APPLICATION NOTE 42499

Elemental analysis: CHNS/O characterization of solid and liquid fertilizers by the Thermo Scientific Flash*Smart* Elemental Analyzer

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Goal

To assess the performance of the Flash*Smart* EA for the characterization of solid and liquid fertilizers.

Introduction

For agronomic research and quality control, the chemical characterization of fertilizers plays a very important role.

In the production process, the elemental composition of fertilizers is periodically monitored for their characterization. The rigorous quality controls begin with the suppliers of the raw materials.

As nitrogen and carbon provide information regarding the deficiency or excess of nutritional elements in soil, they are determined to evaluate organic matter and calculate the amount of fertilizer to be added.

Sulfur is also determined in soils as its deficiency can have negative influence for the growth of vegetables, particularly in the quality of proteins.

For the information provided by elemental analysis, there is a growing need for the elemental determination of fertilizers and the analysis of low level of nitrogen in agricultural *"run-off"* water resulting from fertilizer.

Laboratories need simple and fully automated analytical solution, accurate and precise, enabling fast analysis with an excellent reproducibility, no matter the sample type.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1), based on the dynamic combustion of the sample, provides automatic and simultaneous CHNS determination in a single analysis run and the oxygen determination by pyrolysis in a second run. The Flash*Smart* Elemental Analyzer is equipped with two totally independent furnaces. The Flash*Smart* Elemental Analyzer can also determine simultaneous NC or only nitrogen by a double reactors system: first reactor for combustion and catalytic oxidation of the combustion gases, the second is used to reduce nitrous oxides as N_2. The Flash*Smart* EA ability is to run both high and low levels as well as solid and liquid samples without matrix effect with the same system. The system meets laboratory requirements for modularity, accuracy, day to day reproducibility and high sample throughput. Moreover, safety, precision and reproducibility are ensured, eliminating the challenges coming from traditional methods. The Dumas combustion method is approved by different associations for the analysis of fertilizers (AOAC, ISO and Italian Gazzetta Ufficiale).

Figure 1. Flash*Smart* Elemental Analyzer with MAS Plus Autosampler and AS 1310 Liquid Autosampler

Methods

The Elemental Analyzer operates according to the dynamic flash combustion of the sample. Samples can be weighed in tin containers and introduced into the combustion reactor via the Thermo Scientific™ MAS Plus Autosampler or they can be directly injected by a syringe via the AS 1310 Liquid Autosampler, in both cases together with the proper amount of oxygen.

For nitrogen determination only, after combustion, the produced gases are carried by a helium flow to a second reactor filled with copper, then swept through CO_2 and H_2O traps, a GC column and finally detected by a thermal conductivity detector (see Figure 2). While for NC determination only one H_2O trap is used.

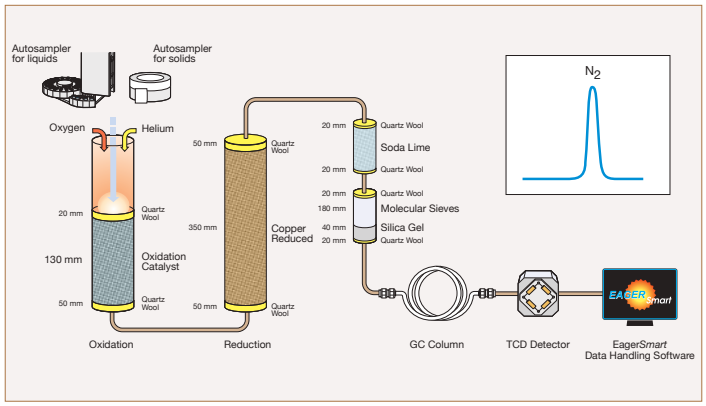

Figure 2. Nitrogen configuration

For simultaneous CHNS, after combustion the resulted gases are carried by a helium flow to a layer filled with copper, a GC column that provides the separation of the combustion gases, and finally, detected by a thermal conductivity detector (TCD) (see Figure 3). For NCS or only sulfur determination a water trap is installed between the reactor and the GC column.

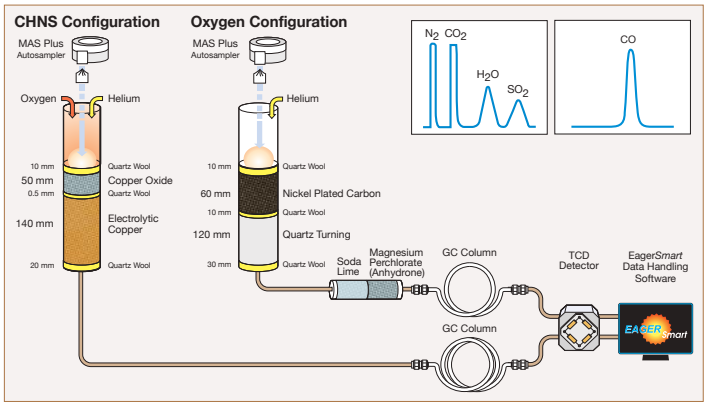

Figure 3. CHNS/O configuration

For oxygen determination, the system operates in pyrolysis mode. Samples are weighed in silver containers and introduced into the pyrolysis chamber (right furnace) via the MAS Plus Autosampler. The reactor contains nickel coated carbon maintained at 1060 ˚C. The oxygen present in the sample, combined with the carbon, forms carbon monoxide which is then gas chromatographically separated from other products and detected by the TCD Detector (Figure 3).

A complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software and displayed at the end of the analysis.

Results

Several solid and liquid fertilizers were analyzed by Flash*Smart* EA using different configurations to demonstrate the repeatability, accuracy and precision in a large range of element concentration. Solid samples were homogenized by a ball mill while liquid samples were analyzed without pre-treatment.

Table 1 shows the nitrogen determination of pure solid samples. Instrument calibration was performed with urea (46.65 %N). Urea was analyzed also as unknown to check the accuracy and precision of the system. The sample for fertilizers was weighed at 90–100 mg urea, 150–160 mg ammonium chloride, 180–200 mg ammonium sulphate, 4–5 mg for ammonium nitrate and 100–120 mg for potassium nitrate.

Table 1. Nitrogen determination in pure solid fertilizers

Sample name	Theoretical	Flash*Smart* EA		
	N%	No. of analysis	Av. N%	RSD%
Urea	46.65	10	46.61	0.12
Ammonium chloride	26.16	10	26.38	0.19
Ammonium sulfate	21.20	10	21.27	0.53
Ammonium nitrate	34.99	3	34.93	0.01
Potassium nitrate	13.85	3	13.85	0.56

Table 2 shows the nitrogen determination of solid inorganic fertilizers indicating the composition of the mixture, the sample weight and the nitrogen data obtained. Instrument calibration was performed with 90–100 mg urea (46.65 %N).

Table 2. Nitrogen determination in solid inorganic fertilizers

No.	Composition	Weight (mg)	N%	RSD%
1	Urea, biammonium phosphate, ammonium sulphate, monobasic calcium phosphate, bibasic calcium phosphate, calcium phosphate, zinc oxide, potassium chloride	180–190	22.94 23.01 23.00 22.87 22.92	0.25
2	Biammonium phosphate	215–220	18.38 18.35 18.37 18.25 18.34	0.28
3	Urea, biammonium phosphate, ammonium sulphate, monobasic calcium phosphate, bibasic calcium phosphate, calcium phosphate, zinc oxide, magnesium oxide, calcium carbonate, boron	195–200	22.02 22.01 21.99 21.97 21.97	0.10
4	Urea, biammonium phosphate, ammonium sulphate, monobasic calcium phosphate, bibasic calcium phosphate, calcium phosphate, magnesium oxide, calcium carbonate, potassium chloride, boron	200–205	10.41 10.19 10.39 10.22 10.31	0.95
5	Urea, biammonium phosphate, ammonium sulphate, monobasic calcium phosphate, bibasic calcium phosphate, calcium phosphate, magnesium oxide, calcium carbonate, potassium chloride, boron	260–275	10.72 10.81 10.79 10.75 10.71	0.40
6	Potassium carbonate, potassium nitrate, monobasic potassium phosphate, ammonium sulphate, iron EDTA, copper EDTA, zinc EDTA, boron	250–290	15.35 15.33 15.31 15.32 15.29	0.15

Table 3 shows the nitrogen determination of liquid fertilizer samples. Samples were analyzed by liquid injection and the volume injected was 100 µl. Instrument calibration was performed with 100 ul of urea water solution (0.3 and 7 N%).

Table 3. Nitrogen determination in liquid fertilizers

Sample	N%	RSD%	Sample	N%	RSD%
1	0.072 0.073 0.072	1.52	6	2.79 2.85 2.83	1.07
2	0.220 0.218 0.220	0.61	7	7.13 7.10 7.15	0.19
3	0.310 0.316 0.316	1.10	8	10.19 10.16 10.17	0.19

Table 4 and 5 shows the nitrogen and carbon determination of solid and liquid fertilizers. The calibration was performed with 4–5 mg of aspartic acid (10.52 N%, 36.09 C%), and the solid fertilizer was weighed at 5–6 mg and the liquid samples at 10–15 mg, adsorbed on about 10 mg of Chromosorb.

Table 6 shows the CHNS/O data of a solid and liquid fertilizers. For CHNS, the calibration was performed with 2–3 mg sulfamethazine, and the sample weight used was 3–4 mg. For oxygen determination, the calibration was performed with 1–1.5 mg aspartic acid, and the sample was weighed at 1–1.5 mg. Table 7 shows the CHNS data of solid (containing different amount of ammonium nitrate) and liquid fertilizers. The calibration was performed with 2–3 mg BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene) and 3–4 mg urea, and the sample weighed 3–4 mg. Table 8 shows the NCS data of solid fertilizer samples. The calibration was performed with 2–3 mg of BBOT, nicotinamide, cystine and urea, and the sample was weighed at 3–4 mg. Table 9 shows the sulfur data of solid samples. The calibration was performed with 2–3 mg of BBOT (7.44 S%) and the sample was weighed at 2–4 mg.

Table 4. NC determination of solid fertilizers

Sample	N%	RSD%	C%	RSD%
1	3.88 3.87 3.89	0.27	29.84 30.48 29.81	1.25
2	9.38 9.36 9.35	0.16	35.66 36.60 35.54	0.17
3	9.77 9.79 9.78	0.10	8.01 8.04 8.04	0.22
4	17.87 17.81 17.87	0.22	0.231 0.227 0.228	0.91
5	33.47 33.51 33.55	0.13	0.038 0.037 0.039	1.86

Table 5. NC determination of liquid fertilizers

Sample	N%	RSD%	C%	RSD%
1	0.7881 0.7752	0.2412	0.4552 0.4675	1.8852
2	1.6335 1.6329	0.0260	0.0133 0.0122	6.1005
3	4.0065 3.9530	0.9506	0.0416 0.0404	2.0696
4	4.0576 4.0105	0.8256	0.3475 0.3552	1.5497
5	0.6753 0.6883	1.3483	0.4791 0.4799	0.1180

Table 6. CHNS/O determination in solid and liquid fertilizers

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%	O%	RSD%
Solid	19.01 18.97 19.08	0.29	27.05 27.00 26.90	0.28	10.57 10.55 10.57	0.11	-	-	40.90 40.85 40.86	0.06
Liquid	12.18 12.21 12.15	0.25	14.03 14.13 14.10	0.36	4.72 4.71 4.73	0.21	11.77 11.70 11.72	0.31	39.23 39.31 39.21	0.13

Table 7. Simultaneous CHNS determination in solid and liquid fertilizers

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Inorganic solid 1	34.27 34.31 34.49	0.34	0.237 0.234 0.238	0.88	5.20 5.20 5.21	0.11	0.767 0.760 0.758	0.62
Inorganic solid 2	18.06 17.99 18.16	0.47	1.04 1.06 1.06	1.10	2.50 2.46 2.47	0.84	1.51 1.49 1.51	0.77
Inorganic solid 3	14.55 14.43 14.40	0.55	6.07 6.02 6.02	0.48	8.14 8.16 8.11	0.31	0.0194 0.0191 0.0196	1.30
Organic liquid 1	8.46 8.40 8.41	0.38	9.67 9.67 9.60	0.42	7.54 7.53 7.54	0.08	0.845 0.837 0.842	0.48
Organic liquid 2	3.47 3.43 3.48	0.76	11.04 11.06 11.08	0.18	7.01 7.05 7.03	0.28	1.86 1.89 1.88	0.81
Organic liquid 3	0.284 0.286 0.281	0.89	10.73 10.75 10.69	0.28	7.32 7.28 7.28	0.32	0.519 0.518 0.510	0.51

Table 8. Simultaneous NCS determination in solid fertilizers

Sample	N%	RSD%	C%	RSD%	S%	RSD%
1	10.54 10.58 10.58	0.23	4.58 4.52 4.69	1.82	0.21 0.22 0.21	1.86
2	24.61 24.73 24.69	0.25	0.221 0.223 0.220	0.69	1.23 1.23 1.23	0.13
3	25.50 25.54 25.55	0.09	0.046 0.042 0.044	3.90	0.085 0.084 0.085	0.71
4	20.63 20.76 20.67	0.31	0.943 0.936 0.939	0.41	23.94 23.99 23.99	0.12

Table 9. Sulfur determination in solid fertilizers

Fertilizer 1		Fertilizer 2		Fertilizer 3	
S%	RSD%	S%	RSD%	S%	RSD%
2.74 2.70 2.72 2.75 2.74	0.74	3.62 3.61 3.66 3.62 3.68	0.86	4.87 4.85 4.86 4.81 4.80	0.64

Conclusions

For agronomic analysis for quality control, elemental analysis enables automated and accurate characterization of fertilizers and agricultural *"run-off"* water.

The Flash*Smart* EA, based on the combustion method (Dumas) determines N, NC, CHNS by combustion and oxygen by pyrolysis for the analysis of solid and liquid fertilizers samples in a wide range from low to high content and without the use of sample digestion or toxic chemicals, which is normally required by traditional methods.

The need for analysis productivity and sample throughput is met, by performing simultaneous CHNS or NCS determination in a single run and analyzing sulfur only with minor modifications of the analytical conditions. Nitrogen only or NC determinations can be performed by increasing the sample weight and changing the configuration. The requirements of modern laboratories for flexibility, accuracy, sensitivity, automation and low cost per analysis are fulfilled by the Flash*Smart* EA, which also enables compliance to official methods. The Dumas combustion method has been approved and adopted by Official Organizations for the analysis of fertilizers as AOAC (Official Method 990.13, total nitrogen in fertilizers 2.4.02), BS ISO 22241-2-2006 (determination of urea content by total nitrogen) and Official Italian Method on Soils Analytical Chemistry (Gazzetta Ufficiale, Method 146, new regulations for fertilizer's control).

All data were obtained with a good reproducibility and no matrix effect was observed when changing from solids to liquid samples. This indicates the complete and accurate detection of the elements.

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