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ADSORBABLE ORGANIC HALIDES (AOX) IN WATER

INTRODUCTION

Following investment in new technology plus a comprehensive R&D development project, ALS now offers NATA Accredited Adsorbable Organic Halide (AOX) analysis.

AOX – WHAT ARE THEY?

Halogenated organic compounds (HOC) have increasingly been used within various industries over the years. Some man-made halogenated compounds are toxic, mutagenic, or carcinogenic and they may have harmful effects on human health and the environment.

Adsorbable Organic Halogen (AOX) Compounds (X = Cl, Br, I)) is a sum parameter for describing the organic halogen compound load in water, sewage sludge and soils.

The parameter covers a large group of substances from simple volatile substances such as trichloromethane (chloroform), or complex organic molecules such as dioxins/furans with a large variety of toxic properties. Most AOXs are chlorine-containing molecules, but bromo- and iodo-AOXs do also occur.

Almost all chemicals known as persistent organic pollutants (POPs), e.g., polychlorinated biphenyls (PCBs), DDT, and dioxins, are halogenated compounds. However, numerous halogenated organic compounds remain to be assessed to find out whether they harm human health or the environment and are therefore captured in the analysis of AOX.

AOX compounds pose a potential concern because they resist breaking down in the environment therefore they have long half-life periods. Some of these molecules are toxic at high concentrations. They may also pose a threat to aquatic organisms living in estuaries because they can bio-accumulate in the food chain. Hence, AOX can be important in effluent quality monitoring from landfill leachates or industry in order to meet discharge limits.

METHOD INFORMATION

ALS METHOD CODE
EP009
Instrumentation
Analytical Jena Multi X 2500
LIMITS OF REPORTING (LOR)
Drinking/Clean Water: 20 µg/L
Method Reference
US EPA 1650C

SOURCES AND FORMATION OF AOX

One of the main sources of AOX discharges world-wide is the pulp and paper industry. When using chlorine and chlorine chemicals to bleach fibres, some of the chlorine reacts with organic matter to form chlorinated organic substances which may then be discharged with the treated effluent and detected as AOXs.

Landfills can also be a source of necessary precursor organic compounds. Landfill leachates rich in organics which are discharged into waterways may flow into the water supply system. Leachates containing aromatic compounds will easily react with active chlorine and may generate halogenated compounds[1].

Smaller quantities of AOX are also formed during the routine chlorination of drinking water, swimming pools, cooling waters and process waters in laundries. In water treatment, the use of disinfectants such as chlorine, calcium hypochlorite and sodium hypochlorite results in the formation of free chlorine and combined chlorine residuals and disinfection by-products. Although many specific chlorine disinfection by-products have been identified, several of the total organic halogens have yet to be identified.

Other sources of AOX discharges are the effluents of industrial facilities which contain chlorine-containing substances from manufacturing or use. Raw hospital wastewater and effluent is also considered as an important source of AOX in municipal wastewater [3]. The chemical industry and other sectors such as metal surface treatment, textiles, waste treatment, printing and dry cleaning are also potential sources.

CLASSES OF HOC's

There are a series of different forms of halogenated organic compounds which can be determined:

AOX (Adsorbable Organically Bound Halogens)
Represents the organically bound halogens - chlorine, bromine and iodine (but not fluorine) contained in a sample which can be adsorbed on activated carbon.
EOX (Extractable Organically Bound Halogens)
Represents the organically bound halogens - chlorine, bromine and iodine (but not fluorine) - which can be extracted with a non-polar solvent.
POX (Purgeable Organically Bound Halogens)
Represents the organically bound halogens - chlorine, bromine and iodine (but not fluorine) - contained in a sample, which can be purged in the gas phase under defined conditions with an auxiliary gas.

AOX is by far the most common of the classes which are monitored and analysed however this is highly dependent upon specific industries.

REGULATORY GUIDELINES

The NSW Solid Waste Landfill Environmental Guidelines include AOX as an indicator parameter for groundwater detection monitoring programs with a required detection limit of 10 mg/L for AOX.

The Queensland Department of Environment Heritage Protection Waste Disposal (ERA 60) includes TOX as an indicator parameter for both surface and groundwater monitoring however doesn't apply a detection limit. The

Draft Guideline for Coal Seam Gas Recycled Water Management Plan and Validation (June 2011) stipulates that TOX is a parameter that must be included in the pre-supply water quality data collection program, aquifer baseline, source water, operational and verification monitoring programs.

ANALYSIS OF ADSORBABLE ORGANICS HALOGENATED COMPOUNDS

The method of determining AOX has been standardized worldwide through a large number of standards. The ALS methodology for the analysis of AOX is based on the US EPA Method 1650 and international standard ISO 9562.

AOX/TOX methodology uses carbon adsorption with a microcoulometric-titration detector to detect all organic halides containing chlorine, bromine & iodine that are adsorbed by granular activated carbon under specific conditions.

The result is a parameter used for water quality control purposes and represents the sum of organically bound chlorine, bromine and iodine (but not fluorine) that can be adsorbed on activated carbon under specified conditions and, if the sample is not filtered, includes that associated with suspended matter.

The Limit of Reporting (LOR) and Application Range is detailed right:

Analyte	Limit of Reporting
Adsorbable Organic Halides (AOX)	20 µg/L

IMPACTS ON HUMAN HEALTH AND ENVIRONMENT

There is no direct relationship between AOX value and toxicity. Excessive exposure to chemicals in this diverse grouping of chemicals may affect health with the possible effects depending on the particular chemical. Many of the chemicals detected under the parameter AOX are also individually listed. Some chlorinated chemicals detected by AOX are toxic to aquatic organisms at low concentrations. Many are persistent and can also bio-accumulate.

AOX compounds pose a potential concern because they resist breaking down in the environment. Some of these molecules are toxic at high concentrations. Because they can accumulate in the food chain, they pose a potential threat to aquatic organisms living in estuaries near bleached pulp effluents.

GENERAL SAMPLING & PRESERVATION REQUIREMENTS

Drinking Water: 500mL Amber Glass Bottle with Teflon Cap, Zero Headspace, pH<2 with HNO_3 .Samples containing residual chlorine (e.g. drinking water) must have sodium thiosulphate added. Storage: Cool to 0 to 4°C Holding Time: 6 months

For further information please contact your local ALS Client Services team.

REFERENCES

[1] Journal of Mater Cycles Waste Management 2001, Adsorbable organic halides (AOX), AOX formation potential, and PCDDs/DFs in landfill leachate and their removal in water treatment processes. Yukio Noma, Sayuri Yamane, Akiko Kida.

[2] Swedish Environmental Protection Agency, Swedish Pollutant Release and Transfer Register, Halogenated Organics Compounds, October 2009.

[3] National Centre for Biotechnology Information, Adsorbable organic halogen compounds and bio-toxicity in hospital wastewater treatment. Sun YX, Zhang F, Wang KL, Gu P. October 2007.