

Characterization of Adsorbable Organic Halogens (AOX) by ion chromatography and inductively coupled plasma-mass spectrometry

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The halogen specific parameters AOCl, AOBr, and AOI in water can be determined by combining the standard AOX procedure (AOX_{DIN}) with off-line ion chromatography (IC) or inductively coupled plasma-mass spectrometry (ICP-MS) detection of the combustion products (Cl⁻, Br⁻, and I⁻) recovered from the AOX analyzer. The IC and ICP-MS methods gave good results with model systems. With IC, the minimum detectable concentrations are near 0.1 mg/L for Cl⁻ and Br⁻, and 5.0 mg/L for I⁻, while with the ICP-MS method, the minimum detectable concentration is 0.0001 mg/L for Cl⁻, Br⁻ and I⁻. Quantitative recoveries of the organic Cl, Br, and I from different standard mixtures were obtained using the IC and ICP-MS methods. A good agreement between the conventional AOX_{DIN} and the described AOX_{IC or ICP-MS} were found.

Keywords: organic halogens; ion chromatography; inductively coupled plasma-mass spectrometry

INTRODUCTION

Water systems are polluted with many harmful organic substances. One important group of these compounds is the organic halogens, whose characteristic is generally toxicity, bioaccumulation and persistence [1–2]. These compounds may come from agriculture, industrial activities, as well natural formation [3–5]. The large number of organic halides which are of environmental concern, has created a need for a detection of such compounds in water systems. An easy, simple, and cheap way of detecting these substances in water is the use of the sum parameter AOX_{DIN} (adsorbable organic halogens) method [6], which indicates the overall level of fluorine, chlorine, bromine

and iodine. The AOX value is referred to the molar mass of chloride. However, this analytical procedure gives no information on the source and nature of halogens present nor on the toxicity [7–10]. And even in advancement in the identification of AOX substances, the identity of the major fraction of the AOX is still unknown [11–12].

For specific determination of halogens in water samples, ion chromatography (IC) and inductively coupled plasma - mass spectrometry (ICP-MS) were applied [13–15]. In this study, an analytical method is developed that further characterizes the AOX into AOCl, AOBr, and AOI components, using the combined procedure: AOX_{DIN}-IC or AOX_{DIN}-ICP-MS.

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EXPERIMENTAL

Reagents. The nitrate and washing solutions were prepared according to the German standard procedure [6]. The nitrate solution contained 17 g NaNO_3 and 1.4 mL conc. HNO_3 diluted with Millipore water to make 1 L solution. The washing solution was prepared by diluting 50 mL nitrate solution to 1 L with Millipore water.

Stock solution halides of 1000 $\mu\text{g/L}$ (calculated as Cl, Br, and I) were prepared from analytical-reagent grade salts (Merck). Working standards with concentrations ranging from 10 to 4000 $\mu\text{g/L}$ halide solutions were prepared immediately before calibration.

For the determination of the recovery the following Cl, Br, and I containing substances (with purity higher than 98%) were used: 4-chloro-, 4-bromo-, and 4-iodophenol.

Wastewater samples were taken from the municipal, biological treatment plant in Neureut, Karlsruhe, Germany. After acidification with HNO_3 to pH 2, the samples were stored at 4°C. Prior to analysis, the wastewater sample was filtered through a prewashed glass filter and subsequently through a 0.45 μm membrane filter. The sample volume taken for analysis depended on the dissolved organic carbon (DOC) value: for $\text{DOC} < 10 \text{ mg/L}$, a volume of 100 mL of the original sample was used; and, for $\text{DOC} > 10 \text{ mg/L}$, a volume of 100 mL of the diluted sample was taken exceeding 1 mg of organic carbon.

Water was used for preparation of standards solutions and sample dilutions was taken from the Millipore Milli-Q system.

AOX determination. AOX was determined according to the German standard DIN 3809-H14 [6]. In brief, to 20 mL of the filtered (0.45 μm) sample, 80 mL deionized water, 85 mg NaNO_3 , 100 μL conc. HNO_3 , and 50 mg activated carbon were added. The pH of the sample was adjusted with HNO_3 to between pH = 2 and pH = 3. The samples were placed in flasks on a laboratory shaker. After 16 h, the activated carbon was separated by filtration (0.45 μm), washed twice with nitrate washing solution and analyzed using an ECS 1200 AOX analyzer (Euroglas). Blank samples were determined simultaneously with deionized water. All given AOX values are blank value corrected. The blank values ranged from 2.0 to 5.7 $\mu\text{g/L Cl}$.

AOCl, AOBr, and AOI determination. The determination of the AOX components was performed using an AOX apparatus. A water sample was added with activated charcoal and other reagents, similarly treated as in the AOX analysis. The activated charcoal was filtered, washed and placed in a boat and burned in the combustion chamber of the AOX apparatus. The combustion gases passed through a dehydration tube, and were collected into a 1:200 mixture of 2 mM Na_2CO_3 and 1 mM

NaHCO_3 , containing also 0.1 mL 30% H_2O_2 solution. The collected absorption solution was further separated and analyzed using the IC or ICP-MS method.

IC measurement. The IC measurement was carried out using the Dionex 4500i instrument in combination with the Shimadzu CR34 integrator. A 60 μL sample was injected into a stream of eluant solutions (0.01 M $\text{Na}_2\text{B}_4\text{O}_7$ –0.01 M H_3BO_3 and 2 mM Na_2CO_3 –1 mM NaHCO_3), and passed through a series of ion exchangers (AS9SC exchanger containing quaternary ammonium bases) at a flow rate of 2 mL/min. The separation was conducted at room temperature. A continuous flow of 0.025 M H_2SO_4 was supplied at the suppressor, where the separated ions were converted to their highly conductive acid forms and the carbonate-bicarbonate eluent was converted to weakly conductive carbonic acid. The separated ions in their acidic forms were measured by conductivity.

ICP-MS measurement. A Perkin Elmer SCIEX Elan 6000 instrument was used to monitor the nuclides of ^{35}Cl , ^{79}Br , and ^{127}I . In the ICP-MS determination, the sample aerosol was generated at the nebulizer and spray chamber, and was carried into the plasma. The plasma consists of the flowing stream of Ar ionized by high frequency radio field. This field was inductively coupled to the ionized gas converting molecules into charged particles. The ions were accelerated to the quadrupole through a series of lenses (which effects dispersion). The fragments were separated according to one particular mass to charge ratio by means of the quadrupole. The charged particles were detected by the electron multiplier and fragmentation pattern called spectra was obtained. A computer-controlled scanning mechanisms allowed the examination of the unknown spectra from a library of known mass spectra.

RESULTS AND DISCUSSION

A schematic flow of the AOX, AOCl, AOBr, and AOI analysis is presented in Fig. 1. The left side of diagram shows the basic steps involved in the AOX determination. Through the combination of steps 1 to 3 with the halogen specific-determination methods, the further determination of AOX into AOX components was made possible. The group parameters AOCl, AOBr, and AOI were determined by combining the standard procedure for AOX with off-line IC or ICP-MS analysis of the collected combustion halide-containing gases from the AOX-analyser.

IC analysis. A typical separation of the ions from a standard calibration solution containing a mixture of halide was performed, as shown in the IC chromatogram (Fig. 2). The chromatogram showed that there was a good separation of Cl^- , Br^- , and I^- . The peaks were identified on the basis of retention time as compared to standards. Quantification was by measurement of the peak height or peak area.

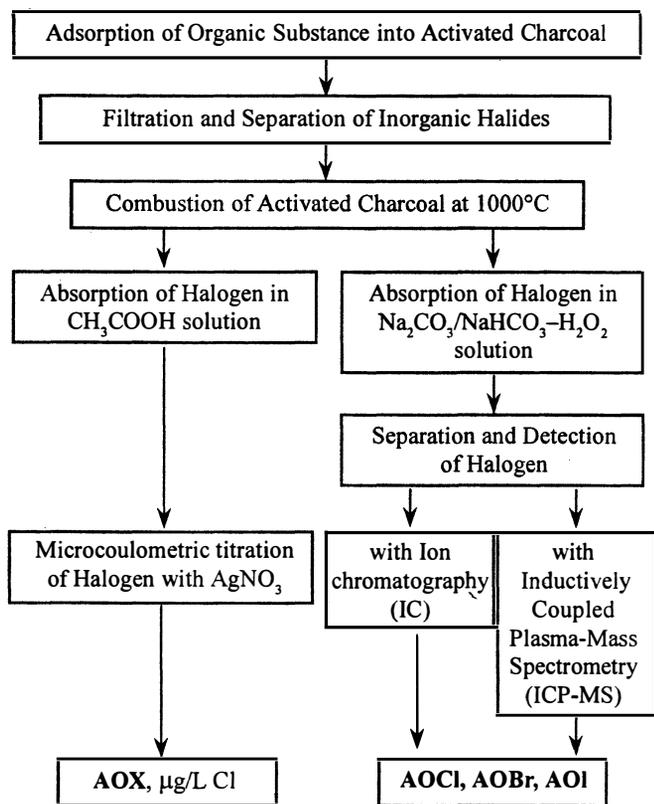


Fig. 1. Schematic diagram of the AOX_{DIN} -analysis (left) and the further characterization of the AOX (right).

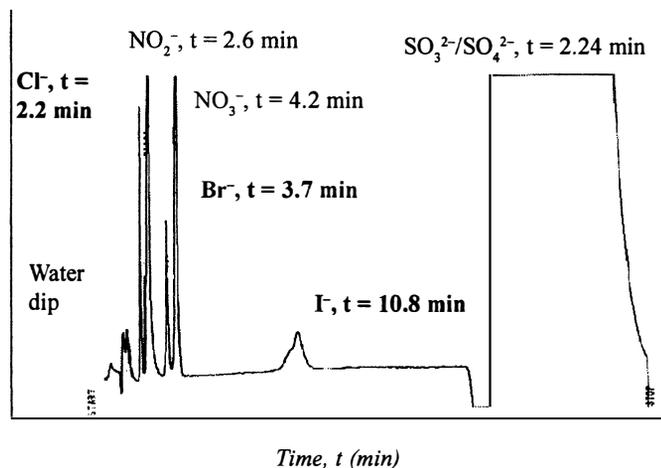


Fig. 2. IC chromatogram showing the separation of ions. IC instrument: Dionex 4500i; Eluant solutions: 0.01 M $Na_2B_4O_7$ - 0.01 M H_3BO_3 , 2 mM Na_2CO_3 - 1 mM $NaHCO_3$; Flowrate: 3.5 mL/min; Injection volume: 60 mL.

For the quantitative determination of bromide, chloride and iodide ions in the absorption solution, calibration of the ion chromatography was performed by injection of mixed ion standards of five concentration levels covering the concentration ranges from 0.1 to 20 mg/L. Each sample was

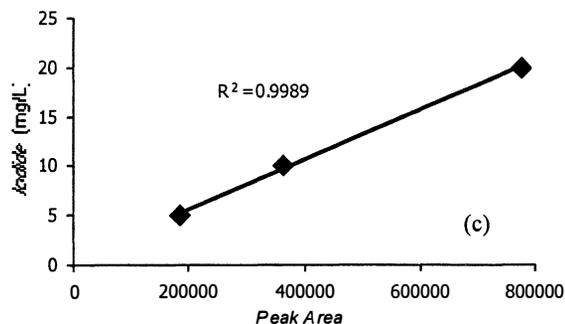
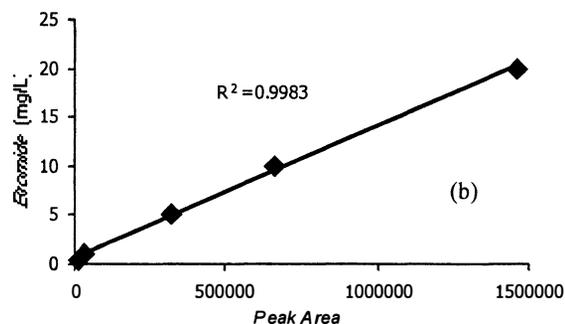
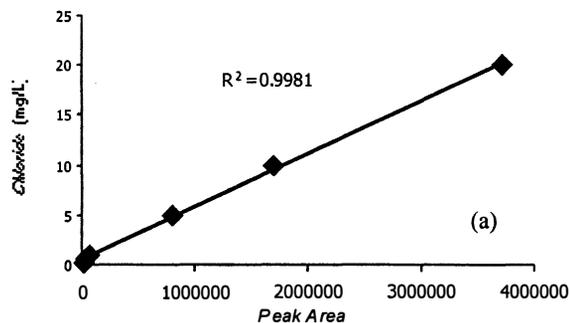


Fig. 3. Calibration curves for (a) chloride, (b) bromide and (c) iodide using the IC method.

injected three times and the mean values of the peak area were set in relation to the standard concentration. The detection limits for the AOCl and AOBr were found to be 0.1 mg/L, and for AOI is 5 mg/L, calculated from deviation of blank values. The calibration curve are shown in Fig. 3.

The analysis method was validated using 4-chloro-, 4-bromo-, 4-iodophenol, which are known to be quantitatively adsorbed on activated carbon. Recoveries of the mixed organic standards, containing the same concentration of the organic Cl, Br and I in the working range of 100–500 µg/L were determined. The standard solutions were analyzed following the first three basic steps of the AOX analyses. Then, the combustion gases was collected through a specified Na_2CO_3 - $NaHCO_3$ - H_2O_2 absorbing solution and further injected into the IC set-up. Each standard solution was analyzed three times and the mean values of found AOCl, AOBr, and AOI concentrations for different concentration levels were correlated to the added values. The

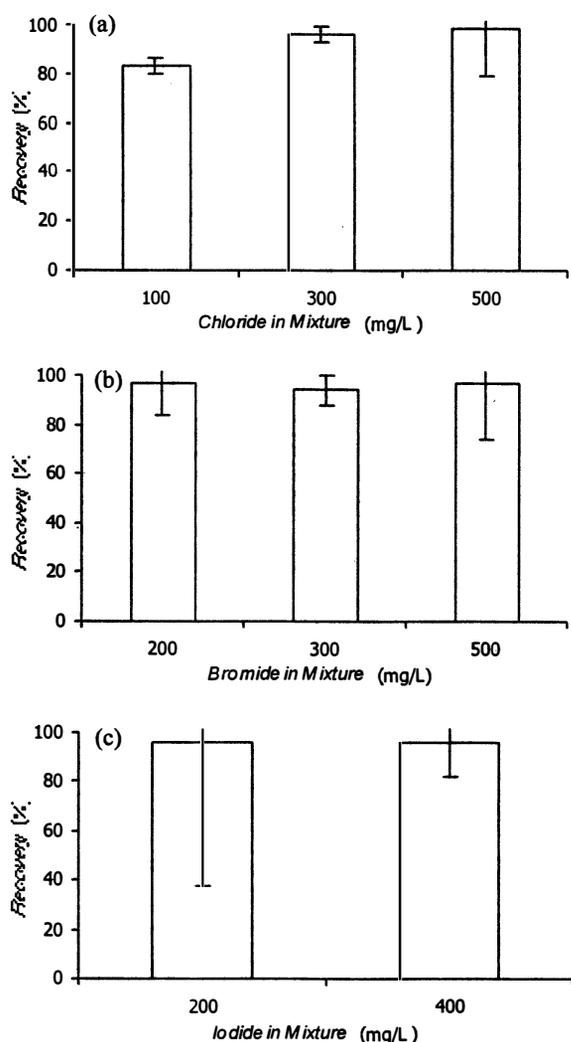


Fig. 4. Recovery of (a) chloride, (b) bromide and (c) iodide using the combined AOX_{DIN}-IC method.

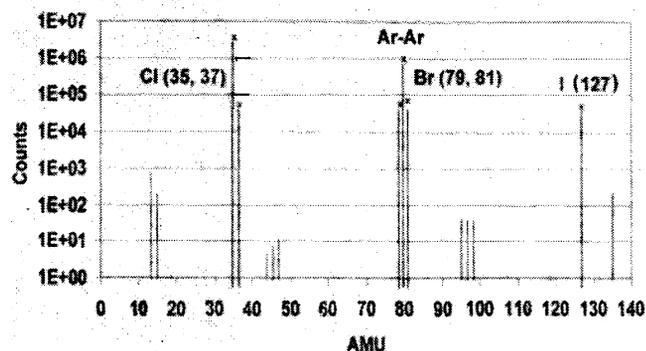


Fig. 5. ICP mass spectra of a solution containing a mixture of Cl⁻, Br⁻, and I⁻ (calculated each at 5 mg/L).

blank values for AOCl, AOBr, and AOI were subtracted from those obtained by the ion chromatography determination of the solution. Calculations were based on an enrichment factor of 20 (i.e., 100 mL water sample and 5 mL absorption solution

containing of Na₂CO₃-NaHCO₃-H₂O₂ solution and are calculated according to Funk [16]). The recovery results expressed in % are presented in Fig. 4. The recovery % ranges from 85 to 98 for Cl, at 95–95% for Br, and 97% for I; indicating a high recovery for 4-chloro, 4-bromo, 4-iodophenol using the combined AOX_{DIN}-IC method.

ICP-MS analysis. Water samples with very low ppb concentrations of the group parameters AOCl, AOBr and AOI can be analyzed by combining the first steps of the standard AOX analysis with ICP-MS method. Fig. 5 shows the typical ICP mass spectra showing the fragmentation pattern of Cl, Br and I ions. Quantification was based on the intensity of the selected isotope emission spectral peak. Calibration curves for quantification and recovery experiments were established by analyzing standard solutions of chloride, bromide and iodide, following similar solution preparation and calculation as

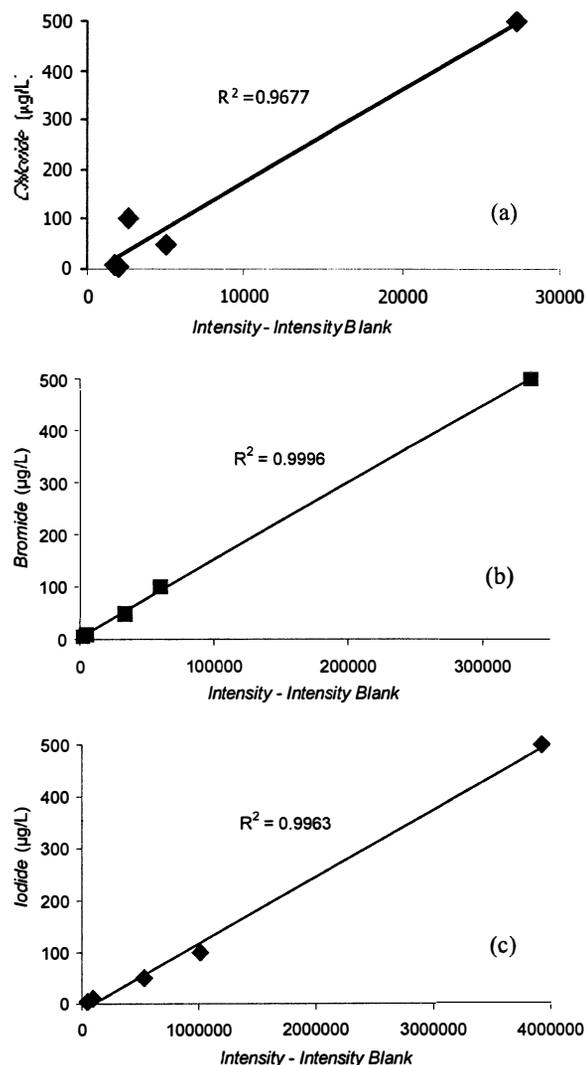


Fig. 6. Calibration curve for (a) chloride, (b) bromide and (c) iodide using the ICP-MS method.

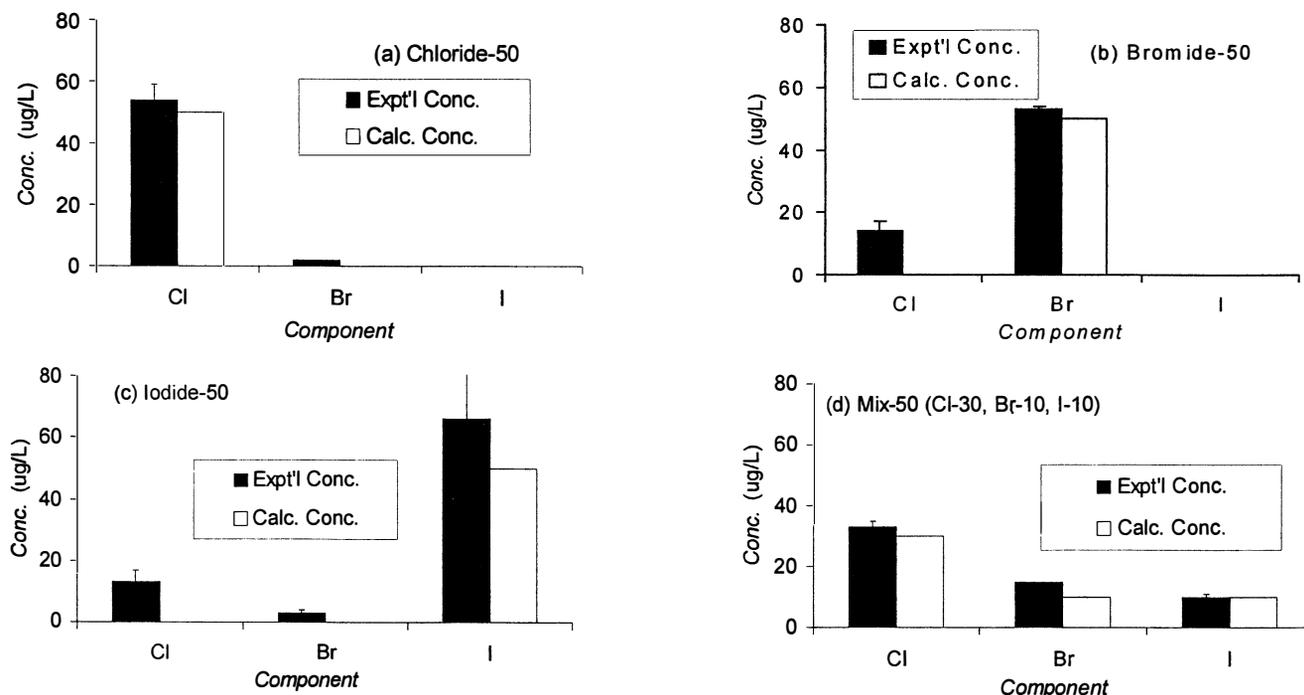


Fig. 7. Recovery of the (a–c) single ion and (d) mixed ions using the combined AOX_{DIN} -ICP-MS method.

Table 1. Results of specific parameters AOCl, AOBr and AOI derived from the combined (AOX_{DIN} -IC or AOX_{DIN} -ICP-MS) methods and comparison with the AOX_{DIN} -method.

Sample	AOCl $\mu\text{g/L Cl}$	AOBr $\mu\text{g/L Cl (Br)}$	AOI $\mu\text{g/L Cl (I)}$	$AOX_{IC-ICP-MS}^1$ $\mu\text{g/L Cl}$	AOX_{DIN} $\mu\text{g/L Cl}$
with IC					
Solution A	100	101 (230)	52 (186)	253	239
Solution B	325	143 (325)	103 (368)	571	499
with ICP-MS					
Solution C	23	15 (34)	9 (32)	47	40
NRT-II (Effluent) ²	32	36 (14)	42 (15)	80	78

¹ $AOX = 1 \cdot AOCl + 0.44 \cdot AOBr + 0.28 \cdot AOI$

²real wastewater sample

mentioned in the IC method. Fig. 6 shows the calibration curve and the detection limits were found to be 0.1 $\mu\text{g/l}$ for the three ions.

Fig. 7 showed the recovery results of organically bound halogens obtained when the model samples were analyzed for AOCl, AOBr, and AOI using combined AOX_{DIN} -ICP-MS. Figs. 7 (a–c) are results of a single ion solution of 50 $\mu\text{g/L}$ while in Fig. 7 (d) is a derived from a solution of a mixture of ions. As can be seen, the amount of chloride, bromide and iodide recovered from the AOX analyzer exceeded the blank level (especially as presented in Fig. 7 a-c), probably due to the impurities present in the activated charcoal, matrix effects, and improper instrument specification settings. The presence of

halogens and other ions in the activated carbon used in the AOX analysis is the major obstacle for more precise estimation of the distribution of AOCl, AOBr, and AOI [14–15].

Comparison of AOX, IC and ICP-MS. The described methods (AOX_{DIN} -IC and AOX_{DIN} -ICP-MS) were applied to the analysis of model samples. In Table 1, the results obtained with the combined AOX_{DIN} -IC and AOX_{DIN} -ICP-MS methods are given and compared with conventional AOX_{DIN} method. In general, there is a good agreement between the results. The AOX_{DIN} -ICP-MS method further proved to be a more sensitive method compared to AOX_{DIN} -IC. The AOX_{IC} and AOX_{ICP-MS} values were a bit higher than the AOX_{DIN} values due to slight impurities in the activated charcoal used. A preliminary examination of the

real wastewater (NRT-II) taken from the treatment plant indicated that the treated wastewater consists mainly on AOCl and AOI.

CONCLUSION

The application of the ion chromatography or inductively coupled plasma permits a differentiation of the classical group parameter AOX into AOCl, AOBr, and AOI. This new approach to the AOX classification gives useful information on the composition of the AOX pool and is a promising basis or further isolation and identification studies. Further improvement of the adsorption techniques and the ICP-MS method are needed to be able to classify the AOX from samples having low AOX concentrations.

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