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Quantification in X-Ray Fluorescence Spectrometry

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1. Introduction

X-ray fluorescence spectrometry (XRF) is a versatile tool in many analytical problems. Major, minor and trace elements can be qualitatively and quantitatively determined in various kinds of samples: metals, alloys, glasses, cements, minerals, rocks, ores, polymers as well as environmental and biological materials. Elements from Na to U are routinely determined using energy-dispersive X-ray fluorescence spectrometry (EDXRF) whereas application of wavelength-dispersive spectrometers (WDXRF) allows efficient determination of low-Z elements down to even Be. Although the samples can be analyzed without treatment, high quality results can be ensured if appropriate sample preparation is applied. This may vary from simple cleaning and polishing of the sample (metals, alloys), powdering and pelletizing with or without binder (ceramics, minerals, ores, soils, etc.), fusing the sample with appropriate flux (ceramics, rocks, ores, etc.) to digestion with acids (metals, alloys). This way errors resulting from surface roughness, particle size effect or inhomogeneity of the material can be eliminated or minimized. Due to the nondestructive character of X-ray measurement, the XRF spectrometry is widely applied in analysis of art, museum and archeological objects such as manuscripts, paintings, icons, pottery, ancient glasses, ceramics, coins. Moreover, XRF spectrometry is utilized for simultaneous determination of thickness and composition of various materials such as semiconductors, electrooptic and solar cell devices, etc., in electronic industry and other branches of technology. Typical detection limits for medium- and high-Z elements are in the ppm range, which is satisfactory for several applications. However, in some cases, the elemental concentrations are too low for a direct analysis. Then, the analytes must be preconcentrated prior to analysis using physical or chemical preconcentration or separation methods.

Quantitative analysis of all types of aforementioned samples requires applying adequate empirical or theoretical methods. In quantitative XRF analysis, the measured fluorescent intensities are converted into the concentration of the analytes. This issue is rather complicated because the measured intensities depend not only on the analyte concentration but also on accompanying elements (matrix), sample type (solid, liquid or powder sample, etc.), method of sample preparation, shape and thickness of the analyzed sample and measurement conditions such as geometrical setup of the spectrometer, irradiated size, flux

and spectral distribution of the exciting radiation and the efficiency of detection systems. The simplest equation relating radiation intensity I_i to weight fraction of analyte W_i can be expressed as follows:

$$I_i = k_i W_i \quad (1)$$

Where k_i is a constant. The radiation intensity I_i in Eq. (1) is corrected for background, line overlap, and so forth. In practice, the subtraction of background is not perfectly performed. Thus, Eq. (1) can be expressed in a more general form:

$$I_i = k_i W_i + b_i \quad (2)$$

Where b_i is the radiation intensity when analyte concentration equals zero. The constant k_i is called the sensitivity and is expressed in counts per second per unit of concentration. The constants k_i and b_i are determined by least-squares fit on the basis of measured reference samples from the following formulas:

$$k_i = \frac{n \sum_{j=1}^n W_{ij} I_{ij} - \sum_{i=1}^n W_{ij} \sum_{i=1}^n I_{ij}}{n \sum_{i=1}^n W_{ij}^2 - \left(\sum_{i=1}^n W_{ij} \right)^2} \quad (3)$$

$$b_i = \frac{\sum_{i=1}^n I_{ij} - K_i \sum_{i=1}^n W_{ij}}{n}$$

Where n is the number of standard samples used for analyte i , W_{ij} is the weight fraction of analyte i in standard j , I_{ij} is the radiation intensity of analyte i in standard j .

In practice, the concentrations of the standard samples have to cover the concentration in unknown sample. Moreover, the calculated concentration is more accurate at the center of the calibration line than at the extremities. The Eq. (2) can be rewritten as follows:

$$W_i = K_i I_i + B_i \quad (4)$$

If the calibration based on Eq. (2) or Eq. (4) and standard samples similar to the unknown are carefully applied, several parameters such as sample type, method of sample preparation, and measurement conditions, i.e. the geometrical setup of the spectrometer, irradiated size, flux and the efficiency of detection systems are included in the slope K_i and can be omitted in further stages of quantification. However, a simple linear calibration is not the rule in the XRF analysis. In general, applying the linear Eq. (2) or Eq. (4) requires not only that all standards are similar to the unknown and but also the set of standards with a very limited range of concentrations must be applied for calibration. Only then, the matrix effects in all samples are similar and linear relationship between radiation intensity and analyte concentration can be obtained. On the other hand, the use of standards with a very limited range of concentrations will lead to a calibration graph with large uncertainty on the slope and intercept. Because the matrix effects play an important role in XRF analysis, a more general equation should be applied:

$$W_i = K_i I_i M_i + B_i \quad (5)$$

Where M_i is the total matrix effects term. The M_i differs from one if matrix effects cannot be neglected. When the analyte radiation is absorbed by the matrix or when the absorption effects are dominating over enhancement effects, M_i is larger than 1. On the other hand, when enhancement effects are dominant over absorption, M_i is smaller than 1.

In matrix correction methods, the radiation intensity I_i is usually replaced with relative radiation intensity R_i defined as fluorescent radiation intensity of analyte in binary, ternary or in multielement specimen $I_{specimen,i}$ to fluorescent radiation intensity of pure element or compound $I_{pure-element,i}$, e.g. oxide:

$$R_i = \frac{I_{specimen,i}}{I_{pure-element,i}} \quad (6)$$

If matrix effects can be neglected, the relative radiation intensity equals weight fraction of analyte:

$$W_i = R_i \quad (7)$$

In practice, the matrix effects play an important role in XRF analysis. Therefore, the relative radiation intensity has to be corrected using total matrix effects term:

$$W_i = R_i M_i \quad (8)$$

Because the matrix effects are the major source of errors in X-ray fluorescence analysis, this chapter is devoted to matrix correction methods applied in quantitative XRF analysis. The matrix effects (absorption and secondary fluorescence) and necessary background information on theoretical relationship between radiation intensity and sample composition will be provided first. In the next part of the chapter, the quantification methods applied in XRF will be discussed.

2. General relationship between radiation intensity and concentration

In 1955, Sherman proposed a mathematical formula to calculate radiation intensity of analyte in a specimen of a known composition (Sherman, 1955). Later, Shiraiwa and Fujino corrected the enhancement part of this formula by introducing a missing factor of $\frac{1}{2}$ (Shiraiwa and Fujino, 1966). The general equation to calculate X-ray fluorescence intensity I_i emitted by an analyte in the specimen of thickness t when it is irradiated by a polychromatic X-ray beam can be expressed as follows:

$$I_i = \frac{d\Omega}{4\pi \sin \phi_i} Q_i q_i W_i \int_{\lambda_{min}}^{\lambda_{edge}} \tau_i(\lambda) I_0(\lambda) \frac{1 - \exp[-\chi(\lambda, \lambda_i)\rho t]}{\chi(\lambda, \lambda_i)} \left(1 + \sum_j W_j S_{ij} \right) d\lambda \quad (9)$$

Where $d\Omega$ is the differential solid angle for the characteristic radiation; i, j are the subscripts for the analyte and matrix element, respectively; Q_i is the sensitivity of the spectrometer for characteristic radiation of analyte i ; W_i, W_j are weight fractions of the analyte i and matrix element j , respectively; λ_{min} and λ_{edge} are short-wavelength limit and wavelength of analyte absorption edge, respectively; $\tau_i(\lambda)$ is the photoelectric absorption coefficient for analyte i and primary radiation of wavelength λ ; $I_0(\lambda)$ is intensity of the primary radiation, ρ is the

density of the sample; t is the sample thickness; q_i is sensitivity of the analyte i (if the K_α line is chosen then $q_i = \omega_{K,i} f_{i,K\alpha} (1 - 1/J_{i,K})$, where $\omega_{K,i}$ is fluorescence yield of K radiation; $f_{i,K\alpha}$ is weight of K_α line within K series; $J_{i,K}$ is absorption edge jump ratio. If the L_α or L_β is chosen as the analytical line, then the Cöster-Kronig transition probabilities have to be additionally taken into consideration); $\chi(\lambda, \lambda_i)$ is total mass-attenuation coefficient of the sample for the incident and fluorescent radiation:

$$\begin{aligned}\chi(\lambda, \lambda_i) &= \frac{\mu(\lambda)}{\sin \phi_1} + \frac{\mu(\lambda_i)}{\sin \phi_2} \\ \mu(\lambda) &= W_i \mu_i(\lambda) + \sum_j W_j \mu_j(\lambda) \\ \mu(\lambda_i) &= W_i \mu_i(\lambda_i) + \sum_j W_j \mu_j(\lambda_i)\end{aligned}\quad (10)$$

Where $\mu(\lambda)$ and $\mu(\lambda_i)$ are the total mass-attenuation coefficients of the specimen for the incident radiation λ and characteristic radiation λ_i , respectively; ϕ_1 and ϕ_2 are the incidence and take-off angles, respectively; $\mu_i(\lambda)$, $\mu_i(\lambda_i)$, $\mu_j(\lambda)$, $\mu_j(\lambda_i)$ are the mass-attenuation coefficients of the analyte i and matrix element j present in the specimen for the incident radiation λ and characteristic radiation λ_i . The S_{ij} (in Eq. 9) is the enhancement term for the matrix element j , which can enhance the analyte i (if analyte is not enhanced by matrix element j then $S_{ij} = 0$):

$$\begin{aligned}S_{ij} &= \frac{1}{2} q_j \tau_j(\lambda) \frac{\tau_i(\lambda_j)}{\tau_i(\lambda)} \frac{\chi(\lambda, \lambda_i)}{1 - \exp[-\chi(\lambda, \lambda_i) \rho t]} D_{ij} \\ D_{ij} &= \int_0^{\pi/2} \tan(\theta) \left[\frac{1 - \exp[-\chi_1(\lambda_i, \lambda_j) \rho t]}{\chi_1(\lambda_i, \lambda_j) \chi_2(\lambda, \lambda_j)} - \frac{1 - \exp[-\chi(\lambda, \lambda_i) \rho t]}{\chi(\lambda, \lambda_i) \chi_2(\lambda, \lambda_j)} \right] d\theta + \\ &\quad \int_{\pi/2}^{\pi} \tan(\theta) \left[\frac{\exp[-\chi_2(\lambda, \lambda_j) \rho t] - \exp[-\chi(\lambda, \lambda_i) \rho t]}{\chi_1(\lambda_i, \lambda_j) \chi_2(\lambda, \lambda_j)} - \frac{1 - \exp[-\chi(\lambda, \lambda_i) \rho t]}{\chi(\lambda, \lambda_i) \chi_2(\lambda, \lambda_j)} \right] d\theta \\ \chi_1(\lambda_i, \lambda_j) &= \frac{\mu(\lambda_i)}{\sin \phi_1} + \frac{\mu(\lambda_j)}{\cos \theta} \\ \chi_2(\lambda, \lambda_j) &= \frac{\mu(\lambda)}{\sin \phi_1} - \frac{\mu(\lambda_j)}{\cos \theta}\end{aligned}\quad (11)$$

It is beyond the scope of this chapter to derive the Eq. (9). Details on the derivation of this equation can be found elsewhere (Mantler, 1986; Van Dyck et al., 1986; He and Van Espen, 1991; Węgrzynek et al. 1993). As seen from Eq. (9), the intensity of characteristic radiation is the complex function of sample composition and sample thickness. The primary and fluorescent radiation are attenuated by atoms of the analyte and by any other atoms present in the matrix (see Eq. (10)). If matrix element emits a characteristic line that has sufficient

energy to excite the analyte, the fluorescent intensity is higher than expected from primary excitation only (the enhancement term S_{ij} in Eq. (9)). The so-called matrix effects (absorption and enhancement) will be discussed in the next section of this chapter.

It should be emphasized that the enhancement term S_{ij} in Eq. (9) cannot be expressed as analytical function and numerical integration is required. Therefore, the matrix correction methods require complex mathematical treatment. Nevertheless, if the thickness of the sample is greater than the so-called saturation thickness ($t \rightarrow \infty$), Eq. (9) simplifies to:

$$I_i = \frac{d\Omega}{4\pi \sin \phi} Q_i q_i W_i \int_{\lambda_{\min}}^{\lambda_{edge}} \frac{\tau_i(\lambda) I_0(\lambda)}{\chi(\lambda, \lambda_i)} \left(1 + \sum_j W_j S_{ij} \right) d\lambda \quad (12)$$

$$S_{ij} = \frac{1}{2} q_j \tau_j(\lambda) \frac{\tau_i(\lambda_j)}{\tau_i(\lambda)} \left[\ln \left(1 + \frac{\mu(\lambda)}{\mu(\lambda_j) \sin \phi} \right) \frac{\sin \phi}{\mu(\lambda)} + \ln \left(1 + \frac{\mu(\lambda_i)}{\mu(\lambda_j) \sin \phi} \right) \frac{\sin \phi}{\mu(\lambda_i)} \right]$$

Eq. (12) is applied in analysis of the so-called infinitely thick specimens. In practice, the sample should satisfy Eq. (13). Then, the relative error resulting from applying Eq. (10) instead of Eq. (7) does not exceed 1%.

$$t \geq \frac{4.61}{\chi(\lambda, \lambda_i) \rho} \quad (13)$$

As seen from Eq. (12), the intensity of characteristic radiation of analyte present in infinitely thick sample depends not only on analyte concentration but also on full matrix composition. Because sample thickness is greater than the saturation thickness, the intensity of characteristic radiation of analyte does not depend on sample thickness, which considerably simplifies mathematical treatment.

If the sample is infinitely thin ($t \rightarrow 0$), then the enhancement effects can be neglected ($S_{ij} \rightarrow 0$) and the approximation $\exp(-x) \approx 1-x$ can be applied and the Eq. (9) simplifies to:

$$I_i = \frac{d\Omega}{4\pi \sin \phi} Q_i q_i W_i \rho t \int_{\lambda_{\min}}^{\lambda_{edge}} \tau_i(\lambda) I_0(\lambda) d\lambda \quad (14)$$

In practice, the sample is not infinitely thin, therefore it should satisfy Eq. (15). Then, the relative error resulting from applying Eq. (14) instead of Eq. (9) does not exceed 0.5 %.

$$\rho t \leq \frac{0.1}{\chi(\lambda, \lambda_i)} \quad (15)$$

For thin samples, the intensity of characteristic radiation of analyte does not depend on matrix composition – matrix effects can be neglected. In consequence, the linear relationship between radiation intensity and mass per unit area of the analyte is observed (mass per unit area of the sample: $m = \rho t$ [g cm⁻²], mass per unit area of the analyte: $W_i m$).

The samples of less than critical thickness for which matrix effects cannot be neglected are called intermediate-thickness samples. Review of quantitative analysis of these samples including many references can be found in Ref. (Markowicz and Van Grieken, 2002; Sitko, 2009). The general division of the sample in X-ray fluorescence analysis is presented in Fig. 1.

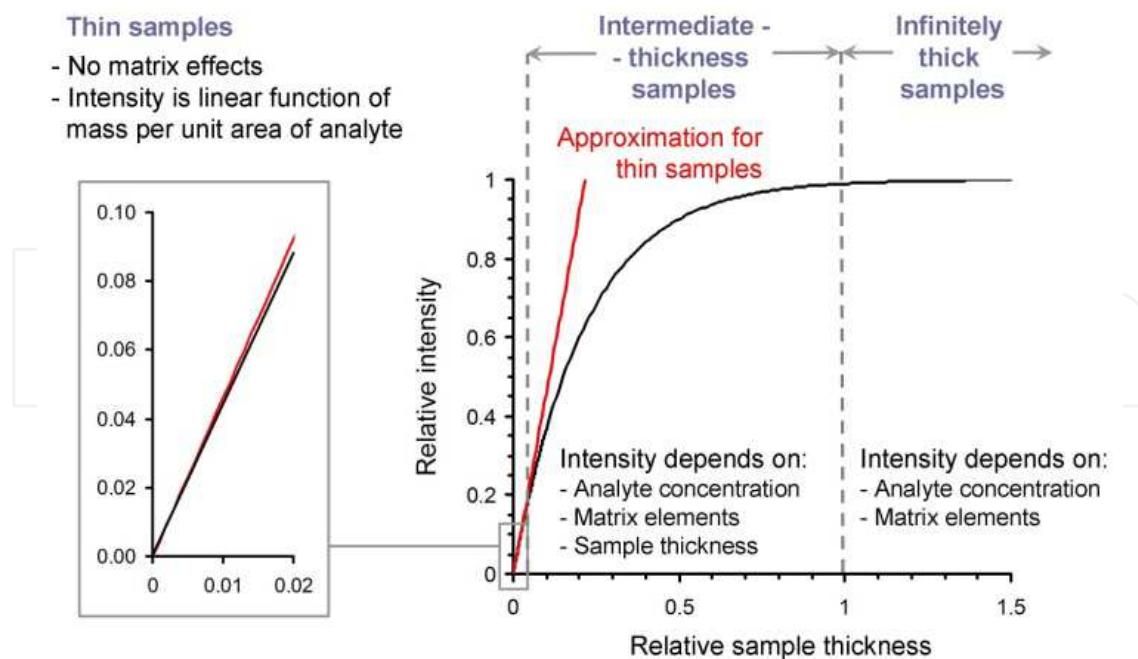


Fig. 1. The general division of the sample in XRF analysis.

3. Matrix effects in XRF analysis

Matrix effects in XRF spectrometry are caused by absorption and enhancement of X-ray radiation in the specimen. The primary and secondary absorption occur as the elements in the specimen absorb the primary and characteristic radiation, respectively. The strong absorption is observed if the specimen contains an element with absorption edge of slightly lower energy than the energy of the characteristic line of the analyte. When matrix elements emit characteristic radiation of slightly higher energy than the energy of analyte absorption edge, the analyte is excited to emit characteristic radiation in addition to that excited directly by the X-ray source. This is called secondary fluorescence or enhancement. The absorption and enhancement effects are shown in Fig. 2 using binaries (FeMn, FeCr and FeNi) as examples. When matrix effects are either negligible or constant, the linear relationship

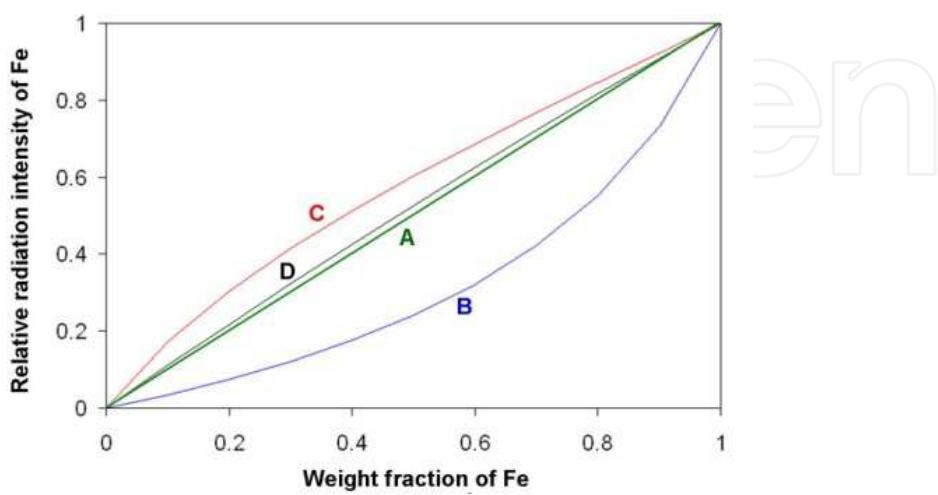


Fig. 2. Relationship between radiation intensity of Fe and weight fraction of Fe: Curve A – matrix effects are negligible, Curve B – FeCr, Curve C – FeNi, Curve D – FeMn.

between radiation intensity and weight fraction of analyte is obtained (Curve A). Curve B is obtained when the absorption by the matrix elements in the specimen is greater than the absorption by the analyte alone (the so-called positive absorption, e.g. determination of Fe in FeCr binaries). Curve C illustrates an enhancement effect, e.g. in the case of determination of Fe in FeNi binaries. Curve D is observed when the matrix element in the specimen absorbs the analyte radiation to a lesser degree than the analyte alone (the so-called negative absorption, e.g. determination of Fe in FeMn binaries).

4. Quantification in XRF analysis

Numerous methods, both empirical and theoretical, have been proposed for quantitative XRF analysis. They are divided into two major groups: compensation and matrix correction methods (Fig. 3). Moreover, only one method allows minimizing matrix effects. This method is based on preparation of thin samples. For these samples, matrix effects are not observed under measurement conditions and linear relationship between radiation intensity and analyte concentration is observed. In other quantitative methods, the matrix effects are still present but they are corrected or compensated.

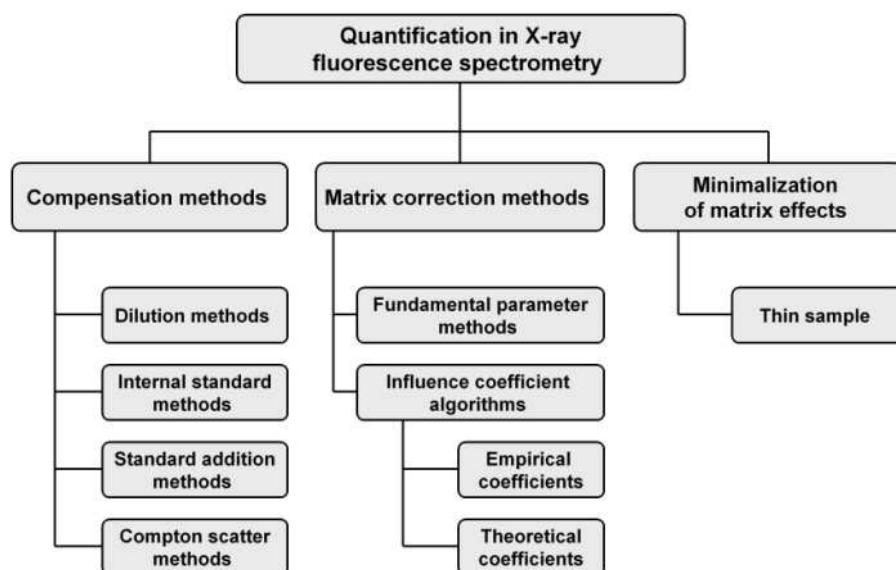


Fig. 3. General division of methods applied in quantitative XRF analysis.

The compensation methods (variations in matrix effects resulting from various specimen compositions are minimized), except Compton scatter, are all well-known in other analytical techniques, e.g. atomic absorption or emission spectrometry. In these methods, special sample preparation is required and only one or few elements can be quantitatively determined. Therefore, the compensation methods are less popular than matrix correction methods. It should be emphasized that radiation intensity of analyte can be calculated from theory. This feature is unique to X-ray spectrometry techniques. No other analytical technique allows such a combination of theoretical calculations and experimental results. Due to the increasing power of computers during the past few years, the theoretical methods, both fundamental parameters and theoretical influence coefficients, became the most popular in routine XRF analysis. Therefore, these methods are discussed in this chapter. Review of the compensation methods including many references can be found in

"Handbook of X-Ray Spectrometry," edited by Van Grieken and Markowicz (de Vries and Vrebos, 2002) and "Handbook of Practical X-Ray Fluorescence Analysis" edited by Beckhoff, Kanngießer, Langhoff, Wedell and Wolff (Vrebos, 2006).

5. Fundamental parameter methods

The fundamental parameter methods are based on Sherman equation (Eq. (9)) considering both primary and secondary fluorescence. The tertiary fluorescence and the effects caused by scattered radiation are usually neglected. Eq. (9) enables to calculate the intensity of fluorescent radiation of analyte in the specimen of known composition. It is possible if all physical constants are known: photoelectric absorption coefficients, mass-attenuation coefficients, Cöster-Kronig transition probabilities, fluorescence yields, weight of analytical line within the series, absorption jump ratios, whose values can be found in updated databases (Elam et al., 2001; Ebel et al., 2003). X-ray tube spectrum, required in calculation, can be obtained from published experimental data. Nevertheless, the experimental spectral distributions are published only for selected voltages and types of X-ray tube (take-off angle and thickness of the Be window although absorption in Be window can be easily corrected). Therefore, X-ray tube spectrum (both characteristic line intensities and continuum intensity) can be calculated from theoretical or semi-empirical algorithms (Ebel, 1999; Pella et al., 1985 and 1991; Finkelshtein and Pavlova, 1999).

In practice, the application of fundamental parameter method consists of two steps: calibration and analysis of unknown sample.

Calibration is a crucial issue in assuring high quality results of quantitative analysis. In fundamental parameter methods, calibration can be performed in different ways:

1. Calibration can be performed using pure-element standards (thin or bulk) for each element or multielement standard similar to unknown sample. Then, the calibration constant $(d\Omega/4\pi\sin\phi_l)Q_i q_i$ in Eq. (9) is calculated from the measured intensity and theoretical intensity of analyte is calculated for a given composition of standard specimen. If multi-element standards similar to unknown sample are applied, then the best analysis results can be expected.
2. The product $(d\Omega/4\pi\sin\phi_l)Q_i$ can be determined for a few pure-element standards, the element sensitivity q_i is calculated from theory. Then, the relationship between $(d\Omega/4\pi\sin\phi_l)Q_i$ and wavelength can be established. This procedure allows the determination of all elements using only a few pure-element standards. The determination of the relationship between $(d\Omega/4\pi\sin\phi_l)Q_i$ and wavelength of analyte in WDXRF is described in Ref. (Sitko and Zawisza, 2005).
3. The fundamental parameter method allows performing standardless analysis. Both Q_i and q_i are calculated from theory. Nevertheless, the element concentrations have to be normalized because absolute radiation intensity of X-ray tube is very difficult to calculate from theory. Such a procedure can be strictly performed in EDXRF spectrometry where Q_i depends on the applied semiconductor detector, filters and measurement atmosphere. In the WDXRF spectrometry, Q_i is a complex function of detection efficiency of proportional and scintillation detectors, measurement atmosphere, as well as the reflectivity of the analyzing crystal (very difficult or even impossible to calculate from theory with efficient accuracy). Therefore, standardless methods included in commercial software packages are not strictly standardless because they are based on spectrometer sensitivities determined experimentally by manufacturer.

Sherman equation enables to calculate radiation intensity of analyte in a sample of known composition. In practice, the aim of the analysis is to calculate analyte concentration from the actual measurements. Unfortunately, the Sherman equation cannot be transformed in order to calculate analyte concentration directly (analyte concentration is included in total mass-attenuation coefficient $\chi(\lambda, \lambda_i)$ and in enhancement term S_{ij}). Therefore, the analysis of unknown sample is performed using iteration. At the beginning, the first estimate of the composition is made, which can be done in several ways. For example, in this step, the matrix effects are neglected and weight fraction of analyte W_i equals relative intensity R_i determined using the calibration data. In the next step, the theoretical intensity R'_i is calculated for the first estimate of composition. Then, the next estimate of composition can be calculated from the difference between measured and theoretical intensities e.g. using linear interpolation. For example, if measured intensity R_i is 10% higher than theoretical intensity R'_i , the weight fraction of analyte is increased by 10%. The process is repeated until convergence is obtained, i.e. the weight fraction element does not change from one step to another by more than a present proportion e.g. 0.0001. In the analysis of specimen containing n elements (or stoichiometric compounds, e.g. oxides), a set of n Eq. (9) has to be solved for the unknown weight fractions by iteration.

The fundamental parameter methods have several advantages. First of all, these methods can be applied in analysis of thick samples, thin films and multilayers (simultaneous determination of composition and thickness is possible). The comprehensive algorithms dedicated to analysis of multiple layer films assume such effects as primary fluorescence, secondary fluorescence within the same layer, secondary enhancement between different layers and also secondary enhancement from the bulk substrate (Mantler, 1986; Willis, 1989; De Boer, 1990). A serious advantage of fundamental parameter methods is the possibility of using any standard specimen for calibration: pure-element thick or thin standard, one standard similar to unknown sample, series of standards similar to unknown sample, etc. Moreover, standardless analysis can be performed. The overview of fundamental parameter methods applied in analysis of thin films and multilayers can be found in Ref. (Sitko, 2009). The fundamental parameter methods have some limitations. They do not usually consider all physical processes in the sample such as: tertiary fluorescence, scatter of both the primary and fluorescence radiation and photoelectrons (important in the case of low-Z elements). Moreover, the accuracy of fundamental parameters methods strongly depends on uncertainty of atomic parameters (mass-attenuation coefficients, fluorescent yield, etc.), measurement geometry and spectral distribution of X-ray tube. Nevertheless, the use of standards similar to unknown will compensate these effects and will lead to more accurate results. The accuracy of fundamental parameter methods is discussed in previously published papers (Mantler and Kawahara, 2004; De Boer et al., 1993; Elam et al., 2004; Sitko, 2007 and 2008a). The "classical" fundamental parameters method can be applied only if all elements in the specimen are detectable. Then, the total mass-attenuation coefficient $\chi(\lambda, \lambda_i)$ and enhancement term S_{ij} can be calculated during iteration. The quantitative analysis is hampered when undetectable low-Z elements (e.g. H, C, N, O) are present in the material, e.g. geological, environmental and biological samples. Then, the methods utilizing scattered primary radiation or emission-transmission method can be successfully applied.

6. Methods based on scattered radiation

The intensity of the Compton scattered radiation can be used to obtain estimate of the attenuation coefficient of the specimen at the wavelength of the scattered photons. Because

the intensity of the scattered radiation is inversely proportional to the mass attenuation coefficient, the Compton scattered radiation I_{Comp} can be used as internal standard:

$$W_i = K_i \frac{I_i}{I_{Comp}} + B_i \quad (16)$$

The most common application of Eq. (16) is in the determination of trace elements, e.g. Sr, in geological samples. The method is limited to those cases where only trace elements have absorption edges between the wavelength of the analyte characteristic radiation and the wavelength of scattered radiation. Otherwise, the characteristic radiation of a major matrix element, e.g. Fe, can be used for matrix correction together with scattered radiation (Nesbitt, 1976). If matrix diversification is significant or heavy absorbers are present in large amounts, the Compton scattered radiation is preferred using a power function rather than a simple inverse proportion (Bao, 1997).

The scattered primary radiation is also used in more sophisticated strategies, i.e. in backscattered fundamental parameter methods. Then, scattered primary radiation is applied for the evaluation of the so-called "dark matrix" which consists of undetectable low-Z elements (e.g. H, C, N, O). Nielson (Nielson, 1977) proposed the backscattered fundamental parameter method which utilizes incoherently and coherently scattered radiations to choose and determine quantities of two light elements representative of the 'dark matrix.' To improve the accuracy of the analysis, Węgrzynek et al. applied differential scattering cross sections instead of total scattering cross sections (Węgrzynek et al., 2003a). Another strategy is the use of average atomic number (e.g. Szalóki et al., 1999). Theory and experiment show that the coherent/incoherent scatter ratio is sensitive to average atomic number of the sample Z_M :

$$\frac{I_{coh}}{I_{Comp}} = aZ_M^n \quad (17)$$

Where I_{coh} is coherent (Rayleigh) scattered radiation intensity, a and n are constants. Average atomic number is defined as follows:

$$Z_M = W_i Z_i + \sum_j W_j Z_j \quad (18)$$

Where Z_i and Z_j are atomic numbers of analyte i and matrix element j , respectively. The summation in Eq. (18) is over all elements present in the specimen. Because the detectable elements can be distinguished from undetectable elements, the average atomic number of the 'dark matrix' Z_{low-Z} can be calculated from the Eq. (19).

$$Z_{low-Z} = \frac{Z_M - \sum_k W_k Z_k}{1 - \sum_k W_k} \quad (19)$$

Where W_k and Z_k are weight fraction and atomic number of detectable element, respectively. If Z_{low-Z} is known, then the mass-attenuation coefficient of the 'dark matrix' for given radiation energy E can be calculated from the empirical Eq. (20).

$$\mu_{low-Z}(E) = b(E) \times Z_{low-Z}^{c(E)} \quad (20)$$

Where $b(E)$ and $c(E)$ are calculated from the least-squares fits applied to the published values of mass-attenuation coefficients.

The backscattered fundamental parameter methods allow calculating contribution of undetectable elements to absorption effects. Therefore, they are usually applied in determination of heavy elements in light matrix samples, e.g. environmental samples (plants, soils, etc.), biological samples and plastics. A strong advantage of the backscattered fundamental parameter methods is the fact that full matrix composition of the sample does not need to be known. Unfortunately, additional calibration has to be performed with the use of the standard samples of known Z_M (determination of constants a and n). It should be noted that the scattered radiation can also be applied to estimate the sample thickness (Araujo et al., 1990; Giauque et al., 1994).

An empirical algorithm for correction of matrix effects in light matrix samples was proposed in Ref. (Sitko, 2006 a). The algorithm was derived for the analysis of samples collected onto membrane filters:

$$W_i m = K_i I_i \left[a_i m \left(\frac{I_{coh}}{I_{Comp}} \right)^b + 1 \right] + B_i \quad (21)$$

Where K_i , B_i and a_i are the constants calculated by the least-squares fit on the basis of experimental results for standard samples, m is the mass per unit area of the sample. The coefficient b depends on the filter applied and the mass per unit area of the collected sample. This coefficient can be described by least-squares fit polynomials of second order in ln–ln scale:

$$b = \exp [p_0 + p_1 \ln m + p_2 (\ln m)^2] \quad (22)$$

Where p_0 , p_1 , p_2 are the constants determined on the basis of experimental results for standard samples. If diversification of sample thickness is limited, this coefficient can be also treated as constant.

7. Emission–Transmission method

The emission–transmission (E-T) method is one of the most popular methods based on transmission measurement (Fig. 4). The method is frequently applied for correction of absorption effects in light matrix samples pressed into pellets or collected onto filters. Nevertheless, applicability of E-T method is limited to the samples that are partially transparent for X-ray beams, i.e. intermediate-thickness samples. The method consists of measuring the X-ray fluorescent radiation from the specimen alone $I_{i,S}$, from specimen with a target located at a position adjacent to the back of the specimen $I_{i,S+T}$ and from the target alone $I_{i,T}$. Taking into account these measurements, the total mass-attenuation coefficient $\chi(\lambda, \lambda_i)$ can be calculated from the following relationship:

$$\exp[-\chi(\lambda, \lambda_i)\rho t] = \frac{I_{i,S+T} - I_{i,S}}{I_{i,T}} \quad (23)$$

The most important advantage of the E-T method is the possibility of determining $\chi(\lambda, \lambda_i)$ without the knowledge of the sample composition. In consequence, the absorption correction can be performed very easily and enhancement term S_{ij} can be calculated without

using iterative approach (Węgrzynek et al., 1993). In multielement analysis, the measurements are usually performed for a few elements and then relationship between $\chi(\lambda, \lambda_i)$ and wavelength is established. If minor and/or major elements are present in a sample, discontinuities in the relationship between $\chi(\lambda, \lambda_i)$ and wavelength resulting from absorption edges are observed. Then, at least two measurements for each wavelength region are performed or appropriate iteration procedure can be applied (Markowicz and Haselberger, 1992). Quantification based on E-T method, including accuracy and calibration can be found in Ref. (Markowicz et al., 1992; Markowicz and Van Grieken, 2002; Węgrzynek et al., 2003b).

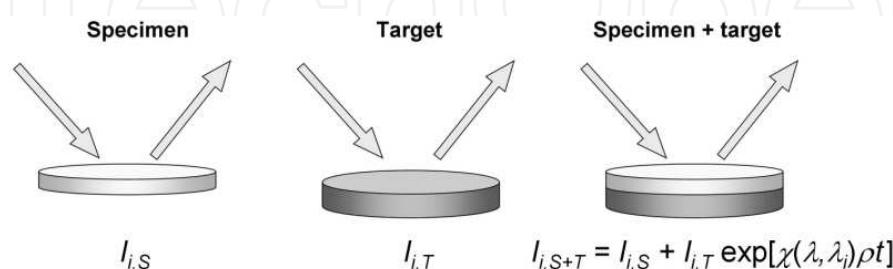


Fig. 4. Measurements in emission-transmission method.

8. Influence coefficient algorithms

Many influence coefficient algorithms have been developed. They were reviewed and discussed in one chapter of "Handbook of X-Ray Spectrometry," edited by Van Grieken and Markowicz (de Vries and Vrebos, 2002) and numerous papers (Rousseau, 2001, 2002, 2004, 2006), (Willis and Lachance, 2000, 2004). The algorithms can be divided in different ways. The influence coefficients can be calculated from theory (using Sherman equation) or from the measurements, therefore the algorithms are generally divided into two groups: theoretical and empirical influence coefficients algorithms (Fig. 5). The algorithms can use a single or more than one coefficient per matrix element. Moreover, the influence coefficients can be constant or can vary with composition of the sample.

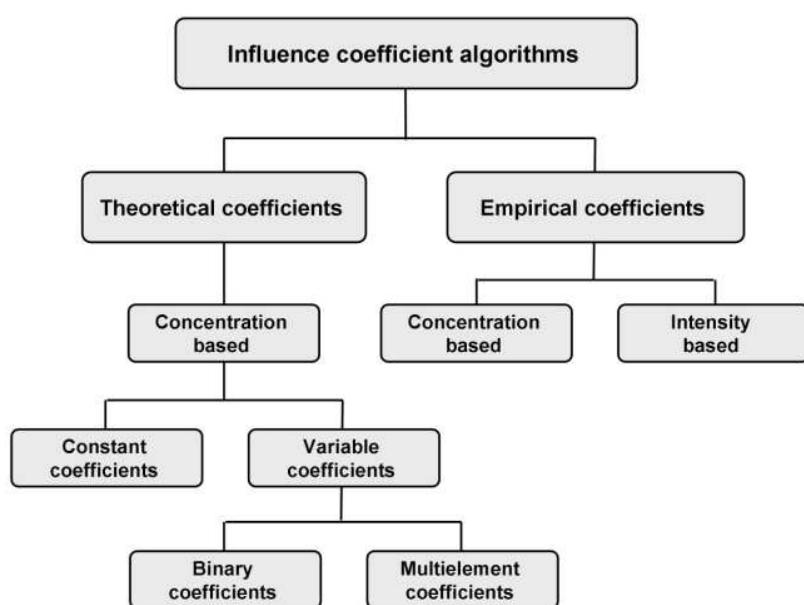


Fig. 5. General division of influence coefficient algorithms.

In general, the total matrix correction term M_i is expressed as a linear combination of weight fractions of matrix elements W_j :

$$M_i = 1 + \sum_j \alpha_{ij} W_j \quad (24)$$

Where α_{ij} is influence coefficient describing the matrix effect of the interfering element j on the analyte i . Combining Eq. (8) with Eq. (24) leads to the general form of concentration based algorithm:

$$W_i = R_i \left[1 + \sum_j \alpha_{ij} W_j \right] \quad (25)$$

Eq. (25) is usually applied if influence coefficients are determined using R_i calculated from theory. The total matrix correction term expressed by Eq. (24) can also be combined with Eq. (5). Then, we obtain the general equation that can be used during calibration if the matrix correction term is calculated from theory for each standard specimen:

$$W_i = K_i I_i \left[1 + \sum_j \alpha_{ij} W_j \right] + B_i \quad (26)$$

Eq. (26) is also used in empirical algorithms if influence coefficients α_{ij} , slope K_i and intercept B_i are determined from multiple-regression analysis on a large suite of standards. One of the simplest algorithms was proposed by Lachance and Traill in 1966 (Lachance and Traill, 1966). The algorithm can be easily derived from the Sherman equation if the following assumptions are made: the sample is infinitely thick, the monochromatic excitation is applied and enhancement effects are negligible. Then, the Sherman equation simplifies to:

$$I_i = \frac{d\Omega}{4\pi \sin \phi} Q_i q_i W_i \tau_i(\lambda) I_0(\lambda) \frac{1}{\chi(\lambda, \lambda_i)} \quad (27)$$

The total mass-attenuation coefficient can be expressed as follows:

$$\chi(\lambda, \lambda_i) = W_i \chi_i(\lambda, \lambda_i) + \sum_j W_j \chi_j(\lambda, \lambda_i) \quad (28)$$

Where:

$$\chi_i(\lambda, \lambda_i) = \frac{\mu_i(\lambda)}{\sin \phi_1} + \frac{\mu_i(\lambda_i)}{\sin \phi_2} \quad (29)$$

$$\chi_j(\lambda, \lambda_i) = \frac{\mu_j(\lambda)}{\sin \phi_1} + \frac{\mu_j(\lambda_i)}{\sin \phi_2}$$

The total mass attenuation coefficient $\chi(\lambda, \lambda_i)$ depends on both matrix elements j and analyte element i . Assuming that the sum of the element weight fractions in the specimen equals

one (then $W_i = 1 - \sum W_j$), the weight fraction of analyte element i can be eliminated from Eq. (28) and then $\chi(\lambda, \lambda_i)$ is given by:

$$\chi(\lambda, \lambda_i) = \chi_i(\lambda, \lambda_i) \left[1 + \sum_j \alpha_{ij} W_j \right] \quad (30)$$

Where:

$$\alpha_{ij} = \frac{\chi_j(\lambda, \lambda_i)}{\chi_i(\lambda, \lambda_i)} - 1 \quad (31)$$

Finally, if the absolute intensity I_i is replaced by the relative radiation intensity R_i the Lachance-Traill equation can be obtained from the simplified Sherman formula (Eq. (27)):

$$W_i = R_i \left[1 + \sum_j \alpha_{ij} W_j \right] \quad (32)$$

In Lachance-Traill algorithm, the influence coefficient α_{ij} corrects for the absorption effects of the matrix element j on the analyte i in the case of monochromatic excitation of wavelength λ . The coefficient can be positive or negative. If the analyte is determined in presence of a heavier matrix element, then $\chi_i(\lambda, \lambda_i) < \chi_j(\lambda, \lambda_i)$ and α_{ij} is positive. If the analyte is determined in presence of a lighter matrix element, then $\chi_i(\lambda, \lambda_i) > \chi_j(\lambda, \lambda_i)$ and α_{ij} is negative. The influence coefficients can be calculated in different ways:

- It can be calculated directly from the Eq. (31).
- It can be determined from multiple-regression analysis on a large suite of standards.
- It can be calculated from the relative radiation intensity R_i .

The influence coefficients can be calculated directly from the Eq. (31) only if monochromatic excitation is applied (or the effective wavelength is used although it is composition dependent) and there are no enhancement effects. The determination of Ni in ternary system FeNiCr is shown here as an example. The analyte is excited by molybdenum radiation (Mo K_α) and following measurement geometry is assumed: $\phi_1 = 60^\circ$ and $\phi_2 = 40^\circ$. In this case, the influence coefficient α_{NiFe} describing influence of Fe on Ni is calculated from the following equation:

$$\alpha_{NiFe} = \frac{\frac{\mu_{Fe}(\lambda_{Mo})}{\sin \phi_1} + \frac{\mu_{Fe}(\lambda_{Ni})}{\sin \phi_2}}{\frac{\mu_{Ni}(\lambda_{Mo})}{\sin \phi_1} + \frac{\mu_{Ni}(\lambda_{Ni})}{\sin \phi_2}} - 1 = \frac{\frac{37.4}{0.87} + \frac{363.3}{0.64}}{\frac{44.6}{0.87} + \frac{59.8}{0.64}} - 1 = 3.21 \quad (33)$$

The influence coefficient α_{NiCr} describing influence of Cr on Ni is calculated in the same way. Finally, the following equation is obtained for determination of Ni in FeNiCr using aforementioned measurement conditions:

$$W_{Ni} = R_{Ni} [1 + 3.21 \times W_{Fe} + 2.47 \times W_{Cr}] \quad (34)$$

The influence coefficients can also be calculated from relative radiation intensity of the analyte. In this case, the influence coefficient α_{ij} is calculated for binary systems. Then Eq. (32) simplifies to:

$$W_i = R_i [1 + \alpha_{ij} W_j] \quad (35)$$

Eq. (35) can be rewritten to obtain α_{ij} :

$$\alpha_{ij} = \frac{W_i/R_i - 1}{W_j} \quad (36)$$

For example, to determine influence coefficient describing influence of Cr on Ni in FeNiCr, the binary system NiCr is taken into account, and R_{Ni} for this system has to be determined. The relative intensity can be determined based on actual measurements. In this case, the pure element specimens and suitable binary specimens must be available. Therefore, R_i is usually calculated from theory using fundamental parameter method. In the first step, the composition of hypothetical binary specimen is assumed. In next step, R_i is calculated from theory for actual measurement conditions (voltage of X-ray tube, incident and take-off angles, medium: air, helium or vacuum). Finally, α_{ij} is calculated from Eq. (36). The influence coefficients can be determined for any quantitative composition of binary systems. Table 1 shows influence coefficients calculated for various compositions of binary systems. The example is given for determination of Ni in ternary system FeNiCr. Thus, in this case the secondary fluorescence does not exist. As can be observed, if monochromatic excitation is applied, the coefficients are constants, i.e. they do not vary with composition. A different situation is observed for polychromatic excitation, where both α_{NiFe} and α_{NiCr} vary with composition of the specimen.

W_{Ni}	W_{Fe}	W_{Cr}	Monochromatic excitation, Mo K α			Polychromatic excitation, Mo target X-ray tube operated at 45kV		
			R_{Ni}	α_{NiFe}	α_{NiCr}	R_{Ni}	α_{NiFe}	α_{NiCr}
0.2	0.8		0.0561	3.21		0.0740	2.13	
0.5	0.5		0.1920	3.21		0.2396	2.17	
0.8	0.2		0.4873	3.21		0.5510	2.26	
0.2		0.8	0.0672		2.47	0.0883		1.58
0.5		0.5	0.2238		2.47	0.2759		1.63
0.8		0.2	0.5355		2.47	0.5972		1.70

Table 1. Influence coefficient calculated from R_i for determination of Ni in ternary system FeNiCr using monochromatic and polychromatic excitation.

A similar situation is observed in determination of Fe in FeNiCr if polychromatic excitation is applied (Table 2). Both α_{FeCr} and α_{FeNi} are variable. The coefficient describing influence of Cr on Fe is positive because only absorption effect is observed in this case. The coefficient describing influence of Ni on Fe is negative because the enhancement effect dominates. Moreover, it strongly depends on specimen composition.

Summarizing, the influence coefficients can be treated as constants only if monochromatic excitation is applied and there are no enhancement effects. Fig. 6 presents results for determination of Cr in stainless steel before and after matrix correction using constant

coefficients (e.g. Lachance-Traill algorithm) and variable linear coefficients (e.g. Claisse-Quintin algorithm). Before matrix correction, the mean error of Cr determination equals 1.11 % Cr. Considerable improvement is obtained after matrix correction with constant coefficient - the mean error is equal to 0.35 % Cr. Even better results are obtained for linear coefficients - the mean error equals 0.14 % Cr.

W_{Fe}	W_{Cr}	W_{Ni}	R_{Fe}	α_{FeCr}	α_{FeNi}
0.2	0.8		0.0717	2.24	
0.5	0.5		0.2329	2.29	
0.8	0.2		0.5405	2.40	
0.2		0.8	0.3017		-0.42
0.5		0.5	0.5985		-0.33
0.8		0.2	0.8431		-0.26

Table 2. Influence coefficient calculated from R_i for determination of Fe in ternary system FeNiCr using polychromatic excitation: Mo target X-ray tube operated at 45kV.

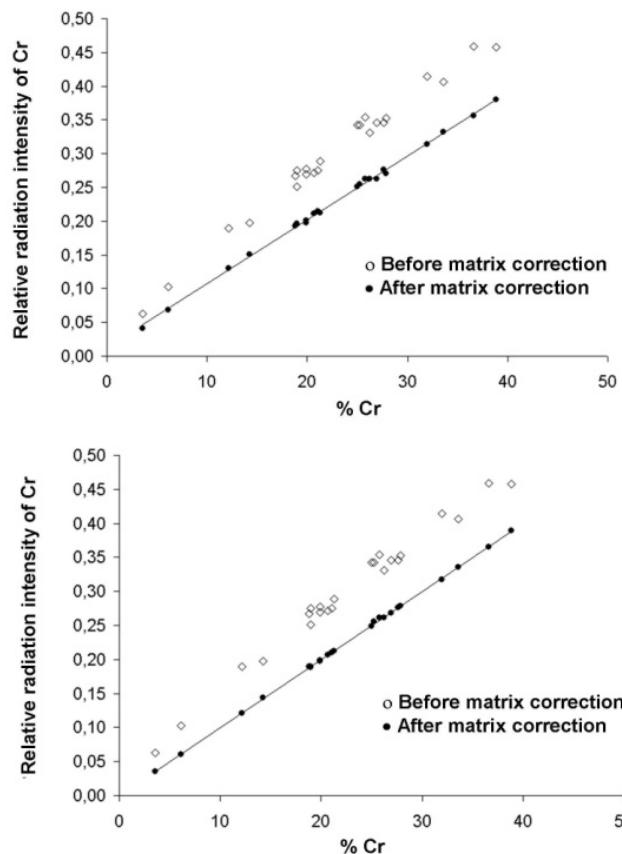


Fig. 6. Determination of Cr in stainless steel before and after matrix correction using (a) Lachance-Traill algorithm and (b) Claisse-Quintin algorithm (see subchapters 8.1 and 8.2).

The coefficients calculated from R_i for binaries are the so-called binary coefficients, i.e. they describe influence of matrix element on analyte but they do not take into account other

matrix elements. Therefore, applying binary coefficients to multielement samples leads to an incomplete matrix correction. It can be explained using simple example: the enhancement of Fe by Ni in two different matrices - Al and Cr matrix. In Cr matrix, Ni radiation is strongly absorbed by Cr. Therefore, Ni excites Fe to a lesser extent in Cr matrix than in Al matrix. In both cases, the same influence coefficient α_{FeNi} is used if binary coefficient algorithm is applied. Therefore, a better solution is the use of multielement coefficient algorithms, e.g. Lachance-Claisse, Broll-Tertain or Rousseau algorithm.

In general, the constant coefficient algorithms (e.g. Lachance-Traill algorithm) give satisfactory results but concentration range should be limited (0-10%). The algorithms using binary variable coefficients (e.g. Claisse-Quintin algorithm) give excellent results over medium concentration range of 0-40%. Multielement coefficient algorithms can be used in a full concentration range between 0 and 100%.

A number of influence coefficient algorithms have been proposed for correction of matrix effects. They can be divided in several ways: by the way of calculating influence coefficients (theoretical or empirical), by the variables used in matrix correction term (concentration or intensity based) or by the analytical context of determination of coefficients (constant or variable, binary or multielement). The general scheme of division and sub-divisions of influence coefficient algorithms is presented in Fig. 5.

In the next part of the chapter, various influence coefficient algorithms will be reviewed. The application of these algorithms for calibration and analysis of unknown specimen discussed here is valid for any of the algorithms. Some differences are observed in the use of theoretical and empirical algorithms during the calibration stage.

In the case of theoretical influence coefficient algorithms, the coefficients are determined from theory e.g. using R_i calculated from Sherman equation for given measurement conditions. In the next stage, the matrix correction term (Eq. (24)) is calculated for all standard specimens and for a given analyte. Then, the calibration graph is plotted: the measured radiation intensity of the analyte multiplied by the corresponding matrix correction versus weight fraction of analyte. Then, slope K_i and intercept B_i are determined by least-squares fit using set of standard specimens.

In the case of empirical algorithms, the influence coefficients, slope K_i and intercept B_i are determined from multiple-regression analysis on a large suite of standards. If there are n matrix elements, $n+2$ coefficients have to be determined (n influence coefficients, slope K_i and intercept B_i). For the calculation of $n+2$ coefficients, $n+2$ standards are required. In practice, a much larger number of standards is used: $2n$ or even $3n$. It should be noted, that the matrix element can be included in matrix correction term only if its influence on the analyte is significant. Otherwise, the matrix element should be omitted in matrix correction term to obtain correct values of other influence coefficients. Moreover, the concentration of all elements in the reference specimens should cover composition of unknown sample. Only then, accurate results can be obtained.

Analysis of unknown sample is similar for both theoretical and empirical algorithms. In this step, a set of equations has to be solved for the unknowns: W_i, W_j, \dots, W_n . If there are n linear equations with n unknowns, the set of equations can be solved algebraically. However, an iterative procedure is usually applied, especially in the case of a set of non-linear equations. General scheme of using theoretical influence algorithm is presented in Fig. 7.

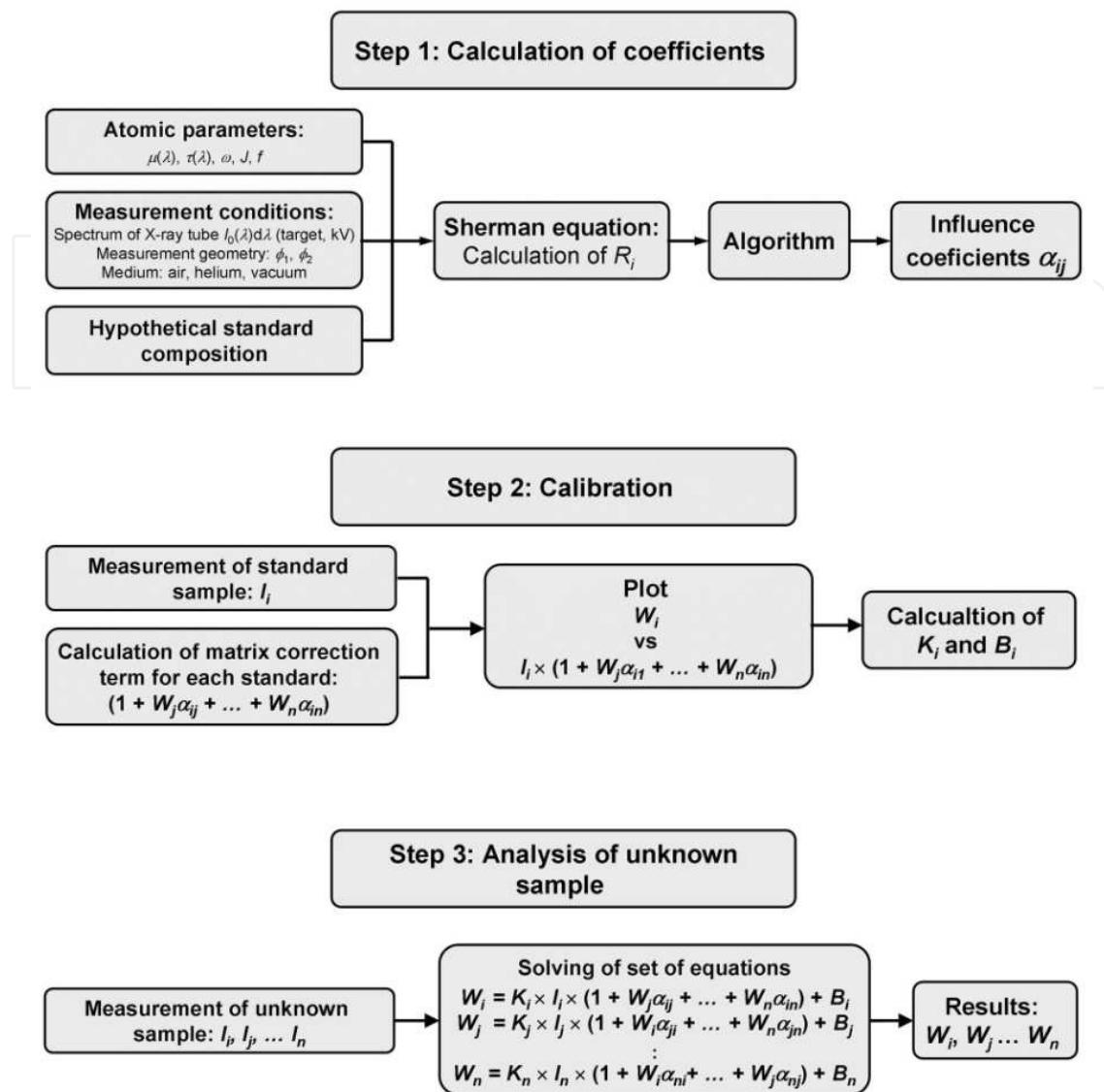


Fig. 7. General scheme of using theoretical influence algorithm.

8.1 Constant coefficient algorithms

The previous section shows that influence coefficients can be treated as constants only if: monochromatic excitation is applied and there are no enhancement effects. However, the monochromatic excitation is rarely used in practice and enhancement effects are usually observed in multielement specimens. Therefore, to obtain accurate results with constant coefficients, the concentration ranges of analyte and matrix elements should be limited. The constant coefficients are calculated for a given composition range or a series of reference samples that cover composition of unknown sample. If composition range is wide, then the sample can be diluted by pelletizing with a binder or by fusion.

The Lachance-Traill algorithm (1966)

$$W_i = R_i \left[1 + \sum_j \alpha_{ij} W_j \right] \quad (37)$$

The algorithm was discussed in detail in the previous section. The influence coefficients can be determined from the relative radiation intensity or from multiple-regression analysis on a large suite of standards. They can also be calculated directly from the Eq. (31) if monochromatic excitation is applied and enhancement effects are not observed. If polychromatic beam is applied, then the effective wavelength can be used, however it is also composition dependent.

The de Jongh algorithm (1973)

$$W_i = E_i R_i \left[1 + \sum_{\substack{j \\ j \neq e}} \alpha_{ij} W_j \right] \quad (38)$$

Where E_i is a constant determined during calibration. The algorithm proposed by de Jongh (de Jongh, 1973) uses theoretical coefficients calculated from fundamental parameters. This algorithm looks similar to the Lachance-Traill equation but the eliminated element e is the same for all equations (in Lachance-Traill algorithm, the analyte is eliminated from each equation, i.e. $\alpha_{ii} = 0$). The influence coefficients are calculated by a Taylor series expansion around an average composition. They are multielement coefficients rather than binary coefficients, i.e. the influence coefficient describes influence of matrix element j on analyte i in the presence of all matrix elements. The advantage of the de Jongh algorithm is that one element can be arbitrarily eliminated from the correction procedure, so there is no need to measure it. For example, in ferrous alloys, iron is often the major element and it is usually determined by difference, and therefore, can be eliminated from the correction procedure.

The Rasberry-Heinrich algorithm (1974)

$$W_i = R_i \left[1 + \sum_j a_{ij} W_j + \sum_k \frac{b_{ik}}{1 + W_i} W_k \right] \quad (39)$$

In this algorithm, two different coefficients are used for correction of absorption effect (coefficient a_{ij}) and enhancement effect (coefficient b_{ik}) and only one coefficient is used for each matrix element. The coefficient a_{ij} is used if absorption is the dominant effect (then $b_{ik} = 0$). The coefficients b_{ik} are used if enhancement is the dominant effect (then $a_{ij} = 0$). The coefficients are determined experimentally on the basis of measured reference samples. The serious disadvantage of the algorithm is the fact that it is not clear which matrix element should be assigned an a_{ij} and which one a b_{ik} . Therefore, the Rasberry-Heinrich algorithm is not considered to be generally applicable, but it gives satisfactory results for FeNiCr alloys. It is for this system that the algorithm was originally developed.

The Lucas-Tooth and Price algorithm (1964)

$$W_i = I_i \left[k_i + \sum_j a_{ij} I_j \right] + B_i \quad (40)$$

Where k_i and a_{ij} are the correction coefficients, B_i is a background term. The coefficients are determined by a least-squares fit on the basis of measured reference samples. The correction

is done using intensities rather than concentrations. The algorithm assumes that the matrix effect of an element j on the analyte i is proportional to its intensity. Because this approximation is unreliable (the measured intensities are modified by matrix effects and are not directly proportional to concentrations), the algorithm has a limited range of applicability. However, determination of a single element is possible using Lucas-Tooth and Price algorithm.

8.2 Variable binary coefficient algorithms

The Claisse-Quintin algorithm (1967)

$$W_i = R_i \left[1 + \sum_j \alpha_{lin,ij} W_j + \sum_j \sum_k \alpha_{ijk} W_j W_k \right] \quad (41)$$

$$\alpha_{lin,ij} = \alpha_{ij} + \alpha_{ijj} W_M$$

In 1967, Claisse and Quintin proposed an improved version of Lachance-Traill algorithm (Claisse and Quintin, 1967). The algorithm uses linear coefficients $\alpha_{lin,ij}$ instead of constant coefficients and can be applied for polychromatic excitation in a medium range of concentration. The cross-product coefficient α_{ijk} included in matrix correction term corrects for the simultaneous presence of both j and k and compensates for the fact that the total matrix effect correction cannot be represented as a sum of binary matrix effect corrections. W_M is matrix concentration ($W_M = 1 - W_i$) proposed by Tertian instead of W_j in the original equation in order to obtain high quality results (Tertian, 1976). Equations for calculating accurate and valid theoretical binary influence coefficients in the Claisse-Quintin algorithm were first proposed by Rousseau and Claisse (1974) and later improved by Rousseau (1984 b). The influence coefficients are calculated from R_i using fundamental parameters at two binaries ($W_i = 0.2$ and 0.8). The algorithm introduces a theoretical mean relative error of 0.04% on the calculated concentrations in the case of cement samples prepared as pressed powder pellets (medium concentration range of 0 - 40%). For a large concentration range (0-100%), e.g. in the case of alloy analysis, the Claisse-Quintin algorithm introduces 0.3% relative error (Rousseau, 2001).

The COLA algorithm (1981)

$$W_i = R_i \left[1 + \sum_j \alpha_{hyp,ij} W_j + \sum_j \sum_k \alpha_{ijk} W_j W_k \right] \quad (42)$$

$$\alpha_{hyp,ij} = \alpha_{ij,1} + \frac{\alpha_{ij,2} W_M}{1 + \alpha_{ij,3} (1 - W_M)}$$

In 1981, Lachance proposed an algorithm called COLA (comprehensive Lachance) with a new approximation to the binary influence coefficients (Lachance, 1981). This time, hyperbolic influence coefficients were applied. The influence coefficients are calculated from R_i using fundamental parameters at three binaries ($W_i = 0.001, 0.5$ and 0.999). Similarly to the Claisse-Quintin algorithm, the cross-product coefficients are calculated from a ternary

system ($W_i = 0.30$, $W_j = 0.35$, $W_k = 0.35$). The applicability of COLA algorithm is similar to the Claisse-Quintin algorithm. The algorithm corrects for both absorption and enhancement effects over a broad range of concentration.

8.3 Variable multielement coefficient algorithms

Binary influence coefficients are based on an approximation: the total matrix effect on the analyte i equals the sum of the effects of each matrix element j and each effect is calculated independently of each other. The binary coefficient algorithms give accurate results if composition range is limited, i.e. 0-10% for the constant coefficient algorithms and 0-40% for binary variable coefficient algorithms. The coefficients are calculated for a given composition range rather than for a given sample composition. The multielement coefficients are exact and are calculated for each individual reference and unknown specimens. Therefore, the multielement coefficient algorithms are applicable in full composition range from 0 to 100%. The most important algorithms were proposed by Broll and Tertian (1983), Rousseau (1984), and Lachance and Claisse (1995).

The Broll-Tertain algorithm (1983)

$$W_i = R_i \left[1 + \sum_j \left(\alpha_{ij} - \varepsilon_{ij} \frac{W_i}{R_i} \right) W_j \right] \quad (43)$$

The Rousseau algorithm (1984)

$$W_i = R_i \frac{1 + \sum_j \alpha_{ij} W_j}{1 + \sum_j \varepsilon_{ij} W_j} \quad (44)$$

The Lachance-Claisse algorithm (1995)

$$W_i = R_i \left[1 + \sum_j \frac{\alpha_{ij} - \varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} W_j} W_j \right] \quad (45)$$

Where α_{ij} and ε_{ij} are influence coefficients correcting for absorption and enhancement effects, respectively. The multielement influence coefficients can be easily calculated for reference specimens of known composition. In the case of unknown specimens, the iteration is used. In Rousseau algorithm, a first estimate of the composition of the unknown specimen is calculated using the Claisse-Quintin algorithm, then the influence coefficients are calculated for this composition. An exact estimate of composition is finally obtained by applying the iterative process to Eq. (44). Willis and Lachance (2004) showed that the aforementioned multielement coefficient algorithms give the same high-quality results and no algorithm can outperform any of the others.

8.4 Influence coefficient algorithms for intermediate-thickness samples

The influence coefficients algorithms are widely applied for quantitative analysis of infinitely thick samples. Influence coefficients algorithms can be deduced from the Sherman

equation because exponential term equals zero for thick samples. In consequence, the matrix correction term can be expressed as a linear combination of matrix elements concentrations. The analysis of intermediate-thickness samples is much more complicated because the exponential term in Eq. (9) cannot be neglected. However, Sitko (2005) proposed a certain approximation to eliminate the exponential term:

$$1 - \exp(-x) = \frac{1}{k_1 + k_0/x} \quad (46)$$

Where k_1 and k_0 are constants, $x = \chi(\lambda, \lambda_i)\rho t$. The proposed approximation allows not only for eliminating the exponential term but also transforming Sherman equation to a form in which the matrix correction term is expressed as a linear combination of all matrix elements concentrations. Thus, the proposed approximation was a base for the first empirical influence coefficient algorithm dedicated for the analysis of intermediate-thickness samples (Sitko, 2005):

$$W_i m = I_i \left[a_i + c_i m + \sum_j \alpha_{ij} W_j m \right] + B_i \quad (47)$$

Where $W_i m$ and $W_j m$ are the masses per unit area of the analyte i and the matrix element j , respectively; α_{ij} is the influence coefficient; a_i and c_i are the coefficients dependent on the range of thickness of calibration samples. The coefficients a_i , c_i , α_{ij} and B_i are calculated by the least-squares fit on the basis of reference samples of various thickness and composition. The influence coefficients in this algorithm are treated as constants. Therefore, to obtain accurate results, sample thickness and composition range should be limited. To overcome this inconvenience, the theoretical influence coefficient algorithm for intermediate-thickness samples was proposed (Sitko, 2006 b):

$$W_i m = K_i I_i \left[a_i + c_i m + \sum_j \alpha_{ij} W_j m \right] + B_i \quad (48)$$

$$\alpha_{ij} = \frac{\alpha_{ij} c_i - S_{ij} (a_i/m + c_i)}{1 + \sum_j S_{ij} W_j}$$

Where K_i , B_i are the calibration constants calculated by the least-squares fit on the basis of experimental results for reference samples; a_i and c_i are the coefficients dependent on the thickness and total mass-attenuation coefficient of the sample; α_{ij} is the absorption influence coefficient; S_{ij} is the enhancement term. The coefficients a_i , c_i , α_{ij} and S_{ij} are multielement coefficients and are calculated directly from theory. The proposed theoretical influence algorithm can be applied in analysis of samples of any thickness and is more general in its form than algorithms for thick samples. It is worth emphasizing that the algorithm takes the well-known form for thick samples, e.g. the Lachance-Claisse algorithm (if sample thickness $\rightarrow \infty$ then $a_i \rightarrow 0$ and $c_i \rightarrow 1$). The theoretical influence algorithm is more flexible than the previously proposed empirical algorithm and can be applied for a wide range of thickness and composition.

In the next paper (Sitko, 2008b), two algorithms of constant and linear coefficients for simultaneous determination of composition and thickness of thin films were proposed. This time, the coefficients are not calculated directly from theory but from the relative radiation intensity (calculated from theory) of hypothetical pure element films and binary films. The potential of the algorithms was demonstrated with hypothetical ternary and binary systems: FeCrNi, FeCr, FeNi, CrNi and experimental data of FeNi and Cu films.

9. Conclusions

Many methods, both empirical and theoretical, have been proposed for quantitative XRF analysis. Method selection usually depends on sample type (thin or bulk, alloys or rocks, etc.), method of sample preparation (without treatment, fusion, etc.), expected results (quantitative or semi-quantitative analysis, determination of a single element or multielement analysis) and availability of standard samples. If the compensation methods are applied, then complicated sample preparation is required, only one or few elements can be quantitatively determined (standard addition, internal standard, Compton scatter) and additional matrix correction may be required (dilution). In influence coefficient algorithm, the matrix correction and calibration is clear, therefore, interpretation of data is very easy. The fundamental parameter methods are like "a black box". Nevertheless, the serious advantage is their versatility: the analysis of bulk, thin samples and multilayers is possible. Fundamental parameter methods are usually considered to be less accurate than the influence coefficient algorithms. This results from the fact that the fundamental parameter methods are usually used with only a few standards. The accuracy of fundamental parameter methods is very similar to that of influence coefficient algorithms when the same standards (many standards similar to the unknown) are used in both cases.

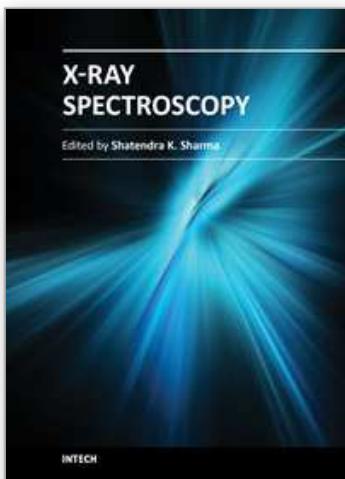
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The x-ray is the only invention that became a regular diagnostic tool in hospitals within a week of its first observation by Roentgen in 1895. Even today, x-rays are a great characterization tool at the hands of scientists working in almost every field, such as medicine, physics, material science, space science, chemistry, archeology, and metallurgy. With vast existing applications of x-rays, it is even more surprising that every day people are finding new applications of x-rays or refining the existing techniques. This book consists of selected chapters on the recent applications of x-ray spectroscopy that are of great interest to the scientists and engineers working in the fields of material science, physics, chemistry, astrophysics, astrochemistry, instrumentation, and techniques of x-ray based characterization. The chapters have been grouped into two major sections based upon the techniques and applications. The book covers some basic principles of satellite x-rays as characterization tools for chemical properties and the physics of detectors and x-ray spectrometer. The techniques like EDXRF, WDXRF, EPMA, satellites, micro-beam analysis, particle induced XRF, and matrix effects are discussed. The characterization of thin films and ceramic materials using x-rays is also covered.

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