

## Application Work AW IC AU6-0510-092013

### The analysis of Fluorine and Chlorine in Zinc slag by Metrohm Combustion IC and a verification between the CIC and existing methods

#### 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, Chlorine

#### Summary

The application work describes the determination fluorine and chlorine in zinc slag using the Metrohm Combustion IC system. Fluorine and Chlorine are deleterious elements in the concentrate due to its corrosive nature and the determination of it is of vital importance to the process metallurgist.

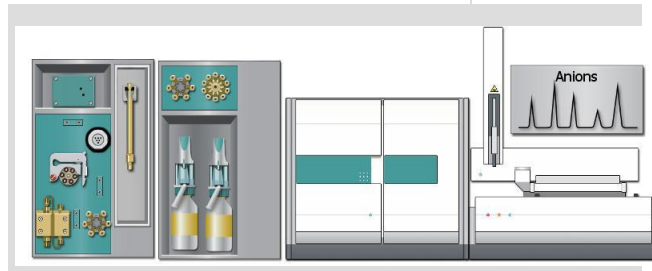
Current laboratory techniques for fluoride involves a long cumbersome fusion with a potentiometric ion selective electrode (ISE) finish. For Chloride the current determination is carried out via XRF. The new combustion IC from Metrohm offers a novel and robust method that is ideal for these types of samples.

#### 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 H<sub>2</sub>O -IC1- 1mg/L
- Hydrogen peroxide, 30% H<sub>2</sub>O<sub>2</sub>, 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™ 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

Zinc Slag concentrates, kindly provided by Nyrstar , Port Pirie, Australia.

#### Standard

Mixed anion standard of 2 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 (up to at least 0.1 mg) with about 10 to 20 mg of the Zinc 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 Solution	200 mg/L H <sub>2</sub> O <sub>2</sub>
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. Several blanks should be carried out to verify if the quartz wool is free of analyte impurities.

## Sample analysis

10 mg to 20 mg of the zinc sample is combusted. Depending on the expected fluorine and chlorine concentration about 25 µL to 200 µL of the combusted sample is pre-concentrated and injected into the IC.

## Calculation

Automatic integration with MagIC Net 2.4 software, using the peak area for all analytes.

## 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 mixed standard anions. Linearity is established by variable volume pre-concentration using the 4 mg/L mixed anion standard.

Volume (µL)	200	100	40	20	10	5
Conc.(µg/mL)	4.0	2.0	1.0	0.5	0.2	0.1

## Results

Sample	Conc F (%) Av # 2	Conc Cl (%) Av # 2
STD 1	0.00216	0.07510
STD 2	0.00185	0.02300
STD 3	0.08900	0.07555
STD 4	0.03625	0.26575
STD 5	0.11135	1.03145

## Appendix

- Appendix 1: Instrumentation setup, calibration curves, chromatograms
- Appendix 2: Result comparison between CIC and ISE for Fluorine and CIC and XRF for Chlorine.

## Date:

Monday, November 11, 2013

## Reference

1. Dietrich, R. and Skinner, B., 1979, Rocks and Rock Minerals.
2. Gilchrist, J.D. (1989). "Extraction Metallurgy"
3. Metrohm IC AW AU6-0483-052013

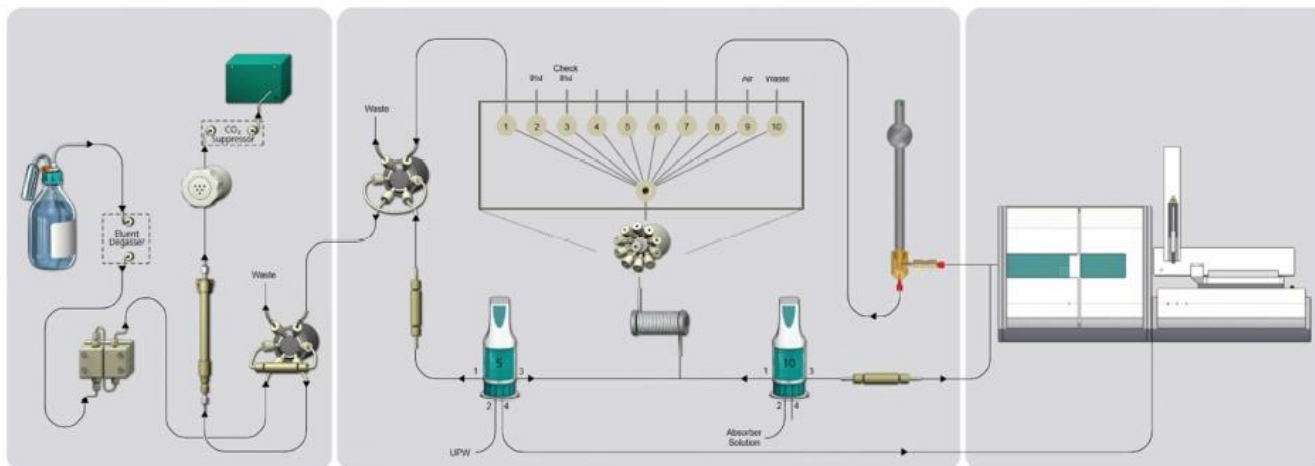
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## Appendix 1

### Instrumentation setup, calibration curves, chromatograms.

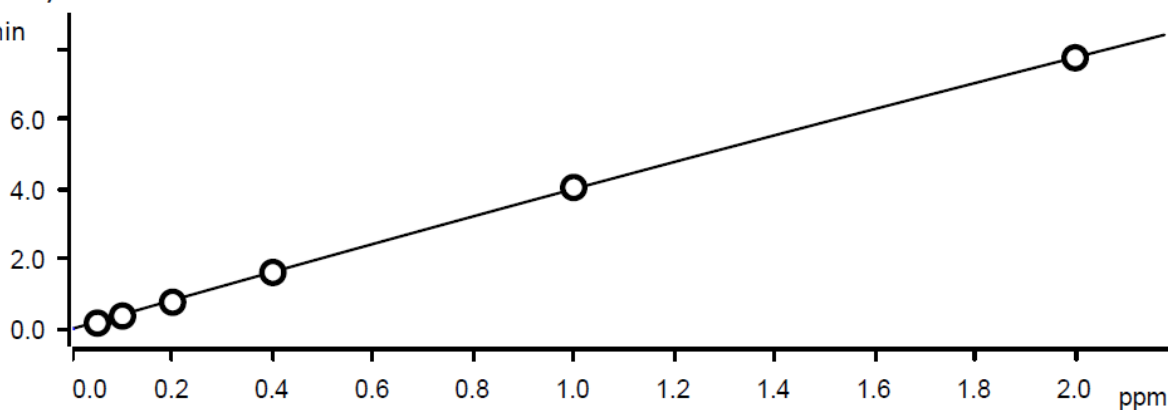
#### Instrumentation setup



**Calibration**

**Fluoride (Anions)**

( $\mu\text{S}/\text{cm}$ ) x min



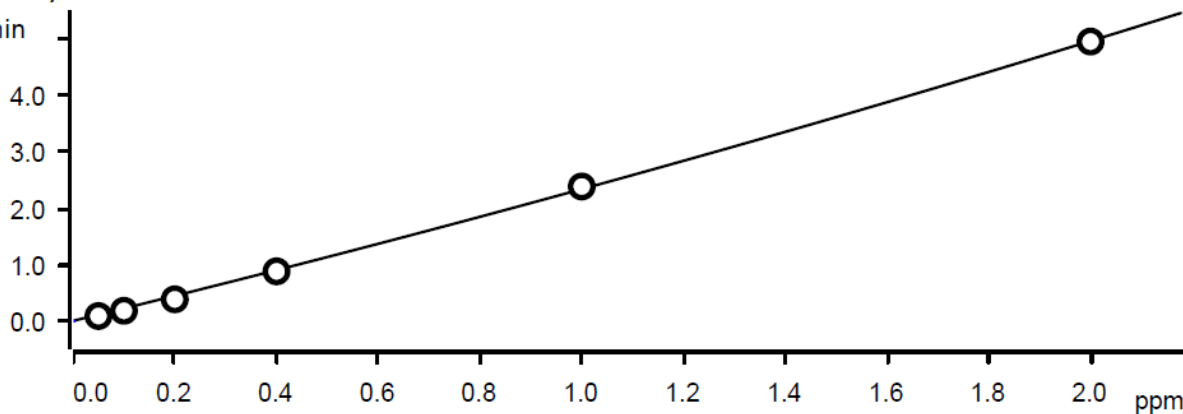
Function: .....  $A = 0.0205538 \times Q - 2.91874E-6 \times Q^2$

Relative standard deviation ..... 2.019499 %

Correlation coefficient ..... 0.999888

**Chloride (Anions)**

( $\mu\text{S}/\text{cm}$ ) x min

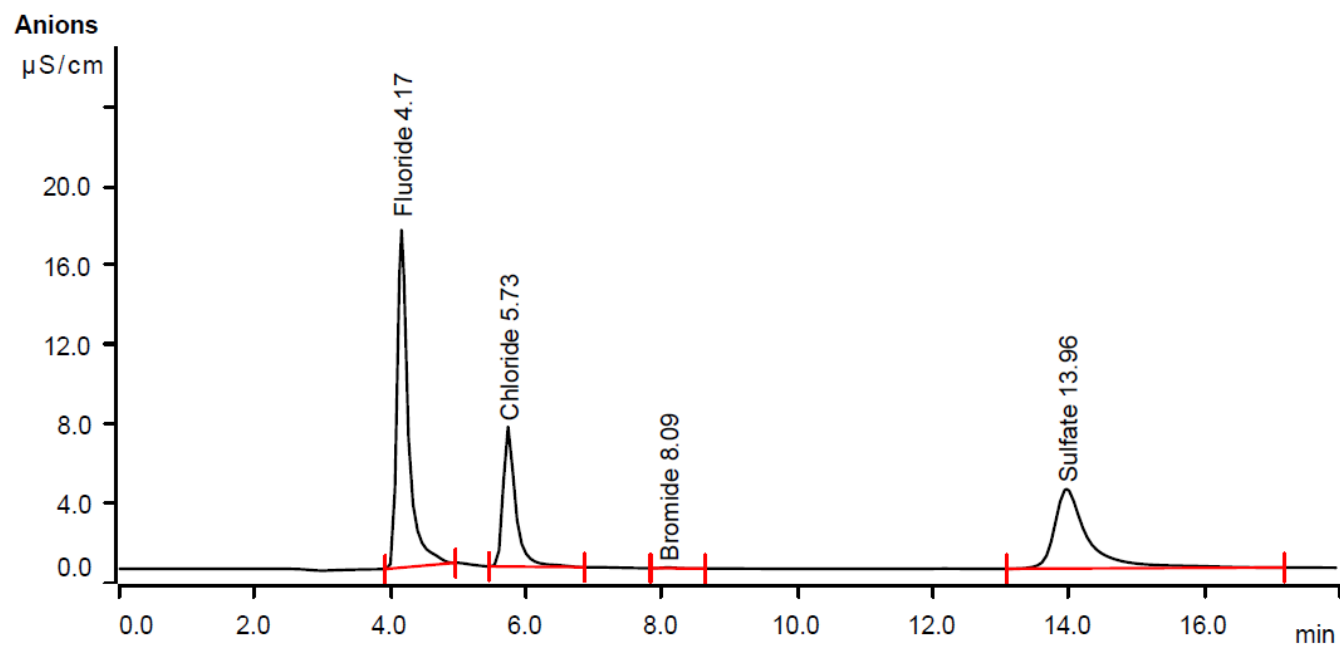


Function: .....  $A = 0.0109678 \times Q + 3.63648E-6 \times Q^2$

Relative standard deviation ..... 3.235694 %

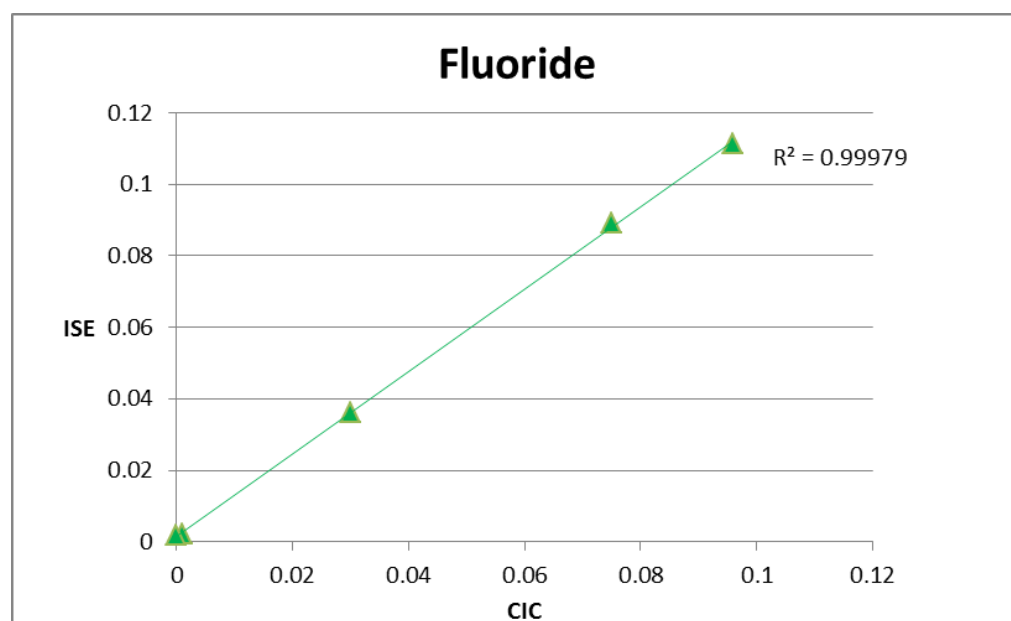
Correlation coefficient ..... 0.999748

## Sample chromatogram STD 3



## Appendix 2: Result comparison between CIC and ISE for Fluorine and CIC and XRF for Chlorine.

Fluoride				
Std	ISE	CIC 1	CIC 2	CIC AV
1	0.001	0.00212	0.0022	0.00216
2	0	0.0018	0.0019	0.00185
3	0.075	0.0898	0.0882	0.089
4	0.03	0.0378	0.0347	0.03625
5	0.096	0.1098	0.1129	0.11135



Chloride				
Std	XRF	CIC 1	CIC 2	AV
1	0.07	0.0732	0.0738	0.0751
2	0.02	0.0256	0.0204	0.023
3	0.08	0.0754	0.0757	0.07555
4	0.27	0.2671	0.2644	0.26575
5	0.96	1.0391	1.0238	1.03145

