Establishing Geochemical Standards and Methods for CHNS Abundances and CNS Isotopes

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ABSTRACT

Purpose: Determination of carbon, nitrogen, hydrogen and sulfur abundances and stable isotopes ratios by combustion method.

Methods: Rock samples with different geological ages and thermal maturity, including reference materials, were analyzed using an elemental analyzer with an autosampler.

Results: Carbon, nitrogen, hydrogen and sulfur data of these rock samples are presented to evaluate the accuracy, precision and repeatability of the analytical method.

INTRODUCTION

Abundances and stable isotope ratios of carbon, nitrogen, sulfur and hydrogen have become important tools for reconstructing the evolution of Earth and life over geologic timescales, requiring accurate and precise analytical methods with high sample throughput. However, appropriate geological reference materials and standardized methods for both abundance and stable isotope measurements currently do not exist.

Studies focused on elemental abundance measurements are most commonly performed with an elemental analyzer (EA), whereas bulk stable isotope analysis is undertaken with an EA coupled to an isotope ratio mass spectrometer (IRMS). However, the use of two different analytical systems to get both determinations makes the analyses more costly and time consuming.

To address these shortcomings, the Thermo Scientific™ Flash IRMS™ Elemental Analyzer (Figure 1) was developed to enable the measurement of elemental abundances and stable isotope ratios with high sample throughput and lower cost per sample analysis. This improved analytical setup has the advantage that abundance measurements can be performed alongside stable isotope analysis without the need for two, independent analytical systems. Importantly, this is achieved whilst ensuring higher data quality with optimized sample sizes and delivering measurement accuracy, reproducibility, day to day reproducibility.

Figure 1. Thermo Scientific Flash IRMS Elemental Analyzer.

MATERIALS AND METHODS

For CHNS abundance determination, the Elemental Analyzer 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.

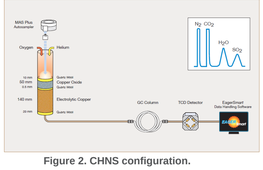


Figure 2. CHNS configuration.

For NCS isotope ratio determination, the Elemental Analyzer operates with the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor via the MAS Plus Autosampler alongside a pulse of oxygen. For nitrogen, carbon and sulfur, after combustion, the produced gases are carried by helium to a layer filled with copper, then to a water trap before entering in the GC column that separates the combustion gases before detection by the Thermo Scientific™ MAT253™ 10kV Isotope Ratio MS (Figure 3). This instrument configuration is known as the Thermo Scientific™ EA IsoLink IRMS System While for nitrogen, after combustion, the analyte gases are carried in a helium carrier gas to a reduction reactor, then to two chemical traps to adsorb the CO_2 and the H_2O, before entering in the GC column that separates the gases (Figure 4). For stable isotope ratio determination, a complete report is automatically generated by the Thermo Scientific™ Isodat™ Software Suite and displayed at the end of the analysis.

The elemental abundance data are compared to a dedicated EA standalone setup in a different laboratory.

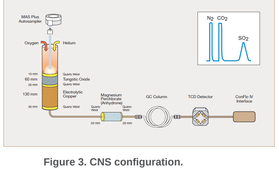


Figure 3. CNS configuration.

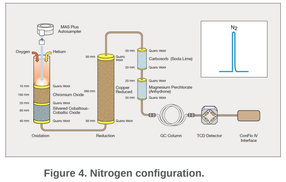


Figure 4. Nitrogen configuration.

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 EA IsoLInk IRMS System. Table 1 shows the sample information, and it can be noted that thermal maturity increases approximately with age in these samples.

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

Table 1. Rock sample information

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

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 Thermo Scientific™ Flash*Smart*™ EA coupled with the Flame Photometric Detector. Table 2 shows the sample weight and the CHNS data and the RSD% obtained for each sample.

Table 2. Rock sample weight and CHNS data.

Code	Weight (mg)	Abundance and RSD%							
		N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
1	3-4.5	0.883	0.77	27.84	0.37	3.17	0.52	1.47	1.22
2	7-10	0.357	0.41	9.62	0.33	1.46	1.25	5.29	0.27
3	7-10	0.275	0.81	7.93	0.49	0.944	0.95	1.03	0.82
4	7-8	0.102	1.99	11.55	0.90	0.747	1.28	1.57	1.11
5	15-20	0.0492	1.28	1.06	1.04	0.608	1.04	0.0219	1.02
6	15-25	0.0578	0.75	2.08	0.85	0.785	0.78	0.259	0.83
7	15-25	0.0008	6.04	0.0221	2.96	0.0246	2.75	0.0092	2.24
8	95-105	0.0030	3.08	0.0547	1.78	0.219	1.56	0.0551	1.24
9	10-15	0.0966	0.97	5.95	0.87	0.878	0.86	9.76	0.63
10	10-15	0.0114	1.87	3.06	0.72	0.869	0.78	2.65	0.64
11	15-25	0.0418	1.71	0.0587	1.47	0.458	1.26	0.0033	4.25
12	15-20	0.0251	1.98	0.584	0.51	0.272	1.44	0.342	0.96
13	15-25	0.0069	2.74	0.430	0.90	0.756	1.34	0.114	1.17
14	15-25	0.0030	3.54	0.179	0.71	0.654	0.87	0.0039	3.35
15	15-25	0	0	0.470	0.30	0.336	0.41	0.379	0.33

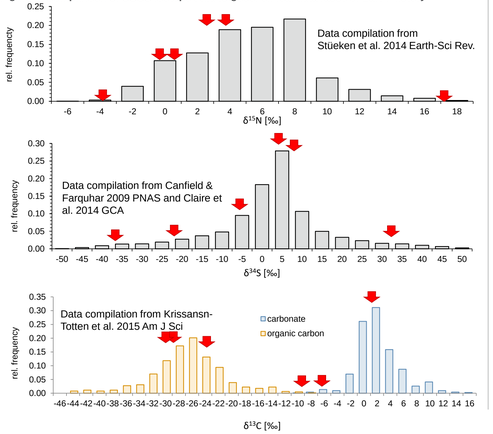
For CNS isotope ratio determination, the calibration was performed with the internationally recognized isotope standards USGS-41 and USGS-40 for carbon and nitrogen isotopes and IAEA-S2 and IAEA-S3 for sulfur isotopes. The rock samples were analyzed 2-5 times. Lower sample weights were used for carbon and sulfur isotope analyses (Table 3); higher weights were used for nitrogen isotope analyses. Table 3 presents the data and the SD obtained.

Table 3. Carbon, nitrogen and sulfur isotope ratio values.

Code	Weight (mg)*	Isotope value [‰] and one standard deviation (1SD)					
		$\delta^{15}N$	1SD	$\delta^{13}C$	1SD	$\delta^{34}S$	1SD
1	0.6-0.9	17.73	0.38	-24.95	0.46	32.93	0.54
2	0.11-0.12 and 1.8-2.0	-0.46	0.33	-29.80	0.23	-22.72	0.45
3	0.6-0.8 and 1.9-2.3	0.24	0.45	-30.05	0.14	7.24	0.36
4	0.4-0.5 and 7.0-7.6	-3.81	0.02	-10.77	0.79	-6.37	0.64
5	10-15	2.90	0.17	-6.30	0.24	5.80	0.76
6	1.1-1.3 and 9.8-10.5	3.83	0.08	0.30	0.30	-38.14	0.47
7	40-46	ND	ND	-23.80	0.11	-0.09	0.22
8	109-114	ND	ND	-14.96	0.12	17.78	0.42
9	0.07-0.11 and 6-7	6.28	0.00	-38.08	0.02	8.47	0.40
10	0.18-0.21 and 17-22	0.20	0.77	-40.51	0.79	4.77	0.27
11	37-51	4.09	0.02	-28.46	0.46	ND	ND
12	1.5-2.2 and 23-27	2.81	0.50	-32.03	0.05	10.02	0.55
13	4-5 and 57-58	1.47	0.84	-30.94	0.07	1.62	0.22
14	50-77	-0.23	0.48	-39.71	0.23	ND	ND
15	1.6-2.0	ND	ND	-39.65	0.78	1.44	0.08

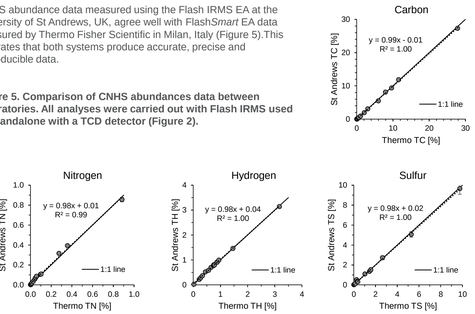
The isotope data for the six commercially available USGS standards spread over nearly the full geological range (histograms) of thousands of sample analyses (red arrows in Figure 4). As these standard reference materials over a wide range of isotope values, they are very useful in determining data reproducibility across the natural range of sample analyses.

Figure 4. Comparison of USGS isotope data to geochemical databases of Earth history.



CHNS abundance data measured using the Flash IRMS EA at the University of St Andrews, UK, agree well with Flash*Smart* EA data measured by Thermo Fisher Scientific in Milan, Italy (Figure 5).This illustrates that both systems produce accurate, precise and reproducible data.

Figure 5. Comparison of CNHS abundances data between laboratories. All analyses were carried out with Flash IRMS used as standalone with a TCD detector (Figure 2).



CONCLUSIONS

- The EA IsoLink IRMS System is the optimal solution for the analysis of CHNS abundances and isotope ratio determination in many application fields, in terms of accuracy, repeatability, automation, speed of analysis and cost per analysis.
- No memory effect was observed changing the sample matrix, indicating complete combustion and detection of all elements.
- The EA IsoLink IRMS System can used to produce elemental abundance data and stable isotope ratios without loss of data quality.
- Appropriate analytical reproducibility was obtained for isotopic in all rock samples with >50ppm concentration, including rocks of Precambrian age with high thermal maturity (samples 9, 10, 14, 15).
- The USGS rocks standards cover a wide range in CHNS abundances and CNS isotopic ratios, making them an ideal suite of reference materials for geochemical studies.

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TRADEMARKS/LICENSING

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