

Instrument: SC832DR

Determination of Sulfur and Carbon in Lithium Iron Phosphate Battery Materials

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Introduction

Lithium Iron Phosphate (LiFePO₄) batteries are a type of Lithium-ion battery that uses LiFePO₄ powder as the cathode material and a graphitic Carbon electrode with a metallic backing as the anode. Lithium Iron Phosphate, also called LFP, is a crystalline, grey-to-black powder with an olivine crystal structure. This unique crystal structure facilitates efficient diffusion of Lithium-ions. Lithium Iron Phosphate offers good electrochemical performance, low resistance, and is one of the safest and most stable cathode materials available for Lithium-ion batteries.

Carbon determination in LiFePO₄ 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 LiFePO₄ is used as an additive, making Sulfur determination in the base material an important quality control parameter.

Instrument Model and Configuration

The LECO SC832DR is a macro combustion Carbon and Sulfur determinator. The instrument utilizes a pure Oxygen environment in a high-temperature, horizontal, ceramic, combustion furnace that is designed to handle macro sample masses. A weighed sample is combusted and the combustion gases are swept from the furnace and passed through anhydrous for the removal of moisture. The combustion gases are then carried to non-dispersive infrared (NDIR) cells for the detection of Carbon (as CO₂) and Sulfur (as SO₂).

NDIR cells function based on the principle that CO₂ and SO₂ absorb infrared (IR) energy at unique wavelengths within the IR spectrum. Incident IR energy at these wavelengths is absorbed as the gases pass through 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.



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 1 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

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

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
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Note: Refer to 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 LiFePO_4) 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 in order 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 1004) LCRM Synthetic Carbon and Sulfur (0.99 % C, 0.97 % S) and LECO 502-905 (Lot 1003) LCRM Synthetic Carbon (5.00 % C). The calibration was verified using LECO 502-964 (Lot 1001) LCRM Synthetic Carbon and Sulfur (0.12 % C, 0.10 % S) and LECO 502-909 (Lot 1003) LCRM Ore (0.18 % C, 0.67 % 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 (%)
LiFePO₄ Sample 1	0.2518	<0.0014**	<0.007**
Sigma Aldrich	0.2516	<0.0014**	<0.007**
PN: 759546	0.2534	<0.0014**	<0.007**
	0.2526	<0.0014**	<0.007**
	0.2531	<0.0014**	<0.007**
	\bar{x} =	--	--
	s =	--	--
LiFePO₄ Sample 2	0.2527	0.0132	1.162
	0.2523	0.0129	1.154
	0.2531	0.0135	1.154
	0.2530	0.0132	1.153
	0.2523	0.0133	1.154
	\bar{x} =	0.0132	1.155
	s =	0.0002	0.004
LiFePO₄ Sample 3	0.2531	0.0164	1.307
MSE Supplies	0.2539	0.0165	1.308
PN: PO0127	0.2508	0.0162	1.311
	0.2516	0.0163	1.306
	0.2513	0.0161	1.310
	\bar{x} =	0.0163	1.308
	s =	0.0002	0.002

**Results were below the lower detection limit of the instrument.

\bar{x} = Sample Mean; s = Sample Standard Deviation