Rapid, Acid-Free Analysis of Cathode Powders

Automated & quantitative determination of major elemental components and impurities

Laser Ablation | ICP Analysis | LaserTRAX Robotic System
Accurate and Precise | Solid Sample Analysis

Figure 1. LaserTRAX system with Avio 500 Series ICP

LaserTRAX: Robotic solid sample handling with automated barcode-reading for LA-ICP

Brief

Battery cathode materials are pressed into pellets and analyzed by laser ablation ICPOES (LA-ICP). Simplification of the sample preparation not only eliminates the need for the time-consuming, hazardous acid digestion steps, but also decreases the time from sample receipt to result to <5 minutes.

The novel method provides quantification of major elements and trace impurities in NMC powders with the benefits of:

1) Reduction in sample preparation time from 30-60 minutes to <3 minutes
2) Elimination of acid related to preparation and waste disposal
3) Major and trace elements determinations with a single automated method

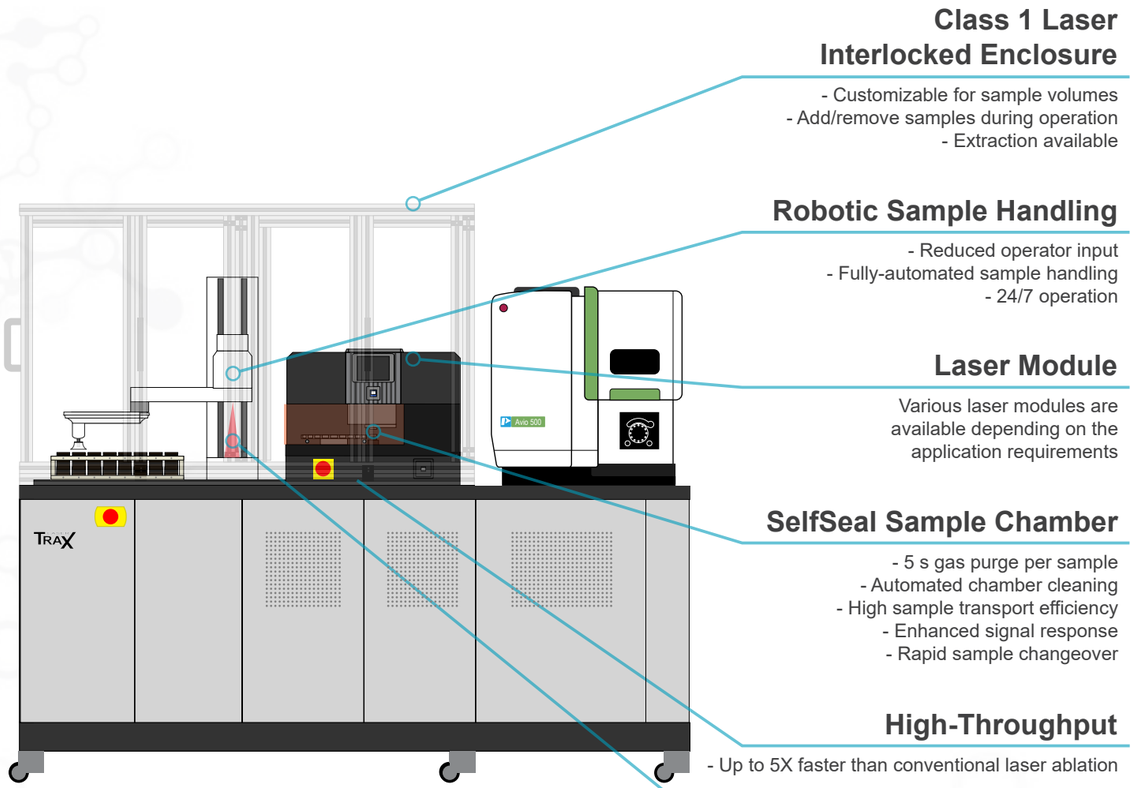

Figure 2. LaserTRAX features diagram

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Introduction

Cathode materials, such as $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC), have been identified as one of the most promising materials for improving the performance of batteries. The performance and qualities of these materials can be greatly impacted by the ratio of Ni-Mn-Co and Li, as well as the impurities in the materials. The analysis of these materials has been reliant on acid digestion and subsequent analysis, for example flame atomic absorption spectrometry (FAAS), complexometric titration, and solution-ICP. These methods are time-consuming, taking 30-60 minutes to digest a sample, all while generating hazardous waste.

LA-ICP completely eliminates all acid waste generated in the sample preparation process and in the operation of the ICP. In addition, samples can be prepared and analyzed in under 4 minutes; all while meeting requirements stated in Chinese Standard YS/T 798-2012. Battery materials, such as LFP, LCO, NMC, or NCA, can also be directly analyzed as a solid, with major and trace determination being done simultaneously.

LaserTRAX

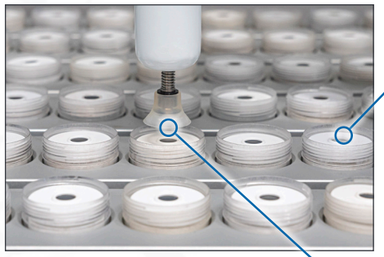
LaserTRAX is a next-generation, single-unit instrument that fully automates the process of sample handling, laser sampling, ICP detection, data reduction and report generation. LaserTRAX is capable of high-throughput (>500 pressed cathode samples per day) solid sampling. The system provides seamless sample flow by combining four main components (Figure 2):

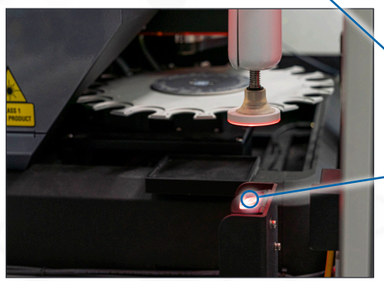
1) Sample delivery and ablation
   a. Robotic arm for sample loading
   b. Sample Changer (SC) carousel
   c. SelfSeal™ laser cell
2) ESL 266 laser (193nm also available)
3) ICP detection system (ICPMS also available)
4) ESL LaserTRAX software for seamless operation and LIMS compatible data reduction

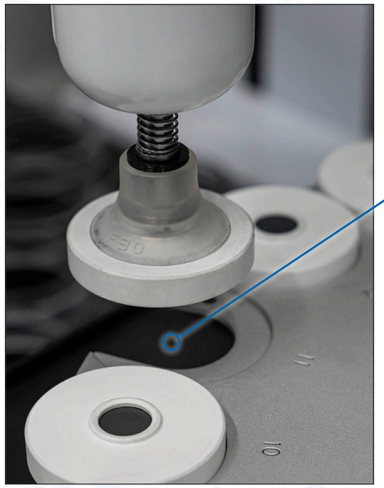
Operation is simplified through the LaserTRAX user interface. Once samples are loaded into the system, the user simply defines the number of samples and the frequency of blanks, standards, and QCs. The sequence is then generated and the user starts the analysis. Figure 3 shows the order of operation for this method.

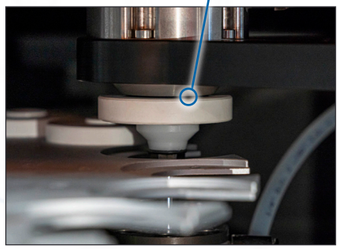
LaserTRAX Analytical Cycle

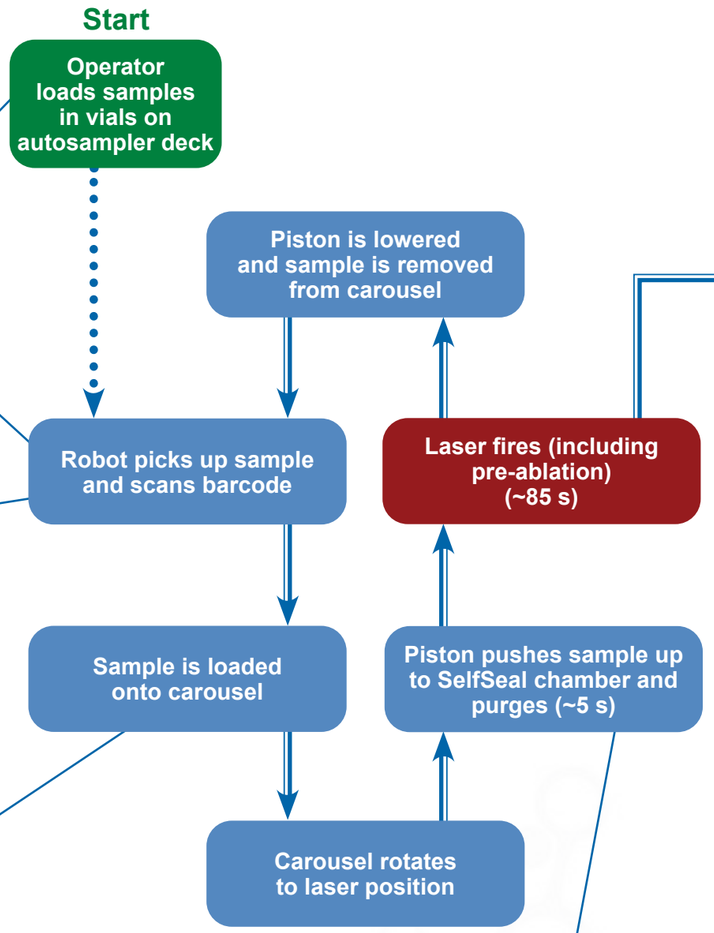
Robotic Sample Handling



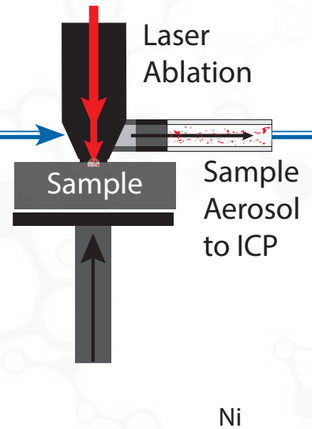


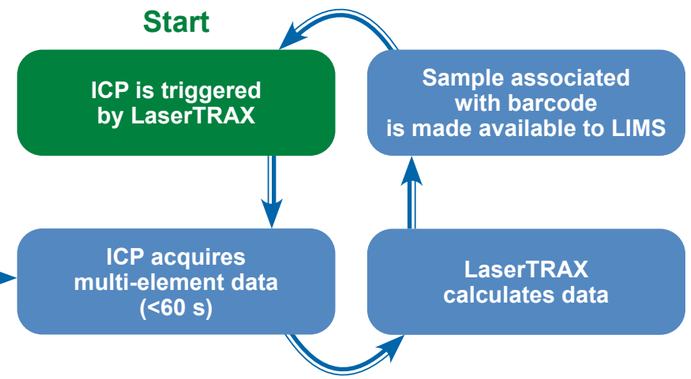






ICP Data Acquisition





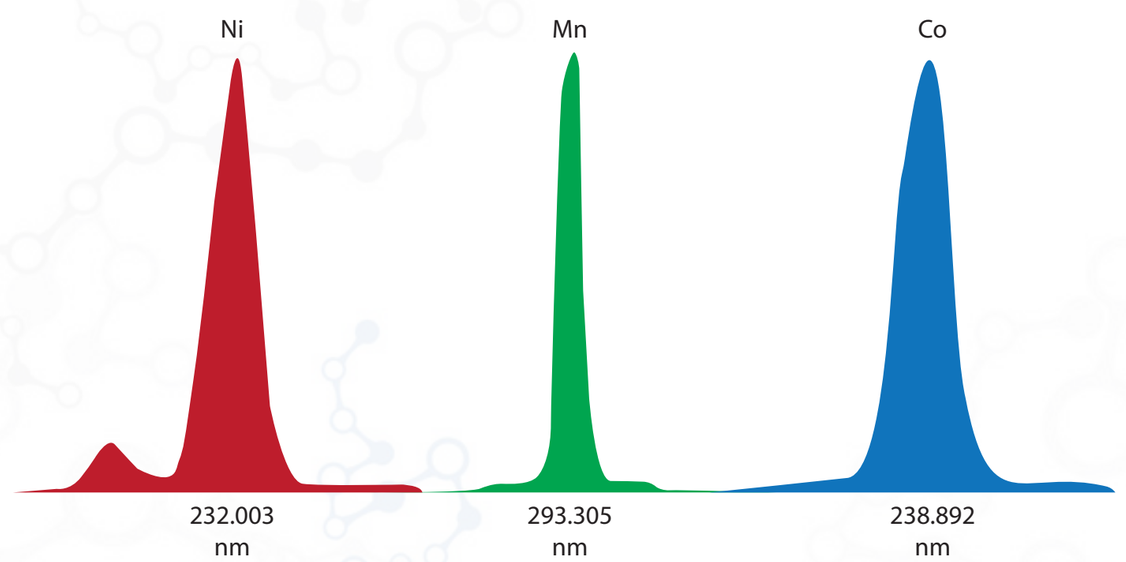


Figure 3. LaserTRAX sample to sample time is defined by the analytical conditions. In this example, the system is purged (5 s), a pre-ablation is done to remove any surface contamination (25 s), major components and trace impurities elements are measured (<60 s), cell is cleaned with N_2 purge and next sample is sealed (10 s) for a total analytical time of <2 minutes. During the analytical cycle, the robot unloads a previously analyzed sample, picks up the next sample, scans barcode, and loads next sample onto carousel.

Instrumentation

A PerkinElmer Avio 500 was implemented with the LaserTRAX for this application. A simultaneous instrument is required for this analysis because it acquires all analytes in one acquisition which produces more stable major component molar ratios. ICP parameters can be found in Table 1 and analyte information can be found in Table 2.

Sample and Standard Preparation

Three ternary cathode materials of different compositions were utilized in these experiments (Table 3). Three mixtures of NMC 111 and NMC 622 were prepared according to the mass fractions shown in Table 4.

Table 1. LaserTRAX and ICP Parameters

Parameters	
LaserTRAX	Setting
Raster Pattern Size	1 mm x 1 mm
Ablation Spot Size (µm)	180
Repetition Rate (Hz)	5
Scan Speed (µm/sec)	100
Warm Up Time (s)	5
Laser Cell Gas Flow Rate (L/min)	0.8
Pre-ablation Passes	1
ICP	
Torch	Quartz ZipTorch for laser only (T20Q-37) Nitride ZipTorch for laser + solution (ZTN-D-37)
Injector Diameter (mm)	2
Plasma Gas Flow (L/min)	14
Auxiliary Gas Flow (L/min)	1
Torch Position	-3
ICP RF Power (W)	1500
Viewing Mode	Axial
Stabilization Delay (s)	15
Integration Time (s)	0.01
Read Time (s)	8
Replicates	3
Laser Mixing Chamber	(S011787)
Ar Addition Gas Flow (L/min)	0.13 (ICP nebulizer gas)

Table 2. Wavelengths for major and trace elements

Major Elements	
Analyte	Wavelength (nm)
Co	238.892
Li	610.362
Mn	293.305
Ni	232.003
Trace Elements	
Analyte	Wavelength (nm)
Al	396.153
Ba	455.403
Be	313.107
Ca	396.847
Cu	324.752
Fe	259.939
Mg	285.213
Na	589.592
Sr	407.771
Zr	343.823

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Table 3. NMC Powders with different molar ratios analyzed

Molar Ratios of Major Components					
Cathode Materials	Li	Ni	Mn	Co	O
NMC 111	1	0.33	0.33	0.33	2
NMC 532	1	0.5	0.3	0.2	2
NMC 622	1	0.6	0.2	0.2	2

Table 4. Mass fractions of NMC 111 and NMC 622 in the mixtures

Sample	NMC 111 Mass Fraction (%)	NMC 622 Mass Fraction (%)
Mix 1	25	75
Mix 2	50	50
Mix 3	75	25

Sample preparation is fast and simple for LaserTRAX samples (Fig. 4). The sample is scooped (~0.2 g) and then pressed in a 13 mm die in a hydraulic press at 10 T for 30 seconds. Samples are then loaded into an ESI sample holder. For the analysis of ternary cathode materials, samples were prepared such that the analytical surface of the pellet was a solid layer of NMC. This prevents any dilution of the sample, resulting in better detection limits and a more homogeneous sample. A sample can be weighed, pressed, and ready for analysis in under 2 minutes.

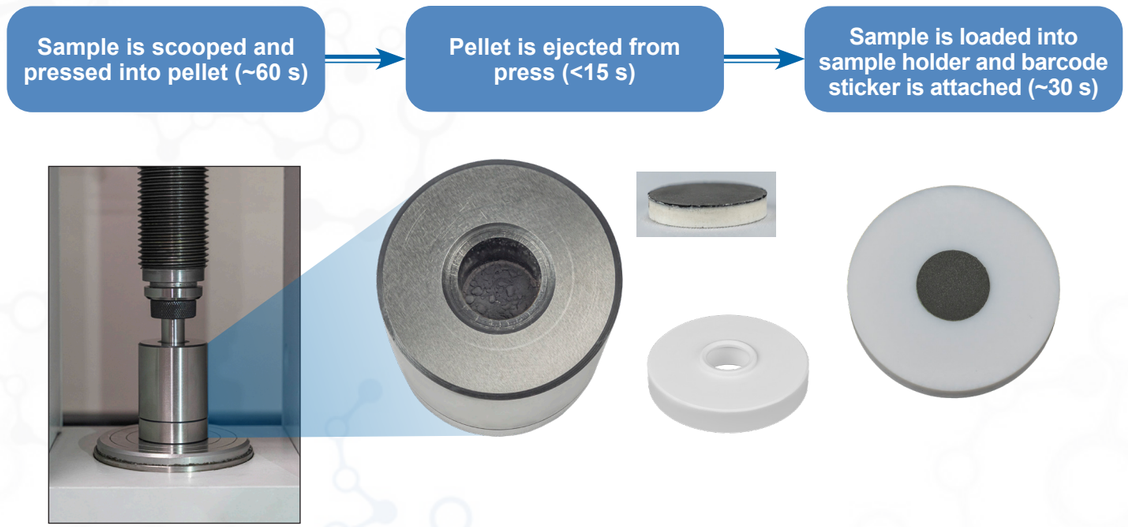

Figure 4. Sample preparation process is reduced from 30-60 minutes acid digestion to <2 minutes for pressed pellets.

Results and Discussion

LaserTRAX automatically processes ICP (can also be used for ICPMS) data and displays the calculated values in real time. The number of standards, standard concentrations, blanks, QC concentrations, and sample ID information can all be imported with barcode IDs, eliminating user error associated with sample ordering or transcription. Together, these features ensure the correct answer is associated with the corresponding sample every time.

Xceleri, the ESL LaserTRAX software, automatically converts the major component data to the final molar ratios. Equations 1 through 5 (Appendix A) show the calculations in detail.

Molar ratios are an important characteristic of the NMC materials with different ratios of metals providing different properties. The undiluted preparation of the NMC allows for more reproducibility between samples, which provides confidence that the results obtained are correct for that material. To show the stability of the LaserTRAX analysis, 8 replicate NMC 111 samples were prepared and analyzed. Excellent precision, < 0.4% RSD, was displayed for the 8 samples analyzed representing a stable and reproducible method. The sample repeatability measurements are shown in Table 5.

Table 5. Pressed pellet sample prep and analysis yields <0.4% RSD

Sample Number	Co Mol %	Mn Mol %	Ni Mol %	$\frac{\text{(Li Mol \%)}}{\text{(Co+Mn+Ni Mol \%)}}$
1	32.91	33.12	32.91	1.04
2	33.11	32.95	32.89	1.04
3	32.87	33.10	32.98	1.05
4	32.77	33.08	33.10	1.05
5	32.79	33.19	33.01	1.04
6	32.93	33.14	32.91	1.04
7	33.01	33.10	32.84	1.04
8	32.81	33.13	33.08	1.04
Average	32.90 ± 0.11	33.10 ± 0.06	32.97 ± 0.09	1.04 ± 0.003
RSD (%)	0.33	0.19	0.26	0.30

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To prove the technique for a range of NMC materials, NMC samples with different metal molar ratios were prepared and analyzed using NMC 111 as the reference standard. The analysis was repeated 5 times to demonstrate the robustness of the analytical method (Table 6). Precision for all sample types was within ±0.24 mol % for Co, ±0.42 mol % for Mn, ±0.59 mol % for Ni, and ±0.03 mol % for Li/Metals for the 5 analytical measurements.

Table 6. LaserTRAX determined mol % compared to reference value

	Co		Mn		Ni		Li/Metals	
Sample	Reference Value (mol %)	LA-ICPOES (mol %)	Reference Value (mol %)	LA-ICPOES (mol %)	Reference Value (mol %)	LA-ICPOES (mol %)	Reference Value (mol %)	LA-ICPOES (mol %)
NMC 532	19.50	19.26 ± 0.17	32.77	32.19 ± 0.42	47.73	48.54 ± 0.59	1.05	1.07 ± 0.02
NMC 622	19.48	19.59 ± 0.19	22.50	22.96 ± 0.20	58.02	57.45 ± 0.36	1.06	1.04 ± 0.02
Mix 1	23.18	22.98 ± 0.08	25.15	25.59 ± 0.16	51.67	51.44 ± 0.21	1.06	1.04 ± 0.03
Mix 2	26.70	26.51 ± 0.08	27.77	28.05 ± 0.19	45.53	45.43 ± 0.25	1.08	1.07 ± 0.02
Mix 3	30.70	30.19 ± 0.24	30.44	30.58 ± 0.39	38.86	39.23 ± 0.57	1.09	1.06 ± 0.02

*All samples were analyzed 5 times (n = 5)

Comparing the results from LaserTRAX and the reference values, there was excellent agreement. The determined molar ratios were within ±0.51 mol % for Co, ±0.58 mol % for Mn, ±0.81 mol % for Ni, and ±0.03 mol % for Li /Metals for the NMC 532, NMC 622, and the 3 mixtures.

For the analysis of trace contaminants, Standard Addition (SA) calibration was utilized by spiking a series of NMC 111 material. Examples of the SA calibration curves are shown in Figure 5 for Mg, Cu, Ca, and Fe. The calibrations show good linearity (>0.95) and LODs are all below recommended manufacturing requirements for ternary cathode quality assurance (Table 7). Concentrations were determined for the common contaminants of interest in these types of cathode materials.

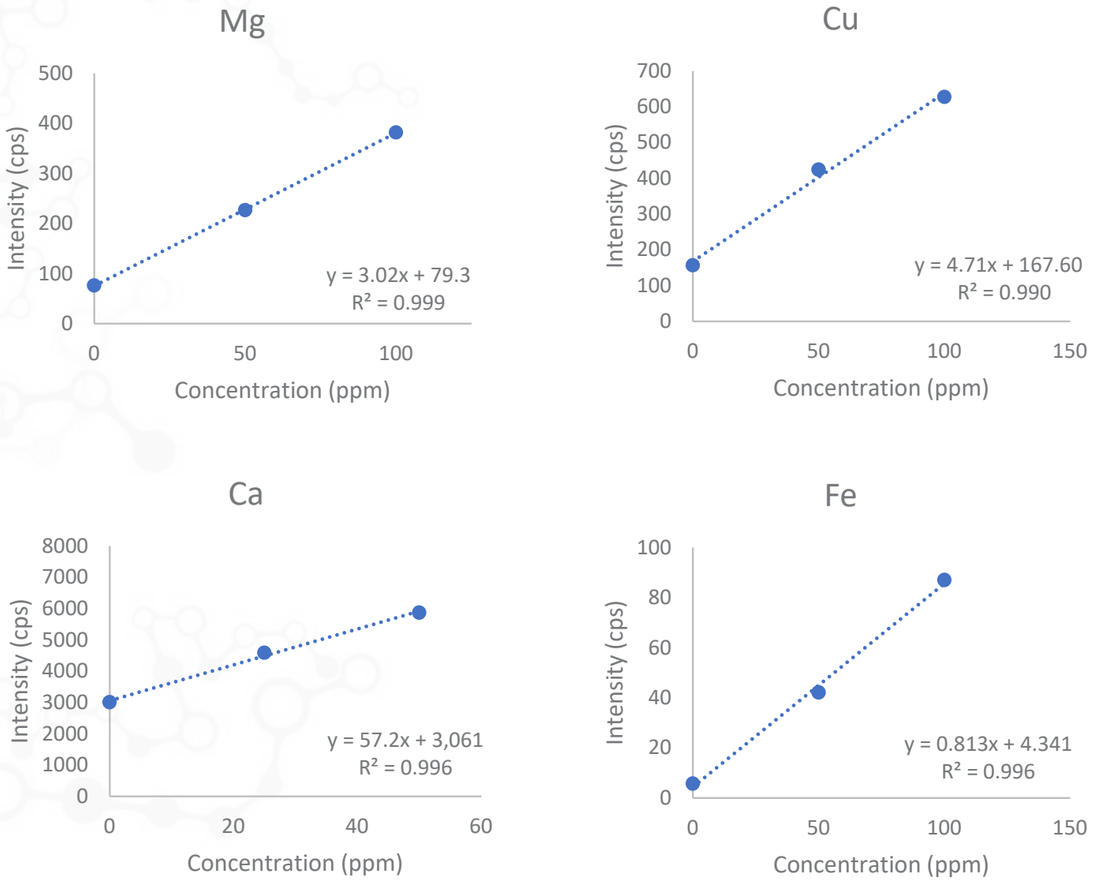

Figure 5. Standard Addition calibration curves for Mg, Cu, Ca, and Fe

Table 7. LaserTRAX determined mol % compared to reference value

Analyte	Al	Ba	Be	Ca	Cu	Fe	Mg	Na	Sr	Zr
R^2	0.993	1.000	0.994	0.996	0.990	0.996	0.999	0.955	0.995	0.993
Manufacturing Requirements (ppm)	N/A	N/A	N/A	<300	<300	<300	<300	<300	N/A	N/A
LOD	9.6	0.58	7.5	0.19	4.1	9.6	3.0	6.2	0.10	0.70
NMC 111	93.4	1.13	14.3	43.0	<LOD	<LOD	27.4	210	0.96	316
NMC 532	1846	4.12	<LOD	32.6	<LOD	19.8	25.0	159	21.0	10.1
NMC 622	1096	1.55	9.18	28.9	<LOD	11.5	21.4	261	12.9	4.21
Mix 1	982	1.27	11.1	29.8	<LOD	<LOD	25.9	228	9.20	87.5

Conclusion

The analysis of NMC can be greatly simplified by analyzing pressed-pellets by LaserTRAX rather than digesting the materials. Sample preparation time is reduced to under 3 minutes and analysis in under 4 minutes. Acid digestion is completely eliminated from the sample preparation procedure. User intervention is drastically reduced after samples have been delivered to the autosampler deck of the robot. Stability of molar ratios is exceptional, with RSD < 0.4% for 8 replicate pellets of NMC 111. LaserTRAX is able to differentiate between samples with small changes in molar ratio. Stability of the analytical method from run to run is excellent, with an RSD less than 3% over 5 runs. LaserTRAX correlated well with established reference values, with ± 2% difference for Co, Mn, and Ni, and within ± 5% difference for Li. LaserTRAX is the ideal tool for the analysis of cathode materials to provide accurate, precise, and rapid results using automation without the need for corrosive acids.

Appendix A
Equations

First, concentration is determined for each analyte by dividing by the slope of the calibration curve created by the standard.

Equation 1.

$$Conc.(X)=Int(X)/m$$

Where X is the analyte and m is the slope determined by the calibration curve.

Next, concentration is converted to moles by dividing the concentration by the molar mass of the analyte.

Equation 2.

$$Moles(X)=Conc.(X)/M$$

Where M is the molar mass of the analyte.

The moles of total metals in NMC can obtained by summing the moles of Co, Mn, and Ni.

Equation 3.

$$Moles(Metals)= Moles(Co)+Moles(Mn)+Moles(Ni)$$

The molar ratio for each of the metals is then calculated by dividing the moles of the analyte by the sum of the moles of the major metal analytes and multiplied by 100 to convert to a percentage.

Equation 4.

$$Molar\ Ratio(X)= \frac{Moles(X)}{Moles(Metals)} *100$$

And the ratio of Li to total metals can be found by dividing the molar ratio of lithium by the molar ratio of total metals.

Equation 5.

$$Li{:}Metals\ Ratio= \frac{Moles(Li)}{Moles(Metals)}$$