Application Note

Instrument: FP928

Determination of Nitrogen in Plastics

LECO Corporation; Saint Joseph, Michigan USA

Introduction

The plastics industry is currently one of the largest manufacturing industries worldwide and shows continued growth. Plastics have a wide array of applications such as packaging, medical supplies, automotive parts, insulation, and many more. Plastics consist of a wide range of synthetic or semi-synthetic materials, such as polyethylene terephthalate (PET), which are composed of polymers. Compounds containing Nitrogen are commonly used in the manufacturing of plastic materials such as initializers, plasticizers, stabilizers, and various polymerization modifiers. These compounds play an important role in the physical and mechanical properties of the plastic material. The determination of Nitrogen is crucial in the material characterization and quality control procedures for the manufacturing and molding process of plastic materials.

The classical method utilized for Nitrogen determination in organic materials is the Kjeldahl method which involves sample digestion, distillation, and ammonia determination typically by titration. This method involves time-consuming sample preparation and the use of hazardous materials. The LECO FP928 is a Nitrogen determinator that utilizes an automated Dumas combustion method and provides accurate and precise results in approximately five minutes. This eliminates involved sample preparation and the use of hazardous materials resulting in a cost-effective method for the quality control of plastic production.

Instrument Model and Configuration

The LECO FP928 is a macro combustion Nitrogen determinator that utilizes a pure Oxygen environment in a high-temperature horizontal ceramic combustion furnace, using ceramic or Nickel combustion boats designed to handle macro sample masses (~1.0 g). 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 carrier gas (Helium or Argon) for analysis. The aliquot of gas is carried through a heated reduction tube, filled with Copper, to convert Nitrogen Oxide combustion gas species (NO_x) to Nitrogen (N_2). The aliquot gas is then carried to a thermal conductivity cell (TC) for the detection of Nitrogen (N_2).

Thermal conductivity detectors work by detecting changes in the thermal conductivity of the analyte gas compared to 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 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.

Note: When changing carrier gas type, the flow needs to be adjusted following instructions provided in the 928 Series Operator's Instruction Manual. The aliquot dose loop size is changed by selecting the desired aliquot dose loop size in the software's Method Parameters.

Sample Preparation

Plastic pellets can typically be analyzed as received. Plastic sheet samples should be cut or folded to lay flat in the combustion boat. Care should be taken to not heat the samples when cutting, which could potentially alter their chemistry.

Accessories

528-203 Ceramic Combustion Boats* with 502-343 Nickel Boat Liners or 625-505-430 Nickel Boats*, deionized or distilled water, disposable pipettes.

**For optimal precision, ceramic and Nickel combustion boats should be baked in a muffle furnace at 1,000 °C for a minimum of 40 minutes. Once the combustion boats have cooled, they should be transferred to a desiccator for storage. If the combustion boats are not used within twenty-four hours, they should be re-baked. After baking, handle combustion boats with clean tongs only; do not use fingers.*

Reference Materials

Calibration should be performed using 502-602 Ammonium Solution (0.1% N). Verification can be performed using 502-601 Ammonium solution (0.01% N).

*Method Parameters***

Gas Type†	Helium
Furnace Temperature	800 °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††	Large (10 cm^3)

***Refer to 928 Series Operator's Instruction Manual for Parameter definitions.*

†Due to the decreased sensitivity of the TC cell when using Argon as a carrier gas, it is recommended that Helium be used as the carrier gas when analyzing samples with low Nitrogen content.

††Due to the low levels of Nitrogen in this sample matrix, a 10 cm^3 dose loop is recommended for optimal accuracy and precision.

Element Parameters**

Parameter	Helium (10 cm^3) Nitrogen
Integration Delay	0 s
Starting Baseline	10 s
Post Baseline Delay	20 s
Use Comparator	No
Integration Time	50 s
Use Endline	Yes
Endline Delay	30 s
Ending Baseline	5 s

***Refer to 928 Series 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

Analysis Considerations

The combustion of many types of plastics will result in some degree of sooting. Steps should be taken to reduce sooting, such as the addition of deionized or distilled water to the samples prior to analysis and reducing the furnace temperature to 800 °C. Reducing the sample mass may minimize sooting; however, care should be taken to not impact the lower detection capabilities of the method. It is important to monitor the primary filter tube for signs of sooting and change the glass wool and steel wool as necessary (approximately every 10 plastic samples).

Plastics containing high levels of halogens may require additional routine maintenance. It is important to monitor the primary filter tube for signs of excessive corrosion of the steel wool and change it as necessary. Increased inspection of the thermoelectric cooler may be necessary as well.

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 (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. Using a pipette, weigh ~2 ml of deionized or distilled water into a 528-203 Ceramic Combustion Boat lined with a 502-343 Nickel Boat Liner or a 625-505-430 Nickel Combustion Boat.
   c. Place the combustion boat containing the water in the appropriate position in the autoloader.
   d. Perform 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.

   Note: The standard deviation of the last five blanks should be less than or equal to 0.001% (10 ppm). 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. Using a pipette, weigh ~1.0 g of 502-602 Ammonium Solution (0.1% N) into a 528-203 Ceramic Combustion Boat lined with a 502-343 Nickel Boat Liner or a 625-505-430 Nickel Combustion Boat.
   c. Enter sample mass and identification into the Login screen.
   d. Tare the balance, and, using a pipette, add ~2 ml of deionized or distilled water to the combustion boat.
   e. Transfer the combustion boat containing the ammonium solution and water to the appropriate position in the autoloader.
   f. Perform steps 4b through 4e a minimum of five times.
   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 ~1.0 g of 502-601 Ammonium solution (0.01% N) with an additional ~2 ml of deionized or distilled water and confirm that the results are within the acceptable tolerance range.
5. Analyze Samples.
   a. Select the desired number of Sample replicates in the Login screen.
   b. Weigh ~1.0 g of the sample into a 528-203 Ceramic Combustion Boat lined with a 502-343 Nickel Boat Liner or a 625-505-430 Nickel Boat.
   c. Enter sample mass and identification information into the Login screen.
   d. Tare the balance, and, using a pipette, add ~2 ml of deionized or distilled water on top of the sample in the Combustion Boat.
   e. Transfer the combustion boat containing the sample and water to the appropriate position in the autoloader.
   f. Perform steps 5b through 5e for each sample to be analyzed.
   g. Initiate the analysis sequence.

‡*The same crucible option should be used for blank determination, calibration, and sample analysis.*

TYPICAL RESULTS

Data was generated utilizing a linear, force through origin calibration using 502-602 Ammonium Solution (0.1% N). The calibration was verified using 502-601 Ammonium Solution (0.01% N). All reference materials and samples were weighed and analyzed at ~1.0 g. Approximately 2 ml of deionized water was added to the samples prior to analysis to reduce sooting.

	10 cm^3 Helium	
	Mass (g)	*% N*
Polypropylene	1.0196	0.022
	0.9998	0.014
	1.0321	0.020
	1.0213	0.022
	1.0037	0.016
	Avg =	***0.019***
	s =	***0.004***
High Density Polyethylene	1.0192	0.012
	1.0108	0.009
	1.0233	0.010
	1.0334	0.012
	1.0536	0.010
	Avg =	***0.011***
	s =	***0.001***
Polyethylene Terephthalate	0.9925	0.017
	0.9934	0.013
	1.0015	0.015
	1.0094	0.013
	1.0048	0.013
	Avg =	***0.014***
	s =	***0.002***

LECO Corporation | 3000 Lakeview Avenue | St. Joseph, MI 49085 | Phone: 800-292-6141 | 269-985-5496
info@leco.com • www.leco.com | ISO-9001:2015 Certified | *LECO is a registered trademark of LECO Corporation.*
LCRM = LECO Certified Reference Material; LRM = LECO Reference Material and are registered trademarks of LECO Corporation.

