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Automated Standard Addition for the Analysis of Battery Cathode Materials

Brief

Digested cathode powders were analyzed with the prep*FAST* MX+ connected to an Avio 500. This setup, powered by Xceleri software, allows for an automated standard addition method that provides more accurate results, less sample preparation, and reduced acid waste.

Highlights:

- Detection of major and trace elements in digested cathode materials
- Comparison of external calibration, manual standard addition, and automated standard addition
- Automated matrix standard addition (MSA) accounts for matrix effects – providing more accurate results
- Autodilution reduces sample preparation
- Xceleri software automates and simplifies the analytical process

Introduction

Lithium cathode materials are important for maximizing the capacity and performance of lithium-ion batteries. In the case of LNMC cathode materials the performance can be related to the ratio of Li to Ni, Mn, and Co, as well as the amount of trace element impurities. The most common way to determine the concentrations of these elements is to digest the materials in acid, dilute the samples, then analyze with an inductively coupled plasma optical emission spectrometer (ICP). In both raw materials and cathode powders, there is a large matrix effect that can bias the accuracy of results. The most accurate way to account for this is to perform standard addition on each sample. However, this process requires extra sample preparation. To counter that, Elemental Scientific, Inc. (ESI) has introduced an automated technique for performing matrix standard addition (MSA). The prep*FAST* MX+ provides an automated analysis that dilutes samples to the correct acid ratio for ICP analysis and automatically performs inline standard addition spikes. Using ESI's Xceleri software, the analyst can easily define dilution factors, elements of interest, standard addition spike ranges, and produce a report of all samples analyzed.

Experimental

prep*FAST* MX+ (Fig. 1) – automated inline sample preparation autosampler that provides autocalibration, automated MSA, and autodilution of samples (samples can be diluted from 1-400x). The system has syringe driven internal standard addition, standard addition spiking, and the option for vacuum or syringe loading of samples. Syringe loading can be used for small sample volumes or to account for samples with varying viscosity. In addition, the SampleSense valve is included which further automates viscous samples and ensures that the sample is always loaded correctly for analysis. The autosampler has a built in dual-rinse station for high-speed rinsing and superior washout. Xceleri operates as the instrument control software providing a fully automated setup. The ESI software triggers the ICP; controls the dilution factors, calibrations, elements of interest, and sample sequence (Fig. 2a) and sample location (Fig. 2b); retreives and processes the data (Fig. 3).

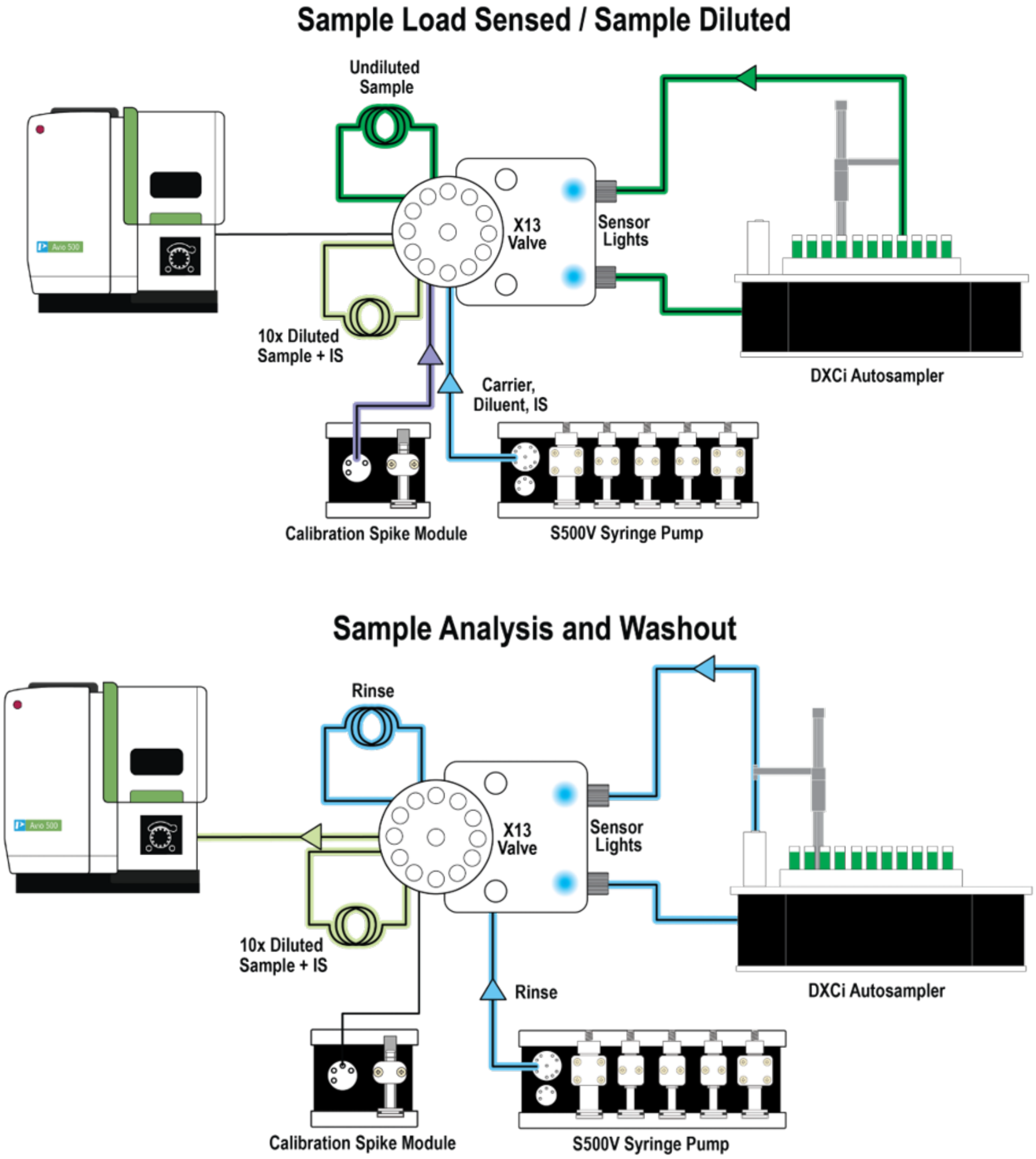
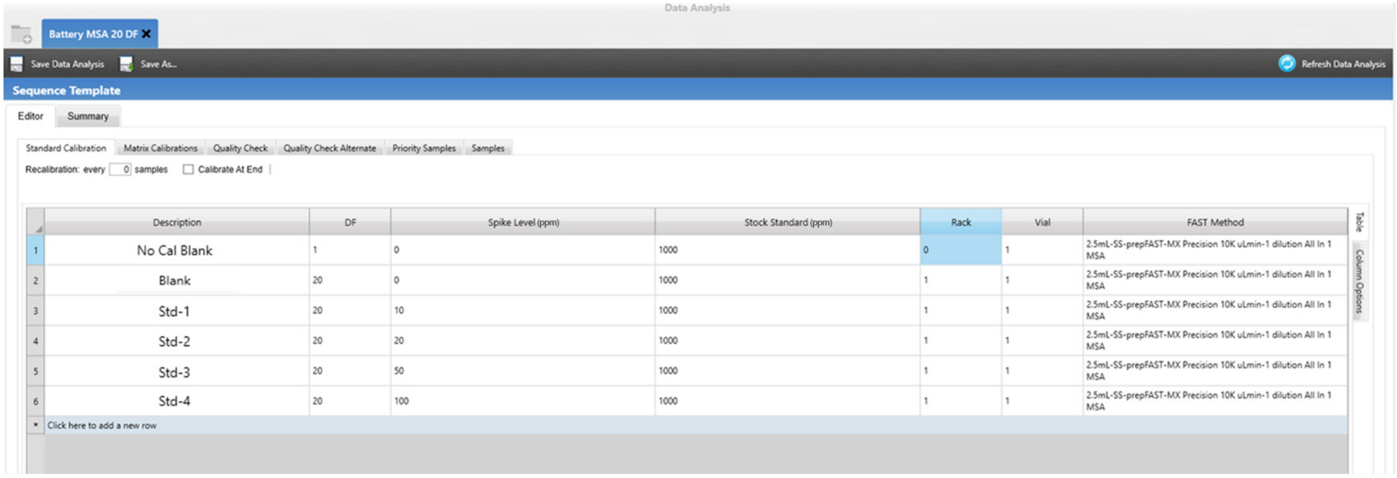


Figure 1. Elemental Scientific's prep*FAST* MX+. (Top) Sample loading and dilution schematic and (Bottom) sample analysis and washout schematic.

Experimental *(Continued)*



Recalibration: every 0 samples ☐ Calibrate At End

	Description	DF	Spike Level (ppm)	Stock Standard (ppm)	Rack	Vial	FAST Method
1	No Cal Blank	1	0	1000	0	1	2.5mL-SS-prepFAST-MX Precision 10K uLmin-1 dilution All In 1 MSA
2	Blank	20	0	1000	1	1	2.5mL-SS-prepFAST-MX Precision 10K uLmin-1 dilution All In 1 MSA
3	Std-1	20	10	1000	1	1	2.5mL-SS-prepFAST-MX Precision 10K uLmin-1 dilution All In 1 MSA
4	Std-2	20	20	1000	1	1	2.5mL-SS-prepFAST-MX Precision 10K uLmin-1 dilution All In 1 MSA
5	Std-3	20	50	1000	1	1	2.5mL-SS-prepFAST-MX Precision 10K uLmin-1 dilution All In 1 MSA
6	Std-4	20	100	1000	1	1	2.5mL-SS-prepFAST-MX Precision 10K uLmin-1 dilution All In 1 MSA
*	Click here to add a new row						

Figure 2a. Screenshot of the Xceleri software tab showing the sequence for running the automated standard addition calibration.
Blank = sample, Std-1 through Std-4 are standard addition spikes correlating to 10-100 ppm.

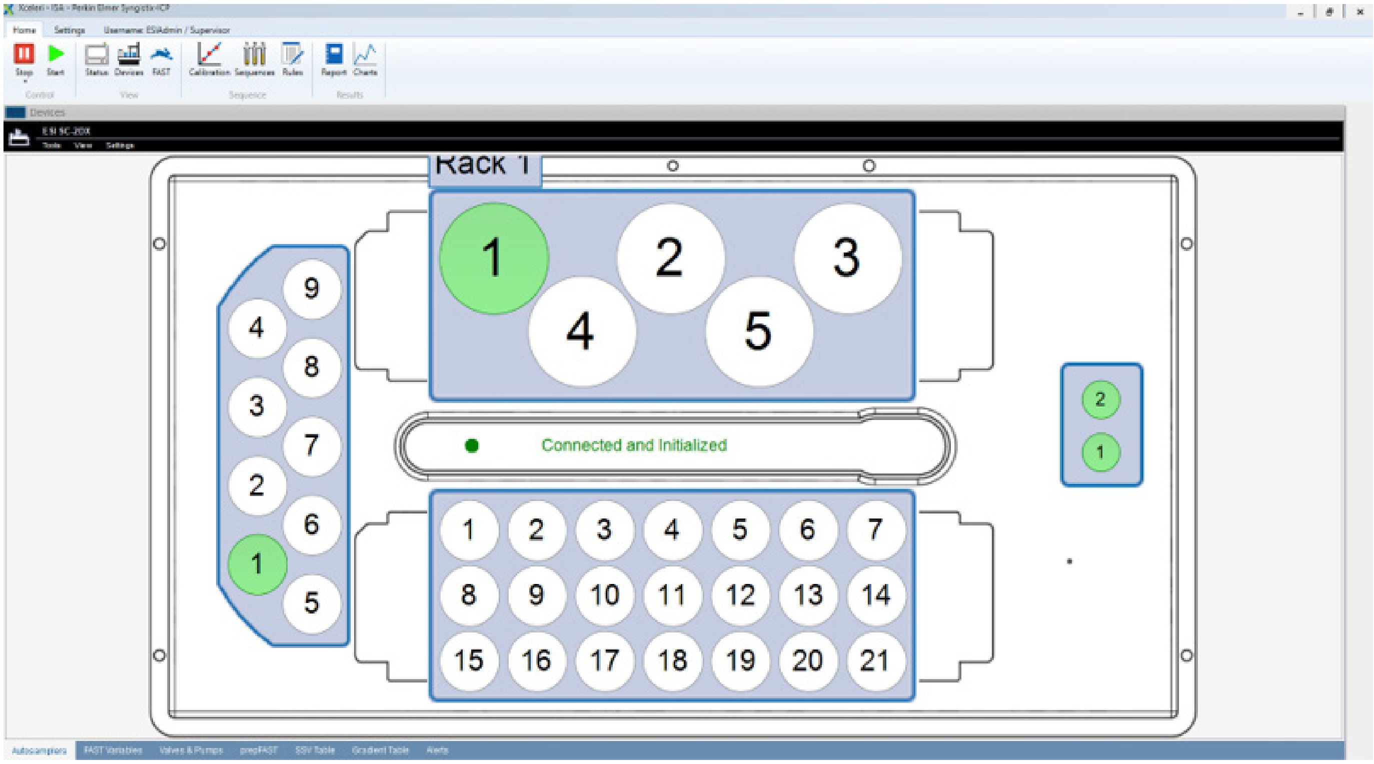
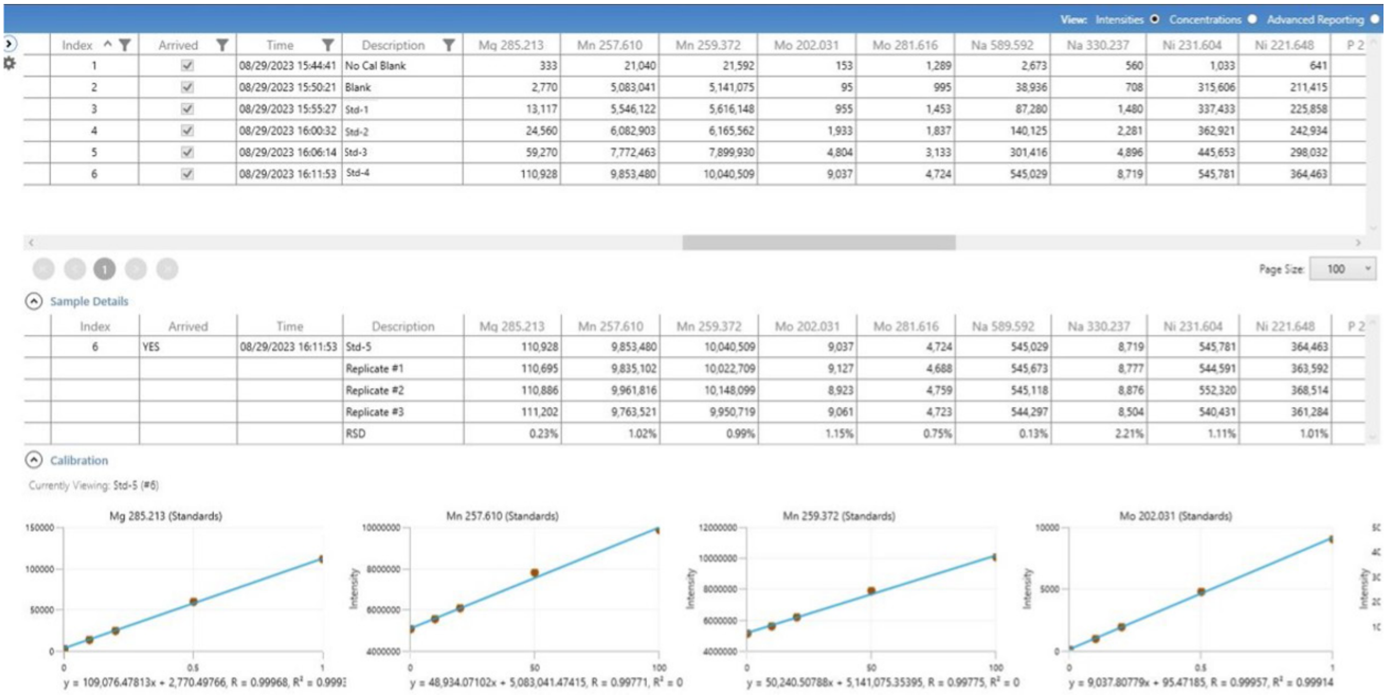


Figure 2b. Screenshot of the Xceleri software tab showing the location in the autosampler.

Experimental *(Continued)*



Index	Arrived	Time	Description	Mg 285.213	Mn 257.610	Mn 259.372	Mo 202.031	Mo 281.616	Na 589.592	Na 330.237	Ni 231.604	Ni 221.648	P 2
1	☑	08/29/2023 15:44:41	No Cal Blank	333	21,040	21,592	153	1,289	2,673	560	1,033	641	
2	☑	08/29/2023 15:50:21	Blank	2,770	5,083,041	5,141,075	95	995	38,936	708	315,606	211,415	
3	☑	08/29/2023 15:55:27	Std-1	13,117	5,546,122	5,616,148	955	1,453	87,280	1,480	337,433	225,858	
4	☑	08/29/2023 16:00:32	Std-2	24,560	6,082,903	6,165,562	1,933	1,837	140,125	2,281	362,921	242,934	
5	☑	08/29/2023 16:06:14	Std-3	59,270	7,772,463	7,899,930	4,804	3,133	301,416	4,896	445,653	298,032	
6	☑	08/29/2023 16:11:53	Std-4	110,928	9,853,480	10,040,509	9,037	4,724	545,029	8,719	545,781	364,463	

Index	Arrived	Time	Description	Mg 285.213	Mn 257.610	Mn 259.372	Mo 202.031	Mo 281.616	Na 589.592	Na 330.237	Ni 231.604	Ni 221.648	P 2
6	YES	08/29/2023 16:11:53	Std-5	110,928	9,853,480	10,040,509	9,037	4,724	545,029	8,719	545,781	364,463	
			Replicate #1	110,695	9,835,102	10,022,709	9,127	4,688	545,673	8,777	544,591	363,592	
			Replicate #2	110,886	9,961,816	10,148,099	8,923	4,759	545,118	8,876	552,320	368,514	
			Replicate #3	111,202	9,763,521	9,950,719	9,061	4,723	544,297	8,504	540,431	361,284	
			RSD	0.23%	1.02%	0.99%	1.15%	0.75%	0.13%	2.21%	1.11%	1.01%	

y = 109,076.47813x + 2,770.49766, R = 0.99968, R² = 0.999

y = 48,934.07102x + 5,083,041.47415, R = 0.99771, R² = 0

y = 50,240.50788x + 5,141,075.35395, R = 0.99775, R² = 0

y = 9,037.80779x + 95.47185, R = 0.99957, R² = 0.99914

Figure 3. Screenshot of the Xceleri software tab showing the report page displaying intensities, replicates, RSDs, and calibration curves.

An Avio 500 ICP was employed for these measurements. An 8 mm quartz O-ring free baffled cyclonic spray chamber (ESI), 2.0 mm sapphire demountable ZipTorch injector for Avio (ESI), demountable NitrideTorch (ESI), and PFA microflow nebulizer (ESI) were used in these experiments. The plasma gas was 12 L/min Ar, auxiliary gas 0.4 L/min Ar, nebulizer gas 0.7 L/min Ar, and plasma power of 1500 W. The ICP method was set to a 2 ms integration time and 1 s read time for each wavelength measured. The elements monitored were Li 670 nm, Co 228 nm, Cu 324 nm, Fe 259 nm, Mn 257 nm, Na 589 nm, Ni 231 nm, and Zr 343 nm.

Samples were prepared by weighing out 2 g of NMC 1:1:1 powder, adding 15 g HCl and 5 g HNO_3 then heated on an Analab Hotplate for 30 minutes at 120 °C. This solution was then diluted to 200 g with UPW offline. The samples were then diluted again inline (20x dilution factor) using the prep*FAST* MX+. Stock standards for the MSA methods consisted of 500 ppm Li, 1,000 ppm Co, Ni, and Mn, and 10 ppm trace elements (Fe, Cu, Zr, etc.).

Experimental *(Continued)*

Three different calibration methods were performed in this study: external calibration, manual MSA, and automated MSA. The results from these experiments are displayed in Table 1. These results include a comparison of linearity (R^2), sample result (wt%), and %RSD. The results show that Li, Co, Mn, Ni, Na, and Zr show a bias for external calibration compared to the MSA methods. This is not surprising as a bias from matrix effects was expected. The difference between the external calibration results and the automated MSA results varied from 2-18 %bias, with Na being the most drastic at 4500 %bias. When comparing the manual MSA and automated MSA results there is a very good correlation (slope = 1.0085) which can be seen in the linear regression displayed in Figure 4. This validates that the prep*FAST* MX+ method can perform accurate and reliable automated standard additions for cathode materials.

Table 1. Comparison of external calibration, manually prepared MSA, and automated MSA for the elements of interest. %RSD is based on 3 replicate measurements.

		External Cal	**Manual MSA**	**Auto MSA**
Li	Linearity (R^2)	0.9996	0.9970	0.9984
	Result (wt%)	8.38	8.11	8.19
	%RSD	0.4	0.4	0.5
Co	Linearity (R^2)	0.9993	0.9984	0.9980
	Result (wt%)	20.6	21.2	21.5
	%RSD	0.7	0.7	0.8
Mn	Linearity (R^2)	0.9998	0.9992	0.9999
	Result (wt%)	18.0	17.0	16.8
	%RSD	0.7	0.7	0.8
Ni	Linearity (R^2)	0.9999	0.9985	0.9978
	Result (wt%)	20.6	21.2	21.5
	%RSD	0.6	0.6	0.7
Na	Linearity (R^2)	0.9977	0.9988	0.9997
	Result (wt%)	0.92	0.02	0.02
	%RSD	0.9	0.9	0.2
Fe	Linearity (R^2)	0.9999	0.9999	0.9998
	Result (wt%)	0.00	0.00	0.00
	%RSD	n/a	n/a	n/a
Cu	Linearity (R^2)	0.9996	0.9999	0.9999
	Result (wt%)	0.003	0.003	0.003
	%RSD	2.2	2.2	2.2
Zr	Linearity (R^2)	0.9999	0.9973	0.9992
	Result (wt%)	0.40	0.47	0.49
	%RSD	0.8	0.8	0.3

Experimental *(Continued)*

Examining the calibration curves for the major and trace elements revealed variations in the slopes, which supports the aforementioned results in Table 1. Figure 5 displays the Mn (major example) calibration curves for the three techniques. The slope for the Mn external calibration curve was ~75,000 as compared to ~79,000 for the MSA techniques. Figure 6 displays the Cu (trace example) calibration curves for the three techniques. In this case the slope for external calibration was higher (~96,000) as compared to the MSA techniques (~91,000). For Cu this points to a suppression of signal in the real samples as compared to the neat external calibration. Further supporting the need for standard addition.

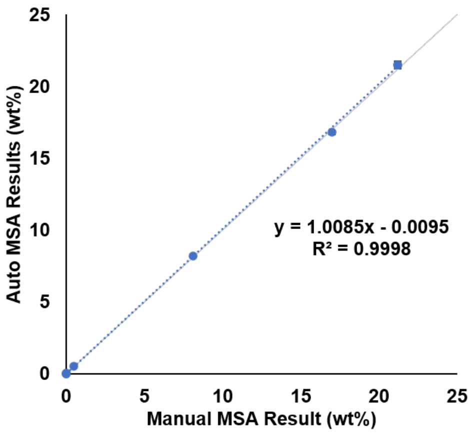


Figure 4. Linear regression comparing the results from the manual MSA and automated MSA. The slope of 1.0085 (perfect correlation = 1) shows an excellent correlation in the two techniques.

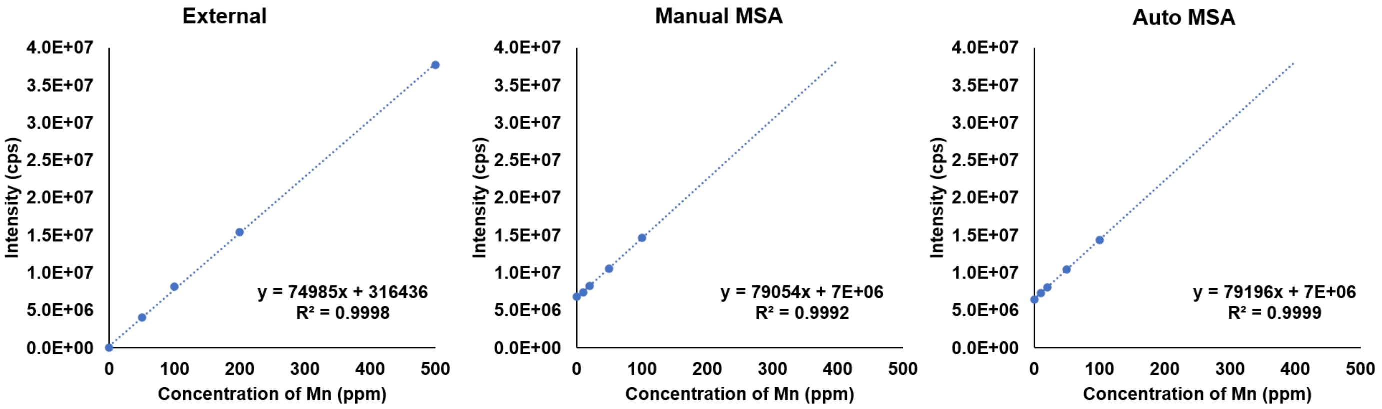


Figure 5. Displays the calibration curves for Mn performed by external calibration, manual MSA, and automated MSA.

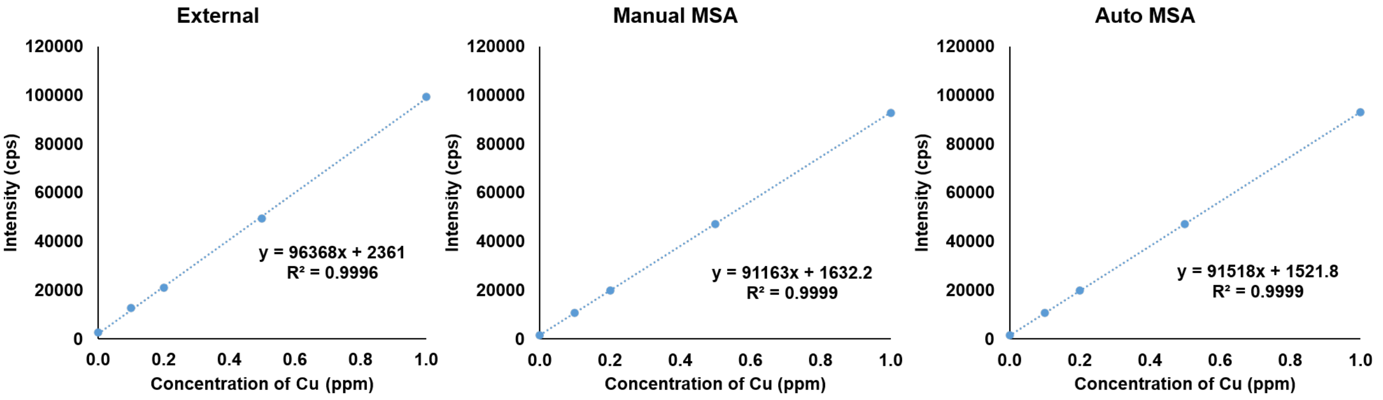


Figure 6. Displays the calibration curves for Cu performed by external calibration, manual MSA, and automated MSA.

Results

The recovery was determined based on evaluating spike #3 for the manual and automatic MSA methods (Table 2). The overall %recovery (average recovery from all the elements measured) for the manual and automatic MSA methods were 98 ± 5% and 98 ± 3%, respectively. As represented in the standard deviation the manual MSA had a bit wider range of recoveries, 91-107%, whereas the automatic MSA method was 94-101%.

Table 2. Percent recoveries for spike #3 from the manual and automatic MSA methods. % Recovery was based on the spike 3 standard value.

	Manual MSA	Auto MSA
Li	91	99
Co	99	95
Mn	95	101
Ni	99	94
Na	96	100
Fe	100	101
Cu	99	101
Zr	107	94

Conclusions

In this work we have developed and validated an automatic MSA method using ESI's prep*FAST* MX+ and Xceleri software. Both MSA methods were more accurate than the external calibration curves, with the most drastic difference seen for Na. The comparison of manual and automatic MSA had very good agreement, further validating the automatic MSA method. The automatic MSA method with the prep*FAST* MX+ provides laboratories with an efficient, time-savings, and more accurate method for the analysis of cathode materials.