



Improving accuracy and capabilities of X-ray fluorescence method using intensity ratios



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ABSTRACT

An X-ray fluorescence analysis algorithm is proposed which is based on a use of ratios of X-ray fluorescence lines intensities. Such an analytical signal is more stable and leads to improved accuracy. Novel calibration equations are proposed which are suitable for analysis in a broad range of matrix compositions. To apply the algorithm to analysis of samples containing significant amount of undetectable elements a use of a dependence of a Rayleigh-to-Compton intensity ratio on a total content of these elements is suggested. The technique's validity is shown by analysis of standard steel samples, model metal oxides mixture and iron ore samples.

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1. Introduction

X-ray fluorescence (XRF) method allows fast and precise determination of elemental composition of samples of various genesis. Different techniques and calibration methods have been proposed since early 1950-s in order to reach the best precision and to broad an application field of the method. A comprehensive review of these techniques including *fundamental parameters method* (FPM) is given by R.M. Rousseau [1]. However, all the techniques were originally designed for analysis of homogeneous samples with flat polished surface, e.g. massive steel samples, fused borate disks, etc. Therefore, none of the techniques (except FPM) can be applied for the analysis of non-conventional samples (finished technical products, samples with unpolished surface, metal filings, various powders with different grain size, etc.) without appropriate calibration and often a great number of reference samples, but adequate standard samples are often unavailable [2]. Besides, when a specimen contains significant amounts of elements that cannot be detected (*undetectable elements* (UE)), most of these techniques fail to give adequate results. Some other methods using primary radiation scattered by a sample were suggested to solve this problem

[3–8], but their application is usually limited to a narrow matrix composition range restricted by calibration samples and often requires a large number of reference standards.

It is shown that if a ratio of XRF lines intensities is applied as an analytical signal, then accuracy of analysis improves and the influence of the sample shape and surface quality decreases significantly [2]. However, matrix effects influence is still strong and should be taken into account.

In a current work, we present a novel equations with theoretical coefficients based on intensity ratios. These equations allow one to improve the accuracy of XRF analysis, to broad the matrix composition range, in which the analysis can be performed with the same accuracy with the same calibration samples, and to analyze non-conventional samples with a reduced number of standard samples.

2. Theory

2.1. Algorithm for samples not containing UE

A dependence of XRF intensity ratio on a concentration ratio occurred to be linear in a broad range of concentration ratios [2]. However, it is still influenced by other elements. Let us consider Ni-Fe-Cr tertiary system under monochromatic approximation. To take into account that the primary radiation is polychromatic and heterogeneous due to its characteristic constituents, it is better to use different *effective* wavelengths λ_i^{pr} of the primary radiation for each element i [9,10]. These wavelengths are chosen so that

Abbreviations: XRF, X-ray fluorescence; FPM, fundamental parameters method; UE, undetectable elements; FA, fundamental algorithm; LSM, least squares method; BFP, backscatter fundamental parameters; DE, detectable elements; NRMSE, normalized root-mean-square error; APE, absolute percentage error.

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their influence is similar to the averaged influence of the whole primary radiation spectrum. Then nickel-to-iron K_{α} -lines intensity ratio is given by the following equation:

$$\frac{I_{NiK\alpha}}{I_{FeK\alpha}} = \frac{g_{Ni}}{g_{Fe}} \frac{C_{Ni}}{C_{Fe}} \frac{k_{Ni}}{k_{Fe}} \frac{p_{NiK\alpha}}{p_{FeK\alpha}} \times \frac{\mu_{Ni}(\lambda_{Ni}^{pr}) \times I_{pr}(\lambda_{Ni}^{pr})/M_{Ni}}{\mu_{Fe}(\lambda_{Fe}^{pr}) \times I_{pr}(\lambda_{Fe}^{pr})/M_{Fe} + 1/2 \times \delta_{Fe,NiK\alpha} + 1/2 \times \delta_{Fe,NiK\beta}}, \quad (1)$$

where $I_{iK\alpha}$ is an intensity of K_{α} -line of an element i , g_i is a proportionality constant dependent upon the instrument used, c_i is a mass fraction of the element i , $I_{pr}(\lambda)$ is an intensity of primary radiation at a λ wavelength,

$$k_i = \frac{S_i - 1}{S_i} \omega_i,$$

S_i is a jump ratio of element i for K -edge of considered line, ω_i is a fluorescence yield for considered line of element i , p_i is a fraction of element's i K_{α} -line in the total intensity of K -series, $\mu_i(\lambda)$ is a mass attenuation coefficient of the element i at the λ wavelength,

$$M_i = \sum_{j=1}^n C_j \times (\mu_j(\lambda_i^{pr}) \times \text{cosec} \phi + \mu_j(\lambda_{iK\alpha}) \times \text{cosec} \psi),$$

$\delta_{i,jK\alpha}$ is an enhancement correction factor:

$$\delta_{ij} = \mu_i(\lambda_{jK\alpha}) k_j C_j \mu_j(\lambda_j^{pr}) \times I_{pr}(\lambda_j^{pr}) \times L_{i,jK\alpha}^i / \left(\sum_{k=1}^n C_k \times (\mu_k(\lambda_j^{pr}) \times \text{cosec} \phi + \mu_k(\lambda_{iK\alpha}) \times \text{cosec} \psi) \right),$$

$$L_{i,jK\alpha}^i = \frac{\sin \phi}{\sum_k C_k \mu_k(\lambda_j^{pr})} \ln \left(1 + \frac{\sum_k C_k \mu_k(\lambda_j^{pr})}{\sin \phi \times \sum_k C_k \mu_k(\lambda_{jK\alpha})} \right) + \frac{\sin \psi}{\sum_k C_k \mu_k(\lambda_{iK\alpha})} \times \ln \left(1 + \frac{\sum_k C_k \mu_k(\lambda_{iK\alpha})}{\sin \psi \times \sum_k C_k \mu_k(\lambda_{jK\alpha})} \right),$$

ϕ is an angle between the sample and an incident x-rays, ψ is an angle at which XRF radiation is detected ("take-off angle") [11].

Rearrangement of (1) gives

$$\frac{I_{NiK\alpha}}{I_{FeK\alpha}} = k_{Ni/Fe} \frac{C_{Ni}}{C_{Fe}} \times \frac{M_{Fe}}{\frac{\mu_{Fe}(\lambda_{Fe}^{pr}) \times I_{pr}(\lambda_{Fe}^{pr})}{\mu_{Ni}(\lambda_{Ni}^{pr}) \times I_{pr}(\lambda_{Ni}^{pr})} M_{Ni} + \frac{M_{Fe} M_{Ni} \times [1/2 \times \delta_{Fe,NiK\alpha} + 1/2 \times \delta_{Fe,NiK\beta}]}{\mu_{Ni}(\lambda_{Ni}^{pr}) \times I_{pr}(\lambda_{Ni}^{pr})}}, \quad (2)$$

where $k_{Ni/Fe} = g_{Ni} k_{Ni} p_{NiK\alpha} / g_{Fe} k_{Fe} p_{FeK\alpha}$. Let us then consider $M_i/M_j \approx \text{const}$ (which is, of course, rather rough approximation). Then, taking into account that $C_{Ni} = (C_{Ni} + C_{Fe}) R_{Ni/Fe} / (1 + R_{Ni/Fe})$ and $C_{Fe} = (C_{Ni} + C_{Fe}) / (1 + R_{Ni/Fe})$, where $R_{Ni/Fe} = C_{Ni} / C_{Fe}$, and that $C_{Ni} + C_{Fe} = 1 - C_{Cr}$ in the considered case, we can rearrange (2) as follows:

$$\frac{I_{NiK\alpha}}{I_{FeK\alpha}} = k_{Ni/Fe} R_{Ni/Fe} \frac{a_0 + a_{Cr} \times C_{Cr}}{b_0 + b_{Cr} \times C_{Cr}}, \quad (3)$$

where

$$\begin{aligned} a_0 &= [R_{Ni/Fe} \times \mu_{Ni}(\lambda_{Fe}^{pr}, \lambda_{FeK\alpha}) + \mu_{Fe}(\lambda_{Fe}^{pr}, \lambda_{FeK\alpha})] / (1 + R_{Ni/Fe}), \\ a_{Cr} &= \mu_{Cr}(\lambda_{Fe}^{pr}, \lambda_{FeK\alpha}) - a_0, \\ b_0 &= \frac{\mu_{Fe}(\lambda_{Fe}^{pr}) I_{pr}(\lambda_{Fe}^{pr}) R_{Ni/Fe} \mu_{Ni}(\lambda_{Ni}^{pr}, \lambda_{NiK\alpha}) + \mu_{Fe}(\lambda_{Fe}^{pr}, \lambda_{NiK\alpha})}{\mu_{Ni}(\lambda_{Ni}^{pr}) I_{pr}(\lambda_{Ni}^{pr})} \frac{1}{1 + R_{Ni/Fe}} \\ &+ \frac{1}{2} \frac{R_{Ni/Fe}}{1 + R_{Ni/Fe}} \sum_{k=1}^n \frac{k_{Ni} M_{Ni} M_{Fe}}{C_k \mu_{Ni}(\lambda_{Ni}^{pr}, \lambda_{FeK\alpha})} \left(\mu_{Fe}(\lambda_{NiK\alpha}) p_{NiK\alpha} L_{NiK\alpha}^{Fe} + \mu_{Fe}(\lambda_{NiK\beta}) p_{NiK\beta} L_{NiK\beta}^{Fe} \right), \\ b_{Cr} &= \frac{\mu_{Fe}(\lambda_{Fe}^{pr}) I_{pr}(\lambda_{Fe}^{pr})}{\mu_{Ni}(\lambda_{Ni}^{pr}) I_{pr}(\lambda_{Ni}^{pr})} \mu_{Cr}(\lambda_{Ni}^{pr}, \lambda_{NiK\alpha}) - b_0, \\ \mu_i(\lambda_j, \lambda_k) &= \mu_i(\lambda_j) \times \text{cosec} \phi + \mu_i(\lambda_k) \times \text{cosec} \psi. \end{aligned}$$

For multielement sample, the Eq. (3) will take the following form:

$$\frac{I_{iK\alpha}}{I_{jK\beta}} = k_{i/j} R_{i/j} \frac{a_0 + \sum_{k \neq i,j} a_k C_k}{b_0 + \sum_{k \neq i,j} b_k C_k} = a R_{i/j}. \quad (4)$$

However, beside approximations used, there is a problem of coefficients a_i , b_i being dependent on the concentration ratio $R_{i/j}$ of the chosen pair of elements i and j . Thus, the Eq. (4) will require a very close first approximation of the sample composition and will allow one to obtain accurate results only in narrow ranges of concentrations of all elements, i.e. in narrow range of the matrix composition. Such a situation took place with Rousseau's fundamental algorithm (FA), which required a use of a Claisse–Quintin algorithm with separate calibration samples set for obtaining the first approximation [1].

An alternative approach was suggested by Pavlinsky and Vladimirova [12]. They first calculated XRF lines intensities for several tens of samples and then used this calculated intensities to find the values of the parameters of their model by the least squares method (LSM). This allows one to broad an operating range of matrix compositions and to reduce bias caused by the approximations used. Therefore, we also apply this approach to calculate the parameters of our model. However, when the concentration ratios $R_{i/j}$ are relatively large, some of the assumptions made do not work, which gives rise to a significant constant term, though the dependence is still linear:

$$\frac{I_{iK\alpha}}{I_{jK\beta}} = a_0 + a_1 R_{i/j}. \quad (5)$$

Nevertheless, both the coefficients a_0 and a_1 were found to be best fit by an expression similar to that of the coefficient a in (4), so after dividing both numerator and denominator of (4) by b_0

$$a_0 = \frac{a_{00} + \sum_{k \neq i,j} a_{01k} C_k}{1 + \sum_{k \neq i,j} b_{01k} C_k}, a_1 = \frac{a_{10} + \sum_{k \neq i,j} a_{1k} C_k}{1 + \sum_{k \neq i,j} b_{1k} C_k}.$$

However, it was found empirically that often second-order terms are necessary to describe a dependence of a_0 on concentrations C_k more accurately. Therefore

$$a_0 = \frac{a_{00} + \sum_{k \neq i,j} a_{01k} C_k + \sum_{k \neq i,j} a_{02k} C_k^2}{1 + \sum_{k \neq i,j} b_{01k} C_k + \sum_{k \neq i,j} b_{02k} C_k^2}.$$

2.2. Algorithm for samples containing UE

Almost all algorithms of XRF analysis of samples with significant content of UE are models based on the use of a scattered radiation. Often they are more or less adequate regression models [13]. Nevertheless, some models have theoretical basis. Among them Bakhtiarov's technique [6], so-called backscatter fundamental parameters (BFP) method [3,4] and Szaloki's algorithm [5] are notable. The first one is suitable for determination of heavy metals in any concentration and in any light matrix. However, empirical regression models are necessary for analysis of samples containing high amounts of other heavy elements, especially heavier than the element being determined [6]. Thus, matrix composition range will be restricted by calibration samples, and errors caused by difference in samples' shape, particle sizes, surface quality are possible. BFP is an attempt to expand FPM to samples containing UE, but it requires using absolute intensities of scattered radiation, that in fact again leads to a dependence of the results on samples' shape, surface quality and other experimental factors difficult to control.

Szaloki's algorithm is also an attempt of expanding FPM to samples containing UE. It utilizes using Rayleigh-to-Compton intensity ratio $I_{R/C}$ to determine an average atomic number of the sample Z_S

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