

# Determination of Fluorine, Chlorine and Bromine in Household Products by means of Oxygen Bomb Combustion and Ion Chromatography

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**A method for routine determination of fluorine, chlorine and bromine in household products was developed and validated. In this work, halogen analyses were made based on oxygen bomb combustion followed by ion chromatography (IC). The chromatographic analysis was performed by an IonPac AS19 hydroxide-selective anion-exchange column, a reagent free ion chromatograph eluent generator and an anion self-regenerating suppressor in 10 min. The response was linear ( $r \geq 0.9995$ ) in the entire investigated domain. The limit of detection for the halogens was in the range of  $2$  to  $9 \times 10^{-3}$  mg/L and the limit of quantification was lower than 8 mg/Kg with 20  $\mu$ L of injection volume. The certified reference material of ERM-EC 681k was pretreated using an oxygen bomb combustion procedure to demonstrate the precision of the proposed method. The quantitative analysis results obtained by IC for the target elements were  $797 \pm 9$  mg/Kg chlorine and  $786 \pm 25$  mg/Kg bromine, which were in good agreement with the certified values of  $800 \pm 4$  mg/Kg chlorine,  $770 \pm 5$  mg/Kg bromine for ERM-EC 681k, respectively. This validated method was successfully applied for the analysis of fluorine, chlorine and bromine in household product samples, and the variation of halogen contained among the tested samples was remarkable.**

## Introduction

Halogen comprises fluorine, chlorine, bromine and iodine that are used in various commercial and industrial applications to improve the performance of materials. For approximately 200 years, synthetic halogenated compounds, especially fluoride, bromide and chlorinated compounds, have been used as pesticides, disinfectants, solvents, pharmaceuticals, cryogen and flame-retardants (1). The widely used halogens in household products have increasingly received concerns because the incineration of halogenated organics leads to the formation of strongly carcinogenic, highly migratory and chronically toxic products. For example, the combustion of waste containing chlorine releases dioxins that are a strong carcinogen. Therefore, more governmental and organization legislative initiatives have been launched that concern the free use of halogens. For instance, to protect the ozone layer, the Montreal Protocol (2) on substances that deplete the ozone layer came into effect in 1987, and China joined the protocol in 1989. With environment protection taken into account, the Montreal Protocol was modified in Copenhagen in 1992, which stipulated that chlorofluorocarbon (CFC) will be completely forbidden to be used after January 1, 1996. The Stockholm Convention (3) has already acted to control the production and use of certain persistent organic pollutants, including chloride, and in November, 2004, this Convention was enforced for China. Today, halogens are prohibited from use in

numerous countries around the world. The member states of the European Union have adopted the directives 2002/96&95/EC and test methods 2008/IEC62321 covering the treatment of waste electrical and electronic equipment (WEEE) and the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) (4–7), respectively. These restrictions will have a global effect on manufacturers and retailers, vigorously pushing forward the halogen-free process. Parts and/or products are considered halogen-free provided each homogenous material has a maximum concentration of 900 mg/Kg bromine or chlorine (4). A homogeneous material has uniform composition throughout and cannot be mechanically disjointed into different materials.

Various analytical methods have been used for elemental analysis after combustion with oxygen in sealed stainless-steel bomb. A few authors (8–9) showed that plasma optical emission spectrometry (ICP-OES) can be successfully applied for anion determination. They also showed that chemical analysis (10) and potentiometric titration (11) could be applied for analyzing anions in the oxygen bomb absorption solution. As the researchers (12) suggested that ion chromatography (IC) is the most sensitive and versatile method for the detection of halogens, because it offers the possibility of a very fast, accurate and simultaneous method for multi-element analysis without the necessary lengthy chemical preparation and conversion pretreatment steps.

Although a considerable amount of literature has already been reported on the analysis of element in solids, e.g., coal (13, 14), rubber (11, 15) and waste (12, 16, 17), and atmospheric (18) and liquid matrices (19, 20), only a few papers are related to the determination of halogens in household products. Hence, the objective of the work discussed in this paper was to develop an oxygen bomb combustion coupled to an IC method to simultaneously determine fluorine, chlorine and bromine in nonmetallic component parts of household products.

## Experimental

### Chemicals and reagents

Standards of fluoride, chloride and bromide were purchased from State Center for Standard Matter (Beijing, China). Certified reference materials of ERM-EC 681k were available from the Institute of Reference Materials and Measurement (IRMM, Geel Belgium). Certified reference material consists of low-density polyethylene (LDPE) granulate that has been fortified with commercially available LDPE with technical mixtures of chlorine ( $0.80 \pm 0.05$  g/Kg) and bromine ( $0.77 \pm 0.04$  g/Kg) for ERM-EC 681k. The figures have been certified by IRMM.

High-purity oxygen, 99.5 %, and liquid nitrogen,  $\geq 99.8$  %, were purchased from South Asia Air Products (Beijing, China). Platinum ignition wire and blank capsule were supplied by Parr Instrument Company (Moline, IL). Sodium carbonate and sodium bicarbonate, analytical reagent (AR) grade, were obtained from Beijing Chemical Works (Beijing, China). All solutions and eluent were prepared by using ultrapure water (18.2 M $\Omega$  cm resistivity, 25°C) from a Millipore Direct-Q water purification system (Billerica, MA).

### Instrumentation

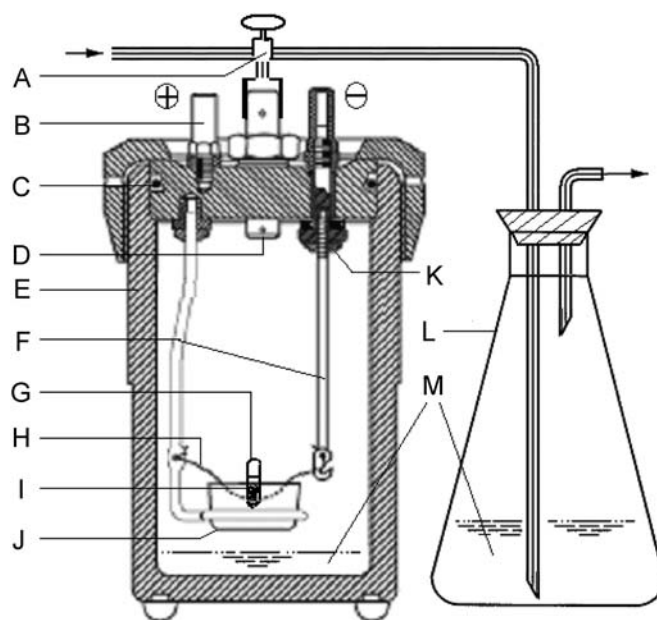
IC analysis were conducted using a Dionex ISC-2000 equipped with an AS40 automated sampler, reagent-free ion chromatograph eluent generator cartridge (RFIC EGCII KOH), CD 20 conductivity detector and anion self-regenerating suppressor (ASRS 300, 4 mm, all Dionex, Sunnyvale, CA). Chromatographic separation was carried out on an AS 19 hydroxide selective anion exchange column (250  $\times$  4 mm i.d., Dionex IonPac). The AG 19 guard column (50  $\times$  4 mm i.d., Dionex IonPac) was installed before the analytical column. For the sample pulverization, an IKA-A11 analytical grinding mill (IKA Works, Guangzhou, China) coupled to a stainless steel cutting blade was adopted. A high pressure stainless steel oxygen bomb (with a capacity of 350 mL, Parr Instrument Company, Moline, Illinois) coupled to a water bucket was used for sample combustion. Polytetrafluoroethylene (PTFE) syringe filters (13 mm  $\times$  0.45  $\mu$ m; 13 mm  $\times$  0.2  $\mu$ m) were purchased from Thermo Fisher Scientific (Shanghai, China). For the preparation of standard solution, Thermo Scientific finnpipette F3 was employed (Thermo Scientific, Finland). All of the glassware for the preparation of samples and standard solutions were cleaned with deionized water and acetone and then baked at 450°C.

### Preparation of standard and absorption solutions

By using a finnpipette, a portion from each standard (100, 100 and 1,000  $\mu$ g/mL for fluoride, chloride and bromide) was withdrawn to obtain the combined solution: 4.00  $\mu$ g/mL of fluoride, 6.00  $\mu$ g/mL of chloride and 20.0  $\mu$ g/mL of bromide. The combined solution was diluted step-by-step with ultrapure water to give four different concentrations of working standard solutions. Concentration levels were: 2.00, 0.80, 0.32 and 0.16  $\mu$ g/mL for fluoride; 3.00, 1.20, 0.48 and 0.24  $\mu$ g/mL for chloride; 10.0, 4.00, 1.60 and 0.80  $\mu$ g/mL for bromide. The combined solutions and four working standard solutions were employed to construct the calibration curves. The absorption solution used for IC studies was prepared by dissolving 2.54 g sodium carbonate and 2.52 g sodium bicarbonate in 1.0 L pure water. All solutions were stored at 4°C in a refrigerator before use.

### Sample pretreatment

Certified reference material of ERM-EC 681k and the real samples were ground to a homogenous powder by using an IKA-A11 analytical grinding mill under liquid nitrogen protection. The milled nonmetallic samples were initially sifted through a 0.45-mm sieve and dried at room temperature to a constant mass before the weighing and combustion step. The weighting amount depended on the calorific value and the amount of the halogen content. Approximately 0.1 g (accurate to



**Figure 1.** Schematic diagram of the oxygen combustion bomb: three-way piece (A); ignition unit (B); gasket and sealing ring (C); oxygen filling connection and gas release valve (D); stainless steel bomb (E); platinum electrode (F); gelatin capsule (G); platinum fuse wire (H); sample powder (I); quartz combustion capsule (J); (K); Erlenmeyer flask (L); absorption solution (M).

0.1 mg) of milled powder for each combustion was weighed into a gelatin capsule. The gelatin capsule was slung up between two platinum electrodes. To trap the combustion gases, the inner wall surface of the bomb was wetted with 10 mL of absorption solution before the bulk transfer of the solution. As shown in Figure 1, the assembled bomb was purged under a 300 mL/min oxygen flow for 3 min; the three-way piece was then screwed and pressurized with oxygen to 30 atm. The bomb was immersed in a water bucket and ignited via an electrical discharge through a platinum ignition wire. After the ignition and cooling step, most of the halogen was absorbed by the combination solution. The three-way piece was carefully unscrewed to reduce the bomb pressure to 1 atm within 3 min before opening. The released gases were trapped after passing through an Erlenmeyer flask filled with the same absorption solution. All of the parts of the interior of the bomb were rinsed with hot pure water, and all of the washings and solutions were collected in 50-mL volumetric flasks and degassed by ultrasonification (40 kHz working frequency and 100 W power) at room temperature. The supernatant and homogeneous solution was filtered through a filtering cartridge with a 0.45- $\mu$ m membrane before the volume was completed the mark with ultrapure water. All samples were analyzed as soon as possible after the preparation.

### IC analysis

For IC analyses, all of the sample solutions were filtered through a filtering cartridge with a 0.2- $\mu$ m membrane into the 5-mL sample vials. The injection (volume: 20  $\mu$ L) was performed by AS 40 automated sampler. Other analytical conditions were as follows: suppressor type, ASRS-4 mm; pump-ECD hydroxide, 38.0; suppressor current, 189 mA; eluent concentration, 30

mMol; pressure limit range: 200–3,000 psi. The analyses were achieved at a flow rate of 2.0 mL/min and the column temperature was fixed at 30°C; the cell temperature was set at 35°C for analysis; the data were collected at the rate of 5.0 Hz and processed by Chromeleon chromatography workstation.

## Results and Discussion

### Validation of method

Validation of the method was performed evaluating the parameters described in the following.

#### Linearity

To verify the linearity of the proposed method, multipoint calibration curves were established by injecting reference standard solutions in triplicate. The slopes of the halogen calibration curves are shown in Table I. For all halogens, the values of the correlation coefficient of the normal linear regression lines were better than 0.9995; that is, these calibration curves were linear over the concentration range 0.16 to 4.00 µg/mL for fluoride, 0.24 to 6.00 µg/mL for chloride and 0.80 to 20.0 µg/mL for bromide. A chromatogram corresponding to five standard solutions at different concentration levels is presented in Figure 2.

#### Precision and accuracy

Certified reference material of ERM-EC 681k containing chlorine and bromine was employed to validation the precision and accuracy of the developed method. To validate the overall method, the ERM standard was analyzed in quintuplicate from the start. As summarized in Table II, the testing value for a newly purchased bottle of certified reference material was matched with the interval certified by IRMM.

As another important criterion of the precision and accuracy, the reproducibility of the techniques was evaluated by repetitive analysis of the polymer-spiked authentic standard. Each blank polymer sample, spiked at two concentration levels for all halogens (i.e., low, 0.5 µg/mL, and high, 10 µg/mL) was pre-treated and analyzed in quintuplicate under the established method, as described previously. The results show that recoveries varied between 92.3 and 98.1% for fluoride, 90.5 and 95.3% for chloride and 88.6 and 98.1% for bromide. The relative error (RE) values for halogens tended to increase at low concentration of the compounds. The RE for all halogens was less than 5% in the samples spiked with 10 mg/L of the compounds. In the study using a sample spiked with 0.5 mg/L, the values for bromine were less than 15%, although the measured values for

**Table I**

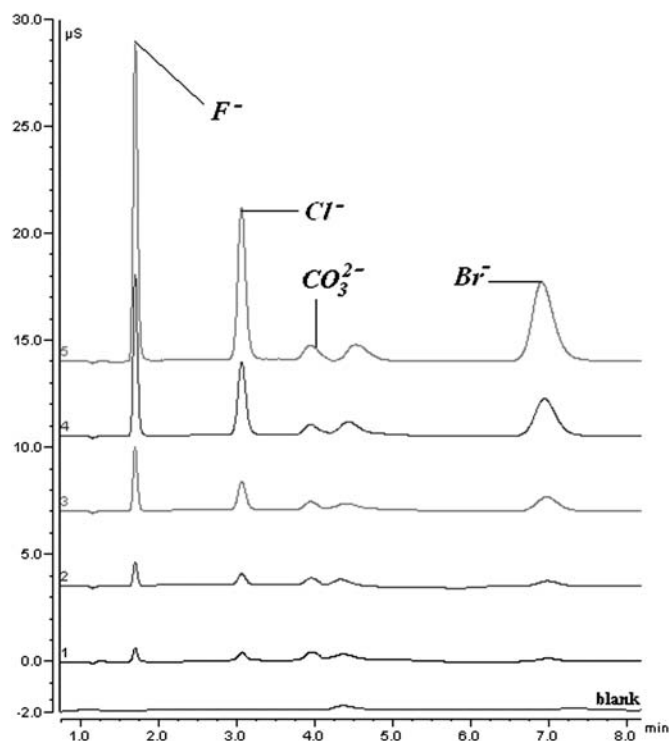
Linearity of the Calibration Curves for Determination of Halogens and the Precision and Accuracy Levels of the Present Analytical Method

Halogens	Calibration curve			ERM-EC 681k		0.5 mg/L*		10 mg/L*	
	Slope	Intercept	<i>r</i>	RSD <sup>†</sup>	RE <sup>‡</sup>	RSD	RE	RSD	RE
Fluoride	0.2613	0.004	0.9999	3.7	-5.3	2.2	7.5	2.6	2.2
Chloride	0.153	0.058	0.9995	4.1	-5.6	2.9	8.3	2.8	2.4
Bromide	0.0659	0.0191	0.9995	5.6	7.4	3.5	14.3	2.3	4.5

\*Amounts of halogens spiked into the the absorption solutions.

<sup>†</sup>RSD values in the studies with assays of five spiked samples (%).

<sup>‡</sup>RE of assayed samples relative to their certified values or spiked concentrations (%).



**Figure 2.** A chromatogram corresponding to five standard solutions at different concentration levels.

**Table II**

Halogen Analysis of Household Products by Oxygen Bomb Combustion and IC

Real sample	Peak order	Halogen found* ( mg/Kg )		
		Fluorine	Chlorine	Bromine
Pure water (system blank)	a1	ND <sup>†</sup>	N.D	ND
Gelatin capsule (travel blank)	a2	ND	N.D	ND
ERM-EC 681k	a4	ND	797 ± 9	786 ± 25
Plastic toy	a3	331 ± 3	696 ± 7	ND
Connector	a5	ND	10,376 ± 38	142,612 ± 273
Printed circuit board	a6	ND	394 ± 11	47,144 ± 157
Insulation material	a7	2,663 ± 16	N.D	ND
Computer components	a8	197 ± 6	636 ± 3	ND
Plastic package	a9	ND	420 ± 13	37,792 ± 79
Cardboard	a10	473 ± 5	3,543 ± 15	ND
Wire jacketing	a11	ND	207 ± 6	89,415 ± 133
Toothbrush	b1	ND	1,012 ± 8	ND
Fill material	b2	ND	2,530 ± 24	ND
Textiles	b3	ND	3,681 ± 19	ND
Mylar	b4	ND	6,005 ± 35	ND
Tableware	b5	ND	1,250 ± 6	ND
Magnetic tape	b6	ND	9,782 ± 45	ND
Vibration dampening part	b7	ND	9,894 ± 52	ND
Thinner	b8	ND	4,662 ± 25	ND
Cable	b9	ND	10,797 ± 62	ND
Nature gas pipe	b10	29 ± 9	2,877 ± 7	ND
Clear coat	b11	ND	4,589 ± 13	ND
Hardener	b12	ND	5,290 ± 11	ND
Rainwear	b13	66 ± 7	7,703 ± 15	ND
Film	b14	ND	8,333 ± 21	ND
Floor tiles	b15	299 ± 15	74,819 ± 97	ND
Beckryflex basecoat	b16	ND	7,528 ± 26	ND
Garden hoses	b17	350 ± 13	80,162 ± 85	ND
Rigid polyurethane foam	b18	264 ± 14	99,543 ± 46	ND

\*Quintuplicate analyses for reference material and triplicate analyses for real samples.

<sup>†</sup>ND: not detected or below detection limits.

all halogens were higher than their concentrations calculated from the spiked amounts.

The precision of the present analytical method was evaluated by the relative standard deviations (RSD) in studies with replicated assays ( $n = 5$ ), and the accuracy of the method was evaluated by the RE of the assayed samples relative to their certified values or spiked concentrations. The RSD and RE values for fluoride, chloride and bromide are summarized in Table I. Accordingly, these values indicate that the verified method can be considered to be precise for the quantification of halogens in polymer samples.

#### Limits of detection and quantification

The limits of detection (LOD) and quantification (LOQ) were calculated on the basis of the concentration giving a signal of three and ten times to background noise at the corresponding retention time of each analyte. The evaluation was carried out by analyzing the diluted solutions that contained  $F^-$ ,  $Cl^-$  and  $Br^-$  in concentrations below and above the limited values. With 20  $\mu\text{L}$  of injection volume, chlorine had the lowest LOD,  $2 \times 10^{-3}$  mg/L. The highest LOD was  $9 \times 10^{-3}$  mg/L, which was obtained for bromine. The investigated LOD of the method for fluoride was  $3 \times 10^{-3}$  mg/L, which is slightly higher than chlorine. Apparently, the  $Br^-$  was much less sensitive than  $F^-$  and  $Cl^-$  in conductivity detector. LOQ depended on the sample weight (0.1 g) or extract volumes (50 mL) and ranged from 8 for chlorine and 12 for fluoride to 44 mg/Kg for bromine. The proposed methodology fully meets the requirements of relational directives.

#### Determination of real samples

To demonstrate the performance of the proposed methodology, various household products were analyzed under the optimized conditions, as described previously. In the case of samples containing large amounts of halogen, the solution obtained after combustion was diluted before IC analysis. The identification of peaks in the real samples was based on retention time, with reference to the standard. It has always been a challenge to quantify micro-halogen with the application of an IC procedure because the analysis is affected by high concentrations of carbonate coming from the absorption solution and sample combustion. Apart from the effects of carbonate, nitrogen and phosphorus were observed to interference with analysis of fluorine and chlorine (17). Recent IC technological advances have resulted in the availability of hydroxide-selective anion-exchange columns, reagent free ion chromatograph eluent generators and the high-capacity electrolytically regenerated suppressors, which can be used to provide much higher resolution and sensitivity. As shown in Figures 2, 3, and 4, no interference was observed in the chromatograms at the retention times of the halogens. A gelatin capsule was used as a travel blank, which was pretreated and determined similarly to the real sample. The system blank values were routinely checked by ultrapure water (before and after the analysis) to avoid the memory effect of the system.

The results presented in Figures 3 and 4 and Table II were obtained by analysis of fluorine, chlorine and bromine in certified reference materials and real samples. Chlorine was the most prominent halogen in the household product samples, with concentrations ranging from  $207 \pm 6$  to  $99,543 \pm 46$  mg/Kg. A

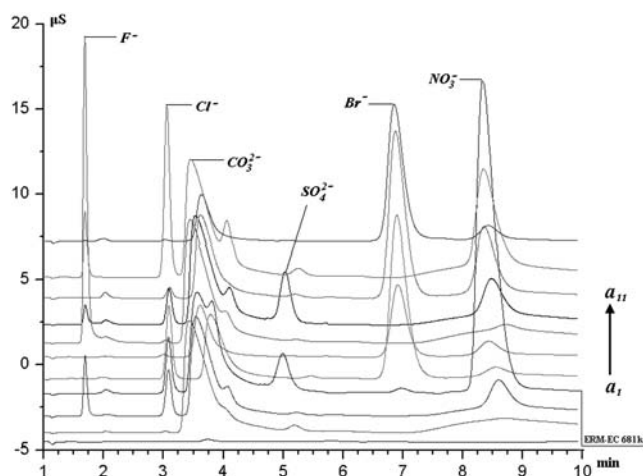


Figure 3. Chromatogram of real samples containing fluoride and bromine.

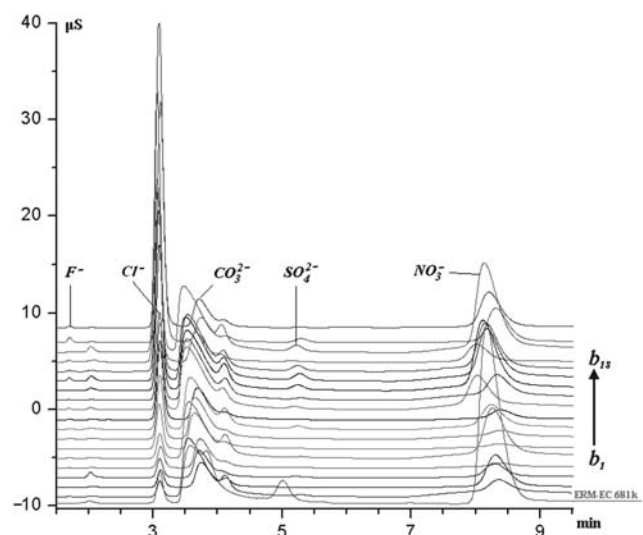


Figure 4. Chromatogram of real samples containing chloride.

possible explanation is that polyvinylchloride (PVC) or chlorinated flame retardants (CFRs) have been used in certain flame-resistant thermoplastic resins. Additionally, the widely used paints and solvent are known to contain a considerable number of chlorinated compounds. It is not surprising to find higher concentrations of fluorine and chlorine in the rigid polyurethane foam, because  $\text{CCl}_3\text{F}$  is commonly used as a foamer in thermal insulation materials. Furthermore, abundant bromine was found in wire jacketing, printed circuit board, connector and plastic package, with values between  $37,792 \pm 7.9$  and  $142,612 \pm 273$  mg/Kg. This is presumably due to brominated flame retardants (BFRs), which are often used as additives because nonmetallic components are subject to high temperatures.

#### Conclusions

The combination of oxygen combustion bomb and IC appeared to produce a simple and reliable method for determination of fluoride, chloride and bromide in household products (or other

complex matrices). The combustion procedure is efficient, resource-saving and easy to handle. In combination, IC is the most convenient and sensitive method for detection of halogens, because it offers the possibility of a very fast, accurate and simultaneous method for multi-element analysis without the necessary lengthy chemical preparation and conversion pretreatment steps. Furthermore, the method was validated for linearity, LOD, LOQ, precision and accuracy. In conclusion, this rapid and versatile method is suitable for quantitative analysis and quality control for manufacturing of household products.

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