

# PARIVESH

NEWSLETTER

## *Adsorbable Organic Halides*



**CENTRAL POLLUTION CONTROL BOARD**  
**Ministry of Environment & Forests**

Website: [www.cpcb.nic.in](http://www.cpcb.nic.in)



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(भारत सरकार का संगठन)

पर्यावरण एवं वन मंत्रालय

### Central Pollution Control Board

(A Govt. of India Organisation)

Ministry of Environment & Forests

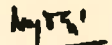
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Organic halogen compounds are a large class of natural and synthetic chemicals that contain one or more halogens (fluorine, chlorine, bromine, or iodine) combined with carbon and other elements. Many of these compounds are recalcitrant and have long half-life periods. Some of them show a tendency to bioaccumulate while some are proven carcinogens and mutagens. The group of organic halogens may be analyzed individually through GC, HPLC or other sophisticated instruments but to analyze them in a group as summary parameter (Adsorbable Organic Halides) adsorption technique is effective, accurate, time saving and economical.

Adsorbable organic halides (AOX) are generated mostly from pulp and paper industry during the bleaching process. These compounds are formed as a result of reaction between residual lignin from wood fibres and chlorine/chlorine compounds used for bleaching. Considering its health hazard and carcinogenic nature, Central Board took the initiative and developed the standards for AOX in the effluent of Large & Small pulp and paper industries.

This compilation about Adsorbable Organic Halides is the outcome of the dedicated efforts of Ms. Namita Mishra, Sc. 'B' and Sh. B. K. Jakhmola, Sc. 'D' under the supervision and guidance of Sh. J. S. Kamyotra, Member Secretary.

I hope that the compilation will prove to be a useful source of information for the regulatory bodies, industries as well as research Institutions.

  
(Ajay Tyagi)

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## Adsorbable Organic Halides

### 1.0 Introduction

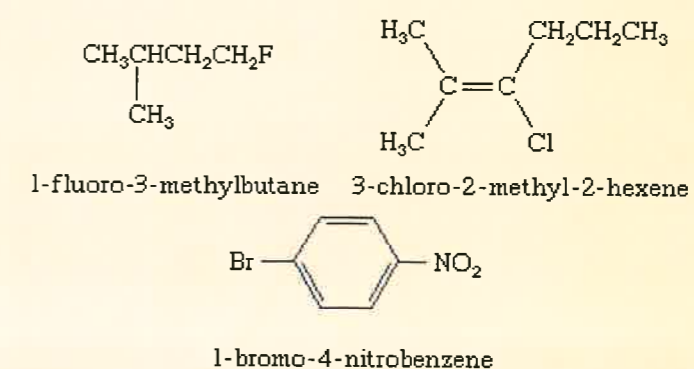
Organic halogens are one of the most threatening groups of chemical compounds. These compounds are a large class of natural and synthetic chemicals that contain one or more halogens (fluorine, chlorine, bromine, or iodine) combined with carbon and other elements. Since the group consists of PCBs, Pesticides, Trihalomethanes (THMS) and several other chloro-bromo organic compounds, with potential to cause toxic, carcinogenic or persistent effects on human beings, therefore monitoring of this group of compounds is of utmost importance.

The group of organic halogens can be analysed individually using GC, HPLC or other sophisticated instruments but their individual assessment is not only time consuming but also very costly. Therefore in absence of any specific requirement, the group compounds can be analysed as summary parameter by adsorption technique which is very effective in terms of accuracy, time consumption and expenditure.

### 2.0 Organic Halogen (General Discussion)

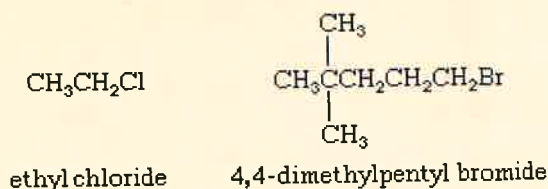
#### 2.i Nomenclature

Two types of IUPAC nomenclature are used when naming organohalogen compounds: substitutive and functional class. In substitutive nomenclature the prefix fluoro-, chloro-, bromo-, or iodo- is added to the name of the hydrocarbon framework along with a number (called a locant) identifying the carbon to which the halogen is attached. Substituents, including the halogen, are listed in alphabetical order. Examples of substitutive nomenclature are given here.



Two separate words are used when naming alkyl halides by functional class nomenclature. The first word is the IUPAC name of the **alkyl group** and the second is the word *fluoride, chloride, bromide, or iodide*—depending on the halogen. The alkyl group chain is numbered beginning with the carbon to which the halogen is attached.





Some chlorinated hydrocarbons are known by long standing common names. These include  $\text{CH}_2\text{Cl}_2$  (methylene chloride),  $\text{CHCl}_3$  (chloroform),  $\text{CCl}_4$  (carbon tetrachloride),  $\text{CH}_2=\text{CHCl}$  (vinyl chloride), and  $\text{CH}_2=\text{CCl}_2$  (vinylidene chloride).

## 2.2 Classification of Organic Halogen

Organic Halogens are typically classified in the same way as the similarly structured organic compounds that have hydrogen atoms occupying the molecular sites of the halogen atoms in halocarbons. Among the chemical families are:

- haloalkanes -- compounds with carbon atoms linked by single bond.
- haloalkenes -- compounds with one or more double bond between carbon atoms
- haloaromatics -- compounds with carbons linked in one or more aromatic rings with a de-localized donut shaped pi cloud.

The halogen atoms in halocarbon molecules are often called "substituents" as though those atoms had been substituted for hydrogen atoms. However halocarbons are prepared in many ways that do not involve direct substitution of halogens for hydrogens.

On the basis of physical & chemical properties halogenated organic compounds may be classified as in Table: 1

Table 1: Simplified classification of Organic Halogen Compounds

Type	Properties	Example
Type-1	Chemical reactive compounds rapidly converted by hydrolysis or oxidation	Allyl chloride Chloroformates
Type-2	Volatile compounds not very water soluble, rather inert to hydrolysis or oxidation generally resistant to bio-degradation	Perchloroethylene, Ethylene dichloride, Chloroform
Type-3	Less volatile compounds, not usually water soluble, generally resistant to bio-degradation, environmentally persistent.	Ethylene dibromide, Propylene dichlorid
Type-4	Alliphatic compounds with functional group, quite water soluble, non-volatile, fairly reactive, environmentally persistent therefore significant from water pollution view point	Chlorinated acids, Alcohols and amines

Type-5	Hydrophobic Aromatic compounds, slightly water soluble and slowly degradable	Chlorinated Benzenes, Toluenes, Xylene and Naphthalenes
Type-6	Aromatic compounds with functional group, frequently water soluble, non-volatile, resistant to degradation, toxic to micro-organisms	Chlorinated phenols, Cresols, Xylenols, Anilines
Type-7	Polymeric material, inert, water insoluble, constituents of plastics	PVC, Teflon, Polychloroprene

### 2.3 Terms & Abbreviations

On the basis of pretreatment & processing of samples for analysis as summary parameter organic halogens may be termed as different names as described below:

- TX (Total Halides)** When an oil or other complex hydrocarbon based sample is analysed as such (without pre-treatment) followed by pyrolysis & titration, the analytical results obtained are reported as Total Halides
- TOX Total Organic Halides** or TOX (also represented as dissolved organic halides or DOX) is a measurement used to estimate the total quantity of dissolved halogenated organic material in a sample.
- AOX Adsorbable Organic Halides** are compound containing organically bound chlorine, bromine, iodine (but not fluorine) substances which can be adsorbed at the surface of activated carbon under specific conditions.
- EOX (Extractable Organic Halides)** The organically bound halogens are extracted from the environmental samples (particularly for solid samples which cannot be adsorbed on active carbon or are difficult to filter through filter devices) by means of suitable solvents like pentane, hexane or heptanes. The extract is sparged directly on pyrolysis zone. The halides produced during mineralization are determined on the basis of an argentometric reaction or by an equivalent method.
- POX (Purgeable Organic Halides)** When organically bound halogens Chlorine, Bromine and Iodine are determined on the basis of purging of a sample with inert gas/ oxygen under specifically defined conditions, the analytical results obtained are reported as POX. This method is employed when easily volatile organic halogens are present in the sample.
- DOX (Dissolved Organic Halogen)** is a measurement used to estimate the total quantity of dissolved halogenated organic matter in water sample. This is similar to literature reference to TOX, AOX and CAOX.

- TOCl (**Total Organo Chlorine**) The organic halogen where Chlorine is bounded as a halide is termed as TOCl.
- OX (**Organic Halides**) Compounds containing carbon, usually hydrogen and at least one of the halogen element - chlorine, bromine, iodine; other elements for example oxygen, nitrogen, sulphur may also be present.
- HCH **Halogenated hydrocarbon** is a compound containing carbon, halogens and no other element except hydrogen is present, however hydrogen may also be not present.
- CHC **Chlorinated hydrocarbon** is a compound containing carbon, chlorine and no other element except hydrogen is present, however hydrogen may also be not present.

## 2.4 Application and use of important organic halogens

- The first halocarbon commercially used was Tyrian purple a natural organobromide of the Murex brandaris marine snail.
- Common uses for halocarbons have been as solvents, pesticides, refrigerants, fire-resistant oils, ingredients of elastomers, adhesives and sealants, electrically insulating coatings, plasticizers, and plastics. Many halocarbons have specialized uses in industry. One halocarbon i.e. sucralose, is a sweetener.
- Before the halogen compounds were regulated, the general public often encountered haloalkanes as paint and cleaning solvents such as trichloroethane (1,1,1-trichloroethane) and carbon tetrachloride (tetrachloromethane), pesticides like 1,2-dibromoethane (EDB, ethylene dibromide), and refrigerants like Freon-22 (duPont trademark for chlorodifluoromethane). Some haloalkanes are still widely used for industrial cleaning, such as methylene chloride (dichloromethane), and as refrigerants, such as R-134a (1,1,1,2-tetrafluoroethane).
- Haloalkenes have also been used as solvents, including perchloroethylene (Per tetrachloroethene), widespread in dry cleaning, and trichloroethylene (TCE, 1,1,2-trichloroethene). Other haloalkenes have been chemical building blocks of plastics such as polyvinyl chloride ("vinyl" or PVC, polymerized chloroethene) and Teflon (duPont trademark for polymerized tetrafluoroethene, PTFE).
- Haloaromatics ( polychlorinated biphenyls, PCBs), once widely used in power transformers and capacitors and in building caulk, the former Halowaxes (polychlorinated naphthalenes,

PCNs), once used for electrical insulation, and the chlorobenzenes and their derivatives used for disinfectants pesticides such as dichloro-diphenyl-trichloroethane (DDT, 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane), herbicides such as 2,4-D (2,4-dichlorophenoxyacetic acid), askarel dielectrics (mixed with PCBs no longer used in most countries), and chemical feedstocks.

- A few halocarbons, including acid halides like acetyl chloride, are highly reactive, these are rarely found outside chemical processing. The widespread uses of halocarbons were often driven by observations that most of them were more stable than other substances. They may be less affected by acids or alkalis; they may not burn as readily; they may not be attacked by bacteria or molds; or they may not be affected as much by sun exposure.

## 2.5 Main source of Organic Halogen

Presence of halogenated organic molecules in environmental matrices is indicative of anthropogenic contamination of environment by synthetic substances, as the carbon halide bond rarely occurs in natural conditions. A few halogenated organic substances of simpler chemical structure are recognized to be derived from natural sources, notably the methyl chloride may be formed by direct reaction of gaseous chlorine and methane in the atmosphere, however, the majority of halogen containing hydrocarbons identified in the atmosphere are probably of man made origin and arise from chemical manufacturing activities and through disposal of consumer products.

### 2.5.1 Man made sources

The major sources of Organic halogens (OX) arising in the environment are manifold. Some of these may include the following:

- **Chemical Industries** : generated due to improper housekeeping, accidental spillage, leakage of raw materials, solvents, additives during process/manufacture.
- **Pulp and Paper Industries** : One of the main sources of AOX releases world-wide is the pulp and paper industry. When using chlorine and chlorine chemicals to bleach fibers, 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.
- **Textile Industries** : produced during chlorine bleaching of cotton/ fabrics & use of organic halogens as processing chemicals.
- **Tanneries** : use of organic halogens during processing/preservation of hides.
- **Metal treatment and finishing units** : chlorination of brighteners, use of organic halogens in metal cleaning.



- **Paints and varnish** : Use of organic halogens as raw material in resin production units
- **Dry Cleaning units** : use of organic halogens as processing chemicals
- **Halogenated insecticides/pesticides industries** : from production process
- **PVC Plastic Industries** : use of organic halogens in manufacture of PVC and plastics.
- **Potable water treatment** : during chlorination, organic substance present in raw water may be transformed in organic halogens i.e. trihalomethane.
- **Sewage and municipal effluent** : effluent discharge, along with runoff water
- **Solid waste slurries and sludge** : generated during chemical manufacturing and recovery operations and from industrial applications of halogenated organics as raw materials, solvents and degreasing agents; sludges also arise from industrial effluent treatment systems.

Residues from the manufacturer , processing and application of halogenated organic products arises as concentrated and dilute liquids, sludges and slurries, tars and solids. They normally contain organic halogens compounds or are as mixture of other and inorganic chemicals, water and various extraneous materials. Mainly organic halogen compounds can be emitted or discharged to the environment through:

- Industrial and municipal effluents
- Sludges and other solid waste
- Exhaust air

### 2.5.2 Natural Sources:

A large amount of the naturally occurring halocarbons are created by wood fire, dioxine for example, or volcanic activities. A second large source is marine algae which produce several chlorinated methane and ethane derivates. There are several thousand more complex halocarbons known, produced mainly by marine species. Although chlorine compounds are the majority of the discovered compounds, bromides, iodides and fluorides have also been found. The tyrian purple, which is a dibromoindigo, is representative of the bromides, while the thyroxine secreted from the thyroid gland, is an iodide, and the highly toxic fluoroacetate is one of the rare organofluorides. These three representatives, thyroxine from humans, tyrian purple from snails and fluoroacetate from plants, also show that unrelated species use halocarbons for several purposes.



## 2.6 Environmental concern and Health Hazard

Halogenated organic products used in industry and commerce vary widely in their properties. Some products exhibit properties of high toxicity, persistence, bioaccumulation or carcinogenicity; while others depict low toxicity and are possibly subject to some measure of degradation in the environment. Typically, compounds having high molecular weight and highly halogenated substituted compounds, tend to be highly toxic, non degradable and bioaccumulative. Some alkyl and aryl halogenated compounds exhibit highly corrosive or irritant properties. Some of the compounds causing harmful effects directly or indirectly to human kind are discussed below :

- Polychlorinated naphthalene may cause chloracne and liver disease in the workers exposed to them. Skin Contact with the hydraulic oils containing PCBs, may cause fatal liver disease in animals and are considered as "too toxic" for use in a submarine
- Since the 1970s there have been longstanding unresolved controversies over potential health hazards of trichloroethylene (TCE) and other halocarbon solvents that had been widely used for industrial cleaning (Anderson v. Grace 1986) (Scott & Cogliano 2000) (U.S. National Academies of Science 2004) (United States 2004). More recently perfluorooctanoic acid (PFOA), a precursor in the most common manufacturing process for Teflon and also used to make coatings for fabrics and food packaging, has become a health and environmental concern (United States 2006), suggesting that halocarbons thought to be among the most inert may also present hazards.
- Halocarbons, including those that might not be hazardous in themselves, can present waste disposal issues. Because they do not readily degrade in natural environments, and tend to accumulate. Incineration and accidental fires can create corrosive by products like hydrochloric acid and hydrofluoric acid and poisons like halogenated dioxins and furans.

## 3.0 Analytical Techniques for determination of Organic Halogen

Monitoring of organic halogen group of compounds is of paramount importance. These compounds can be determined individually in an environmental sample using chromatographic techniques like gas chromatograph or high pressure liquid chromatography (GC, HPLC etc.), while complete group of organic halogens can be screened in a single analysis using AOX/TOX analyzer. The analytical options using GC/HPLC techniques have advantage of determining the individual concentrations but are more time consuming & cost prohibitive, while using AOX/TOX analyzer for analysis of organic halogens, the results obtained are as sum mass concentration of organic halogens in single analysis, which is economical as well as time saving. This analysis can be termed as summary parameter analysis.

**3.1 Available Methods for Analysis:** Presently for determination of organic halides representing the sum of organically bound chlorine, bromine and iodine (but not fluorine) in environmental samples several methods are existing. Some of them are described below:

- i. Total Organic Halide method 450.1- Interium", prepared as Stephen Brillefs and James J, Lichterberg, USEPA, Office of the Research and Development, Physical and chemical methods Branch. EMSC – Cincinnati 45268 EPA 600/4-81-056 (1981)
- ii. Method 9020 USEPA Office of the solid waste. "Test methods for evaluating solid waste. SW-846" Third edition 1987.
- iii. (a) German Standards methods: Determination of adsorbable organic halogens (AOX). "German Standard method for the analysis of water, waste water and sludge- General parameter of effects and substances", Deutsche Industrie Norm (DIN) methods 38409 part 14, DIN German standards Institute Beuth Verlag Berlin Germany.  
  
(b) Determination of Extractable Halogens in Organic bounding (EOX) DIN 38409 part 8 Sept 1984 in water sample. Draft proposed for a German standard method for the Examination of water, waste water and sludge. Determination of purgeable Organic Halogens in water (POX) (H25).  
  
(c) Determination of organically bound halogens amenable to stripping and to extraction (S17) (DIN 38414 part 17) November 1989 in sludge and sediments  
  
(d) Determination of organically bound halogens (AOX) (S18) DIN 38414 part 18 November 1989.
- iv. "Water quality – Determination of adsorbable organic Halogens (AOX)" International Organization for Standards ISO9562:1989(E).
- v. Pulp, Paper and Board – Determination of total chlorine and organically bound chlorine ISO/TCS/-1 WG 4N36. Third working Draft
- vi. Organically bound chlorine by the AOX method "SCAN-W 9;89, Secretariate Scandinavian pulp, paper and Board Testing committee, AOX 5604-5-11486, Stockholm, Sweden (1989)
- vii. Water Quality- Determination of adsorbable organically bound halogens (AOX): Document (EN/TC 230/) WG-1/TGN 18, Revised GTG8 in Vienna Sept 1998
- viii. Method 5320, " Dissolved Organic halogen" " Standard method for the examination of water and waste water" 5320. American Health association 1015, 15<sup>th</sup> NW Washington DC 20005 22<sup>nd</sup> Edition.

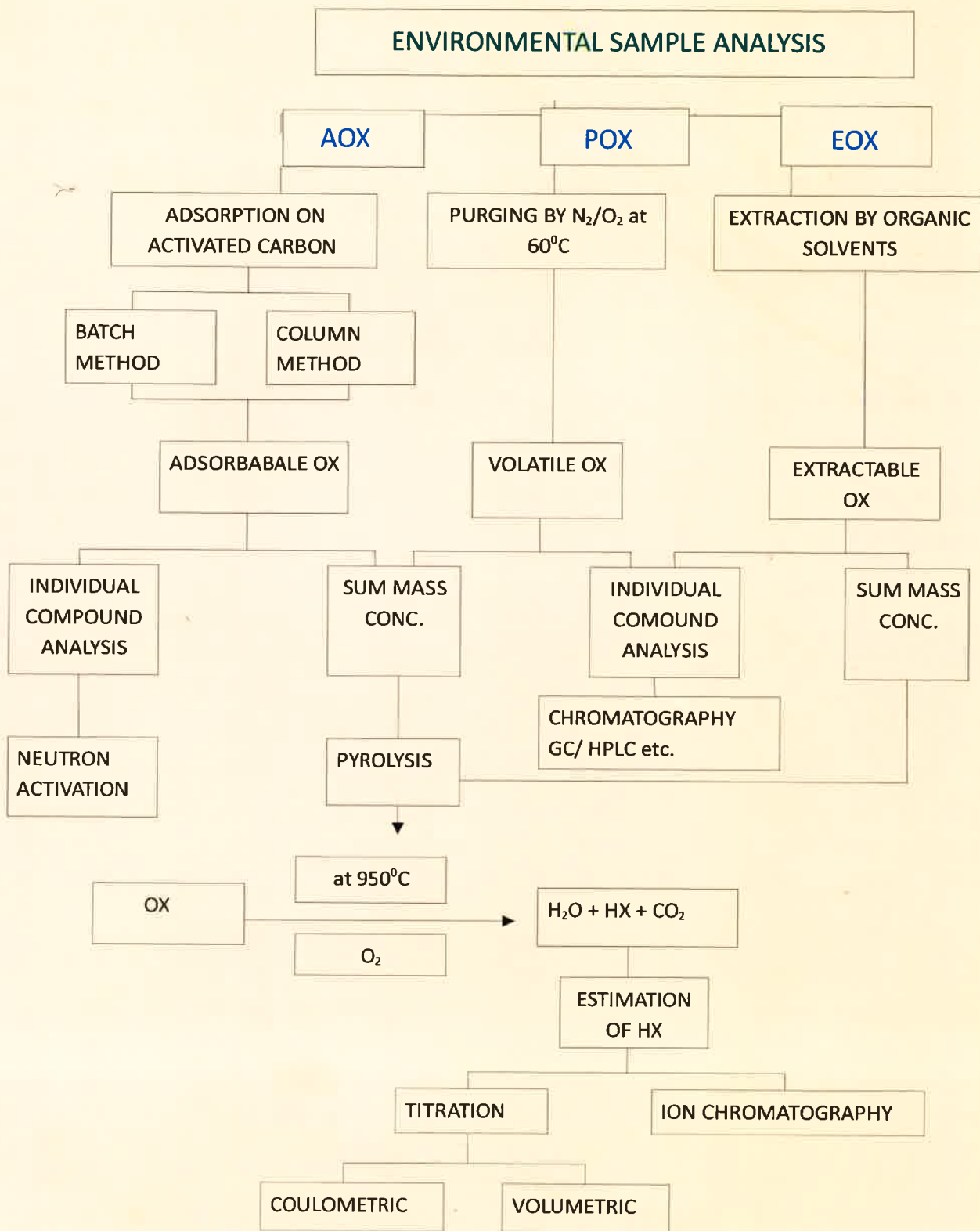


Figure-1 Simulative flow diagram depicting measurement of AOX, POX and EOX in Environmental Samples

ix. "Canadian Standard method for the determination of adsorbable Organic Halide (AOX) in water and waste water", Environment Canada and the Canadian pulp and paper association (1990)

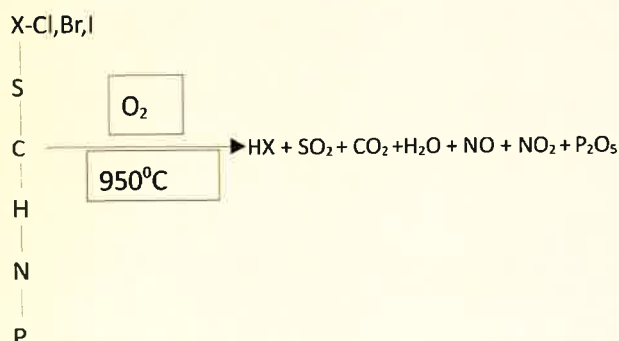
x. Methods 1650 may 1991 USEPA; Adsorbable organic halides by adsorption and coulometric titration

xi. Water quality – Determination of adsorbable organically bound halogens (AOX). British Standard BSEN 1485: 1997676068: Section 56: 1997 (The European Standard EN 1485: 1996 has the status of a british standard)

## 4.0 Measurement of AOX through AOX/TOX Analyzer

### 4.1 Principle & Application of analytical method

The organic halides present in the aqueous sample, which has been acidified with nitric acid are adsorbed on the activated carbon. By treating, activated carbon with halides free sodium nitrate solution, the inorganic halide compounds are removed during the course of various adsorption steps. The organic halides (AOX) burn with the activated carbon in the oxygen flow and is converted into hydrogen halides (HX).



The HX (HCl, HBr, HI) is determined quantitatively by any suitable means or devices i.e. argentometric devices.

This method is suitable for determination of organic halides in aqueous sample containing more than 10µg/l of the organically bound halogens & less than 10µg/l of dissolved organically bound carbon (DOC). The detection limit of the method is usually dependent on interference rather than instrumental limitations. The minimum detectable concentration may be influenced by the analytical repeatability, equipment used, activated carbon quality and the operator technical ability.

The mass concentration of organic halides is reported as on equivalent concentration of organically bound chloride.



## 4.2 Basic AOX Analyzer and Peripherals

Basically, various makes of instruments are based on the identified principle, but these may differ in details like compact or flexible system for AOX, POX and EOX. However, the basic AOX analyzer comprises following parts:

a) **Sample Introduction module**

The sample introduction module comprise of quartz tube with quartz boat. Injection speed of the boat can either be controlled manually or (automatic). Sample introduction modules are generally designed separately for POX, EOX & AOX compounds.

b) **Combustion apparatus**

Combustion apparatus is a horizontal tubular furnace having quartz combustion tube connected to sample introduction module on one side and scrubber to the other side. The middle section of furnace can be achieved up to at least 1000°C. The sample boat from the sample module can be moved from the cold end of the tube to its hot section.

c) **Scrubber**

Scrubber containing sulphuric acid is placed between the outlet of combustion tube and titration cell for cleaning and drying the gases/ steam coming from combustion tube.

d) **Titration cell**

Titration cell consists of generator, electrodes & measuring electrodes (coulometric type) or measuring electrode (volumetric type) dipped in the receiving solution for the gases

e) **Control module**

Control module of the instrument regulates analysis of the titration cell & consists of PC and printer for sample and analysis reports.



Figure: 2 AOX Analyzer

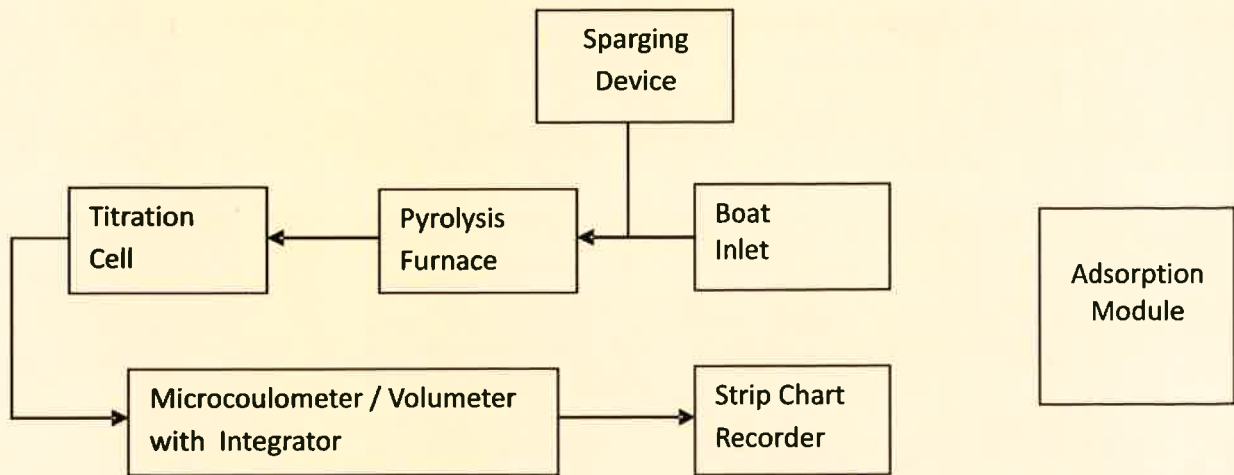


Figure: 3 Flow chart of Analytical system

#### 4.3 Additional Equipment/ Apparatus

- Mechanical Shaker
- Filter device for vacuum filtration
- Conical flasks with standard tapered glass stopper or PTFE-line screw caps
- Polycarbonate membrane filter, chloride free or least chloride content with pore size  $0.4\mu$
- Vacuum sources: Pressure/ Vacuum Pump

#### 5.0 Sampling Plan , Collection, Transportation and Preservation

- i. Sample should be collected in such a way that there are atleast 4-5 nos of field samples for a day to conduct analysis conveniently and cost effectively.
- ii. After site selection, collect a representative sample of waste water having minimum quantity of 500ml in an amber brown glass bottle with ground glass stopper already washed with chromic acid and rinsed with distilled water.
- iii. Immediately after collecting the sample adjust  $\text{pH} < 2$  by adding analytical grade  $\text{HNO}_3$ . Fill the bottle up to top, avoiding entrapping of air bubbles. If sample contains active chlorine, remove this by adding sodium sulphite solution (less than 1ml/l) or crystal (minimum 5 mg/l).
- iv. The sample should be kept at  $4^\circ\text{C}$  during transportation and analyze as soon as possible after collection. Otherwise, it can be stored upto 28 days in  $4^\circ\text{C}$  after getting it acidified. Care should be taken to allow the sample to be equilibrated with room temperature prior to analysis.

## 6.0 Sample Analysis

1. Sample dilution: shake well the sample and a small portion of the sample in such quantity and dilute it to 100ml to have an AOX value within the working range of the instrument which is generally 25 to 250 $\mu$ g/l or 2.5-25 absolute.
2. Pretreatment (Batch procedure – Shaking Technique): For the analysis of organic halogens as summary parameter, the sample must be pretreated before mineralization; Pretreatment is carried out as per the following steps:
  - Transfer 100 ml of test sample after dilution if required into a stoppard 250 ml conical flask in order to restrict the head space.
  - Add 5 ml of nitrate stock solution to the flask and ensure the pH < 2.
  - Add one level scoop of activated carbon (50mg) and shake well for 1hr to ensure proper adsorption.
  - Filter the suspension through 25mm or 47mm polycarbonate membrane filter using filtration device with vacuum pump. Take the same dia filter for blank also.
  - Wash activated carbon inside the filter funnel with approximately 25 ml of nitrate wash solution in several portions
  - Carefully remove the top of filter holder, making sure that no carbon is lost.
  - Using the forceps carefully fold the polycarbonate filter into half, then into four fold, making sure that no carbon is lost.
  - Transfer (after calibration of the instrument) polycarbonate filter along with activated carbon in to quartz boat for mineralization.



**Figure: 4 Organic Halide Adsorption by Shaking Technique (Batch Method)**

### **6.1 Calibration**

Before analysis of environmental samples, calibration of the instrument is essential. It is performed when the instrument is set-up and when calibration is not verified. While calibrating the instrument, following steps are involved

- Cell performance
- Combustion system test
- Standard organic halide combustion test
- Background level of  $\text{Cl}^-$
- Calibration by external standard

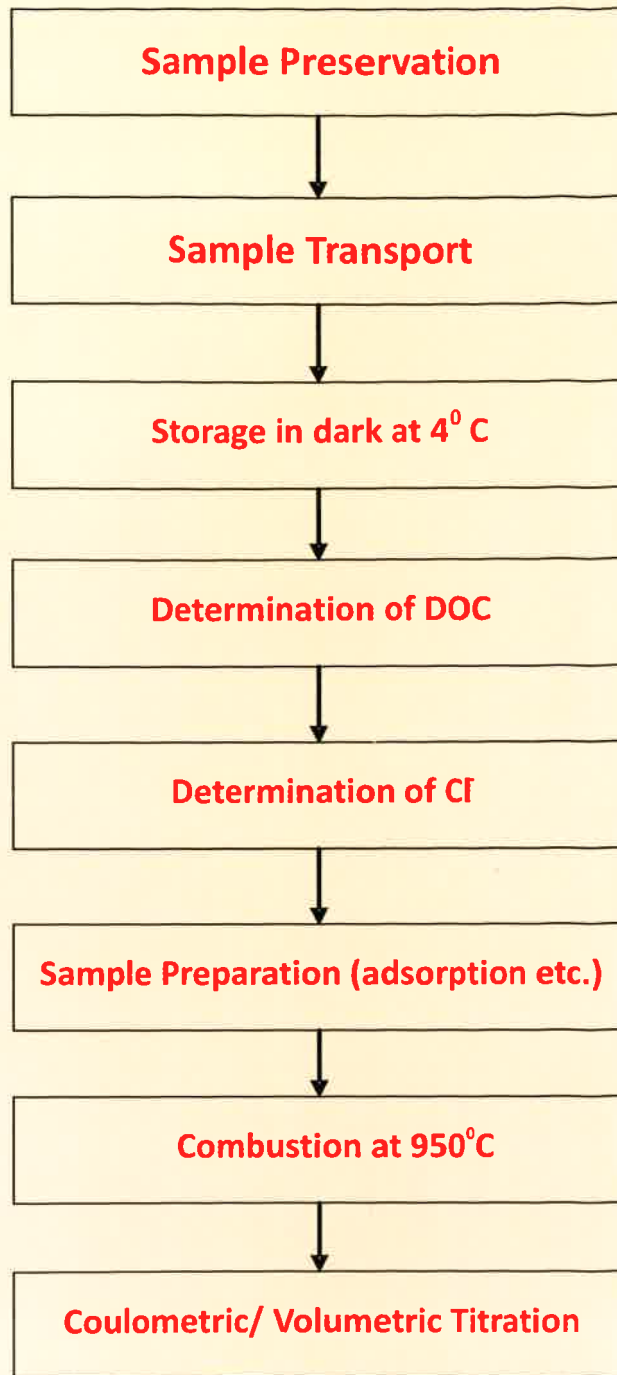
### **6.2 Combustion**

After calibration of instrument the pre-treated sample in a poly-carbonate filters or quartz frit in a quartz combustion boat or in the cassette (for quartz frit) is pyrolysed by introducing it in a pre heated and regulated furnace at  $950^\circ\text{C}$ . The AOX burns with the activated carbon in the oxygen at regulated flow of 6-8 liter/ hour and is converted into Hydrogen halide (HX). These product gases are dehydrated and cleaned in a scrubber (Dehydration tube having concentrated  $\text{H}_2\text{SO}_4$ ) with an Argon/Oxygen carrier and are introduced into the titration cell.

### **6.3 Titration**

During Incineration, organic halogens are transformed to hydrogen halides (HCl, HBr, HI) which are led into titration cell and are subsequently determined by volumetric titration with  $\text{AgNO}_3$  or by:





**Figure-5 Procedure of AOX Analysis Overview**

coulometric titration. The difference between the two methods (Volumetric and Coulometric) is solely in the manner of dosing the reagent. In case of coulometric  $\text{Ag}^+$  ions are produced at a generator electrode by electric current. In the volumetric titration the  $\text{Ag}^+$  ions are added as solution with a high resolution piston burette. In order to reduce the solubility product of  $\text{AgCl}$ , the titration should be conducted in acetic acid (min 70%)

The coulometric and volumetric AOX determinations are carried out as end point titration. Depending on the difference between the measured value and the nominal value the reagent is closed till the per-selected end point potential is exactly reached. As soon as the titration of a sample is completed the receiver is immediately ready for introducing the next sample, i.e. the end point titration permits multiple titration in one and the same solvent vessel.

## 7.0 Regulatory Limits of organic Halogen (AOX)

For protecting and improving the quality of the environment and preventing and abating environmental pollution, the standards for emission or discharge of environmental pollutants from the industries, operations or processes are specified in Schedule I of Environment (Protection) Act, 1986. Central Pollution Control Board has developed the standards for AOX in Pulp & Paper industries, which are a major source of AOX. The regulatory limits are given below in Table-2.

Table: 2 AOX Standards as specified under Environment (Protection) Rules, 1986, in schedule I

S. No	Industry	Parameter	Standard
01.	Small Pulp and Paper Industry (Capacity up to 24000 MT/Annum)	Absorbable Organic Halogens (AOX) in effluent discharge	2.0 Kg/ton of Paper produced with effect from the 1 <sup>st</sup> day of March, 2006
02.	Large Pulp & Paper News Print/ Rayon Grade Plants of Capacity above 24000 MT per Annum	Absorbable Organic Halogens (AOX) in effluent discharge	1.0 Kg/ton of Paper produced with effect from the 1 <sup>st</sup> day of March, 2008

## 8.0 Status of AOX in selected Industries

AOX is generated largely from the Pulp and Paper industry during the bleaching process. These compounds are formed as a result of reaction between residual lignin from wood fibers and chlorine/ chlorine compounds used for bleaching. To assess the quantity of AOX generated through Pulp and Paper sector, five units in U.P. and Haryana, having bleaching process for whitening of pulp were identified and the status was monitored. Samples were collected and analyzed to assess AOX generation from these units. A short description of units with their bleaching products and their process sequence is given below:

### Unit-1

Product : Unbleached, Bleached Paper & Board  
Production Capacity : 75,000 MT/Annum  
Raw Material : Wood, Bamboo, Veneer Chip  
Bleaching Sequence : O – C – Eop - H1 - H2  
ODL Chlorination – Alkali Extraction & H<sub>2</sub>O<sub>2</sub> – Hypo 1&2

### Unit-2

Product : Writing and Printing Paper, Specialty Paper, Coated Paper  
Production Capacity : 72680 MT/Annum  
Actual Production : 89004 MT/Annum  
(2011-12)  
Raw Material : Bamboo – 15%  
: Veneer Waste – 50%  
: Eucalyptus – 33-34%  
: Popular Wood – 3-4%  
Bleaching Sequence : Chlorine Dioxide – Caustic + O<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> –  
Chlorine Dioxide - Chlorine Dioxide

### Unit-3

Product : Writing and Printing Paper  
Production Capacity : 200 MT/Day  
Raw Material : Agro Waste (Bagasse & Wheat Straw)  
Bleaching Sequence : Chlorine Dioxide – Caustic + O<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> –  
Chlorine Dioxide

### Unit-4

Product : Duplex Board Paper  
Production Capacity : 50 MT/Day  
Raw Material : Waste Paper  
Bleaching Sequence : Hypochlorite

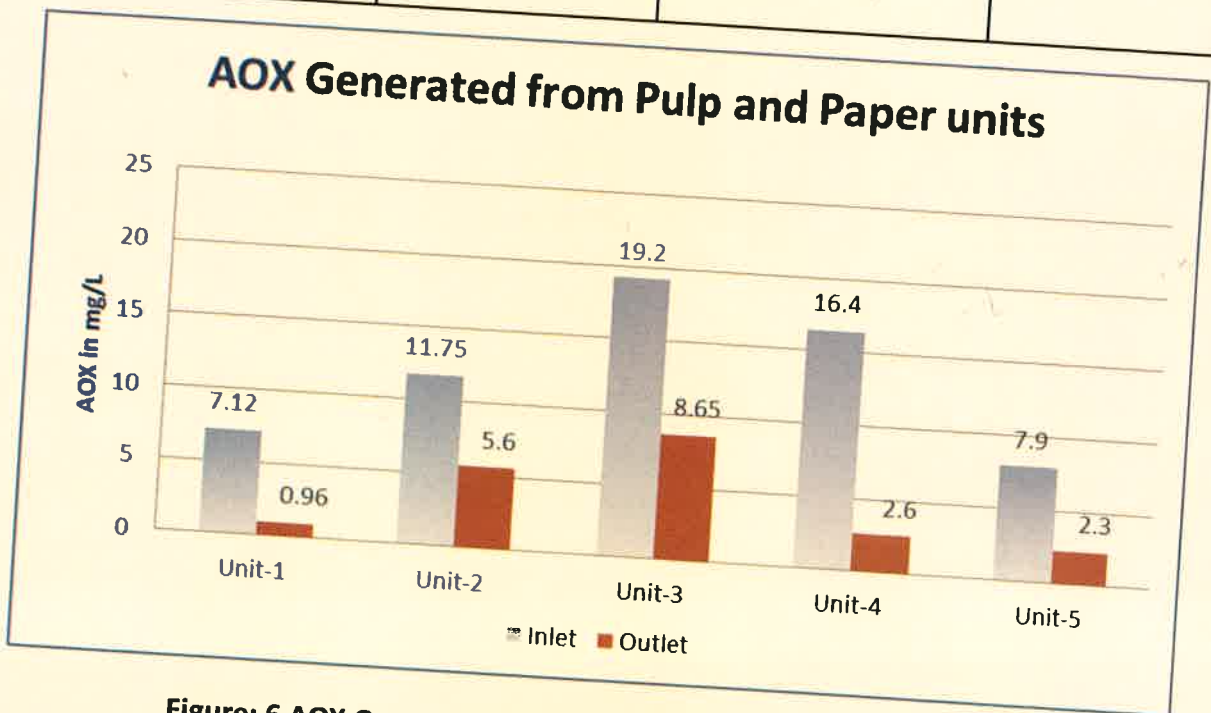
### Unit-5

Product : Duplex & MG Poster & Kraft  
Production Capacity : 60 TPD Duplex  
: 20 TPD MG Poster  
Raw Material : 100% Recycled fibers  
Bleaching Sequence : Hypochlorite

The findings analysis results of the samples collected from these five units are given in Table-3 and depicted graphically at Figure-6.

**Table: 3 Result of AOX generated from selected units of Pulp & Paper units**

S.No.	Units	INLET	OUTLET	
		in mg/l	in mg/l	in Kg/Ton
01.	Unit - 1	7.12 mg/l	0.96	0.04
02.	Unit - 2	11.75 mg/l	5.60	0.3
03.	Unit - 3	19.20 mg/l	8.65	0.5
04.	Unit - 4	16.40 mg/l	2.60	0.1
05.	Unit - 5	7.9 mg/l	2.3	0.07



**Figure: 6 AOX Generated from selected units of Pulp and Paper**

The grab waste water samples were collected from the outlet of Effluent Treatment Plants of selected Pulp and Paper units and the results give an assessment of AOX generation per tonne of bleached pulp. Except unit 4 & 5 all the other three units are covered under Large Pulp and Paper category and the AOX values observed are well within the prescribed standard of AOX i.e. 1Kg/Tonne as the values put in the range of .04 to 0.5 Kg/Tonne. The two small pulp and paper units also had the AOX within the prescribed limit (2 Kg/Tonne) having the values as 0.07 and 0.1 Kg/Tonne respectively.



## 9.0 Laboratories Having AOX Analyzer

Based on the information collected from suppliers and the laboratories, following organization are equipped with AOX/ TX/ TOX analyzer having facility for analysis of organic halogens as summary parameter:

1. Central Pollution Control Board  
'Parivesh Bhawan' East Arjun Nagar,  
Delhi 110032
2. Central Pulp & Paper Research Institute  
P.O. Box – 174, Star Paper Mill Road, Saharanpur -  
247001
3. Gujrat Pollution Control Board  
Sector-10-A, Gandhinagar – 382043, Gujrat
4. Orissa Pollution Control Board  
A/118, Nilakantha Nagar, Unit -VIII,  
Bhubaneswar – 751012
5. NEERI Nagpur  
National Highway 7  
Nagpur
6. Shriram Institute for Industrial Research,  
19, University Road,  
Delhi
7. Centre for Environmental Sciences,  
Anna University,  
Chennai - 600025
8. Andhra Pradesh Paper Mills Ltd.,  
V Floor, Swapnalok Complex, 92 /93,  
S.D. Road, Secundrabad - 500003

9. Century Pulp & Paper,  
Ghanshyamdham, P.O. Lalkuan – 262402  
Distt. Nainital
10. Madhya Pradesh Pollution Control Board,  
E-5, Paryavaran Parisar, Arera Colony,  
Bhopal - 462015
11. Andhra Pradesh Pollution Control Board,  
Maitrivanam, 2<sup>nd</sup> Floor, HUDA Complex  
S R Nagar, Hyderabad – 500038 (A.P)
12. Karnataka State Pollution Control Board,  
Public Utility Building, Mahatma Gandhi Road,  
Bangalore - 560001
13. Rajasthan State Pollution Control Board,  
4, Industrial Area, Jhalana Doongri,  
Jaipur - 320004
14. Kerala State Pollution Control Board,  
Gandhi Nagar,  
Kochi - 682020
15. Hindustan Paper Corporation Limited  
Kagjinagar – 782413  
Jagiroad, Morgaon, Assam
16. Tamilnadu Pollution control Board,  
76, Mount Salai, Guindy  
Chennai
17. Indian Institute of Technology,  
Post Office IIT- Roorkee,  
Haridwar, UK - 247667
18. Regional Research Laboratory,  
CSIR, Hoshangabad Road, Near Habib ganj Naka,  
Bhopal 462026

19. Agharkar Research Institute,  
Microbial Science Division, Agharkar Road,  
Pune - 411004
20. Central Pollution Control Board, ZO,  
Southernd Conclave, Block 502, 5<sup>th</sup> & 6<sup>th</sup> Floors  
1582, Rajdanga Main Road, Kolkata - 700107
21. Central Pollution Control Board, 1<sup>st</sup> & 2<sup>nd</sup> Floors,  
Nisagra Bhavan, A- Block, Thimmaiah Main Road,  
7<sup>th</sup> D Cross, Shivnagar, Bengaluru

*Remarks: Working/ Non-working/ Obsolete status of the AOX Analyzer with the above organization/institution is not available with CPCB*

## 10.0 List of Some of the Manufacturer of AOX Analyzer

1. **behr Labor-Technik GmbH.** Spangerstraße 8  
40599 Düsseldorf Postfach 16 01 64 40564 Düsseldorf  
Tel.: +49 - (0)211 - 7 48 47 17.  
Fax: +49 - (0)211 - 7 48 47 48.
2. **Analytik jena AG**  
Konrad-Zuse-Straße 1.D 07745 Jena, Germany  
Tel.: +49 3641 201-0  
Fax:+49(3641)201-160
3. **Thermo Fisher Scientific** 1400 Northpoint Parkway,  
Suite 50. West Palm Beach, FL 33407. United States  
Tel: +1 800-532-4752. Fax: +1 877-373-4006
4. **Mitsubishi Chemical Industries Ltd.**  
5-2, Marunouchi 2-chome  
Chiyoda-ku, Tokyo 100-0005  
Japan  
Tel.: (03) 3283-6111  
Fax: (03) 3283-5874

## 11.0 References

- i. Determination of Adsorbable organic halogens (AOX). (H-14) German standard method for the examination of water, waste water and sludge.
- ii. Water quality – determination of adsorbable organic halogens (AOX), International organization for standard, International standard method – 9562 1989-09-01.
- iii. Method 5320 “Dissolved organic halogen” from “Standard methods for the examination of water and waste water” 5320, American Public Health association 22<sup>nd</sup> Edition
- iv. Adsorbable organic halides by adsorption and coulometric titration – US EPA method 1650 May 1991 “Draft”
- v. Method 9020 A, 9022A, US EPA of solid waste “Test method for evaluating solid waste SW-846” Revision 1 November, 1990.
- vi. Organically bound chlorine by the AOX method” SCAN-W 9:89, Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, S-11486, Stockholm, Sweden (1989)
- vii. Determination of chlorine and organically bound chlorine, ISO/TC 5/-/WG4 N36 P.O. Bethge 1993-06-11, 3<sup>rd</sup> working draft.
- viii. Waste Management Paper No. 9 Halogenated hydrocarbon solvents waste from cleaning process. HMSO, London 1976.
- ix. Waste Management Paper NO. 15 Halogenated Organic Waste, HMSO London 1978.
- x. Pollution Control Law Series; PCLS/02/2010 Published by CPCB Delhi.
- xi. Laboratory Analytical Techniques Series: LATS/14/1998-99, Published by CPCB Delhi.