Application Note: 30194

Simultaneous N, C and S Isotope Ratio Determination on a DELTA V Isotope Ratio MS using a Flash Elemental Analyzer

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Key Words

- ConFlo IV
- DELTA V Series
- Elemental Analyzer
- smartEA™
- Multi-Element Analysis
- Isotope Ratio MS

Introduction

Multi-element isotope ratio analysis is becoming increasingly important, particularly in food authenticity control and forensic applications. With increasing numbers of samples for analysis, reduced sample preparation and measurement time are required. The ability to measure N, C and S isotopes from a single sample drop was demonstrated by Avak in 1996 with an analysis time of 30 minutes.[1]

With the introduction of the Thermo Scientific ConFlo IV universal interface in July 2007, the ability for multi-element isotope ratio determination was both enhanced and simplified. The ConFlo IV interface allows software-controlled switching of up to five reference gases and automatic dilution of sample gases down to 1:100 according to the varying amounts of the three elements in the samples. Using the Thermo Scientific smartEA option, the simultaneous analysis of N, C and S is simplified even further. The smartEA™ option adjusts the dilution of sample gases as a direct response to the TCD signals from the Flash Elemental Analyzer (EA). The optimized chromatography now reduces the analysis time to less than 18 minutes.

This technical note explains the modifications needed for triple measurements of N, C and S isotope ratios and shows the performance that can be achieved.

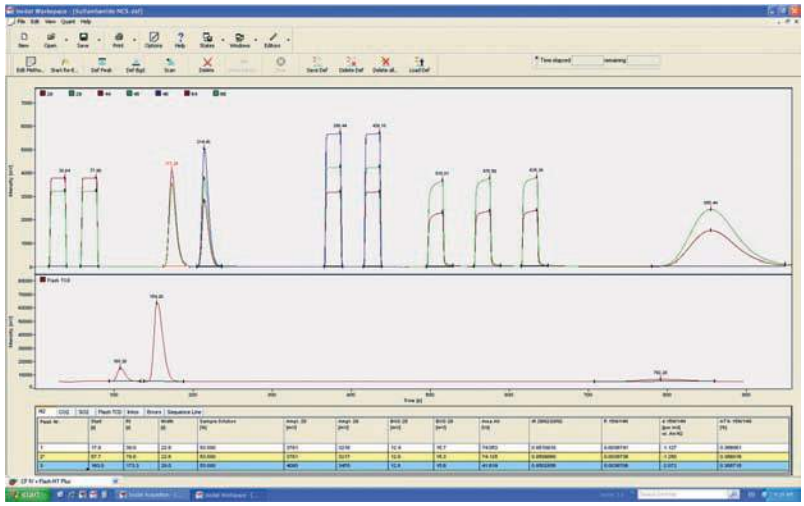

Figure 1: N, C and S triple measurement of sulfanilamide. Top: mass traces, middle: TCD trace of Flash EA, bottom: tabs with comprehensive data and results for each isotope.

Method

Optimal conditions for sulfur isotope ratio analysis require a short transfer line and reduced volumes in a water-free environment. Therefore a single reactor filled with WO_3 and electrolytic copper wires is used for the triple N, C and S analysis. A chemical trap of magnesium perchlorate removes water produced in the combustion process. Tubing in the Flash EA and the connection to the ConFlo IV interface is made of 1/16" Sulfinert® capillary to avoid the formation of acidic compounds by SO_2 with adsorbed water. The commonly used Teflon® tubing cannot be used for triple analysis of N, C and S due to increased nitrogen background. An optimized chromatographic column separates N_2 and CO_2 with an improved retention time of the SO_2. The Flash elemental analyzer used was a Thermo Scientific FlashEA 1112, system parameters are given in Table 1.

FlashEA 1112 settings NCS triple analysis

Reactor temperature	1,020 °C
GC temperature	70 °C
Carrier flow	80 mL/min
Autosampler type	MAS 200R

Table 1: System settings for triple measurement.

The ConFlo IV universal interface and the Flash EA were connected with the smartEA™ option to make use of the automatic dilution ability. The isotope ratio mass spectrometer (IRMS) used was a Thermo Scientific DELTA V Plus with a universal triple collector. A fast magnet field jump of the IRMS takes place automatically between the N_2 and CO_2 peaks followed by a slow magnet field jump to SO_2.

Results

The chromatogram in Figure 1 shows flat top reference gas pulses from the ConFlo IV interface and the chromatographically separated sample peaks of N_2, CO_2 and SO_2 from the elemental analyzer (400 µg of sulfanilamide). N_2 and CO_2 show a separation of 17 seconds which is required to perform a fast magnet field jump immediately after the detection of the N_2 sample peak at 191 seconds. The change of the magnet field from CO_2 to SO_2 is performed slowly between the CO_2 and SO_2 reference gas pulses at 460 seconds.

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Sample Identifier	Amount [mg]	$\delta^{15}N$ [‰]	$\delta^{13}C$ [‰]	$\delta^{34}S$ [‰]	Mean $\delta^{15}N$ [‰] S.D.	Mean $\delta^{13}C$ [‰] S.D.	Mean $\delta^{34}S$ [‰] S.D.	C/S Ratio
Sulfanilamide	0.245	-1.76	-28.76	3.09	-1.84 **0.07**	-28.77 **0.03**	3.04 **0.12**	2.2
Sulfanilamide	0.192	-1.87	-28.80	2.90				
Sulfanilamide	0.244	-1.89	-28.73	3.13				
Vitamin B1	0.192	-1.02	-32.88	-4.94	-0.96 **0.06**	-32.85 **0.04**	-4.96 **0.09**	4.4
Vitamin B1	0.240	-0.89	-32.86	-5.06				
Vitamin B1	0.196	-0.96	-32.81	-4.89				
Vitamin H	0.412	-12.34	-29.23	10.42	-12.30 **0.04**	-29.26 **0.03**	10.42 **0.10**	3.8
Vitamin H	0.468	-12.31	-29.30	10.32				
Vitamin H	0.474	-12.27	-29.24	10.52				
Cysteine	0.299	10.03	-14.26	7.13	10.12 **0.17**	-14.25 **0.02**	7.11 **0.07**	1.1
Cysteine	0.288	10.32	-14.23	7.17				
Cysteine	0.280	10.01	-14.27	7.03				
Soil	95.540	7.01	-23.61	3.73	7.00 **0.05**	-23.62 **0.05**	4.00 **0.25**	67.0
Soil	100.979	7.05	-23.67	4.23				
Soil	103.211	6.95	-23.57	4.04				
Octopus Tissue	2.041	10.48	-16.09	15.91	10.50 **0.02**	-16.07 **0.02**	15.97 **0.11**	n.d.
Octopus Tissue	2.033	10.49	-16.06	16.10				
Octopus Tissue	2.070	10.52	-16.06	15.91				
Bird Feather	1.148	7.60	-15.42	5.42	7.71 **0.10**	-15.53 **0.09**	5.23 **0.17**	n.d.
Bird Feather	1.002	7.75	-15.58	5.13				
Bird Feather	1.065	7.78	-15.57	5.14				
Pesticide	0.445	-9.28	-31.78	-4.77	-9.21 **0.17**	-31.74 **0.06**	-4.68 **0.11**	3.0
Pesticide	0.457	-9.01	-31.77	-4.73				
Pesticide	0.438	-9.34	-31.67	-4.56				
River Sediment	5.173	6.00	-22.75	-22.65	6.37 **0.33**	-22.57 **0.17**	-22.30 **0.38**	7.3
River Sediment	5.327	6.65	-22.42	-21.89				
River Sediment	5.304	6.46	-22.52	-22.36				

Table 2: Various sample types analyzed simultaneously for N, C and S isotope ratios. Samples were measured in triplicates.

The smartEA option delays the peaks after TCD detection. The shift in retention time of the sample peaks between TCD and mass trace is 60 seconds. This time is needed to adjust the automatic sample dilutions in the ConFlo IV interface. Each gas peak is individually diluted with respect to its abundance in the sample. This results in an acquisition time of 19 minutes which allows the analysis of three samples per hour.

The precision (S.D.) shown in Table 2 is ≤ 0.17‰ for $\delta^{15}N$, ≤ 0.1‰ for $\delta^{13}C$ and ≤ 0.17‰ for $\delta^{34}S$. For heterogeneous samples and samples with low sulfur contents (e.g. soil, river sediment, see Table 2) reduced precision has to be expected. The C/S ratio should not exceed 70. Sulfur contents are best analyzed from 30 µg on.

Conclusion

The triple analysis of N, C and S isotopes can be performed with any DELTA V series mass spectrometer using a Flash elemental analyzer for IRMS with a sulfur applicable reactor, tubing, and a chromatographic column described in Table 3. It is recommended to use Sulfinert capillaries instead of permeable Teflon or stainless steel tubing in order to reduce background and to avoid water adsorption. The analysis time can be reduced to less than 18 minutes.

Parts	Possible Supplier	Part Number
NCS Reactor (sulfur reactor with WO_3 and reduced Cu)	Thermo Fisher Scientific	468 020 21
Adsorption Trap (Water Trap) with connectors	Thermo Fisher Scientific	281 131 02
Aluminium Ferrule, 1.6 mm (Olive, 10 pcs)	Thermo Fisher Scientific	290 340 44
Stainless Steel Tubing Nut ss 304 6MB (10 pcs)	Thermo Fisher Scientific	350 404 03
Sulfinert Separation Column PP-QS, 2 m, 1/4", 50/80 mesh	Restek	PC4974
Sulfinert Tubing (1.5 m plus distance EA-ConFlo) 0.03"ID, 1/16"OD	Restek	22504

Table 3: Required parts for simultaneous N, C and S triple isotope analysis.

This setup can also be used to analyze N or C or S in a single mode. Analysis time for single sulfur isotope analysis can be reduced by increasing the column temperature allowing for a faster SO_2 elution to the disadvantage of the N_2/CO_2 separation.

Modifications and maintenance are minor and equal to a dedicated setup for sulfur isotope analysis. All parts can be installed quickly and easily on site at reasonable costs.

References

[1] Avak, H. Triple Element Mode – C, N, S from a single combustion. *Application Flash Report No. 16*, Finnigan MAT, **1996.**

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