STUDY OF NET INTENSITY CALCULATION METHOD IN X-RAY FLUORESCENCE ANALYSIS

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Abstract - The semiquantitative analysis, which is called as 'Standardless Analysis' allows to obtain the compositions of samples directly from qualitative scan data without knowing sample information. The new methods on peak separation and background curve fitting demonstrated as powerful tools for the semi-quantitative analysis. The peak separation can also be applied to determine line overlapping coefficients for the conventional fundamental parameter method and the coefficients showed accurate line overlapping corrections.

Key words x-ray fluorescence analysis, semiquantitative analysis
peak separation, background curve fitting

The semi-quantitative analysis[1], which allows to obtain compositions of samples directly from qualitative scan data, recently plays one of major roles in x-ray fluorescence analysis. However, line overlapping and curved background could cause errors in predicting the net intensities of the lines for the analysis. This paper describes the new net intensity calculation methods using peak separations and background curved fitting. The method can be applied to the conventional fundamental parameter analysis as well.

EXPERIMENTAL

The studies in this paper have been done using the new Rigaku wavelength dispersive spectrometer RIX3000. The computer system available for the spectrometer is either IBM PS/2 or NEC PC9801 and the software supports full multi-tasking and multi-window. The function of the multi-tasking is not limited, so any combination of programs can be run simultaneously. The multi-window and mouse operation give friendly user interface.

PEAK SEPARATION

Peak separation techniques have not been commonly used in wavelength dispersive type of spectrometers(WDXRF). Because the line overlappings are corrected with a calibration formula using line overlapping coefficients in quantitative analysis. The peak separation techniques described in this paper are used to correct the line overlappings in qualitative scan data for semi-quantitative analysis. There are two kinds of peak separation methods developed. One is function separation using pseudo-Voigt function, which contains both Gaussian and Lorentzian and makes good fitting for the peak profiles of WDXRF[2]. The other is standard profile separation which uses standard profiles obtained by measuring standard materials instead of using mathematical function. Table 1 exhibits the formulas for the peak separations. A profile for the separation is fitted as the summation of individual profile and background. The background is calculated using a polynomial function. In the function separation, individual peak is treated as asymmetric and the widths for the left and right sides from the peak are calculated independently. All coefficients are calculated by least square fit. The standard profile separation adjusts the x-axis shift of the standard profiles. A background can also be used as a standard profile.

Table 1 Peak separation formulas

$$I(2\theta) = \sum_k f_k(2\theta) + B(2\theta)$$

$f_k(2\theta)$: Profile of peak k

$B(2\theta)$: Background function

Function separation (Pseudo-Voigt function)

$$f_k(2\theta) = h_k \{ r_k f_G(2\theta) + (1-r_k) f_L(2\theta) \}$$

$f_G(2\theta)$: Gaussian $f_L(2\theta)$: Lorentzian

$$f_G(2\theta) = \exp \left\{ -\ln 2 \frac{(2\theta - 2\theta_P)^2}{W^2} \right\}$$

$$f_L(2\theta) = \frac{1}{1 + \frac{(2\theta - 2\theta_P)^2}{W^2}}$$

h_k : Peak intensity

r_k : Gauss content

W : Half of 50% width

$2\theta_P$: Peak 2θ

Standard profile separation

$$f_k(2\theta) = \alpha_k S_k(2\theta + \beta_k)$$

$S_k(2\theta)$: Measured standard profile for peak k

α_k : Peak intensity ratio

β_k : Adjusted 2θ

Fig. 1 shows the comparison of the peak separations of both the methods using Mn-K α and Cr-K β_1 using a stainless steel. In the Fig. 1, mark x is measured data point. The broken line is individual fitted profile with the calculated background and the solid line is synthetic fitted profile. As the results show, both methods gave excellent fitting and the difference is the fitting around 62.0 degree. In the function fitting, the peak of the Cr-K β_5 line is not included in the calculation and calculated as the skirt of the Cr-K β_1 line. On the other hand, the Cr-K β_5 line is included in the standard profile of Cr-K β_1 line in the standard profile separation and it gave the perfect fitting.

Fig. 1 Comparison of peak separation methods
(sample : stainless steel)

Fig. 2 shows the peak separation results of V-K α and Cr-K α lines from a titanium alloy using the standard profile separation. The V-K α and Cr-K α lines are seriously overlapped with Ti-K β_1 and V-K β_1 . Table 2 lists the semi-quantitative analysis results of the titanium alloy NBS 654a which is a 6Al-4V titanium alloy using the peak separation shown in Fig. 2. The analyzed results of V and Cr without peak separation gave higher concentrations than the chemical values because of the line overlappings. The results with the peak separation are well matched with the chemical values.

Table 2 Semi-quantitative analysis result (%) of titanium alloy using peak separation (sample : NBS654a (6Al-4V))

Element	Line	Chemical	with separation	Deviation	without separation	Deviation
Cr	Cr-K α	0.02	<u>0.02</u>	0.00	0.45	0.43
Fe	Fe-K α	0.20	0.22	0.02	0.21	0.01
Al	Al-K α	6.34	6.16	-0.18	6.10	-0.24
V	V-K α	3.95	<u>4.00</u>	0.05	4.76	0.81

Fig. 2 Peak separations in titanium alloy (standard profile separation)

$$I_c = I_{net} - \sum I_j$$

I_c : Corrected intensity
 I_j : Correcting intensity
 I_j : Overlapping coefficient

Calculate by regression in
 fundamental parameter method

Calculate using peak separation

Fig. 3 Calculation of overlapping coefficients for fundamental parameter analysis

The peak separations can also be used to calculate overlapping correction coefficients for the conventional fundamental parameter analysis. Fig. 3 illustrates calculation methods of overlapping coefficients. The overlapping correction coefficients may be calculated by regression calculation of sensitivity calibration in the fundamental parameter method if appropriate standards can be prepared as shown in the figure. In the calculation using the peak separation, the coefficient is calculated by the ratio of interfering intensity at the analyzing line to the correcting line intensity. Table 3 lists the quantitative analysis results of stainless steel using the overlapping coefficients for P, S, Mn and Co which are typical elements for line overlapping correction. The coefficients were determined by the standard profile separation. As the results show, the coefficients gives excellent corrections for serious line overlappings.

Table 3 Quantitative analysis results (%) with overlapping coefficients
(coefficients determined by peak separation for P, S, Mn and Co)

Sample : Stainless steel

Sample	Element	Si	Mn	P	S	Ni	Cr	Mo	Co
JSS 650	Chemical	0.38	0.55	0.023	0.0026	0.30	16.66	0.044	—
	XRF	0.38	0.55	0.022	0.0019	0.30	16.74	0.043	—
	Deviation	0.00	0.00	-0.001	-0.0009	0.00	0.08	-0.001	—
JSS 652	Chemical	0.40	1.71	0.030	0.0055	11.15	16.85	2.13	0.22
	XRF	0.39	1.70	0.028	0.0080	11.03	16.93	2.10	0.22
	Deviation	-0.01	-0.01	-0.002	0.0025	-0.12	0.08	-0.03	0.00
BAS SS61	Chemical	0.42	0.78	0.016	0.016	6.26	15.20	—	0.040
	XRF	0.43	0.78	0.017	0.015	6.23	15.39	—	0.036
	Deviation	0.01	0.00	0.001	-0.001	-0.03	0.19	—	-0.004
BAS SS66	Chemical	0.51	0.81	0.020	0.023	9.48	17.60	2.43	0.063
	XRF	0.51	0.81	0.019	0.026	9.46	17.74	2.42	0.061
	Deviation	0.00	0.00	-0.001	0.003	-0.02	0.14	-0.01	-0.002

Concentrations calculated by fundamental parameter method

Standards used : BAS 63 for S, JSS 651 for others

Fig. 4 Background fitting for Bi determination in solders

BACKGROUND FITTING

The background fitting is used to obtain the net intensity of a peak located on a curved background or the skirt of a giant peak. The functions available are polynomial, Lorentzian and hyperbolic. The Lorentzian or hyperbolic function gives good fitting for curved backgrounds. The multi-point curve fitting can be used for either qualitative scan data or quantitative analysis. Fig. 4 exhibits the results of the background fitting for Bi determination in solder samples. The function used is hyperbolic. The data points for the fitting calculation were selected before and after the peak position. The concentrations of Bi were determined by the semi-quantitative analysis. The results without fitting are obtained using the net intensities calculated assuming straight backgrounds.

CONCLUSION

The results of the new peak separation and background fitting methods proved that they are powerful tools for the semi-quantitative analysis. And the methods can also be adapted to the conventional fundamental parameter analysis and improve the reliability of the results.

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