Chemical Use of the Absorption of Soft γ-Rays, β-Ray-excited X-Rays and K-Capture X-Rays. I. Improvement in Fundamental Technique and Introduction of a Differential Absorption Method*

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Soft γ-rays, β-ray-excited X-rays and K-capture X-rays are absorbed mainly by the photoelectric effect in most cases, the absorption coefficient depending much on the atomic number of the absorber material. The mass absorption coefficient (σ) for the photoelectric absorption of a photon whose energy is over the absorption edge of the absorber material is expressed by[1]

$$\sigma = C(Z^5/A)E^{-\lambda} \qquad (8/3 < \lambda < 7/2) \qquad (1)$$

where Z and A are respectively the atomic number and the atomic weight of the absorber material and C is a constant.

This phenomenon is to be applied to a vast field of chemistry as well as radiography. Recently, several kinds of works by the use of the absorption of such photons have been published[2-4], including the determination of sulfur in petroleum, of chlorine and bromine in solid organic substances, and of uranium and heavy metal salts. The thickness and density of several kinds of material were also measured by similar techniques. The fundamental technique which has been adopted in these works, however, is useful only for either of the following two cases; (1) when a mono-energetic photon-beam source of a suitable

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* A part of this paper was reported at the 2nd Isotope Conference of Japan, February, 1958.

[1] e. g., E. Segrè, "Experimental Nuclear Physics", Vol. 1, John Wiley & Sons, Inc., New York (1953), p. 310.

[2] W. W. Meinke, *Anal. Chem.*, **28**, 737 (1956).

[3] W. W. Meinke, ibid., **30**, 688 (1958).

[4] W. W. Meinke, ibid., **32**, No. 5-106R (1960).

energy is used (i. e. when the exponential absorption law holds), and (2) when a relationship between the absorbance and the quantity (or concentration) of the element (or substance) to be determined can easily be obtained empirically under a given condition.

To extend the applicability of the absorption phenomenon, according to the present author's opinion, it is essential to improve the fundamental technique so that an exponential absorption curve and an accurate absorption coefficient could be obtained for a photon-beam even when it is not exactly mono-energetic.

Thus, the following studies have been undertaken: (1) examination of a source giving photons of required energy, (2) examination of a detector which enables an efficient measurement of the radiation and gives an absorption curve as near as possible to the exponential with a given absorber, (3) introduction of the differential absorption method which is useful for obtaining a better absorption curve and a more accurate absorption coefficient in the presence of photons of different energies, (4) examination of apparent change in the absorption coefficient with geometrical arrangement, and (5) establishment of an empirical relationship between the absorption coefficient and the photon energy.

Photon-beam Source. — Absorptiometry in quantitative analysis is usually based on Lambert-Beer's law, regardless of the photon-beam energy (wavelength). For a mono-energetic photon-beam an exponential absorption curve can be obtained easily. Radioisotopes emitting such photons are desirable as the source, and have been used in several works[2-4]. Various nuclides including the following are useful for this purpose: ^{51}Cr, ^{133}Ba, ^{203}Hg, ^{139}Ce, ^{141}Ce, ^{185}W, ^{153}Gd, ^{97m}Tc, ^{170}Tm, ^{109}Gd, ^{204}Tl, ^{241}Am, ^{145}Sm, ^{73}As, ^{210}Pb (RaD), ^{125}I, ^{93}Mo, ^{68}Ge, ^{59}Ni, ^{55}Fe and ^{49}V. (The photon energy decreases in the order given.) In using a radio-isotope emitting also β-rays for the source, the Bremsstrahlung should be made as weak as possible with a suitable enveloping substance (e. g. polystyrene).

Since a relatively small number of nuclides among those written above are usually accessible, another kind of source, generating β-ray-excited X-rays, is required for increasing the energy variety. With β-ray-excited X-rays as the source, such improvements in the fundamental technique as shown later are necessary, as they are not exactly mono-energetic. The yield and the purity (absence of photons of unsuitable energies) depend on the target (converter) and the arrangement of the generator. For the present purpose the purity of the X-rays and the ease in the change of the target material are more important than the yield. A reflection-type generator with a K_β-filter holder, (Fig. 1) serves conveniently.

Figure 2 shows the spectra observed by a scintillation counter (sodium iodide 1″×1″ crystal with aluminum cover), and Fig. 3 those by the scintillation and a proportional counter.

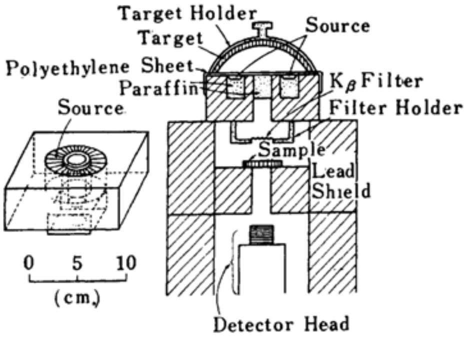

Fig. 1. Generator of β-ray-excited X-rays.

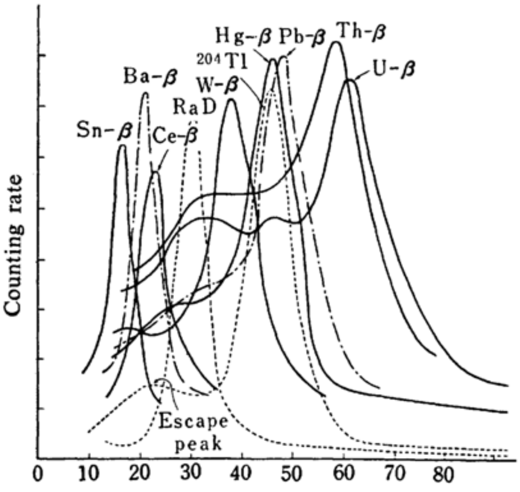

Fig. 2. Spectra of photon-beam sources.

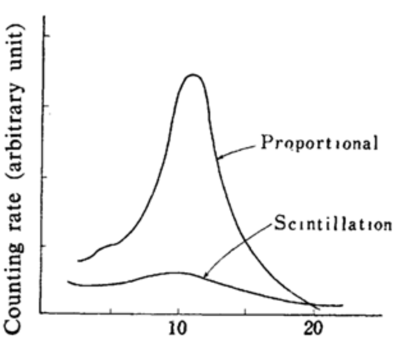

Fig. 3. Spectra of Br-β.

(For convenience, β-ray-excited X-ray of element M is written as M-β in this paper.)

Detector. — The counting efficiency and the shape of the absorption curve depend much on the detection method. When ^{55}Fe is used as a source, a simple G-M counter works satisfactorily. But this counter is a poor detector for a photon-beam having a higher energy than 10 keV. and the pulse height cannot be discriminated. Thus, an ordinary G–M counter can be used only for a few sources: e. g. ^{55}Fe, ^{59}Ni.

Measurement of photon-beams by counting only a narrow region of photo-peak (photo-peak counting) by a low-noise scintillation counter with a single channel analyzer offers a better result in general; the efficiency is high for photons of 20 to 300 keV. and the absorption curve is more similar to a typical exponential curve. For a photon having an energy under 20 keV., however, the following three problems are encountered: (1) the absorption by the cover of the scintillator, (2) the multiplier noise, and (3) the broadening of photo-peak (e. g. those in Fig. 2). The first can be made small by the use of a beryllium-covered crystal, which, however, is not always readily available. On the other hand, a proportional counter tube filled with xenon, krypton or a mixture of these serves, as a still better detector for such a measurement. Fig. 3 shows the spectra of Br-β measured by a xenon-filled proportional counter and by the scintillation counter. No marked photo-peak is observed by the latter. Though the photo-peak obtained by the proportional counter is not so sharp as inferred from literature[5], probably owing to the end effect, the counter is proved to be a very useful detector for such a photon-beam. A krypton-filled tube works as either a proportional or a G-M counter according to the applied voltage, though the dead time of the G-M tube is as long as 1 millisecond. By the use of an external quenching circuit, however, such a tube could be used also as a G-M tube and provides a cheaper technique for measuring photons below 50 keV.

In Fig. 4 the absorption curves of photon-beam from ^{204}Tl and of Hg-β are shown. Both emit the characteristic X-rays of mercury. The curve measured by a usual G-M counter is far from the exponential curve; the absorption coefficients are much larger at the initial stage, and an absorption tail is observed. The former phenomenon can be attributed to the L-series X-rays which are more sensitive to counter than the K X-rays. The same is seen with ^{203}Hg, which emits a γ-ray and characteristic X-rays of thallium owing to internal conversion. The tailing should be due to the Bremsstrahlung. The curves obtained by the photo-peak counting with a scintillation counter are greatly superior. For ^{203}Hg, the curve maintains the exponential form even when the counting rate decreases to 1/1000 of the initial. For other sources, especially for β-ray-excited X-rays, however, the absorption tailing exists to a considerable degree.

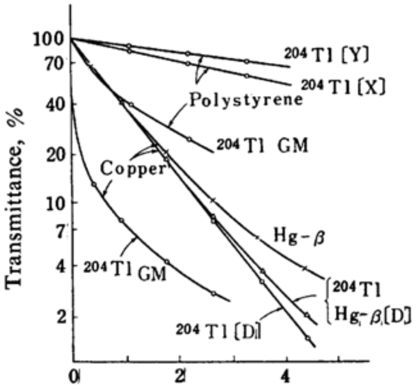

Fig. 4. Absorption curves.

GM; Measured by a G-M counter
[D]; The differential absorption curve
[X]; Absorber at the position in Fig. 1
[Y]; Absorber on the scintillator

The energy resolution of the counter should be taken into account, since K_α X-rays of the β-ray-excited X-ray are always accompanied with K_β rays and Bremsstrahlung of similar energies. On measuring a mono-energetic photon-beam by a scintillation or a proportional counter, the photo-peak is expressed by the Gaussian distribution curve,

$$R = k \exp[-h^2(E_\mathrm{m} - E)^2] \qquad (2)$$

where R is the counting rate, E is the energy, E_m is the observed energy giving maximum R on the spectrum, and k and h are constants. And,

$$(\varDelta E)_{1/2} = C\sqrt{E_\mathrm{m}} \qquad (3)$$

where $(\varDelta E)_{1/2}$ is the full width of photo-peak at 1/2 counting rate and C is a constant. By the use of a good source, i. e. RaD, the value C in Eq. 3 can be determined, and from this value and Eq. 2 the fraction of K_β involved in the measurement range is calculated under a given experimental condition. For a common experimental condition described in the experimental part, the effect of K_β is usually of less significance in case of a source giving a higher

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[5] W. Parrish et al., *Rev. Sci. Instr.*, **27**, 795 (1956).

energy than Hg-β, but must be considered for a source giving a lower energy than Ce-β. In the latter case a K_β filter is useful to some extent; the shape in a higher energy region than the top of the photo-peak is improved and the photo-peak itself becomes sharper.

Differential Absorption Method. — As mentioned above, the absorption curve obtained by the above technique is in general not entirely satisfying for an accurate work. Inevitably there is absorption tailing to a certain degree, which is a nuisance when trying to obtain an accurate absorption coefficient, especially when the absorbance is large.

Two useful methods for the removal of the effect of absorption tailing (differential method and auxiliary absorption method) are presented, which have been devised anew in consideration of the causes of the tailing.

There must be three causes:

(1) Photons of a higher energy suffer the Compton scattering in the detector and escape with an energy loss in the vicinity of the measurement range.

(2) The same scattering also occurs in the absorber and surrounding materials, and a part of the scattered photons can have a similar energy as that of the main photo-peak and enter the detector.

(3) The escape-peak of a photon whose energy is higher by the energy of the K_α of the detector material appears in the measurement range.

For effects 1 and 2, the following relationship is known[6].

$$E_e = \boldsymbol{h}\nu_0 \frac{2\boldsymbol{h}\nu_0/\boldsymbol{m}\boldsymbol{c}^2}{1\boldsymbol{h}+2\nu_0/\boldsymbol{m}\boldsymbol{c}^2} \tag{4}$$

where E_e is the maximum energy that an electron can obtain after a collision. When E_e is smaller than $\boldsymbol{m}\boldsymbol{c}^2/5$, $\boldsymbol{h}\nu_0/E_e$ is greater than 7/2. This relathionship shows that photons giving the effect 1 must have had much higher energies than the observed range, when the photons were subjected to only one scattering. The chance of multiple scattering giving rise to effect 1 must be very small.

The effect 2 must result either from a small-angle scattering or from a multiple scattering. When the measurement is made in an arrangement shown in Fig. 1, the probability of the latter is negligible. A photon scattered with a small change of direction (e. g. a few degree), θ, loses so small an amount of energy that it is hardly ever distinguished from the unscattered photon. The following familiar equation elucidates such a relationship[7]

$$\boldsymbol{h}\nu = \frac{\boldsymbol{h}\nu_0}{1+(\boldsymbol{h}\nu_0/\boldsymbol{m}\boldsymbol{c}^2)(1-\cos\theta)} \tag{5}$$

where $\boldsymbol{h}\nu$ and $\boldsymbol{h}\nu_0$ are respectively the energy of the photon after and before the scattering. Thus, the tailing due to effect 2 is not serious.

Complete elimination of the effect 3 is practically impossible. But when the geometrical arrangement is so adjusted as to make the photon-beam enter the center of the detector, the escape-peak is less distinct.

Thus, the main cause of the tailing should be the single Compton scattering (in the detector) of photons having much higher energies.

Differential Method. — Several sheets of absorber made of the same material and having the same thickness are prepared. The counting rate is measured, the number of the sheets being changed one by one. When the decrease in the counting rate caused by placing one additional sheet is plotted against the number of the sheets used, the curve is more similar to an ideally exponential than the ordinary curve.

That curve, which is tentatively called "differential absorption curve" can be formulated as follows: the ordinary absorption curve is generally expressed by

$$R = A\exp(-\Phi T) + B(T) \tag{6}$$

where Φ and T are respectively the absorption coefficient and the absorber thickness and A is a constant, and $B(T)$ is written as

$$B(T) = \sum_n B_n \exp[-\Phi_n T] \tag{7}$$

For simplicity, the following case is considered.

$$B(T) = B\exp[-\Phi' T] + C \tag{8}$$

That is to say, the source gives only two kinds of photon, and there is a constant back ground. Then, the difference between the counting rates measured through n and $n+1$ sheets of the absorber of thickness ΔT is expressed by

$$\begin{aligned} R_n - R_{n+1} &= A\exp(-\Phi n\Delta T)[1-\exp(-\Phi\Delta T)] \\ &\quad + B\exp(-\Phi' n\Delta T)[1-\exp(-\Phi'\Delta T)] \\ &= [1-\exp(-\Phi\Delta T)]\Big[A\exp(-\Phi T) \\ &\quad + \frac{1-\exp(-\Phi'\Delta T)}{1-\exp(-\Phi\Delta T)} B\exp(-\Phi' T)\Big] \end{aligned} \tag{9}$$

where $T = n\Delta T$. Comparison of Eq. 9 with Eq. 6 shows that the effect of a photon of a higher energy is reduced with the aid of the differential curve by a factor of $[1-\exp(-\Phi'\Delta T)]/[1-\exp(-\Phi\Delta T)]$. With an infinite number of

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6) e. g. Ref. 1, p. 319.

7) e. g. ibid., p. 318.

infinitely thin absorbers this factor becomes Φ'/Φ, the ratio of the absorption coefficient for the photon of the higher energy to that for the lower energy. This ratio must be much less than unity. Because, as mentioned above, the energies of the two photons should differ largely from each other, and the absorption, at least for the photon of the lower energy, is mostly due to photoelectric effect. This is why the differential absorption curve is superior to the ordinary absorption curve. Such a consideration also holds in an actual case, where the source gives more photons of varying energies than shown in Eq. 8. When the counts taken are large enough in each measurement with varying numbers of the absorber sheet, the secondary differential absorption curve offers a still better result.

The differential absorption curves of ^{204}Tl and Hg-β with copper are shown in Fig. 4. For other kinds of source and absorber material a similar improvement is observed.

Auxiliary Absorber Method.—For the measurement of the differential absorption curve, several sheets of the same absorber material having the same thickness are required. Practically, this requirement is hardly fulfilled. The "auxiliary absorber method" finds more general use. A thin foil of a certain material (auxiliary absorber) having as large an absorption coefficient as possible specifically for the photon in question is placed in the path of the photon-beam. Further, the decrease in the counting rate caused by this absorber is measured both in the presence and the absence of the sample. When the decrease in counting rate in the presence of the sample is divided by that in its absence, the quotient gives a fairly accurate transmittance (denoted by fraction and not by percentage) of the photon through the sample. This is true even when the absorbance of the sample is considerably great. This can be explained by the following equations. (Subscript A indicates figures for auxiliary absorber.)

$$R(T)=A\exp(-\Phi T)+B(T)$$
$$R(0)=A+B(0)$$
$$R(T_A)=A\exp(-\Phi_A T_A)+B(T_A)$$
$$R(T+T_A)=A\exp(-\Phi T-\Phi_A T_A)+B(T+T_A)$$

Hence, the quotient D becomes

$$D=\frac{R(T)-R(T+T_A)}{R(0)-R(T_A)}$$
$$=\frac{\left(\begin{array}{c}A\exp(-\Phi T)\,[1-\exp(-\Phi_A T_A)]\\+B(T)-B(T+T_A)\end{array}\right)}{A[1-\exp(-\Phi_A T_A)]+B(0)-B(T_A)} \quad (10)$$

When

$$\left.\begin{array}{l}B(0)=B(T_A)\ \text{and}\ B(T)=B(T+T_A)\\ D=\exp(-\Phi T)\end{array}\right\}\quad(11)$$

The larger the Φ_A is and the smaller the T_A is, the better are satisfied the assumptions in Eq. 11. It is clear from a similar argument given in the "differential absorption method" that the auxiliary absorber method offers an improved absorption curve. This curve is also always superior to the differential absorption curve. The differential method can be regarded as a special case of the auxiliary absorber method, each of the absorbers in the former being itself the auxiliary absorber in the latter.

Absorption curves of a solution of barium chloride (0.114 g./ml.) in dilute hydrochloric acid are shown in Fig. 5 with the absorption curve of hydrochloric acid containing the same quantity of chlorine. The auxiliary absorber is a thin tin foil, through which about 53% of photons transmit.

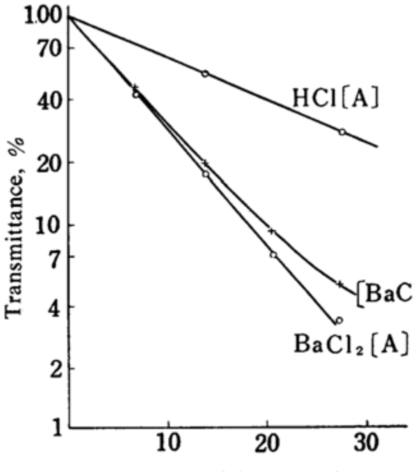

Fig. 5. Absorption curves. $BaCl_2$ [A] and HCl [A] are the auxiliary absorption curves. [$BaCl_2$] is the ordinary absorption curve.

Effect of Geometrical Arrangement.—A change of apparent absorption coefficient is clearly observed for an absorber having a small absorption coefficient according to the geometrical arrangement. For such an example, absorption curves of polystyrene for the photon from ^{204}Tl are shown in Fig. 4. The curve denoted by [X] means that the absorber is placed as shown in Fig. 1, and the one denoted by [Y] means that it is placed on the scintillator. When a detector, an absorber and a source are placed close to one another, the apparent absorption coeffieient is small, and increases toward a definite value with the increase in the distances between the source and the absorber and between the absorber and the detector.

This effect is attributable to the small-angle Compton scattering with a negligible energy loss. With such an absorber, the photolectric effect and the coherent scatterings contribute only slightly, and the absorption is caused almost entirely by the Compton scattering. However, the addition of the correction value, which can be obtained from the theoretical result⁸⁾, offers a definite value independent of the geometrical arrangement, unless the source, absorber and detector are close to one another. Such a corrected value is thought to be the true absorption coefficient. For the geometrical arrangement shown in Fig. 1, the correction value to be added is 0.007 cm^2/g. for atoms in the absorber having an equal number of protons and neutrons. This value is about 1/20 of the total Compton-scattering cross section of the atom for a photon of 100 keV. Thus, this correction value can be used for all kinds of absorber material and for all kinds of photon-beam with quite a little final fractional error, so far as the absorption is mainly due to the photoelectric effect.

Relationship between the Absorption Coefficient and the Photon Energy. — Fairly good absorption curves and accurate absorption coefficients are obtained with the aid of techniques described above. The total cross section of the Compton scattering by an electron is almost independent of the binding state. The relationship between the total cross section of the Compton scattering and the photon energy is found in various literatures.

Amidst the coherent scatterings of photons⁹⁾ with which we are concerned here, only the Rayleigh scattering has a significant contributions, though its cross section is much smaller than that of the photoelectric absorption. The dependence of Rayleigh-scattering cross section on the photon energy is not greatly different from that of the photoelectric effect.

Thus, ϕ, the absorption coefficient excluding the contribution of the Compton scattering is proportional to $E^{-\lambda}$, or,

$$\phi = kE^{-\lambda} \qquad (13)$$

where $8/3 < \lambda < 7/2$, and k is a constant.

The experimental results shown in Fig. 6 agree with Eq. 13. They agree also with other absorber materials such as tungsten, neodymium, barium, iodine and aluminum. These experimental results indicate that Eq. 13 is valid not only above but also under the K-absorption edge, with a change of the magnitude of k at the edge. This relationship plays an important role in further extension of the present study. However, it is doubtful, whether an extrapolation of a curve in Fig. 6 to a region of much lower energy (e. g. ^{55}Fe as the source) provides a correct value.

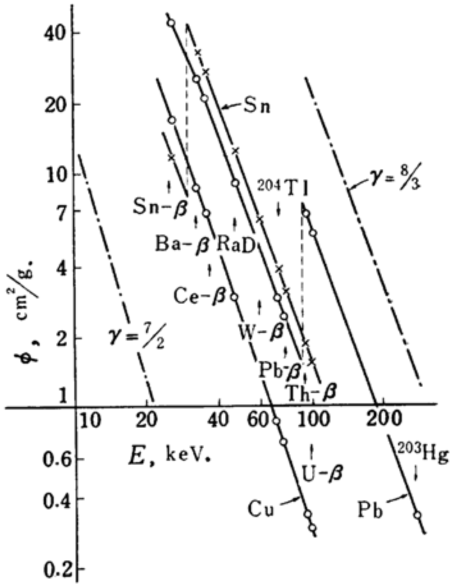

Fig. 6. Relationship between Absorption coefficient and photon energy.

There are numerical tables and charts calculated theoretically for the absorption coefficient against the photon energy. The value, however, is not entirely trustworthy for a photon having an energy not much larger than the binding energy of an electron in the absorber material, because of the invalidity of the Born approximation¹⁰⁾. For the region under the K-absorption edge, the experimental values are usually considerably larger than the theoretical.

Experimental

Photon-beam Source. — A solution containing radioisotopes of high specific activity emitting useful photons together with β-rays, was dried up in a hole dug in a small piece of polystyrene block, and the hole was filled with solid paraffin. When such a radioisotope was dried up in an iron dish or kept without β-ray absorber, the absorption curve, deviated further from the exponential curve. To improve the absorption curve, a solution containing ^{204}Tl was dried up on a crossing of polystyrene fibers at the center of a cubic polystyrene box of 5 cm. dimension, and the air in the box was replaced by hydrogen. However, only a little improvement was observed.

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8) e. g. K. Siegbahn, " Beta- and Gamma-ray Spectroscopy ", North Holland Pub. Co., Amsterdam (1954), p. 33.

9) e. g. ibid., p. 528.

10) e. g. ibid., p. 857.

About 50 mc. of ^{90}Sr of a high specific activity was dried up on a ring-formed filter paper for use as a β-ray source of the β-ray-excited-X-ray generator. It was essential to shield the detector from scattered photons by thick lead blocks. Targets of the generator were prepared as follows. Metal plates of a suitable thickness were formed as shown in Fig. 1, for use as the target. For other materials, compounds with lighter elements, such as uranium oxide, thorium oxide, mercury(I) chloride, tungsten oxide, cerium(IV) oxide, barium carbonate and ammonium bromide were placed on polystyrene target holders to a layer of due thickness with the aid of a benzene solution of polystyrene. The polyethylene sheet covering the lead block of the generator suffered radiation damage and had to be renewed with great care within a year.

Detector.—A scintillator (NaI, 1″×1″, Harshow) was mounted with the aid of a silicone oil on a photomultiplier tube (du Mont 6292), which was selected out of several tubes by examining their stability and thermal noise (a thinner crystal would be preferable for some cases). Heater voltage for the linear amplifier and preamplifier must be stabilized. The unit having the longest resolving time in the counter assembly was the pulse-height analyzer (5 μsec.), others having much smaller resolution time. Throughout the work, the gain of the linear amplifier and the preamplifier and the applied voltage to the photomultiplier tube were kept constant, unless a γ-ray having a higher energy than 200 keV. was measured. The scale in the abscissa of Fig. 2 was the bias voltage (base line) of the single channel analyzer under that condition. The window width for the photo-peak counting was 5.4 V. for a source of a higher energy than RaD and 3.6 V. for that of a lower energy than Ce-β respectively under the same condition. The counting rate without absorber was about 10^4 to 2×10^4 c. p. m. in other cases than ^{203}Hg, in which the rate was about 10^5 c. p. m.

Under the condition of the photo-peak counting, the fraction of K_β rays appearing in the measurement range was as follows (denoted by percentage); U-β 9, Th-β 9, Pb-β 15, Hg-β 17, W-β 22, Ce-β 33, Ba-β 35 and Sn-β 44. For K_β-filter, barium carbonate powder and iodoform were used for Ce-β and Ba-β respectively, both being painted on a thin filter paper in viscous benzene solution of polystyrene.

Proportional counter tubes (1.6 cm. diameter, 10 cm. effective length) of end-window type (1.9 mg./cm^2 mica) filled with methane (4 cm.Hg) and xenon, krypton or a mixture of these (ca. 40 cm.Hg) were set up and their characteristics measured. The output pulse of the tube was preamplified and introduced into the same electronic devices as those used with the scintillation head. The tube was also connected to a simple G-M counter circuit.

Absorbers and Measurement of Absorption Coefficient.—Metal-plate absorbers of aluminum, copper, tin, molybdenum and lead were obtained commercially or by rolling the pure metal to a desired thickness. A known quantity of pure iodine was dissolved in ethanol and made up to a definite volume. Pure barium and neodymium carbonates were dissolved in hydrochloric acid of a suitable concentration, and the content of the element was determined gravimetrically. Absorption curves of both the solution and the solvent were determined, and the absorption coefficient of the element was calculated, volume change due to the dissolution being taken into account.

Summary

Studies for the improvement of fundamental techniques for the chemical use of the absorption of soft γ-rays, β-ray-excited X-rays and K-capture X-rays were undertaken. The exponential absorption curve, which is essential for the measurement of the accurate absorption coefficient and for many quantitative works, was obtained by the use of a proper detection method and the differential absorption technique, even in the presence of some photons having various energies. The relationship between the absorption coefficient thus obtained and the photon energy proved to agree with the theoretical result.

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