Chemical Use of the Absorption of Soft γ-Rays, β-Ray-excited X-Rays and K-Capture X-Rays. II. Application to the Analysis of a Binary Alloy and the Determination of a Heavy Element in a Multi-component System

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The technique described in Part I[1] provides a method of chemical analysis by the use of the absorption phenomenon of the photon-beams. Determination of a heavier element in a given sample was tried by using a single source of a suitable energy and the exponential-absorption law[2]. In applying such a method, the use of a pair of sources appears to be suitable for a greater variety of samples. This is easily to be understood by analogy with the so-called absorption-edge method in X-ray absorptiometry.

The present author has intended to extend this technique by the use of radio-isotopes as the radiation source. Mono-energetic soft X-rays (less than 25 keV.) can be obtained, of course, by the use of an X-ray tube and a proper diffraction crystal. Almost mono-energetic photon-beams of a higher energy, however, are required or preferable when a certain kind of element is to be analyzed or when the absorbance due to the matrix elements is too large for a photon of a lower energy. Radio-isotopes giving soft γ-rays, β-ray-excited X-rays and K-capture X-rays are more useful, and the discussion[3] concerning the comparison of K-capture spectroscopy with ordinary X-ray absorptiometry for sulfur in petroleum appears to hold in other cases.

In this paper, the use of two photon-beam sources with suitable energies is generally discussed, and the application to the analysis of a binary alloy (solder) and of a heavy element in a multi-component system (glass) is proposed.

With a binary system, there are two alternative modes in the choice of the sources: (1) the K absorption edge of one of the two elements, usually of the higher atomic number, is to fall between the energies of the two sources, and (2) both sources are to have higher energies than any of the K absorption edges of the elements, but the absorption coefficients of the two elements for one of the photon-beams are to be markedly different from each other and those for the other photon-beams are to be narly equal (The latter demand is fulfilled by a γ- ray of more than 1 MeV. in energy, to which the photoelectric effect contributes only slightly.). Choice 1 is useful for a sample of this foil, while choice 2 is suitable when the sample is a thick plate or block. The composition of solders without appreciable impurity was determined by using two pairs of sources. (1) U-β and ^{204}Tl, (2) ^{203}Hg and ^{60}Co. (For convinience, M-β is used in this paper for the β-ray-excited X-ray of element M.)

1) T. Naoki, This Bulletin, **34**, 1769 (1961).
2) H. K. Hughes et al., *Anal. Chem.*, **26**, 1889 (1954).
3) W. R. Doughman et al., ibid., **30**, 1924 (1958).

For a plate (either a foil or a block) of a binary alloy consisting of x(g./cm^2) of element A and y(g./cm^2) of element B, there are the following relationships:

$$\left.\begin{aligned}\Phi(E_1\ \mathrm{A})x+\Phi(E_1\ \mathrm{B})y&=-\ln D(E_1)\\ \Phi(E_2\ \mathrm{A})x+\Phi(E_2\ \mathrm{B})y&=-\ln D(E_2)\end{aligned}\right\} \quad (1)$$

$$[\text{Thickness of the plate}]=x+y \quad (2)$$

where Φ (E M) is the total absorption coefficient of element M for a photon-beam of energy E, and $D(E)$ is the transmittance (denoted by a fraction) of a photon-beam of energy E through the plate. Thus, simultaneous determination of the composition and of the plate thickness is possible.

When the element to be determined is in a multi-component system, the situation is slightly more complicated. The use of a number of sources of suitable energies equal to the number of the component elements offers the necessary relationships for determining all the component elements and the plate thickness. Such an argument, however, is only theoretical and impracticable. In practice, the plate thickness must be measured by some other method. Therefore, the measurement of the transmittances of two photon-beams, between the energies of which lies the absorption edge of only the element to be determined, offers a relationship for calculating the content. This relationship (indicated by Eq. 5) is derived as follows:

Eq. 13 in Part I can also be written as

$$\frac{\phi(E_1\ \mathrm{M})}{\phi(E_2\ \mathrm{M})}=(E_1/E_2)^{-\lambda}\quad (8/3<\lambda<7/2) \quad (3)$$

where $\phi(E$ M) is the absorption coefficient (of an element or a material M for a photon-beam of energy E) excluding the contribution of the Compton scattering. When one gram of the sample contains x gram of the element A to be determined and y_m gram of a matrix element M_m, there are the following relationships, where G means the sample (glass):

$$\left.\begin{aligned}\phi(E_1\ \mathrm{A})x+\sum_m[\phi(E_1\ \mathrm{M}_m)y_m]&=\phi(E_1\ \mathrm{G})\\ \phi(E_2\ \mathrm{A})x+\sum_m[\phi(E_2\ \mathrm{M}_m)y_m]&=\phi(E_2\ \mathrm{G})\end{aligned}\right\} \quad (4)$$

On assuming that λ in Eq. 3 remains constant for all elements, Eq.s 3 and 4 offer this relationship for calculating x:

$$x=\frac{\begin{vmatrix}\phi(E_1\ \mathrm{G}) & 1\\ \phi(E_2\ \mathrm{G}) & (E_1/E_2)^{-\lambda}\end{vmatrix}}{\begin{vmatrix}\phi(E_1\ \mathrm{A}) & 1\\ \phi(E_2\ \mathrm{A}) & (E_1/E_2)^{-\lambda}\end{vmatrix}} \quad (5)$$

For a β-ray-excited X-ray or a K-capture X-ray, the E_1 and E_2 should be the weighed means of the energies of K_{α_1} and K_{α_2}. A source pair consisting of RaD and Ce-β and that of U-β and ^{204}Tl were used for the determination of barium and lead respectively.

The error of results is discussed below.

Experimental

Sample.—Solder containing no appreciable ammount of any elements other than tin and lead was rolled to a plate or a foil. Plates of barium glass and lead glass of uniform thickness (about 2 mm.) were prepared. The barium glass contained sodium, boron, silicon, barium and oxygen, while the lead glass consisted of boron, sodium, aluminum, zinc, lead and oxygen. The thickness (g./cm^2) of the glass plates and of the solder foils was determined by measuring the weihgt and the area, while that of the solder plates was done by measuring the thickness and the specific gravity.

Counting.—In all cases a scintillation counter was used with the geometrical arrangement shown in Fig. 1, Chapter I.

The sources were chosen as described above. The measurement was done by using the techniques in Part I, tin foil and lead foil being used as the auxiliary absorbers for Ce-β and U-β respectively. With ^{60}Co as the source, only the γ-ray of the higher energy was counted. For the analysis of solder, the total count taken in each measurement was over 5×10^4, while for that of glass at least 3×10^3 (when the counting rate was smallest) or 3 minutes' counting (when it is largest) was taken.

Chemical Analysis.—Chemical analyses by ordinary methods were carried out for comparison. Solders were analyzed by determining tin gravimetrically as tin(IV) oxide and lead, electrochemically as lead(IV) oxide. A part of any of the glass samples was decomposed with hydrofluoric and sulfuric acid, and barium was determined gravimetrically as barium sulfate, while lead was converted into lead chromate and determined iodometrically by the standard technique.

Results and Discussion

In Tables I, II, III and IV are shown the results. The values with the sign ± indicate the error due to the standard error of counting. In general, all values are in good agreement with those obtained by ordinary chemical analysis. Moreover, the usefulness of Eq. 5 is proved.

TABLE I. ANALYSIS OF SOLDER BY THE USE OF ^{204}Tl AND U-β

Source	Φ(Sn)	Φ(Pb)
^{204}Tl	4.02	3.06
U-β	1.68	5.51

	Absorption method		Chem. anal.	
	mg./cm^2	%	mg./cm^2	%
Tin	64.6±2.0	42.4±1.5	64.3	42.9
Lead	87.6±1.4	57.6±1.3	85.5	57.1
Solder	152.2±2.5		149.8	

TABLE II. ANALYSIS OF A SOLDER BY THE USE OF ^{60}Co AND ^{203}Hg

Source	Φ(Sn)*	Φ(Pb)*
^{60}Co	0.0464	0.0510
^{203}Hg	0.162	0.431

	Absorption method		Chem. anal.	
	g./cm²	%	g./cm²	%
Tin	2.12±0.22	35.7±3.7	2.01	35.0
Lead	3.81±0.19	64.3±3.2	3.73	65.0
Solder	5.93±0.29		5.74	

* Values under the given geometrical arrangement

TABLE III. ANALYSIS OF BARIUM IN GLASS

Sample No.	Barium content, %			
	λ=3/8	λ=2/7	Mean	Chem. anal.
I	25.6	25.6	25.6±0.5	25.6
II	18.3	18.4	18.3±0.4	17.8
III	8.8	9.0	8.9±0.2	9.0
IV	4.5	4.7	4.6±0.1	4.61
V	0.00	0.16	0.08±0.1	0.00

ϕ(Ba) for RaD and for Ce-β are 16.36 and 8.87 respectively.

TABLE IV. ANALYSIS OF LEAD IN GLASS

Sample No.	Lead content, %			
	λ=3/8	λ=2/7	Mean	Chem. anal.
1	−0.4	−0.07	−0.2±0.3	0.00
2	1.78	2.04	1.9±0.3	1.77
3	3.30	3.48	3.4±0.4	3.15
4	8.15	8.43	8.3±0.5	8.2
5	17.7	17.9	17.8±0.6	17.5
6	35.4	35.6	35.5±1.0	34.0
7	54.7	54.9	54.8±1.1	54.6

The error in the final result due to the standard error of counting is calculated as follows: When $\Phi(E\,\mathrm{M})$ in Eq. 1 has been preliminarily determined accurately, the final error in x and y in the same equations depends on that of the determination of $D(E)$. When it is assumed that total counts C is taken during time t without the sample, and C', during t' with the sample, the fractional standard error in $\ln D(E)$, denoted by $\Delta \ln D(E)$, is the standard error in

$$\ln\left[\frac{(C'+\Delta C')/t'}{(C+\Delta C)/t}\right]-\ln\left[\frac{C'/t'}{C/t}\right]$$

where ΔC equals $\pm\sqrt{C}$ and $\Delta C'$, $\pm\sqrt{C'}$. For large values of C and C', for which the approximation

$$\ln\left(1\pm\sqrt{\frac{1}{C}+\frac{1}{C'}}\right)=\pm\sqrt{\frac{1}{C}+\frac{1}{C'}}$$

is valid,

$$\Delta \ln D(E)=\sqrt{\frac{1}{C}+\frac{1}{C'}} \qquad (6)$$

because, the fractional standard error in

$$\frac{C'+\Delta C'}{C'}\Big/\frac{C+\Delta C}{C} \quad \text{is equal to}$$

$$\sqrt{\left(\frac{\Delta C'}{C}\right)^2+\left(\frac{\Delta C}{C}\right)^2} \quad \text{or} \quad \sqrt{\frac{1}{C}+\frac{1}{C'}}$$

The errors in Tables I and II are calculated by Eq. 6. For a multi-component system, when $\phi(E\,\mathrm{A})$ in Eq. 4 and the thickness of the sample have been preliminarily determined with precision, the final error is derived either from the determination of $\phi(E\,\mathrm{G})$ or from the uncertainty of λ in Eqs. 3 and 5. The latter can be regarded as small, as is shown in Part I. By a calculation similar to that for the binary system, the standard error in the final result due to the error of counting for $\Phi(E\,\mathrm{G})$ is obtained and is shown in Tables III and IV. When the optimum determination accuracy within a given counting time is required, the time should be so divided that the determination of $\phi(E\,\mathrm{G})$ for the photon-beam of the higher energy may be done more precisely than for that of the lower energy, owing to the factor of $(E_1/E_2)^{-\lambda}$ in Eq. 5. There are, of course, some uncertainties in $\Phi(E\,\mathrm{A})$, but they can be made insignificantly small when determined once with precision.

The value x in Eq. 5 varies with the value of λ for a given value of $\phi(E\,\mathrm{A})$ and ϕ $(E\,\mathrm{G})$. However, the mean value of x for λ=8/3 and λ=7/2 agrees well with the result of ordinary chemical analysis. This mean value is not significantly different from the value for λ=3.

The physical meaning of the denominator of Eq. 5 is the coefficient of the photoelectric absorption by only the K-shell for a photon-beam of energy E_2 (with a negative sign) with a small contribution of the coherent scatterings. There are several theoretical formulas for the photoelectric absorption cross section by the electrons in the K-shell, (σ_k). The formula obtained by the Born approximation[4] is:

$$\sigma_k=\phi_0\,4\sqrt{2}\,\frac{Z^5}{137^4}\,\frac{(mc^2)^{7/2}}{E} \qquad (7)$$

$$\phi=\frac{8\pi}{3}\,(e^2/mc^2)^2=6.651\times10^{-25}\ \mathrm{cm}^2$$

However, application of the correction factor from the chart[3] to the value of Eq. 7 usually offers a value higher than the experimental result by several per cent, in spite of the contribution of the coherent scatterings to the latter. Other, simpler formulas provide poorer results.

4) E. Segrè, "Experimental Nuclear Physics", Vol 1, John Wiley & Sons, Inc., New York (1953), pp. 310—311.

Summary

The absorption phenomenon of soft γ-rays, β-ray-exited X-rays and K-capture X-rays was applied to the following two kinds of analyses (1) Analysis of solder (simultaneous determination of the composition of a binary system and the sample thickness), and (2) Determination of barium or lead in glasses (determination of an element of high atomic number in a multi-component system). Two photon-beams of energies suitable for each purpose were chosen, and for the latter purpose the relationship between the absorption coefficient of an element and the photon-beam energy was used. The results were in good agreement with those obtained by usual chemical analysis.

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