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Elemental analysis: CHNS characterization of rocks by flash combustion

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Goal

To assess the performance of the elemental analyzer for CHNS determination of rocks in terms of the accuracy, precision, and repeatability.

Introduction

Elemental analysis is used for the characterization of rocks. The determination of Nitrogen and Carbon in rocks is important for the evaluation of organic matter. The differentiation of Total Carbon and Total Organic Carbon as the determination of sulfur are also useful parameters to characterize rocks.

Traditional methods are no longer suitable for routine analysis of rocks, due to their time-consuming preparation and the use of environmentally hazardous reagents. For these reasons, the use of an accurate instrumental analytical techniques is required. As the demand for improved sample throughput, reduction of operational costs and minimization of human errors is increasing notably, a simple and automated technique, which allows fast analysis with an excellent reproducibility is the key for the elemental determination of rocks.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1), based on the dynamic flash combustion of the sample, copes effortlessly with the wide array of laboratory requirements such as accuracy, day to day reproducibility and high sample throughput. The Flash*Smart* EA allows the automated elemental determination of rock samples and the same analytical conditions can be used for the differentiation between the Total Carbon and Total Organic Carbon determination after an acid pre-treatment of the sample. Through its flexibility, the Flash*Smart* EA allows also the simultaneous NCS analysis while for trace Sulfur determination, the analyzer has been coupled with the flame photometric detector (FPD). This method combines the advantages of the elemental analyzer with the sensitivity, selectivity, and robustness of the FPD Detector.

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Figure 1. Thermo Scientific™ Flash*Smart*™ Elemental Analyzer.

Methods

For CHNS abundance determination, the Flash*Smart* EA operates with 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 alongside a pulse of oxygen. After combustion, the produced gases are carried in a helium carrier gas to a layer filled with copper. The analyte then enters the GC column, which separates the produced gases before detection by a Thermal Conductivity Detector (TCD) (Figure 2). For weight percent determination a complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software and displayed at the end of the analysis. For S (single determination) or simultaneous NCS configuration, after combustion of the sample the resultant gases are carried by a helium flow to a layer filled with copper, then through a water trap, a GC column and finally, detected by the thermal conductivity detector (TCD) (Figure 3), while for trace sulfur analysis, after the water trap, the gases are carried by a helium flow through a short GC column and finally, detected by the Flame Photometric Detector (FPD), (Figure 4).

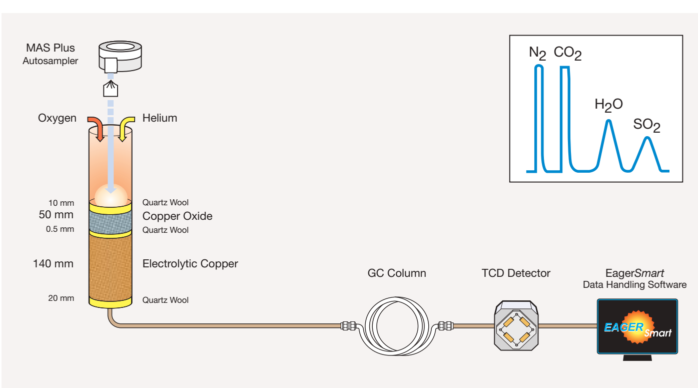

Figure 2. CHNS configuration.

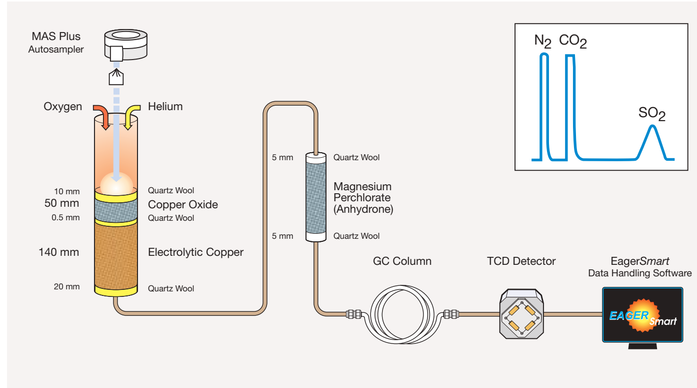

Figure 3. Single Sulfur or NCS configuration.

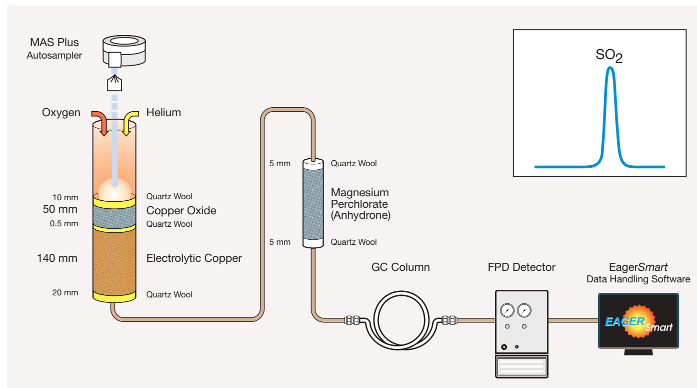

Figure 4. Sulfur configuration by FPD Detector.

The differentiation of Total Carbon (TC) and Total Organic Carbon (TOC) was performed by sample manipulation prior to analysis following the Official Italian Method on Soils Analytical Chemistry, Method 248 (Gazzetta Ufficiale).

TOC was determined after removing carbonates by acidification of the sample with HCl 1:1 (Figure 5) using the kit showed in Figure 6. The two analyses TC and TOC were performed consecutively using the same analytical conditions of the instrument.

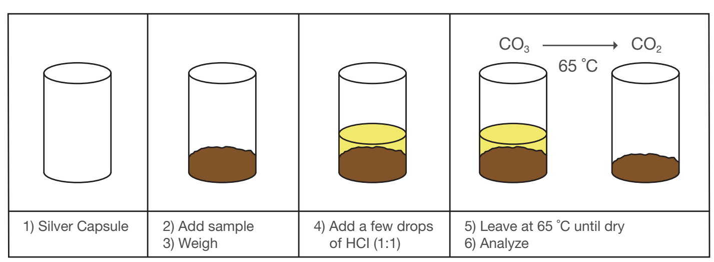

Figure 5. Method for TOC determination.

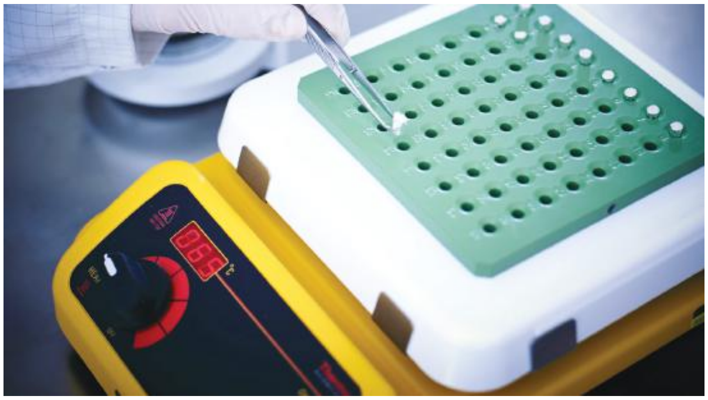

Figure 6. Kit for Total Organic Carbon (TOC) for solid samples.

Results

The analysis of 15 rock samples with different geological ages and thermal maturity, including 8 USGS* rock standards, were performed to demonstrate the performance of the Analyzer. Samples were homogenized by a ball mill.

*USGS: the United States Geological Survey is a government organization that studies the geological history of the United States and provides analytical reference materials.

For CHNS abundance determination, the calibration curve was produced by analyzing 2–3 mg BBOT and using the K factor as the calibration method. The rock samples were analyzed 10 times to evaluate the repeatability. The trace sulfur content of sample code 11 and 14 was determined using the Flash*Smart* EA coupled with the Flame Photometric Detector. Table 1 shows the sample information (the thermal maturity increases approximately with age in these samples), and the sample weight used for CHNS and TOC determination. Table 2 shows the CHNS and TOC data with the relative RSD% obtained for each sample.

Table 1. Rock sample information.

Code	Rock sample name	Geological unit origin	Age (billion of years)	Weight (mg) for CHNS	Weight (mg) for TOC
1	USGS SGR-1	Green River Shale, USA	0.05	3–4.5	3–4.5
2	USGS SDO-1	Devonian Ohio Shale, USA	0.37	7–10	8–10
3	USGS SHWFD-1	Woodford Shale,USA	0.36	7–10	8–10
4	USGS SHBOQ-1	Boquillas Shale, USA	0.07	7–8	8–10
5	USGS SCO-1	Cody Shale, USA	0.07	15–20	8–10
6	USGS SBC-1	Brush Creek Shale, USA	0.31	15–25	8–10
7	USGS BHVO-2	Hawaiiian Basalt, USA	Modern	15–25	8–10
8	USGS SDC-1	Mica Schist, USA	Unknown	95–105	8–10
9	MR21011	Mt McRae Shale, Australia	2.50	10–15	8–10
10	J18	Jeerinah Formation, Australia	2.66	10–15	8–10
11	NS1282-1	Nonesuch Shale, USA	1.10	15–25	8–10
12	SC20-1	Sheep Creek, Belt Supergroup, USA	1.45	15–20	8–10
13	SC20-51	Sheep Creek, Belt Supergroup, USA	1.45	15–25	8–10
14	MC-4	Mosquito Creek Group, Australia	2.85	15–25	8–10
15	T37	Tumbiana Formation, USA	2.72	15–25	8–10

Table 2. CHNS and TOC data of rocks.

Code	CHNS abundance and RSD%								TOC abundance and RSD%	
	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%	TOC%	RSD%
1	0.883	0.77	27.84	0.37	3.17	0.52	1.47	1.22	24.56	0.25
2	0.357	0.41	9.62	0.33	1.46	1.25	5.29	0.27	9.33	0.09
3	0.275	0.81	7.93	0.49	0.944	0.95	1.03	0.82	7.70	0.49
4	0.102	1.99	11.55	0.90	0.747	1.28	1.57	1.11	5.27	0.55
5	0.0492	1.28	1.06	1.04	0.608	1.04	0.0219	1.02	0.2831	1.15
6	0.0578	0.75	2.08	0.85	0.785	0.78	0.259	0.83	1.11	0.40
7	0.0008	6.04	0.0221	2.96	0.0246	2.75	0.0092	2.24	0.0198	1.98
8	0.0030	3.08	0.0547	1.78	0.219	1.56	0.0551	1.24	0.0331	1.85
9	0.0966	0.97	5.95	0.87	0.878	0.86	9.76	0.63	5.62	0.33
10	0.0114	1.87	3.06	0.72	0.869	0.78	2.65	0.64	2.93	0.66
11	0.0418	1.71	0.0587	1.47	0.458	1.26	0.0033	4.25	0.0562	0.98
12	0.0251	1.98	0.584	0.51	0.272	1.44	0.342	0.96	0.5485	0.35
13	0.0069	2.74	0.430	0.90	0.756	1.34	0.114	1.17	0.4000	1.02
14	0.0030	3.54	0.179	0.71	0.654	0.87	0.0039	3.35	0.1482	1.05
15	0	0	0.470	0.30	0.336	0.41	0.379	0.33	0.3768	0.88

Other four rock samples were anayzed for NCS and TOC determination. The calibration curve was performed analyzing 2–3 mg BBOT and using the K factor as the calibration method. The rock samples were homogenized by a ball mill and analyzed in triplicate to evaluate the repeatability. For NCS determination, the sample weight was 5–10 mg for samples A and B, and 15–20 mg for samples C and D, while for TOC determination the sample weight was 5–6 mg. Table 3 shows the data obtained.

Table 3. NCS and TOC determination of rocks.

Sample	N%	RSD%	C%	RSD%	S%	RSD%	TOC%	RSD%
Rock A	0.0546 0.0544 0.0543	0.28	12.2622 12.2625 12.2624	0.001	1.0097 1.0095 1.0209	0.64	1.6601 1.6543 1.6702	0.48
Rock B	0.0540 0.0552 0.0550	1.17	5.2900 5.3362 5.3191	0.44	4.1788 4.1469 4.1327	0.57	4.6462 4.6003 4.6381	0.53
Rock C	0.0062 0.0065 0.0064	2.40	0.1791 0.1733 0.1800	2.05	0.1643 0.1774 0.1690	3.89	0.1511 0.1559 0.1577	2.20
Rock D	0.0033 0.0035 0.0031	6.06	0.0997 0.0982 0.0975	1.14	0.3677 0.3684 0.3682	0.10	0.0269 0.0255 0.0260	2.68

Three silicate rock samples were analyzed using CHNS configuration. The calibration curve was performed analyzing 2–3 mg BBOT and using the K factor as the calibration method. The samples were homogenized by a ball mill and analyzed in triplicate to evaluate the repeatability, sample weight 15–20 mg. Table 4 shows the data obtained.

Table 4. CHNS data of silica rock samples.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
1	-	-	0.0491 0.0498 0.0478	1.40	0.272 0.275 0.272	0.63	0.0082 0.0079 0.0080	1.90
2	0.0024 0.0027 0.0028	7.91	0.0136 0.0128 0.0132	3.03	0.128 0.124 0.125	1.66	-	-
3	-	-	0.0643 0.0644 0.0652	0.76	0.184 0.181 0.183	0.84	-	-

Finally, a rock sample was analyzed at about 100 mg in CHNS configuration using the large tin container to weight the sample to demonstrate the repeatability of ten replicates. The calibration curve was performed analyzing 2–3 mg BBOT and using the K factor as the calibration method. Table 4 shows the data obtained.

Table 5. CHNS data a rock sample at about 100 mg sample weight.

Weight (mg)	N%	C%	H%	S%
101.5	0.0031	0.0559	0.223	0.0551
102.5	0.0030	0.0551	0.220	0.0543
101.6	0.0031	0.0557	0.222	0.0549
101.2	0.0031	0.0558	0.223	0.0550
102.9	0.0030	0.0549	0.219	0.0541
106.0	0.0029	0.0545	0.218	0.0562
100.6	0.0029	0.0536	0.215	0.0553
100.2	0.0029	0.0538	0.216	0.0555
102.2	0.0029	0.0544	0.218	0.0561
103.5	0.0029	0.0531	0.213	0.0548
Average	0.0030	0.0547	0.219	0.0551
Std.Dev.	0.0001	0.0010	0.0034	0.0007
RSD%	2.08	1.78	1.56	1.24

Conclusions

For the quantitative determination of nitrogen, carbon, hydrogen and sulfur and TOC, the all-in-one Flash*Smart* EA is the optimal solution in geology in sample matrices with a wide range of concentrations spanning low to high amounts. Specifically, the Flash*Smart* EA demonstrates excellent repeatability, reproducibility, accuracy, and precision, as automation, speed of analysis and cost per analysis.

No memory effect was observed when changing the sample type, indicating the complete conversion and detection of all elements.

Thanks to the modularity of the Flash*Smart* EA, the hardware, autosamplers and software can be readily used for other configurations such as CHN/O, CHN/S, CHNS/O, CHNS/CHNS, CHN/CHN, NC (single reactor)/S, N-Protein (single reactor)/S and more. This can be achieved only by changing consumables.

The USGS rocks standards cover a wide range in CHNS abundances, making them an ideal suite of reference materials for geochemical studies.

Acknowledgments

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