Application Note

Instrument: SC832DR

EMPOWERING RESULTS
Elemental Analysis | GC Mass Spectrometry | Metallography

Determination of Sulfur and Carbon in Lithium, Nickel, Manganese, and Cobalt Battery Materials

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Introduction

Lithium, Nickel, Manganese, and Cobalt (Li-NMC) batteries are a type of Lithium-ion battery that uses Li-NMC powder as the cathode material and a graphitic Carbon electrode with a metallic backing as the anode. Li-NMC batteries combine the benefits of Lithium with the three main elements used in different Lithium-ion battery cathodes: Nickel, Manganese, and Cobalt. Nickel cathodes on their own have high specific energy but are not very stable. Manganese cathodes are exceptionally stable but have a low specific energy. Cobalt cathodes have high specific energy but low specific power. Combining Lithium with the three different cathode materials yields a stable battery with a high specific energy suitable for high-load applications.

Carbon determination in Li-NMC is important as the Carbon content directly impacts the performance of this battery material. In addition, emerging battery technologies can take advantage of improved Sulfur utilization when Li-NMC is used as an additive, making Sulfur determination in the base material an important quality control procedure.

Instrument Model and Configuration

The LECO SC832DR is a macro combustion Sulfur and Carbon determinator. The instrument utilizes a pure Oxygen environment in a high-temperature, horizontal, ceramic combustion furnace designed to handle macro sample masses. A weighed sample is combusted, and the combustion gases are swept from the furnace and passed through anhydrone for the removal of moisture. The combustion gases are then carried to non-dispersive infrared (NDIR) cells for the detection of Sulfur (as SO_2) and Carbon (as CO_2).

NDIR cells function on the principle that SO_2 and CO_2 absorb infrared (IR) energy at unique wavelengths within the IR spectrum. Incident IR energy at these wavelengths is absorbed as the analyte gases pass through the IR absorption cells, with the absorption being dependent upon the path length of the cell. The Dual Range (DR) SC832 model has a wider Sulfur range due to the use of both a short and long path length IR cell for Sulfur determination. This allows for the measurement of both high and low range Sulfur signals. The software automatically selects which cell to use for optimum Sulfur determination using the SC832DR.

Sample Preparation

Samples should be a uniform, representative powder or granular material.

Note: Please reference the appropriate Safety Data Sheets (SDS) for safe handling of all materials and samples.

Accessories

528-203 Ceramic Combustion Boats*, 502-321 Com-Cat™, 761-929 Crucible Tongs, and 501-614 Spatula

**For optimal precision, combustion boats should be baked in a muffle furnace at 1,000 °C for a minimum of one hour prior to use. Once the combustion boats have cooled, they should be transferred to a desiccator for storage until use. 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

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

General Parameters

Furnace Temperature	1450 °C
Lance On Delay	20 s
Manual Loading Model	Single Sample
Nominal Mass	1.0000 g
Cooling Delay	0 s

Element Parameters

Parameter	*Sulfur*	*Carbon*
Wait for Baseline Stability	Yes	Yes
Starting Baseline	2 s	2 s
Use Comparator	Yes	Yes
Comparator Level	1.00 %	1.00 %
Minimum Integration Time	160 s	90 s
Maximum Integration Time	450 s	180 s
Range Select	Auto	--
Range Lower Limit	800	--
Range Upper Limit	950	--
Automatically Started Analyses		
Auto Detect Data Missed Time	3 s	3 s
Low Cell Autostart Level	0.010 V	--
High Cell Autostart Level	0.010 V	--
Autostart Level	--	0.010 V
Manually Started Analyses		
Integration Delay	0 s	0 s

Note: Refer to the 832 Series Operator's Instruction Manual for parameter definitions.

Procedure

1. Prepare instrument for operation as outlined in the operator's instruction manual.
2. Condition the System.
   a. From the Analysis Screen, use the Login Bar to add three sample replicates.
   b. Weigh ~0.25 g of a similar matrix (to Li-NMC) into a pre-baked 528-203 Ceramic Combustion Boat.
   c. Enter sample mass and identification into the Analysis Screen.
   d. Tare the combustion boat containing the sample and add ~1.0 g of 502-321 Com-Cat. Mix the Com-Cat thoroughly with the sample and spread the mixture evenly within the combustion boat.
   e. Place the combustion boat containing the sample and Com-Cat in front of the furnace entrance (for manual loading systems), or into the appropriate position in the autoloader.
   f. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the combustion boat containing the sample into the furnace and press the Analyze button.
   g. Perform steps 2b through 2e (or 2b through 2f for manual loading systems) three times.
   h. For auto-loading systems, initiate the analysis sequence.
3. Determine Blank.
   a. From the Analysis Screen, use the Login Bar to add five or more blank replicates.
   b. Weigh ~1.0 g of 502-321 Com-Cat into a pre-baked 528-203 Ceramic Combustion Boat and spread the material evenly within the combustion boat.
   c. Place the combustion boat containing the Com-Cat in front of the furnace entrance (for manual loading systems) or place the required number of combustion boats containing Com-Cat (minimum of five) into the appropriate positions in the autoloader.
   d. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the combustion boat into the furnace and press the Analyze button.
   e. For manual loading systems, perform steps 3b through 3d a minimum of five times.
   f. For auto-loading systems, initiate the analysis sequence.
   g. Set the blank following the procedure outlined in the operator's instruction manual.

   Note: The standard deviation of the last three blanks should be less than or equal to 0.001 % (10 ppm) for both Sulfur and Carbon. Additional blanks beyond the recommended five may be required to achieve the recommended precision.
4. Calibrate/Drift Correct.
   a. From the Analysis Screen, use the Login Bar to add the desired number of calibration/drift replicates (minimum of five).
   b. Weigh an appropriate mass of a suitable reference material into a pre-baked 528-203 Ceramic Combustion Boat.
   c. Enter sample mass and identification into the Analysis Screen.
   d. Tare the combustion boat containing the reference material and add ~1.0 g of 502-321 Com-Cat. Mix the Com-Cat thoroughly with the reference material and spread the mixture evenly within the combustion boat.
   e. Place the combustion boat containing the reference material and Com-Cat in front of the furnace entrance (for manual loading systems), or into the appropriate position in the autoloader.
   f. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the combustion boat containing the sample into the furnace and press the Analyze button.
   g. Perform steps 4b through 4e (or 4b through 4f for manual loading systems) a minimum of five times for each calibration/drift sample used.
   h. For auto-loading systems, initiate the analysis sequence.
   i. Calibrate or drift correct the instrument following the procedure outlined in the operator's instruction manual.
   j. Verify the calibration/drift correction by analyzing an appropriate mass of another/different suitable reference material, following steps 4b through 4h, and confirm that the results are within the acceptable tolerance range.
5. Analyze Samples.
   a. From the Analysis Screen, use the Login Bar to add the desired number of sample replicates.
   b. Weigh ~0.25 g of the sample into a pre-baked 528-203 Ceramic Combustion Boat.
   c. Enter sample mass and identification into the Analysis Screen.
   d. Tare the combustion boat containing the sample and add ~1.0 g of 502-321 Com-Cat. Mix the Com-Cat thoroughly with the sample and spread the mixture evenly within the combustion boat.
   e. Place the combustion boat containing the sample and Com-Cat in front of the furnace entrance (for manual loading systems), or into the appropriate position in the autoloader.
   f. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the combustion boat containing the sample into the furnace and press the Analyze button.
   g. Perform steps 5b through 5e (or 5b through 5f for manual loading systems) for each sample to be analyzed.
   h. For auto-loading systems, initiate the analysis sequence.

Typical Results

Data was generated utilizing a linear, force through origin calibration using LECO 502-914 (Lot 1005) LCRM Synthetic Carbon and Sulfur (1.03 % C, 1.00 % S). The calibration was verified using LECO 502-964 (Lot 1001) LCRM Synthetic Carbon and Sulfur (0.12 % C, 0.10 % S). Samples and reference materials were mixed with ~1.0 g of LECO 502-321 Com-Cat prior to analysis.

Samples	*Mass (g)*	*Sulfur (%)*	*Carbon (%)*
Li-NMC Sample 1	0.2517	<0.0014**	1.151
Li-NMC Oxide	0.2546	<0.0014**	1.149
Sigma Aldrich	0.2510	<0.0014**	1.149
Part Number: 761001	0.2532	<0.0014**	1.150
	0.2517	<0.0014**	1.145
	$\bar{x}$ =	**--**	***1.149***
	***s* =**	**--**	***0.002***
Li-NMC Sample 2	0.2530	0.135	0.075
Li-NMC 111	0.2542	0.137	0.075
BAM	0.2513	0.137	0.075
Part Number: S014	0.2547	0.138	0.074
0.1421 ±0.0071 % S	0.2504	0.138	0.074
	$\bar{x}$ =	***0.137***	***0.075***
	***s* =**	***0.001***	***0.001***

***Results were below the lower detection limit of the instrument.*
$\bar{x}$ = Sample Mean; s = Sample Standard Deviation

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