Combustion Ion Chromatography - Enhancing Halogen Detection Using Preconcentration Methods

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Overview

Purpose: Demonstrate the method sensitivity of adding sample preconcentration to Combustion Ion Chromatography.

Methods: Samples were combusted in a Mitsubishi AQF-2100H furnace equipped with a GA210 sparging unit. One mL samples were transferred to an anion concentrator column mounted on the injection valve of a Thermo Scientific™ Dionex™ ICS-2100 Integrated Reagent-Free™ Ion Chromatography (RFIC™) system. The anion analysis was performed using a Thermo Scientific™ Dionex™ IonPac™ AS15 column.

Results: Limit of detection for the anions determined by combustion ion chromatography (IC) was shown to be as low as approximately 10 ppb, with limits of quantitation being approximately 25 ppb. Outstanding retention time stability (0.08% RSD for chloride) was also demonstrated.

Introduction

Combustion can be used to oxidize a sample so that the combustion products can be analyzed and the sample composition determined. Combustion of organic samples for CHN analysis is a technique with a long and rich history.[1,2] Combustion may also be used to prepare samples for halogen and sulfur content analysis. Under high temperature oxidizing conditions, the halogens are converted to volatile HX and X_2 and the sulfur to SO_x. These volatile products are trapped in an aqueous solution which can subsequently be analyzed by ion chromatography to give the concentrations of the individual halides. The sulfur species are further oxidized in solution and sulfate is determined by IC.

Combustion of samples for halogen and sulfur content has been practiced for years, using techniques such as oxygen bombs (Parr, etc), Schöniger flasks and the Wickbold apparatus. In some cases such as oxygen bombs the heat is derived internally, via chemical reaction. In open tube methods such as the Wickbold apparatus, heat is applied externally. Recently microwave ovens have been used to heat the sample. All of these methods require the manual transfer of the sample into a reaction vessel and, after combustion, from the vessel to the ion chromatograph. In many cases they require extensive methods development to optimize the combustion conditions. In addition the closed vessel approaches are inherently labor intensive, slow and require skilled operators to perform them.

Automation of the combustion process is now available using apparatus from several manufacturers, including Mitsubishi Analytech, Inc. The AQF-2100 from Mitsubishi is comprised of an autosampler designed to handle the particular physical form of the sample, the combustion furnace and controller, and the absorption unit which includes a sample injection valve. Gases, liquids and solid samples can all be managed with the appropriate autosampler. Solids and semi-solid samples are placed in a quartz sample boat and pushed into the hot quartz tube furnace. Figure 1 shows a schematic of the combustion apparatus.

Combustion ion chromatography is an inherently dilutive technique, with a relatively small amount of sample gases being trapped in a relatively larger volume of water, resulting in low analyte concentrations in the injection sample. In addition, sulfate analysis requires the addition of hydrogen peroxide to the sparger water, to oxidize to sulfate the various sulfur species produced. The peroxide will sometimes interfere with the fluoride peak in the ion chromatograms.

There are several potential solutions to these problems. Initial sample size can be increased but is limited by the combustion capability of the system to about 100 mg; sometimes as much as 500 mg can be used. Volumes injected into the IC can be increased, but these too have practical limits and applications limitations. For instance unusually large sample volumes can cause problems for fluoride quantitation due to the increased size of the adjacent water dip. The solution studied in this work is to adapt sample preconcentration methodology for ion chromatography to this application.

FIGURE 1. Diagram of a combustion ion chromatography system.
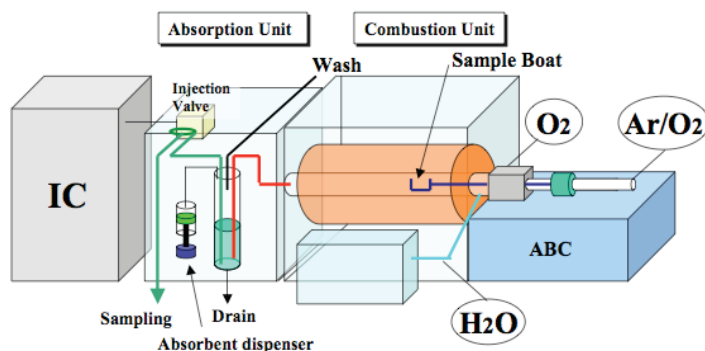
Methods

Equipment:

Combustion apparatus: Mitsubishi Chemical Analytech AQF-2100H including ASC-250L liquid sample changer, ABC-210 automatic boat controller, HF-210 horizontal furnace and GA-210 sample absorption unit with 1 mL sample loop. Combustion samples: 90 µL xylene solutions.

Ion Chromatograph: Dionex ICS-2100 IC system

Column: Dionex IonPac AG15 and AS15 column set, 4 x 250 mm
Column Temperature: 30 °C
Eluent: 33.5 mM KOH, from Thermo Scientific Dionex EGC-KOH Eluent Generator Cartridge
Flow Rate: 1.2 mL/min
Concentrator Column: UTAC-XLP1
Sample transfer: Thermo Scientific Dionex AXP Auxiliary Pump with a Dionex ATC-HC Anion Trap Column, 1 mL/min
Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor, 4 mm, 100 mA current, recycle mode, detector temperature 35 °C

Samples were combusted using standard methods and the resulting volatile components absorbed into 3 mL of deionized (DI) water with hydrogen peroxide. The sparger fluid was loaded into a 1 mL sample loop on the GA-210 valve using the fluidics on board the GA-210. Loop contents were transferred to the concentrator column using an AXP pump. See Figure 3 for a plumbing schematic.

FIGURE 2. Combustion ion chromatograph.

FIGURE 3. Schematic, principal fluidics pathways.
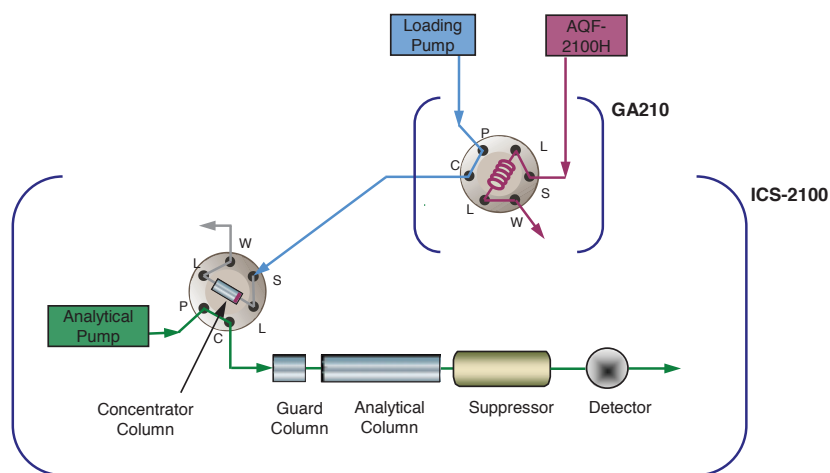
Results

Blank runs of sample solvent were compared to those obtained by running the sample combustion with an empty sample boat. Low background levels of fluoride, chloride and sulfate were detected, with no appreciable difference between the empty boat and solvent. This demonstrates that the background is potentially due to low level contamination of the sparger water, transfer water or plumbing.

FIGURE 4. Blank injections, solvent blank (blue trace) compared to an empty sample boat.
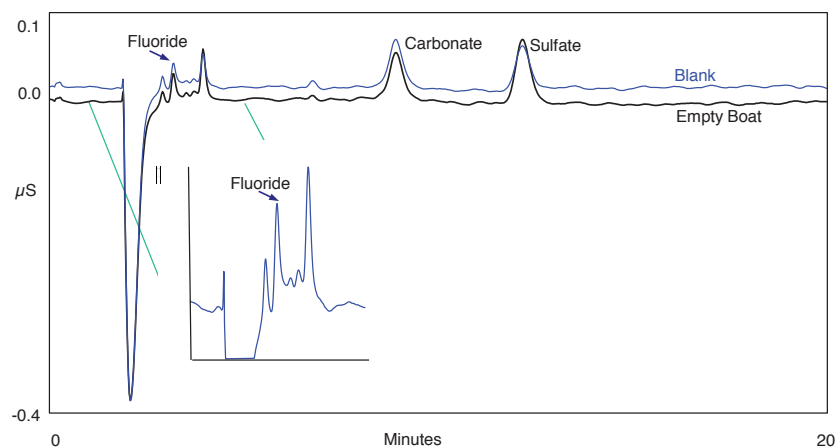
Note the early elution section of the blank chromatograms in Figure 4, in the expanded section above. The combined performance of the column and chromatograph provide for excellent separation between the fluoride and the water dip, as well as the peak, probably peroxide, which precedes fluoride. In addition, the fluoride is well resolved from the trailing peaks, likely to be acetate and formate which are frequently observed in combustion IC. The result of this high resolution is to afford quantitative results for fluoride which are less than 1% RSD for repeat sample injections. The highly reproducible chromatography along with the high resolution as provides confidence in assigning the identity of fluoride to an individual peak.

Standards were prepared in xylene, combusted before absorption and absorbed into aqueous hydrogen peroxide. One mL aliquots were passed through a concentrator column and analyzed on the ion chromatograph. Figure 5 demonstrates the 5-fold improvement in signal size resulting from the sample preconcentration.

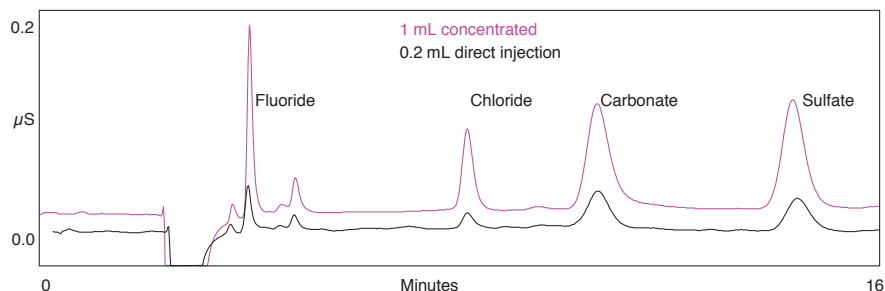**FIGURE 5. Overlaid 10 ppb standards: 0.2 mL direct injection vs. 1 mL concentrated.**

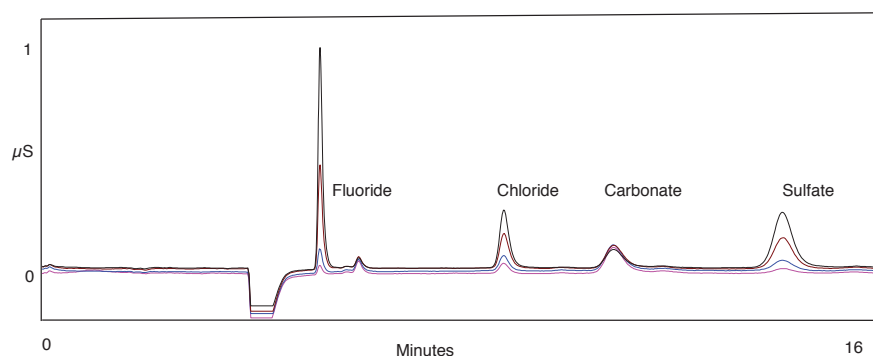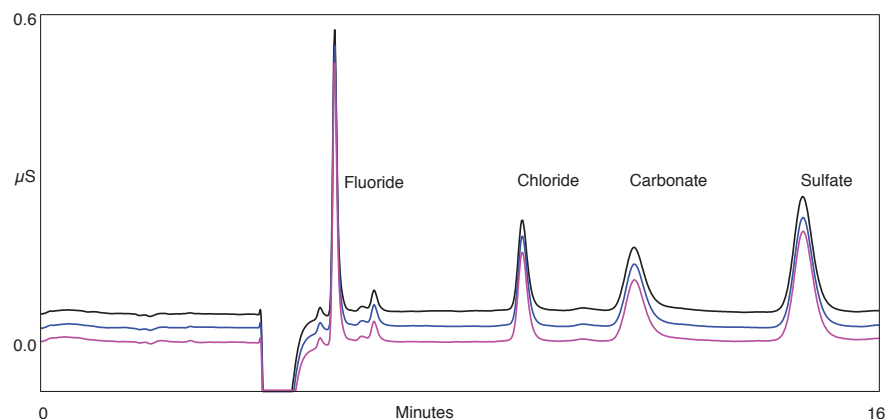**FIGURE 6. Overlaid standards: 0, 10, 50, 100 µg/L.**

FIGURE 7. Overlaid repeat injections of the same sample.

The excellent run to run reproducibility of 0.08% RSD for the method is shown in Figure 7 where consecutive, repeat injections of a low concentration sample (approximately 50 ppb) are compared. Table 1 shows the improvement in the quantitation for fluoride afforded by the increased sample size from sample preconcentration. The table compares the reproducibility of area and height measurements for direct injection and pre-concentrated samples. Since sample volumes have been increased by a factor of five, peak areas and heights are proportionally increased. This provides for improved reliability of peak integration and signal to noise, both of which reduce the variability of the quantitation.

Table 1. Area and height reproducibility for fluoride; direct injection compared to sample preconcentration

	Direct Injection, 0.2 mL		Preconcentration, 1 mL	
	Area (μS*min)	Height (μS)	Area (μS*min)	Height (μS)
Run 1	0.01612	0.1366	0.06049	0.5733
Run 2	0.01533	0.1335	0.06034	0.5711
Run 3	0.01666	0.1369	0.06034	0.5720
Standard Deviation	0.00072	0.0000	0.00011	0.0000
% Relative Standard Deviation	**4.19%**	**1.38%**	**0.15%**	**0.20%**

Conclusion

- Combustion ion chromatography automates the analysis of halogens and sulfate in difficult to process samples.

- The combination of the high performance Dionex IonPac AS15 column and the Dionex ICS-2100 IC system provides superior resolution and reproducibility- as low as 0.08% RSD.

- Sample preconcentration provides significant improvements in quantitation of low concentration samples.

- Future work may evaluate smaller sample trapping volumes, approaches to ultra-high purity transfer solutions, increased sample concentration volumes and faster ion chromatography methods.

References

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2. Strouts, C.R.N; Gilfillan, J.H.; Wilson, H.N. Chapter 14. *Analytical Chemistry;* Vol 1; Oxford University Press, 1955.

Acknowledgements

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