Determination of Total Sulfur in Refractory Samples: Comparing Various Elemental Analysis Techniques

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Introduction

Total sulfur determination in refractory materials is a common analysis that has been historically performed with resistance or induction furnace instruments. Many factors influence which furnace style is optimal, such as water content (free and crystalline), the presence of organic binders, and decomposition temperature. Instruments with resistance furnaces are better suited for the analysis of materials with elevated moisture or organic content, and require the use of promoters to achieve full sulfur recovery. Induction furnace instruments are better suited for the analysis of materials with high decomposition temperatures, and also require the use of combustion promoters. New resistance furnace technology with elevated analysis temperature capabilities, up to 1550 °C, allow for new methods in the analysis of refractory materials without the use of combustion promoters.

This poster presentation will compare the results of total sulfur determination by various elemental analysis techniques featuring an induction furnace instrument and resistance furnace instruments, with and without the use of combustion promoters. Data will be examined that includes refractory materials such as lime, limestone, glass, cement, and other industrial raw materials.

Published Methods

- ASTM C25: Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
- ASTM C114: Standard Test Methods for Chemical Analysis of Hydraulic Cement
- ASTM E1915: Standard Test Methods for Analysis of Metal Bearing Ores and Related Materials for Carbon, Sulfur, and Acid-Base Characteristics

Methodology

S744

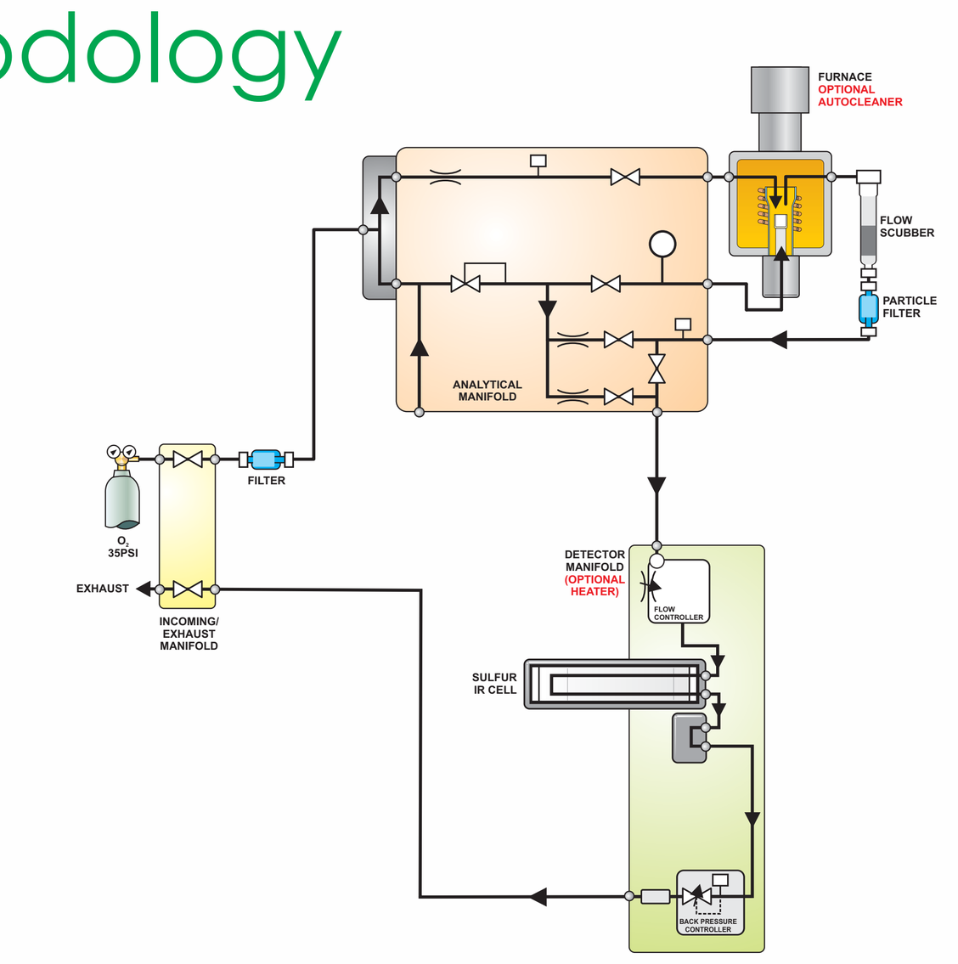

Figure 1: S744 Flow Diagram

The S744 sulfur analyzer is an induction furnace system designed for determination of sulfur content of metals, ores, ceramics, and other inorganic materials.

A pre-weighed sample is placed in a crucible and combusted, with aid from a combustion accelerator, in a stream of purified oxygen using radio-frequency (RF) induction to heat the sample. Sulfur present in the sample is liberated as sulfur dioxide (SO_2) and swept by the oxygen carrier through a dust filter, and a drying reagent. The combustion gases then pass through a non-dispersive infrared cell (NDIR), for detection of sulfur as SO_2.

The use of combustion accelerators is required for analysis of most materials. The accelerators will inductively couple with the sample material, hastening combustion and acting as a flux to ensure a completely fluid melt, which is essential for oxidation of sulfur species in a relatively short time frame. When analyzing nonconductive materials, such as limestone, lime, cements, and glass, the use of an accelerator with good inductive capabilities, such as iron, is essential. Typically, for sulfur determination, a combination of tungsten, tin, and iron accelerators are utilized for analysis.

S832DR

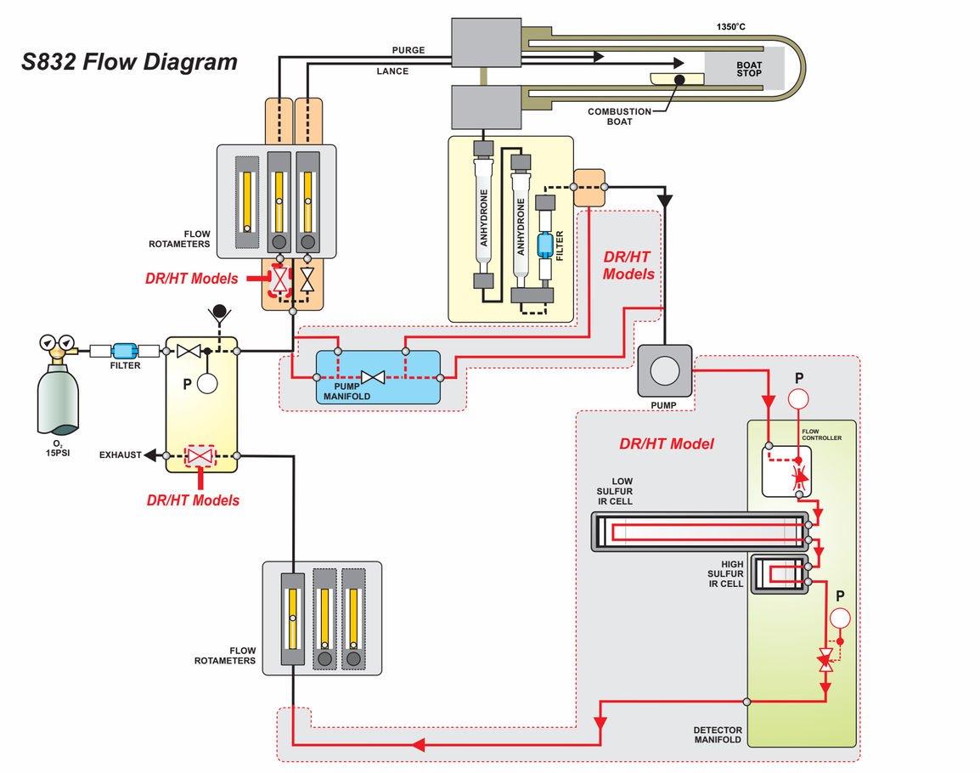

Figure 2: S832DR/S832HT Flow Diagram

The S832 sulfur analyzer is a resistance furnace system designed for determination of sulfur content in a multitude of matrices from coals, cokes, graphitic compounds, ores, and cements to soils, plant tissues, and fertilizers.

Analysis begins as a sample is weighed into a combustion crucible and may be mixed with a promotor, such as Com-Cat™. The sample is then introduced into a resistance furnace with a pure oxygen environment heated to 1350-1550 °C. Sulfur present in the sample is liberated as sulfur dioxide (SO_2) and the gases are swept from the furnace by the oxygen carrier. The liberated gases are then passed through a drying agent and on to the flow controller, setting the flow of the combustion gases through the non-dispersive infrared (NDIR) sulfur detection cells.

For the purposes of this poster presentation, the S832DR and S832HT models will be examined. The S832DR model has two sulfur NDIR cells providing the widest sulfur range and improved precision in samples with low sulfur compositions. The maximum temperature of 1450 °C for the furnace is utilized for this method and also requires the addition of the combustion promoter Com-Cat™ to the sample. The S832HT model also has two sulfur NDIR cells providing the widest sulfur range and improved precision in samples with low sulfur compositions. In addition, the S832HT has the ability to support a furnace temperature of 1550 °C. The higher furnace temperature allows for sample analysis to be performed without the use of a combustion promoter.

Background Information

Current combustion instrumentation methodology requires the use of combustion promoters/accelerators to achieve full sulfur recoveries in refractory samples, which consequently increases the cost-per-analysis. Additionally, material characteristics, such as water content and decomposition temperature, restrict some materials to analysis on a specific combustion instrument furnace type. This presents an issue when multiple matrices are required to be analyzed for sulfur with some of the materials containing organic constituents, moisture, or crystalline water. Often this situation will require the use of multiple instrument types.

Limitations of Current Methodology

Water and the S744

The presence of water in a sample material can impact sulfur recoveries on induction furnace instruments, such as the LECO S744. The water present will react with the sulfur dioxide produced during combustion/decomposition, causing low analyte recovery. This water can be present in the sample as either residual or crystalline forms. Residual water can be removed by drying the material at 105 °C for one hour. However, crystalline water requires much higher temperatures (up to 1300 °C) for removal from the sample material. These elevated temperatures can also result in the loss of sulfur species. The water produced during combustion of hydroxides, such as Calcium Hydroxide, will also have the same effect on reducing sulfur recovery. As such, hydrated, hydride, and hydroxide samples are typically analyzed for sulfur using resistance furnace instruments, such as the S832DR/S832HT.

Temperature Limitations and the S832DR

Resistance furnace technology currently being employed for sulfur analysis of refractory materials has a maximum temperature range of 1450 °C. This temperature is sufficient to facilitate decomposition of most sulfur matrices, but will require the addition of a combustion promoter to achieve complete analyte recovery from refractory materials. The new high temperature resistance furnace model of the LECO S832 (S832HT) allows for a maximum sustained furnace temperature of 1550 °C. This elevated furnace temperature facilitates full sulfur analyte recovery in refractory materials without the use of a combustion promoter. This new high temperature model allows for a reduction of the cost-per-analysis and allows for a single instrument to be utilized for the analysis of a wide range of sulfur- containing materials.

Analysis Time and the S832DR/S832HT

A major factor in determining the appropriate instrumentation for analysis of refractory materials is the analysis time of the respective instruments. The analysis time will not only determine the sample throughput, but will also play a role in the effective cost-per-analysis. Due to the lower furnace temperatures utilized by the S832 instruments, analysis times of three to six minutes are typically observed when analyzing refractory materials. The S832DR demonstrates the shortest time of analysis of this instrument type, likely due to the orthophosphate flux present in the Com-Cat™ combustion promoter used for analysis. The elevated temperatures of the S744 analyzer, typically ~1800 °C, and use of combustion accelerators demonstrated analysis times of two minutes for all refractory materials. This allows the S744 analyzer to have the highest sample throughput of all instrument types examined in this presentation.

Sample Preparation

To achieve the most accurate and precise results, a representative and uniform sample is required for analysis. It is recommended that samples are ground to pass through a No. 100 (150 micron) sieve to ensure sample homogeneity. For the purposes of this poster presentation, a sample mass of 100 to 250 mg was utilized for analysis on all instruments.

S832DR – 1450 °C Analysis

For analysis of the sample set on the LECO S832DR, a sample of homogenized material is accurately weighed into a pre-baked LECO 528-203 Combustion Crucible*. The sample mass and identification are entered into the instrument software, and the weighed sample is then mixed with ~1.0 g LECO 502-321 Com-Cat™.

S832HT – 1550 °C Analysis

For analysis of the sample set on the LECO S832HT, a sample of homogenized material is accurately weighed into a pre-baked LECO 528-203 Combustion Crucible*. The sample mass and identification are entered into the instrument software, and the sample is analyzed without additional preparation or combustion promoter.

S744 – Induction Furnace Analysis

For analysis of the sample set on the LECO S744, a sample of homogenized material is accurately weighed into a pre-baked LECO 528-018HP Combustion Crucible*. The sample mass and identification are entered into the instrument software. The sample is then covered with ~1.0 g LECO 502-173 LECOCEL II HP and ~1.0 g LECO 502-231 HP Iron Chip Accelerator.

*Prior to analysis, LECO 528-203 Combustion Crucibles are pre-baked at 1000 °C for one hour and cooled in a desiccator until time of use. LECO 528-018HP Combustion Crucibles are pre-baked at 1350 °C for 15 minutes and cooled in a desiccator until time of use.

Results

Calibration and Verification

To allow for a direct comparison of the analysis techniques, an effort was made to utilize similar calibration schemes for each instrument and matrix type. For the data that will be examined in this poster presentation, two different calibration schemes were utilized.

For the NIST Soda Lime Glass material, a Synthetic Carbon and Sulfur LECO Certified Reference Material (LCRM) was utilized for calibration. This Synthetic Carbon and Sulfur LCRM contains a refractory sulfur species with thermal decomposition characteristics similar to this sample matrix. For the data that will be examined, a linear, forced through origin calibration was utilized.

For all remaining sample types that we will examine in this poster presentation, a NIST Portland Cement reference material was utilized for calibration. The data generated for these materials also utilized a linear, forced through origin calibration.

These calibrations were verified, prior to data collection, utilizing a variety of LECO and NIST certified reference materials. These certified reference materials covered multiple sample matrices including, but not limited to, Portland cements, ores, fly ash, and limestone.

Sample Data

A sample suite was chosen to demonstrate the analytical performance and application capabilities of the three instrument types presented. These materials were chosen to cover a wide range of refractory matrices and raw materials that are typically analyzed for sulfur content and include limestone, hydrated lime, cement, fly ash, and soda-lime glass. Where possible, materials with certified total sulfur values were utilized to assess accuracy and precision.

Table 1: Determined sulfur results for all instruments

Sample	Number of Replicates		S832DR	S832HT	S744
NIST 1d Argillaceous Limestone 0.1028% S	n = 5	Sulfur Average (%)	0.108	0.109	0.105
		Std Dev (%)	0.001	0.002	0.005
		RSD (%)	0.93	1.83	4.76
Hydraulic Cement Commercial Grade	n = 5	Sulfur Average (%)	1.738	1.742	1.685
		Std Dev (%)	0.025	0.021	0.017
		RSD (%)	1.44	1.21	1.01
Hydrated Lime Commercial Grade	n = 5	Sulfur Average (%)	0.336	0.347	N/A
		Std Dev (%)	0.004	0.004	N/A
		RSD (%)	1.19	1.15	N/A
NIST 633a Portland Cement 0.8723% S	n = 5	Sulfur Average (%)	0.872	0.873	0.863
		Std Dev (%)	0.002	0.007	0.002
		RSD (%)	0.23	0.80	0.23
NIST 2690 Fly Ash @ 0.15% S	n = 5	Sulfur Average (%)	0.151	0.151	0.149
		Std Dev (%)	0.0004	0.001	0.001
		RSD (%)	0.26	0.66	0.67
NIST 80a Soda-Lime Glass (Beads) 0.087% S	n = 5	Sulfur Average (%)	N/A	0.084	0.084
		Std Dev (%)	N/A	0.004	0.001
		RSD (%)	N/A	4.76	1.19

The total sulfur results obtained for the sample suite, summarized in Table 1, indicate comparable analyte recoveries across all three instruments. As discussed previously, some analytical limitations were present when analyzing this sample suite. First, due to the elevated water content of Hydrated Lime, this material was not analyzed on the LECO S744. The water present in this material will react with sulfur dioxide produced during sample combustion/decomposition, causing low analyte recovery. This sample type is typically analyzed on resistance furnace combustion instruments only, such as the S832DR/S832HT analyzers. Secondly, due to the highly refractory nature of Soda-Lime Glass, this material was not analyzed on the LECO S832DR. It was determined that a furnace temperature of 1450 °C was insufficient to achieve full sulfur recovery, even with the use of a combustion promoter. Analysis of this material on the S832HT, at a furnace temperature of 1550 °C, produced comparable results to those obtained on the S744. Lastly, the S744 demonstrated the shortest analysis time for all samples examined, please refer to Table 2 below.

The shorter analysis time highlights the increased sample throughput associated with the induction furnace instruments, while still maintaining comparable analytical results. Data generated for this sample suite also indicates that the LECO S832HT will produce suitable results for refractory materials without the use of costly combustion promoters. Thus reducing the cost-per-analysis associated with analysis of these materials.

Table 2: Observed analysis times

Sample	S832DR	S832HT	S744
NIST 1d Argillaceous Limestone	4 min	5 min	2 min
Hydraulic Cement	3 min	4 min	2 min
Hydrated Lime	5 min	6 min	N/A
NIST 633a Portland Cement	3 min	5 min	2 min
NIST 2690 Fly Ash	3 min	4 min	2 min
NIST 80a Soda-Lime Glass	N/A	6 min	2 min

Cost-per-Analysis Comparison

The cost-per-analysis (CPA) of the instruments utilized for this poster presentation are comprised of costs associated with compressed gases, reagents, combustion accelerators, and a few hardware parts that will need replacement based upon instrument usage. For the purposes of this comparison, the costs associated with analysis time/sample throughput were not examined.

In addition to the robustness of the S832HT, comparison of the CPA of these instruments demonstrates another advantage of this analyzer. The elevated analysis temperature and subsequent elimination of the requirement for a combustion promoter reduced the S832HT CPA by ~$0.36/replicate, or a CPA reduction of ~46%, in comparison to the S832DR analyzer. Additionally, the CPA analysis demonstrates an improvement of the S832HT over the S744 analyzer. A CPA reduction of ~$0.21/replicate, or a CPA reduction of ~33%, was observed in comparison to the S744.

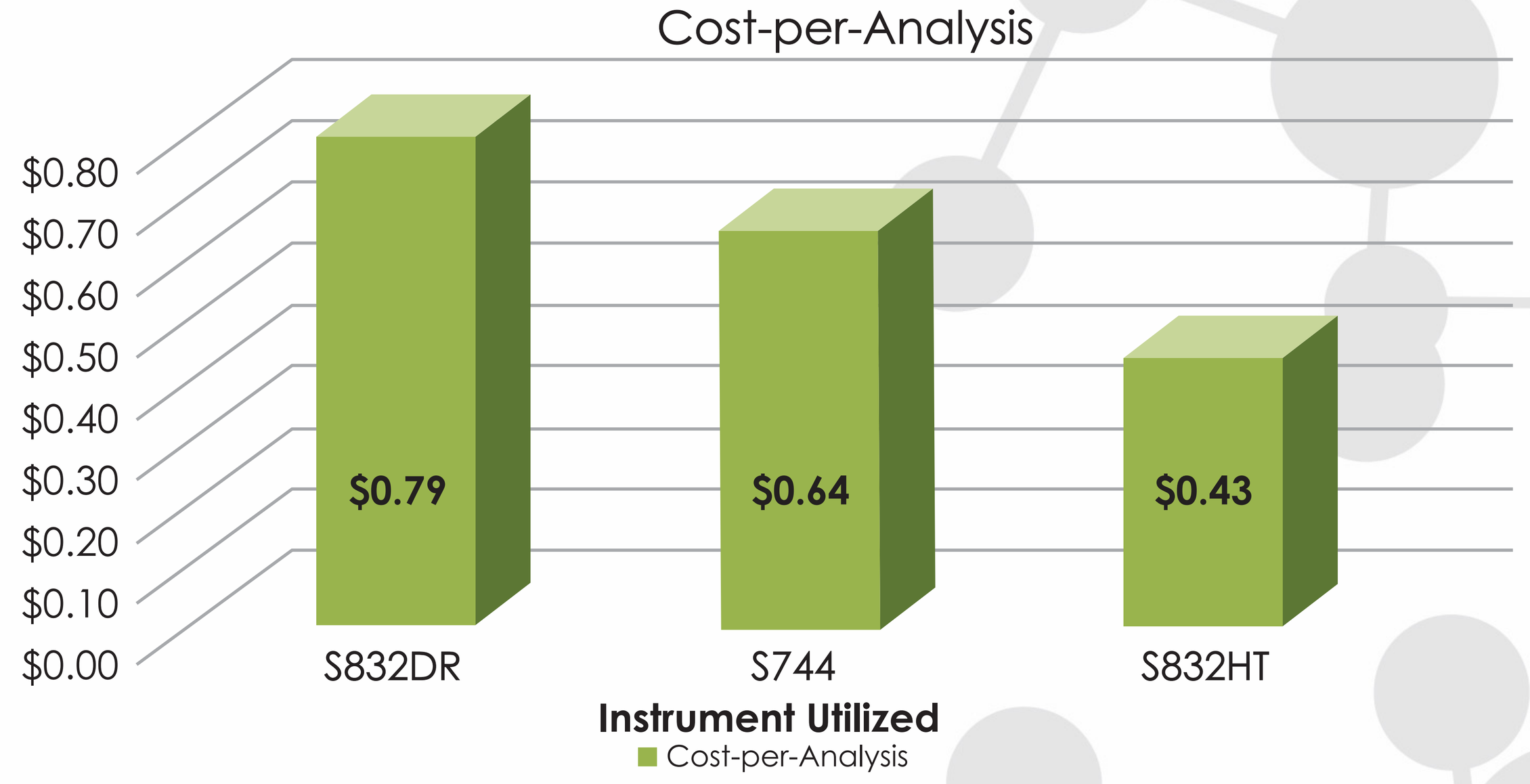

Figure 3: Cost-per-analysis summary for all instruments

Conclusion

The primary objective of this presentation was to demonstrate the analytical performance and application capability of LECO total sulfur analyzers that have been optimized for the analysis of refractory materials. The methods and results presented demonstrate that consistent results can be obtained when utilizing any of the instrumentation examined.

Analysis on the S832DR provides a shorter analysis time in comparison to the S832HT, while still allowing for the analysis of high moisture samples not applicable to the S744. The S744 analyzer demonstrates the shortest analysis time and highest furnace temperature of the instruments examined. This allows for the analysis of highly refractory materials, such as Soda-Lime Glass, to be performed in roughly two minutes, increasing sample throughput in comparison with the S832 resistance furnace instruments. The S832HT analyzer demonstrates a reduced cost-per-analysis, in comparison with the S832DR and S744 analyzers, while still maintaining analytical performance for all materials examined. Additionally, the S832HT potentially reduces the need for multiple instrument types for analysis of refractory materials, further lowering analysis costs.

Delivering the Right Results