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APPLICATION NOTE 42241

Elemental Analysis: Nitrogen determination of inorganic fertilizers using argon as carrier gas

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Keywords

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Goal

This application note demonstrates the performance of the Thermo Scientific Flash*Smart* Elemental Analyzer for fertilizer analysis and show the repeatability and reproducibility of data obtained when using argon and helium as carrier gas.

Introduction

The chemical composition of fertilizers is important in agronomy for research and quality control purposes. One of the tests used in the production process of fertilizers is the determination of the nitrogen content. The determination of nitrogen provides useful information on the characterization of the fertilizers and it affects agricultural decisions. Therefore, an automated technique allowing accurate analysis and high throughput with excellent reproducibility is key for agronomy applications.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1), based on the dynamic combustion method (Dumas method) performs nitrogen determination by providing advantages over the traditional methods, for example with the removal of the need for hazardous chemicals. Considering also the need for cost efficiencies and the likely increase in helium gas cost, the Flash*Smart* EA offers an alternative for the carrier gas. Argon can be used as alternative to helium in the Flash*Smart* EA.

The note presents data on nitrogen determination for inorganic fertilizers. The analysis are performed helium and argon as carrier gas and the results are then compared.

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

Methods

The Flash*Smart* EA operates according to 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 with oxygen. After combustion, the produced gases are carried by a helium or argon flow to a second reactor filled with copper, then swept through CO_2 and H_2O traps, and a GC column. Finally, they are detected by a Thermal Conductivity Detector (TCD) (Figure 2). A complete report is automatically generated by Thermo Scientific™ Eager*Smart*™ Data Handling Software.

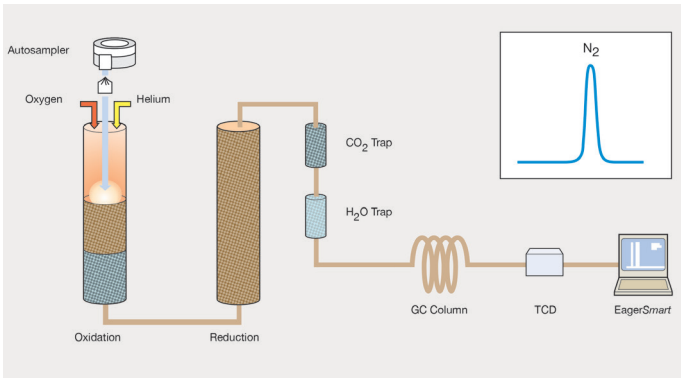

Figure 2. Nitrogen configuration.

Analytical Conditions		
Parameter	**Helium Gas**	**Argon Gas**
Combustion Reactor Temperature	950°C	950°C
Reduction Reactor Temperature	840°C	840°C
Oven Temperature	50°C	50°C
Carrier Gas Flow	140 mL/min	60 mL/min
Reference Gas Flow	100 mL/min	60 mL/min
Sample Delay	10 sec	10 sec
Oxygen Flow	300 mL/min for pure standards and test A, 270 mL/min for test B	300 mL/min
Oxygen Injection Time	10 sec for pure standards and test A, 5 sec for test B	10 sec for pure standards and test A, 5 sec for test B

Note: The Eager*Smart* Data Handling Software provides the option AGO (Argon Gas Option), allowing to manage the flow of argon gas during the run.

Results

To evaluate the performance of the Elemental Analyzer for fertilizers analysis using helium and argon as carrier gas, pure standards with different nitrogen concentration were chosen. Instrument calibration was performed with about 90–100 mg of urea (46.65 N%) standard using K factor as calibration method. Then urea (90–100 mg), ammonium chloride (150–160 mg) and ammonium sulfate (180–190 mg) were analyzed 10 times to evaluate the repeatability. Table 1 shows the theoretical data and the uncertainty of each standard while Table 2 shows the experimental results obtained using argon and helium as carrier gas. The results obtained fall within the uncertainty value declared.

Table 1. Standards information.

Sample Description	Theoretical N%	Uncertainty (±%)
Urea Thermo Scientific standard	46.65	0.30
Ammonium Chloride	26.18	0.25
Ammonium Sulfate	21.20	0.21

Table 2. Experimental nitrogen data of standards.

Sample	Thermo Scientific Urea		Ammonium Chloride		Ammonium Sulfate	
Carrier Gas	He	Ar	He	Ar	He	Ar
Element	N%	N%	N%	N%	N%	N%
	46.58	46.63	26.36	26.45	21.18	21.36
	46.68	46.46	26.42	26.37	21.15	21.27
	46.52	46.44	26.42	26.42	21.35	21.25
	46.62	46.65	26.32	26.42	21.05	21.31
	46.58	46.57	26.38	26.20	21.23	21.42
	46.66	46.60	26.40	26.35	21.32	21.34
	46.65	46.36	26.36	26.41	21.37	21.32
	46.63	46.34	26.40	26.32	21.35	21.38
	46.52	46.33	26.46	26.42	21.30	21.33
	46.62	46.48	26.33	26.34	21.40	21.40
Average %	46.61	46.49	26.38	26.36	21.27	21.34
RSD%	0.12	0.26	0.16	0.27	0.53	0.25

Different mixtures of inorganic fertilizers were chosen to compare the results when using helium or argon as carrier gas. Two tests, A and B, were performed over a range of sample weight for both carrier gases. Table 3 shows the composition of each sample while Table 4 shows the standard and the sample weight used for each test. K factor was used as calibration method in all cases.

Table 3. Inorganic fertilizers composition.

Sample No.	Mixture Composition
1	Urea
2	Urea, biammonium phosphate, ammonium sulfate, monobasic calcium phosphate, bibasic calcium phosphate, calcium phosphate, zinc oxide, potassium chloride
3	Biammonium phosphate
4	Urea, biammonium phosphate, ammonium sulfate, monobasic calcium phosphate, bibasic calcium phosphate, calcium phosphate, zinc oxide, magnesium oxide, calcium carbonate, boron
5	Urea, biammonium phosphate, ammonium sulfate, monobasic calcium phosphate, bibasic calcium phosphate, calcium phosphate, magnesium oxide, calcium carbonate, potassium chloride, boron
6	Urea, biammonium phosphate, ammonium sulfate, monobasic calcium phosphate, bibasic calcium phosphate, calcium phosphate, magnesium oxide, calcium carbonate, potassium chloride, boron
7	Potassium carbonate, potassium nitrate, monobasic potassium phosphate, ammonium sulfate, iron EDTA, copper EDTA, zinc EDTA, boron

Table 4. Standard and fertilizer samples for tests A and B.

Test	Urea Standard	Fertilizer			
	Helium and Argon Carrier Gas	Helium Carrier Gas		Argon Carrier Gas	
	Weight (mg)	Sample No.	Weight (mg)	Sample No.	Weight (mg)
A	95–100	1	98–100	1	92–95
		2	180–190	2	170–190
		3	216–222	3	198–212
		4	194–201	4	191–197
		5	202–208	7	200–227
		6	259–278	8	260–280
		7	250–290	9	262–305
B	45–50	1	48–50	1	43–50
		2	94–96	2	91–100
		3	108–111	3	105–113
		4	97–98	4	93–100
		5	198–211	7	176–183
		6	197–203	8	183–190
		7	148-177	9	165-184

Table 5 shows the nitrogen data obtained from tests A and B using helium carrier gas while Table 6 shows the data obtained using argon carrier gas for both tests.

Table 5. Nitrogen data of tests A and B using helium carrier gas.

Sample No.	Test A			Test B		
	N%	Avg. %	RSD%	N%	Avg. %	RSD%
1	46.86 46.65 46.84 46.81 46.89	46.81	0.20	46.70 46.86 46.89 46.89 46.87	46.84	0.17
2	22.94 23.01 23.00 22.87 22.92	22.95	0.25	23.26 23.04 23.18 23.03 23.22	23.15	0.34
3	18.38 18.35 18.37 18.25 18.34	18.34	0.28	18.35 18.48 18.48 18.48 18.39	18.44	0.34
4	22.02 22.01 21.99 21.97 21.97	21.99	0.10	22.14 22.22 21.89 22.16 22.00	22.08	0.61
5	10.41 10.19 10.39 10.22 10.31	10.30	0.95	10.31 10.43 10.45 10.32 10.47	10.40	0.73
6	10.72 10.81 10.79 10.75 10.71	10.76	0.40	10.82 10.81 10.79 10.85 10.85	10.82	0.24
7	15.35 15.33 15.31 15.32 15.29	15.32	0.15	15.38 15.44 15.39 15.37 15.48	15.41	0.30

Table 6. Nitrogen data of tests A and B using argon carrier gas.

Sample No.	Test A			Test B		
	N%	Avg. %	RSD%	N%	Avg. %	RSD%
1	46.68 46.74 46.61	46.68	0.14	46.50 46.75 46.83	46.69	0.37
2	23.34 23.23 23.43	23.33	0.43	23.06 22.90 22.93	22.96	0.37
3	18.31 18.33 18.26	18.30	0.20	18.63 18.40 18.53	18.52	0.62
4	22.04 22.06 22.06	22.05	0.05	21.72 21.96 21.64	21.77	0.76
5	10.36 10.45 10.51	10.44	0.72	10.50 10.45 10.38	10.44	0.58
6	11.06 10.94 11.02	11.01	0.56	10.69 10.72 10.72	10.71	0.16
7	15.34 15.08 15.05	15.16	1.05	15.44 15.24 15.29	15.32	0.68

Table 7 shows a summary of the nitrogen average data of tests A and B using helium and argon carrier gases, which show highly comparable data.

Table 7. Summary of nitrogen data.

Sample No.	Test A				Test B			
	Helium Carrier Gas		Argon Carrier Gas		Helium Carrier Gas		Argon Carrier Gas	
	N%	RSD%	N%	RSD%	N%	RSD%	N%	RSD%
1	46.81	0.20	46.68	0.14	46.84	0.17	46.69	0.37
2	22.95	0.25	23.33	0.43	23.15	0.45	22.96	0.37
3	18.34	0.28	18.30	0.20	18.44	0.34	18.52	0.62
4	21.99	0.10	22.05	0.05	22.08	0.61	21.77	0.76
5	10.30	0.95	10.44	0.72	10.40	0.72	10.44	0.58
6	10.76	0.40	11.01	0.56	10.82	0.24	10.71	0.16
7	15.32	0.15	15.16	1.05	15.41	0.30	15.32	0.68

Conclusions

For nitrogen analysis of inorganic fertilizers the Flash*Smart* Elemental Analyzer provides accurate data, which are obtained with good repeatability considering the inhomogeneity of the fertilizer mixtures, with no matrix effect when changing the sample.

The data obtained when using argon as carrier gas are comparable with those obtained when using helium as carrier gas, providing operational efficiences and potentially reducing analysis costs.

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