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APPLICATION NOTE

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Accurate and Precise Sulfur Analysis using the Thermo Scientific Flash*Smart* Elemental Analyzer

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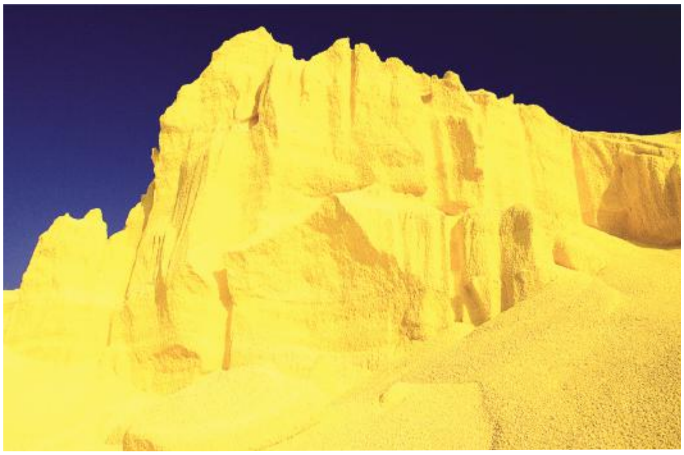

Key Words
Accuracy, Combustion, Precision, Repeatability, Reproducibility, Sulfur

Goal

To demonstrate the performance of the Thermo Scientific Flash*Smart* Elemental Analyzer for sulfur determination.

Introduction

The importance of sulfur determination has grown significantly in geology, agronomy, petrochemistry, environmental sciences, food authenticity and forensics. Today many of the classical methods are no longer suitable for routine analysis. However, analytical instruments improve the reliability of data and laboratory productivity, without the use of hazardous chemicals.

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

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1), copes effortlessly with the wide array of laboratory requirements such as accuracy, reproducibility, and high sample throughput.

Methods

The Flash*Smart* Elemental Analyzer operates according to the dynamic flash combustion of the sample (modified Dumas method). Samples are weighed in tin containers and introduced into the combustion reactor from the Thermo Scientific™ MAS Plus Autosampler with the proper amount of oxygen.

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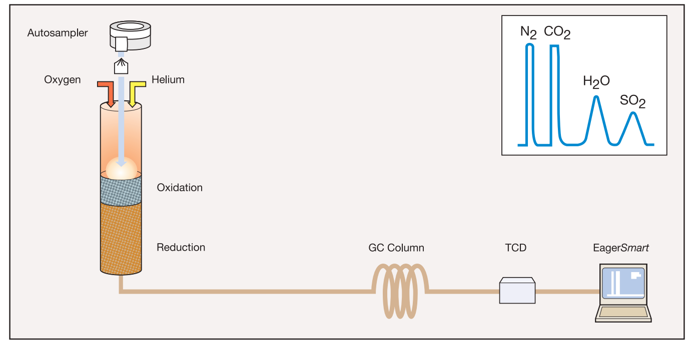
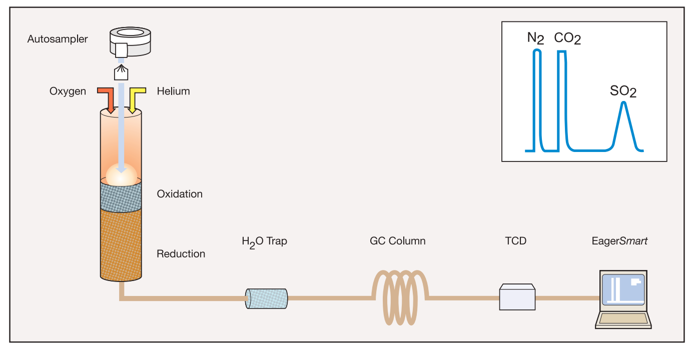
For simultaneous CHNS determination, after combustion, the analyte gases are carried by helium to a layer filled with copper, then onto the GC column (2 meters) that separates the combustion gases before detection by a Thermal Conductivity Detector (TCD), Figure 2.

Figure 2. Flash*Smart* CHNS Configuration.



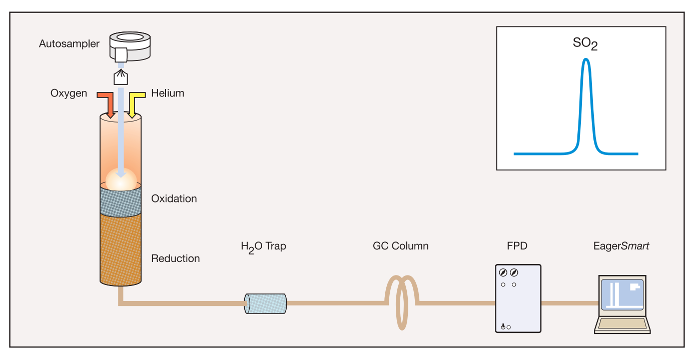
For single sulfur determination or simultaneous NCS, after combustion, the analyte gases are carried by helium to a layer filled with copper, then swept through a water trap before entering the GC column (0.80 or 2 meters) which separates the combustion gases before detection by a Thermal Conductivity Detector (TCD), Figure 3.

Figure 3. Flash*Smart* NCS or single S Configuration.



For trace sulfur determination, after combustion, the analyte gases are carried by helium to a layer filled with copper, then swept through a water trap before entering the GC column (0.15 meter) which separates the combustion gases before detection by a Flame Photometric Detector (FPD), Figure 4 and Figure 5.

Figure 4. Flash*Smart* Sulfur Configuration by FPD Detector.



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 5. The Flash*Smart* EA with the Flame Photometric Detector.

Results

To demonstrate the performance of the Flash*Smart* Analyzer for sulfur determination in CHNS, NCS and S-only configurations, three systems were set-up to perform typical analytical tests. For CHNS and NCS, the calibration was performed with Methionine standard using K factor as the calibration method.

Then, three analyses of sulfanilamide were performed as unknown. Table 1 shows the correlation between the CHNS theoretical percentages of the sulfanilamide standard, the accepted range according to the technical specification of the system and the experimental data obtained in triplicate measurements for each instrument. Table 2 shows the relative NCS data.

The sulfur data obtained in CHNS configuration are comparable with those obtained in NCS configuration confirming the proper quantification of the sulfur content without adsorption of sulfur in the water trap or on the GC columns. All data are acceptable and comparable confirming the repeatability and reproducibility expected under different configurations.

Table 1. Sulfur data on Sulfanilamide in CHNS configuration.

Technical Specification			Flash*Smart* Analyzers									
Element	Theoretical	Range	1		2		3		4		5	
	%	(±)	%	RSD%	%	RSD%	%	RSD%	%	RSD%	%	RSD%
N	16.27	0.16	16.25 16.28 16.28	0.11	16.28 16.29 16.28	0.04	16.32 16.29 16.31	0.09	16.23 16.24 16.21	0.09	16.28 16.30 16.27	0.09
C	41.84	0.30	41.96 41.97 41.96	0.01	41.77 41.79 41.68	0.14	41.80 41.87 41.94	0.17	41.91 41.92 41.92	0.01	41.66 41.65 41.63	0.04
H	4.68	0.07	4.65 4.66 4.64	0.21	4.68 4.68 4.68	0.00	4.64 4.65 4.65	0.12	4.68 4.68 4.69	0.12	4.69 4.69 4.69	0.00
S	18.62	0.20	18.75 18.74 18.73	0.05	18.77 18.77 18.73	0.12	18.68 18.62 18.70	0.22	18.77 18.55 18.77	0.68	18.75 18.71 18.78	0.19

Table 2. Sulfur data on Sulfanilamide in NCS configuration.

Technical Specification			Flash*Smart* Analyzers									
Element	Theoretical	Range	1		2		3		4		5	
	%	(±)	%	RSD%	%	RSD%	%	RSD%	%	RSD%	%	RSD%
N	16.27	0.16	16.34 16.28 16.32	0.19	16.29 16.31 16.28	0.09	16.28 16.28 16.26	0.07	16.31 16.30 16.26	0.16	16.24 16.27 16.21	0.18
C	41.84	0.30	41.95 41.94 41.84	0.15	42.00 41.93 41.94	0.09	41.87 41.75 41.68	0.23	41.69 41.68 41.63	0.08	42.03 41.95 42.03	0.11
S	18.62	0.20	18.61 18.68 18.64	0.19	18.74 18.78 18.77	0.11	18.59 18.61 18.79	0.59	18.71 18.68 18.78	0.27	18.79 18.76 18.71	0.21

For trace sulfur determination by FPD Detector, Thermo Scientific™ Pasta Reference Material was analyzed. The calibration method used was Quadratic Fit.

Table 3 shows the certified sulfur data, the accepted range and the experimental sulfur data obtained on five Flash*Smart* Analyzers demonstrating accuracy and precision on the different instruments.

Table 3. Sulfur data measured on Thermo Scientific Pasta Reference Material.

Technical Specification			Flash*Smart* Analyzers									
Element	Theoretical	Range	1		2		3		4		5	
	%	(±)	%	RSD%	%	RSD%	%	RSD%	%	RSD%	%	RSD%
S	0.135	0.04	0.135 0.136 0.135	0.427	0.137 0.138 0.137	0.420	0.136 0.135 0.135	0.425	0.135 0.135 0.134	0.429	0.137 0.137 0.136	0.422

The validation of the concentration range for sulfur, which is determined using the TCD Detector from low to high amounts, was checked by the analysis of three samples at low, medium and high sulfur concentrations. For the low range a Soil Reference Material (0.0140 S%) was used; for the medium range, sulfanilamide standard (theoretical 18.62 S%, accepted range ±0.2) was chosen for analysis. For the high range, sulfur powder was chosen (99.98 S%).

Table 4 reports the analytical data that demonstrates the accuracy and precision of the Analyzer for sulfur determination.

Table 4. Performance of sulfur determination by TCD Detector.

Low Range			Medium Range			High Range		
Sample	S%	RSD%	Sample	S%	RSD%	Sample	S%	RSD%
Soil Ref. Mat (0.0140 S%)	0.0141 0.0136 0.0138 0.0144 0.0140	2.1696	Sulfanilamide (18.62 S%)	18.68 18.65 18.68 18.64 18.71	0.1486	Sulfur Powder (99.98 S%)	99.99 99.90 99.85 99.86 99.99	0.0684

In order to evaluate the accuracy of the analyses in matrices that are different from pure organic standards, several Reference Materials were analyzed in simultaneous NCS and for sulfur as single determination. The calibration was performed with BBOT using K factor as the calibration method.

Table 5 shows the certified percentages and the relative uncertainty while Table 6 shows the experimental results obtained. The sulfur data obtained are reproducible and comparable between both configurations, confirming the complete conversion and quantification of sulfur.

Table 5. Certified values of Reference Materials.

Reference Material Information	Specification					
	N%	Uncertainty (±)	C%	Uncertainty (±)	S%	Uncertainty (±)
Low Organic Content Soil	0.13	0.023	1.61	0.09	0.01	n.a.
Loamy Soil	0.27	0.02	2.75	0.12	0.04	n.a.
Sandy Soil	0.07	0.01	0.83	0.05	0.01	n.a.
Birch Leaves	2.12	0.06	48.09	0.51	0.17	0.03
Orchard Leaves	2.28	0.04	50.40	0.40	0.16	0.01
Alfalfa	3.01	0.20	n.a.	n.a.	0.27	0.04
Bladderwrack Algae	1.25	0.02	33.67	0.29	2.29	
Spirulina Algae	10.81	0.06	47.21	0.39	0.60	0.03

Table 6. Experimental NCS and S data from several Reference Materials.

Reference Material	Simultaneous NCS analysis						Sulfur single analysis	
	N%	RSD%	C%	RSD%	S%	RSD%	S%	RSD%
Low Organic Content	0.130 0.132 0.131	0.88	1.605 1.615 1.612	0.32	0.0134 0.0133 0.0132	0.75	0.0131 0.0132 0.0130	0.76
Loamy Soil	0.272 0.268 0.270	0.74	2.73 2.74 2.74	0.20	0.0432 0.0425 0.0431	0.88	0.0432 0.0428 0.0429	0.48
Sandy Soil	0.0705 0.0711 0.0715	0.71	0.844 0.848 0.851	0.56	0.0152 0.0154 0.0155	0.98	0.0156 0.0157 0.0159	0.97
Birch Leaves	2.14 2.14 2.13	0.10	48.11 48.31 41.25	0.21	0.167 0.169 0.168	0.60	0.168 0.169 0.169	0.34
Orchard Leaves	2.29 2.28 2.29	0.15	50.25 50.35 50.22	0.14	0.153 0.154 0.155	0.64	0.152 0.153 0.154	0.65
Alfalfa	3.04 3.06 3.06	0.38	43.77 43.69 43.75	0.10	0.268 0.271 0.269	0.57	0.277 0.274 0.273	0.56
Bladderwrack Algae	1.26 1.26 1.26	0.00	33.69 33.66 33.62	0.11	2.282 2.276 2.286	0.22	2.278 2.274 2.283	0.20
Spirulina Algae	10.81 10.89 10.85	0.37	47.22 47.26 47.29	0.07	0.594 0.595 0.598	0.35	0.594 0.593 0.590	0.35

Finally, different matrices were analyzed using CHNS and NCS configuration by TCD Detector (Tables 7 and 8) and trace sulfur by FPD Detector (Table 9) to show the aplicability of sulfur determination in different application fields.

The data obtained show an excellent repeatability without matrix effect, which indicates complete combustion of the samples, no memory effect and proper quantification of the elements.

Table 7. CHNS determination of different matrices by TCD Detector.

Application field	Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Geological	Rock 1	0.0062 0.0065 0.0064	2.399	0.1511 0.1559 0.1577	2.202	0.1643 0.1774 0.1690	3.899	0.1791 0.1733 0.1800	2.049
	Rock 2	0.0033 0.0035 0.0031	6.060	0.0997 0.0982 0.0975	1.140	0.368 0.368 0.368	0.098	0.0269 0.0255 0.0260	2.682
Food	Supplement	0.330 0.333 0.329	0.533	40.615 40.396 40.630	0.323	6.274 6.331 6.323	0.488	0.366 0.368 0.357	1.581
	Gelatine	15.796 15.835 15.838	0.148	44.615 44.647 44.624	0.037	6.623 6.658 6.622	0.309	0.531 0.536 0.537	0.601
Petrochemical	Black Coal	1.335 1.330 1.328	0.271	79.863 79.668 79.685	0.136	4.563 4.569 4.559	0.110	0.345 0.340 0.351	1.595
	Bio-Fuel	0.503 0.499 0.500	0.425	45.197 45.179 44.952	0.303	5.671 5.638 5.596	0.663	0.0324 0.0317 0.0327	1.590
Material Characterization	Carbon Fiber	3.7880 3.7667 3.8433	1.0406	93.6306 93.2411 93.6027	0.2324	0.3133 0.3290 0.3125	2.9233	0.0324 0.0359 0.0339	5.1544
	Rubber	0.626 0.628 0.622	0.470	81.962 81.866 82.361	0.320	11.218 11.249 11.272	0.243	1.561 1.553 1.572	0.606

Table 8. NCS determination of different matrices by TCD Detector.

Application field	Sample	N%	RSD%	C%	RSD%	S%	RSD%
Agronomy	Soil	0.059 0.058 0.058	0.260	0.874 0.871 0.870	0.240	0.010 0.010 0.010	1.490
	Leaves	2.420 2.458 2.436	0.782	42.060 42.092 42.085	0.041	0.319 0.314 0.310	1.450
Food	Meat	12.939 12.979 13.013	0.286	51.064 50.886 50.879	0.206	0.724 0.732 0.721	0.742
	Animal Feed	3.892 3.845 3.810	1.069	44.752 44.893 44.235	0.776	0.287 0.282 0.277	1.773
Petrochemical	Carbon Black	0.135 0.134 0.140	2.156	96.329 96.241 96.300	0.046	0.711 0.704 0.709	0.505
	Lubricant	0.121 0.118 0.121	1.042	84.505 84.540 84.418	0.075	0.649 0.648 0.654	0.472
Environmental	Solid Compost	1.607 1.622 1.601	0.672	16.711 16.791 16.844	0.399	2.920 2.897 2.903	0.425
	Liquid Compost	0.143 0.146 0.144	0.822	2.362 2.332 2.389	1.210	0.050 0.050 0.050	0.614
Material Characterization	Paper	0.028 0.030 0.028	3.027	42.337 42.366 42.327	0.047	0.039 0.042 0.039	4.337
	Additive	0.925 0.930 0.917	0.665	75.437 75.299 75.319	0.099	2.988 2.980 2.969	0.318

Table 9. Sulfur determination of different matrices by FPD Detector.

Application field	Sample	ppm S	RSD%	Application field	Sample	ppm S	RSD%
Geological	Sand	17 15 17	7.070	Petrochemical	Graphite	46 46 45	1.264
Food	Maize Starch	65 63 65	1.795	Material Characterization	Catalyst	13 11 11	9.897

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Conclusions

The Thermo Scientific Flash*Smart* Elemental Analyzer is a robust solution for weight percent sulfur analysis in all type of sample matrices (solids, viscous and liquid samples) in terms of accuracy, precision, repeatability and sensitivity of results.

The inherent automation and high speed of analysis improves efficiency and help reduce overall operational costs.

The Flash*Smart* Analyzer can determine sulfur concentration in simultaneous CHNS and NCS mode, and also as sulfur measured on its own TCD Detector (100 ppm–100 S%). Additionally, with a simple upgrade, trace sulfur amounts can be measured when the Analyzer is coupled with a FPD Detector (5–500 ppm S).

The analyses show that no differences for sulfur percent determination between CHNS, NCS or single S determination modes, indicating:

- No interference from the hydrogen peak on sulfur peak.
- No matrix effect, even when changing the sample and element content.
- No adsorption of sulfur by the water trap.
- No adsorption of sulfur on the GC columns used.
- No influence from the nitrogen or carbon content.
- Complete combustion of all sample matrices.
- Complete conversion of sulfur to SO_2.
- Proper quantification of the sulfur in all types of matrices.

The Eager*Smart* Data Handling Software controls the TCD and FPD Detectors without any upgrade needed.

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

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