Application Note

Instrument: CN928/FP928

Determination of Nitrogen in Fertilizer

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Introduction

Nitrogen is one of the most important elements for plant development and is the macronutrient that is most often found to be deficient in arable soils used for crop production. Nitrogen plays a key role in the formation of enzymes and proteins, which promotes lush, vigorous growth and development in plants that often leads to an increase in the yield from the plant. Fertilizers are utilized to re-introduce nitrogen back into arable soils. Fertilizers can be grouped by their makeup and/or origins into categories including inorganic and/or synthetic (including nitrates, ammonium, and urea) and organic (including compost materials and manures). The accurate and precise determination of nitrogen in all fertilizer types is not only important in the process of blending and preparing the fertilizer material for use, but also will have significant impact on the commercial value and guarantee of the fertilizer.

The CN928/FP928 is a macro combustion carbon and nitrogen/protein determinator that utilizes a pure oxygen environment in a high-temperature horizontal ceramic combustion furnace designed to handle macro sample mass. A thermoelectric cooler removes moisture from the combustion gases before they are collected in a ballast. The gases equilibrate and mix in the ballast before a representative aliquot (3 cm^3 or 10 cm^3 volume) of the gas is extracted and introduced into a flowing stream of inert gas (helium or argon) for analysis. The aliquot gas is carried to a thermal conductivity cell (TC) for the detection of nitrogen (N_2).

Instrument Model and Configuration

Thermal conductivity detectors work by detecting changes in the thermal conductivity of the analyte gas compared to the constant thermal conductivity of the reference/carrier gas. The greater the difference between the thermal conductivity of the carrier gas and the analyte gas, the greater the sensitivity of the detector. The CN928/FP928 supports either the use of helium or argon as the instrument's carrier gas. When used as a carrier gas, helium provides the highest sensitivity, and the best performance at the lower limit of the nitrogen range. The thermal conductivity difference between argon and nitrogen is not as great as the thermal conductivity difference between helium and nitrogen, therefore the detector is inherently less sensitive when using argon as a carrier gas.

The CN928/FP928 offers the additional advantage of utilizing either a 10 cm^3 aliquot loop or a 3 cm^3 aliquot loop within the instrument's gas collection and handling system. The 10 cm^3 aliquot loop optimizes the system for the lowest nitrogen range and provides the best precision. The 3 cm^3 aliquot loop extends reagent life expectancy by approximately three fold when compared to the 10 cm^3 aliquot loop, while providing the lowest cost-per-analysis with minimal impact on practical application performance (see Typical Results section).

Note: When changing carrier gas type, the flow needs to be adjusted following instructions provided in the CN928/FP928 Operator's Instruction Manual. The aliquot loop size is changed by selecting the desired aliquot loop size in the software's Method Parameters.

Sample Preparation

Samples must be of a uniform consistency to produce suitable results. Reference materials should be prepared as directed by the certificate, prior to analysis.

Accessories

528-203 Ceramic Combustion Boats*, 502-343 Nickel Boat Liners, 761-929 Crucible Tongs, and 501-614 Spatula

**Note: For optimal precision, when analyzing samples with low nitrogen concentrations, ceramic combustion boats should be baked in a muffle furnace at 1000 °C for a minimum of 40 minutes prior to use. Once the ceramic combustion boats have cooled, they should be transferred to a desiccator for storage. If the ceramic combustion boats are not used within twenty-four hours, they should be re-baked. After baking, handle ceramic combustion boats with clean tongs only; do not use fingers.*

Reference Materials

LCRM®, LRM®, NIST, or other suitable reference materials.

Method Reference

AOAC 993.13 Nitrogen (Total) in Fertilizers, Combustion Method

Analysis Parameters**

Gas Type	Helium or Argon
Furnace Temperature	1350 °C
Dehydration Time	0 s
Nominal Mass	1.0000 g
Purge Cycles	3
Ballast Equilibrate Time	10 s
Ballast Not Filled Timeout	300 s
Aliquot Loop Fill Pressure Drop	200 mm Hg
Aliquot Loop Equilibrate Time	4 s
Dose Loop Size	10 cm^3 or 3 cm^3

Element Parameters**

	Helium 10 cm^3 & 3 cm^3	Argon 10 cm^3 and 3 cm^3
Integration Delay	0 s	0 s
Starting Baseline	10 s	10 s
Post Baseline Delay	28 s	25 s
Use Comparator	No	No
Integration Time	40 s	35 s
Use Endline	Yes	Yes
Endline Delay	30 s	30 s
Ending Baseline	5 s	5 s

***Refer to CN928/FP928 Operator's Instruction Manual for Parameter definitions.*

Burn Profile

Burn Step	Lance Flow	Furnace Flow	Time
1	No	Yes	5 s
2	Yes	Yes	5 s
3	Yes	No	End

Procedure

1. Prepare instrument for operation as outlined in the operator's instruction manual.
2. Condition the system.
   a. Select five or more Blank replicates in the Login screen (ceramic combustion boat is not required).
   b. Initiate the analysis sequence.
3. Determine Blank.
   a. Select five or more Blank replicates in the Login screen.
   b. Weigh ~ 0.4 g ground sucrose[†] into a 528-203 Ceramic Combustion Boat.
   c. Place ceramic combustion boat containing sucrose[†] in the appropriate position in the autoloader.
   d. Repeat steps 3b through 3c a minimum of five times.
   e. Initiate the analysis sequence.
   f. Set the blank following the procedure outlined in the operator's instruction manual.

[†]Liquid fertilizer samples do not require the addition of sucrose; therefore, sucrose is not used for blank determination when analyzing liquid fertilizer samples. When determining the blank for liquid fertilizers, a 502-343 Nickel Boat Liner should be added to the 528-203 Ceramic Combustion Boat.

Note: The standard deviation of the last three blanks should be less than or equal to 0.001% (10 ppm) when utilizing helium as a carrier gas, and less than or equal to 0.005% (50 ppm) when utilizing argon as a carrier gas. Additional blanks beyond the recommended five may be required in order to achieve the recommended precision.

4. Calibrate/Drift Correct.
   a. Select the desired number of calibration/drift replicates in the Login screen (minimum of five).
   b. Weigh ~ 0.10 g of NIST 913b Uric Acid or another suitable reference material into a 528-203 Ceramic Combustion Boat.
   c. Enter sample mass and identification into the Login screen.
   d. Add ~ 0.4 g of ground sucrose to the reference material and mix thoroughly.
   e. Transfer the ceramic combustion boat containing the reference material mixed with sucrose to the appropriate position in the autoloader.
   f. Repeat steps 4b through 4e a minimum five times for each calibration/drift sample used.
   g. Initiate the analysis sequence.
   h. Calibrate or Drift Correct the instrument following the procedure outlined in the operator's instruction manual.
   i. Verify the calibration by analyzing ~ 0.1g of another appropriate reference material following steps 4b through 4g, and confirm that the results are within the acceptable tolerance range for that material.

Note: A multi-point calibration (fractional weight or multiple calibration samples) may be used to calibrate if desired. Typically, the LECO CN/FP928 can be calibrated using several replicates of a single mass range (0.1 g) of uric acid or other suitable reference material utilizing a single standard calibration. This is a cost-effective and simple process. The calibration can be verified by analyzing different compounds such as ammonium sulfate (~ 0.1 g) and/or urea (~ 0.1 g).

5. Analyze samples (powder/granular samples).
   a. Select the desired number of sample replicates in the Login screen.
   b. Weigh ~ 0.1 g of the fertilizer sample into a 528-203 Ceramic Combustion Boat.
   c. Enter sample mass and identification information into the Login screen.
   d. Add ~ 0.4 g of ground sucrose to the sample and mix thoroughly.
   e. Transfer the ceramic combustion boat containing the sample mixed with sucrose to the appropriate position in the autoloader.
   f. Repeat steps 5b through 5e for each sample to be analyzed.
   g. Initiate the analysis sequence.
6. Analyze samples (liquid samples).
   a. Select the desired number of sample replicates in the Login screen.
   b. Place a 502-343 Nickel Boat Liner into a 528-203 Ceramic Combustion Boat.
   c. Weigh ~ 0.1 g to 2.0 g (depending on the nitrogen concentration) of the liquid fertilizer sample into the Nickel boat liner within the ceramic combustion boat.
   d. Enter sample mass and identification information into the Login screen.
   e. Transfer the ceramic combustion boat/nickel boat liner containing the sample to the appropriate position in the autoloader.
   f. Repeat steps 6b through 6e for each sample to be analyzed.
   g. Initiate the analysis sequence.

Notes:

! *Liquid reference material and liquid fertilizer samples do not require the addition of sucrose.*

! *If soot (carbon black) is observed in the primary filter (steel wool filter), the sample mass should be reduced to prevent further sooting. Some sample types will produce soot when analyzed at larger sample masses, and reducing the sample mass will prevent soot from building up in the primary filter.*

TYPICAL RESULTS

Data was generated utilizing a single standard, forced through origin calibration using ~ 0.1 g of NIST 913b Uric Acid (33.23% N). Alternatively, LECO 503-530 LCRM Urea may be used for calibration.

	10 cm^3 Helium		3 cm^3 Helium		10 cm^3 Argon		3 cm^3 Argon	
	Mass (g)	*% N*	*Mass (g)*	*% N*	*Mass (g)*	*% N*	*Mass (g)*	*% N*
Urea	0.1038	46.78	0.1030	46.67	0.0985	46.63	0.1007	46.51
Sigma Aldrich	0.1001	46.69	0.0960	46.78	0.1011	46.66	0.1053	46.59
Lot: SLBH9709V	0.1067	46.63	0.0958	46.70	0.0993	46.67	0.1065	46.57
Theoretical Value:	0.1023	46.49	0.1047	46.72	0.1034	46.80	0.1002	46.07
46.65% N	0.1035	46.59	0.1034	46.73	0.0986	46.71	0.1084	46.65
	0.1020	46.73	0.0996	46.70	0.1095	46.74	0.1003	46.65
	0.1003	46.80	0.0975	46.69	0.0998	46.82	0.0994	46.34
	0.0988	46.68	0.1040	46.58	0.0997	46.75	0.1056	46.49
	0.1023	46.63	0.1049	46.76	0.1001	46.68	0.1052	46.60
	0.1050	46.53	0.1024	46.67	0.0919	46.70	0.0968	46.54
	Avg =	***46.66***	***Avg =***	***46.70***	***Avg =***	***46.72***	***Avg =***	***46.50***
	s =	***0.10***	***s =***	***0.06***	***s =***	***0.06***	***s =***	***0.18***
Ammonium Sulfate	0.1013	21.36	0.1081	21.16	0.1095	21.22	0.1028	21.09
Sigma Aldrich	0.0992	21.12	0.1045	21.15	0.1035	21.16	0.0958	21.24
Lot: MKBN1032V	0.0999	21.19	0.0972	21.15	0.0983	21.18	0.0944	21.14
Theoretical Value:	0.1083	21.14	0.0995	21.21	0.1022	21.20	0.1053	21.10
21.20% N	0.1026	21.24	0.0992	21.19	0.1004	21.21	0.1009	21.15
	0.1011	21.18	0.1091	21.16	0.1030	21.20	0.0976	21.19
	0.1062	21.25	0.1021	21.16	0.1043	21.21	0.0993	21.06
	0.0955	21.24	0.1044	21.18	0.0980	21.28	0.0964	21.09
	0.0963	21.20	0.1022	21.17	0.1107	21.15	0.1034	21.03
	0.0987	21.10	0.0946	21.22	0.1018	21.15	0.0982	21.17
	Avg =	***21.20***	***Avg =***	***21.18***	***Avg =***	***21.20***	***Avg =***	***21.13***
	s =	***0.08***	***s =***	***0.02***	***s =***	***0.04***	***s =***	***0.06***
Potassium Nitrate	0.1070	13.82	0.1032	13.84	0.0920	13.91	0.0921	13.76
Sigma Aldrich	0.0983	13.86	0.0963	13.87	0.0925	13.88	0.1040	13.85
Lot: ER07220BR	0.0966	13.78	0.1058	13.86	0.0983	13.80	0.0952	13.86
Theoretical Value:	0.0923	13.87	0.1090	13.62	0.0962	13.79	0.0995	13.77
13.8% N	0.0953	13.85	0.1026	13.69	0.0951	13.85	0.1041	13.79
	0.1002	13.82	0.1012	13.97	0.0917	13.80	0.1015	13.83
	0.1097	13.90	0.1017	13.86	0.1032	13.80	0.1087	13.83
	0.1000	13.85	0.1007	13.94	0.1006	13.86	0.0977	13.81
	0.1000	13.87	0.1090	13.88	0.0993	13.80	0.0994	13.71
	0.0936	13.87	0.0985	13.80	0.1003	13.88	0.1077	13.98
	Avg =	***13.85***	***Avg =***	***13.83***	***Avg =***	***13.84***	***Avg =***	***13.82***
	s =	***0.03***	***s =***	***0.11***	***s =***	***0.05***	***s =***	***0.07***
Ammonium	2.0186	0.012	1.9936	0.010	2.0136	0.013	1.9829	0.012
LECO 502-601	2.0226	0.012	1.9591	0.011	2.0579	0.013	2.0192	0.015
Lot: CT-0435	2.0089	0.012	2.0482	0.012	2.0469	0.011	2.0567	0.020
Certified Value:	2.1602	0.012	2.0234	0.011	2.1141	0.011	2.0136	0.012
0.01% N	2.0492	0.011	2.0981	0.011	2.0736	0.009	2.0113	0.019
	2.0647	0.010	1.9916	0.010	2.0828	0.008	2.0453	0.009
	2.0504	0.010	2.0174	0.010	2.0124	0.007	2.0150	0.012
	2.0238	0.010	2.1771	0.010	2.0463	0.011	2.0570	0.011
	2.0134	0.009	2.0850	0.010	2.0785	0.011	2.0184	0.014
	2.0346	0.011	2.0510	0.009	2.7725	0.013	2.0035	0.014
	Avg =	***0.011***	***Avg =***	***0.010***	***Avg =***	***0.011***	***Avg =***	***0.014***
	s =	***0.001***	***s =***	***0.001***	***s =***	***0.002***	***s =***	***0.003***
Ammonium	1.0140	0.097	1.0967	0.099	1.0503	0.100	1.0948	0.103
LECO 502-602	1.0122	0.097	1.0189	0.099	1.0508	0.098	1.0417	0.105
Lot: CT-0859	1.1113	0.096	1.1251	0.100	1.1191	0.099	1.0623	0.109
Certified Value:	1.0153	0.098	1.1218	0.101	1.0899	0.096	1.0132	0.110
0.10% N	1.0006	0.098	1.0379	0.100	1.0175	0.098	1.0765	0.102
	1.0077	0.098	1.1665	0.099	1.0207	0.103	1.0313	0.111
	1.0465	0.099	1.2596	0.100	1.0366	0.104	1.0199	0.099
	0.9990	0.101	1.1228	0.099	1.0093	0.106	1.0292	0.098
	1.0699	0.099	1.0928	0.101	1.0183	0.105	1.0404	0.108
	1.1192	0.100	1.2308	0.104	1.0377	0.104	1.0216	0.101
	Avg =	***0.098***	***Avg =***	***0.100***	***Avg =***	***0.101***	***Avg =***	***0.105***
	s =	***0.001***	***s =***	***0.001***	***s =***	***0.003***	***s =***	***0.005***

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