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CALCULATION OF THE CORRECTIONS TO THE CHEMICAL COMPOSITION
OF SOLIDS IN THE FLUORESCENT X-RAY ANALYSIS OF SLURRIES
ZAVODSKAYA LABORATORIYA, 36, 937 (1970).

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FOREWORD
(by Translator)

This translation was made to assist our own work in the field of X-ray fluorescence on-stream analysis, and it was felt it might be of interest to other Canadian workers in the field.

SUMMARY

In the X-ray fluorescence analysis of slurries, a method is developed for the calculation of the chemical composition of the solids, which is independent of the solids content of the slurry.

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The peculiarity of X-ray fluorescence analysis of slurries lies in the necessary calculation of the degree of dilution of the solid samples by the water. That is why one determines a supplementary parameter -- the intensity of radiation of known energy, scattered, and attenuated by the slurry [1,2]. At a fixed degree of dilution of the sample, this intensity depends on the chemical composition of the solid.

The effective wavelength of primary radiation exciting X-ray fluorescence of the elements analysed depends on the target composition⁽¹⁾. In slurry analysis, this quantity can be considered as constant, because dilution of the solid sample by water reduces the filtration of the primary lines and, consequently, the attenuation of the effective wavelengths.

At low concentrations of element A in the solid sample and at great dilutions, it is possible to disregard the magnitude of the absorption jumps for the given elements. In this case, the absolute intensity of the analytical line I_A for the "solids contents" lines can be written:

$$I_A = I_A^\pi - I_\phi^\pi = k_1 \frac{C_{A\pi}}{\mu_{A\pi}^*} \dots \quad (\text{Eq. 1})$$

where I_A^π - observed intensity of the analytical line; I_ϕ^π - intensity of the background near the analytical line; k_1 - a quantity fixed by the given conditions of fluorescent excitation; $C_{A\pi}$ - concentration of element A in the slurry; $\mu_{A\pi}^*$ - mass attenuation coefficient of the slurry for the analytical line of element A.

Representing the slurry attenuation coefficient by $\mu_{A\pi}^*$, the coefficients of attenuation by the solid as μ_{AT}^* and by the water as μ_{AB}^* , in place of equation (1) we have

$$I_A^\pi - I_\phi^\pi = k_1 \cdot C_{A\pi} / \left\{ (\mu_{AT}^* - \mu_{AB}^*) \cdot C_T + \mu_{AB}^* \right\} \dots \quad (\text{Eq. 2})$$

(C_T = concentration of the solid in the slurry).

From this equation, it is clear that the specific intensity (the intensity $I_A^{1\pi}$, containing 1% of element B in the slurry) increases with increased degree of dilution; it has as limit

$$\lim_{C_T \rightarrow 0} \frac{I_A}{C_{A\pi}} = \lim_{C_T \rightarrow 0} I_A^{1\pi} = \frac{k_1}{\mu_{AB}^*} = I_A^{1B} \quad \dots \quad (\text{Eq. 3})$$

Substituting from equation (2)

$$k_1 = \mu_{AB}^* \cdot I_A^{1B} \quad \text{and} \quad C_{A\pi} = C_{AT} \cdot C_T \quad \dots \quad (\text{Eq. 4})$$

we obtain after rearrangement

$$I_A^\pi - I_\phi^\pi = I_A^{1B} \cdot C_{AT} \cdot C_T / \left\{ (\mu_{AT}^* - \mu_{AB}^* - 1) \cdot C_T + 1 \right\} \quad \dots \quad (\text{Eq. 5})$$

The intensity formulae for the scattered radiations at wavelength λ_p [3] appropriate to slurries as "thick" emitters can be written:

$$I_p^\pi = k_2 \cdot (\sigma_\pi^* - \mu_{p\pi}^*) = k_2 \cdot \sigma_\pi^* / \left\{ (\mu_{pT}^* - \mu_{pB}^*) C_T + \mu_{pB}^* \right\} \quad \dots \quad (\text{Eq. 6})$$

where k_2 = a constant; σ_π^* mass coefficient for scattering by the slurry; $\mu_{p\pi}^*$, μ_{pT}^* , and μ_{pB}^* = mass coefficients for the attenuations respectively of the slurry, of the solid, and of the water at the wavelength of the scattered radiation.

Coefficient k_2 can be determined by the size of the scattering of pure water. As a consequence of expression (6) we derive

$$\Delta \epsilon_p = \frac{I_p^B}{I_p^\pi} - 1 = \frac{\sigma_B^*}{\sigma_\pi^*} \cdot \left(\frac{\mu_{pT}^*}{\mu_{pB}^*} - 1 \right) C_T \quad \dots \quad (\text{Eq. 7})$$

It has been experimentally established that this mean atomic number of the suspended matter in the slurry changes negligibly, and it is possible to assume were in wavelength interval $1 - 2\text{\AA}$:

$$\sigma_B^* \approx \sigma_\pi^* \quad \dots \quad (\text{Eq. 8})$$

Then with known solids, equation (7) sets forth directly the proportional relationship (Figure 1, lines 1 and 2). Under normal circumstances, the mass coefficient for scattering by the slurry increases with increase in slurry densities (Figure 1, curve 3).

Equations (5), (7) and approximation (8) permit the proposal of an analytical method for slurries with variable chemical composition of (their) solids. As long as, between analytical lines of the elements determined and the scattering wavelengths, there are no absorption edges, it is possible to write

$$\mu_{A_T}^* / \mu_{A_B}^* = \mu_{P_T}^* / \mu_{P_B}^* \quad \dots \quad (\text{Eq. 9})$$

From this we have:

$$\Delta \epsilon_A = \left(I_A^\pi - I_\phi^\pi \right) / I_P^\pi = \left(I_P^{1B} / I_P^B \right) \cdot C_{A_T} \cdot C_T \quad \dots \quad (\text{Eq. 10})$$

Because the final results of the analysis must be the content of element A in the solid, it is determined jointly by equations (7) and (10), and with regard to C_{A_T} we obtain

$$C_{A_T} = \left\{ I_P^{1B} (\mu_{P_T}^* \mu_{P_B}^* - 1) / I_A^{1B} \right\} (\Delta \epsilon_A / \Delta \epsilon_P) = k_A \cdot (\Delta \epsilon_A / \Delta \epsilon_P) \quad (\text{Eq. 11})$$

It is evident that as long as the transformed quantities $\mu_{P_T}^*$ can be neglected, the elements (to be) determined in the slurry are adequately measured by the intensities of the analytical lines and the scattering.

We assume that the solids consist of elements M, N, --. For these elements with the given approximations, it is possible to write down equation (11). Then the mass coefficient of attenuation by the solid

$$\mu_{P_T}^* = \sum_i^{M,N..} \mu_{P_i}^* \cdot C_{i_T} = \mu_{P_M}^* \cdot k_M \cdot \frac{\Delta \epsilon_M}{\Delta \epsilon_P} + \mu_{P_N}^* \cdot k_N \cdot \frac{\Delta \epsilon_N}{\Delta \epsilon_P} + \dots \quad (\text{Eq. 12})$$

By calculation of formula (12), equation (11) will have the form:

$$C_{A_T} = \frac{\Delta \epsilon_A}{\Delta \epsilon_P} \cdot \frac{I_P^B}{I_A^{1B}} \cdot \left(\frac{\mu_{P_M}^*}{\mu_{P_B}^*} \cdot k_M \cdot \frac{\Delta \epsilon_M}{\Delta \epsilon_P} + \frac{\mu_{P_N}^*}{\mu_{P_B}^*} \cdot k_N \cdot \frac{\Delta \epsilon_N}{\Delta \epsilon_P} + \dots \right) \quad (\text{Eq. 13})$$

Equation (13) shows that for carrying out an analysis, besides the intensities of scattering and of the analytical lines of element A, it is necessary to measure the fluorescent intensities of the interfering elements.

Experimental verification of the above reduced formulae were carried out on an X-ray quantometer ϕ PK-5 having four Soller spectrometric channels with LiF analyzing crystals. The X-ray tube was a BXV-7, fed by a VIP-50-100 rectifier. The radiation detector was a scintillator. The slurry of volume $\sim 1 \ell$ was circulated continuously through a circulating cell whose construction guaranteed obtaining a "thick" emitter. The coefficient of variance of the measured intensities was 1%.

The intensities of the X-ray fluorescence and scattering of the pulp depended on particle size of the solid, [4, 5]; however, in these experiments, the granulometric composition of the solid was constant.

For the calculation of the quantity $\Delta \epsilon_A$, it was assumed that the ratio of the background intensity and the scattering intensity was constant and likewise the ratio of the determinations on water:

$$\Delta \epsilon_A = I_A^\pi / I_P^\pi - I_\phi^\pi / I_P^\pi = I_A^\pi / I_P^\pi - I_\phi^\pi / I_P^B \quad \dots \quad (\text{Eq. 14})$$

From tables of reduced data there exist tests for verifying formula (11). Slurries were prepared by mixing with water portions of known weight from the same ore, containing 0.67% copper. A record was made of the intensity of the $K\alpha$ fluorescence of copper and the slurry scattering of the characteristic radiation ($\text{Au } L\beta_1$) from the anode of the X-ray tube.

It is evident from Table 1 that, with a constant chemical composition of the solid, the coefficient K_A does not depend on the percentage solid content of the slurry.

TABLE 1
Calculation of the Coefficient K_A (11) of the Slurry with
Constant Chemical Compositions of the Solid

| Sample No. | Percent Solids in Slurry | Number of Counts in 40 sec | | $\frac{\Delta \epsilon_{Cu}}{\Delta \epsilon_p}$ | K_{Cu} |
|------------|--------------------------|----------------------------|---------------------|--|----------|
| | | $N_{CuK\alpha}$ | $N_{P(AuL\beta_1)}$ | | |
| Water | 0 | 6,200 | 82,270 | - | - |
| 1 | 9.1 | 15,900 | 66,900 | 0.725 | 1.081 |
| 2 | 16.7 | 21,760 | 57,600 | 0.718 | 1.071 |
| 3 | 23.1 | 25,700 | 52,470 | 0.736 | 1.100 |
| 4 | 28.6 | 28,000 | 47,900 | 0.714 | 1.066 |
| 5 | 33.3 | 30,100 | 44,900 | 0.717 | 1.071 |

Samples with different chemical compositions were produced by mixing with barren rock - fluorite and different concentrations of zinc, of lead, and pyrite. The contents of Zn, Pb, and Fe in the solids varied from 0 to 4%. The solids contents of the slurries, prepared for these tests, were between 5 and 30%. The analytical lines were $ZnK\alpha$, $PbL\beta_1$, $FeK\alpha$, and the scattered anodic radiation $ReL\beta_1$.

Experimental results confirmed that determination of concentrations of elements and solids is possible with adequate precision by the use of analytical lines and scattering in the presence of small fluctuations of the absorption of the analytical lines in the solid. In this case, the analytical graph is a straight line (Figure 2). If the zinc content of the solid is to be determined by this graph, then correction for variations in the chemical composition of the solid, as calculation shows, is given by the equation

$$C_{Zn_T} = C_{Zn}^{\circ} (0.59 + 0.04^{\circ} \frac{\Delta \epsilon_{Pb}}{\Delta \epsilon_{Re}} + 0.20 \frac{\Delta \epsilon_{Fe}}{\Delta \epsilon_{Re}} \dots \dots) \quad (Eq. 15)$$

where C_{Zn_T} - true zinc content of the solid; C_{Zn}° - zinc content of the solid determined from the graph.

The terms in parenthesis for standard samples are equal to unity. The precision achieved in the determination is characterized by a coefficient of variance of 5.5%. It is clear that, in the general case, the analytical error, apart from the instrumental error will depend on how accurately the above-mentioned assumptions turns out to be.

The effect of particle size of the solid was checked by the analytical results of the method described.

The grinding of the sample variously affected the intensity of the analytical lines: it increased the range of specific intensity I_A^{1b} and enlarged the effective mass (attenuation) coefficient of the solid μ_{AT}^* . The character and the function described are preserved. However, in analyses (equation 11) there arise partial compensations for the effect of particle size. For example, the variation in the quantity K_A in a sample of copper ore of diverse particle size (grade product - 0.10 mm fluctuating between 300 and 100%) is characterized by a coefficient of variance of 4%, because, at the same time, the absolute intensity of the CuK α line increased from 10 to 40% with the grinding of the solid and depended on the degree of dilution.

REFERENCES

1. SMALLBONE, A.H., Briquetting Rock Prod. 1965, 68, No. 12, 60-63.
2. FULLER, M.L., McGARVY, P.W., Engineering and Mining Journal, 1962, 163, No. 4, 95.
3. SMAGUNOVA, A.H., BELOVA, P.A., ALFONIN, B.P., LOSEV, H.E., Zavod. Lab. 1864, XXX, No. 4, 426.
4. LOSEV, H.F., SMAGUNOVA, A.H. BELOVA, P.A., and STUDENNIKOV, G.A., Zavod, Lab. 1966, XXXII, No. 2, 154.
5. CARR-BRION, K.G., Analyst, 1966, 91, No. 1081, 289-290.

Percentage solid content in the slurry.

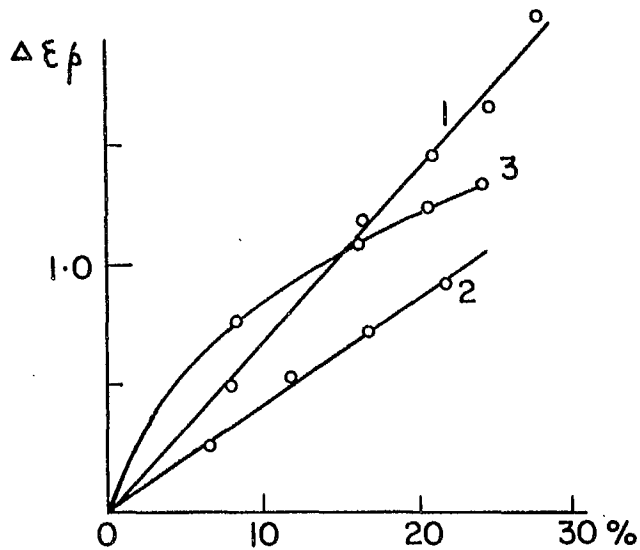


Figure 1. Relationship of the variation in the scattered intensity ($\text{Re}L\beta_1$) with the percentage solid content in the pulp with different mean atomic number of the suspended matter (Z_T): 1-3- Z_T respectively $\sim 19, 16, 75$.

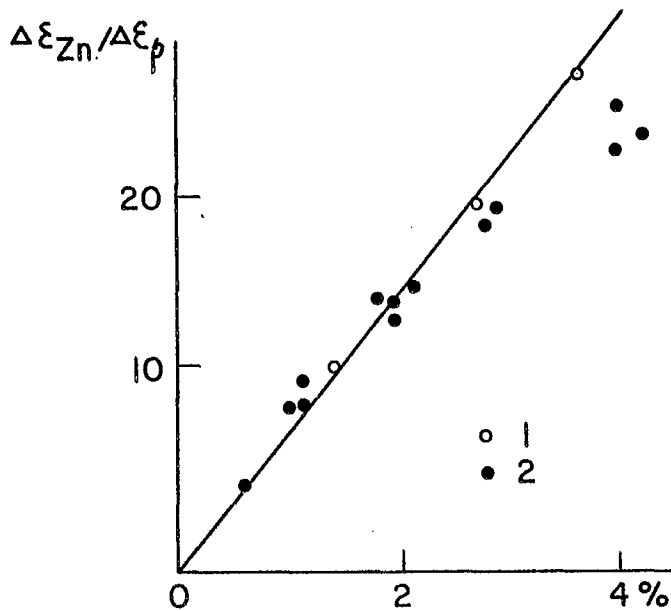


Figure 2. Analytical graph for the determination of zinc in slurries.
1 - standard samples;
2 - chemical composition of solids different from the standards.

