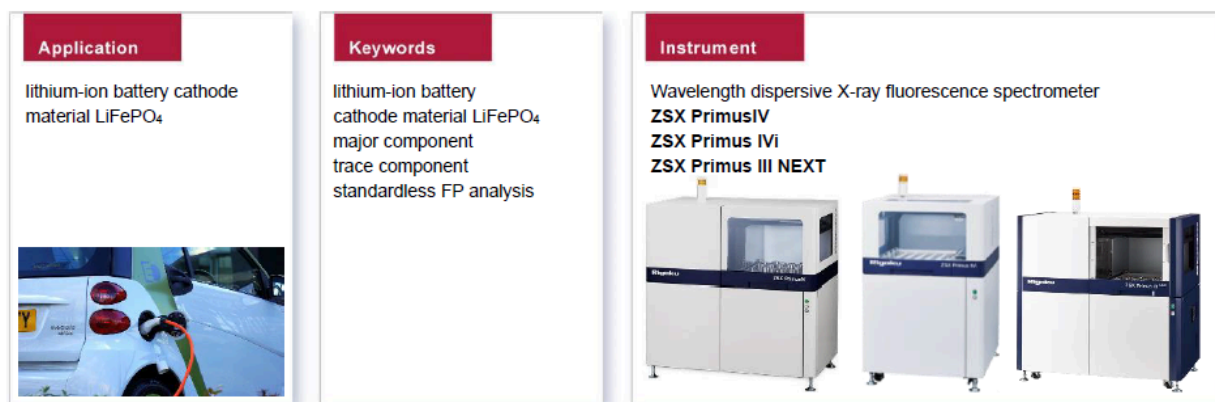


# XRF1131 Standardless FP Analysis of Lithium-ion Battery Cathode Material $\text{LiFePO}_4$ by ZSX PrimusIV



## Introduction

In recent years, the demand for lithium-ion batteries (LIBs) has increased significantly with the widespread adoption of battery electric vehicles (BEVs) and energy storage systems (ESSs) aiming for carbon neutrality. Lithium iron phosphate ( $\text{LiFePO}_4$ ), which is used as a low-cost and safe cathode material in LIBs, contains Fe as a major component. Because the composition of the electrode active material and trace impurities affect battery performance, the concentration of main components Li, Fe, P and trace impurities such as Cu, Na, Ca and Zn should be controlled. As a non-destructive elemental quantification method, X-ray fluorescence allows sample analysis for powders and electrode plates without complicated sample preparation such as acid digestion. In standardless FP analysis (SQX analysis)<sup>[1,2]</sup>, qualitative scan analysis is run at first and then composition is calculated by the fundamental parameter (FP) method using X-ray intensities of detected elements and FP sensitivity libraries. Compositional calculation can be performed without preparing any standard samples and calibration curves. In this application note, SQX analysis was performed for cathode material  $\text{LiFePO}_4$  to determine the concentration of Fe, P and trace components using the wavelength dispersive X-ray fluorescence spectrometer ZSX Primus IV. In addition, applicability of the ZSX Primus IV was evaluated with reference to the Nonferrous Metals Industry Standard of the People's Republic of China, YS/T 1028.5-2015<sup>[3]</sup>, a standard for the chemical analysis of trace components in  $\text{LiFePO}_4$  by using ICP atomic emission spectrometry (ICP-AES).

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## Instrument

Wavelength dispersive X-ray fluorescence spectrometer (WDXRF) ZSX PrimusIV is capable of analyzing elements from Be to Cm and can perform qualitative and quantitative analyses from ppm to 100%. X-ray fluorescence spectra obtained by using analyzing crystals have high resolution and low peak overlap, ensuring highly reliable analysis results. The standard measurement condition for SQX analysis is to perform qualitative analysis sequentially by scanning the angle of the analyzing crystals over a wide range of elements. By using the fixed-angle measurement function, which specifies the element and adds the accumulation time at the fixed angle, the accuracy of trace element analysis can be improved. In addition to standard sensitivity libraries, matching libraries can be registered for each analysis sample. By registering sensitivities of a reference sample similar to the analysis sample as a matching library, the reliability of the calculated result is improved. SQX analysis also has a function to calculate the estimated error (theoretical standard deviation) based on sample composition, X-ray intensity and measurement time, which can be useful to evaluate the uncertainty of SQX analysis result.

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## Sample Preparation

Three powder samples of  $\text{LiFePO}_4$  were used for analysis, one pure reagent (sample A, FUJIFILM Wako Pure Chemical Corporation) and two battery-grade electrode materials (sample B and sample C). Each sample was mixed with binder (Chemplex SpectroBlend) at a ratio of 10 mass% and then pelletized into a 32 mm aluminum ring at a pressure of 100 kN.

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## Measurement

For each sample, sequential scan analysis from F to Cm was performed in a vacuum with a measurement diameter of 30 mm. The results obtained were used for SQX analysis. In the SQX calculation, the component type was selected as oxide powder and the content of  $\text{Li}_2\text{O}$  was set as a fixed value in advance. For the trace elements defined in YS/T 1028.5-2015, fixed angle measurements were applied to improve precision. Measurement times for peak and background are shown in Table 1.

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## Result

Table 2 shows the SQX analysis results of the main components Fe and P, the theoretical standard deviation, and the composition ratio (molar ratio) of Fe/P for each sample. These results were calculated from the matching library using sample A ( $\text{LiFePO}_4$  reagent) as a reference sample. Analytical line X-ray intensities and stoichiometric values of Fe and P were used for matching library registration. SQX analysis results of samples B and C using the matching library indicated slightly lower Fe content than the stoichiometric value. As the theoretical standard deviations (0.03 mass% for Fe and 0.02 mass% for P) in Table 2 are shown, there are significant differences between SQX results of samples B and C and the stoichiometric values. Figure 1 shows the qualitative spectrum of each sample. In sample A ( $\text{LiFePO}_4$  reagent), almost no impurity components were observed. In sample B, in addition to peaks derived from the main components (Fe, P), small peaks of impurities (Ni, Mn, Cr) and an additive component (Ti) were also observed. In sample C, small peaks derived from impurities (Ni, Mn) were observed. Figure 2 shows the F-K $\alpha$  peak profile for each sample. The F-K $\alpha$  peak was observed in sample B, and the SQX analysis result (described later) indicated that it contained approximately 1 mass% fluorine. WDXRF can analyze not only metallic elements but also fluorine.

Analytical line	Na-K $\alpha$	Mg-K $\alpha$	Al-K $\alpha$	Si-K $\alpha$	S-K $\alpha$	Ca-K $\alpha$	Ti-K $\alpha$	Cr-K $\alpha$
Peak (sec)	200	100	20	20	20	20	20	20
BG (sec)	100 x 2	50 x 2	10 x 2	10 x 2	10 x 2	10 x 2	10 x 2	10 x 2
Analytical line	Mn-K $\alpha$	Co-K $\beta$	Ni-K $\alpha$	Cu-K $\alpha$	Zn-K $\alpha$	Zr-K $\alpha$	Pb-L $\alpha$	
Peak (sec)	20	200	20	20	20	20	20	
BG (sec)	10 x 2	100 x 2	10 x 2	10 x 2	10 x 2	10 x 2	10 x 2	

Table 1 Fixed angle measurement condition for trace components

		Sample A		Sample B	Sample C
	Stoichiometric value	SQX result (w/o matching library)	SQX result (w/ matching library)	SQX result (w/ matching library)	SQX result (w/ matching library)
Fe (mass%)	35.40	37.26	35.37	34.01	34.91
Theoretical standard deviation (mass%)	-	0.03	0.03	0.03	0.03
P (mass%)	19.64	18.56	19.62	19.64	19.81
Theoretical standard deviation (mass%)	-	0.02	0.02	0.02	0.02
Fe/P (molar ratio)	1.00	1.11	1.00	0.96	0.98

Table 2 SQX analysis results of Fe and P, theoretical standard deviation and molar ratio of Fe/P

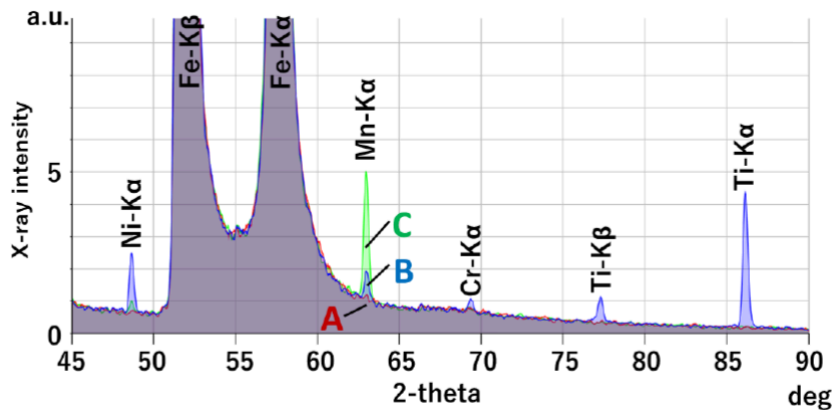


Fig. 1 Qualitative spectrum of each sample.

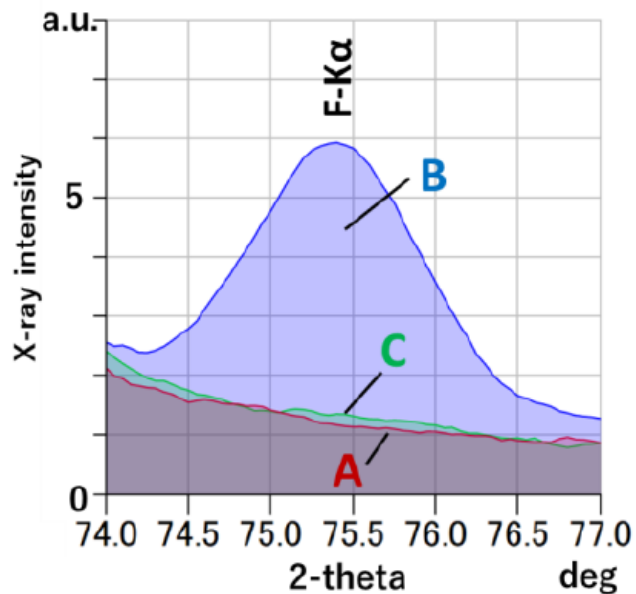


Fig. 2 F-Kα peak profile of each sample.

Sample		F	Na	Mg	Al	Si	S	Ca	Ti	Cr	Mn	Co	Ni	Cu	Zn	Zr	Pb
A	SQX result	N.D.	N.D.	N.D.	22	100	57	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Theoretical standard deviation	-	-	-	0.9	1.8	3.4	-	-	-	-	-	-	-	-	-	-
B	SQX result	9000	45	N.D.	2760	86	81	32	1590	44	120	41	210	N.D.	N.D.	16	N.D.
	Theoretical standard deviation	740	2.5	-	8.1	1.7	0.4	1.1	7.1	1.3	1.7	2.2	1.6	-	-	0.4	-
C	SQX result	N.D.	690	N.D.	41	78	98	55	N.D.	N.D.	520	N.D.	29	22	N.D.	N.D.	N.D.
	Theoretical standard deviation	-	4.4	-	1.1	1.7	4.3	1.1	-	-	2.7	-	1.0	0.9	-	-	-

Table 3 SQX analysis results and theoretical standard deviations of each sample (unit: ppm)

※ N.D.: less than LLD (detection limit value)

LLD: 3 times statistical error of background intensity

Sample A-C	F	Na	Mg	Al	Si	S	Ca	Ti	Cr	Mn	Co	Ni	Cu	Zn	Zr	Pb
SQX	4500	20	17	9	13	20	9	15	11	12	20	9	8	7	16	15
ICP-AES	-	20	20	20	-	-	20	-	20	20	20	20	20	20	-	20

Table 4 Comparison of the LOQ of SQX with the lower limit of ICP-AES measurement range (unit: ppm)

※ -: ICP analysis specification not described

LOQ: 9 times statistical error of background intensity

Table 3 shows the SQX analysis results of trace components in each sample. Theoretical standard deviations for each component are also listed. Impurities Al, Si, and S were detected in sample A. On the other hand, in battery grade electrode materials samples B and C, metal impurities and additive components on the order of tens to thousands of ppm were detected. Theoretical standard deviations of several hundred ppm for fluorine and several ppm for other elements were calculated from the SQX analysis results. Table 4 shows a comparison of the limit of quantitation (LOQ) of each element with the lower limit measurement range of ICP-AES in YS/T 1028.5-2015. The results of SQX analysis with fixed angle measurement meet the YS/T 1028.5-2015 standard.

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## Conclusions

Standardless FP analysis (SQX analysis) of cathode material  $\text{LiFePO}_4$  was performed by ZSX PrimusIV. In battery-grade samples, the Fe contents were found to be slightly lower than the stoichiometric value. A wide variety of impurities and additive components on the order of tens to thousands of ppm were detected in the samples. SQX analysis with fixed angle measurement can meet the standard of ICP-AES in YS/T 1028.5-2015. WDXRF can analyze fluorine, which usually requires ion chromatography, as well as other components in non-destructively. ZSX Guidance software has a wide variety of functions for high-precision analysis. The matching library function using any desired reference sample gives accurate quantitative results. For the analysis of trace metal components at 20 ppm level, fixed angle measurement can be applied to meet the required quantitation limit. X-ray fluorescence analysis, which is a non-destructive, rapid and accurate analytical method, is suitable for the compositional analysis of battery materials.

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## References

- [1] Yasujiro Yamada, Advanced ZSX Guidance – Semi-quantitative analysis (SQX analysis) , Rigaku Journal 50(1), 2019
- [2] Hikari Takahara, Hironori Kobayashi, Standardless FP XRF analysis for lithium ion battery electrode materials, Rigaku Journal 52(1), 2021
- [3] Nonferrous Metals Industry Standard of the People's Republic of China, Methods for chemical analysis of lithium iron phosphate, YS/T 1028.5-2015

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## Related products



### ZSX Primus IV

High power, tube above, sequential WDXRF spectrometer with new ZSX Guidance expert system software



### ZSX Primus IVi

High-power, tube-below, sequential WDXRF spectrometer with new ZSX Guidance expert system software



### ZSX Primus III NEXT

Affordable, high-end, tube-above Industrial WDXRF for the analysis of solid samples