

X-ray fluorescence analysis: Contribution of different wavelengths in the primary tungsten spectrum and molybdenum spectrum to the excitation of nickel, copper and zinc

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Abstract—First it is established that Zn is excited by the $WL\beta_1$ line. This must be taken into account when calculating the mass absorption coefficient of Zn at the $WL\beta_1$ wavelength. The contribution of different wavelengths in the polychromatic primary spectrum to the excitation of Ni, Cu and Zn is investigated. This is done in two ways:

- (1) By calculating and measuring how the intensity from a metal in solution is influenced by the addition of another metal to the solution.
- (2) By calculating and measuring the relation between intensity and concentration for the two component systems CuO-Ni(OH)_2 and CuO-ZnO .

The calculations are done for different primary wavelengths and the results are compared with experiment. Indeed the mass absorption coefficient of Zn at the $WL\beta_1$ wavelength turns out to be consistent with the assumption that Zn is excited by the $WL\beta_1$ line. Furthermore it appears that the wavelength of the exciting radiation has (nearly) no influence upon the course of the intensity/concentration curve for two component systems, if both components are excited by (nearly) the same wavelength range in the primary spectrum, and the considered fluorescence line cannot excite the other component in the mixture.

1. INTRODUCTION

IN X-RAY fluorescence spectrometry an X-ray tube is used as excitation source. An X-ray tube emits a polychromatic continuous spectrum, on which are superimposed the characteristic lines from the anode material. An element is excited by that part of the tube spectrum, which is of shorter wavelength than the absorption edge of the element. This implies that an element is excited by a part of the continuum, and, in many cases, moreover by one or more characteristic tube lines. The excitation efficiency of the primary radiation becomes greater as its wavelength approaches the absorption edge.

We shall make further inquiries into the excitation of the K lines of the elements Ni, Cu and Zn by the most intensive characteristic lines, emitted by the tungsten X-ray tube. We can derive from the wavelengths of the tungsten lines and the absorption edges of Ni, Cu and Zn, which tungsten lines can contribute to the excitation of these elements. It appears from the data in Table 1 that Cu and Zn are excited very efficiently by the $WL\beta_1$ line but not by the $WL\alpha_1$ line, while Ni is excited by both the $WL\beta_1$ line and the $WL\alpha_1$ line.

We can derive likewise from the course of the absorption coefficient with wavelength and atomic number, which tungsten lines can contribute to the excitation of Ni, Cu and Zn. During recent years several tables, containing the mass absorption coefficients of the elements at a number of wavelengths, have

Table 1. Wavelengths of the most intensive W lines and the K absorption edges of Ni, Cu and Zn

Spectral line or Absorption edge	Wavelength Å
$WL\beta_1$	1.28176
$WL\alpha_1$	1.47635
Zn K abs.	1.28329
Cu K abs.	1.38043
Ni K abs.	1.48802

Data copied from: "X-ray wavelengths for Spectrometer". X-ray department, General Electric Company, 4th Edition (1966).

been published. The tables, published by HEINRICH [1] and THEISEN and VOLLATH [2] can be considered as being the most useful, because these tables mention the absorption coefficients at the most frequently used characteristic lines. The mass absorption coefficients, in which we are interested here, are mentioned in Table 2. The high absorption coefficients of Ni and Cu at the $WL\beta_1$ wavelength and of Ni at the $WL\alpha_1$ wavelength are caused by excitation of these elements by the W lines. Cu and Zn are not excited by the $WL\alpha_1$ line, that is why here the absorption coefficients are low. Theisen and Vollath calculated however for Zn a low absorption coefficient at the $WL\beta_1$ line. These authors assumed obviously that Zn is not excited by this line. Heinrich does not mention a value for the absorption coefficient of Zn at the $WL\beta_1$ wavelength.

Table 2. Mass absorption coefficients of Ni, Cu and Zn at the most intensive W lines

Element	$\mu(WL\beta_1)$ (cm ² /g) according to [1]	$\mu(WL\beta_1)$ (cm ² /g) according to [2]	$\mu(WL\alpha_1)$ (cm ² /g) according to [1]	$\mu(WL\alpha_1)$ (cm ² /g) according to [2]
Ni	227.2	226.487	332.9	329.361
Cu	248.6	246.988	47.6	47.821
Zn	—	36.074	52.8	52.762

In contrast to this MÜLLER [3] states that Zn is excited by the $WL\beta_1$ line. The same can be concluded from Rabillon's data [4], concerning the excitation efficiencies of different anode materials in the X-ray tube.

A possible approach to this problem is to plot a curve, which shows for different elements, including Zn, the ratios of the fluorescence intensities, which we measure with a tungsten X-ray tube and an other X-ray tube. SCHREIBER [5] showed a

[1] K. F. J. HEINRICH, *The Electron Microprobe* (Edited by T. D. MCKINLEY, K. F. J. HEINRICH and D. B. WITTRY), p. 296. John Wiley, New York (1966).

[2] R. THEISEN and D. VOLLATH, *Tabellen der Massenschwächungskoeffizienten von Röntgenstrahlen*. Verlag Stahleisen M.B.H., Düsseldorf (1967).

[3] R. MÜLLER, *Spektrochemische Analysen mit Röntgenfluoreszenz*. Oldenbourg (1967).

[4] R. RABILLON, *Revue univille Mines* (9) 17, 291 (1961).

[5] H. SCHREIBER JR., *Adv. X-ray Analysis* 5, 370 (1962).

plot of the intensities, obtained with the tungsten X-ray tube, in comparison with the intensities, obtained with the chromium and molybdenum tubes. MÜLLER [6] measured the fluorescence intensities, obtained with tungsten excitation and molybdenum excitation. We have plotted in Fig. 1 a curve, showing the fluorescence intensities from a number of elements, obtained with a tungsten X-ray tube, in proportion to the intensities, obtained with a molybdenum tube. Our measuring results lead to the same conclusions as Schreiber's and Müller's results, viz:

The intensity ratio W tube/Mo tube increases continuously from element 39 up to and including element 33. This is caused mainly by the continuous decrease of the excitation efficiency of the characteristic molybdenum lines over this region. The elements 32 and 31 will be excited by the $WL\gamma_1$ radiation from the W tube. This accounts for the small but sharp increase in the intensity ratio between element 33 and element 32. Then there is a sharp and large increase in the curve from element 31 to element 30 (Zn). This points to the fact that element 30 is excited by the characteristic $WL\beta_1$ line from the W tube. If element 30 was not excited by the $WL\beta_1$ line, there would be a sharp increase from element 30 to element 29.

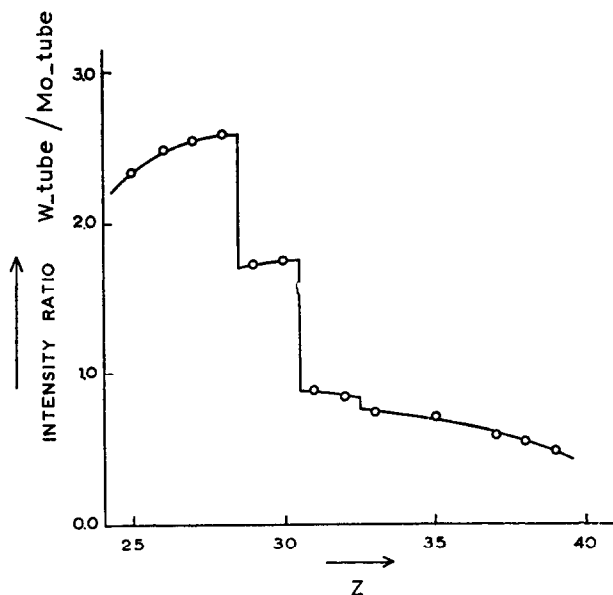


Fig. 1. Ratio of the $K\alpha$ fluorescence intensities, measured with tungsten and molybdenum excitation, as function of the atomic number.

Samples: cellulose briquets, containing little amounts of the elements. Apparatus: Philips PW 1540 plane crystal spectrometer. Measuring circumstances: 48 kV X-ray tube voltage. Primary collimator with 0.18° angle of divergence. LiF 220 analyzing crystal, first order reflections. However: LiF 200 analyzing crystal, second order reflections, for $GaK\alpha$ and $GeK\alpha$ lines. Scintillation counter, without pulse height discrimination.

Finally the sharp increase from element 29 to element 28 is due to excitation of the elements 28 and lower by the $WL\alpha_1$ line from the W tube.

So we must assume that Theisen and Vollath give an incorrect value for the mass absorption coefficient of Zn at the $WL\beta_1$ wavelength. The correct absorption coefficient can be calculated from the equation, derived by Theisen and Vollath:

$$\mu_{\text{el.}}(\lambda) = C\lambda^a Z^b \quad (1a)$$

where $\mu_{\text{el.}}(\lambda)$ is the mass absorption coefficient of an element at wavelength λ ,
 Z is the atomic number of that element,

C , a and b are constants within a period of the periodic system of the elements,
 and within a wavelength range between two absorption edges of
 the absorbing element.

We must however use the values of C , a and b , given by Theisen and Vollath for $\lambda < \lambda_k$.

Thus:

$$\mu_{\text{Zn}}(WL\beta_1) = 3.12 \cdot 10^{-2} \cdot (\lambda_{WL\beta_1})^{2.68} \cdot (Z_{\text{Zn}})^{2.47} = 268.5.$$

Heinrich's still frequently used formula

$$\mu_{\text{el.}}(\lambda) = C'\lambda^a \quad (1b)$$

contains the empirical factor C' , the value of which changes with the absorbing element. Assuming that Zn is excited by the $WL\beta_1$ line:

$$\mu_{\text{Zn}}(WL\beta_1) = 138.000 \cdot (\lambda_{WL\beta_1})^{2.70} = 269.9.$$

We investigated more exactly the contribution of different wavelengths in the primary spectrum to the excitation of Ni, Cu and Zn, not only for the primary tungsten spectrum, but also for the primary molybdenum spectrum.

2. INTERELEMENT EFFECTS IN SOLUTIONS

2.1. Mathematics

The intensity of a characteristic line, emitted by a component A in a weight fraction C_A in a solution, is calculated from the well known equation:

$$\begin{aligned} I_A^0 &= \int_{\lambda_{\min}}^{\lambda_{K_A}} \frac{KC_A\mu_A(\lambda)I_0(\lambda) d\lambda}{C_A\left\{\frac{\mu_A(\lambda)}{\sin \alpha} + \frac{\mu_A(\lambda_A)}{\sin \beta}\right\} + \{1 - C_A\}\left\{\frac{\mu_D(\lambda)}{\sin \alpha} + \frac{\mu_D(\lambda_A)}{\sin \beta}\right\}} \\ &= \int_{\lambda_{\min}}^{\lambda_{K_A}} \frac{K \sin \alpha C_A\mu_A(\lambda)I_0(\lambda) d\lambda}{C_A\varepsilon_A(\lambda, \lambda_A) + \{1 - C_A\}\varepsilon_D(\lambda, \lambda_A)} \end{aligned} \quad (2)$$

with

$$\varepsilon_A(\lambda, \lambda_A) = \mu_A(\lambda) + q\mu_A(\lambda_A)$$

$$\varepsilon_D(\lambda, \lambda_A) = \mu_D(\lambda) + q\mu_D(\lambda_A)$$

$$q = \frac{\sin \alpha}{\sin \beta}$$

K = a constant for a given component A and a given spectrometer arrangement,

λ = wavelength in the primary spectrum,

λ_A = wavelength of the analytical line,

λ_{\min} = the short wavelength limit of the primary spectrum,

λ_{K_A} = the K absorption edge of component A , if a K line is measured for I_A^0 ,

$I_0(\lambda)$ = the intensity in the incident beam at the wavelength λ ,

$\mu_A(\lambda)$ = mass absorption coefficient of component A at wavelength λ ,

$\mu_D(\lambda)$ = mass absorption coefficient of the solvent at wavelength λ ,

$\mu_A(\lambda_A)$ = mass absorption coefficient of component A at wavelength λ_A ,

$\mu_D(\lambda_A)$ = mass absorption coefficient of the solvent at wavelength λ_A ,

α = angle between primary beam and specimen surface,

β = angle between secondary beam and specimen surface.

When another component B is added to the solution, in a concentration C_B , the intensity I_A^0 will change, according to the equation:

$$I_A' = \int_{\lambda_{\min}}^{\lambda_{K_A}} \frac{K \sin \alpha C_A' \mu_A(\lambda) I_0(\lambda) d\lambda}{C_A' \varepsilon_A(\lambda, \lambda_A) + C_B \varepsilon_B(\lambda, \lambda_A) + \{1 - C_A' - C_B\} \varepsilon_D(\lambda, \lambda_A)} \quad (3)$$

with

$$\varepsilon_B(\lambda, \lambda_A) = \mu_B(\lambda) + q\mu_B(\lambda_A).$$

The addition of the component B to the solution causes a small change in the weight fraction C_A . The changed concentration is called C_A' . Combining the equations (2) and (3):

$$\frac{I_A'}{I_A^0} = \frac{\int_{\lambda_{\min}}^{\lambda_{K_A}} \frac{K \sin \alpha C_A' \mu_A(\lambda) I_0(\lambda) d\lambda}{C_A' \varepsilon_A(\lambda, \lambda_A) + C_B \varepsilon_B(\lambda, \lambda_A) + \{1 - C_A' - C_B\} \varepsilon_D(\lambda, \lambda_A)}}{\int_{\lambda_{\min}}^{\lambda_{K_A}} \frac{K \sin \alpha C_A \mu_A(\lambda) I_0(\lambda) d\lambda}{C_A \varepsilon_A(\lambda, \lambda_A) + \{1 - C_A\} \varepsilon_D(\lambda, \lambda_A)}} \quad (4)$$

In the case of a pure monochromatic primary radiation with wavelength λ :

$$\begin{aligned} \frac{I_A'}{I_A^0} &= \frac{C_A'}{C_A \varepsilon_A(\lambda, \lambda_A) + \{1 - C_A\} \varepsilon_D(\lambda, \lambda_A)} \\ &= \frac{C_A'}{C_A} \times \frac{C_A \{\varepsilon_A(\lambda, \lambda_A) - \varepsilon_D(\lambda, \lambda_A)\} + \varepsilon_D(\lambda, \lambda_A)}{C_A \{\varepsilon_A(\lambda, \lambda_A) - \varepsilon_D(\lambda, \lambda_A)\} + C_B \{\varepsilon_B(\lambda, \lambda_A) - \varepsilon_D(\lambda, \lambda_A)\} + \varepsilon_D(\lambda, \lambda_A)} \end{aligned} \quad (5)$$

2.2. Procedure

In practice the specimen is excited as a rule by a polychromatic beam, which complicates a comparison of the theory with practical measuring results. It is necessary to calculate the theoretical intensity ratio I_A'/I_A^0 for different primary wavelengths, and to combine the results.

Measurements and calculations have been done for the $\text{CuK}\alpha$ intensity, emitted by CuSO_4 solutions, to which various amounts of NiSO_4 or ZnSO_4 have been added and for the $\text{ZnK}\alpha$ intensity, emitted by ZnSO_4 solutions, to which various amounts of CuSO_4 have been added. The solutions were prepared using pro analysis chemicals (Merck, Darmstadt), to wit $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

1, 2, 3 or 4 ml standard solution of component *B* was added to 5 ml standard solution of component *A*, after which the solution was made up to 10 ml by water. The reference solutions were prepared by adding 5 ml water to 5 ml solution of component *A*. The concentrations of anhydrous NiSO_4 , CuSO_4 and ZnSO_4 in the solutions were calculated, in mg/ml, for an easy reproduction in the figures, as well as in weight fraction, for the theoretical calculations of I_A'/I_A^0 . It will be clear that the concentration of *A* in mg/ml is not influenced by the presence of component *B* in the solutions.

Calculations have been done for some wavelengths in the exciting spectrum, emitted by a tungsten X-ray tube, namely the $WL\beta_1$ wavelength, the $WL\gamma_1$ wavelength and an arbitrary wavelength in the continuous tube spectrum. For that we chose 0.90 Å, in order to have three wavelengths regularly spread over the most exciting part of the tube spectrum. The mass absorption coefficients of the sulfates and of H_2O have been calculated from the equation

$$\mu_{\text{comb.}}(\lambda) = \sum W_{\text{el.}} \mu_{\text{el.}}(\lambda) \quad (6)$$

with $\mu_{\text{comb.}}(\lambda)$ = mass absorption coefficient of the combination at wavelength λ ,
 $\mu_{\text{el.}}(\lambda)$ = mass absorption coefficient of an element at wavelength λ ,
 $W_{\text{el.}}$ = weight fraction of that element in the combination.

We used the numerical values of the absorption coefficients of the elements, as calculated by THEISEN and VOLLATH [2]. However, this table does not mention the absorption coefficients at some of the desired wavelengths. We calculated these from equation (1a). For this we used the numerical values of the factors *C*, *a* and *b*, which are mentioned in [2]. The contribution of the hydrogen to the absorption coefficients of the combinations have been neglected. Table 3 shows the absorption coefficients of the three sulfates and of H_2O at the considered primary and secondary wavelengths. Two possible values of μ_{ZnSO_4} at the $WL\beta_1$ wavelength are mentioned.

Figures 2a, b and c show for the three mentioned solution series the calculated variations of I_A'/I_A^0 with C_B , together with practical measuring points. It is assumed in the calculations that $q = 1.58$. This value applies to the Philips PW 1540 plane crystal spectrometer, which we used. At that the average angle between the divergent primary beam and the specimen surface is considered.

In Fig. 2b two curves have been drawn for the primary $WL\beta_1$ line, one where it is assumed that Zn is excited by the $WL\beta_1$ line, and one where it is assumed

Table 3. Mass absorption coefficients of NiSO_4 , CuSO_4 , ZnSO_4 and H_2O at some primary and secondary wavelengths

Spectral line	λ (Å)	μ_{NiSO_4} (cm^2/g)	μ_{CuSO_4} (cm^2/g)	μ_{ZnSO_4} (cm^2/g)	$\mu_{\text{H}_2\text{O}}$ (cm^2/g)
	0.900	38.64	43.35	47.37	2.09
$WL\gamma_1$	1.098	65.93	73.94	80.80	3.74
$WL\beta_1$	1.282	99.47	111.54	121.82*	5.82
$WL\beta_1$	—	—	—	27.69†	—
$\text{ZnK}\alpha$	1.436	—	35.88	37.86	8.12
$\text{CuK}\alpha$	1.542	41.35	43.68	46.06	9.99

* Supposing that Zn is excited by the $WL\beta_1$ line, obtained with the mass absorption coefficient of Zn, calculated in Section 1.

† Supposing that Zn is not excited by the $WL\beta_1$ line, obtained with the mass absorption coefficient of Zn, mentioned in [2].

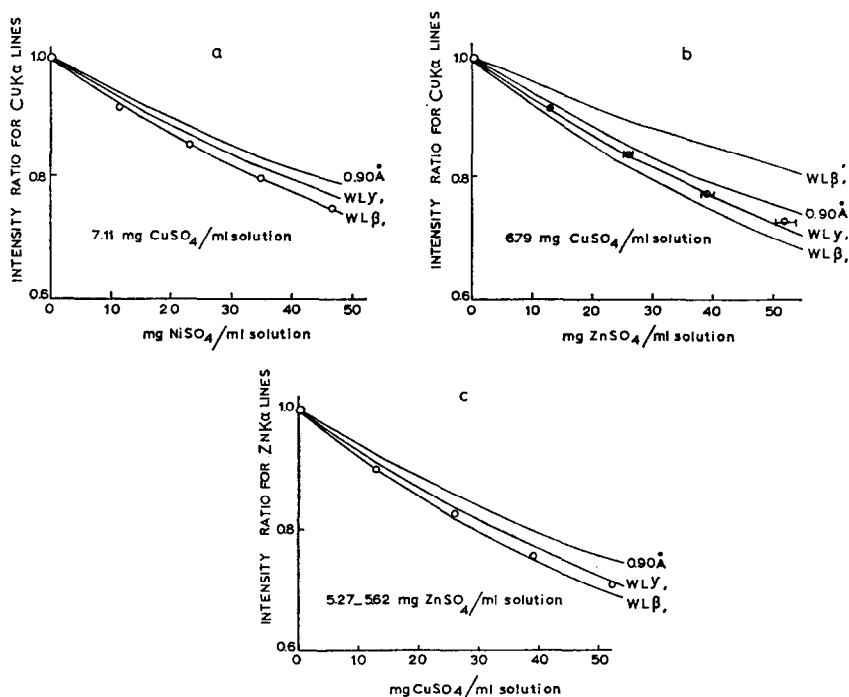


Fig. 2. Influence of the NiSO_4 concentration or the ZnSO_4 concentration in a CuSO_4 solution upon the $\text{CuK}\alpha$ intensity ratio, and influence of the CuSO_4 concentration in a ZnSO_4 solution upon the $\text{ZnK}\alpha$ intensity ratio. Drawn lines: Calculated intensity ratios at the marked exciting wavelengths. Circlets: Practical measured intensity ratios. Measuring circumstances: Tungsten X-ray tube, 40 kV voltage. Primary collimator with 0.18° angle of divergence. LiF 220 analyzing crystal, first order reflections. Scintillation counter, without pulse height discrimination.

that Zn is not excited by the $WL\beta_1$ line (indicated by $WL\beta_1'$). Ranges have been indicated for the $ZnSO_4$ concentrations. The reason for that is that the composition of the used zinc sulfate will probably lie between $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$, owing to weathering, instead of conforming to pure $ZnSO_4 \cdot 7H_2O$. The concentration range between these limits is indicated, and it is seen that the $ZnSO_4$ concentration hardly affects the calculated curves in Fig. 2c. The absolute standard deviation in the measured intensity ratios, caused by the statistical counting error, is continually about 0.002.

2.3. Conclusions

It follows from the measuring results in Fig. 2a that Cu is excited mainly by the $WL\beta_1$ line in the primary spectrum. The measuring results in Fig. 2b prove clearly that for $\mu_{ZnSO_4}(WL\beta_1)$ the value holds good, whereby it is assumed that Zn is excited by the $WL\beta_1$ line. The measured intensity ratios are somewhat higher than the calculated intensity ratios for the $WL\beta_1$ line. This fact is caused rather by secondary excitation of Cu by the $ZnK\beta$ lines, than by the contribution of shorter wavelengths in the primary spectrum to the excitation of Cu.

It follows from the measuring results in Fig. 2c that Zn is excited nearly equally by the various wavelengths in the tungsten spectrum.

3. INTERELEMENT EFFECTS IN BINARY OXIDE MIXTURES

3.1. General mathematics

We shall summarize the theory concerning the relation between concentration and emitted X-ray fluorescence intensity, as several authors [3, 7, 8, 9] have established it. The intensity of a characteristic line, emitted by a component A in a binary mixture of component A and component B , is calculated from the equation, similar to (2):

$$I_A(C_A) = \int_{\lambda_{\min}}^{\lambda_{K_A}} \frac{K \sin \alpha C_A \mu_A(\lambda) I_0(\lambda) d\lambda}{C_A \varepsilon_A(\lambda, \lambda_A) + C_B \varepsilon_B(\lambda, \lambda_A)} \quad (7)$$

with

$$\varepsilon_A(\lambda, \lambda_A) = \mu_A(\lambda) + q\mu_A(\lambda_A)$$

$$\varepsilon_B(\lambda, \lambda_A) = \mu_B(\lambda) + q\mu_B(\lambda_A)$$

C_A = weight fraction of component A in the specimen,

C_B = weight fraction of component B in the specimen,

$$C_A + C_B = 1.$$

The pure component A ($C_A = 1$, $C_B = 0$) emits an intensity:

$$I_A(C_A = 1) = \int_{\lambda_{\min}}^{\lambda_{K_A}} \frac{K \sin \alpha \mu_A(\lambda) I_0(\lambda) d\lambda}{\varepsilon_A(\lambda, \lambda_A)}. \quad (8)$$

[7] A. GUINIER, *Revue univlle Mines* (9) **17**, 143 (1961).

[8] H.-J. KOPINECK, *Arch. Eisenhüttenw.* **33**, 327 (1962).

[9] R. MÜLLER, *Spectrochim. Acta* **18**, 123 (1962).

Combining the equations (7) and (8):

$$\begin{aligned} \frac{I_A(C_A)}{I_A(C_A = 1)} &= \frac{\int_{\lambda_{\min}}^{\lambda_{\kappa_A}} \frac{K \sin \alpha C_A \mu_A(\lambda) I_0(\lambda) d\lambda}{C_A \varepsilon_A(\lambda, \lambda_A) + C_B \varepsilon_B(\lambda, \lambda_A)}}{\int_{\lambda_{\min}}^{\lambda_{\kappa_A}} \frac{K \sin \alpha \mu_A(\lambda) I_0(\lambda) d\lambda}{\varepsilon_A(\lambda, \lambda_A)}} \\ &= \frac{\int_{\lambda_{\min}}^{\lambda_{\kappa_A}} \frac{C_A}{C_A + C_B R(\lambda, \lambda_A)} \frac{K \sin \alpha \mu_A(\lambda) I_0(\lambda) d\lambda}{\varepsilon_A(\lambda, \lambda_A)}}{\int_{\lambda_{\min}}^{\lambda_{\kappa_A}} \frac{K \sin \alpha \mu_A(\lambda) I_0(\lambda) d\lambda}{\varepsilon_A(\lambda, \lambda_A)}} \end{aligned} \quad (9)$$

with $R(\lambda, \lambda_A) = \frac{\varepsilon_B(\lambda, \lambda_A)}{\varepsilon_A(\lambda, \lambda_A)}$, the so-called regression coefficient.

In the case of pure monochromatic primary radiation with wavelength λ :

$$\frac{I_A(C_A)}{I_A(C_A = 1)} = \frac{C_A}{C_A + C_B R(\lambda, \lambda_A)}. \quad (10)$$

Here too a comparison of the described theory with practical measuring results is complicated, because in practice the specimen is excited by a polychromatic primary beam. However, in many cases R is nearly independent of λ . Then we may write in the numerator of formula (9) the factor

$$\frac{C_A}{C_A + C_B R(\lambda, \lambda_A)}$$

before the integral. In this way formula (9) is reduced to formula (10). This means that in those cases it is sufficient to calculate the intensity ratio $I_A(C_A)/I_A(C_A = 1)$ only for one primary wavelength, for example the wavelength of the most intensive line in the exciting part of the primary spectrum.

KOPINECK [8] found that in the binary systems, which he discussed, R can be independent of λ over the λ range, by which both components in a system can be excited, on condition that the considered fluorescence line cannot excite the other component in the mixture. This author did not make further inquiries into this subject. We shall try to do that.

It is evident that $R(\lambda, \lambda_A)$ is independent of λ if

$$\frac{\mu_B(\lambda)}{\mu_A(\lambda)} = \frac{\mu_B(\lambda_A)}{\mu_A(\lambda_A)}$$

over the whole exciting wavelength range. If the components A and B are pure elements, the following relations hold [2]:

$$\begin{aligned} \mu_A(\lambda) &= C \lambda^a Z_A^b \\ \mu_B(\lambda) &= C \lambda^a Z_B^b \end{aligned} \quad (1a)$$

where Z_A and Z_B are the atomic numbers of the elements A and B . For elements in the period $19 \leq Z \leq 36$:

$$\mu(\lambda) = 3.12 \cdot 10^{-2} \cdot \lambda^{2.66} \cdot Z^{2.47}, \quad \text{if } \lambda < \lambda_K$$

$$\mu(\lambda) = 9.59 \cdot 10^{-4} \cdot \lambda^{2.70} \cdot Z^{2.90}, \quad \text{if } \lambda_K < \lambda < \lambda_{LI}.$$

If A and B are *two neighbouring elements*, we may assume generally that the two elements are excited by (nearly) the same wavelengths in the primary spectrum. In this case we may write:

$$\frac{\mu_B(\lambda)}{\mu_A(\lambda)} = \frac{3.12 \cdot 10^{-2} \cdot \lambda^{2.66} \cdot Z_B^{2.47}}{3.12 \cdot 10^{-2} \cdot \lambda^{2.66} \cdot Z_A^{2.47}} = \left(\frac{Z_B}{Z_A}\right)^{2.47}, \quad \text{independent of } \lambda.$$

For the factor $\mu_B(\lambda_A)/\mu_A(\lambda_A)$ there are two possibilities:

(1) $\lambda_{K_B} < \lambda_A < \lambda_{LI_B}$. λ_{K_B} and λ_{LI_B} are the wavelengths at the K and LI absorption edges of element B .

Then:

$$\frac{\mu_B(\lambda_A)}{\mu_A(\lambda_A)} = \frac{9.59 \cdot 10^{-4} \cdot \lambda_A^{2.70} \cdot Z_B^{2.90}}{9.59 \cdot 10^{-4} \cdot \lambda_A^{2.70} \cdot Z_A^{2.90}} = \left(\frac{Z_B}{Z_A}\right)^{2.90}.$$

The ratio Z_B/Z_A is nearly equal to 1 in the case of two neighbouring elements. At that there is only little difference between the numerical values of

$$\left(\frac{Z_B}{Z_A}\right)^{2.47} \quad \text{and} \quad \left(\frac{Z_B}{Z_A}\right)^{2.90}.$$

Consequently in this case $R(\lambda, \lambda_A)$ is nearly independent of λ , and equal to

$$\frac{\mu_B(\lambda)}{\mu_A(\lambda)} \quad \text{and} \quad \frac{\mu_B(\lambda_A)}{\mu_A(\lambda_A)}.$$

Here we may ignore the absorption of the primary radiation, when calculating the intensity ratio $I_A(C_A)/I_A(C_A = 1)$, a simplification suggested by JENKINS [10].

(2) $\lambda_A < \lambda_{K_B}$.

Then:

$$\frac{\mu_B(\lambda_A)}{\mu_A(\lambda_A)} = \frac{3.12 \cdot 10^{-2} \cdot \lambda_A^{2.66} \cdot Z_B^{2.47}}{9.59 \cdot 10^{-4} \cdot \lambda_A^{2.70} \cdot Z_A^{2.90}} = 32.5 \cdot \lambda^{-0.04} \cdot \frac{Z_B^{2.47}}{Z_A^{2.90}}.$$

In this case there is much more difference between

$$\frac{\mu_B(\lambda)}{\mu_A(\lambda)} \quad \text{and} \quad \frac{\mu_B(\lambda_A)}{\mu_A(\lambda_A)}.$$

[10] R. JENKINS, *Philips Analytical Equipment Bulletin* 79.117/FS 27. Philips, Eindhoven (1969).

This involves a great variation of $R(\lambda, \lambda_A)$ with λ :

(a) When element A is excited by a wavelength λ much shorter than λ_{K_A} and λ_{K_B} , it holds:

$$\begin{aligned}\mu_B(\lambda) &\ll \mu_B(\lambda_A) \\ \mu_A(\lambda) &< \mu_A(\lambda_A).\end{aligned}$$

Then $R(\lambda, \lambda_A)$ approaches to $\mu_B(\lambda_A)/\mu_A(\lambda_A)$:

(b) When element A is excited by a wavelength λ only a little shorter than λ_{K_A} and λ_{K_B} , it holds:

$$\begin{aligned}\mu_B(\lambda) &< \mu_B(\lambda_A) \\ \mu_A(\lambda) &\gg \mu_A(\lambda_A).\end{aligned}$$

Then $R(\lambda, \lambda_A)$ approaches to $q\mu_B(\lambda_A)/\mu_A(\lambda)$. If $Z_A < Z_B$, there is in the primary spectrum yet a short wavelength range, which can excite element A , but not element B . This can be important if an intensive primary line occurs in it. It can be seen easily that a great difference exists between the $R(\lambda, \lambda_A)$ values for this wavelength range, and the $R(\lambda, \lambda_A)$ values for the wavelength range $< \lambda_{K_B}$.

3.2. Calculations for the systems CuO–Ni(OH)₂ and CuO–ZnO

The variation in the fluorescence intensity as a function of the concentration has been calculated for the systems CuO–Ni(OH)₂ and CuO–ZnO. The absorption behaviour of these oxides is determined mainly by the metals. Calculations have been done for the $K\alpha$ and $K\beta$ lines from the metals and for some wavelengths in the exciting spectra from the tungsten X-ray tube and the molybdenum X-ray tube. The mass absorption coefficients of the oxides were calculated from equation (6), using again the numerical values of the absorption coefficients of the elements, as mentioned by Theisen and Vollath, or calculated, according to THEISEN and VOLLATH [2]. We may neglect the contribution of the oxygen [6, 9], on condition that we take into account the concentration of the metal in the oxide. Then:

$$\mu_{\text{comb.}}(\lambda) = W_{\text{metal}}\mu_{\text{metal}}(\lambda). \quad (6a)$$

Table 4 mentions the calculated absorption coefficients of the oxides at the various primary and secondary wavelengths. It has been proved that, at least in the considered wavelength ranges, the absorption coefficients of the combinations can be expressed as

$$\mu_{\text{comb.}}(\lambda) = C\lambda^a \quad (11)$$

where the factors C and a are constant for a combination, within the wavelength ranges between the absorption edges of the component elements.

Tables 5a and 5b show for the oxide mixtures the regression coefficients, as they vary with the exciting wavelength. Here too it is admitted that $q = 1.58$. Indeed the regression coefficient hardly varies with the exciting wavelength if the secondary line cannot excite the other metal in the mixture (Ni $K\alpha$, Ni $K\beta$ and Cu $K\alpha$ line from the CuO–Ni(OH)₂ system, Cu $K\alpha$, Cu $K\beta$ and Zn $K\alpha$ line from the CuO–ZnO system). In those cases the calculated regression coefficients agree well with the values of the ratios $\mu_B(\lambda)/\mu_A(\lambda)$ and $\mu_B(\lambda_A)/\mu_A(\lambda_A)$, which can be derived

Table 4. Mass absorption coefficients of $\text{Ni}(\text{OH})_2$, CuO and ZnO at some primary and secondary wavelengths

Spectral line	λ (Å)	$\mu_{\text{Ni}(\text{OH})_2}$ (cm^2/g)	μ_{CuO} (cm^2/g)	μ_{ZnO} (cm^2/g)
$\text{MoK}\beta_1$	0.632	22.20	30.32	33.11
$\text{MoK}\alpha_{1,2}$	0.711	30.30	41.39	45.20
	0.900	56.84	77.57	84.69
$W\text{L}\gamma_1$	1.098	96.65	131.8	144.0
$W\text{L}\beta_1$	1.282	145.7	198.7	216.9*
$W\text{L}\beta_1$	1.282	—	—	30.25†
$W\text{L}\alpha_1$	1.476	211.9	40.20	—
$\text{ZnK}\beta_1$	1.295	—	204.1	31.10
$\text{ZnK}\alpha_{1,2}$	1.436	—	37.32	41.14
$\text{CuK}\beta_1$	1.392	181.3	34.30	37.82
$\text{CuK}\alpha_{1,2}$	1.542	34.64	45.25	49.88
$\text{NiK}\beta_1$	1.500	32.13	41.99	—
$\text{NiK}\alpha_{1,2}$	1.659	42.28	55.17	—

* Supposing that Zn is excited by the $W\text{L}\beta_1$ line, obtained with the mass absorption coefficient of Zn, calculated in Section 1.

† Supposing that Zn is not excited by the $W\text{L}\beta_1$ line, obtained with the mass absorption coefficient of Zn, mentioned in [2].

from the data in Table 4. The $W\text{L}\alpha_1$ line can excite Ni, but not Cu. Therefore the regression coefficient, which we obtain at the excitation of Ni by the $W\text{L}\alpha_1$ wavelength, differs strongly from the regression coefficients, which we obtain at the excitation of Ni by the other primary wavelengths. If the secondary line can excite the other metal in the mixture ($\text{CuK}\beta$ line from the CuO – $\text{Ni}(\text{OH})_2$ system, $\text{ZnK}\beta$ line from the CuO – ZnO system), the regression coefficient varies strongly with the primary wavelength, as was to be expected.

Table 5a. Regression coefficients in the $\text{Ni}(\text{OH})_2$ – CuO system

Exciting wavelength (Å)	$\frac{\varepsilon_{\text{CuO}}(\lambda, \text{NiK}\alpha)}{\varepsilon_{\text{Ni}(\text{OH})_2}(\lambda, \text{NiK}\alpha)}$		$\frac{\varepsilon_{\text{Ni}(\text{OH})_2}(\lambda, \text{CuK}\alpha)}{\varepsilon_{\text{CuO}}(\lambda, \text{CuK}\alpha)}$	
	$\frac{\varepsilon_{\text{CuO}}(\lambda, \text{NiK}\beta)}{\varepsilon_{\text{Ni}(\text{OH})_2}(\lambda, \text{NiK}\beta)}$		$\frac{\varepsilon_{\text{Ni}(\text{OH})_2}(\lambda, \text{CuK}\beta)}{\varepsilon_{\text{CuO}}(\lambda, \text{CuK}\beta)}$	
$\text{Mo K}\beta_1$	0.632	1.320	1.323	0.755
$\text{Mo K}\alpha$	0.711	1.324	1.328	0.753
	0.900	1.333	1.337	0.748
$W\text{L}\gamma_1$	1.098	1.339	1.343	0.745
$W\text{L}\beta_1$	1.282	1.345	1.349	0.742
$W\text{L}\alpha_1$	1.476	0.457	0.405	—

Table 5b. Regression coefficients in the CuO – ZnO system

Exciting wavelength (Å)	$\frac{\varepsilon_{\text{ZnO}}(\lambda, \text{CuK}\alpha)}{\varepsilon_{\text{CuO}}(\lambda, \text{CuK}\alpha)}$		$\frac{\varepsilon_{\text{CuO}}(\lambda, \text{ZnK}\alpha)}{\varepsilon_{\text{ZnO}}(\lambda, \text{ZnK}\alpha)}$	
	$\frac{\varepsilon_{\text{ZnO}}(\lambda, \text{CuK}\beta)}{\varepsilon_{\text{CuO}}(\lambda, \text{CuK}\beta)}$		$\frac{\varepsilon_{\text{CuO}}(\lambda, \text{ZnK}\beta)}{\varepsilon_{\text{ZnO}}(\lambda, \text{ZnK}\beta)}$	
$\text{Mo K}\beta_1$	0.632	1.099	1.099	0.910
$\text{Mo K}\alpha$	0.711	1.098	1.098	0.911
	0.900	1.097	1.096	0.9125
$W\text{L}\gamma_1$	1.098	1.096	1.096	0.913
$W\text{L}\beta_1$	1.282	1.094*	1.094*	0.914
$W\text{L}\beta_1$	1.282	0.404†	0.356†	—

* Supposing that Zn is excited by the $W\text{L}\beta_1$ line, $\mu_{\text{ZnO}}(W\text{L}\beta_1) = 216.9$.

† Supposing that Zn is not excited by the $W\text{L}\beta_1$ line, $\mu_{\text{ZnO}}(W\text{L}\beta_1) = 30.25$.

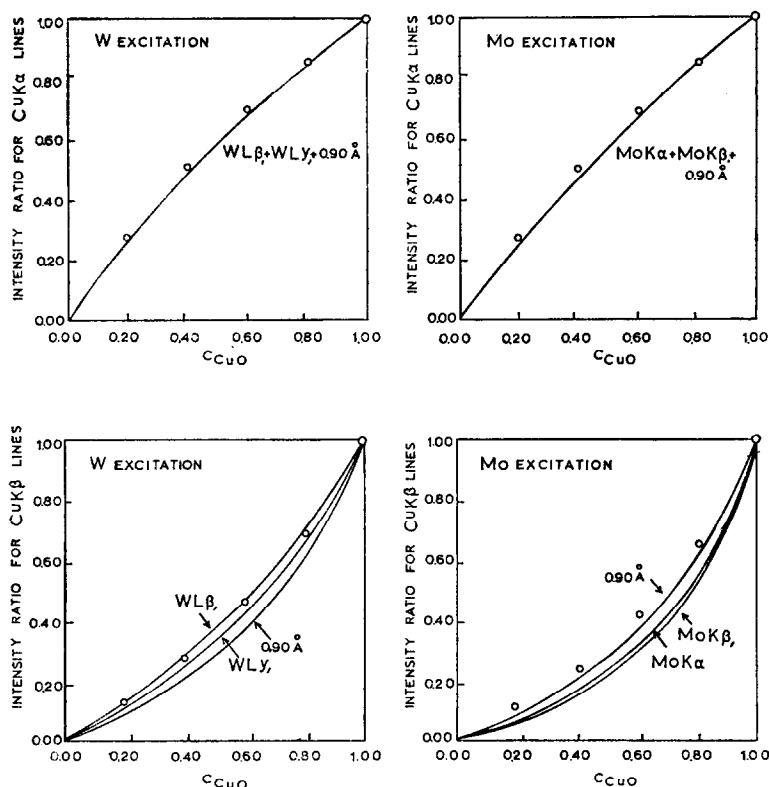


Fig. 3. Correlation between the intensity ratio for the Cu lines and the CuO concentration in CuO-Ni(OH)_2 mixtures. Drawn lines: Calculated intensity ratios at the marked exciting wavelengths. An addition of different primary wavelengths means, that the same theoretical curve holds for these wavelengths. Circlelets: Practical measuring results. Measuring circumstances: Tungsten X-ray tube, 20 kV voltage. Molybdenum X-ray tube, 30 kV voltage. Primary collimator with 0.18° angle of divergence. LiF 200 analyzing crystal, second order reflections. Scintillation counter, without pulse height discrimination.

So it appears from the previously mentioned that, contrary to Müller's suggestion [3], the regression coefficient is not always clearly dependent on the spectral composition of the exciting beam. Figures 3, 4, 5 and 6 show for the oxide mixtures the calculated fluorescence intensity ratios as functions of the concentrations. In Fig. 6 again two curves have been drawn for the $WL\beta_1$ line, one, where it is assumed that Zn is excited by the $WL\beta_1$ line, and one, where it is assumed that Zn is not excited by the $WL\beta_1$ line (indicated by $WL\beta_1'$).

3.3. Experiments

An adequate experimental verification of the theory is a little difficult, because it is not easy to prepare exact homogeneous oxide mixtures. Mixtures were prepared using pro analysis chemicals, CuO and ZnO from Merck, Darmstadt, and Ni(OH)_2 from the British Drug Houses. The average particle size was so small, that particle size effects were non-existent. Three mixing methods were tried by

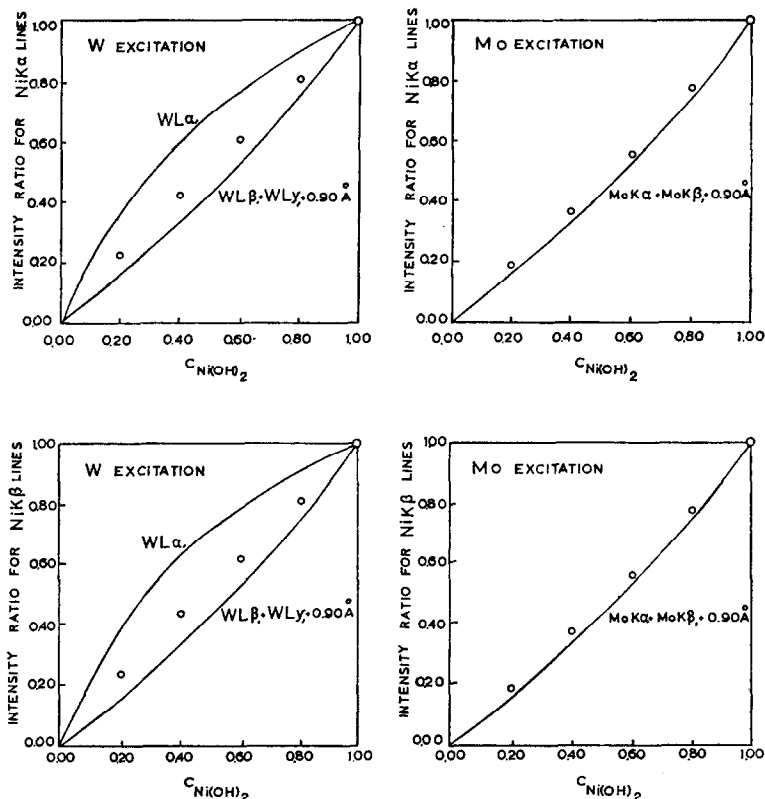


Fig. 4. Correlation between the intensity ratio for the Ni lines and the Ni(OH) $_2$ concentration in CuO-Ni(OH) $_2$ mixtures. Explanation and measuring circumstances: See subscription Fig. 3.

different operators:

- (1) Stirring with a spatula in a vessel for 15 min.
- (2) Grinding in a ceramic mortar for 15 min.
- (3) Grinding in an agate mortar for 15 min.

The mixtures were hand pressed over a mylar film in the specimen holders, which rotated during the measurements. The pure reference oxides were handled in the same manner as the mixtures. Again the Philips PW 1540 plane crystal spectrometer was used. In Tables 6a and 6b some measuring results for the three mixing methods are compared with each other. The standard deviations, due to the statistical counting errors in the measured intensities, are also mentioned.

It is evident that the mixing method affects the measured intensity ratios, considering the small differences in the concentrations. The relative variations advance to 5–10 per cent. Continually the results for the third mixing method are between the results for the other two mixing methods, or agree with the results for another mixing method. So the third mixing method can be considered as presenting the most reliable measuring results. That is why we verified the theory with test samples, prepared by the third method. The practical measuring points have been inserted in Figs. 3–6.

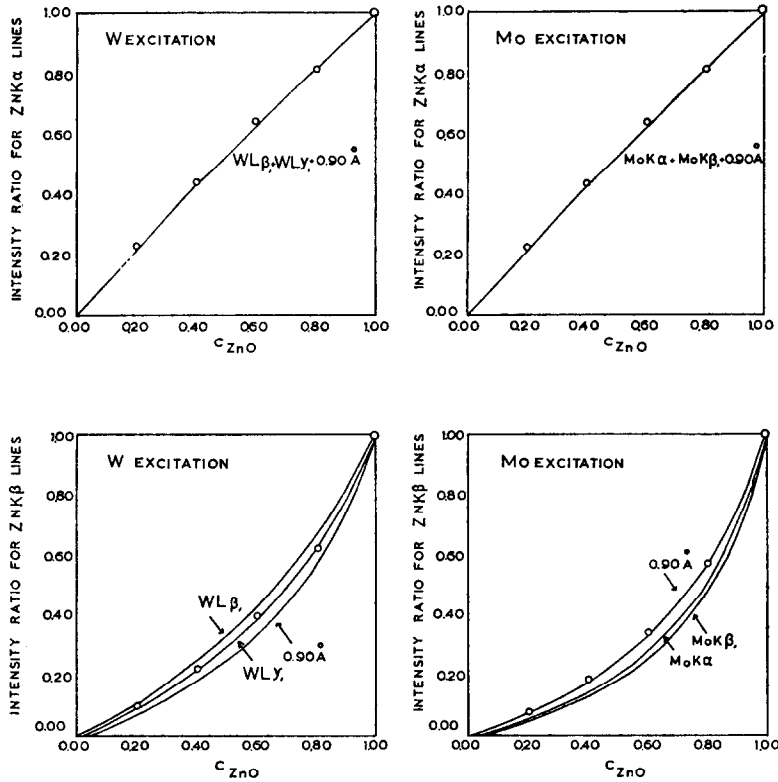


Fig. 5. Correlation between the intensity ratio for the Zn lines and the ZnO concentration in CuO-ZnO mixtures. Explanation and measuring circumstances: See subscription Fig. 3.

3.4 Conclusions

We can conclude from Fig. 3: The measured $\text{CuK}\alpha$ intensities agree well with the theoretically calculated curves. This is a good criterion for the reliability of the test samples. It appears from the measured $\text{CuK}\beta$ intensities that Cu is mainly excited by the $\text{WL}\beta_1$ line if a tungsten X-ray tube is used. If a molybdenum X-ray tube is used, the continuous tube spectrum with $\lambda > \lambda_{\text{MoK}\alpha}$ contributes much to the excitation of Cu. As to Fig. 4: The enhancement of the intensities of the $\text{NiK}\alpha$ and $\text{NiK}\beta$ lines by the $\text{CuK}\beta$ lines can be observed clearly from the measuring results, obtained with the molybdenum X-ray tube. It follows from the measuring results, obtained with the tungsten X-ray tube, that Ni is excited by the $\text{WL}\alpha_1$ line, but mainly by the $\text{WL}\beta$ and $\text{WL}\gamma$ lines and shorter wavelengths, considering the enhancement by the $\text{CuK}\beta$ lines.

Conclusions from Fig. 5 are: The measured $\text{ZnK}\alpha$ intensities agree well with the theoretically calculated curves. It appears from the measured $\text{ZnK}\beta$ intensities that, if the tungsten X-ray tube is used, Zn is excited nearly equally by the $\text{WL}\beta$ lines, the $\text{WL}\gamma$ lines and the continuous tube spectrum. If we use the molybdenum X-ray tube, the continuous tube spectrum with $\lambda > \lambda_{\text{MoK}\alpha}$ contributes much to

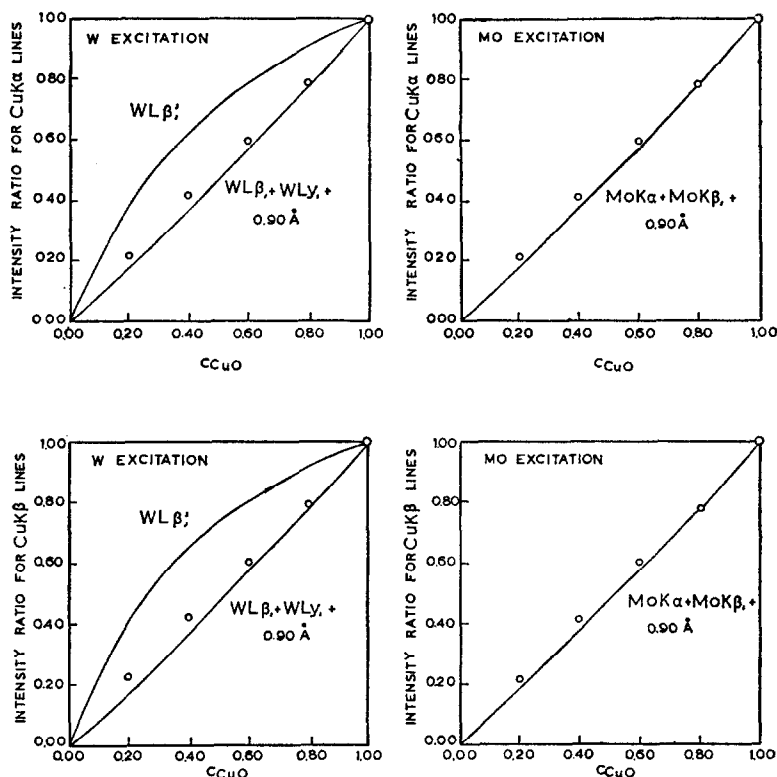


Fig. 6. Correlation between the intensity ratio for the Cu lines and the CuO concentration in CuO-ZnO mixtures. Explanation and measuring circumstances: See subscription Fig. 3.

the excitation of Zn. As to Fig. 6: The enhancement of the intensities of the $\text{CuK}\alpha$ and $\text{CuK}\beta$ lines by the $\text{ZnK}\beta$ lines can be observed clearly if we measure the Cu lines with the molybdenum X-ray tube. The results of the measurements of the $\text{CuK}\alpha$ and $\text{CuK}\beta$ intensities with the tungsten X-ray tube prove clearly that for $\mu_{\text{ZnO}}(\text{WL}\beta_1)$ the value holds good, whereby it is assumed that Zn is excited by the $\text{WL}\beta_1$ line. These measurements too show the influence of the excitation of Cu by the $\text{ZnK}\beta$ lines.

4. APPLICATION TO MULTICOMPONENT SYSTEMS

Equation (10) can be applied also to a multicomponent system:

$$\frac{I_A(C_A)}{I_A(C_A = 1)} = \frac{C_A}{C_A + C_B R_{BA}(\lambda, \lambda_A) + C_C R_{CA}(\lambda, \lambda_A) + \dots + C_N R_{NA}(\lambda, \lambda_A)}$$

with

$$R_{NA}(\lambda, \lambda_A) = \frac{\varepsilon_N(\lambda, \lambda_A)}{\varepsilon_A(\lambda, \lambda_A)}.$$

Table 6a. Influence of the mixing method upon the relative intensities of the X-ray fluorescence lines, emitted by CuO-Ni(OH)_2 mixtures

Mixing method	$C_{\text{Ni(OH)}_2}$	$\frac{I_{\text{NiK}\alpha}(\text{C}_{\text{Ni(OH)}_2})}{I_{\text{NiK}\alpha}(\text{C}_{\text{Ni(OH)}_2} = 1)}$	$\frac{I_{\text{NiK}\beta}(\text{C}_{\text{Ni(OH)}_2})}{I_{\text{NiK}\beta}(\text{C}_{\text{Ni(OH)}_2} = 1)}$	C_{CuO}	$\frac{I_{\text{CuK}\alpha}(\text{C}_{\text{CuO}})}{I_{\text{CuK}\alpha}(\text{C}_{\text{CuO}} = 1)}$	$\frac{I_{\text{CuK}\beta}(\text{C}_{\text{CuO}})}{I_{\text{CuK}\beta}(\text{C}_{\text{CuO}} = 1)}$
Spatula	0.804	0.782 ± 0.002	0.781 ± 0.002	0.196	0.242 ± 0.001	0.113 ± 0.001
Ceramic mortar	0.803	0.776 ± 0.002	0.780 ± 0.002	0.197	0.260 ± 0.001	0.103 ± 0.001
Agate mortar	0.800	0.774 ± 0.002	0.776 ± 0.002	0.200	0.260 ± 0.001	0.107 ± 0.001
Spatula	0.397	0.376 ± 0.001	0.377 ± 0.001	0.603	0.667 ± 0.002	0.434 ± 0.001
Ceramic mortar	0.399	0.367 ± 0.001	0.370 ± 0.001	0.601	0.695 ± 0.002	0.404 ± 0.001
Agate mortar	0.400	0.367 ± 0.001	0.371 ± 0.001	0.600	0.683 ± 0.002	0.411 ± 0.001

Table 6b. Influence of the mixing method upon the relative intensities of the X-ray fluorescence lines, emitted by CuO-ZnO mixtures

Mixing method	C_{CuO}	$\frac{I_{\text{CuK}\alpha}(\text{C}_{\text{CuO}})}{I_{\text{CuK}\alpha}(\text{C}_{\text{CuO}} = 1)}$	$\frac{I_{\text{CuK}\beta}(\text{C}_{\text{CuO}})}{I_{\text{CuK}\beta}(\text{C}_{\text{CuO}} = 1)}$	C_{ZnO}	$\frac{I_{\text{ZnK}\alpha}(\text{C}_{\text{ZnO}})}{I_{\text{ZnK}\alpha}(\text{C}_{\text{ZnO}} = 1)}$	$\frac{I_{\text{ZnK}\beta}(\text{C}_{\text{ZnO}})}{I_{\text{ZnK}\beta}(\text{C}_{\text{ZnO}} = 1)}$
Spatula	0.400	0.440 ± 0.001	0.437 ± 0.001	0.600	0.612 ± 0.001	0.355 ± 0.001
Ceramic mortar	0.402	0.411 ± 0.001	0.418 ± 0.001	0.598	0.661 ± 0.001	0.340 ± 0.001
Agate mortar	0.400	0.411 ± 0.001	0.418 ± 0.001	0.600	0.636 ± 0.001	0.345 ± 0.001
Spatula	0.200	0.237 ± 0.001	0.238 ± 0.001	0.800	0.813 ± 0.002	0.601 ± 0.001
Ceramic mortar	0.200	0.216 ± 0.001	0.221 ± 0.001	0.800	0.854 ± 0.002	0.577 ± 0.001
Agate mortar	0.200	0.214 ± 0.001	0.218 ± 0.001	0.800	0.813 ± 0.002	0.570 ± 0.001

Measuring circumstances: Molybdenum X-ray tube, 30 kV voltage. Primary collimator with 0.18° angle of divergence.

LiF 200 analyzing crystal, first order reflections.

Scintillation counter, without pulse height discrimination.

According to LACHANCE and TRAILL [11] the equation can be rewritten in the form:

$$\frac{I_A(C_A)}{I_A(C_A = 1)} = \frac{C_A}{1 + C_B \alpha_{BA}(\lambda, \lambda_A) + C_C \alpha_{CA}(\lambda, \lambda_A) + \dots + C_N \alpha_{NA}(\lambda, \lambda_A)} \quad (12)$$

with $\alpha_{NA}(\lambda, \lambda_A) = R_{NA}(\lambda, \lambda_A) - 1$, the so-called α correction factor.

TRAILL and LACHANCE [12] assumed, that a polychromatic primary beam practically behaves like a monochromatic one, and that therefore the α coefficients would be constant for a certain system. CLAISSE and QUINTIN [13] meant, that this is not the case, and they modified equation (12) to take care of that fact. The truth is that in a system the α coefficients, for which the condition

$$\frac{\mu_N(\lambda)}{\mu_A(\lambda)} = \frac{\mu_N(\lambda_A)}{\mu_A(\lambda_A)}$$

is fulfilled, are constant and independent of the exciting wavelength. These α coefficients can be calculated quickly from the mass absorption coefficients, which

[11] G. R. LACHANCE and R. J. TRAILL, *Can. Spectrosc.* **11**, 43 (1966).

[12] R. J. TRAILL and G. R. LACHANCE, *Can. Spectrosc.* **11**, 63 (1966).

[13] F. CLAISSE and M. QUINTIN, *Can. Spectrosc.* **12**, 129 (1967).

results in a considerable abbreviation of the analysis time. But this only applies when the characteristic radiation from component A is not enhanced appreciably by the characteristic radiation from component N .

The remaining α coefficients in the system can be ascertained empirically by using measuring results from suitable standard samples, for example binary mixtures of the concerning components.

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