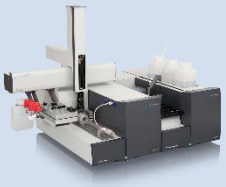
Accurate Determination of Fluoride, Chloride, and Sulfur at Trace Level (<100 ppb) by Combustion-IC

Combustion Ion Chromatography enables the determination of speciated halides and sulfur compounds by a single analysis. TE Instruments developed a fully automated, extremely compact sample preparation system covering the pyrohydrolytic combustion, fraction collection, and sample injection towards any IC. The XPREP C-IC is the only configuration capable of introducing liquid samples both via optimized direct injection module and conventional boat-inlet system into a horizontal furnace. Sample introduction by direct injection improves the analytical results for trace level applications such as aromatic hydrocarbons and ultrapure chemicals. A larger sample volume (100 µL) can be introduced into the direct injection module compared with boat-inlet systems. Controlled sample evaporation at 1 µL/s eliminates the need for a boat program and decreases the time of sample combustion dramatically. Multiple sample combustions can be collected in the same absorption tube, which increases the concentration of analytes in the absorbance medium. The analytical results at trace level are significantly improved by adjusting the number of sample combustions, volume of absorbance liquid, size of the IC sample loop, and use of a pre-concentrator.

Solution

XPREP C-IC

ARCHIE
Liquid Autosampler



XPREP C-IC
Combustion Tube

Sample Information	
Sample Type	Xylene – Spiked Solvent
Component	Fluoride, Chloride, Bromide, Sulfur
Concentration	0 – 100 µg/L
Methods Applicable	-

Table 1 - Sample Information

Summary

The XPREP C-IC sample preparation system was connected to a high-end IC to generate a fully automated C-IC configuration. Calibration standards made from Fluorobenzene (F), Chlorobenzene (Cl), Bromobenzene (Br), and Dibenzothiophene (S) in Xylene were analyzed, covering a range of 25 – 100 mass/volume ppb for each element. Excellent calibration line fits (>0.995 r^2) were created by optimizing the number of sample combustions. The table below demonstrates the high precision of analyzed results at trace level (<100 ppb), which is well below the scope of international test methods currently available such as the ASTM D7359 and UOP 991. The direct injection module allows faster and more controlled combustion of larger sample volumes in comparison with boat-inlet systems. More ions will be trapped in the absorbance medium, creating a higher concentration of analytes, which provides the best possible results for analyzing liquid samples with Combustion-IC at trace level.

Results

Standard (n=3)	F (µg/L)	RSD (%)	Cl (µg/L)	RSD (%)
25 ppb	24	9.62	27	8.52
50 ppb	50	3.11	54	6.41
75 ppb	78	2.17	83	3.79
100 ppb	101	0.84	105	0.96

Table 2 – Results of Spiked Solvent

Standard (n=3)	Br (µg/L)	RSD (%)	S (µg/L)	RSD (%)
25 ppb	25	0.67	29	10.55
50 ppb	50	0.93	53	10.24
75 ppb	75	1.52	76	2.55
100 ppb	100	0.70	92	3.86

Table 3 – Results of Spiked Solvent

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Trace Elemental Instruments

System Description

Introduction - The ARCHIE liquid autosampler introduces samples at a controlled rate into the heated liquids module (500 °C). The liquids module is specifically designed for the direct injection of liquid samples with a final boiling point up to 420 °C, which corresponds with the boiling range of matrices listed in the ASTM D7359 and UOP 991.

Combustion - The Combustion Unit is fitted with a dual-zone furnace. Every sample is completely oxidized by pyrohydrolitic combustion in an oxygen-rich environment at high temperature. The specially developed pyrohydrolitic combustion tube includes a single-stage capturing and collision flow technique. The single stage capturing filter protects the downstream flow path against soot deposition. The capturing filter is "self-cleaning", as it continuously regenerates itself by the high temperatures and presence of oxygen flow. The collision flow technique provides maximum oxidation power for samples that are difficult to oxidize.

Collection – After combustion, absorber solution is added automatically to the output gas stream to guarantee a complete absorption of the analytes in the Fraction Collection Unit. In this process the H-X, X_2 and SO_x are converted to F^-, Cl^-, Br^-, and SO_4^{2-}. These negatively charged ions will be separated in the IC column. Up to 65 combusted samples can be absorbed and stored in the individual absorption vials. The combusted and collected samples can be transferred to the IC immediately or stored for later analysis. Re-run of combusted samples is possible at any time if desired.

IC-Injection – Once sample preparation has been finalized, the absorbent containing the analytes is automatically transferred from the fraction collection unit towards any renowned IC. The internal syringe pumps of the collection unit load and rinse the IC sample loop. A six-way-valve and 100 µL sample loop are by default integrated at the front of the fraction collection unit. For this particular application, a 500 µL sample loop was utilized. This sample loop may be used to fill the pre-concentrator when present in the IC.

System Settings

Parameter	Setting
Oxygen flow	300 mL/min
Argon flow	100 mL/min
Oxygen collision flow	100 mL/min
Furnace temperature I	1000 °C
Furnace temperature II	1000 °C
Introduction module	Direct Injection Module
Absorption solution	100 mg/L Hydrogen Peroxide in Ultrapure Water
Absorption vials	23 mL PP vials
Initial volume absorption solution	3 mL
Sample volume combustion	500 µL (five sample combustions of 100 µL)
Rinsing volume absorption solution after combustion	2 mL
Total volume absorption solution before IC injection	8 mL
Sample loop IC	500 µL

Table 4 - System Settings for Trace Level C-IC Analysis

Calibration

Calibration standards were made from Fluorobenzene (F), Chlorobenzene (Cl), Bromobenzene (Br) and Dibenzothiophene (S) in Xylene. Each calibration standard was analyzed three times. All calibration curves have a correlation coefficient (r^2) better than 0.995.

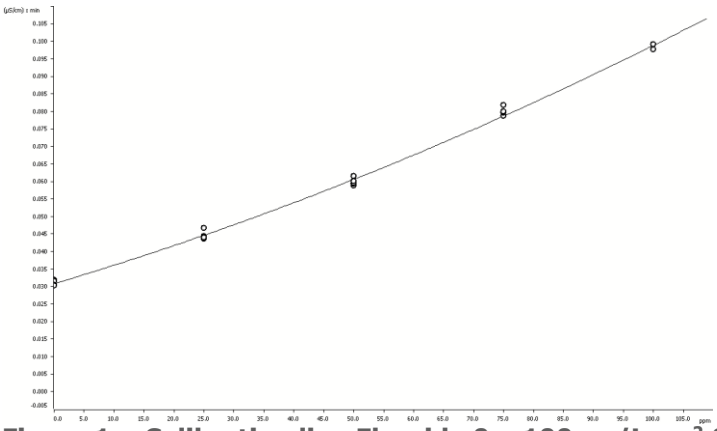

Figure 1 – Calibration line Fluoride 0 – 100 µg/L - r^2 0.9996

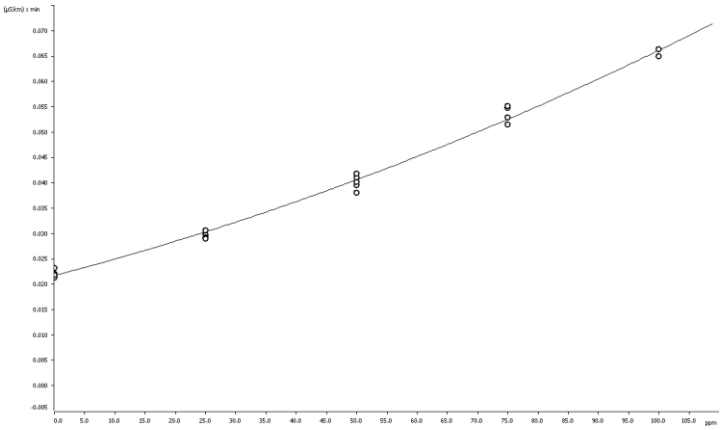

Figure 2 – Calibration line Chloride 0 – 100 µg/L - r^2 0.999

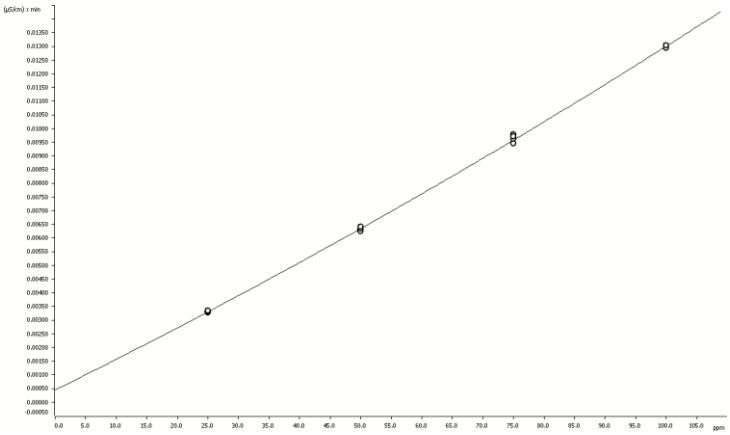

Figure 3 – Calibration line Bromide 0 – 100 µg/L - r^2 0.9999

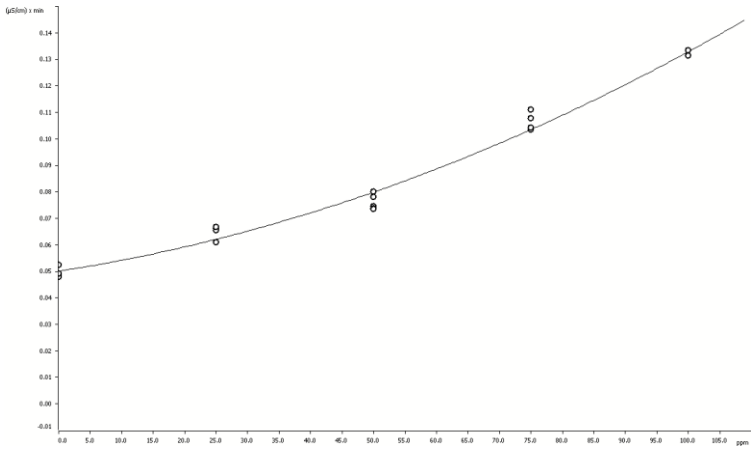

Figure 4 – Calibration line Sulfur 0 – 100 µg/L - r^2 0.996

Example Peaks

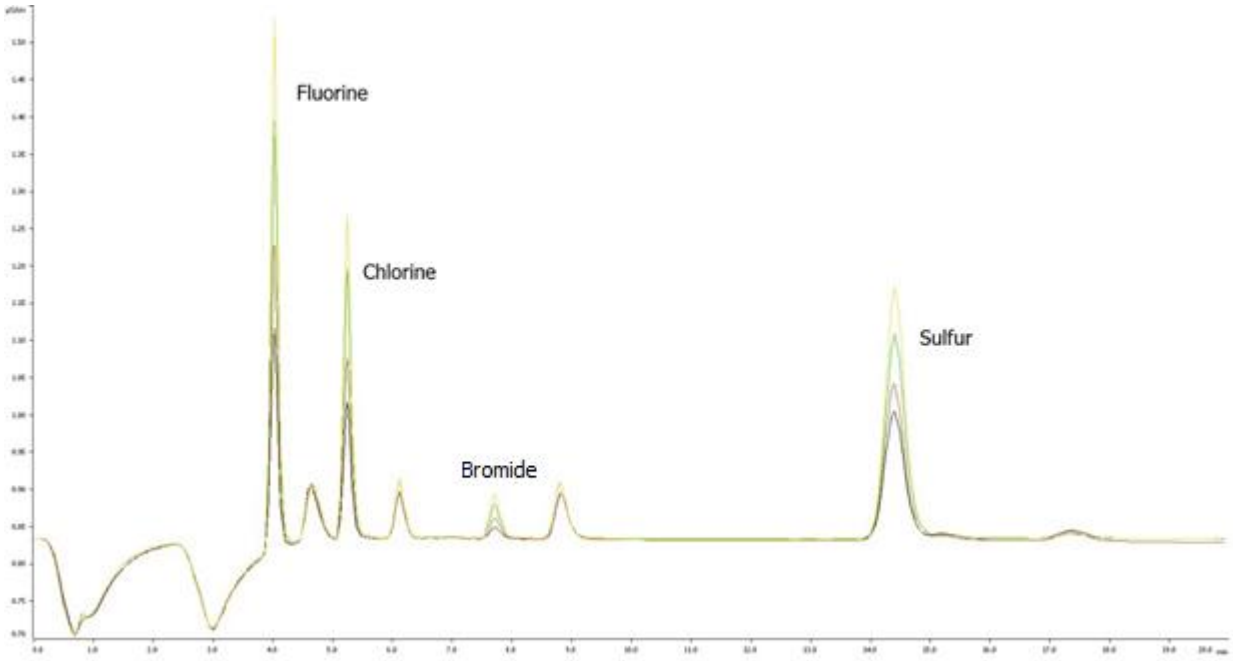

Figure 5 – Peak Overlay Calibration Standards 25 – 100 µg/L