cl/l	72	22
	Synthetic sample <sup>b</sup>	190 µg Cl/l	90	9

<sup>a</sup>KIWA, 1988.

<sup>b</sup>ASTM, unpublished.

## 3 ORGANIC HALOGEN DETERMINATIONS APPLIED TO MARINE SAMPLES

Selected monitoring data for marine samples subjected to organic halogen analyses are given in Table 4.

Marine samples have mainly been analysed by means of EOX methods, although one example has been reported of the determination of volatile organohalogen compounds in the tissues of marine organisms by means of steam distillation and NAA of the distillate (Lunde and Gether, 1976).

The EOX methods applied include extraction of the sample, concentration of the extracts, and detection by NAA, or by combustion and coulometry (see Table 4). The types of samples investigated have mainly been sediments and marine organisms.

Data on the precision and accuracy of a published method for the determination of EOX in marine organisms employing the coulometric detection technique are summarized in Table 5.

The results obtained using detection by NAA and by combustion/coulometry have been compared in an investigation (Martinsen and Grøn, unpubl.). In view of the expected analytical accuracy and precision of the two methods, the agreement in the results was considered satisfactory. In the same investigation (Martinsen and Grøn, unpubl.), the complete removal of inorganic halide from the extracts was ascertained, in accordance with previously published results (Lunde and Gether, 1976).

Treatment of the extracts with sulfuric acid has been employed to remove organohalogen compounds of natural origin and leave behind the xenobiotic organohalogens (Lunde and Gether, 1976). The resulting parameter, extractable persistent organic halogen (EPOX) (or chlorine (EPOCl)), has been compared to EOX for a number of marine organisms (Lunde and Gether, 1976). EPOX constituted 4-55% of the total EOX. No investigation has been conducted on the nature and origin of those halogenated organic compounds removed by the sulfuric acid treatment.

The amount of halogen in identified organic compounds generally amounts to 1-20% of EOX and to 2-100% of EPOX (Knutzen *et al.*, 1984; Lunde and Gether, 1976; Lunde *et al.*, 1975; Ofstad and Martinsen, 1983; Watanabe *et al.*, 1987). The types of compounds determined specifically are PCBs, hexachlorobenzene, DDTs, and hexachlorocyclohexanes. In general, the sum of organohalogens identified as individual compounds constitute a substantially greater fraction of the EPOX than of the EOX.

From the data compiled in Table 4, it appears that concentrations of EOX are comparatively high in all matrices. The levels vary with the degree of pollution and with the matrix analysed. EOX concentrations in blue mussels (Mytilus edulis) are particularly high.

Table 4. Selected data for the EOX analysis of marine samples.

SAMPLE MATRIX	SAMPLING AREA DESCRIPTION	METHOD	ORGANIC HALOGEN CONTENT (as Cl)	REFERENCE
Sea water	Oslofjord, Norway	EOX/NAA	20-200 ng/l	37
	Halsefjord, Norway <sup>1</sup>	EOX/NAA	15-50 µg/l	37
Marine sediments	Limfjord, Denmark	EOX/MC <sup>2</sup>	5-15 µg/g ww <sup>3</sup>	23
	Kristiansandsfjord, Norway <sup>4</sup>	EPOX/NAA <sup>5</sup>	0.3-20 µg/g dw <sup>6</sup>	35
	Osaka Bay, Japan	EOX/NAA	5-10 µg/g dw	64
Blue mussels	Køge Bugt, Denmark	EOX/MC	2 mg/g lw <sup>7</sup>	24
	Kattegat, Denmark	EOX/MC	0.8 mg/g lw	23
	Holbæk Fjord, Denmark	EOX/MC	1.2 mg/g lw	23
	Lillebælt, Denmark	EOX/MC	0.5 mg/g lw	23
	Lillesand, Norway	EOX/NAA	0.25 mg/g lw	38
	Lillesand, Norway	EPOX/NAA <sup>5</sup>	0.05 mg/g lw	38
	Kristiansandsfjord, Norway <sup>4</sup>	EPOX/NAA <sup>5</sup>	0.2-2.5 µg/g ww	35
Japan	EOX/NAA	0.06-0.25 mg/g lw	64	
Fish muscle	Oslofjord, Norway	EOX/NAA	0.05-0.25 mg/g lw	38
	Oslofjord, Norway	EPOX/NAA <sup>5</sup>	0.01-0.03 mg/g lw	38
	Kristiansandsfjord, Norway <sup>4</sup>	EPOX/NAA <sup>5</sup>	0.07-0.48 mg/g lw	35
	Japan	EOX/NAA	0.01-0.035 mg/g lw	64
Fish liver	Kristiansandsfjord, Norway <sup>4</sup>	EPOX/NAA <sup>5</sup>	0.02-0.12 mg/g lw	35
Seals	Norway	EPOX/NAA <sup>5</sup>	0.005-0.03 mg/g lw	46

<sup>1</sup> discharge area of PCB industry

<sup>2</sup> combustion and coulometric detection

<sup>3</sup> data given relative to wet weight

<sup>4</sup> samples taken proximal and distant to industrial discharge area

<sup>5</sup> the basic methods employed give EPOX or EPOCl: extractable organic halogen or chlorine resistant to chemical degradation (H<sub>2</sub>SO<sub>4</sub> treatment of extracts)

<sup>6</sup> data given relative to dry weight

<sup>7</sup> data given relative to lipid weight

Table 5. Performance characteristics for the determination of EOX in blue mussels employing coulometric detection (Grøn and Folke, 1985)

SAMPLE TYPE	MEAN VALUE ( $\mu\text{g Cl/g ww}$ )	RECOVERY OF ADDED STANDARD (%)	COEFFICIENT OF VARIATION (%)
Blue mussels	9.9	-	12
Blue mussels, spiked <sup>1</sup>	29.6	90	9.9

<sup>1</sup> 22  $\mu\text{g Cl/g ww}$  added in the form of p-dichlorobenzene and 2,4,6-trichlorophenol in equal amounts.

## 6 SUMMARY

Analytical methods with satisfactory performances are available for the determination of fractions of halogenated organic compounds (AOX, EOX, VOX) as group parameters for the analysis of waste water samples and samples of polluted recipient fresh water. For the analysis of marine waters, only the determination of EOX with detection by means of combustion/coulometry or NAA seems useful at present.

Marine sediments and biological samples can be analysed advantageously for EOX to obtain a picture of the total load of organohalogen compounds on a marine area. Further research regarding the nature and origin of organic halogens not accounted for by individually detected, xenobiotic halogenated organic compounds is necessary.

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