Rapid Analysis of Gamma-Emitters Using Gamma-Ray Scintillation Spectrometer. II. Determination of ^{137}Cs in Fission Products[*]

By Fumio AOKI, Seishi YAJIMA[**] and Toshio KUROSAWA

(Received June 20, 1958)

The rapid and accurate determination of ^{137}Cs in fission products is very important for instance, in the determination of the "fine structure" of the fission yield curve, or in the treatment of the fuel elements and radioactive wastes.

Beta-ray assay, which has been generally used, involves many tedious procedures and requires skill[1)], because the object must be isolated prior to the activity measurement. The chemical yield through the procedures is not always highly reliable.

A gamma-ray scintillation spectrometer has been favorably used owing to the speediness of its procedure and

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[*] Read at 11th Annual Meeting of the Chemical Society of Japan.

[**] Present address, Japan Atomic Energy Research Institute, Tokai, Ibaragi-Prefecture.

1) F. Brown, *J. Inorg. Nuclear Chem.*, **1**, 248 (1955).

eliability. But when the sample contains nany gamma-emitters, it is, in general, lifficult or impossible to determine the ndividual activity accurately without eparation, because of the possible superosition of the spectra of the gamma-rays.

Peirson[2] analysed the fission products from uranium 235 without chemical separations using a two-crystal gamma-ray scintillation spectrometer, which does not give rise to the Compton continua but shows only the photopeaks in the recorded spectrum. Even if such an excellent instrument is available, chemical separations will still be necessary in such cases as:

i) When the gamma-energy of a nuclide in question can not be resolved from superposing spectra of other nuclides.

ii) When the gamma-intensity of the nuclide is weak and overwhelmed by those of others.

Woodhead et al.[3] determined the activity of ^{137}Cs in fission products. They separated ^{137}Cs solely by anion exchange resin using carriers, and measured its gamma-intensity with a gamma-ray scintillation spectrometer. If it were not necessary to separate ^{137}Cs solely, the procedures would become more simple.

The authors have worked out a method for the rapid determination of ^{137}Cs in fission products combining the partial separation of nuclides with anion exchange resin followed by gamma-ray spectrometry.

Method. — *Extraction of Uranium.* — The bulk of the uranium is extracted from the solution of the irradiated fuel elements with a mixture of tributyl phosphate (T. B. P.) and diethyl ether. (1:1), together with most of neptunium formed. The residual neptunium is removed by the resin treatment shown below (Table I). In this process the loss of ^{137}Cs is in the order of 10^{-5}, which is negligible in its determination.

Anion Exchange.—In treating the fission product solution, free from uranium, by a mixed bed of carbonate- and oxalate-form anion exchange resin (see section III), alkali metals go completely through the column together with some of alkali earths, while almost all of the other ions are retained in the column[4].

The leakage of alkali earths is reduced by the addition of strontium ions. Tables I and II show the retention and leakage of some elements.

TABLE I
RETENTION OF MAIN ELEMENTS (%)

pH of the soln.	Retention of				
	I	Ru	Rare earths. Y	Transition metals	Np
6	93	96	100	100	100
8	96	96	100	100	100
10	98	98	100	100	100

TABLE II
LEAKAGE OF Ba AND Sr (%)

Addition of Sr^{2+} mg/20 ml	Leakage of	
	Ba	Sr
0	89	80
5	53	65
10	46	10
20	36	0
30	30	0
40	42	0
60	42	0

Measurement.—The fission product solution after the resin treatment will contain ^{140}Ba-^{140}La and ^{137}Cs-^{137m}Ba, when it is short-aged, and ^{137}Cs-^{137m}Ba only, when it is long-aged. (^{133m}Cs and ^{135m}Cs are also formed in fission, but their lives are extremely short. ^{135}Cs, the daughter of ^{135m}Cs, emits no gamma-ray and its life is very long. They are all left out of consideration.)

The activity of ^{137}Cs is represented by the peak height of 0.661 MeV gamma of ^{137m}Ba in equilibrium with ^{137}Cs, the parent. Some of ^{137m}Ba is retained in the resin column, but the parent and daughter soon (about 30 min. after the resin treatment) reach a state of equilibrium. Because of the short half life of ^{137m}Ba (2.6 min.) compared with that of ^{137}Cs (30 y.), the difference between the activities of ^{137m}Ba in equilibrium before and after the resin treatment is negligible.

^{140}La, originally present in the sample, is also removed by the resin treatment, but it grows form^{140}Ba in the effluent and reaches a state of equilibrium within a week.

When the effluent is measured by a scintillation spectrometer for long-aged samples, the 0.661 MeV peak height gives the activity of ^{137}Cs without correction, because no other nuclides are present. But when the sample is short-aged, the peak is superposed by the Compton pulses of ^{140}Ba-^{140}La gammas, which must be subtracted from the observed peak

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[2] D. H. Peirson, *Brit. J. Appl. Phys.*, **6.**, 444 (1955).
[3] J. L. Woodhead et al., *Analyst*, **81**, 570 (1956).
[4] S. Yajima et al., not yet published.

height[5]. The correction factor depends on the crystal dimensions and geometry. In our case pure ^{140}Ba-^{140}La source (in equilibrium) gives Compton pulses of 59% of the 0.82 MeV peak height at the photopeak of ^{137m}Ba gamma.

Experimental

Chemical Procedures.—Two kinds of sample were prepared, one for the long-aged and the other for the short-aged, which are:

a) F. P. (about 0.4 μC) + uranyl nitrate (several mg.) + pure ^{137}Cs solution (x ml).

b) Sample a) (F. P. and pure ^{137}Cs activities suffered a little change) + ^{140}Ba-^{140}La (about 0.2 μC)*.

The cooling time of the fission products, which had been supplied by United State Atomic Energy Commitee, was about 3 years. The quantity of the ^{137}Cs (x) was taken as 0, 0.1, 0.3, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0. One ml. of the pure ^{137}Cs solution corresponded to about 0.01 μC and 0.05 μC in sample a and b, respectively. Other elements of fission products than ^{140}Ba-^{140}La are almost completely retained in the resin column; hence they were left out of consideration. After the samples were dissolved in 50 ml of 5 N nitric acid, uranium was extracted with a mixture of T. B. P. and diethyl ether (1 : 1).

The same quantities of two forms of anion exchange resin (Dowex 1—X7.5, 50—100 mesh, treated by 5% oxalic acid solution and by 10% ammonium carbonate solution) were mixed in a beaker. After carbon dioxide gas was thoroughly removed, a column of about 6 mm. in diameter and 100 mm. in length was set up out of the mixture.

Each fission product sample in nitric acid solution free from uranium was taken in a beaker. After evaporating off most of the nitric acid, the residue was dissolved in 20 ml. of 3 N hydrochloric acid solution and again evaporated to dryness. This process was taken so that the resin column could retain almost all ^{106}Ru, which had been proved empirically. Each of the short-aged samples was dissolved in 20 ml. of 0.5% ammonium chloride solution which contains 30 mg. of strontium ion. The pH value was adjusted to 9 with aqueous ammonia solution. The solution was allowed to run through the resin column followed by a passage of 30 ml. of 1% aqueous ammonia solution. Each effluent was concentrated to 2 ml. and transferred to a polyethylene tube in order to measure the gamma-intensity in the same condition.

Measurements.—The same scintillation spectrometer as that used in the previous study[6] was used. One week after the resin treatment, the samples in polyethylene tubes were placed in the well of the sodium iodide (activated with thallous ions) crystal and the activity was measured. Typical gamma-ray spectra of the samples are shown in Figs. 1 and 2.

The effluents of the long-aged samples contained no other radioactive nuclides than ^{137}Cs-^{137m}Ba,

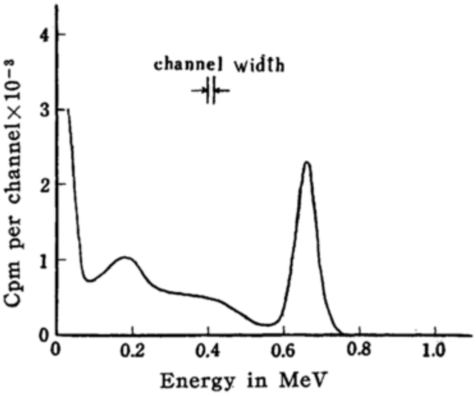

Fig. 1. Gamma-ray spectrum of the long-aged sample treated by the resin column.

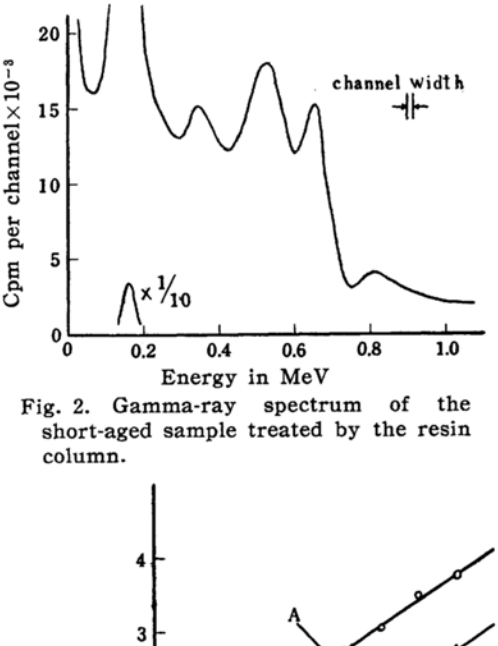

Fig. 2. Gamma-ray spectrum of the short-aged sample treated by the resin column.

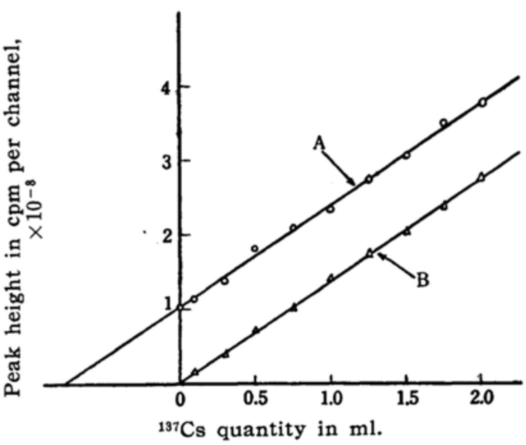

Fig. 3. 0.66 MeV peak heights vs. added ^{137}Cs quantities of the long-aged samples.

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[5] R. E. Connally M. Leboeuf, *Anal. Chem.*, **25**, 1075 (1953).

* In practice this case was first investigated, but because of the unexpected results, as shown in Fig. 4, the sample a) was next studied. The changes of the activities were due to the shortage of the F. P. and pure ^{137}Cs solution.

[6] F. Aoki et al., This Bulletin, **30**, 583 (1957).

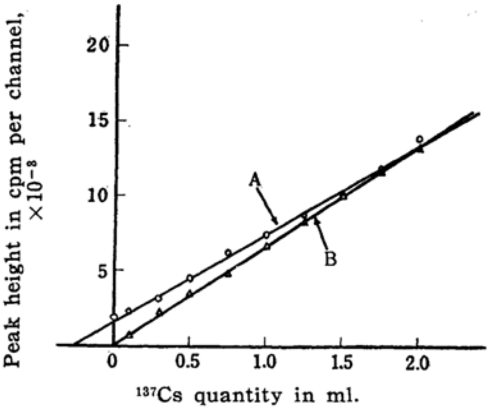

Fig. 4. 0.66 MeV peak heights vs. added ^{137}Cs quantities of the short-aged samples.

but those of the short-aged contained ^{137}Cs-^{137m}Ba and ^{140}Ba-^{140}La, which were identified by the gamma-energies.

The real peak heights of the 0.66 MeV gamma were plotted against the quantities of the added ^{137}Cs solutions (Figs. 3 and 4).

The straight lines, 'A' and 'B' show the 0.66 MeV peak height of the samples and that of pure ^{137}Cs solution added to the fission products, respectively; both have good linearities. In Fig. 3, both lines are parallel, but in Fig. 4 the slope of the straight line 'B' is a little greater than that of 'A'. This fact shows that the peak height, in spite of the correction for the Compton pulses of ^{140}Ba-^{140}La gammas, does not represent the ^{137}Cs quantity, but always gives too low a value. This phenomenon has not yet been sufficiently investigated, but one possible explanation is that some of the 0.66 MeV gamma pulses are summed up with photoelectric or Compton pulses of ^{140}Ba-^{140}La gammas to form higer pulses. However, the length between the origin of the coordinate and the intersection of the straight line 'A' and the abscissa gives the quantity of ^{137}Cs originally present in the fission products, which does not depend on the presence of ^{140}Ba-^{140}La. When the straight line 'A' is determined by the method of least squares, the most probable value of the quantity in question is obtained.

The results are shown in Table III, where N is the 0.66 MeV peak height in counts per minute per channel and x the volume of ^{137}Cs solution in milli litres. The analysed ^{137}Cs quantity corresponds to the absolute value of x at N=O, and is given in the same unit as that of the added ^{137}Cs solution whose activity is temporarily shown in milli litres.

TABLE III
ANALYSIS OF ^{137}Cs IN THE FISSION PRODUCTS

Sample	Straight line	^{137}Cs quantity (ml)
Long-aged	$N=1037.44-1370.83x$	0.757
Short-aged	$N=1553.51-5963.95x$	0.260

In this experiment the quantities of ^{137}Cs originally present in the fission products were unkown, so the errors of the measured quantities can not be shown. The maximum deviations of the peak heights from the straight lines determined by the method of least squere are 6% and 10% in the case of the long-aged and the short-aged, respectively.

Summary

A method for the rapid determination of ^{137}Cs in fission products has been studied. Simple and reliable analysis is possible by combining oxalate- and carbonate-form anion exchange resin and a gamma-ray scintillation spectrometer as follows.

Take several samples of equal quantity from a given fission products solution. Add various known quantities of pure ^{137}Cs to them respectively. Extract the bulk of uranium with T. B. P. in diethyl ether. Treat them through a mixed bed of carbonate- and oxalate-form anion exchange resin. Measure each aliquot using a gamma-ray scintillation spectrometer. Plot the real peak height of the 0.66 MeV gamma vs. the added ^{137}Cs quantity, and determine the straight line by the method of least square. Find the intersection of the straight line and the abscissa.

The quantity in question is given by the length of the abscissa between the intersection and the origin.

The authors wish to thank Dr. S. Uchida and Mr. K. Hashimoto for encouraging the prosecution of this work.

Government Chemical Industrial
Research Institute
Shibuya-ku, Tokyo