Challenge

A simple method to determine F in geological samples

Solution

Direct determination of F in solids using solid sampling technique and HR-CS MAS

Determination of Fluorine in Geological Samples on the contrAA® 800 G Continuum-Source AAS

Introduction

Fluorine is a common element in the earth's crust formed in minerals and rocks as fluorides. The abundance of fluorine in the crust averages about 650 ppm (parts per million) and is commonly found in basalts, gabbros, andesites, granodiorites, rhyolites and granites. Marine phosphorites contain significantly higher concentrations of fluorine, averaging more than 30,000 ppm.

Fluorine mineral deposits occur in a wide variety of geological environments and in a multitude of forms associated with or enclosed within volcanic rocks, intrusive igneous rocks, metamorphic rocks or sedimentary rocks. Fluorite (CaF_2), the most common and abundant fluorine mineral occurs as vein fillings in rocks that have been subjected to hydrothermal activity and these veins often contain metallic ores which can include sulfides of tin, silver, lead, zinc, copper, and other metals. Fluorite is also found in the fractures and vugs of some limestones and dolomites. Fluorite can be massive, granular or euhedral as octahedral or cubic crystals. Fluorite is a common mineral in hydrothermal and carbonate rocks worldwide.

Fluorite (CaF_2), also known as fluorspar in industry, also has important uses in metallurgy including steel production, in the manufacture of ceramics and for the production of hydrofluoric acid as a precursor for other manufactured products. Optical grade fluorite with exceptional clarity is used for lenses in optical system, while specimens with exceptional color are cut into gemstones and ornaments.

In this study, the fluorine content in rock samples was determined by graphite furnace AAS using the contrAA® 800 G High-Resolution Continuum Source Atomic Absorption Spectrometer with solid sampler for direct analysis of finely ground samples.

Instrumentation

The contrAA® 800 G graphite furnace AAS with SSA 600L direct-solid autosampler equipped with a liquid dosing unit was used to analyze a range of geological reference materials for the determination of fluorine. The finely ground samples were analyzed as received requiring no additional sample preparation. Fluorine was determined by measuring molecular absorption bands of gallium monofluoride (GaF) in which fluorine is converted stoichiometrically when mixed with a gallium solution.

The SSA 600L autosampler can perform a fully automated analysis of up to 84 solid samples including the weighing of samples, the addition of modifiers and reagents and transport to the graphite furnace. The samples were manually dosed onto graphite sample carriers (typically between 0.05 and 0.5 mg) and automatically weighed using the integrated microbalance. Samples were weighed to a precision of 1 µg and process modifiers and molecule forming reagents added via the liquid dosing unit, including 8 µL of aqueous gallium standard (1000 mg/L). Graphite sample carriers were also conditioned with zirconium standard solution (1 g/L) and calcium standard solution (2 mg/L) prior to analysis. Solutions Pd/Mg/Zr (0.1 %/0.05 %/20 ppm) and sodium acetate (NaAc 10 g/L) were used as modifiers to stabilize fluoride during the drying process.

Method Parameters

Two furnace methods were developed to cover the expected fluorine concentration range of the samples using a combination of two GaF molecular absorption lines. Table 1 below shows the wavelengths selected and their respective concentration ranges. A multi-point calibration for lower fluorine concentrations, using the more sensitive 212.181 nm absorption line, was created from United States Geological Survey AGV-2 (Andesite) reference material. Accordingly, GPS-1 (Grandiorite) reference material was used with the less sensitive 209.419 nm absorption line to determine higher concentrations of fluorine. Multi-point calibrations for each wavelength were generated from single reference standards by varying the weight of material, and therefore, the absolute mass of fluorine.

Table 1: Wavelength, reference material and calibration range used to generate calibration curves

Wavelength (nm)	USGS Reference Material	Certified Value [mg/kg]	Conc. Range [mg/kg]
GaF 212.181	AGV-2	440	50 - 500
GaF 209.419	GSP-1	3630	500 - 5000

Graphite Furnace Temperature-Time Program

Table 2 and Figure 1 show the temperature program and profile for GaF 212.181 nm. A similar program was used for GaF 209.419 nm, although with a slightly higher atomization temperature.

Table 2: Temperature-Time program for GaF 212.181 nm

Wavelength (nm)	T_{Pyr} [°C]	T_{Atom} [°C]	Ramp [°C/s]
GaF 212.181	250	1750	1400
GaF 209.419	250	1850	1400

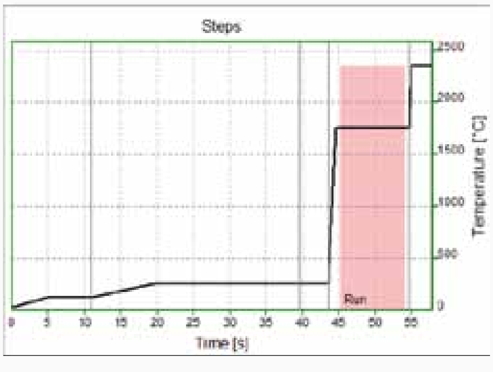

Figure 1: Temperature-Time profile for GaF 212.181nm

Evaluation Parameters

The evaluation parameters including the number of pixels used for peak integration, measurement time, the width of the spectral window for observation and the background correction technique used are displayed in table 3. Iterative Background Correction was selected to minimize the influence of other molecular structures within the spectral observation window.

Table 3: Measurement and spectral evaluation parameters

Wavelength (nm)	Eval. pixel	Measurement Time	Spectral Observation Width		Background Correction
		[s]	[nm]	[pixel]	
GaF 212.181	3	9.0	0.23	200	IBC-m
GaF 209.419	4	5.0	0.25	200	IBC-m

Results and Discussion

The results of seven geological samples, including five certified reference materials are reported in tables 4 and 5 below. Basalt and two Andesite samples containing fluorine in the range of approximately 200 - 400 mg/kg were measured using the 212.181 nm molecular absorption line. Higher concentrations of fluorine ranging from approximately 800 – 4400 mg/kg were measured in a Rhyolite, Granite and two unknown samples using the less sensitive 209.419 nm absorption line.
Each analysis was performed in triplicate and the average results are reported as well as the variability of the measurements. The measured concentrations compared well with the certified values for the known reference materials, validating the accuracy of the method.

Table 4: Results for fluorine in Basalt and Andesite reference materials using GaF 212.181 nm

Calibrated on AGV-2 (Andesite) - 440 mg/kg	Measured Concentration [mg/kg]	Certified Concentration [mg/kg]
BHVO-1 (Basalt)	421 ± 25	385 ± 31
JA-2 (Japanese Andesite)	245 ± 24	223 (200-485)
JA-3 (Japanese Andesite)	266 ± 24	286 (SD=45)

Table 5: Results for fluorine in Rhyolite and Granite reference materials using GaF 209.419 nm

Calibrated on GSP-1 (Grandiorite) - 3630 mg/kg	Measured Concentration [mg/kg]	Certified Concentration [mg/kg]
JR-1 (Japanese Rhyolite)	860 ± 99	991 (SD=112)
PYR-1A	1170 ± 98	NA
NIG-1A	2720 ± 92	NA
NIM-G (Granite)	4300 ± 91	4200

Calibration

Figures 2 and 3 display the multi-point calibration graphs generated for the two molecular absorption lines of GaF.
Figure 2 shows the calibration graph generated for the GaF 212.181 nm molecular absorption line using USGS AGV-2 Andesite reference standard using different sample weights.
Figure 3 shows the calibration graph generated for the GaF 209.419 nm molecular absorption line using USGS GSP-1 Grandiorite reference standard using different sample weights.

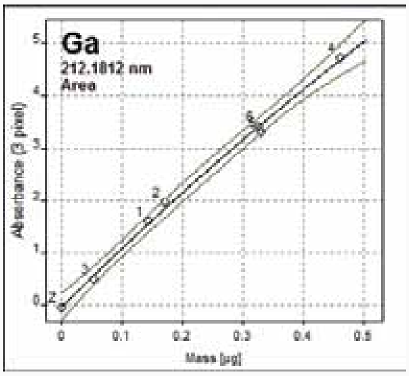

Figure 2: Solid calibration with AGV-2 (440 mg/kg)
R^2= 0.994
Calibration function: nonlinear rational

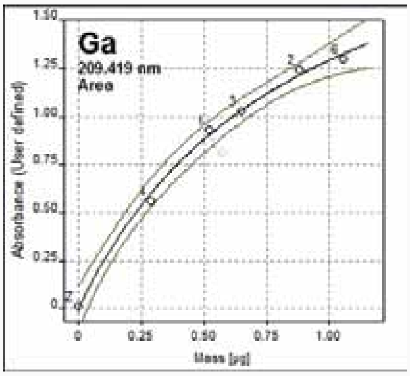

Figure 3: Solid calibration with GSP-1 (3630 mg/kg)
R^2= 0.992
Calibration function: nonlinear rational

Signal Profile and Spectral Region

Fine-structured, molecule absorption spectra of gallium mono-fluoride were observed at wavelengths 212.181 nm and 209.419 nm as shown in figures 4 and 5 below. Figure 4 below shows the signal profile and spectral region for the GaF 212.180 nm molecular absorption line when measuring the AGV-2 Andesite calibration standard. Figure 5 shows the signal profile and spectral region for the GaF 209.419 nm molecular absorption line when measuring the GSP-1 Grandiorite calibration standard.

The contrAA® ASpect CS software provides comprehensive display and editing of the data, including both 2D and 3D views of the spectral region during atomization.

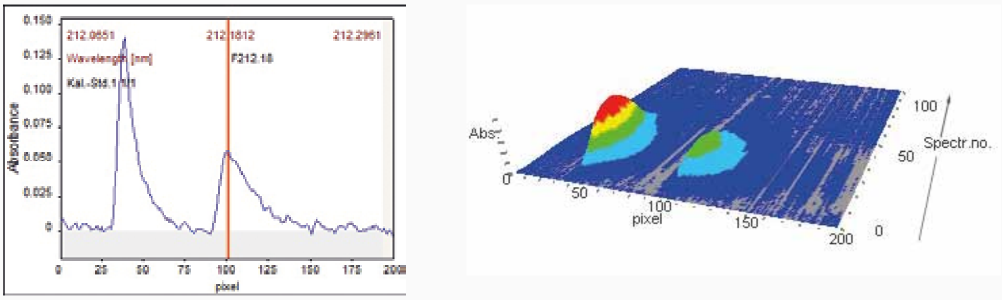

Figure 4: Signal profile and spectral region for GaF 212.180 nm (sample AGV-2)

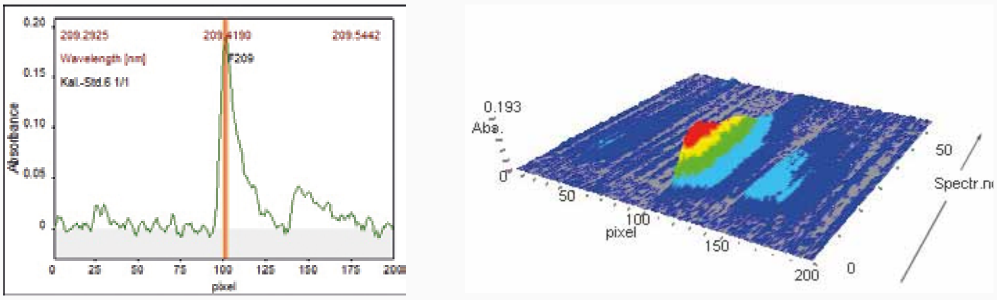

Figure 5: Signal profile and spectral region for GaF 209.419 nm (sample GSP-1)

Correction of Spectral Interferences – CSI

On rare occasions where background structure from matrix elements overlap with the desired analyte wavelength, they are easily removed using the CSI software tool provided with the ASpect CS software. While these interferences can potentially occur on the contrAA®, just like on any AAS, continuum-source AAS is unique in that spectral information is visible to the user and easy to identify. Hence, making it simple to remove interferences using correction spectra of the interfering substances as shown in figure 6 below for the 212.181 nm line.

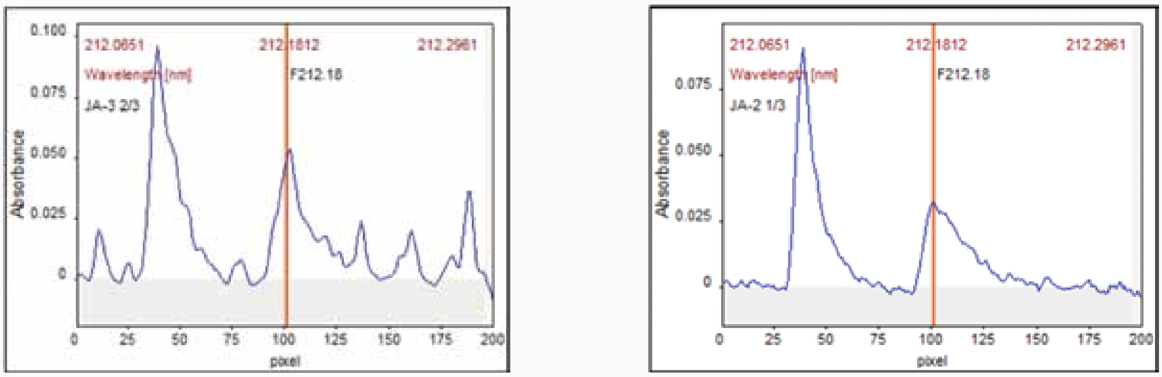

Figure 6: Signal profile for GaF 212.181 nm with and without Spectral Correction

Conclusion

The contrAA® 800 G with continuum source Xenon lamp and high-resolution optical design offers the unique capability of determining non-metals such as fluorine in geological samples. The direct-solid autosampler also eliminates the need for sample digestion and accurately weighs the sample prior to loading into the graphite furnace.

The contrAA® 800 G has also demonstrated successful determination of other halogens including chlorine and bromine in foods, waters and pharmaceutical samples 1-3.

References

1. Ozbek, Nil; Akman, Suleyman; *Determination of Fluorine in Milk and Water via Molecular Absorption of Barium Monofluoride by High-Resolution Continuum Source Atomic Spectrometer*; Microchemical Journal, **2014**, 117, pages 111-115

2 Ozbek, Nil; Akman, Suleyman; *Determination of Chlorine in Milk via Molecular Absorption of SrCl using High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry*; J. Agric. Food Chem., **2016**, 64 (28), pages 5767-5772

3. Gunduz, Sema; Akman, Suleyman; *Determination of bromine by high resolution molecular absorption of strontium mono bromide generated in a graphite furnace*; Microchemical Journal, **2014**, 116, pages 1-6

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