Application Work AW IC AU6-0522-052013

Fluorine and Chlorine in Cu-concentrates and Cu-ores by Metrohm Combustion IC

Branch

1. General analytical chemistry / 10. Metals, electroplating/
15. Mineral resources

Keywords

IC 881 / Metrosep A Supp 5 - 150/4.0 / MMS 5000 / 920 / Absorber Module / Combustion Module / combustion ion chromatography / CIC / mining / matrix elimination / fluorine / branch 16; branch 1; branch 2

Summary

The application work describes the determination fluorine in copper sulfide concentrates using the Metrohm Combustion IC system.

This work is also suitable for the copper containing ores. Copper concentrate is the first commercial product of the copper production line and is composed of approximately equal parts of copper, iron and sulfide. Concentrates are the raw material for all copper smelters, which by processing it obtain an impure form of metallic copper, anode or blister copper, which is later used to produce high purity refined copper. The production of concentrates implies the crushing and later milling of the ore down to a particle size allowing copper to be released by flotation. The concentrates from different regions have approximately between 24% up to 36% of copper. Copper concentrates are then submitted to a final filtration and drying process to decrease the humidity to 8-9%. Fluorine is a deleterious element in the concentrate due to its corrosive nature and the determination of it is of vital importance not only to the analytical laboratory but also to the process metallallurgist and the end buyer. Due to this penalties have been set by the buyer depending on the amount present.

Current laboratory techniques involve a long cumbersome fusion with a potentiometric ion selective electrode finish. However this method is prone to huge analytical errors. The new combustion IC from Metrohm offers a novel and robust method that is ideal for these types of samples.

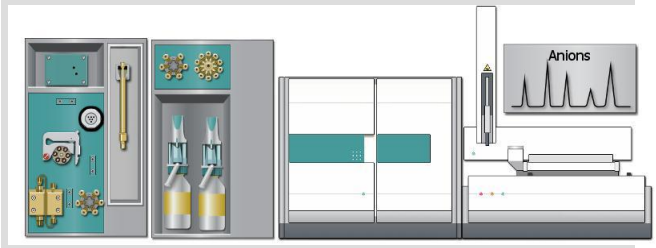
This application work provides the reproducibility on a series of fluoride analysis in copper concentrates.

Reagents

- Sodium carbonate , CAS 497-19-8
- Sodium bicarbonate, 144-55-8
- Sulfuric acid, CAS 7664-93-9
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)
- Multicomponent Anion Standard in H2O -IC1- 1mg/L
- Hydrogen peroxide, 30% H2O2, TraceCert®, from Sigma Aldrich 16911

Instruments

881 Compact IC pro – Anion – MCS	2.881.0030
IC conductivity detector	2.850.9010
Combustion Module	2.136.0700
Autosampler MMS 5000	2.136.0800
Kit for solid sampling	6.7302.000
920 Absorber Module	2.920.0010
MagIC Net TM 2.4 Compact	6.6059.241
Metrosep A Supp 5 - 150/4.0	6.1006.520
Metrosep A Supp 4/5 Guard column	6.1006.500
Metrosep A PCC 1 HC	6.1006.310



Samples

Copper Sulfide concentrates, kindly provided by Newcrest Mining Limited, NSW

Standard

Mixed anion standard of 4 mg/L is prepared from 10 mg/L of multi anion high purity standard.

Method Description

A quartz wool prefilled tube (refer to Picture 1) is tarred and filled accurately (accurate to at least 0.1 mg) with about 10 to 20 mg of the copper concentrate sample, and finally packed with some extra quartz wool.

The main reason for using this sampling method is to protect the quartz combustion tube from being degraded by the alkaline and alkaline earth metals.

Finally, the packed tube is transferred in a quartz boat for a fully automated analysis via the automatic boat drive of the combustion IC unit.

IC Parameters

Eluent Flow	0.7 mL/min
Column temperature	30°C
Absorber Solultion	200 mg/L H_2O_2
Sample loop	250 µL
Inj. Vol. (Standards)	5 - 200 µL
MSM Regenerent	100 mmol/L Sulfuric acid
MSM Rinsing	water
Carbonate Suppressor	ON

Combustion Parameters

Argon	100 mL/min
Oxygen	300 mL/min
Oven temperature	1050 °C
Time for post-combustion	180 sec
Initial volume of absorbing solution	2 mL
Water addition	0.2 mL/min
Absorbtion solution addition	0.2 mL/min

Boat Blank

It is important to bake the boats and tubes before using them for sample analysis in order to remove the ionic impurities present. The quartz boat is much cleaner compared to a ceramic boat and doesn't leach out ionic impurities. For trace analysis it is essential to keep the boats and the pyrotubes clean. For trace analysis analyte concentration from the boat blank should be, ideally, less than 2 µg/L (ppb).

Sample analysis

10 mg to 20 mg of the copper concentrate is combusted. Depending on the expected fluorine concentration about 50 µL to 200 µL of the combusted sample is preconcentrated and injected into the IC.

Calculation

Automatic integration with MagIC Net 2.4 software, using the peak area for both components.

Time program

The time program was set up with sub-routines which are activated depending on the sample type (e.g. sample, standard, check standard and blank) defined in the determination series table.

Calibration

IC is calibrated separately using a mixed standard anions. Standard linearity is established by variable volume pre concentration using the 1 mg/L mixed anion standard.

Volume (µL)	200	100	50	25	12.5	6.25
Conc.(µg/mL)	4.000	2.000	1.000	0.500	0.250	0.125

Sample Results

The full validation includes:

1. Linearity check
2. Robustness / Reproducibility
3. Blanks, LOD , LOQ
4. Carry - Over
5. Accuracy / Repeatability

Appendix

Appendix 1: Validation results

Appendix 2: Calibration curves, chromatograms.

Date:

Wednesday, December 04, 2013

Reference

- Dietrich, R. and Skinner, B., 1979, Rocks and Rock Minerals.
- Gilchrist, J.D. (1989). "Extraction Metallurgy"

Authors

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Metrohm Australia - MEP Instruments

Appendix 1: Validation results

1.Linearity:

For verification on the linearity multiple standards over the whole calibration range were injected multiple times and matched against the calibration curve.

The average linearity coeficient is 0.9997 for Fluorine and 0.99540 for Chlorine.

Component		Fluorine			Chlorine		
Calibration		**A = 0.0210918× Q - 4.76118E-6× Q²**			**A = 0.0130780× Q + 4.81818E-7× Q²**		
Correlation Coeff		**0.99997**			**0.99995**		
RSD %		**0.00897**			**0.01298**		
Standard	**Conc (ppm)**	**Series 1**	**Series 2**	**Series 3**	**Series 1**	**Series 2**	**Series 3**
Std 1	0.125	0.10200	0.12900	0.12800	0.12800	0.11100	0.11100
Std 2	0.250	0.22900	0.25200	0.25300	0.25300	0.22800	0.23000
Std 3	0.500	0.51200	0.51200	0.51300	0.48100	0.48100	0.48300
Std 4	1.000	1.00900	1.00900	1.01000	0.99400	0.99400	0.99600
Std 5	2.000	1.98600	1.98600	1.98400	2.01500	1.98600	2.01600
Std 6	4.000	4.00000	4.00800	4.00400	4.01300	3.99700	3.99700
Correlation Coeff		**0.99995**	**0.99998**	**0.99998**	**0.99998**	**0.99998**	**0.99997**
Linearity		**0.99741**	**1.00065**	**1.00184**	**0.99490**	**0.99640**	**0.99489**

2. Robustness:

The robustness test was carried out over different days by different analysts using different batches of chemicals such as mobile phase and scrubber solution.

To get a good understanding about the long term stability, a single system calibration was used prior to the investigation.

The main variables “sample weight” and “pre-concentration volume” were investigated by varying the target value systematically. The target value for the sample weight was set at 10, 15 and 20 mg respectively while the pre-concentration value was set at 50, 100 and 150 µL.

#	Date	Time	Volume (uL)	Target Weight (mg)	Exp. Weight (mg)	C Fluorine (ppm)	C Chlorine (ppm)	Remarks	Analyst
1	27/11/2013	12:11:39 PM	50	20	20.5	395	7.6		dk
2	27/11/2013	12:32:39 PM	100	20	22.6	389	18.4		dk
3	27/11/2013	12:53:46 PM	150	20	20.8	390	19.9		dk
4	27/11/2013	1:14:59 PM	50	10	9.8	391	23.1		dk
5	27/11/2013	1:36:00 PM	100	10	10.3	401	18.8		dk
6	27/11/2013	1:57:06 PM	150	10	9.9	382	21.4		dk
7	27/11/2013	5:28:20 PM	50	15	15.7	400	18.8		dk
8	27/11/2013	5:49:21 PM	100	15	15	400	17.4		dk
9	27/11/2013	6:10:28 PM	150	15	15	393	17.5		dk
10	28/11/2013	9:35:50 AM	50	20	18.1	386	23.2		bc
11	28/11/2013	11:35:03 AM	100	20	22.9	405	17.9		bc
12	26/11/2013	11:56:10 AM	150	20	18.9	377	20.6		bc
13	26/11/2013	12:17:22 PM	50	10	9.6	402	27.9		bc
14	28/11/2013	12:38:24 PM	100	10	7.9	401	22.8		bc
15	28/11/2013	12:59:30 PM	150	10	10.1	385	30.1		bc
16	28/11/2013	1:20:43 PM	50	15	16.3	396	10		bc
17	28/11/2013	1:41:44 PM	100	15	15.6	400	22		bc
18	28/11/2013	2:02:51 PM	150	15	14.1	395	28.5		bc
19	28/11/2013	2:24:03 PM	50	20	21.6	397	10.5		bc
20	28/11/2013	2:45:04 PM	100	20	21.7	393	15.8		bc
21	28/11/2013	3:06:10 PM	150	20	19.5	394	25.8	1*	bc
22	28/11/2013	7:19:33 PM	50	10	12	400	294.7	2*	bc
23	28/11/2013	6:58:27 PM	100	10	13.9	400	15.3		bc
24	28/11/2013	6:37:26 PM	150	10	7.8	409	32		bc
25	28/11/2013	6:16:13 PM	50	15	15.3	399	23		bc
26	28/11/2013	5:55:07 PM	100	15	13.8	405	15		bc

27	28/11/2013	5:34:06 PM	150	15	15.4	405	37		bc
28	28/11/2013	5:12:53 PM	50	20	23.1	389	27		bc
29	28/11/2013	4:51:46 PM	100	20	18.2	399	15		bc
30	28/11/2013	4:30:45 PM	150	20	19.2	396	24		bc
31	28/11/2013	4:09:32 PM	50	10	7.6	405	35		bc
32	28/11/2013	3:48:25 PM	100	10	7.8	402	19		bc
33	28/11/2013	3:27:23 PM	150	10	9.1	408	34		bc
34	29/11/2013	10:46:20 AM	50	15	16.1	409	27		dk
35	29/11/2013	11:19:37 AM	100	15	15.3	395	15		dk
36	29/11/2013	11:40:43 AM	150	15	14.6	394	23		dk
37	29/11/2013	12:01:55 PM	50	20	20.8	401	25		dk
38	29/11/2013	12:22:56 PM	100	20	21.8	396	25		dk
39	29/11/2013	12:44:02 PM	150	20	19.6	417	29		dk
40	29/11/2013	1:05:14 PM	50	10	10.8	392	26		dk
41	29/11/2013	1:26:14 PM	100	10	10.4	407	17		dk
42	29/11/2013	1:47:21 PM	150	10	11.1	413	30		dk
43	29/11/2013	2:08:36 PM	50	15	15.8	406	21		dk
44	29/11/2013	2:29:37 PM	100	15	14.5	399	18		dk
45	29/11/2013	2:50:44 PM	150	15	14.6	402	23		dk
46	29/11/2013	3:11:56 PM	50	20	21.5	396	8		dk
47	29/11/2013	3:32:57 PM	100	20	22	399	17		dk
48	29/11/2013	3:54:03 PM	150	20	20.4	405	19		dk
49	29/11/2013	4:15:16 PM	50	10	11.7	398	20		dk
50	29/11/2013	4:36:16 PM	100	10	10.8	427	17		dk
51	29/11/2013	4:57:22 PM	150	10	11.6	406	22		dk
52	3/12/2013	10:14:32 AM	50	15	16.2	460	39		dk
53	3/12/2013	10:54:56 AM	100	15	16.1	389	18		dk
54	3/12/2013	11:16:03 AM	150	15	15.3	408	23		dk
55	3/12/2013	11:37:17 AM	50	20	20.8	402	9		dk
56	3/12/2013	11:58:18 AM	100	20	20.9	398	20		dk
57	3/12/2013	12:19:25 PM	150	20	20.4	405	23		dk
58	3/12/2013	12:40:39 PM	50	10	9.5	389	25		dk
59	3/12/2013	1:01:41 PM	100	10	10.6	408	22		dk
60	3/12/2013	1:22:50 PM	150	10	10.8	409	26		dk
61	3/12/2013	1:44:04 PM	50	15	16.6	396	8		dk
62	3/12/2013	2:05:05 PM	100	15	14.8	414.7	18.8		dk

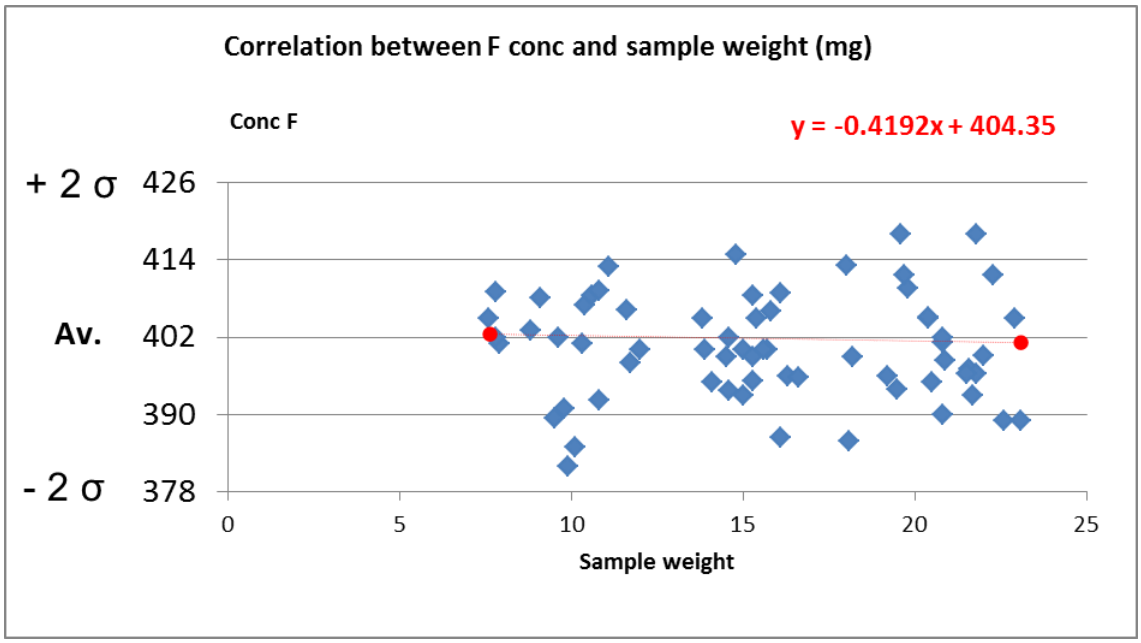
63	3/12/2013	4:32:53 PM	150	15	21.8	**418**	**22**		**dk**
64	3/12/2013	4:11:47 PM	50	20	18.9	**429**	**19**		**dk**
65	3/12/2013	3:50:46 PM	100	20	22.3	**412**	**22**		**dk**
66	3/12/2013	3:29:33 PM	150	20	19.8	**410**	**20**		**dk**
67	3/12/2013	3:08:26 PM	50	10	18	**413**	**18**		**dk**
68	3/12/2013	2:47:25 PM	100	10	8.8	**403**	**8.8**		**dk**
69	3/12/2013	2:26:12 PM	150	10	19.7	**412**	**20**		**dk**
Mean						**402**	**21**		
St Dev.						**12**	**7**		
Rel STD (%)						**2.87**	**32**		

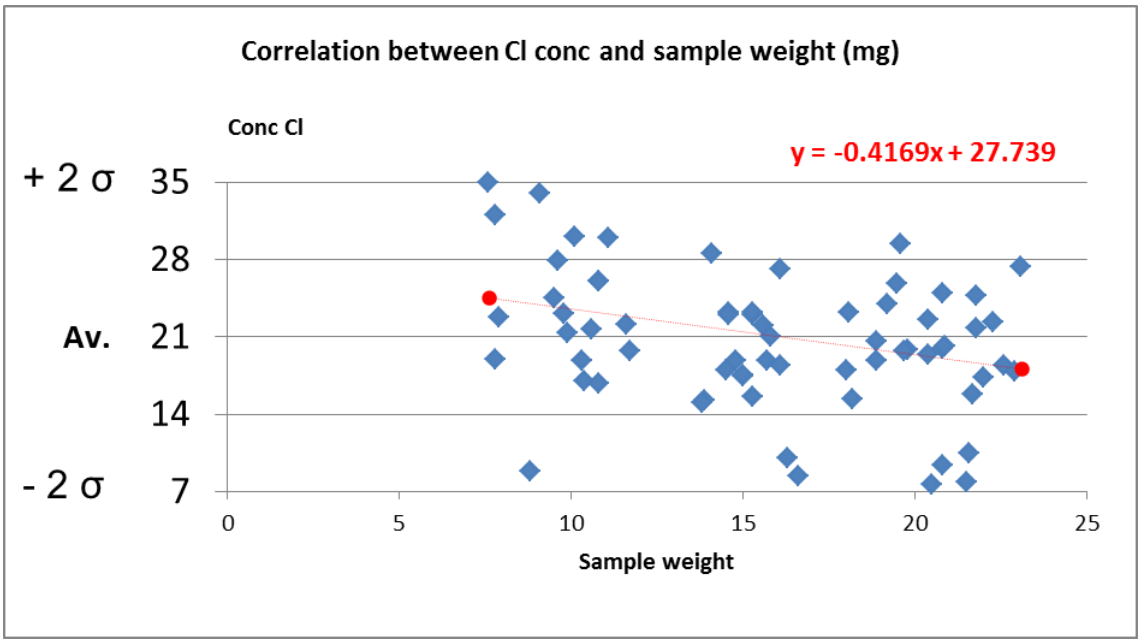
Remark 1*: Mobile phase ran out and replaced by new batch.

Remark 2*: Sample boat was touched with fingers while not wearing latex gloves: Due to the high salt level the chloride content is exceeding the expectation and the result is faulty. Hence why, this value is excluded for the statistical calculations.

Impact of the sample weight on the analytical results:

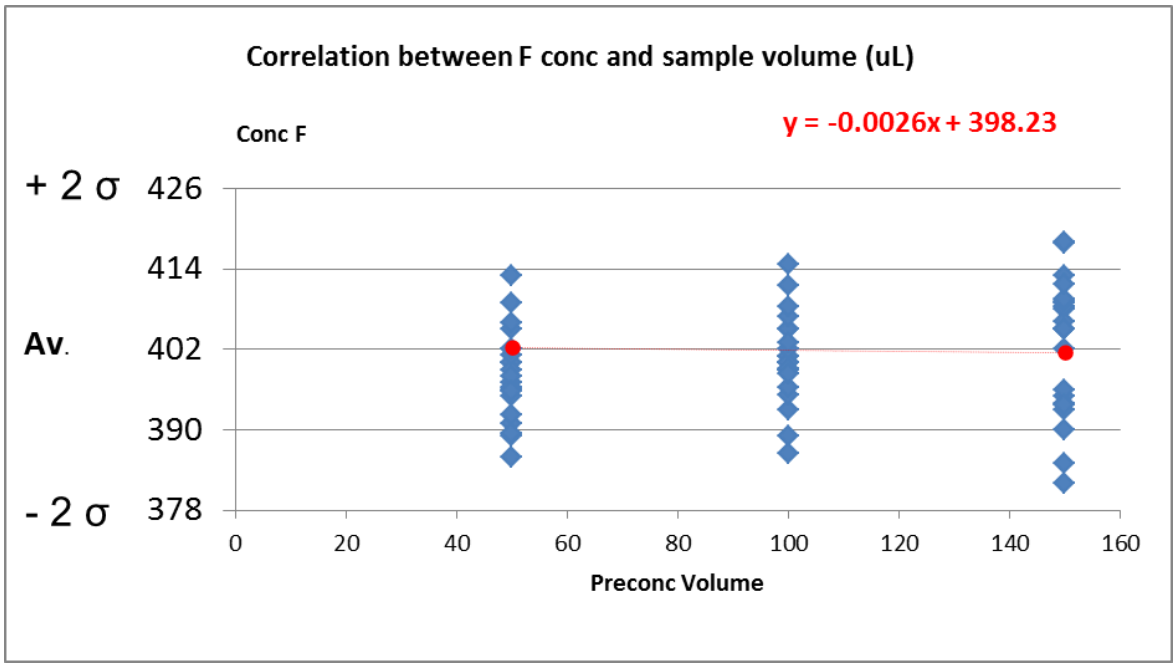
The theoretical value of the linear regression (red dot) in the lower and higher end of the sample weight lies perfectly in the 68 percentile or 1 sigma interval, hence why no evident impact of the sample weight on the final result of chlorine and fluorine can be expected.

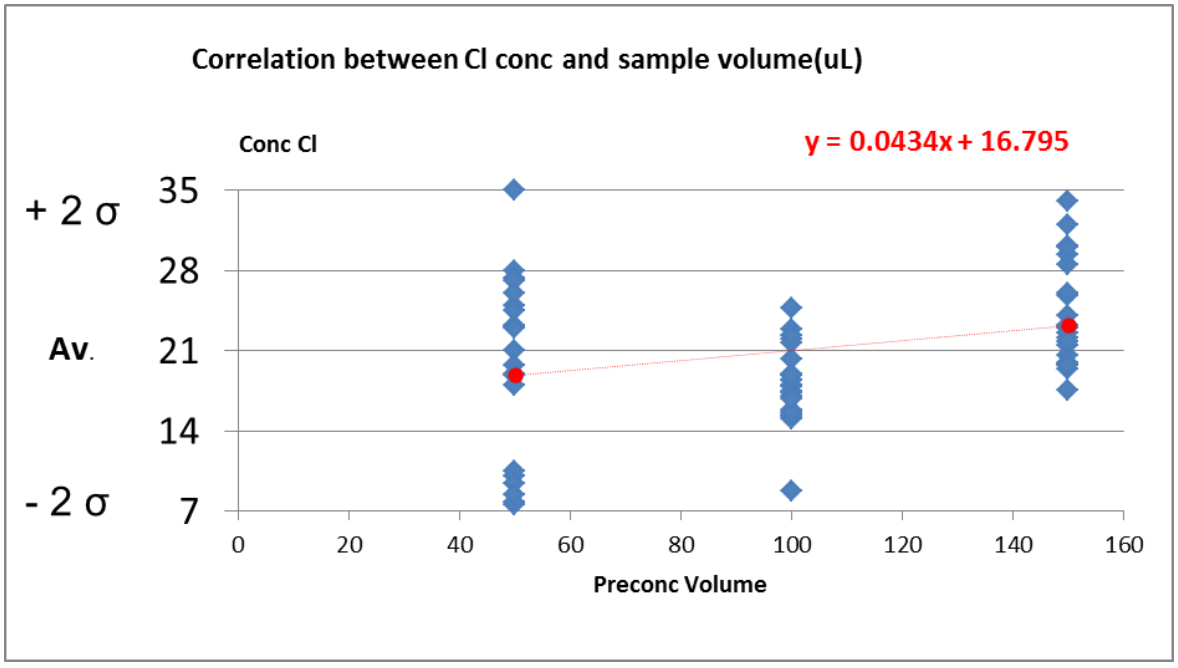




Impact of the sample pre-concentration volume on the analytical results:

The theoretical value of the linear regression (red dot) in the lower and higher end of the sample volume lies perfectly in the 68 % or 1 sigma interval, hence why no evident impact of the volume on the final result of fluorine and chlorine can be expected.





3. Determination blanks, LOD, LOQ:

The determination blank is defined as the sum of the system- and sample blank.

The system blank is the potential error as a result of the liquid handling and gas contamination, while the sample blank refers to the potential contamination of the quartz sample vial, quartz boat and quartz wool as well as the contamination that might occur during sample handling and sample introduction.

For the calculation a 10 mg sample weight and 200 µL preconcentration volume was used. Based on these sample settings an LOD < 3 for fluorine and an LOD < for chlorine were determined.

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Determination	Fluorine (ppm)	Chlorine (ppm)
1	1.8	2
2	1.8	1.9
3	2	1.9
4	2.1	1.9
5	2.3	1.9
6	2.8	1.7
7	2.2	1.8
8	2.3	1.8
9	2.4	1.8
10	2.6	1.9
Av.	2.23	1.86
St.dev.	0.941	0.064
LOD	2.823	0.192
LOQ	9.41	0.64

4. Carry-over:

For this experiment the worst case scenario has been used where a sample was run a second time without emptying and cleaning the vial and sample boat. In reality the sample vials are emptied and should be backed out with the boat using a muffle oven.

Higher blanks can be expected for chloride because the higher potential contamination with dust and natural aerosols containing sodium chloride

		Fluorine			Chlorine		
# Sample	Sample ID	1st combustion	2nd combustion	carry over (%)	1st combustion	2nd combustion	carry over (%)
1	Cu Con 8	390.1	3.5	0.90	19.9	0.3	1.51
2	Cu Con 8	391	6.4	1.64	23.1	1.3	5.63
3	Cu Con 8	392.2	3.7	0.94	18.8	2.3	12.23
4	Cu Con 8	401.1	3.8	0.95	21.4	2	9.35
5	Cu Con 8	382.5	3.9	1.02	18.8	0	0.00
6	Cu Con 8	400.3	3.9	0.97	17.4	0.7	4.02
7	Cu Con 8	400.5	2.4	0.60	17.5	0.8	4.57
Av				1.00			5.33

5. Accuracy and repeatability:

Sample	Type	Metrohm	Ref Lab.	Ref Lab	Cert values	Cert values	Ref Lab	Cert values
Method		CIC	Fusion ISE1	Std. dev.	Fusion ISE2	Std. dev.	Diff. %	Diff. %
CUF 1	Con	2641.6	2100.0					
CES01	Geological	1955.1	1732.0	155.0	1770.0	158.0	11.4	9.5
CES02	Geological	999.0	1222.0	149.0	1245.0	92.0	-22.3	-24.6
CES03	Geological	1770.6	1786.0	133.0	1760.0	130.0	-0.9	0.6
CAD68	Geological	656.5	688.0	175.0	650.0	52.0	-4.8	1.0
CAD69	Geological	970.4	958.0	34.0	965.0	97.0	1.3	0.6
RR2013CVO-1	Con	310.2	320.0				-3.2	
RR2013CVO-2	Con	322.2	320.0				0.7	
RR2013CVO-3	Con	287.4	320.0				-11.4	
RR2013CVO-4	Con	323.3	320.0				1.0	
NL011730 T1/T2	Con	862.6	790.0	740-840			8.4	