

Determination of Arsenic in Rocks and Ores with a Sequential X-Ray Spectrometer

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The determination of As making use of the $K\alpha$ net intensity requires subtraction of the overlapping Pb $L\alpha$ peak. As the interfering intensity cannot be measured directly, a calculated value has to be obtained from measurement at the Pb $L\beta$ line. A mathematical approach was developed which is based on a typical mean value for the ratio between the Pb $L\alpha$ and $L\beta$ net intensities. Three measurements per sample are required and the routine calibration procedure is set up with three standard samples. Measurements are fed into a computer programmed to calculate both As and Pb concentrations. The programme corrects for matrix effects by means of one of the measurements that is taken at a chosen background point.

The method was devised for fast routine analysis and can be applied to samples of varied composition with the limitation that the As and Pb emission lines are not subjected to significant enhancement. Samples are prepared by grinding the material to a suitable fineness and then pressing it into a tablet. The attainable accuracy and limit of detection for As depend on the Pb level present in each sample.

INTRODUCTION

The possibilities offered by sequential x-ray spectrometers for the determination of parts per million levels of As (less than 0.5%) have to be considered within a general theoretical scheme dealing with the determination of low concentrations in a group of elements having lines in the wavelength range from 0.4 to 1.4 Å.

The basic theoretical relationships can be considered to have been reliably settled and the predictions of the theory have been thoroughly checked.¹⁻⁵ Therefore, we can limit ourselves to summarizing the basic relationships and state the conditions and concepts that have been made use of in this work. These are as follows.

In the case of As, fusion of samples is not possible and the analysis has to be made directly on finely powdered and pressed material. The grinding process should then be effective enough to ensure that grain size and mineralogical effects are kept within acceptable limits.

A restrictive condition of the theory is that the characteristic radiation analysed should not be subjected to significant enhancement effects. This condition implies that any element capable of enhancing the analysed radiation can be present only in low concentrations (less than 1.0%). In particular, the As K radiation will be enhanced by Ba, Mo, Zr, Sr and Rb. Hence, the level of these commonly occurring elements ought to be checked.

It is assumed that suitable instrumental conditions have been chosen and are kept fixed throughout. For this study, a Philips PW 1450 automatic sequential spectrometer with a 3 kW tungsten tube at 70 kV was used. Measurements were made with an LiF 200 crystal and a scintillation counter with an additional collimator.

We define as a pure background point (PBP) any point of the spectrum generated by the sample where

the corresponding photons of wavelength $\bar{\lambda}$ are originated only by scattering in the atoms of the sample and in parts of the instrument.

Consider now a group of samples in all of which the same PBP can be chosen at $\lambda = \bar{\lambda}$. The composition of the samples is well known and the coefficient μ is calculated for all samples at $\lambda = \bar{\lambda}$. If the pure background intensity I_b is measured at the point $P(\bar{\lambda})$ for each sample, then the theory indicates that the I_b value obtained will comply with the equation

$$I_b(\bar{\lambda}) = I_r(\bar{\lambda}) + \frac{m(\bar{\lambda})}{\mu(\bar{\lambda})} \quad (1)$$

where I_r and m behave as constants. I_r is a measure of a residual intensity scattered by parts of the instrument and is not related to the sample matrix; m is a proportionality constant that links the value of μ^{-1} in the matrix with the intensity ($I_b - I_r$) that is scattered by the sample atoms. I_r and m take different values if another PBP with a different $\bar{\lambda}$ value is chosen.

One flexible feature of the theory lies in the fact that the form of Eqn (1) is maintained if μ is calculated at a different wavelength λ_0 in the range 0.4-1.4 Å. In fact, the chosen value of λ_0 may lie fairly distant from $\bar{\lambda}$. Clearly, a new value of m must appear in Eqn (1) if μ is now calculated at the new value λ_0 .

Consider a group of samples where two fixed PBPs can be chosen in each sample at wavelengths λ_1 and λ_2 . If the coefficient μ for these samples is calculated at a chosen wavelength λ_0 , Eqn (1) can be applied at the two points:

$$I_{b1} = I_{r1} + \frac{m_1}{\mu(\lambda_0)}$$

$$I_{b2} = I_{r2} + \frac{m_2}{\mu(\lambda_0)}$$

Thus, the two background intensities appear mathematically related in every sample:

$$I_{b2} = M_{21}(I_{b1} - I_{r1}) + I_{r2} \quad (2)$$

where $M_{21} = m_2/m_1$. It is often found in practice that if the two points are very near each other ($|2\theta_1 - 2\theta_2| \leq 0.5^\circ$) then $M_{21} \approx 1$ and also $I_{R2} \approx I_{R1}$. In such a case, Eqn (2) can be replaced by the approximate expression

$$I_{b2} = M_{21}I_{b1} \quad (3)$$

Theory predicts that the matrix effect can be satisfactorily corrected by means of the coefficient μ calculated at a chosen wavelength λ_0 which is kept fixed for standard and unknown samples. Moreover, this value λ_0 may be chosen at any point in the range 0.4–1.4 Å.

We denote by I_n the net intensity measured in the unknown sample for a given element and by I_{ns} the corresponding intensity measured in a standard sample S; then, the concentration C in the unknown sample is given by

$$C = C_s \cdot \frac{I_n}{I_{ns}} \cdot \frac{\mu(\lambda_0)}{\mu_s(\lambda_0)} \quad (4)$$

where C_s is the concentration of the element of interest in the standard sample which has a mass absorption coefficient $\mu_s(\lambda_0)$. Now, if the chosen value of λ_0 used in Eqn (4) corresponds to a PBP and the background intensity I_b is measured at that point in both standard S and unknown samples, one obtains

$$\frac{\mu(\lambda_0)}{\mu_s(\lambda_0)} = \frac{I_{bs} - I_r}{I_b - I_r} \quad (5)$$

As I_r can be determined experimentally, it follows from Eqn (5) that the matrix effect can be corrected using the background intensities measured at a suitably chosen PBP.

The most serious difficulty in the application of this theory arises when the peak of the element to be analysed is affected by spectral interference. In the case of As, the $K\alpha_1$ line has a wavelength of 1.177 Å and the $L\alpha_1$ line of Pb has a wavelength of 1.175 Å. As a result, the 2θ interval for the two peaks is about 0.03° and it was calculated that 84% of the net peak intensity from the Pb $L\alpha$ line enters the detector positioned at the As $K\alpha$ peak. As the interfering intensity cannot be measured directly, it has to be calculated by resorting to the net peak intensity of the Pb $L\beta$ line.

BASIS OF THE MATHEMATICAL APPROACH

Subtraction of the interfering Pb $L\alpha$ intensity

This problem required a study of the factors that bear on the value of the ratio between the net intensities of the Pb $L\alpha$ and $L\beta$ lines. This ratio will be henceforth denoted α/β .

A simplified situation with monochromatic excitation was considered and calculations of α/β were carried out for each of the main rock-forming compounds (see Appendix). The results indicate that α/β depends on the matrix composition and the spectral distribution of

the exciting radiation. The list of values calculated for a chosen exciting wavelength allows one to calculate that in usual rocks and ores the variation of α/β should lie in a range defined by $\pm 4\%$ round a mean value. Considerations based on the concept of an effective wavelength⁶ lead to the assumption that a similar result should hold good in the general case with radiation from a x-ray tube.

A variation of 4% in the value of α/β implies an absolute error in the calculation of the As concentration that is proportional to the Pb level present in the sample. To gauge the significance of this potential error, the case of sample GXR-2 presented in Table 1 can be considered. This sample has a Pb level of about 600 ppm; if a 4% variation in α/β is assumed, an error of 11 ppm in an As determination has to be allowed for.

The procedure presented in this paper is based on a fixed mean value of α/β . In our view, if this mean value is carefully determined and the Pb level is under 600 ppm, the variations of α/β should not significantly impair the overall accuracy of the method.

Calculation of background intensity under the As $K\alpha$ and Pb $L\beta$ peaks

The method requires the following three measurements, which are carried out on calibration and on unknown samples;

(i) I_b : intensity at a point that was chosen at $\lambda = 0.999$ Å ($2\theta = 28.76^\circ$). This point is normally free from characteristic radiation and can be considered as a pure background point.

(ii) $I_{K\alpha}$: total intensity at the As $K\alpha$ peak ($\lambda = 1.177$ Å, $2\theta = 33.96^\circ$).

(iii) $I_{L\beta}$: total intensity at the Pb $L\beta$ peak ($\lambda = 0.983$ Å, $2\theta = 28.26^\circ$).

According to Eqn (2), the background intensity I_b is mathematically related to the background under the As $K\alpha$ and Pb $L\beta$ peaks; moreover, Eqn (5) indicates that I_b can be used to correct the matrix effect. If a suitable calibration graph is set up, all these calculations can be carried out by means of a computer.

EXPERIMENTAL BASIS

Determination of α/β

A working mean value and the range of variation of α/β with matrix composition, eventual grain size and mineralogical effects have to be found experimentally. For this purpose, a fairly large group of samples were selected, which fulfilled the following requirements; (i) the As content in all samples was negligible; (ii) all samples had a Pb content between 100 and 2000 ppm; and (iii) the group included a few samples with compositions which could be considered as extreme cases of usual rock matrixes, that is, samples having only very light compounds and others with high percentages of heavy compounds. The described group of samples is not easy to obtain. To avoid the difficulties, we had to select among the available international standard

samples for firebricks, cements, limes, clays, etc. Synthetic samples made up of pure oxides and carbonates proved to be most useful because in these samples the composition can be fixed at will.

The required levels of Pb were obtained by adding to the chosen samples small amounts of pure Pb compounds. All the measured values of α/β lay in the range 0.65 ± 0.04 .

The interfering intensity I_i from the Pb $L\alpha$ line could then be calculated in all samples from the measured Pb $L\beta$ net peak intensity I_β :

$$I_i = I_\beta \times 0.65 \times 0.84 = 0.546 I_\beta \quad (6)$$

The factor 0.84 results from the fact that the As $K\alpha$ peak does not coincide with the Pb $L\alpha$ peak. This value depends on the collimation system and has to be determined for each spectrometer.

Construction of the calibration graph for background determinations

To construct the required calibration graphs the procedure as follows.

A suitable standard S was chosen, with a typical matrix and having a fairly high As level (900 ppm) and a Pb level of 167 ppm. The calibration is based on the time T_0 corresponding to a pre-set count of 4×10^4 for the total intensity $I_{K\alpha}$ measured on the standard sample S, which will be henceforth used as a monitor.

A group of about ten samples with well known matrix composition was selected according to the following criteria: (i) over 99% of the matrix was made up by elements with $Z < 27$; (ii) the As and Pb contents were each under 50 ppm; and (iii) the group included samples with compositions at the extremes of the usual ranges for rocks and ores. The mass absorption coefficient, μ for the samples was calculated at $\lambda = 1 \text{ \AA}$ and covered a range from 10 to 40.

The intensities I_b , $I_{L\beta}$ and $I_{K\alpha}$ were measured for the above-described group of calibration samples. In samples with detectable levels of As or Pb, a suitable calculation procedure was applied to obtain the corresponding pure background level (under-the-peak background).

The resulting values, N , were plotted against the corresponding value of μ^{-1} calculated at $\lambda = 1 \text{ \AA}$. Figure 1 shows the calibration graphs obtained; according to Eqn (1) they form a system of three straight lines, each defined by a pair of values for I_r and m .

Each line was defined by about ten experimental values. As a final step, two samples of the calibration group were selected. In our case, they were a sample of pure TiO_2 and a sample of pure SiO_2 ; the choice was made according to the following criteria: (i) the samples had no detectable levels of either As or Pb; (ii) their matrix compositions give values of μ that are near the extremes of the range for usual samples; at $\lambda = 1 \text{ \AA}$ the μ values for TiO_2 and SiO_2 are 36.6 and 9.7, respectively; (iii) the values of N obtained for these two samples coincided with points on the calibration lines. Hence the whole calibration group could be replaced by two samples without a decrease in accuracy. From now onwards, this pair of samples will enable the analyst to

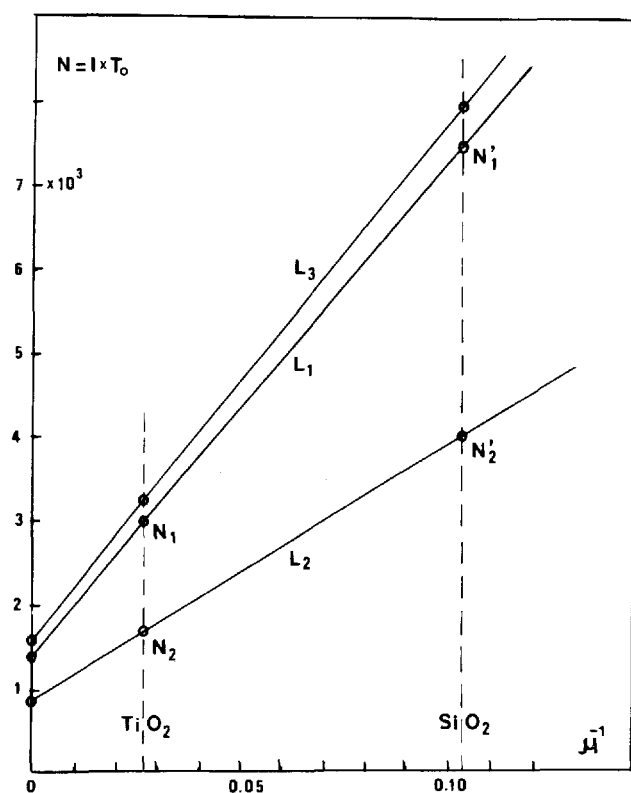


Figure 1. Graph for calculating under-the-peak backgrounds. L_1 is defined by intensities I_b measured at the pure background point chosen at $\lambda = 0.999 \text{ \AA}$. L_2 gives the background under the As $K\alpha$ peak and L_3 gives that under the Pb $L\beta$ peak.

monitor at suitable intervals the conditions in the scintillation detector and the x-ray emission of the tube. These conditions in the course of time are subject to random changes or electronic drift which may significantly affect the measurement of pure background intensities.

Recalibration procedure

As the PBP corresponding to calibration line L_3 is very near that corresponding to L_1 , the N values for $I_{L\beta}$ can be calculated from those of I_b making use of the Eqn (3). The value for the constant $M_{31} = m_3/m_1$ is calculated in the original calibration system and is kept constant in the recalibrations. Hence the recalibration procedure is reduced to only four measurements: N_1 , N_2 on the TiO_2 sample and N'_1 , N'_2 on the SiO_2 sample; these four measurements are to be made in the time T_0 that is determined by the pre-set counting $N = 4 \times 10^4$ fixed for standard S.

Procedure for the analysis of unknown samples

The procedure is made up of the following steps.

1. With a pre-set count of $N = 4 \times 10^4$ for $I_{K\alpha}$ (total peak intensity of the As $K\alpha$ line) in the standard S (As level 900 ppm) the time T_0 is determined and used in all following measurements.

2. Measure I_b and $I_{L\beta}$ in the standard S; the N values obtained are designed b_0 and c_0 , respectively.

Table 1. Determination of Pb and As in six standard ores

Sample	<i>a</i>	<i>b</i>	<i>c</i>	<i>q</i>	<i>r</i>	<i>s</i>	<i>t</i>	<i>u</i>	<i>v</i>	<i>w</i>	[Pb] (ppm)	[As] (ppm)
S	40.0	5.1	10.5	5.5	2.8	4.9	2.7	37.1	34.4	3.8	167	900
GXR-1	18.8	3.5	15.5	3.8	1.9	11.6	6.4	16.8	10.3	2.2	681	469
GXR-2	21.7	7.3	36.1	7.9	4.1	28.1	15.4	17.5	2.0	6.0	602	35
GXR-3	89.0	3.4	3.9	3.7	1.9	0.2	0.1	87.0	86.9	2.1	12	4117
GXR-4	9.4	6.0	8.2	6.5	3.3	1.6	0.9	6.0	5.0	4.7	45	108
GXR-5	4.7	6.6	7.8	7.1	3.7	0.6	0.3	0.9	0.6	5.3	15	12
GXR-6	21.1	5.8	9.4	6.3	3.2	3.0	1.7	17.8	16.1	4.5	88	356

3. Make careful measurements to obtain statistically accurate values of N_1 , N_2 , N'_1 and N'_2 with the calibration samples TiO_2 and SiO_2 .

4. Measure $I_{K\alpha}$, I_b and $I_{L\beta}$ in the unknown sample. The N values obtained are designed a , b and c , respectively.

5. With the set of data N_1 , N_2 , N'_1 , N'_2 and the corresponding values of μ^{-1} for TiO_2 and SiO_2 a computation programme sets up the calibration system. The μ^{-1} values for TiO_2 and SiO_2 are 0.027 and 0.103, respectively, and of course are constant in all recalibrations. With the obtained calibration line L_1 the computer calculates the value

$$N_{br} = 1.355 N_1 - 0.355 N'_1$$

This value corresponds to the residual background for L_1 and will be used in the next steps.

6. With the values a , b and c obtained from the unknown sample, the computer proceeds with the following calculations:

$$q = bM_{13}$$

$$r = (b - N_1) \frac{(N'_2 - N_2)}{(N'_1 - N_1)} + N_2$$

$$s = c - q$$

$$t = 0.546 s$$

$$u = a - r$$

$$v = u - t$$

$$w = b - N_{br}$$

$$[\text{As}] = 900 \left(\frac{v}{v_0} \cdot \frac{w_0}{w} \right) \text{ ppm}$$

$$[\text{Pb}] = 167 \left(\frac{s}{s_0} \cdot \frac{w_0}{w} \right) \text{ ppm}$$

The terms s_0 , v_0 and w_0 are the corresponding s , v and w values calculated for the standard S.

The physical meanings of the above terms can be described as follows:

q = Background under Pb $L\beta$ peak; in our case, $M_{31} = 1.088$.

r = Background under As $K\alpha$ peak given by L_2 .

s = Net peak intensity at Pb $L\beta$.

t = Interfering intensity due to Pb $L\alpha$.

u = Net peak intensity at As $K\alpha$ with Pb interference included.

v = Net peak intensity at As $K\alpha$ with Pb interference removed.

w = Scattering intensity from PBP at $2\theta = 28.76^\circ$ with residual scattering N_{br} removed.

[As] = As concentration in unknown sample. The standard sample S contained 900 ppm of As.

[Pb] = Pb concentration in unknown sample. The standard sample S contained 167 ppm of Pb.

RESULTS

Table 1 shows the results obtained with our programme for six standard reference ore samples supplied by the US Geological Survey (GXR-1-GXR-6). The a , b and c values represent measurements made on each sample divided by 10^3 . The calculated concentrations of Pb and As are given in the two last columns.

A study of the Pb and As concentrations in these samples shows that the results obtained using different analytical techniques vary greatly. Good agreement is found with the values obtained at the Los Alamos Scientific Laboratory⁷ using neutron activation analysis and atomic absorption spectrometry (Table 2). For the Pb level in GXR-4 other sources give a range of 41–54 ppm.

CONCLUSIONS

The procedure described for the determination of As using the $K\alpha$ lines provides a means for the expeditions monitoring of As and Pb levels in geological surveys. The reliability of the method must be previously ensured

Table 2. Reported concentrations of Pb and As in standard ores⁷

Sample	[Pb] (ppm)	[As] (ppm)	Sample	[Pb] (ppm)	[As] (ppm)
GRX-1	670 ± 20	460 ± 30	GRX-4	—	98 ± 10
GRX-2	615 ± 15	31 ± 5	GRX-5	22 ± 2	12 ± 3
GRX-3	15 ± 2	4000 ± 450	GRX-6	110 ± 10	340 ± 30

by careful experimental work. After the tube anode and operating conditions have been chosen, the analyst must determine a suitable mean value for α/β and set up an accurate calibration graph for calculating under-the-peak backgrounds.

The limit of detection and accuracy attainable depend mainly on the Pb level present in the sample. The method

can be expected to give satisfactory results for samples having Pb levels up to 600 ppm. For higher Pb levels the method can be supplemented by measuring the As $K\beta$ net intensity. Except for the small $W_{L\gamma^4}$ peak, the $K\beta$ line is normally free from spectral interferences; if a Mo tube is used, careful measurement at this line should detect As levels over 60 ppm.

REFERENCES

1. C. E. Feather and J. P. Willis, *X-Ray Spectrom.* **5**, 41 (1976).
2. H. Bougault, P. Cambon and H. Toulhoat, *X-Ray Spectrom.* **6**, 66 (1977).
3. E. A. Th. Verdurmen, *X-Ray Spectrom.* **6**, 117 (1977).
4. R. Vié le Sage, J. P. Quisefit, R. Dejean de la Bâtie and J. Faucherre, *X-Ray Spectrom.* **8**, 121 (1979).
5. J. Hower, *Am. Mineral.* **44**, 25 (1959).
6. R. Müller, *Spectrochemical Analysis by XRF*, Chap. 6. Plenum Press, New York (1972).
7. E. Gladner, D. Perrin, J. Owens and D. Knab, *Anal. Chem.* **51**, 1557 (1979).
8. T. Shirawa and N. Fujino, *Jpn. J. Appl. Phys.* **5**, 886 (1966).

APPENDIX

A study of the factors that affect the value of α/β can be made with the mathematical scheme provided by the basic equation⁸ that gives the fluorescence intensity of an element in a known matrix. In the present case, it is assumed that the Pb atoms are not subjected to significant enhancement; the problem then can be dealt with by using only the first term of the basic equation. Further, as the Pb level is assumed to be in the ppm range, this element can be neglected in the calculation of the absorption coefficient of the sample. The model, however, requires a great amount of physical data; hence, it is convenient to consider first the simpler case in which the sample is irradiated with a monochromatic beam of intensity I_0 and wavelength λ_0 .

For the net intensities I_α and I_β corresponding to the Pb $L\alpha$ and $L\beta$ lines, the basic equation gives the following relationships;

$$I_\alpha = GP(\alpha) \frac{\mu^*(\lambda_0)CI_0}{\mu(\lambda_0)/\sin \psi_1 + \mu(\alpha)/\sin \psi_2} \quad (6)$$

$$I_\beta = GP(\beta) \frac{\mu^*(\lambda_0)CI_0}{\mu(\lambda_0)/\sin \psi_1 + \mu(\beta)/\sin \psi_2} \quad (7)$$

G = constant defined by instrumental conditions.

$P(\)$ = constant defined by the product of three parameters characteristic of the Pb atom and the corresponding line.

$\mu(\lambda_0), \mu(\alpha), \mu(\beta)$ = values of the matrix absorption coefficient calculated at $\lambda = \lambda_0$, at the wavelength of $L\alpha$ (1.18 Å) and at the wavelength of $L\beta$ (0.98 Å), respectively.

$\mu^*(\lambda_0)$ = value of the Pb absorption coefficient at $\lambda = \lambda_0$.

C = Pb concentration.

Assuming the condition that $\psi_1 = \psi_2$, one obtains from Eqns (6) and (7) that α/β is proportional to the ratio

$$\frac{\mu(\lambda_0) + \mu(\beta)}{\mu(\lambda_0) + \mu(\alpha)} \quad (8)$$

which makes it possible to gauge the variations of α/β likely to occur in practice. For a chosen wavelength λ_0 one can calculate the values of the ratio (8) corresponding to the main compounds in rocks and ores. Table 3 shows the values of $\mu(\beta)$, $\mu(\alpha)$ and the ratio (8) for various compounds and elements. The value of $\mu(\lambda_0)$ was calculated for two values of λ_0 , viz. $\lambda_0 = 0.75$ Å and

Table 3. Calculated values of the ratio (8) for various compounds and elements under two different excitation conditions

	$\mu(\beta)$ ($\lambda = 0.98$ Å)	$\mu(\alpha)$ ($\lambda = 1.18$ Å)	$\mu(\lambda_0)$ ($\lambda_0 = 0.75$ Å)	Ratio (8) ($\lambda_0 = 0.75$ Å)	$\mu(\lambda_0)$ ($\lambda_0 = 0.40$ Å)	Ratio (8) ($\lambda_0 = 0.40$ Å)
Cu	115	195	57	0.68	9.6	0.61
S	23	38	11	0.74	1.8	0.62
Fe ₂ O ₃	62.6	102.2	29.3	0.70	5.1	0.63
TiO ₂	34.3	57.1	16.3	0.69	2.8	0.62
CaO	31.2	51.1	14.7	0.70	2.6	0.63
K ₂ O	31.3	51.4	14.8	0.70	2.5	0.63
SiO ₂	9.1	14.5	4.3	0.71	0.8	0.65
Al ₂ O ₃	8.2	13.4	3.9	0.70	0.7	0.63
MgO	7.3	12.1	3.5	0.69	0.6	0.62
Na ₂ O	6.8	10.5	3.2	0.72	0.6	0.67
CO ₂	2.8	4.0	1.3	0.77	0.3	0.72
H ₂ O	2.9	4.3	1.4	0.76	0.3	0.71

0.40 Å; these values were chosen to define a range which should contain the effective wavelength⁶ equivalent to the x-ray tube exciting output.

The values of the ratio (8) indicate that, in a usual rock or ore matrix, it should vary within a range defined by $\pm 4\%$. For a given compound the ratio (8) is a monotonously increasing function of λ_0 ; hence, one can assume that the $\pm 4\%$ range holds good for any value of λ_0 between 0.40 and 0.75 Å.

A study of the general case with excitation by an x-ray tube can be carried out following the above-described pattern. In accordance with the basic equation, Eqns (6) and (7) should now take the form of integrals to be calculated over well defined wavelength intervals. The intensity I_β must be expressed as the sum $I_{\beta 1} + I_{\beta 2}$. The integrals can be transformed⁶ by making use of the mean-value theorem of the integral calculus and one obtains

$$I_\alpha = GP(\alpha) \frac{\mu^*(\bar{\lambda})CI(\bar{\lambda})}{\mu(\bar{\lambda}) + \mu(\alpha)} (\lambda_3 - \lambda_m) \quad (9)$$

$$I_{\beta 1} = GP(\beta_1) \frac{\mu^*(\bar{\lambda}')CI(\bar{\lambda}')}{\mu(\bar{\lambda}') + \mu(\beta)} (\lambda_2 - \lambda_m) \quad (10)$$

$$I_{\beta 2} = GP(\beta_2) \frac{\mu^*(\bar{\lambda})CI(\bar{\lambda})}{\mu(\bar{\lambda}) + \mu(\beta)} (\lambda_3 - \lambda_m) \quad (11)$$

where

λ_m = minimal wavelength of the tube output.

λ_2 = wavelength of Pb L_{II} absorption edge.

λ_3 = wavelength of Pb L_{III} absorption edge.

$\bar{\lambda}$ = effective wavelength for I_α and $I_{\beta 2}$.

$\bar{\lambda}'$ = effective wavelength for $I_{\beta 1}$.

It is easy to verify that with the assumption that $\bar{\lambda} = \bar{\lambda}'$, Eqns (9)–(11) allow one to obtain the ratio (8) with $\lambda_0 = \bar{\lambda}$. Calculations with Eqns (9)–(11) for a given tube output have not been carried out by the author. Qualitative considerations for the case of the W tube spectrum indicate that the assumption $\bar{\lambda} = \bar{\lambda}'$ can be taken as an acceptable approximation. The conclusions obtained from the ratio (8) should then remain valid in the general case.