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Empirical Relations for Matrix Effects in Synthetic Thick Samples Comprising Low Z Elements

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In x-ray fluorescence, matrix effects disturb the proportionality between characteristic x-ray intensity of an element and its amount in the sample. To find relations for matrix effects of thick samples comprising low Z elements, the absorption term1 for selective analyte 'a' x-rays and enhancement term1 for analyte 'c' x-rays in the presence of enhancer a in the sample are experimentally evaluated and empirically correlated with elemental amounts in a category of samples. The correlations are independent of measured x-ray counts.

Key Words: X-ray fluorescence, matrix effects, absorption, enhancement.

INTRODUCTION

Under XRF technique for elemental analysis, the correlation of characteristic x-ray intensities with concentrations of the elements in a sample is cumbersome due to matrix effects. For thin samples, the effects are nil and increase with thickness of the sample. Beyond a thickness, the effects become constant and sample is called thick sample. The elements with close atomic numbers Z's present in the sample magnify the effects. Presently, a study of absorption and enhancement terms has been made with synthetic samples of known concentrations as $CaCO_3$+KNO_3+borax (Set-I) and $CaCO_3$+$CdCO_3$+borax (Set-II). Under excitation of Ca K x-rays, absorption of Ca K x-rays and enhancement of each potassium K x-rays and Cd L X-rays due to Ca K x-rays are studied. The fractional amounts, α of Ca and β of K/Cd, are varied in such a way that either the fractional substrate amount$1-\alpha-\beta$ remains constant or the amount of KNO_3/$CdCO_3$ and borax are fixed with variable amounts of $CaCO_3$. All the samples, in addition to Ca, K and Cd, contain elements Na, O, N, C and H that comprise a low Z substrate. The proportions of the elements and substrate in samples almost resemble to that of plants and biological samples.

EXPERIMENTAL

Set-I comprises total 19 targets and Set-II comprises 20 targets in thick pellet form of dia. 2.5 cm with weights in the range 300-700mg depending upon its constituents. Thick target of only borax material is used to correct the counts recorded in the detector for the contributions of background and scattered incident photons from the sample targets and a target of each $CaCO_3$, KNO_3 and $CdCO_3$ is used for the relative measurements. In set-I, 9 samples are for absorption study with variable fractions α and β (in the range, 0.007-0.036) in a fixed amount of borax. Remaining 10 samples are for enhancement studies with fixed amount of potassium and borax and variable fractional amounts of calcium (in the range, 0.017-0.125). Similarly in the set-II, 10 targets are made for each absorption and enhancement study.

For selective excitation[1] of Ca K x-rays, the targets and standards are irradiated, in turn, with 5.959 keV Mn K x-rays from ≈100 mCi Fe-55 source in a 90° reflection geometry[2]. For each target, counts under the x-ray photo peaks are collected with AMPTEK XR-100CR Si-PIN detector coupled to ORTEC MCA(model 465) having energy resolution ~200 eV at 5.959 keV Mn K x-rays. The counts are collected for the time intervals to have statistics in photo peak counts less than 1%. The background and scattered photons obtained with borax target in place of sample targets are subtracted from the actual spectrum. The background subtracted spectrum of a target each from set-I and set-II with 5.959 keV irradiations from ^{55}Fe source are shown in figs. 1 and 2. Though, there are overlapping of K Kβ and Ca Kα peaks and Cd L(β+γ) and Ca Kα peaks, but to extract the only counts under the Kα+Kβ peaks of K and that of Ca and Lα+L(β+γ) peaks of Cd, the method already followed in our laboratory[3] is used.

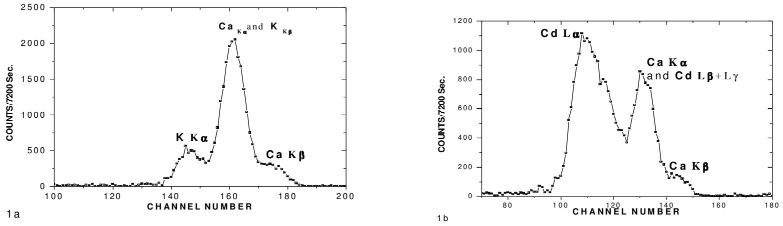


Fig.1. Background subtracted spectrum of a target from irradiations with 5.959 keV photons from ^{55}Fe source from set-I (1a) and from set-II (1b).

ABSORPTION TERMS

For a sample 'S' and its standard 'Sp' (made by adding amount α′ of analyte element ***a*** or its compound **A** in unit amount of S), the absorption term[1] $\left[\mu_a^{S(Sp)}/\mu_a^{A}\right]$ of the sample or its standard relative to that of **A** material can be evaluated from the analyte amount α or α+α′ and ***a*** x-ray counts from S or Sp and A targets using relation 1(2).

$$\frac{\mu_a^S}{\mu_a^A} = \alpha \frac{M_A}{nM_a}\left[\frac{N_a^S}{N_a^A}\right]^{-1} \quad \cdots \quad (1) \qquad \frac{\mu_a^{Sp}}{\mu_a^A} = \left[\frac{\alpha + \frac{nM_a}{M_A}\alpha'}{1+\alpha'}\right]\left[\frac{M_A}{nM_a}\right]\left[\frac{N_a^{Sp}}{N_a^A}\right]^{-1} \quad (2)$$

Where $M_{\boldsymbol{a}}$ is atomic weight of element $\boldsymbol{a}$; M_A is the molecular weight of compound A; n is number of atoms of $\boldsymbol{a}$ in one mole of A; $N_{\boldsymbol{a}}^{S(Sp)(A)}$ is count under the $\boldsymbol{a}$ x-ray photo peak from S, Sp or A; $\mu_{\boldsymbol{a}}^{S(Sp)(A)}$ is the composite absorption coefficient of target material S, Sp or A at incident photon and emitted $\boldsymbol{a}$ x-ray energies.

In the present work, analyte $\boldsymbol{a}$ is Ca and its compound A is $CaCO_3$, the absorption ratios for set-I and set-II, $\left[\mu_{Ca}^{Set\text{-}I}/\mu_{Ca}^{CaCO_3}\right]$ and $\left[\mu_{Ca}^{Set\text{-}II}/\mu_{Ca}^{CaCO_3}\right]$, are evaluated and plotted against Ca concentrations (fig. 2a and 2b). With the statistical error in counts <1%, weighing precision 0.1mg and taking utmost precaution for mixing the materials, the error in absorption ratios is nearly <2%.

Further, a search for empirical relation between the determined absorption terms and the analyte amounts is made in each case. For this different order polynomials in amount are tried on α and $\ell n\left[\mu_{Ca}^{Set\text{-}I(Set\text{-}II)}/\mu_{Ca}^{CaCO_3}\right]$ with μ's ratios from relation 1 for first 9 targets of set I and first 10 targets of set II. For remaining 10 targets of each set, in which only $CaCO_3$ amounts are varied, the lowest Ca fraction in each set is taken as α and the additional Ca fractions in other targets are treated as α´, polynomial in α+α´ are tried on $\ell n\left[\mu_{Ca}^{Set\text{-}I(set\text{-}II)}/\mu_{Ca}^{CaCO_3}\right]$ with μ's ratios from relation 2. Following the criteria of lowest powers of amount terms and closeness between actual and generated values, the polynomial relation for different categories comes as given in table 1 and the values generated from the polynomials are shown in figure 2a and 2b

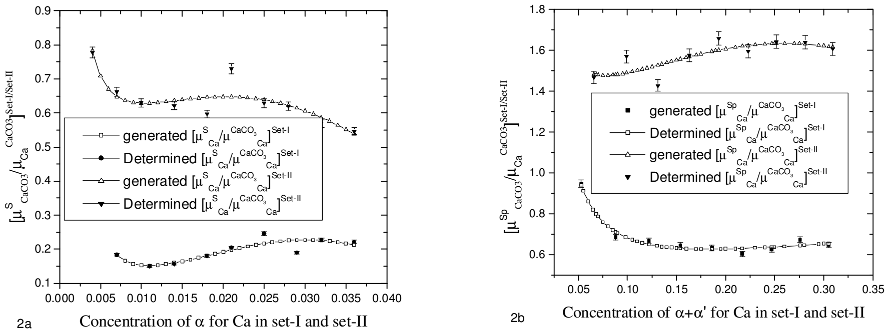


Fig. 2. Plot of determined and generated values of absorption ratios $\left[\mu_{Ca}^{Set\text{-}I(Set\text{-}II)}/\mu_{Ca}^{CaCO_3}\right]$ versus fractions of calcium α (2a) and α+α´ (2b).

Table1. List of relative absorption terms in excitation of Ca, its empirical relations with analyte amounts and co-efficients of fit along with mean absolute percent deviation D_p for each case.

Ratios $\ell n\left[\frac{\mu_{Ca}^{S/Sp}}{\mu_{Ca}^{CaCO_3}}\right]$	$\sum_{j=-p}^{q} Acof_j\left[[\alpha]^j([\alpha+\alpha']^j)\right]$	Coefficients of fit, *Acof*$_j$, and Mean absolute Percentage deviation, Dp Set-I	Set-II
$\ell n\left[\frac{\mu_{Ca}^{S}}{\mu_{Ca}^{CaCO_3}}\right]$ for Ca K x-rays and 5.959 keV excitations for first 9 samples of set-I & 10 samples of set-II	$\sum_{j=-1}^{2} Acof_j[\alpha]^j$	A_{-1}=0.1197714E-01 A_0=-0.436007E+01 A_1=0.1514395E+03 A_2=-0.229233E+04 D_p=5.30	A_{-1}=0.2721844E-02 A_0= -0.108918E+01 A_1=0.4471804E+02 A_2=-0.937474E+03 D_p=3.18
$\ell n\left[\frac{\mu_{Ca}^{Sp}}{\mu_{Ca}^{CaCO_3}}\right]$ for Ca K x-rays and 5.959 keV excitations for next 10 targets of each, set-I and set-II	$\sum_{j=-1}^{2} Acof_j[\alpha+\alpha']^j$	A_{-1}=0.3582136E-01 A_0=-0.131616E+01 A_1=0.6174554E+01 A_2=-0.127822E+02 D_p=2.33	A_{-1}=0.152249E-01 A_0=-0.2462374 A_1=0.7934327E+01 A_2=-0.2450114E+02 D_p=2.00

In the polynomial relations, Acof$_j$'s are coefficients of fit[1]. The mean absolute percent deviation $D_p = 100/nC_{im}\left[\sum|C_i - C_{i'}|\right]$ that is the measure of analysis error is calculated for each set and is included in table 1. Here C_i and $C_{i'}$ are the evaluated and actual weight fractions and C_{im} are the mean of C_i.

ENHANCEMENT TERMS

For enhancement of analyte ***c*** x-rays due to x-rays of analyte ***a***, the relative ratio of absorption terms, $\left[\mu_c^{S(Sp)}/\mu_c^{C}\right]$ for ***c***'s x-rays in S(Sp) and in compound ***C*** of ***c***, comes in terms of amounts α, α′ and β and counting rates N_c^S, N_c^C and N_c^{Sp} as[1]

$$\frac{\mu_c^S}{\mu_c^C}/G = \frac{\beta M_C}{lM_c}\alpha\left[\frac{N_c^S}{N_c^C}\right]^{-1} \quad \ldots (3) \qquad \frac{\mu_C^{Sp}}{\mu_C^C}/G = \frac{\beta}{1+\alpha'}\frac{M_c}{lM_C}\frac{\left(\alpha+\alpha' n\frac{M_a}{M_A}\right)}{1+\alpha'}\left[\frac{N_c^{Sp}}{N_c^C}\right]^{-1} \quad \ldots (4)$$

Where M_c is atomic weight of element ***c***. M_C is molecular weight of compound ***C***. *l* is number of atoms of ***c*** in one mole of ***C***; $N_c^{S(Sp)(C)}$ is count under the ***c*** x-ray photo peak from S, Sp or ***C***.

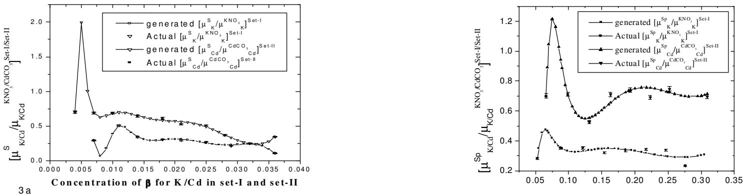
Similarly $\mu_c^{S(Sp)(C)}$ is the composite absorption coefficient of target material S, Sp or ***C*** at incident photon and emitted x-ray energies. β is fractional amount of ***c*** in sample S.

$G = \frac{N_0}{M_a}\frac{\sigma_a^i \sigma_c^a}{\sigma_c^i}$ and $\sigma_{a(c)}^{i(a)}$ is the x-ray production cross-section of ***a(c)*** x-rays at incident energy *i* or at ***a*** x-ray energy. N_0 is the Avogadro's number. However, all parameters involved in G are constants at photon energy *i* and for analytes ***a*** and ***c***. Thus, $\left[\mu_c^{S(Sp)}/\mu_c^{C}\right]$ ratios, expressed in G units, represent relative enhancement of ***c*** and can be determined from relation (3) and (4) from counting rate ratios and amounts β and α.

The enhancement of each, potassium K x-rays and cadmium L x-rays, because of calcium K x-rays in μ's ratios, $\left[\mu_{K(Cd)}^{S(Sp)} \Big/ \mu_{K(Cd)}^{KNO_3(CdCO_3)}\right]^{set-I(set-II)}$, are evaluated from the observed counts under the K/L photo peak of K/Cd and with known amounts α for calcium and β for K/Cd. Some plots of calculated ratios for different β and α+α′ combinations are shown in figures 3a and 3b. The evaluated μ′s terms are correlated with α, α+α′ and β amounts irrespective of its x-ray counts by finding their empirical relations. The agreement between most of the fitted and actual ones comes out to be with in 10% for the fits listed in table 2. The results are also shown in fig. 3a and 3b for S and Sp. All this lends support to the relation (5).

$$\ell n\left(\frac{\mu_K^{S(Sp)}}{\mu_K^{KNO_3}}\right) = \sum_{j=-p}^{q} Ecof_j[\alpha]^j([\beta]^j)([\alpha+\alpha']^j) \qquad \ldots. \quad (5)$$

Here $Ecof_j$'s are the coefficients of fit for enhancement effect and are similar to $Acof_j$'s. Different relations and mean absolute percent deviation D_p is measure of the analysis error are listed in table 2.



3a

3b

Figure 3 Plot of calculated values of enhancement ratios $\left[\mu_{K/Cd}^{S/Sp} \Big/ \mu_{K/Cd}^{KNO_3/CdCO_3}\right]^{set-I/set-II}$ versus β fractions of K/Cd (Fig.3a) and α+α′ fractions of Ca (Fig. 3b) along with the generated values

Table 2. Listing of relative enhancement terms for K K x-rays and Cd L x-rays, their empirical relations with enhanced and enhancer amounts, β and α, and co-efficients of fits along with mean absolute percent deviation D_p in set-I and set-II.

Ratios $\ell n\left[\frac{\mu_{K/Cd}^{S/Sp}}{\mu_{K/Cd}^{KNO_3/CdCO_3}}\right]$	$\sum_{j=-p}^{q} Ecof_j[\alpha]^j/[\beta]^j/[\alpha+\alpha']^j$	Coefficients of fit, *Acof*$_j$, and Mean absolute Percentage deviation, Dp	
		Set-I	Set-II
$\ell n\left[\frac{\mu_{K/Cd}^{S}}{\mu_{K/Cd}^{KNO_3/CdCO_3}}\right]$ for K K x–rays/Cd L x-rays and Cd in 5.959 keV excitation	$\sum_{j=-3}^{4} Ecof_j[\alpha]^j$	E_{-3}=0.7074366E-03	E_{-3}=-0.1104936E-04
		E_{-2}=-0.3330547	E_{-2}=0.7532714E-02
		E_{-1}=0.637156E+02	E_{-1}=-01999052E+01
		E_0=-0.6446864E+04	E_0=0.2696828E+03
		E_1=0.3738251E+06	E_1=-0.2018248E+05
		E_2=-0.1247288E+08	E_2=0.8392349E+06
		E_3=0.2224124E+09	E_3=-0.1810043E+08
		E_4=-0.1640501E+10	E_4=0.1563601E+09
		D_p=2.27	D_p=2.08
	$\sum_{j=-2}^{3} Ecof_j[\beta]^j$	E_{-2}=-0.8074049E-04	E_{-2}=0.1014426E-02
		E_{-1}=-0.3951813E-01	E_{-1}=-0.1605312
		E_0=0.1186182E+02	E_0=0.6641102E+01
		E_1=-0.1280927E+04	E_1=-0.1526626E+03
		E_2=0.4927046E+05	E_2=0.1647646E+04
		E_3=-0.6381886E+06	E_3=-0.6797466E+04
		D_p=10.82	D_p=1.8
$\ell n\left[\frac{\mu_{K/Cd}^{Sp}}{\mu_{K/Cd}^{KNO_3/CdCO_3}}\right]$ for K and Cd in 5.959 keV excitation	$\sum_{j=-3}^{2} Ecof_j[\alpha+\alpha']^j$	E_{-3}=-0.168670E-02	E_{-3}=-0.1149686E-01
		E_{-2}=0.1252093	E_{-2}=0.6713236
		E_{-1}=-0.3451197E+01	E_{-1}=-0.1473483E+02
		E_0=0.4307859E+02	E_0=0.1514945E+03
		E_1=-0.2618954E+03	E_1=-0.7382029E+03
		E_2=0.5734057E+03	E_2=0.1364107E+04
		D_p=7	D_p=2
	$\sum_{j=-2}^{3} Ecof_j[\beta]^j$	E_{-2}=0.2466747E+02	E_{-2}=-0.1163307E+03
		E_{-1}=-0.4443699E+04	E_{-1}=0.8750831E+04
		E_0=0.3194291E+06	E_0=-0.262833E+06
		E_1=-0.1195376E+08	E_1=0.3939747E+07
		E_2=0.2048781E+09	E_2=-0.2947063E+08
		E_3=-0.146242E+10	E_3=0.880047E+08
		D_p=3.447	D_p=3.868

RESULTS AND DISCUSSION

The terms for known samples in set-I and set-II are calculated simply from count rates that are mostly within 1% statistics and utmost care has been taken in weighing, mixing, grinding and making targets, therefore, the errors in calculated values are at the most 2%. The Ca amounts in two sets are evaluated using our earlier method for elemental determinations for thick samples[3] that are within 7% for set-I and 8% for set II of absolute percent deviations Dp. This proves the reliability of count rate ratios. The mean absolute deviations listed in tables 1-2 are less than or near to 5% for
almost all the cases except in case of enhancement term versus calcium amount in Sp that is nearly 10%. This justifies the reliability of relations. In empirical relations found for absorption terms with analyte Ca amount, the powers of amount term varies from -1 to 2 for selective excitation of x-rays. But, for enhancement of K/Cd, the terms came in polynomial with calcium amount powers varying from -3 to 4 for low amounts but changes to -2 to 3 for increased amounts. This shows that enhancement is relatively more sensitive and large with initial variations in low Ca amounts as the Ca amounts increases enhancement changes become a little bit stable. In both the sets, enhancement varies with powers of enhanced element amounts as -2 to 3.

From all these explanations it is concluded that in case of excitations of an analyte in the organic samples where H, C, O, N etc. are the main constituents, the absorption terms for each Ca and K follow the (-1 to 2) polynomial fit with analyte concentrations when constituents of atomic number higher than that of analyte are absent in the substrate. For the presence of higher Z constituent in the sample, whether it is selective excitation or enhanced excitation, the relative absorption terms follow (-2 to 3) polynomial order for analyte amounts.

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