Advanced ZSX Guidance—Semi-quantitative analysis (SQX analysis)

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1. Introduction

Wavelength dispersive X-ray fluorescence (XRF) spectrometers have high spectral resolution and can therefore identify peaks with high accuracy. However, if the analysis line overlaps with a higher order line, peak identification and semi-quantitative analysis results may not be reliable. To perform accurate analysis for such cases, measurement conditions that reduce the influence of the higher order lines need to be set up, followed by remeasuring the sample with the optimized conditions. This can require advanced knowledge of XRF principles and a high level of familiarity with the software. This is not in line with the demand for semi-quantitative analysis being easily and quickly able to give accurate and reliable results for unknown samples.

The new software feature described in this article was developed to overcome this obstacle. It performs semi-quantitative analysis by the FP method using a new procedure that accurately calculates results after the software automatically selects data from the optimal measurement conditions when a higher order line interferes with the analysis line. This allows anyone, including users with little experience in X-ray analysis, to obtain analysis results with higher accuracy and reliability.

2. Principle of higher order line generation and its influence on measurement line intensity

Diffraction of X-rays by an analyzing crystal occurs when Bragg's condition "$2d \sin \theta = n\lambda$" (n: order of diffraction as an integer) is satisfied. The first order line (n = 1), is the measurement line. Diffracted lines with n > 1 are known as higher order lines. The energy of a higher order line is larger than the first order line by a factor of n. These interfering lines can usually be eliminated with a pulse height analyzer (PHA), but not in every case. Large higher order line intensity and the escape peak of the higher order line can affect the analysis results. Figure 1 shows an example of a pulse height distribution curve at a 2θ angle where the higher order line interferes with the first order line.

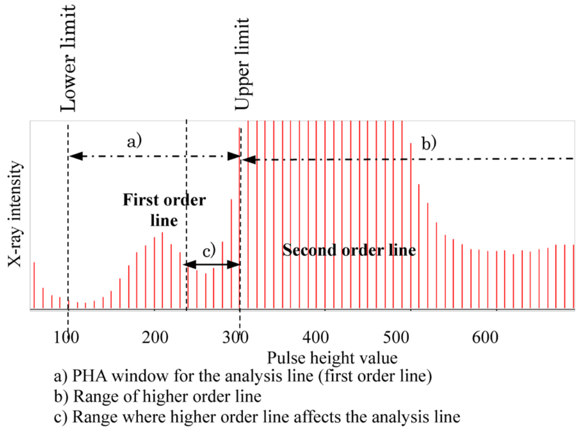

Fig. 1. Pulse height distribution curve showing higher (second) order line affecting the first order line.

The amount of interference of a higher order line on the intensity of the first order line (measurement line) varies depending on the PHA setting. The wider the PHA window, the larger the interference by the higher order line. Lowering the upper limit of the PHA window can reduce or eliminate the effect of the higher order line. Table 1 shows some examples of higher order lines that interfere with analysis lines.

Influence of higher order lines can also be reduced by selecting certain analyzing crystals that do not reflect these interfering lines. Selecting such a crystal may not be optimal with respect to sensitivity, for example, but may be preferred for the elimination of interfering higher order lines.

Table 1. Examples of higher order lines interfering with analysis lines. Value in parentheses indicates order number.

Analysis line	Interfering higher-order line		
Zn-Kα	Mo-Kα(2)	U-Lβ(2)	Y-Kβ(2)
Cu-Kα	Sr-Kβ(2)		
Ni-Kα	Pb-Lγ(2)	Y-Kα(2)	
Fe-Kα	Pb-Lβ3(2)		
Mn-Kα	As-Kβ(2)	Hg-Lβ(2)	Zr-Kβ(3)
V-Kα	Hg-Lα(2)	Y-Kα(3)	
Ti-Kα	Hf-Lα(2)		
Ca-Kα	Ni-Kα(2)	W-Ll(2)	
S-Kα	Co-Kα(3)		
P-Kα	Ca-Kβ(2)	Cu-Kα(4)	
Al-Kα	Ag-Lα(2)	Ba-Lα(3)	
Mg-Kα	Ca-Kα(3)		
Na-Kα	Zr-Lα(2)	Zr-Lβ(2)	

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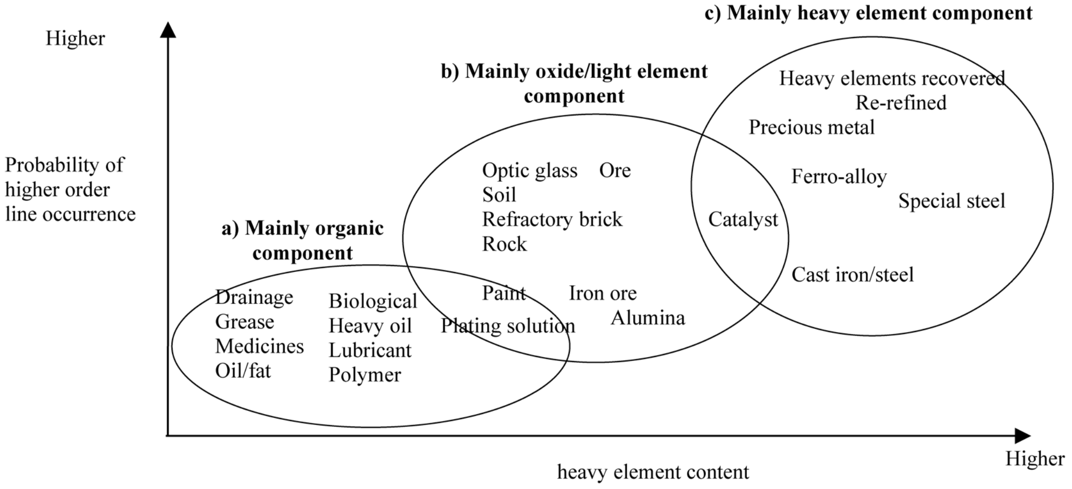


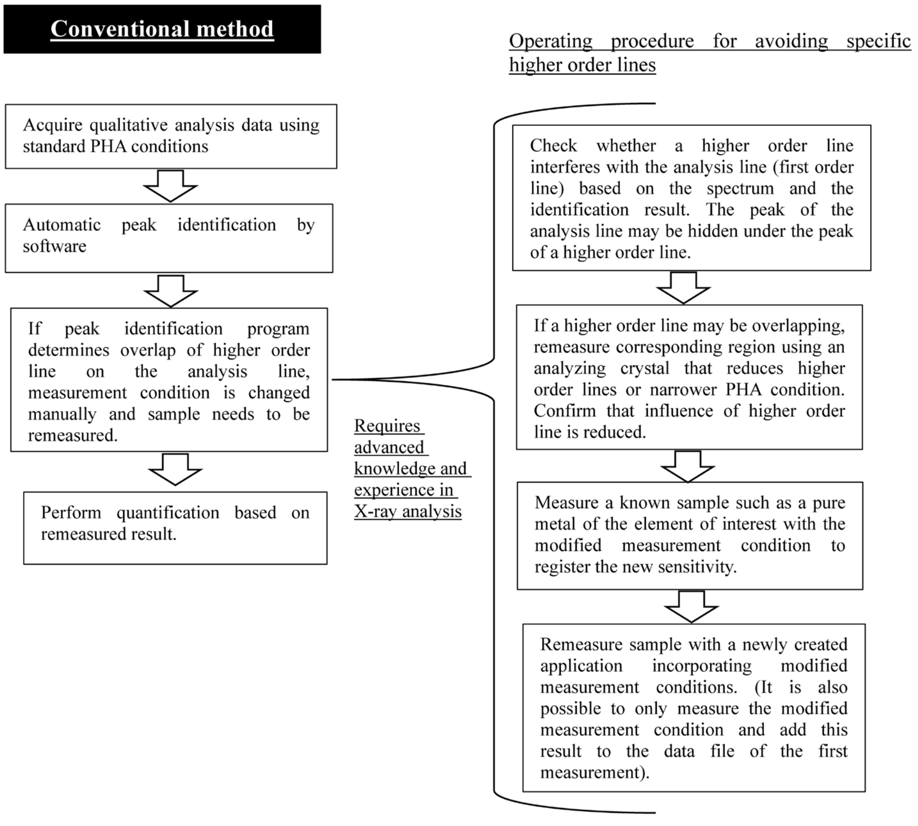
Fig. 2. Relationship between the probability of higher order line occurrence and heavy element content in various samples.

3. Number of higher order lines by sample type

The energy of a higher order line is an integer multiple of the first order line. Therefore, samples containing more heavy elements generally tend to feature a greater number of higher order lines in the analysis data. Figure 2 depicts the relationship between the probability of higher order line occurrence and the heavy element content in various samples. The heavy element content in samples increases from a) mainly organic to b) mainly oxide/light element to c) mainly heavy metal components. The probability of higher order line occurrence increases from a) to c) as well. For example, samples classified as c), such as material collected for the purpose of recycling and recovering heavy elements, can contain many heavy elements and can have high amounts of copper (Cu) and lead (Pb). Such samples can have many higher order lines and therefore require more attention for accurate analysis than samples classified as a).

4. SQX analysis with minimized influence of higher order lines

Presence of interference by a higher order line on the measurement line can be determined from the qualitative analysis result. However, if the higher order line is large, finding the optimum measurement condition that



Acquire qualitative analysis data using standard PHA conditions

Automatic peak identification by software

If peak identification program determines overlap of higher order line on the analysis line, measurement condition is changed manually and sample needs to be remeasured.

Perform quantification based on remeasured result.

Check whether a higher order line interferes with the analysis line (first order line) based on the spectrum and the identification result. The peak of the analysis line may be hidden under the peak of a higher order line.

If a higher order line may be overlapping, remeasure corresponding region using an analyzing crystal that reduces higher order lines or narrower PHA condition. Confirm that influence of higher order line is reduced.

Measure a known sample such as a pure metal of the element of interest with the modified measurement condition to register the new sensitivity.

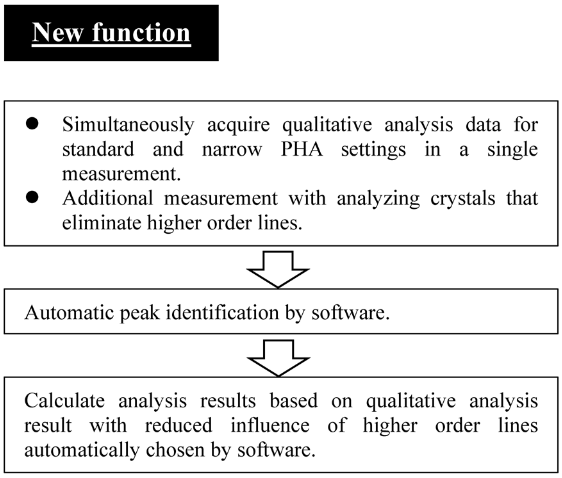
Remeasure sample with a newly created application incorporating modified measurement conditions. (It is also possible to only measure the modified measurement condition and add this result to the data file of the first measurement).

Fig. 3. Conventional procedure for SQX analysis manually reducing influence of interfering higher order lines.

minimizes its influence requires advanced knowledge of XRF principles. To calculate the analysis result based on the optimum measurement condition also requires a high level of familiarity with the software, and therefore it has been an obstacle to obtaining accurate results for samples emitting higher order lines.

Figure 3 shows the conventional method of coping with the interference of a higher order line on the measurement line, and outlines the software operating procedure. As can be seen, reducing the effect of higher order lines requires several complex manual steps.

By applying the new software function, qualitative analysis data with a narrow PHA window width is collected in addition to the data with the standard PHA width. Furthermore, measurements are performed with analyzing crystals that do not reflect higher order lines, supplementing the standard crystal measurement. When calculating analysis results with this additional data available, the software automatically chooses the qualitative result of the measurement condition that eliminates or minimizes the influence of higher order



New function

- Simultaneously acquire qualitative analysis data for standard and narrow PHA settings in a single measurement.
- Additional measurement with analyzing crystals that eliminate higher order lines.

Automatic peak identification by software.

Calculate analysis results based on qualitative analysis result with reduced influence of higher order lines automatically chosen by software.

* Narrow PHA measurement conditions: PHA window narrower than standard setting to reduce influence of higher order line

Fig. 4. Procedure of new function that automatically reduces influence of higher order lines.

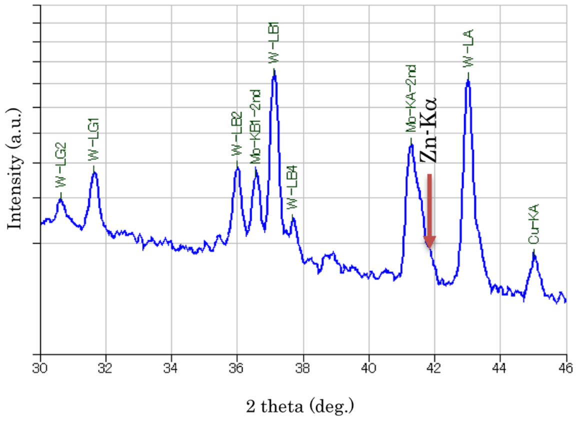
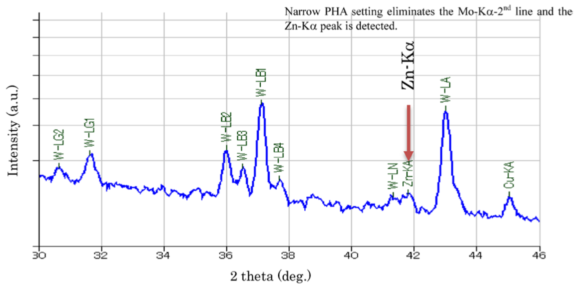


Fig. 5. Qualitative analysis chart with standard PHA setting.



Narrow PHA setting eliminates the Mo-Kα-2^{nd} line and the Zn-Kα peak is detected.

Fig. 6. Qualitative analysis chart with narrow PHA setting.

Table 2. SQX analysis measurement conditions with the new function.

Measurement region	Elements	Higher order line elimination	Analyzing crystal	Detector
Heavy elements	Ru to Cd	Simultaneous acquisition of standard and narrow PHA condition data	LiF(200)	SC
	Ti to U (to Cm)			
Light elements	K to Ca	standard measurement		PC
	Cl		Ge	
	P to S			
	Al to Si		PET	
	F to Mg		RX25	
	Light (1) K, Ca	Additional measurement with analyzing crystal that does not reflect secondary lines	Ge	
	Light (2) Al to S	Additional measurement with analyzing crystal that does not reflect higher order lines	RX25	

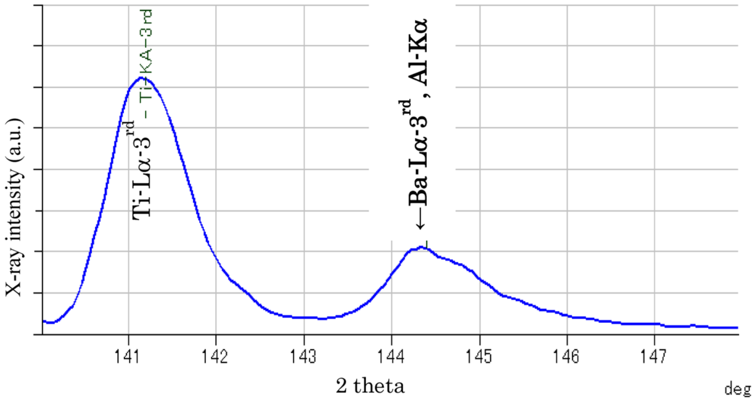


Fig. 7. Qualitative analysis chart for Al-Kα using the standard analyzing crystal PET.

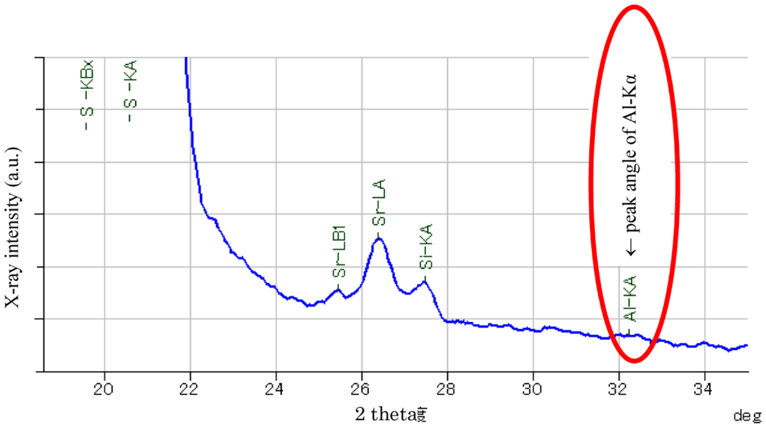


Fig. 8. Qualitative analysis chart including Al-Kα with analyzing crystal RX25.

lines.

Figure 4 shows the software sequence when the new function is applied. The manual procedures required in the former software to reduce the influence of higher order lines have been automated, simplifying the analysis procedure.

Table 2 shows the measurement conditions that reduce the influence of higher order lines. For the heavy element region, data collection with both the standard and narrow PHA window is performed simultaneously in a single qualitative analysis measurement (measurement time is not increased). Simultaneous measurement with multiple PHA settings has been made possible due to the incorporation of a digital multichannel analyzer (D-MCA) into the counting system. For higher order lines in the light element region, the analyzing crystal Ge, which does not reflect second order lines, and RX25, which does not reflect higher order lines, are used for measurement in addition to the standard measurement condition.

5. Application examples of SQX analysis reducing influence of higher order lines

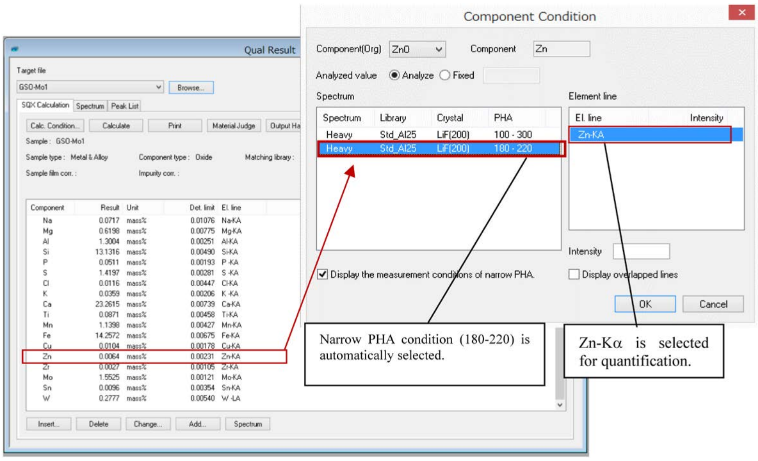
5.1. Heavy element region

SQX analysis was performed on a molybdenum ore sample containing Zn impurity. The qualitative chart with a standard PHA setting (lower limit 100, upper limit 300) around Zn-Kα is shown in Fig. 5. The Zn-Kα peak cannot be seen due to interference by Mo-Kα-2nd, Mo being a major component in the ore. Analysis of Zn impurities in such samples has been difficult by the conventional method.

The qualitative chart of the same sample using the new function is shown in Fig. 6. Since the measurement was performed with the narrow PHA setting, the higher order line Mo-Kα-2nd is eliminated and the Zn-Kα peak is detected. The net intensity of Zn-Kα obtained with the narrow PHA setting is then used in combination with the instrument's sensitivity to calculate the concentration. The calculated result for Zn having a standard value of 66 ppm is 64 ppm.

5.2. Light element region

In the light element region, measurement using an analyzing crystal that can eliminate higher order lines is performed in addition to the standard crystal. Figure 7 shows the Al-Kα chart using the standard PET crystal for a sample mixture of reagent grade $BaSO_4$ and TiO_2. Barium being a major component in the sample, the Ba-Lα-3rd line overlaps with Al-Kα, resulting in the peak



Target file: GSO-Mo1

Sample : GSO-Mo1

Sample type : Metal & Alloy
Component type : Oxide
Matching library :
Sample film corr. :
Impurity corr. :

Component	Result	Unit	Det. limit	El. line
Na	0.0717	mass%	0.01076	Na-KA
Mg	0.6198	mass%	0.00775	Mg-KA
Al	1.3004	mass%	0.00251	Al-KA
Si	13.1316	mass%	0.00490	Si-KA
P	0.0511	mass%	0.00193	P -KA
S	1.4197	mass%	0.00281	S -KA
Cl	0.0116	mass%	0.00447	Cl-KA
K	0.0359	mass%	0.00206	K -KA
Ca	23.2615	mass%	0.00739	Ca-KA
Ti	0.0871	mass%	0.00458	Ti-KA
Mn	1.1398	mass%	0.00427	Mn-KA
Fe	14.2572	mass%	0.00675	Fe-KA
Cu	0.0104	mass%	0.00178	Cu-KA
Zn	0.0064	mass%	0.00231	Zn-KA
Zr	0.0027	mass%	0.00105	Zr-KA
Mo	1.5525	mass%	0.00121	Mo-KA
Sn	0.0096	mass%	0.00354	Sn-KA
W	0.2777	mass%	0.00540	W -LA

Component(Org): ZnO
Component: Zn
Analyzed value: ● Analyze ○ Fixed

Spectrum

Spectrum	Library	Crystal	PHA
Heavy	Std_Al25	LiF(200)	100 - 300
Heavy	Std_Al25	LiF(200)	180 - 220

Element line

El. line	Intensity
Zn-KA	

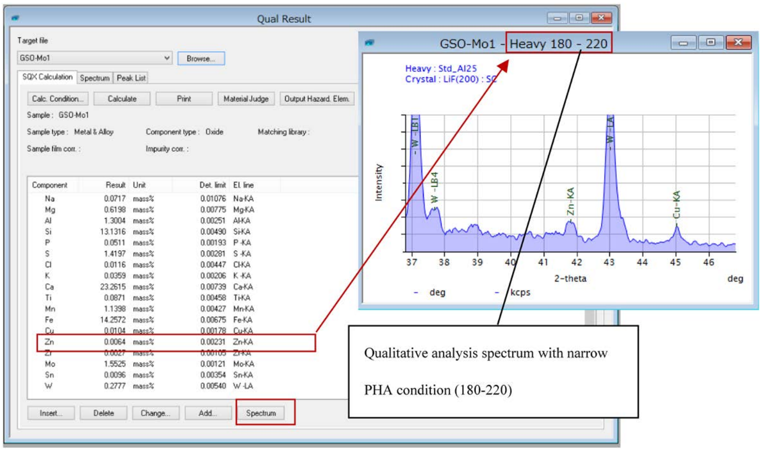
Intensity:

☑ Display the measurement conditions of narrow PHA.
☐ Display overlapped lines

Narrow PHA condition (180-220) is automatically selected.

Zn-Kα is selected for quantification.

Fig. 9. SQX analysis result in software with new function eliminating higher order lines.



Target file: GSO-Mo1

Sample : GSO-Mo1

Sample type : Metal & Alloy
Component type : Oxide
Matching library :
Sample film corr. :
Impurity corr. :

Component	Result	Unit	Det. limit	El. line
Na	0.0717	mass%	0.01076	Na-KA
Mg	0.6198	mass%	0.00775	Mg-KA
Al	1.3004	mass%	0.00251	Al-KA
Si	13.1316	mass%	0.00490	Si-KA
P	0.0511	mass%	0.00193	P -KA
S	1.4197	mass%	0.00281	S -KA
Cl	0.0116	mass%	0.00447	Cl-KA
K	0.0359	mass%	0.00206	K -KA
Ca	23.2615	mass%	0.00739	Ca-KA
Ti	0.0871	mass%	0.00458	Ti-KA
Mn	1.1398	mass%	0.00427	Mn-KA
Fe	14.2572	mass%	0.00675	Fe-KA
Cu	0.0104	mass%	0.00178	Cu-KA
Zn	0.0064	mass%	0.00231	Zn-KA
Zr	0.0027	mass%	0.00105	Zr-KA
Mo	1.5525	mass%	0.00121	Mo-KA
Sn	0.0096	mass%	0.00354	Sn-KA
W	0.2777	mass%	0.00540	W -LA

Qualitative analysis spectrum with narrow

PHA condition (180-220)

Fig. 10. Higher order line eliminated qualitative analysis result.

being falsely identified as Al-Kα. Although the sample contains almost no Al, the calculated result for Al in this case was 0.050 mass%.

By applying the new function, the qualitative analysis result of the measurement performed by analyzing crystal RX25, which eliminates higher order lines, is automatically selected to carry out the calculation for quantification. Figure 8 shows the qualitative analysis chart of the same sample with analyzing crystal RX25. Since higher order lines are not reflected, Ba-Lα-3rd peak is eliminated at the Al-Kα position. The quantitative analysis result calculated based on the Al-Kα net intensity of the automatically selected RX25 qualitative chart was below the detection limit of 0.009 mass%.

5.3. Results from new function in ZSX Guidance software

When performing SQX analysis with the new function, the higher order line eliminated qualitative analysis result is automatically selected for quantification. The new function incorporated in the software is shown below. The SQX analysis result of the molybdenum ore sample discussed in §5.1 is shown in Fig. 9. Double clicking on "Zn" displays the measurement condition used to calculate the result. It can be seen that the Zn-Kα of the higher order line eliminated data (PHA 180-220) is selected automatically for quantification of Zn.

Furthermore, by clicking "Spectrum", the qualitative analysis result selected for quantification can easily be displayed (Fig. 10).

6. Summary

Minimizing the interference of higher order lines used to require advanced knowledge of XRF analysis and extensive understanding of the software. The newly developed software takes advantage of D-MCA technology to realize automatic elimination of interference by higher order lines. As a result, highly accurate analysis and reliable results can be obtained without any special skills even when higher order lines are present. This new feature for the ZSX Guidance is unique to the Rigaku ZSX Primus IV because the D-MCA has been integrated into the counting system.