

THE ROLE OF THE MEASUREMENT CONSTANT IN X-SPECTROMETRY

JOSIP TUDORIĆ-GRMO, NIKOLA GODINOVIĆ, LOVORKA RADA-LJUBIĆ

*Fakultet elektrotehnike strojarstva i brodogradnje,
University of Split, Split, Croatia, Yugoslavia*

JOSIP ČEPLE

*Elektrotehnički studij, Osijek, University of Zagreb
Osijek, Croatia, Yugoslavia*

TATJANA TOMIĆ

Zavod za zaštitu zdravlja - Split, Croatia, Yugoslavia

The role and importance of the measurement constant in X-spectrometry is considered with the problem of the sample composition analysis without the use of standard samples. It is shown that it is possible to determine the sample composition even when the characteristic X-ray intensity for one of the elements in the sample is not detectable. The duraluminum sample and the brass sample compositions have been analyzed as two essentially different examples of the presented approach. Iron in brass shows the case when the corresponding intensity is undetectable since the element is present only in traces. In case of duraluminum, the undetectable aluminum is a dominant component of the sample composition.

1. Introduction

In the last decade the EDXRF spectrometry has developed into the most reliable, non-destructive and rapid analytical method. The X-energy spectrometry requires a minimal sample preparation (thick target), in which case the matrix effects occur. The X-ray intensity from an element in the matrix of other elements is not linear with composition because of the selective absorption or secondary fluorescence within the sample¹⁾. The most common approach for correcting the matrix effects in the X-energy spectrometry is the fundamental parameter method with the use of corresponding standards¹⁾ in order to avoid determining the measurement constant and a series of other relevant parameters.

These standards make the measurement more complex and are unwelcome. This paper presents a new approach to the fundamental parameter method without the use of standards, which also allows avoiding the most undesirable parameter, the measurement constant.²⁾

The problem of determining the sample composition, when the characteristic X-ray intensity of one of the elements in sample is not detectable, is also considered. Here the fundamental parameter method without using the standards, cannot avoid determining the measurement constant. The value of the measurement constant is obtained by analyzing an "independent" sample³⁾. This sample of course, must contain only the elements with detectable characteristic radiation. Obviously, it need not to be a special standard. It is desirable for both this "independent" sample and the sample involved to have the same excitation conditions (working condition of X-ray tube, irradiator, geometry, collection time). If these conditions are not fulfilled it is necessary to perform the renormalization of the measurement constant.³⁾

2. Avoiding the measurement constant in the analysis of a sample composition without the use of standards

The detected characteristic X-ray intensity for an element has been found to be²⁾:

$$I_{ix} = KMF_{ix}(w_i) = K \sum_{\gamma} \frac{n_{o\gamma}}{n_o} \frac{\sigma(x_i) \omega_{xi} \sigma_i(\gamma) w_i \text{kor}_{xi} (1-1/J_{xi})}{\mu_{em}(\gamma) + \mu_{em}(x_i) \cos\beta / \cos\theta}$$

$$\left\{ 1 + \frac{1}{2\sigma_i(\gamma)} \sum_{y_j} w_j (1-1/J_{y_j}) \sigma_i(y_j) \sigma_j(\gamma) \text{kor}_{y_j} w_{y_j} \right\}$$

$$\left[\frac{\cos\beta}{\mu_{em}(\gamma)} \ln \left(1 + \frac{\mu_{em}(\gamma)}{\mu_{em}(y_j) \cos\beta} \right) + \frac{\cos\theta}{\mu_{em}(x_i)} \ln \left(1 + \frac{\mu_{em}(x_i)}{\mu_{em}(y_j) \cos\theta} \right) \right] \quad (1)$$

where:

K - measurement constant (product of irradiator γ -photon number per unit solid angle and mean detector solid angle);

$\mu_{em}(\gamma)$ - mass attenuation coefficient of the sample for incident γ -photon (linear function of unknowns - w_i);

- $\mu_{em}(x_i)$ - mass attenuation coefficient of the sample for x-photon from element-i; $\mu_{em}(y_j)$ - the same for y photon from element-j;
- ω_{xi} - x-shell fluorescence yield for element-i; ω_{yj} - the same for y-shell of element-j;
- $\sigma_i(\gamma)$ - photoelectric cross section for incident γ -photon on element-i; $\sigma_i(y_j)$ - the same for y-photon from element-j;
- J_{xi} - x-shell absorption-edge-jump ratio for element-i; J_{yj} - the same for y-shell for element-j;
- w_i - mass fraction of element-i in the sample, searching values;
- $\epsilon(x_i)$ - relative detection efficiency for x-photon of element-i;
- kor_{xi} - the relative intensity of x-characteristic photon from x-shell one hole state deexcitation for element-i, kor_{yj} - the same for y-shell for element -j;
- $\frac{n_{\alpha\gamma}}{n_0}$ - relative intensity for incident γ -photons;
- β - mean incident angle of γ -photons;
- θ - mean exit angle of x-photons.

The relation (1) is in full analogy with the relation (9) by Criss and Birks¹⁾. The factors kor , ω and J are measurable physical quantities and can be found in references^{4,5,6,7)}. Detection efficiency $\epsilon(x_i)$ can also be found, or can be measured. Thus only the measurement constant K is left unknown.

If the sample composition consists of n elements with the corresponding mass fractions w_j ($j=1\dots n$), the solving of the composition problem requires n measured characteristic intensities N_i ($i=1, \dots, n$, one for each element). Then the system

$$N_i = K * F_i(w_j) \quad \begin{matrix} i=1, \dots, n \\ j=1, \dots, n \end{matrix} \quad (2)$$

$$\sum_j w_j = 1$$

has $(n+1)$ unknowns (K, w_j) and $(n+1)$ independent equations, so the searching for solution is justified. The system is nonlinear and the solution requires the iterative process based on the successively better estimates of mass fraction until the differences between the corresponding calculated intensities and

the measured intensities are within the desired limits. In each iteration step these obtained differences are used to adjust the new assumed mass fractions.

In applying this iteration process it is necessary to avoid determining the measurement constant K. There is no possibility for the corresponding corrections. For this purpose it is convenient to define the measured relative intensities as

$$r_{im} = \frac{N_i}{\sum_i N_i} \quad (3), \text{ where}$$

N_i - is the measured characteristic intensity for element-i, obtained by decomposition of the corresponding spectrum.

The calculated relative intensities are defined in the same manner:

$$r_{ic} = \frac{F_i}{\sum_i F_i} \quad (4)$$

The composition problem is reduced to solve the system of n independent equations with n unknowns:

$$r_{im} = r_{ic}(w_j) \quad (i=1, \dots, n; j=1, \dots, n) \quad (5)$$

$$\sum_j w_j = 1$$

The most simple iterative process is based on the linear interpolation of the mass fraction compositions and on the scaling of these fractions so that their sum is a unity at the start of each iteration step. It can be shown that results converge to the unique solution.

In solving the problem of sample analysis when the characteristic X-ray intensity of an element cannot be detected, the above fundamental parameter method without using the standards²⁾ cannot be applied. Namely, the system of n independent equations with (n+1) unknowns has no unambiguous solution. The number of unknowns must be reduced by one. The measurement constant K is the most advisable unknown which can be determined separately. There are two essentially different cases.

If an intensity is missing because of the corresponding element being present only in traces in the sample, the measurement constant K can be determined in the allowed approximation by

composition analysis of the same sample, assuming the corresponding element not being present at all in the sample. If the corresponding element of the undetectable intensity is a dominant fraction in the sample composition, the above assumption is not allowed. Then the measurement constant K must be determined by analysing an "independent" sample. In both cases the relations (3) can be written as

$$r_{im} = \frac{N_i}{\sum_{i \neq l} N_i + K \cdot F_l(w_j)} \quad \begin{matrix} i \neq l \\ i=1, \dots, (n-1) \\ j=1, \dots, n \end{matrix} \quad (6)$$

and the corresponding system of equations (5) consists of n independent equation with n unknowns and can again be solved by the same iteration method.

3. Measuring and results

To verify both specific ways in determining the sample composition, in case when the characteristic intensity of one of the sample elements cannot be determined, the duraluminum sample and the brass sample have been analyzed.

Duraluminum sample analysis

Duraluminum is an alloy of Al, Fe, Cu, and Zn. The aluminum is present in the highest concentration, but its characteristic radiation is not detectable with the applied detector system. Figure 1. is indicative. Only the characteristic peak of Fe, Cu and Zn can be seen with no characteristic peak of Al.

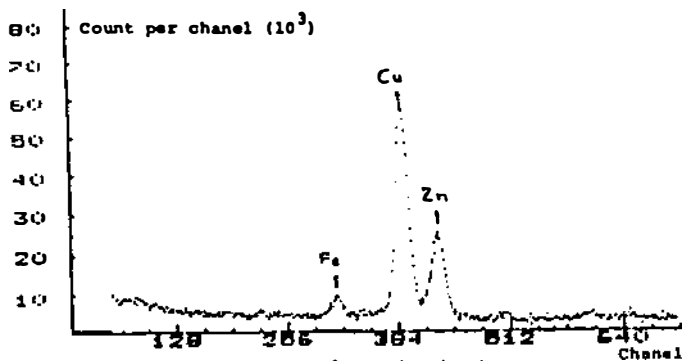


Fig. 1. X-spectrum from duraluminum.

An "independent" sample has been analyzed (Table 1.) and the measurement constant determined.

TABLE 1.

Cr(%)	Mn(%)	Fe(%)	Cu(%)	Zn(%)
1.14 ± 0.02	0.90 ± 0.02	97.7 ± 0.1	0.24 ± 0.02	0.067 ± 0.005

Independent sample composition.

$$K(\text{measur. const.}) = (5,70 \pm 0.02) * 10^6$$

This constant is used directly in the sample analysis since the excitation conditions for the duraluminum sample and those of the "independent" one were the same.

The results of duraluminum sample analysis are given in Table 2. The sample has also been analyzed by chemical analysis method.

TABLE 2.

	Al(%)	Fe(%)	Cu(%)	Zn(%)
X-spectrometry	93.9 ± 0.5	0.29 ± 0.03	5.6 ± 0.5	0.042 ± 0.005
Chemical analysis	93.8 ± 0.2	0.25 ± 0.02	5.5 ± 0.2	*

Duraluminum sample composition.

* - Zn being present in traces only, and it was not possible to separate it by classical chemical methods.

The errors in X-spectrometry analysis include the counting statistical error and uncertainties in the fundamental parameters²⁾. The errors in chemical analysis are estimated by superposition of errors in the corresponding measurements.

The comparative analysis of the results shows the reliability of the described approach in solving the problem of the sample composition analysis when the characteristic intensity of the dominant component in the sample is not detectable.

Brass sample analysis:

Brass sample (alloy of Fe, Cu, Zn) is an example when the characteristic X-ray intensity for an element cannot be determined because the element is present in traces only, as is the case of

iron (Fe). Figure 2. presents the X-ray spectrum from brass. It can be seen that the characteristic X-ray intensity for Fe is of the same order as the background noise.

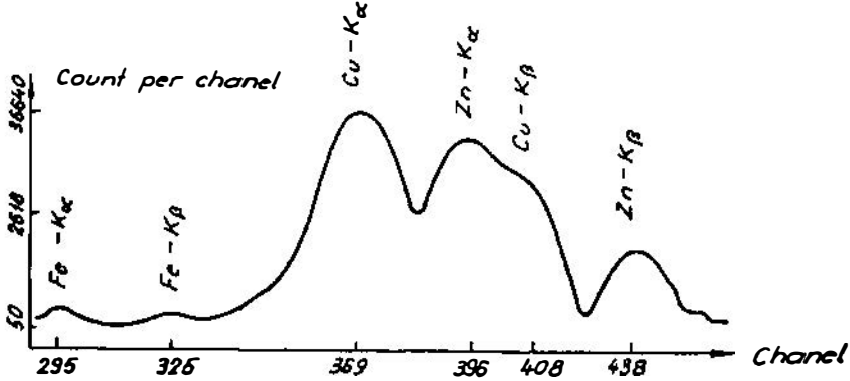


Fig. 2. X - spectrum from brass

This fact naturally allows the assumption that iron is not present in the sample. The aim of this assumption is to determine the measurement constant solving the corresponding system (5).

The true composition of brass sample, now when the measurement constant is estimated, is determined on the basis of relations (6). The analysis results are:

$$w_{Fe} = (0.047 \pm 0.006)\%$$

$$w_{Cu} = (74.8 \pm 0.3)\%$$

$$w_{Zn} = (25.1 \pm 0.3)\%$$

The same brass sample has also been analyzed by the atomic absorption spectrophotometry method and the results are the following:

$$w_{Fe} = (0.047 \pm 0.005)\%$$

$$w_{Cu} = (73.7 \pm 1.5)\%$$

$$w_{Zn} = (26.2 \pm 0.8)\%$$

The errors in X-spectrometry are of the same meaning as before. The errors in the atomic absorption spectrophotometry include the chemical analysis errors and the inherent spectrophotometry errors. The comparative analysis of the presented results shows the reliability of approximate determination of the measurement constant when the characteristic X-ray intensity of an element in traces is hardly detectable.

4. CONCLUSION

In the applied X-spectrometry many improvements can be obtained not only by advancing the detection technique and spectrum deconvolution, but also by the improvement of the physical approach. The presented analysis results, when the characteristic X-ray intensity for one of the elements in the sample is missing, confirms the above statement. It further suggests considering the problem in case the characteristic X-ray intensities for two elements in the sample are undetectable.

Acknowledgement

The authors gratefully acknowledge the support and hospitality of the Laboratory for Nuclear Microanalysis - Institute R.Bošović - Zagreb, where the X-ray spectra were recorded.

References

- 1) W. Criss and L. S. Birks, *Anal. Chem.* 40, (1968), 1080.
- 2) J. Tudorić, M. Grbac and J. Čeple: *A Contribution to the Development of The Fundamental Parameters method in x-ray Energy Spectrometry*, Zbornik radova ISEMEC-87, Ionizirno sevanje, 13. međunarodni seminar, 109-118, Ljubljana 1987.
- 3) N. Godinović, J. Tudorić-Ghemo, J. Čeple, M. Grbac, T. Tomić: *On The Possibility of X-ray analysis of an Alloy With a Dominant Component Whose Characteristic Radiation Is Hardly Detectable in Applied Spectrometry*, Zbornik radova JUKEM 13, 1115-1120, Split 1988.
- 4) W. H. McMaster, N. Kerr Del Grande, J. M. Mallet, J. H. Hubbel: *Compilation of X-ray Cross Section*, University of California, Livermore, May 1969.
- 5) Lederer, Hollander, Perlman: *Table of Isotopes*, John Willey & Sons, New York 1967.
- 6) T. P. Thinh & J. Leroux, *X-ray Spectrometry*, Vol. 8. No. 2. 1979.
- 7) H. O. Krause, *J. Phys: Chem. Ref. Data*, Vol. 8 No. 2. 1979.