DETERMINATION OF TOTAL HALOGEN CONTENT IN HALOGEN-FREE FLUXES BY INDUCTIVELY COUPLED PLASMA AND SOME LIMITATIONS OF ION CHROMATOGRAPHY

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ABSTRACT

Brominated flame retardants (BFRs) are coming under heavy scrutiny due to increasing evidence of the risks they pose to the environment and human health. Therefore, it is important for industrial quality laboratories to follow robust methods to assure commercial products meet the safety requirements established by the governing bodies of the world. Currently, the most common method to determine halogen content is oxygen combustion, followed by ion chromatography. The oxygen combustion test is widely established in environmental as well as in industrial laboratories. One current accepted test method, EN14582, may under-report bromine and chlorine content by as much as 65%. The use of inductively coupled plasma (ICP) methods of detection appears to resolve this discrepancy. Flux marketed as “zero intentionally-added halogens” was combusted in a bomb calorimeter vessel under 30atm of high-purity oxygen in the presence of 25ml of water. The resultant solution was analyzed using both ion chromatography (IC) and ICP. The flux was found to contain <10ppm of each element using both techniques. Samples were then spiked using a common flux additive containing chlorine and bromine, combusted in the same manner, and analyzed. At a low concentration (15ppm Br, 6ppm Cl), the average %recovery of Br was 60.7% by IC and 100.8% by ICP; the %recovery of Cl was 109.5% by IC and 84.8% by ICP. At a moderate concentration (150ppm Br, 65ppm Cl), the %recovery of Br was 25.5% by IC and 86.9% by ICP; the %recovery of Cl was 81.8% by IC and 104.2% by ICP. The effect of pH and buffering capacity of the absorbing solution was explored by ICP in an attempt to optimize the sequestration of Cl and Br in the solution as stable oxyanions; however, the results of hypothetically optimal solutions were no more accurate than those using analytical water as the absorbing solution. Additionally, thirty samples of flux containing 275ppm intentionally-added organic bromine were combusted and analyzed using the techniques described. The average %recovery of bromine by IC was 64.3% and 105.1% by ICP.

Key words: Halogen, halogen content, measuring halogen

INTRODUCTION

EN 14582(a) [1] is one of the most widely-employed test methods for determining the halogen content of organic materials, worldwide. It calls for the utilization of an oxygen bomb combustion vessel to destroy organic matrices and convert bound halogens to their freely-soluble halide form, which are then detected and quantified by ion chromatography (IC). IC is a very versatile technique in that it can provide results for fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate ($NO3^-$), phosphate ($PO4^{-3}$), sulfate ($SO4^{-2}$), and iodide (I^-) in a single 30–45 minute analysis over a four to five order of magnitude concentration range. There are several caveats to EN14582, however. Selection of the absorption solution is critical to method performance and depends on the expected result; analytical-grade water is used for very low concentrations of anions while carbonate or caustic solutions are used to neutralize high concentrations. Each reagent you add to the absorption solution has the potential to increase the blank value for each anion. EN14582 states that pure analytical-grade water may be used as an absorption solution if the expected halogen and sulfate content is less than 10g/kg (10,000ppm or 1%). This recommendation does not hold up when applied to flux due to its high load of nitrogen, phosphorus, and sulfur-containing chemicals, which will also contribute to the overall acidification of the absorption solution. The combustion products from a 1g halogen-free flux sample have been found to drop the pH of analytical-grade water absorption solution to below pH 1. This is undesirable because in an environment of high temperature, low-pH, and high partial-pressure of oxygen, halides can form oxyanions which will not be detected using common IC. Unfortunately, using absorption solutions with carbonate, bicarbonate, or hydroxides has the potential to introduce levels of halides greater than that which is in the sample. Silva, et al. suggested combining the results of IC with the results of a sodium thiosulfate titration of hypochlorate (OCl^-) to generate a total chlorine content (TCC) result [2]. In the case of flux analysis, it is important to quantify all halogens, and not just chlorine. To address the possibility that combusted flux samples have a high probability of producing oxyanions proportionate to the concentration of halides, and thus producing under reported values, we have explored the possibility of conducting the analysis of chlorine, bromine, and iodine by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The determination of chlorine by this method is only possible using instruments with oxygen-free sealed optics, and fluorine must still be quantified by IC.

EQUIPMENT AND REAGENTS

Combustion

A Parr 1108CL oxygen combustion vessel was used for all combustions. This model resists corrosion by chlorine and bromine in excess of 1% of sample weight. It was operated in accordance with the manufacturer's recommended operating procedures. Silva, et al. theorized that the most accurate chlorine results would be generated using an absorption solution which would maintain a pH of >10, the pKa of OCl^-. Three molar strengths of KOH absorber solution were evaluated for their ability to maintain a pH above 10 and stabilize chlorine in the solution. The KOH was verified to be free of significant chloride and bromide (<10ppm) prior to use by ICP.

Anion-IC

Analysis was performed using a Metrohm 883 Basic IC system with a MSM suppressor module and conductivity detector. The eluent used was 4.8mmol/L Na2CO3/1.5mmol/L NaHCO3 at a flow rate of 0.7ml/min. This eluent has been selected because it maintains the elution order of common anions while reducing the elution time, facilitating quantitation of iodide. Separation utilized a Metrosep A Supp 5 250cm/4.0mm column and a Metrosep A Supp 4/5 Guard column. The calibration curve from 0.01ppm to 10ppm was created using fresh dilutions from a custom NIST-traceable standard solution from Inorganic Ventures containing 1000mg/L each of F^-, Cl^-, NO_2^-, Br^-, NO_3^{-2}, PO_4^{-3}, SO_4^{-2}, and I^-. 20µL of standards and samples were injected using a Metrohm 863 Compact Autosampler.

ICP

Analysis was performed using a Spectro Ciros system. Calibration was performed using 1ppm and 100ppm fresh dilutions of the same standard solution used for anion-IC analysis.

SAMPLE PREPARATION

1g portions of no intentionally-added halogens flux were combusted under 30-35atm of ultra-high purity oxygen. The products were absorbed in 25ml 18.2MOhm analytical-grade water; this is the maximum volume of absorbing solution that could be added to the combustion vessel without compromising the sample. The effect of increasing Cl/Br concentration was investigated by spiking samples with varying amounts of 1% solution of bromochloroacetophenone in tetraethylene glycol dimethyl ether to maintain the flux matrix. Additional data were compiled from routine quality control data from a halogen-free flux with a formulated bromine content of 275ppm.

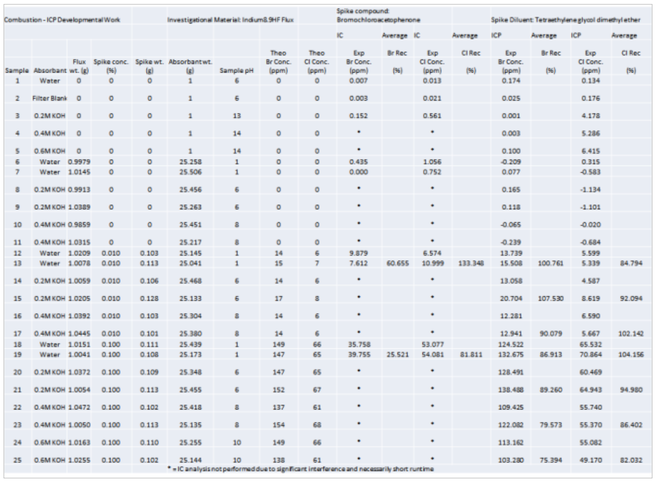
RESULTS

Silva, et al. investigated the content of various refuse-derived fuels and reported TCC levels of 6-24g/kg, 6000-24000ppm [2]. The content of halogen-free fluxes is much lower, making the sensitivity of the test much more important. For this reason, the KOH absorption solutions could not be analyzed by anion-IC because a dilution of >1000 was required to reduce the potassium interference at the beginning of the chromatogram. KOH absorption solutions were analyzed by ICP alone.

All unspiked samples of flux with no intentionally-added halogens were verified to contain 10ppm or less of bromine and chlorine by both IC and ICP, regardless of absorption solution. Samples spiked with 0.01% bromochloroacetophenone had a theoretical content of 14ppm bromine and 6ppm chlorine. Samples spiked with 0.1% bromochloroacetophenone had a theoretical content of 147ppm bromine and 65ppm chlorine.

Only samples using analytical-grade water as the absorption solution were tested using both analytical methods. These samples produced inconsistent results when analyzed by IC. Using ICP, the results were more consistent and more accurate. At these Br/Cl levels, increasing molarity KOH absorption solutions produced decreasingly favorable results. All results are summarized in Table 1 (see end of paper for enlarged table).

Table 1. Summary of experimental results and calculated data

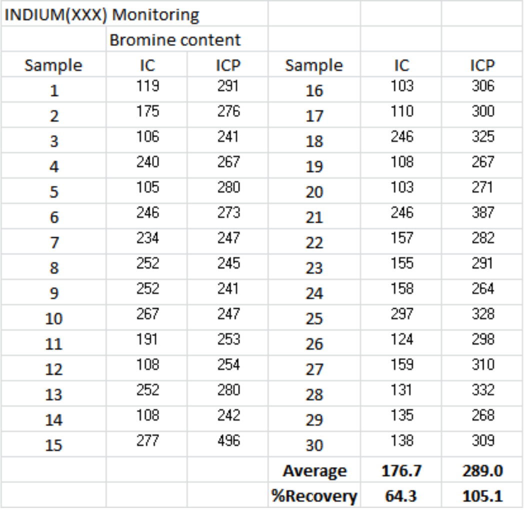


Combustion - ICP Developmental Work					Investigational Material: Indium8.9HF Flux				Spike compound: Bromochloroacetophenone				Spike Diluent: Tetraethyleneglycol dimethyl ether			
									IC	Average	IC	Average	ICP	Average	ICP	Average
Sample	Absorbant	Flux wt. (g)	Spike conc. (%)	Spike wt. (g)	Absorbant wt. (g)	Sample pH	Theo Br Conc. (ppm)	Theo Cl Conc. (ppm)	Exp Br Conc. (ppm)	Br Rec (%)	Exp Cl Conc. (ppm)	Cl Rec (%)	Exp Br Conc. (ppm)	Br Rec (%)	Exp Cl Conc. (ppm)	Cl Rec (%)
1	Water	0	0	0	1	6	0	0	0.007		0.013		0.174		0.134	
2	Filter Blank	0	0	0	1	6	0	0	0.003		0.021		0.025		0.176	
3	0.2M KOH	0	0	0	1	13	0	0	0.152		0.561		0.001		4.178	
4	0.4M KOH	0	0	0	1	14	0	0	*		*		0.003		5.286	
5	0.6M KOH	0	0	0	1	14	0	0	*		*		0.100		6.415	
6	Water	0.9979	0	0	25.258	1	0	0	0.435		1.056		-0.209		0.315	
7	Water	1.0145	0	0	25.506	1	0	0	0.000		0.752		0.077		-0.583	
8	0.2M KOH	0.9913	0	0	25.456	6	0	0	*		*		0.165		-1.134	
9	0.2M KOH	1.0389	0	0	25.263	6	0	0	*		*		0.118		-1.101	
10	0.4M KOH	0.9859	0	0	25.451	8	0	0	*		*		-0.065		-0.020	
11	0.4M KOH	1.0315	0	0	25.217	8	0	0	*		*		-0.239		-0.684	
12	Water	1.0209	0.010	0.103	25.145	1	14	6	9.879		6.574		13.739		5.599	
13	Water	1.0078	0.010	0.113	25.041	1	15	7	7.612	60.655	10.999	133.348	15.508	100.761	5.339	84.794
14	0.2M KOH	1.0059	0.010	0.106	25.468	6	14	6	*		*		13.058		4.587	
15	0.2M KOH	1.0205	0.010	0.128	25.133	6	17	8	*		*		20.704	107.530	8.619	92.094
16	0.4M KOH	1.0392	0.010	0.103	25.304	8	14	6	*		*		12.281		6.590	
17	0.4M KOH	1.0445	0.010	0.101	25.380	8	14	6	*		*		12.941	90.079	5.667	102.142
18	Water	1.0151	0.100	0.111	25.439	1	149	66	35.758		53.077		124.522		65.532	
19	Water	1.0041	0.100	0.108	25.173	1	147	65	39.755	25.521	54.081	81.811	132.675	86.913	70.864	104.156
20	0.2M KOH	1.0372	0.100	0.109	25.348	6	147	65	*		*		128.491		60.469	
21	0.2M KOH	1.0054	0.100	0.113	25.455	6	152	67	*		*		138.488	89.260	64.943	94.980
22	0.4M KOH	1.0472	0.100	0.102	25.418	8	137	61	*		*		109.425		55.740	
23	0.4M KOH	1.0050	0.100	0.113	25.135	8	154	68	*		*		122.082	79.573	55.370	86.402
24	0.6M KOH	1.0163	0.100	0.110	25.255	10	149	66	*		*		113.162		55.082	
25	0.6M KOH	1.0255	0.100	0.102	25.144	10	138	61	*		*		103.280	75.394	49.170	82.032

* = IC analysis not performed due to significant interference and necessarily short runtime

ICP quantitation of chlorine and bromine was practically implemented and the results of ongoing quality monitoring of a flux formulated with 275ppm bromine are summarized in Table 2 (see end of paper for enlarged table).

Table 2. Summary of thirty quality control samples analyzed by both IC and ICP



INDIUM(XXX) Monitoring					
	Bromine content				
Sample	**IC**	**ICP**	**Sample**	**IC**	**ICP**
1	119	291	**16**	103	306
2	175	276	**17**	110	300
3	106	241	**18**	246	325
4	240	267	**19**	108	267
5	105	280	**20**	103	271
6	246	273	**21**	246	387
7	234	247	**22**	157	282
8	252	245	**23**	155	291
9	252	241	**24**	158	264
10	267	247	**25**	297	328
11	191	253	**26**	124	298
12	108	254	**27**	159	310
13	252	280	**28**	131	332
14	108	242	**29**	135	268
15	277	496	**30**	138	309
			Average	**176.7**	**289.0**
			%Recovery	**64.3**	**105.1**

CONCLUSIONS

It appears from these results that ICP detection of bromine and chlorine may be favorable to IC detection at concentrations less than 300ppm and potentially at all concentrations. Experimental results demonstrate a reduction in error of about 75% at the concentrations tested, from 35–40% to 5–10%.

It is possible that KOH absorption solutions could be analyzed by Anion-IC following treatment with cation exchange filters; this may be evaluated during future work. The use of sodium carbonate/bicarbonate solutions for absorption was not explored but may be useable on newer IC systems which remove carbonate from the eluent post-separation pre-detection. In past experiences, high concentrations of carbonate in sample solutions interfered with bromide determination. This artifact may not be as much of an issue when quantifying bromine at higher concentrations.

REFERENCES

[1] European Committee for Standardization, 2007, “EN 14582, Characterization of waste – Halogen and sulfur content – Oxygen combustion in closed systems and determination methods”

[2] Silva, R. B. et al, 2014, “Which chlorine ions are currently being quantified as total chloride on solid alternative fuels?” Fuel Processing Technology 128, pp.61-67.

RELATED ARTICLES

Jensen, T., 2011, “A Review of Test Methods and Classifications for Halogen-Free Soldering Materials” Indium Corp. Tech Paper as presented at APEX EXPO 2011.

Jensen, T. and Lasky, R., 2010, “Challenges Toward Implementing a Halogen-Free PCB Assembly Process” Indium Corp. Tech Paper as presented at APEX EXPO 2010.

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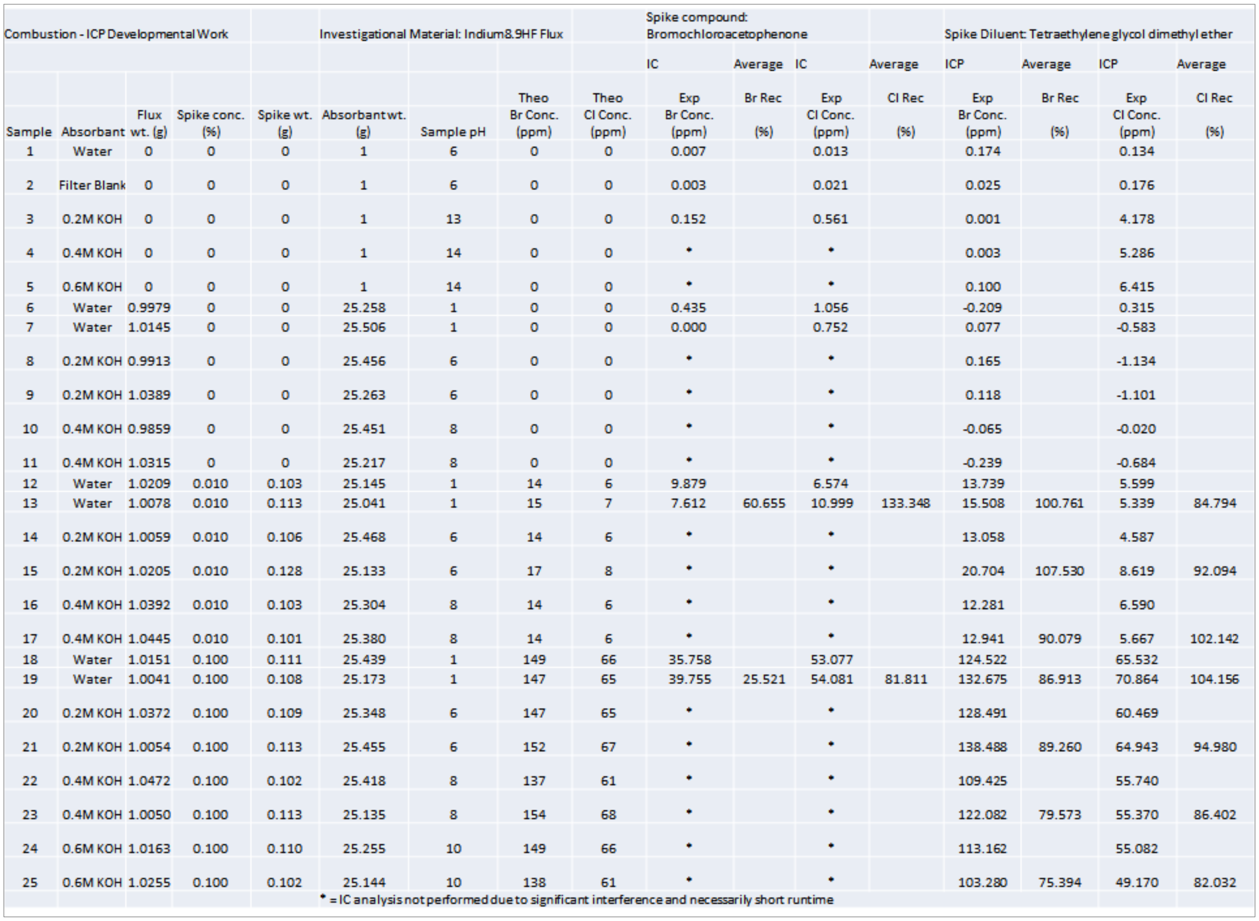

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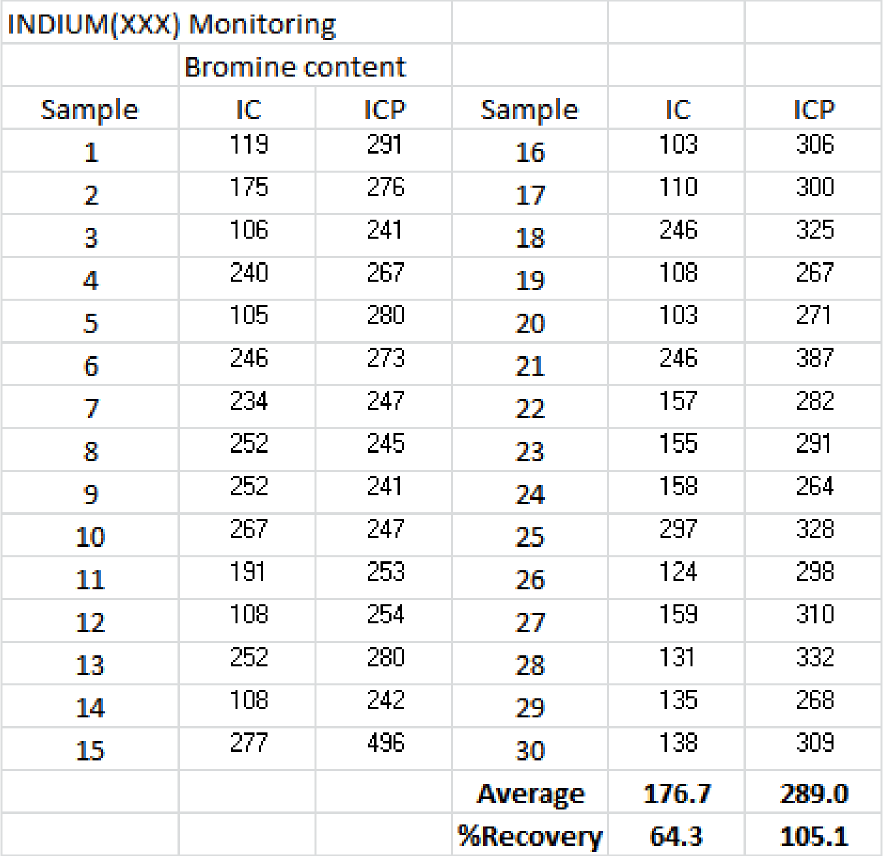

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