Assessment of total chlorine and bromine content in semi-volatile organic substances in water

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Abstract. The integral indicators for assessment of total concentration of chlorine and bromine in semi-volatile organic substances (SVOS) of water are presented. The method is based on liquid/liquid extraction of SVOS from a sample of water (natural, potable, industrial, purified sewage water etc.), concentrating the extract and without derivatization or conversion analyzed by the method of gas chromatography, coupled with atomic emission detecting (GC-AED). In this case the AED operates in two modes: the chlorine selective channel with detection at a wavelength of 479 nm and the bromine selective channel – at 478 nm. Under the given conditions of sample preparation and the chromatographic procedure the components are registered with Kovats retention index on non-polar phases from 900 to 3200. The range of the analytical procedure covers classes of SVOS, such as halogen-containing pesticides, aromatic and aliphatic hydrocarbons, fatty acids, ethers, polyaromatic hydrocarbons, phenols and their halogen derivatives. The total concentration of chlorine and bromine is calculated by component-independent calibration which is available by using an AED. The indexes are named Technogenic Organic Chlorine and Technogenic Organic Bromine, because analyzed compounds have technogenic or secondary technogenic origin. The sensitivity of determination is $1 \times 10^{-6}$ mg/dm$^3$ for the specified elements.

1. Introduction

The control of water contaminates is usually reduced to the definition of a specific list of compounds: global pollutants that have become ubiquitous and some site-specific emerging contaminant groups, which may be present in the water. The number of such compounds is not large, and it is defined on practical grounds taking into account the possible availability of laboratories and necessary rapidness of the analysis. Under this approach the informative value of the received data is not sufficient to assess the total water pollution because of the fact that a significant amount of the contaminants including chlorinated by-products has not been estimated [1].

In heavily industrial regions and megapolises the reservoir water usually has a complex matrix of organic pollutants. Especially in view of possible rain-storm flows from the territory of river watershed which can be agricultural lands or industrial sites, atmospheric transfers and other anthropogenic sources of contamination. Chemical plant wastewaters also pose risk to normal functioning of water resources [2]. First of all it depends on their complex chemical composition. The water treatment technologies
available at the plant not always cope with sewage treatment. The toxicity of the sewage increases at the disinfection stage, special by using chlorine-containing agents. Eventually, organic compounds including toxic halogenated xenobiotics, which are irrelevant to the biosphere, enter the water body [3, 4]. Also the formation of a large number of halogenated chlorination by-products in potable water is a known problem. Many of these compounds have not been identified and not quantitatively determined by routine control [5].

Most of the natural water bodies are receivers of treated wastewater and used as centralized drinking water resources simultaneously [6]. Therefor monitoring of them is relevant. Despite of the fact that only traces of halogen-containing organic compounds are often present in the purified effluent, they can accumulate in the water bodies not undergoing biotransformation and photooxidation due to their stability.

So, organization of a reliable system for monitoring the quality of water from natural water resources and potable water after chlorinated stage is an important task. Availability of information about growing general level of pollution provides for measures of strategic water management and control of the compliance with the standards for water protective areas.

2. Existing Assessment Methodology

In order to address the task of informational monitoring management, it is practical to use survey methods of analysis which allow for monitoring the general background pollution level and incidental emissions [7, 8], combined with control of the most toxic indicator compounds which are characteristic of the given object under observation [2].

In general, the survey methods of analysis can be subdivided into three categories: methods which allow for assessing the general group composition of pollutants, general ultimate composition and methods assessing the possibility of the pollutants to interact (to oxidize under the action of strong oxidizers, to be extracted, sublimated with steam and reduced, etc.). These are some examples of integral water quality indicators: Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Ultraviolet Absorption 254 nm, Steam-volatile Phenols, Permanganate index, Chemical oxygen demand, Total Organic Halogen (TOX), Adsorbable Organic Halogen (AOX) and Extractable Organic Halogen (EOX) [9-11].

The increased focus on the total content of halogen-containing organic water pollutants is due to their high toxicity, mutagenic and carcinogenic activity [12, 13].

According to the method for determination of extractable halogen-containing organic compounds in water (EOX), analytes are extracted from water and placed into the reactor where chlorine organic compounds are converted to HCl under oxygen atmosphere, bromine organic compounds – to HBr, etc. Then the conversion products are absorbed by water. The absorbate solution is analyzed by ion chromatography [11]. The degree of conversion is about 100%, the minimum detected level is $10^{-5} - 10^{-6}$ g/mm$^3$ depending on the element.

3. Results and discussion

This paper presents a new approach to assessing the total chlorine, bromine content in semi-volatile organic substances (SVOS) of water without derivatization or conversion stages. The new approach methodology is as follows. The sample of natural or drinking water is extracted with an organic solvent (e.g. methylene chloride), the extract is boiled down and analyzed by gas chromatography with atomic emission detection (GH-AED), the detector being adjusted for chlorine (479 nm) or bromine (478 nm) emission line.

Under the given conditions of sample preparation and analysis, the chromatograms record the components with Kovats retention index on non-polar phases from 900 to 3200, i.e. boiling out in the range of 150-500°C. This range covers such classes of limited-volatile organic compounds as pesticides (including highly molecular decil), aromatic and aliphatic hydrocarbons, fatty acids, ethers, phenols, polyaromatic hydrocarbons and also halogen derivative organic compounds produced upon chlorination of water [14]. The resulting element selective chromatograms show the total area of chlorine- and
bromine-containing compounds (figure). The total concentration of chlorine and bromine in the analyzed compounds is calculated by component independent calibration available when using the AED [15]. As far as the compounds are mostly of technogenic or secondary technogenic origin, the values are named Technogenic Organic Chlorine (TgOCl) and Technogenic Organic Bromine (TgOBr). The sensitivity of determination is $1 \times 10^{-6}$ mg/dm$^3$ on the given elements.

Definition of such values does not require a close-cut component separation of the sample, still the pollutants can be identified, if necessary, by the elements content in the molecule of the component or in combination with the results of chromatography mass-spectrometry. Such data cannot be obtained with the known composite indices.

![Figure 1. The element selective chromatograms of natural water extract after chlorination, registered on the characteristic wave lengths: CL (479 nm), Br (478 nm).](image)

The integral indicators TgOCl and TgOBr give much information when assessing not only the background pollution of water bodies with halogen compounds, but also when assessing the efficiency of water purification and water treatment at any stage of production and control. The using of these indicators is especially informative in selecting the type and dose of chlorinating agent during the water treatment to minimize the formation of halogenated derivatives.

4. Conclusion

The increased focus on the total content of halogen-containing organic water pollutants is due to their high toxicity, mutagenic and carcinogenic activity. Most of them belong to semi-volatile organic substances. A new approach to assessing the total chlorine and bromine content in semi-volatile organic substances of different type water without derivatization or conversion stages is present. The approach allows one to evaluate the total concentration of these halogens. The sensitivity of determination is $1 \times 10^{-6}$ mg/dm$^3$ on the given elements. The proposed indicators are named Technogenic Organic Chlorine and Technogenic Organic Bromine because analyzed compounds have technogenic or secondary technogenic origin.

5. Acknowledgments

The work was performed within the framework of State Task No. 5.12863.2018 / 8.9 “Development of a system for identification and quantitative analysis of environmental risks arising from the water supply of a large urban agglomeration”.

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