The Sum of Chlorinated and of Brominated Non-Polar Hydrocarbons in Water

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Summary

It is proposed to use chlorine as a common parameter in the study of the non-polar chlorinated hydrocarbons in the aquatic environment. Also the ratio of the sum of chlorine to bromine may be useful indicator of pollution by such compounds. Detector of chlorine and of bromine in this form is based on neutron activation analysis.

Further information on the nature of organochlorine material is obtained by studying variations in the chlorine content with chemical and physical manipulations. Simultaneous determination of known organochlorine micropollutants allows the level of unidentified chlorinated hydrocarbons to be assessed.

In samples of fresh- and sea-water so far analyzed, the total content of non-polar organic bound chlorine exceeds that which can be accounted for as polychlorinated biphenyls (PCB) by a factor of 10 to 100.

Introduction

Most work carried out today in the field of organic micropollutants is based on the determination of known compounds and their metabolites in biological material and in water. Notable examples are various pesticides, polyaromatic hydrocarbons (PAH) and the polychlorinated biphenyls (PCB). This approach has proved to be a rational on where suitable standards may be obtained. Using this approach there is, however, a tendency to overlook substances about which no previous knowledge exists. These substances may be formed naturally, or by non-specific processes such as incomplete combustion. They may also originate from the multitude of products and by-products of industrial chemical processes.

Among the more important groups of organic micropollutants are the non-polar chlorinated hydrocarbons, both known and those of unidentified nature. Determination of the total amount of chlorine will reveal whether known substances such as the PCB form a minor part only, or represent a major portion of this group.

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Unknown man-made chlorinated substances may originate from the large production and extensive use of such substances as polyvinyl chloride and chlorinated solvents and from their destruction and metabolic breakdown. Gaseous chlorine released to the environment may result in direct chlorination of natural substances, e.g. by photo-chlorination processes. Non-enzymic chlorination and bromination of unsaturated hydrocarbons in surface films in the oceans may also occur.

Some chlorinated organic compounds are known in various microorganisms, lichens and sea-weeds (MILLER 1961, BENDZ et al. 1967, SIMS, et al. 1971), but natural chlorinated compounds and metabolites are commonly considered to be rare (SUIDA et al. 1973, HYLIN et al. 1969). Fair amounts of non-specifically brominated hydrocarbons have, however, been shown to be present in marine oils (LUNDE 1972), and recent results show that this may be so with respect to chlorine as well (LUNDE and STEINNES 1973, TANANGER and JORDAL 1973). These results may indicate that natural formation of chlorinated and brominated hydrocarbons are much more extensive that what has previously been supposed.

To attain a better understanding of the level of chlorinated and also of brominated non-polar hydrocarbons in nature, analytical methods are required that allow the precise and specific measurement of chlorine and bromine, present in the organic bound form. Non-destructive neutron activation analysis (NDAA) provides a means to such a total analysis. The only requirement is that inorganic halides may be removed to a sufficiently low level not to disturb the analysis for the organic form. When using the short-lived radioactive isotopes of chlorine and bromine, an irradiation time of 5 min. at a flux of $1.3 \cdot 10^{13}$ n/cm^2 sec. and 5 min. registration with a Ge-Li detector, the minimum detectable amounts are appox. 50 ng for chlorine, and 10 ng for bromine (SOETE et al. 1973). Coupled with the use of efficient, in situ liquid/liquid extraction of water (see below), this translates to about 0.5 ppt for Cl and 0.1 ppt for Br. (1 ppt = 1 part per 10^{12}). Background levels, however, at present may limit sensitivity for chlorine to about ten times the above value. In comparison, the content of PCB in marine waters is of the order of 1 ppt (AHNOFF and JOSEFFSON 1974, AHLING and JENSEN 1970.

Experimental

The analytical procedure is outlined in Fig. 1 and consists of the following steps:

The non-polar organic micropollutants are isolated from approx. 200 litres of water by continuous extraction with about 0.2 litres of a non-polar solvent such as cyclohexane (AHNOFF and JOSEFSSON 1974). Inorganic halides are subsequently removed from this base extract by washing with halide-free water. Previous work in this

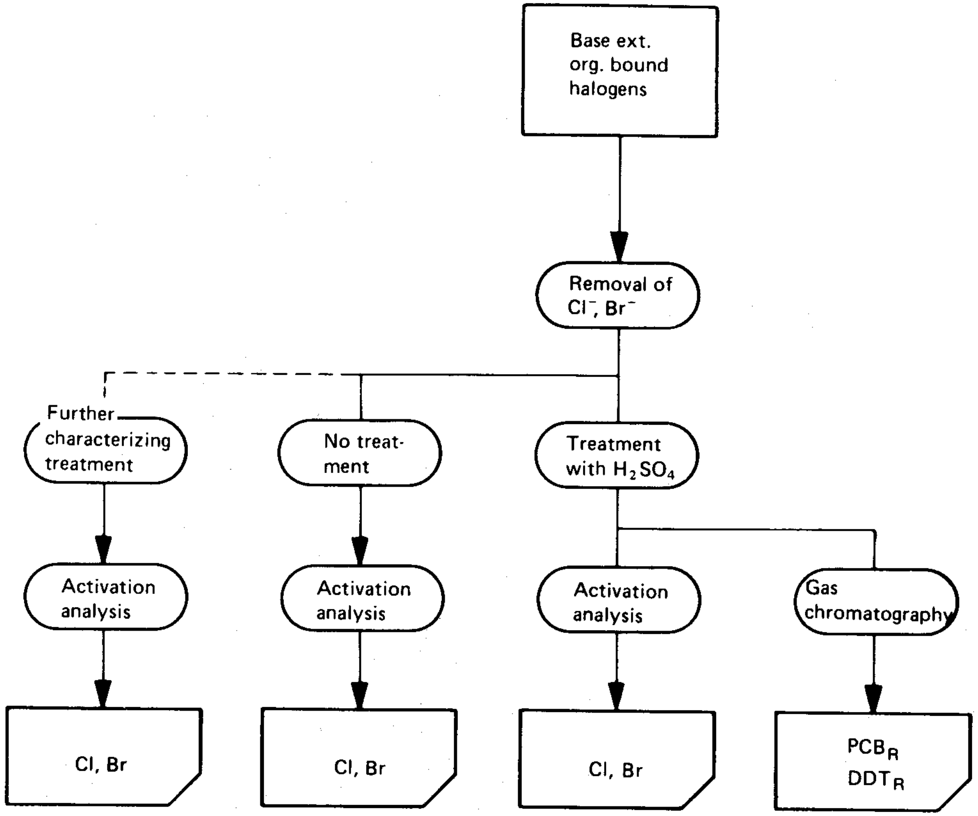

Figure 1. Outline of Analytical Procedure

TABLE 1

ORGANIC BOUND HALOGENS AND PCB IN WATER (ppt)

SAMPLE	MODE OF PREPARATION	UNTREATED SAMPLE		SAMPLE TREATED WITH H_2SO_4		PCB
		Cl	Br	Cl	Br	
Sea water	continuous					
Oslofjord, Drøbak	extraction					
November 1973		195	18	102		1.6
December 1973		40	6	13		1.1
Fresh water supply	continuous					
Maridalsvannet, Oslo	extraxtion					
April 1973		60	12	15	0.2-0.5	0.6
Tap water	continuous					
Maridalsvannet, Oslo	extraction					
April 1973		57	12	15	0.1-0.3	0.5
Fresh water	continuous					
Göta River, Gothenburg	extraction	5300	10			0.3
Nordre River, Gothenburg		2100	5			0.3
October 1972						
Blank		10	0.05	7	0.05	0.1
Sea water	distilled					
Halsefjord	sample					
5 *m*		49200	480			
18 *m*		15600	36			
September 1972						

laboratory and elsewhere (SCHMITT 1962, LUNDE 1971, LUNDE 1973) has shown inorganic halides to be efficiently removed by this process. It has been further substantiated by experiments with radioactive bromide tracers for this work (STEINNES et al.). The extract is concentrated (e.g. in a Kuderna-Danish apparatus) to a few millilitres, and divided into aliquots for chemical treatment (see Fig. 1).

The treated aliquots are finally neutron activated at the reactor facility in halide-free polythene vials together with chlorine and bromine standards, and the induced activity recorded with a multichannel spectrometer as described above. The isotopes ^{38}Cl with $T_{1/2}$ = 37 min, and 80Br with $T_{1/2}$ = 17 min. are used for the determination of chlorine and bromine respectively in this study. The experimental procedure is to be described in further detail elsewhere(STEINNES, et al.).

Results and Discussion

The results of some analyses so far carried out on extracts from salt- and fresh-water are shown in Table 1. While the PCB level in the water samples is approximately at 1 ppt, the level of chlorinated compounds seems to be much higher. In the samples from the Gota river and Nordre river (West Coast, Sweden) the content of organically bound non-polar bromine is approximately at the same level as in samples from the Oslofjord and lake Maridalsvannet, while the level of chlorine is a hundred times higher. Thus, clearly a large excess of chlorinated hydrocarbons are present here, indicating release of such compounds. A PVC production plant is located in the area where the Halsefjord samples have been taken. These samples have been isolated by a method particularly designed for volatile material.

On the basis of results and experience so far attained, it appears that non-destructive determination of organic bound chlorine and bromine may become a useful instrument in the control of chlorinated hydrocarbons in water. In addition to attaining a knowledge of the absolute amounts of organic chlorine, determination of the chlorine/bromine ratio may give information on the origin of chlorine-containing hydrocarbons.

The degree of toughness(chemical persistency)of the compounds present may be judged by a suitable selection of chemical reactions (see Fig. 1), as indicated by the amounts of chlorine present prior to and after treatment with concentrated sulfuric acid.

Work is under way to extend these studies also to biological material.

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