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Photon-Activation Analysis for Iodine by Using Cesium as the Internal-Reference Element*1

Hui-Tuh Tsai, Toyoaki Kato and Yoshinaga Oka

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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The internal-reference method proposed previously has been applied to the determination of iodine by photon-activation analysis, using cesium as the internal-reference element. The present method is based on the measurement of the ^{126}I, ^{124}I and ^{123}I activities produced by the neutron-emitting reactions in iodine, and on the comparison of these activities with that of ^{130}I coming from cesium by the (γ, 2pn) reaction. A lithium-drifted germanium diode with a sensitive volume of 36 cm^3 was used as the detector. The yields of various photonuclear reactions in both elements have also been examined as a function of the bremsstrahlung maximum energies up to 65 MeV. A series of synthetic mixtures of iodine-cesium with known weight ratios has been used to check the sensitivity and the accuracy of this method. We found that we could determine amounts of iodine down to 0.2 μg under the present experimental conditions.

Recently, photon-activation analysis has been established as a useful analytical method for the determination of a number of elements in the periodic table. One of the advantages of photon-activation analysis, as compared with high-flux thermal neutron activation analysis, is that interferences due to ^{24}Na and ^{38}Cl encountered in the thermal neutron activation of various biological materials can be eliminated. Thus, Anderson *et al.*[1] and Wilkniss and Linnenbom[2] utilized the ^{19}F-(γ,n)^{18}F reaction in the determination of fluorine in biological samples and in sea water respectively. The bremsstrahlung-activation technique was also applied to the determination of iodine in biological materials,[3,4] in pharmaceuticals,[5] and in sodium chloride and sodium bromide media.[6]

On the other hand, the present authors have proposed the internal-reference method of activation analysis and have applied this method to the determination of silver in palladium[7] and to that of antimony in tin[8] by activation with thermal neutrons. By this method, the sources of errors associated with activation analysis, such as flux irregularities, can be avoided and no correction for the chemical yield is necessary. Another possible application of this method lies in photon-activation analysis. The residual activities from (γ,xn) reactions in an element to be determined can be compared with those from the (γ,p), the (γ,2pn), the (γ,α), or another charged particle emitting reactions in an internal-reference element. Recently, methods of photon-activation analyses for the determinations of arsenic and niobium have been reported; these methods use selenium and molybdenum respectively as the internal reference elements.[9,10]

The present work concerns a method for the determination of iodine by using cesium as the internal-reference element, along with bremsstrahlung from a linear electron accelerator. The present method depends on the much greater resolving power of a lithium-drifted germanium detector. A study is also included of the yields of photonuclear reactions at several different bremsstrahlung maximum energies up to 65 MeV.

*1 Study of the Activation Analysis Using the Internal-Reference Method. Part XIII. Part XII: Y. Oka, T-C. Pung and T. Saito, This Bulletin, **43**, 1083 (1970).

1) G. H. Anderson, F. M. Graber, V. P. Guinn, H. R. Lukens and D. M. Settle, Proceedins of the Symposium on Nuclear Activation Techniques in the Life Sciences, Amsterdam, IAEA (1967), p. 99.

2) P. E. Wilkniss and V. J. Linnenbom, *Limnol. Oceanog.*, **13**, 530 (1968).

3) P. F. Mulvey, Jr., J. A. Cardarelli, M. Zonkis, R. D. Cooper and B. A. Burrows, *J. Nucl. Med.*, **7**, 603 (1966).

4) R. D. Cooper, D. M. Linekin and G. L. Brownell, Proceedings of the Symposium on Nuclear Activation Techniques in the Life Sciences, Amsterbam, IAEA (1967), p. 65.

5) D. Brune, S. Mattsson and K. Liden, *Anal. Chim. Acta*, **44**, 9 (1969).

6) S. Abe, *Nippon Kagaku Zasshi*, **87**, 426 (1966).

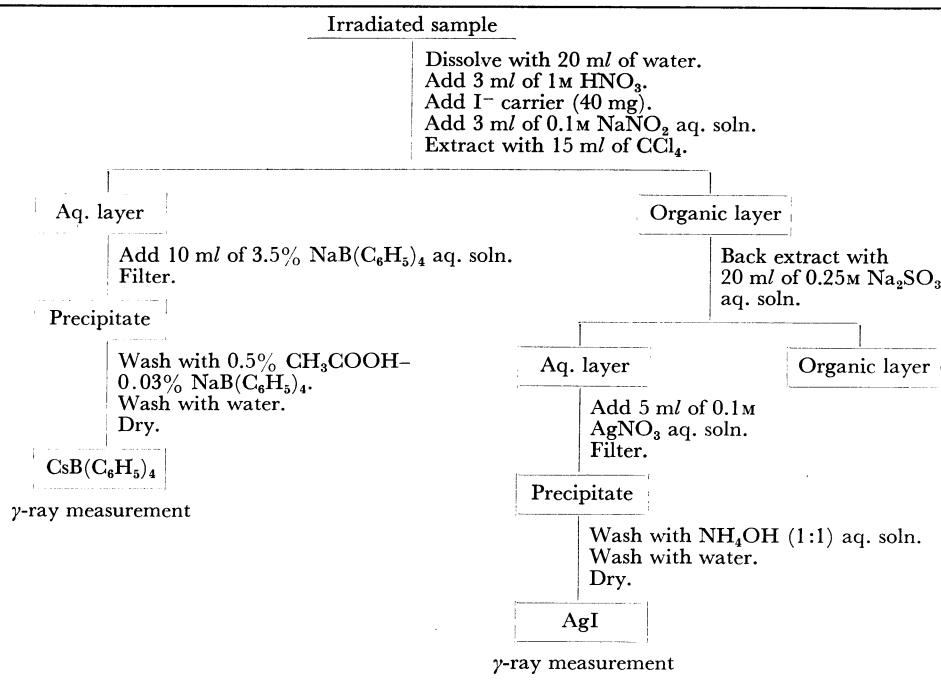
7) Y. Oka, T. Kato, H-T. Tsai and K. Nomura, This Bulletin, **41**, 329 (1968).

8) Y. Oka, T. Kato and H-T. Tsai, *ibid.*, **41**, 2427 (1968).

9) Y. Oka, T. Kato and Y. Konami, *Bunseki Kagaku*, **18**, 971 (1969).

10) Y. Oka, T-C. Pung and T. Saito, This Bulletin, **43**, 1083 (1970).

Table 1. Separation scheme



Experimental

Materials and Irradiation. Cesium chloride and potassium iodide of guaranteed reagent grades were used as the sample materials. A series of synthetic iodine-cesium mixtures with known weight ratios, ranging from 8.87×10^{-3} to 2.64×10^{-4}, were prepared by mixing these two kinds of compounds. Each sample, weighing about 500 mg, was placed in a quartz tube with an internal diameter of 6 mm, and was irradiated by bremsstrahlung with maximum energies up to 65 MeV. Irradiations were terminated after from 30 min to 2 hr. A linear electron accelerator of Tohoku University was used as the bremsstrahlung source. The electron beam was converted to bremsstrahlung photons by a platinum converter with a thickness of 3 mm. In the energy range from 40 to 65 MeV, the range used in this experiment, the average beam current was at least 100 μA, measured at the position of the converter using a current monitor. The pulse-repetition rate was 250 pps, with a pulse width of 3 μsec. During irradiation, the samples were located in a water-cooled sample holder on the bremsstrahlung-beam axis immediately behind the converter. To monitor the bremsstrahlung flux to which the samples were exposed, a thin sheet of gold was wrapped around each sample tube; this was irradiated together with the sample.

Radiochemical Separation. After irradiation, each sample was dissolved with water, and 40 mg of an iodine carrier were added; the sample was subjected to the radiochemical procedure diagrammed in Table 1.

After oxidation with sodium nitrite, the iodine was extracted with chloroform and then back-extracted with an aqueous solution of sodium sulfite. The iodide was precipitated as silver iodide, filtered, washed, and dried. After the removal of the radioiodine, cesium was precipitated as its tetraphenylborate from the aqueous layer, filtered, washed, and dried. The final precipitates were packed in thin aluminum foil for the determination of the chemical yield and for the measurement of the γ-ray spectra. The chemical yield of iodine was 70—75%.

Radioactivity Measurements. The γ-ray spectra were measured with a lithium-drifted germanium detector with a sensitive volume of 36 cm^3, coupled to a TMC 1024-channel pulse-height analyzer. A sample was measured at a fixed position, 9 mm from the active surface of the detector. The counting efficiencies of this detector had previously been determined as a function of the source distance and the γ-ray energy, by counting a series of calibrated sources of known activities. The counting system had a resolution of 4 keV for the 661.6 keV γ-line of ^{137}Cs.

Yield Determination. A photonuclear yield is defined as the rate of the production of a given radioactive nuclide per mole of the target nuclide when a standard amount of bremsstrahlung radiation with a given maximum energy has passed through the target during the irradiation period. In the present experiment, the initial decay rates of the various activities produced were determined from a decay curve analysis of the counting rate of the relevant photopeak area. The corresponding saturation rates were computed and normalized for the bremsstrahlung dose rate, which was measured in terms of the amount of ^{196}Au activity produced by the $^{197}Au(\gamma,n)^{196}Au$ reaction in gold foil irradiated together with the sample.

After correcting for chemical yields, counting efficiencies, branching ratios,[12] and the internal conversion

12) The decay schemes used were those listed in G. M. Lederer, J. M. Hollander and I. Perlman, "Table of Isotopes," Sixth Ed., John Wiley & Sons, New York (1967).

Table 2. Photonuclear reactions and nuclear characteristics of the product iodine nuclides[a)]

Parent nuclide	Reaction path	Threshold energy (MeV)	Product nuclide	Half-life of product	γ-Ray (MeV) (Branching ratio, %)
^{133}Cs	(γ,2p)	17.3	^{131}I	8.05 d	0.284(5.1), 0.364(85.6), 0.637(6.9), others
	(r, pd) (r, 2pn)	21.9 24.1	^{130}I	12.4 hr	0.419(35.0), 0.538(100), 0.743(87), 0.669(100), 1.15(13)
	(γ, αn), (γ, ^{3}He2n), (γ, 2dn), (γ, pd2n), (γ, 2p3n), (γ,dt),	11.2, 31.8, 35.0, 37.2, 39.5, 28.8	^{128}I[b)]	25 min	0.411(~13), 0.528, 0.743, others
	(γ, α3n), (γ, ^{3}He4n), (γ, 2d3n), (γ, pd4n), (γ, 2p5n), (γ, dt2n),	27.1, 47.7, 51.0, 53.2, 55.4, 44.7	^{126}I[b)]	13.0 d	0.386(34.2), 0.48(4.15), 0.667(29.3), 0.751(3.6), 0.870(0.85), 1.43 (3.6)
	(γ, α5n), (γ, dt4n), (γ, ^{3}He6n)	43.8, 61.4, 64.5	^{124}I[b)]	4.2 d	0.603(~61), 0.644(21), 0.722(17.9), 0.714(11), 1.298(0.385), 1.326(0.34), 1.692(13.8), others
	(γ,α6n)	51.4	^{123}I	13.3 hr	0.159(98.8), 0.430(4.56), others(weak)
^{127}I	(γ,n)	9.2	^{126}I[b)]	13.0 d	0.386(34.2), 0.48(4.15), 0.667(29.3), 0.7151(3.6), 0.870(0.85), 1.43(3.6)
	(γ,3n)	25.8	^{124}I[b)]	4.2 d	0.603(61), 0.644(21), 0.722(17.9), 0.714(11), 1.298(0.385), 1.326(0.34), 1.692(13.8), others
	(γ,4n)	33.2	^{123}I	13.3 hr	0.159(98.8), 0.430(4.56), others(weak)
	(γ,6n)	51.3	^{121}I[b)]	2.1 hr	0.212(90)
	(γ,7n)	61.3	^{120}I[b)]	1.3 hr	0.562(100)

a) The data for ^{125}I and ^{122}I are not included because the former nuclide emites only very weak γ-ray (35 keV, 100%) and the latter has a short half-life (3.5 min).
b) Positron emitter.

electrons,[13)] the yields were expressed relative to that of the ^{133}Cs(γ,n)^{132}Cs processes, which was measured by means of the amount of the 0.667 MeV γ-ray (95.6%) of 6.5d-^{132}Cs.

Results and Discussion

Photonuclear Reaction. Although the yield is strongly dependent on the photon energy, and, although, hence, higher sensitivities can be expected with higher maximum electron energies, it should be noted that interferences due to the competitive nuclear reactions would also increase in such circumstances. In order to determine the most suitable conditions for the determination of iodine in iodine-cesium mixtures, therefore, the induced photonuclear reactions and their production rates were investigated by irradiating the two elements individually by bremsstrahlung with several different maximum energies, 40, 45, 60, and 65 MeV. The possible reactions leading to the production of radionuclides of the present importance in this energy region, as well as their nuclear characteristics, are summarized in Table 2. The Q-values of the reactions were calculated on the basis of the difference in mass between the target and the product nuclei.

The threshold energy considerations show that the excitation of a nucleus by photons with energies up to 65 MeV produces excited states of the compound nucleus which can emit up to seven nuclei, leading to the production of several activities. Iodine and cesium are both elements with a single-isotopic composition. This makes the assignment of reaction paths for the (γ,xn) processes easy. On the other

Table 3. Photopeak activities of iodine nuclides formed by ^{127}I (γ,xn) reaction with 45 MeV bremsstrahlung

Nuclide	γ-ray energy (MeV)	Photopeak activity[a)] (cpm/mg)	Limit of determination (μg)
^{126}I	0.386	5.20×10^4	0.2
	0.48	2.73×10^3	3.7
	0.751	2.47×10^3	4.0
	0.870	4.92×10^2	20
^{124}I	0.603	2.69×10^3	3.7
	0.722	3.45×10^2	29
^{123}I	0.159	1.79×10^4	0.6

a) At the end of 2 hr-irradiation with a dose rate of bremsstrahlung with which 0.60 μCi^{196}Au is produced by the (γ,n) process in 1 mg Au.

13) The tables in M. E. Rose, "Internal Conversion Coefficients," North-Holland Publ. Co., Amsterdam (1958), were used.

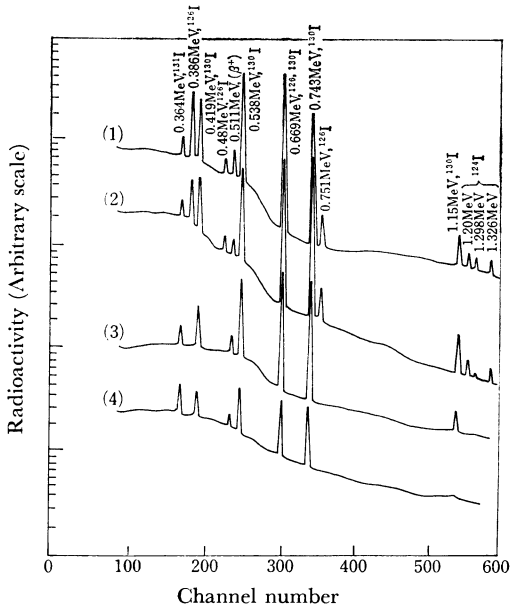


Fig. 1. γ-Ray spectra of iodine activities separated from cesium samples.
1) Irradiated with 65 MeV bremsstrahlung for 30 min; 13 hr after irradiation.
2) Irradiated with 60 MeV bremsstralung for 1 hr; 5.5 hr after irradiation.
3) Irradiated with 45 MeV bremsstrahlung for 1 hr; 9 hr after irradiation.
4) Irradiated with 40 MeV bremsstrahlung for 1 hr; 30 hr after irradiation.

hand, as Table 2 shows, all the iodine nuclides from ^{133}Cs except ^{131}I, can be formed through several different reaction paths.

When an iodine sample was irradiated by 45 MeV bremsstrahlung for a period of 2 hr, the production of ^{126}I, ^{124}I, and ^{123}I was recognized by means of their characteristic γ-rays in the γ-ray spectra. The areas under the photopeaks of the principal γ-rays from those nuclides are given in Table 3. The radioactivity strength of the 0.386 MeV γ-ray from ^{126}I produced by the (γ,n) reaction on ^{127}I was the highest over the energy range investigated; hence it provided the most sensitive method for the determination.

Figure 1 shows the γ-ray spectra of the iodine fractions separated from the cesium samples. It can be seen that ^{131}I, ^{130}I, and ^{126}I were produced at 60 MeV and at 65 MeV, but that the ^{126}I activities can not be detected in any appreciable amounts at excitation energies below 45 MeV. The data listed in Table 2 show that the only possible reaction leading to the production of ^{126}I from cesium at 45 MeV is the ^{133}Cs(γ,α3n)^{126}I reaction. The Coulomb barrier height for this reaction can be calculated as 14.5 MeV; this would restrict the emission of α-particles from an excited state of the cesium nucleus. The yields of the photonuclear reactions for the productions of those nuclides are shown in Table 4.

It should be noted that, with a maximum excitation energy of more than 60 MeV, the more deficient in neutron number the iodine nuclides are, the higher are their yields. This behavior has been emphasized in the previous photospallation work with bremsstrahlung photons up to 250 MeV.[14]

The Determination of Iodine. In the determination of iodine, irradiation were performed by

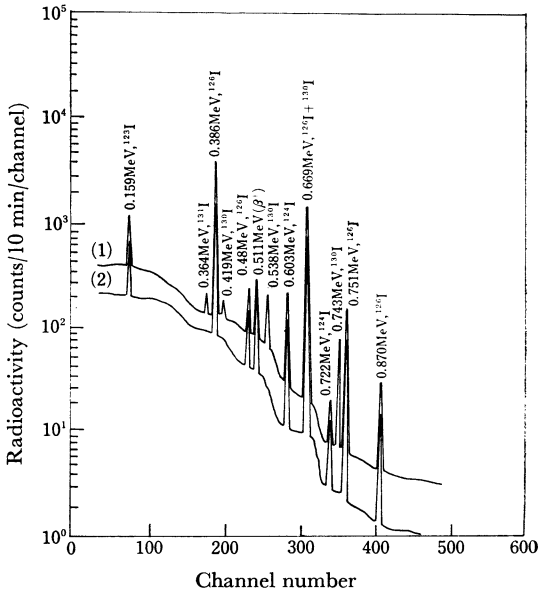


Fig. 2. γ-Ray spectra of radioiodine; (1) separated from an irradiated iodine-cesium mixture (I/Cs=2.64×10^{-4}), 7.5 hr after irradiation, and (2) of iodine sample.

TABLE 4. THE YIELDS OF ^{133}Cs (γ, 2pxn) REACTIONS AS A FUNCTION OF BREMSSTRAHLUNG MAXIMUM ENERGY

Reaction	Yield relative to ^{133}Cs(γ,n))^{132}Cs			
	40 MeV	45 MeV	60 MeV	65 MeV
^{133}Cs(γ, 2p)^{131}I	7.20×10^{-7}	2.32×10^{-6}	1.27×10^{-5}	1.44×10^{-5}
^{133}Cs(γ,2pn)^{130}I	3.27×10^{-7}	1.87×10^{-6}	1.39×10^{-5}	1.61×10^{-5}
^{133}Cs(γ,2p5n)^{126}I	Not detected	Not detected	1.65×10^{-4}	2.48×10^{-4}

14) T. Kato, H-T. Tsai and Y. Oka, This Bulletin, **43**, 576 (1970).

TABLE 5. R_W *vs* R_{A_0} FOR IODINE-CESIUM MIXTURES

R_W	R_W/R_{A_0}						
	^{126}I				^{124}I		^{123}I
	0.386 MeV	0.48 MeV	0.751 MeV	0·870 MeV	0.603 MeV	0.722 MeV	0.159 MeV
8.87×10^{-3}	5.07×10^{-5}	1.00×10^{-3}	1.01×10^{-3}	5.31×10^{-3}	0.93×10^{-3}	0.74×10^{-2}	1.39×10^{-4}
3.47×10^{-3}	5.05×10^{-5}	0.94×10^{-3}	1.01×10^{-3}	5.52×10^{-3}	0.91×10^{-3}	0.73×10^{-2}	1.41×10^{-4}
1.82×10^{-3}	4.94×10^{-5}	0.95×10^{-3}	1.07×10^{-3}	5.48×10^{-3}	0.96×10^{-3}	0.79×10^{-2}	1.35×10^{-4}
5.25×10^{-4}	4.94×10^{-5}	0.94×10^{-3}	1.00×10^{-3}	5.45×10^{-3}	0.94×10^{-3}	0.71×10^{-2}	1.49×10^{-4}
2.64×10^{-4}	5.02×10^{-5}	0.94×10^{-3}	1.06×10^{-3}	5.98×10^{-3}	0.97×10^{-3}	0.76×10^{-2}	1.46×10^{-4}
Mean:	$5.0_0\times10^{-5}$	$0.9_6\times10^{-3}$	$1.0_3\times10^{-3}$	$5.5_5\times10^{-3}$	$0.9_4\times10^{-3}$	$0.7_5\times10^{-2}$	$1.4_2\times10^{-4}$
Std. dev.:	$\pm0.0_5\times10^{-5}$	$\pm0.0_2\times10^{-3}$	$\pm0.0_3\times10^{-3}$	$\pm0.2_3\times10^{-3}$	$\pm0.0_2\times10^{-3}$	$\pm0.0_3\times10^{-2}$	$\pm0.0_5\times10^{-4}$
	(±0.9%)	(±2.4%)	(±2.8%)	(±4.1%)	(±2.2%)	(±3.7%)	(±3.4%)

bremsstrahlung with a maximum energy of 45 MeV, and the photopeak activities due to ^{126}I, ^{124}I and ^{123}I were compared with the reference activity, ^{130}I, from cesium. The synthetic iodine-cesium mixtures were irradiated for a period of 2 hr. A typical γ-ray spectrum of the iodine fraction is shown in Fig. 2, together with that of the iodine sample. From the composite spectra obtained, the photopeak areas under the 0.386, 0.480, 0.751 and 0.870 MeV γ-rays from ^{126}I, the 0.603 and 0.772 MeV γ-rays from ^{124}I, and the 0.159 MeV γ-ray from ^{123}I were measured. Then the ratios of all of those activities to the photopeak area under the 0.538 MeV of ^{130}I were computed. All the activity data were corrected for decay to the end of irradiation. Table 5 shows the results, where the R_{A_0}'s represent the activity ratios and where the R_W's are the weight ratios, I/Cs. A good proportionality is given in each case between the R_{A_0}'s and the R_W's. A relative standard deviation of within ±4% was obtained in the weight-ratio range examined here. When the amount of iodine needed to give 100 cpm is defined as the limit of determination, the sensitivities of this method can be calculated to be as given in the last column of Table 3.

Under the present experimental conditions, amounts of iodine down to about 0.2 μg can be determined.

An increase in sensitivity may be expected with a higher bremsstrahlung dose rate and with a longer period of irradiation. A general applicability of this method will be found in the determination of the iodine content in samples to be analyzed when we add a proper amount of cesium as the internal-reference element.

Considerations were then given to the elements which would cause interferences in this method. The iodine nuclides can be produced by the (γ,pxn) reactions on xenon, *e. g.*, ^{129}Xe(γ,p2n)^{126}I, $-Q=$ 24.22 MeV. However, considering the abundance of xenon in samples ordinarily encountered, it may not appear to be a serious source of interference. The ^{130}Ba(γ,3pn)^{126}I ($-Q=29.36$ MeV) reaction is also a possible source of interference. However, the production rate of this reaction is low because of the small natural abundance of ^{130}Ba(0.101%) and because of the Coulomb barrier restriction inherent in this reaction. In the present case, the neutron reactions which arise from photoneutrons cause no serious problems.

In conclusion, the authors believe that the method presented here holds considerable promise for the accurate determination of iodine in samples of various origins.