thermo scientific

APPLICATION NOTE 42187

Elemental Analysis: Low sulfur determination in geological and agronomy samples by FPD Detector

Authors

Dr. Liliana Krotz and
Dr. Guido Giazzi
Thermo Fisher Scientific,
Milan, Italy

Keywords

Agronomy, Cellulose, Elemental Analysis, Geology, Rocks, Sands, Soils, Trace Sulfur Analysis, Wood

Goal

This application note demonstrates the characterization of a wide range of matrices whilst analyzing geological material, using the Thermo Scientific Flash*Smart* EA coupled with FPD Detector.

Introduction

Chemical composition of geological samples is closely connected with the origin of earth matter and often serves as an indicator of geological processes. Monitoring key elements at lower concentrations is routinely applied to exploration programs, geosciences research and various environmental projects. Sulfur, for example gives important information when analyzing rocks, sand and soils.

Sulfur is an essential component of living matter. The lack of sulfur has a negative influence in the growth of vegetable crops and the quality of proteins produced through the synthesis of amino acids such as cysteine, cystine and methionine and synthesis of vitamins. The levels of sulfur in living matter, such as leaves and pine needles, are also an indicator of pollution.

The importance of sulfur testing has grown in recent years, and many of the classical methods are now no longer suitable for routine analysis. Analytical systems based on the combustion of samples improve the reliability of the data available to the geologist and agronomist, and remove the need for hazardous chemicals.

ThermoFisher SCIENTIFIC

Low total sulfur content can be accurately determined by using the Thermo Scientific™ Flash*Smart* EA coupled with a Flame Photometric Detector (FPD) (Figure 1). This method combines the advantages of an elemental analyzer with the sensitivity, selectivity and robustness of FPD Detector. The coupling is simple and it allows the determination of total sulfur at high and low concentrations (5 – 10 ppm) using the same instrument without matrix effect.

Figure 1. Thermo Scientific Flash*Smart* Elemental Analysis coupled with Flame Photometric Detector (FPD).

Methods

The Flash*Smart* EA operates according to the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor via the Thermo Scientific™ MAS Plus Autosampler with oxygen. After combustion, the resultant gases are carried by a helium flow to a layer filled with copper, then to a trap filled with anhydrone and swept through a GC column that provides the separation of the combustion gases. Finally, they are being detected by the Flame Photometric Detector (FPD) (Figure 2). Total run time is 5 - 6 minutes. A complete report is generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software and displayed at the end of the analysis.

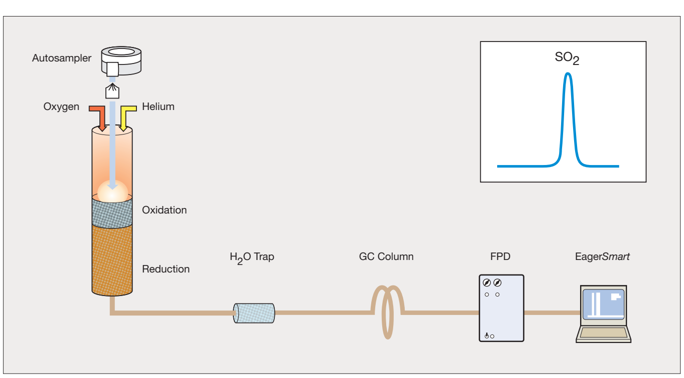

Figure 2. Sulfur configuration.

Results

Different soils, rock, sand, clay, sawdust, wood, cellulose, leaves and plants samples were chosen to show the reproducibility obtained with the system in a large range of trace sulfur content. All samples were homogenized by a ball mill.

Table 1 shows a typical sequence of analysis. Instrument calibration was performed with Montana Soil NIST Reference Material (0.0420 S%), using Quadratic Fit as calibration method (runs 3 to 6). Figure 3 shows the relative calibration curve obtained. The accuracy of the system was verified analyzing the Thermo Scientific Soil Reference Material (0.0320 S%) and Montana Soil NIST Reference Material (0.0420 S%) as unknown (run 7 to 12), as reported in Table 2.

Table 1. Typical sequence.

Run	Sample	Type	Weight (mg)
1	Montana Soil Ref. Mat. (NIST)	Bypass	
2	Montana Soil Ref. Mat. (NIST)	Bypass	
3	Montana Soil Ref. Mat. (NIST)	Standard	2.201
4	Montana Soil Ref. Mat. (NIST)	Standard	7.901
5	Montana Soil Ref. Mat. (NIST)	Standard	4.424
6	Montana Soil Ref. Mat. (NIST)	Standard	9.998
7	Soil Ref. Mat.. (Thermo Scientific)	Unknown	3.785
8	Soil Ref. Mat.. (Thermo Scientific)	Unknown	4.012
9	Soil Ref. Mat.. (Thermo Scientific)	Unknown	3.922
10	Montana Soil Ref. Mat. (NIST)	Unknown	4.121
11	Montana Soil Ref. Mat. (NIST)	Unknown	3.872
12	Montana Soil Ref. Mat. (NIST)	Unknown	4.256

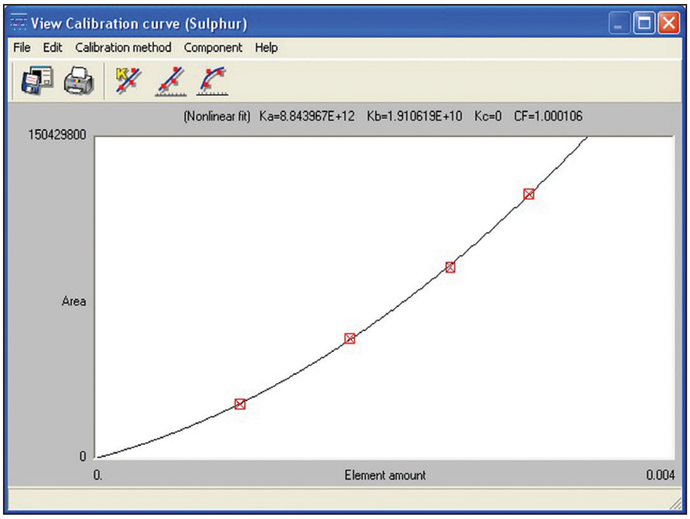

Figure 3. Typical sulfur curve calibration.

Table 2. Test of accuracy.

Sample	S%	Av. S%	RSD%
Soil 1	0.0138 0.0129 0.0129 0.0137 0.0129	0.0132	3.53
Soil 2	0.0272 0.0269 0.0264	0.0268	1.51
Soil 3	0.0661 0.0637 0.0660	0.0652	2.08
Soil 4	0.0031 0.0030 0.0027 0.0030 0.0032	0.0030	6.24
Soil 5	0.0044 0.0041 0.0042 0.0042 0.0042	0.0042	2.60

Table 3 shows sulfur data in various soil samples analyzed several times. All data were obtained with a good reproducibility.

Table 3. Reproducibility of sulfur determination in soil samples.

Sample	S%	Av. S%	RSD%
Soil 1	0.0138 0.0129 0.0129 0.0137 0.0129	0.0132	3.53
Soil 2	0.0272 0.0269 0.0264	0.0268	1.51
Soil 3	0.0661 0.0637 0.0660	0.0652	2.08
Soil 4	0.0031 0.0030 0.0027 0.0030 0.0032	0.0030	6.24
Soil 5	0.0044 0.0041 0.0042 0.0042 0.0042	0.0042	2.60

The accuracy and precision of the Flash*Smart* EA was evaluated through the analysis of soil samples coming from an International WEPAL (Wageningen Evaluating Programs for Analytical Laboratories, Wageningen University, Netherlands) Round Robin Test. The data was compared with the range accepted by WEPAL statistic studies, including all methods for sulfur determination.

Table 4 shows the comparison of the sulfur data obtained fall within the range of sulfur concentration approved by the WEPAL statistical studies. The sulfur data is the average of three analyses results by the Flash*Smart* EA.

Figure 4 shows a typical sulfur chromatogram obtained with FPD Detector.

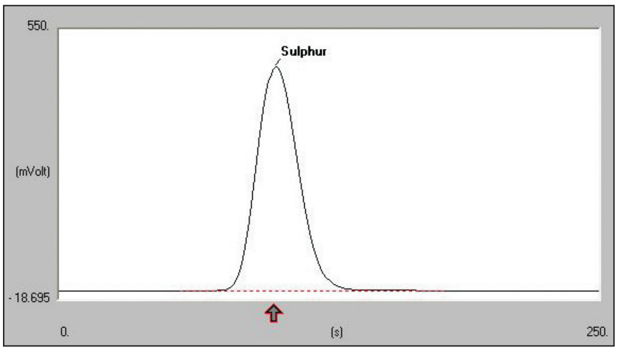

Figure 4. Typical sulfur chromatogram.

Table 4. Reproducibility of sulfur determination in WEPAL Soil samples.

Sample	WEPAL Data		Flash*Smart* EA
Name	Median S%	Range accepted S%	Average S%
Clay	0.0438	0.0398 – 0.0460	0.0456
Sandy Soil-90	0.0512	0.0449 – 0.0550	0.0549
Moist Clay	0.0100	0.0080 – 0.0120	0.0112
River Clay	0.0313	0.0285 – 0.0338	0.0310
Sandy Soil	0.0502	0.0450 – 0.0558	0.0450
Clay	0.0219	0.0161 – 0.0282	0.0222
Moist Clay	0.0125	0.0110 – 0.0159	0.0136
Clay	0.0243	0.0221 – 0.0260	0.0240
River Clay-91	0.0649	0.0600 – 0.0680	0.0660
Sandy Soil	0.0220	0.0184 – 0.0252	0.0228
Sandy Soil	0.0513	0.0468 – 0.0560	0.0500
Riverclay	0.0161	0.0141 – 0.0181	0.0181
Braunerde Pseudogley	0.0285	0.0273 – 0.0286	0.0285

Table 5 shows the trace sulfur data obtained in rock, clay, sand, sawdust, wood and cellulose samples. No memory effect was observed changing the sample matrix or the sulfur content.

Table 5. Sulfur reproducibility.

Sample	S%	Av. S%	RSD%
Rock 1	0.0174 0.0166 0.0170	0.0170	2.3529
Rock 2	0.0759 0.0750 0.0745	0.0751	9.9443
Clay	0.0059 0.0061 0.0064	0.0061	4.103
Sand 1	0.0013 0.0011 0.0011	0.0012	8.3330
Sand 2	0.0017 0.0015 0.0017	0.0016	7.0696
Sawdust	0.0277 0.0260 0.0266	0.0268	3.221
Wood	0.0036 0.0035 0.0037 0.0037 0.0034	0.0036	3.6400
Cellulose	0.0012 0.0013 0.0012	0.0012	4.681

Table 6 shows the sulfur data obtained of the analyses of leaves and plants by FPD Detector.

Conclusions

The Thermo Scientific Flash*Smart* Elemental Analyzer coupled with the FPD Detector is the ideal solution for the analysis of low and high concentration sulfur in geology and agronomy samples in terms of accuracy and reproducibility.

The sulfur data obtained for soil samples fall within in the reference of the WEPAL International Round Robin Tests, demonstrating the superior performance of the Flash*Smart* EA.

Table 6 - Sulfur determination in leaves and plants.

Sample	S%	Av. S%	RSD%
Pine needles 1	0.1156 0.1095 0.1127 0.1108 0.1107 0.1117 0.1159 0.1125 0.1084 0.1110	0.1119	2.1500
Pine needles 2	0.0331 0.0318 0.0320	0.0323	2.168
Oak Leaf	0.0991 0.0992	0.0992	0.0713
Potato	0.2515 0.2531 0.2529	0.2525	0.3453
Alfalfa (herbal medicine)	0.2989 0.3058 0.2957	0.3001	1.7198
Silage (fodder)	0.1727 0.1708 0.1701	0.1712	0.7858

Find out more at **thermofisher.com/OEA**

ThermoFisher SCIENTIFIC