

Accurate and Precise Sulfur Analysis using the Thermo Scientific FlashSmart Elemental Analyzer

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Key Words

Accuracy, Combustion, Precision, Repeatability,
Reproducibility, Sulfur

Goal

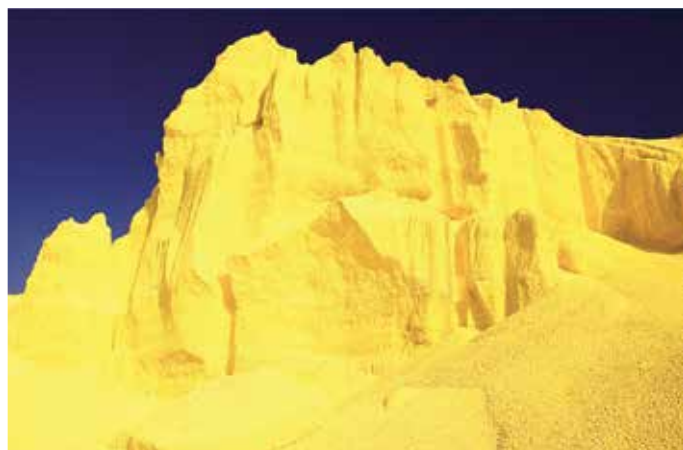
To demonstrate the performance of the Thermo Scientific FlashSmart Elemental Analyzer for sulfur determination.

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 FlashSmart Elemental Analyzer.



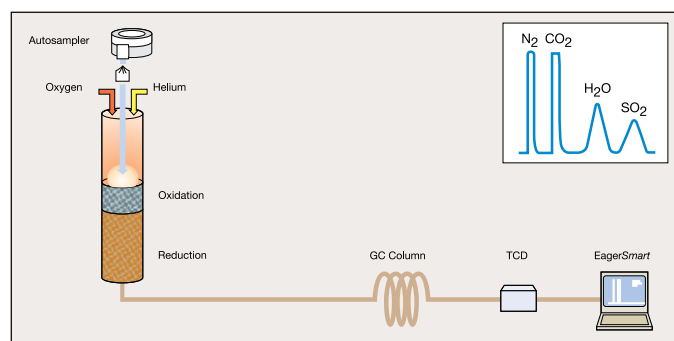
The Thermo Scientific™ FlashSmart™ Elemental Analyzer (Figure 1), copes effortlessly with the wide array of laboratory requirements such as accuracy, reproducibility, and high sample throughput.

Methods

The FlashSmart 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.

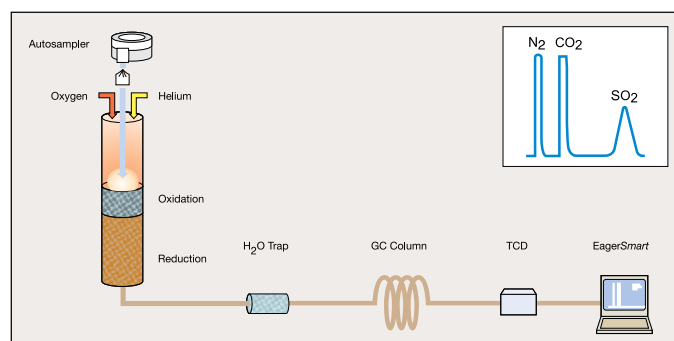
For simultaneous CHNS determination, after combustion, the analyte gases are carried by helium to a layer filled with copper, then onto the GC column (2 meters) that separates the combustion gases before detection by a Thermal Conductivity Detector (TCD), Figure 2.

Figure 2. FlashSmart CHNS Configuration.



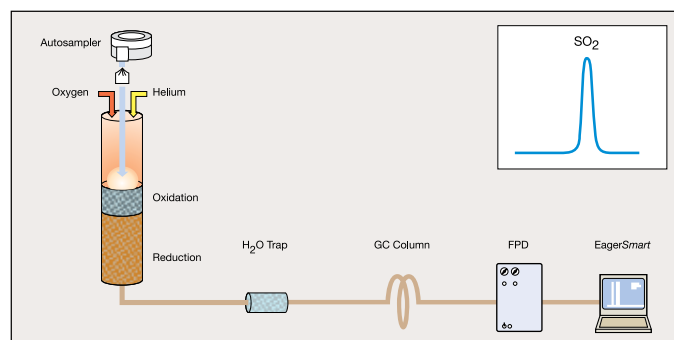
For single sulfur determination or simultaneous NCS, after combustion, the analyte gases are carried by helium to a layer filled with copper, then swept through a water trap before entering the GC column (0.80 or 2 meters) which separates the combustion gases before detection by a Thermal Conductivity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

Figure 3. FlashSmart 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. FlashSmart Sulfur Configuration by FPD Detector.



For weight percent determination a complete report is automatically generated by the Thermo Scientific™ EagerSmart™ Data Handling Software and displayed at the end of the analysis.

Figure 5. The FlashSmart EA with the Flame Photometric Detector.



Results

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

Table 2. Sulfur data on Sulfanilamide in NCS configuration.

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

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 FlashSmart Analyzers demonstrating accuracy and precision on the different instruments.

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

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

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	2.1696	Sulfanilamide (18.62 S%)	18.68	0.1486	Sulfur Powder (99.98 S%)	99.99	0.0684
	0.0136			18.65			99.90	
	0.0138			18.68			99.85	
	0.0144			18.64			99.86	
	0.0140			18.71			99.99	

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

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

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

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

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	7.070	Petrochemical	Graphite	46	1.264
		15				46	
		17				45	
Food	Maize Starch	65	1.795	Material Characterization	Catalyst	13	9.897
		63				11	
		65				11	

Conclusions

The Thermo Scientific FlashSmart 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 FlashSmart 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 SO₂.
- Proper quantification of the sulfur in all types of matrices.

The EagerSmart Data Handling Software controls the TCD and FPD Detectors without any upgrade needed.

Find out more at thermofisher.com/OEA

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