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Technical Note

STANDARDLESS X-RAY FLUORESCENCE SPECTROMETRY (Fundamental Parameter Method using Sensitivity Library)

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1. Introduction

It is possible to calculate the theoretical X-ray intensities using fundamental parameters provided that the sample composition and instrumental parameters (e.g., tube excitation voltage, X-ray optical geometry) are known. The fundamental parameter method (FP) uses the calculated theoretical intensities and the measured intensities to determine the composition of a sample. The development of a practical FP method began around 1966 [1]-[5]. With the advent of modern computers, substantial improve-ments have been made to the FP method.

In order to use a conventional FP method, one needs to have one or more standards with a matrix similar to the unknown samples or at least a set of standards that contain the analyze elements. There are many situations in which "standards" do not exist. This is particularly true in laboratories developing new materials and those involved in one of a kind and/or trouble shooting production problems. For this reason, there is a large demand for a standardless fundamental parameter method.

The Rigaku Fundamental Parameter method [6] meets this demand. Rigaku introduced the concept of a Sensitivity Library which contains the instrument sensitivity, i.e., the relationship between the theoretical and measured intensity of an element. Using this Library, one can analyze unknowns without any standard or prior knowledge of the unknown sample matrix.

Two of the features of the Rigaku FP method are the "Semiquantitative" Analysis Mode and the Group Quatitative Analysis Mode. In the "Semiquantitative" Analysis mode, one may define a set of conditions for performing a qualitative scan with automatic peak and element identification with or without automatic calculation of the concentration of the elements identified. Thus a complete unknown may be analyzed without the need for standards. In the Group Quantitative Analysis mode, one may use one or more standards of similar or completely different matrix. For those elements for which no standards exist, one may use the Sensitivity Library. Thus, by using a few standards and the Sensitivity Library, elements in virtually any sample matrix type can be quantified. As an added feature, the FP method may be used for thin film analysis, for both composition and thickness. Up to four (4) layers may be analyzed.

The Rigaku Fundamental Parameter program is provided as the standard software on the System 3270/3271 and 3370/3371 sequential X-ray spectrometers. It has substantially broadened the applications for which X-ray fluorescence may be applied. This report presents some details of the Rigaku FP method.

2. Theoretical Intensity Formula of Fluorescent X-rays

The derivation of the fundamental parameter formula has taken place over several years. The basic form was presented by Sherman in 1955 [7]. Shiraiwa and Fujino, in 1966 [1], modified the formula of the secondary excitation term. In 1977, a report was given showing the application of the theoretical intensity formula for thin film analysis.

The theoretical calculations of the intensity of nuorescent X-rays are made based on the following premises.

A. All elements are evenly distributed in the sample

B. The intensity of generated X-rays is proportional to the concentration of the measured element. The intensity is affected by the absorption and enhancement effects of the matrix elements.

C. The effects of the matrix elements can be calculated using physical constants, e.g., absorption coefficients, etc.

D. The intensity of the fluorescent X-rays produced from the sample and thus detected by the instrument are dependent on the instrumental configuration and measurement conditions.

Shown below are theoretical intensity formulas for bulk samples.

$I_i = I_{Pi} + I_{Si}$

$$I_{P_i} = \frac{K(\lambda_i)}{\sin\psi_2}\int_{\lambda_{\min}}^{\lambda_e^i}\frac{Q_i(\lambda)}{X}I_0(\lambda)d\lambda$$

$$I_{S_i} = \frac{K(\lambda_i)}{2\sin\psi_2}\sum_j\int_{\lambda_{\min}}^{\lambda_e^j}\frac{Q_j(\lambda)Q(\lambda_j)}{X}I_0(\lambda)\cdot Y\cdot d\lambda$$

I_{Pi}: Primary excitation

I_{Si} : Secondary excitation

$$Q_i(\lambda) = \tau_i(\lambda)W_i\left(1-\tfrac{1}{J_i}\right)\omega_i R_p^i$$

$$X = \frac{\mu(\lambda)}{\sin\psi_1}+\frac{\mu(\lambda_i)}{\sin\psi_2}$$

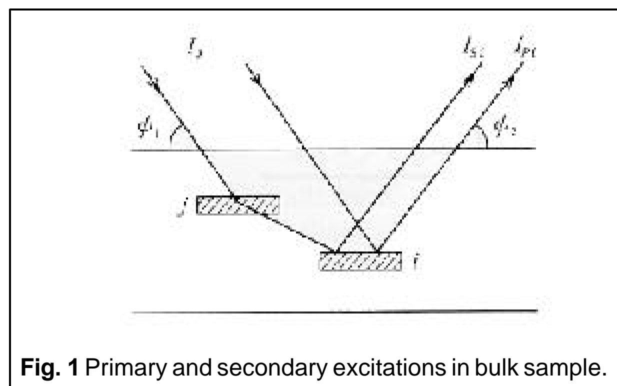

Fig. 1 Primary and secondary excitations in bulk sample.

$$Y = \frac{\sin\psi_1}{\mu(\lambda)}\ln\left(1+\frac{\mu(\lambda)}{\mu(\lambda_j)\sin\psi_1}\right) + \frac{\sin\psi_2}{\mu(\lambda_i)}\ln\left(1+\frac{\mu(\lambda_i)}{\mu(\lambda_j)\sin\psi_2}\right)$$

For thin film samples, consideration must be given to the intralayer and interlayer absorption/enhancement effects. Shown below are the theoretical intensity expressions for the absorption/enhancement in a single layer [3].

Table 1 Abbreviations in theoretical inensity formula.

Category	Item
Chemical composition	Chemical composition of measuring element: W_i
	Chemical composition of co-existing element: W_j
	Density and thickness: ρ, t
Physical constants	Total mass absorption coefficient: $\mu(\lambda)$
	Photo absorption coefficient: $\tau_i(\lambda)$
	Fluorescence yield ω_i
	Jump ratio: J_i
	Transition probability: R_p^i
	Wavelength of fluorescent X-ray and absorption edge: λ_i, λ_e^i

$I_i = I_{Pi} + I_{Si}$

$$I_{P_i} = \frac{K(\lambda_i)}{\sin\psi_2} \int_{\lambda_{\min}}^{\lambda_e^i} \frac{Q_i(\lambda)}{X} \{1 - \exp(-X\rho t)\} I_0(\lambda) d\lambda$$

$$I_{S_i} = \frac{K(\lambda_i)}{2\sin\psi_2} \sum_j \int_{\lambda_{\min}}^{\lambda_e^j} Q_j(\lambda) Q_i(\lambda_j) I_0(\lambda) \cdot \left[\int_0^{\pi/2} \left\{ \frac{1-\exp(-X_1\rho t)}{X_1 X_2} - \frac{1-\exp(-X\rho t)}{X_2 X} \right\} \tan\theta d\theta + \int_{\pi/2}^{\pi} \left\{ \frac{\exp(-X_2\rho t) - \exp(-X\rho t)}{X_1 X_2} - \frac{1-\exp(-X\rho t)}{X_2 X} \right\} \tan\theta d\theta \right] d\lambda$$

$$X = \frac{\mu(\lambda)}{\sin\psi_1} + \frac{\mu(\lambda_i)}{\sin\psi_2},\ X_1 = \frac{\mu(\lambda_\iota)}{\sin\psi_2} + \frac{\mu(\lambda_j)}{\cos\theta}$$

$$X_2 = \frac{\mu(\lambda)}{\sin\psi_1} + \frac{\mu(\lambda_j)}{\cos\theta}$$

In the integral part of the above formula, the following are used as the value in braces for θ integration when X, or X2 is approximately 0.

For the integration term of 0-π2:

$\{\ \} = \{1-(1+X\rho t)\exp(-X\rho t)\}/X^2$

For the integration term of $\pi/2$-π:

$\{\ \} = -\{1+(1+X\rho t)\exp(-X\rho t)\}/X^2$

Fig. 2 shows the double layer thin film model. Thin films can be analyzed with up to four layers.

If the physical constant, instrument factor and sample composition are known, the theoretical intensity can be calculated from the above formulas. By measuring standard samples the instrument sensitivity can be obtained from the relationship between the measured and theoretical X-ray intensities. For an unknown analysis, the measured intensity is converted to the theoretical intensity scale by multiplying by the instrument sensitivity. This converted measured intensity is then used to calculate the composition of the unknown sample.

For example, the following three steps outline the unknown analysis procedure.

1. The measured intensities are converted to theoretical intensity scale. This is then used to make a first approximation of the composition.

2. The above approximate composition is used to calculate theoretical intensities. These are compared to the above converted measured intensities and used to calculate a new approximation of the composition.

3. This step involves a check for convergence between the newest composition and the pre-vious one. If the two compositions agree within a preset limit value, a report is made of the final composition. If the two compositions have not converged sufficiently, Step 2 is repeated until they converge.

3. Sensitivity Library

The instrument sensitivity is basically a conversion factor between the measured intensity and the theoretical intensity. It is a function of the optical system of the instrument, the reflection efficiency of the analyzing crystal, the counting efficiency of the detector, etc. Thus, the instrument sensitivity varies with each element.

Using a conventional fundamental parameter method the instrument sensitivity must be determined for each element to be analyzed. This means that a standard must exist for each element. Except in the case of some routine analysis, standards may be difficult or impossible to obtain for certain elements in some matrices. The Rigaku Fundamental Parameter Sensitivity Library solves this problem.

By using standards spiked with equal concentrations of selected elements, correlations were estab-

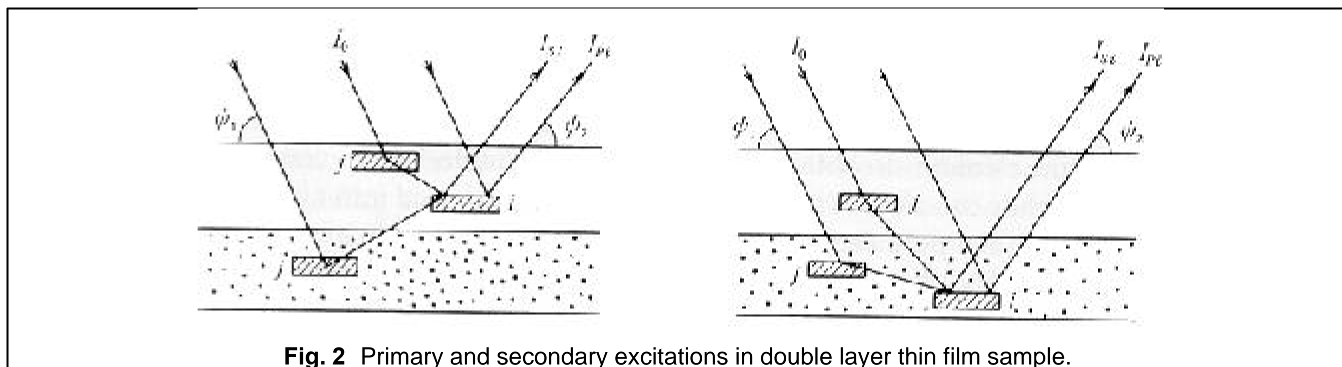

Fig. 2 Primary and secondary excitations in double layer thin film sample.

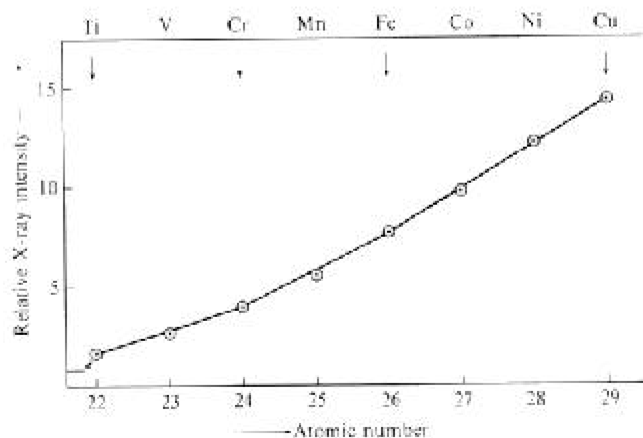

Fig. 3 Relationship between X-ray intensity and atomic number of pure materials. (Note) Arrow stands for library sample.

Table 2 Library Division for Semiquantative Analysis

No.	Elements range	Measured spectrum	Analyzing Crystal	Detector	Excitation condition
1	$_{9}$F ~ $_{12}$Mg	Kα	TAP	F-PC	Both Rh-Lα and Rh-Lβ contribute to excitation
2	$_{13}$Al ~ $_{14}$Si		PET		
3	$_{15}$P ~ $_{16}$S		Ge		
4	$_{17}$Cl				Rh-Lβ contributes to excitation but Rh-Lα does not contribute to excitation
5	$_{18}$Ar ~ $_{21}$Sc		LiF(200)		Both Rh-Kα and Rh-Kβ contribute to excitation
6	$_{22}$Ti ~ $_{42}$Mo	Kα or Kβ$_1$	LiF(200)	SC	
7	$_{43}$Tc ~ $_{44}$Ru				Rh-Kβ contributes to excitation, but Rh-Kα does not contribute to excitation
8	$_{45}$Rh ~ $_{55}$Cs				Rh characteristic X-rays do not contribute to excitation, but only continuous X-ray contribute to excitation
9	$_{56}$Ba ~ $_{92}$U	Lα or Lβ$_1$			Both Rh-Kα and Rh-Kβ contribute to excitation

lished for the measured intensity, instrument sensitivity and element atomic number. These correlations are dependent on the X-ray tube, analyzing crystal, etc. Once these relationships are established and stored in the Sensitivity Library for several elements, they may be used to calculate relationships by interpolation, for elements for which no standards can be made. To maximize the versatility of the Sensitivity Library and minimize the amount of work and standards necessary to analyze a variety of matrices, the following are measured and stored in the instrument at the factory:

a. spectral intensity ratios for Kα to Kβ and Lα to Lβ.
b. intensity ratios for different observed sample areas, i.e., different diaphram diameters, and
c. intensity ratios for the attenuator.

Fig. 3 shows the relationship between the X-ray intensity and the atomic number of a pure element. Generally, it is best to use pure elements to obtain this relationship but pure compounds can also be used. In the latter case, the intensity for the pure element can be calculated knowing the compound formula. In addi-tion, standard samples, e.g., stainless steel, cement, etc., may also be used to establish this relationship by making use of the fundamental parameter method.

From Fig. 3 it is obvious that interpolation between elements is practical. However, in order to do this the sensitivity relationship must be continuous in the atomic number region of interest. Discontinuities result from the use of different analyzing crystals, excitation conditions, etc. To cope with this, the periodic table, and consequently the Sensitivity Library, is divided into nine regions as shown in Table 2. Thus, it is possible to analyze all elements from F to U by using the stored sensitivities of only 17 elements. In actual practice, the sensitivities of a greater

number of elements are usually used in order to improve the accuracy of the data.

4. Automatic Qualitative and Semiquantitative Analysis

For many years analysts have wanted to be able to automatically perform both qualitative and quantitative analysis on an unknown sample. To do this requires automatic peak (i.e., element) identification and quantification from the X-ray spectrum. The Rigaku FP method solves this problem with the automatic qualitative analysis program and the Sensitivity Library.

4.1 Automatic Qualitative Analysis

Accurate elemental identification and X-ray intensity determination is essential in order to perform an analysis of the composition of the sample. The qualitative analysis portion of this program involves two steps.

1. Peak Search and Background Subtraction

The spectrum is prepared for elemental identification by continuous on-line, i.e., Real Time, data processing, including smoothing and peak search. Basically three steps are involved in the algorithm.

a. The raw data (corrected for counting losses) is smoothed while the step scan data is collected.

b. Peaks are found using the second derivatives of smoothed spectrum. Several criteria must be met in order for a peak to be considered "real". The program distinguishes between real peaks and pseudo peaks, i.e., intensity fluctuations in the background or on a peak.

c. the background is then subtracted so that an accurate net peak intensity is obtained.

2. Elemental Identification

Ahigh level decision making process is used to perform elemental identification. Criteria included are the intensity ratios of $K\alpha$ to $K\beta$ and $L\alpha$ to $L\beta$, for strong lines considering line overlap. And also intensity ratios of strong lines to weak lines such as $L\beta_2$ $L\beta_3$, $L\gamma_1$ as well as higher order lines are included in the criteria. The identification algorithm is built with six stages including the identification of characteristic lines from the X-ray tube and very small peaks so that most possible lines are identified.

4.2 Semiquantitative Analysis

The semiquantitative analysis program uses the net peak intensities and element list directly from the qualitative analysis. So, once the semiquantitative option is chosen, automatic qualitative scans, peak identification and quantification can be performed for any number of samples including storage and printout of results. There are five important features of this program.

a. Since the Sensitivity Library is used for the concentration calculations, all elements from F to U may be quantified. The semiquantitative analysis routine calculates all the interelement corrections.

b. The calculations of sample composition may be made as elements or oxides.

c. Dilution factors for fused disks or pressed pellets may be incorporated.

d. An unmeasured component, e.g., a polymer in a plastic. Fe in a steel, etc., may be specified and calculated as the balance.

e. Since the raw data and all the analysis results can be stored, they can also be recalled for user interaction. Thus the analyst can examine, change or modify the results as desired.

4.3 Examples of Semiquantitative Analysis Applications

Table 3 shows the semiquantitative analysis results of a copper alloy, aluminum alloy and a stainless steel. The analysis for each was performed under identical analytical conditions. All values are expressed in percent. The certified values are listed as the "chemical" values. Very good agreement can be seen by examining the "DIFF" column.

Table 4 contains the results for a pressed powder pellet and a fused disk. In both cases the elemental composition was calculated as the oxides. A dilution factor of 10 was used for the glass disk. As with the above metals, the agreement here is excellent for a semiquantitative procedure. For the major constituent in both Tables 3 and 4, the relative error is within ±5%.

5. Group Quantitative Analysis

The group quantitative analysis method employs the full fundamental parameter calculations for specified elements for which an instrument sensitivity has been obtained. For those elements for which it is not possible to establish the instrument sensitivity, the Sensitivity Library is used. This program may be used for bulk sample analysis or for multi-layer thin film (both elemental composition and layer thickness) analysis.

In order to optimize the analytical conditions for each measured element within a sample, a given group may be configured with one or more of the following.

Table 3 Analytical results of metal samples by Semiquantitative Analysis.
(1) Copper alloy (NBSC1103)

Element	Chemical	XRF	Diff
Cu	59.18	58.	-1.18
Zn	35.73	37.	1.27
Pb	3.82	2.9	-0.92
Fe	0.26	0.26	0.0
Sn	0.88	0.85	-0.03
Ni	0.16	0.18	0.02

(2) Aluminium alloy (Showa Alumi 604)

Element	Chemical	XRF	Diff.
Mg	0.60	0.81	0.21
Si	0.38	0.42	0.04
Ti	0.004	--	-0.004
V	0.011	0.015	0.004
Cr	0.015	0.026	0.011
Mn	0.002	0.0034	0.0014
Fe	0.19	0.19	0.00
Cu	0.014	0.016	0.002
Zn	0.003	0.0024	-0.0006
Ga	0.014	0.016	0.002

(3) Stainless steel (NBS D846)

Element	Chemical	XRF	Diff.
Si	1.19	1.0	-0.19
Mn	0.53	0.49	-0.04
Ni	9.11	8.0	-1.11
Cr	18.35	19.0	0.65
Mo	0.43	0.32	-0.11
Cu	0.19	0.18	-0.01
V	0.03	0.04	0.01
W	0.04	0.04	0.0
Ti	0.34	0.31	-0.03
Sn	0.02	0.02	0.0
Nb	0.60	0.50	-0.10
Ta	0.03	0.04	0.01

a. For elements for which standards can be measured, the instrument sensitivity is obtained using the FP method. The sensitivity calibration curve, i.e., Theoretical Intensity vs. Measured Intensity, may be made using either ratio, linear or quadratic equations.

b. For elements for which no standards are available, the FP method uses the Sensitivity Library.

c. For elements for which the FP method is not suitable, e.g., B, C, N and O, any one of several empirical methods may be used.

Table 4 Analytical results of powder and fused bead samples by Semiquantitative Analysis.
(1) Refractory (BCS315) (Powder)

Component	Chemical	XRF	Diff.
SiO_2	51.2	50.	-1.2
TiO_2	1.23	1.3	0.07
Al_2O_3	42.3	42.	-0.3
Fe_2O_3	3.01	3.8	0.79
CaO	0.34	0.36	0.02
MgO	0.57	0.68	0.11
K_2O	0.52	0.59	0.07
Na_2O	0.13	0.12	-0.01
MnO	0.02	0.025	0.005

(2) Rock (JA-1) (Fused disk)

Component	Chemical	XRF	Diff
SiO_2	64.06	63.	-1.06
TiO_2	0.87	0.91	0.04
Al_2O_3	14.98	15.	0.02
Fe_2O_3	6.95	7.4	0.45
MnO	0.15	0.15	0.0
MgO	1.61	1.8	0.19
CaO	5.68	5.9	0.22
Na_2O	3.86	3.9	0.04
K_2O	0.82	0.79	-0.03
P_2O_5	0.16	0.16	0.00

Table 5 Analytical results of bulk sample by Group Analysis.
Stainless steel (JSS 655).
Standard: JSS 654 (sensitivity library used for Nb)

Element	Chemical	X-ray	Diff.
Si	0.60	0.59	-0.01
Mn	1.58	1.58	0.00
Cu	0.089	0.091	0.002
Ni	11.53	11.42	-0.11
Cr	18/54	18.66	0.12
Mo	0.052	0.071	0.019
Nb	0.59	0.63	0.04

To account for those elements in a sample that are not measured, e.g., a polymer in a plastic, oxygen in an oxide, etc., the following may be used.

a. The components may be calculated as the oxides or other compounds.

b. The major constituent may be calculated as the balance component, e.g., Fe in a steel or CxHy in a plastic.

Table 6 Analytical results of thin film samples by Group Analysis. (Sensitivity library used for all spectral lines)

	STD Value	X-ray	Diff.
(1) Cu Foil			
Thickness (mg/cm^2)	8.23	8.55	0.32
(2) Single Layer of Ni P alloy			
Sample 1	STD Value	X-ray	Diff.
Thickness (μm)	1.2	1.18	-0.02
Ni (%)	88.6	89.8	1.2
P(%)	11.4	10.2	-1.2
Sample 2	STD Value	X-ray	Diff.
Thickness(μm)	19	18.9	-0.1
Ni (%)	88.6	88.7	0.1
P(%)	11.4	11.3	-0.1
(3) Double Layer of NiCo alloy on Cr			
Sample 3	STD value	X-ray	Diff.
Thickness of NiCo (A)	401	407	
Ni(%)	80.2	79.6	6-0.6
Co(%)	19.8	20.4	0.6
Thickness of Cr (A)	1040	975	-65
Sample 4	STD value	X-ray	Diff.
Thickness of NiCo (A)	1208	1235	27
Ni(%)	80.2	80.7	0.5
Co(%)	19.8	19.3	-0.5
Thickness of Cr (A)	3133	2967	-166

c. The dilution factor for a fusion flux or pellet binder may be incorporated in the concen-tration calculations.

d. Chemical information from other analytical techniques may be put into the group manually for use in calculating the final results.

e. The film thickness and composition of a multi-layer thin film may be determined at the same time. However, if either the thickness or composition are known in advance they may be put into the group manually and the unknown value determined.

5.1 Examples of Group Quantitative Analysis Applications

Table 5 show the results of the analysis of a JSS655 stainless steel using a JSS654 as a standard. Since the JSS654 does not contain Nb, the Sensitivity Library was used for quantifying this element. The certified values (in percent) are listed as the "chemical" values. In the analysis, Fe was treated as the balance element. Examination of the "DIFF" column shows the excellent agreement of the results.

Table 6 shows the results of the analysis of thin film samples for which no standards were available. The Sensitivity Library was used for the all specified elements. The first set of data shows a comparison be-tween the thickness (mg/cm^2) of a Cu foil calcula-ted using the group method and the standard value ob-tained by weighing the foil. The second set of data is for two samples of a single layer Ni-P thin film. The thickness and composition were calculated for both samples. In the last data set, thin double layers on a glass substrate were measured simultaneously. The first layer was a Ni-Co alloy and the second was pure Cr. The thickness and composition for the first layer and the thickness of the second were calculated for two different samples. A comparison of the accepted standard value and the value calculated from the group quantitative method shows excellent agree-ment.

6. Conclusion

Generally, a fundamental parameter method analysis with similar standards to unknowns in composition gives better accurancy than that with standards having completely different composition [8]. With this respect, the FP method with the Sensitivity Library uses standard materials as references and better accurancy can be expected in the FP method with similar standards. However, there are many situations where no standards are available particularly in the field of research and development. The FP method with the Sensitivity Library, which gives accurate result without standards as verified above, should be a great help in these situations. Especially, the semiquantitative analysis method allows to analyze completely unknown samples ac-companied with qualitative information. The FP method using the Sensitivity Library could release analysts from shackles of standards and has remark-ably broadened the application of X-ray spectro-metry.

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