S 67. *The Extraction of Carrier-free* ^{131}I *from Pile-irradiated Tellurium.*

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A method is described for the routine production, in two working days, of carrier-free ^{131}I from pile-irradiated tellurium. The overall yield is better than 90%.

NATURAL tellurium is a mixture of seven stable isotopes, four of which (^{120}Te, ^{126}Te, ^{128}Te, and ^{130}Te) yield radioactive isotopes by bombardment with slow neutrons. Each active isotope exists in two isomeric states, one of which decays to the other, although both are formed directly by (n, γ) reactions. Subsequently, by β-emission, the iodine isotopes ^{127}I, ^{129}I, and ^{131}I are formed from ^{127}Te, ^{129}Te, and ^{131}Te, respectively. The reactions, elucidated by Seaborg, Livingood, and Kennedy (*Physical Rev.*, 1940, **57**, 363) may be summarised as follows (e^- stands for internal conversion electrons; half lives are in parentheses):

$$\begin{array}{lllll}
{}^{131}\text{Te (30 hours)} & \xrightarrow{e^-} {}^{131}\text{Te (25 min.)} & \xrightarrow{\beta\text{ max?}} & {}^{131}\text{I (8 days)} & \xrightarrow{\beta\text{ max. 0·6 Mev.}} {}^{131}\text{Xe} \\
{}^{129}\text{Te (32 days)} & \xrightarrow{e^-} {}^{129}\text{Te (72 min.)} & \xrightarrow{\beta\text{ Max. 1·8 Mev.}} & {}^{129}\text{I (stable or very long-lived)} & \\
{}^{127}\text{Te (90 days)} & \xrightarrow{e^-} {}^{127}\text{Te (9·3 hours)} & \xrightarrow{\beta\text{ Max. 0·6 Mev.}} & {}^{127}\text{I (stable).} &
\end{array}$$

To estimate the efficiency of extraction of ^{131}I, the 0·6-Mev. β-ray of half-life 8 days must be measured. This can be done only by means of a decay curve, which, with the necessary analysis, is shown in Fig. 1. To perform the normal analysis of successively extracting each period, commencing with the longest, observations should be made for about 200 days. However, after 70 days, only the two longest-lived isotopes are present in appreciable amount and each can be estimated from the observed rate of decay at any point. Alternatively, from an absorption curve of the radiations after this time the relative amounts of each may be estimated.

In the first recorded separation of ^{131}I from tellurium (Seaborg and Livingood, *ibid.*, 1938, **54**, 775) the latter was dissolved in nitric acid after addition of sodium iodide carrier, and the iodine liberated during solution was distilled into sodium hydrogen sulphite solution. Perlman,Chaikoff, and Morton (*J. Biol. Chem.*, 1941, **139**, 433) failed to obtain a reasonable yield of carrier-free ^{131}I by this method and they subsequently (*J. Endocrinol.*, 1942, **30**, 487) dissolved the tellurium in a hot solution of chromic oxide and sulphuric acid, distilling off the iodine after reduction with an excess of oxalic acid. The first detailed directions were published by Kamen (" Radioactive Tracers in Biology," Academic Press Inc., New York, 1947, p. 231). No

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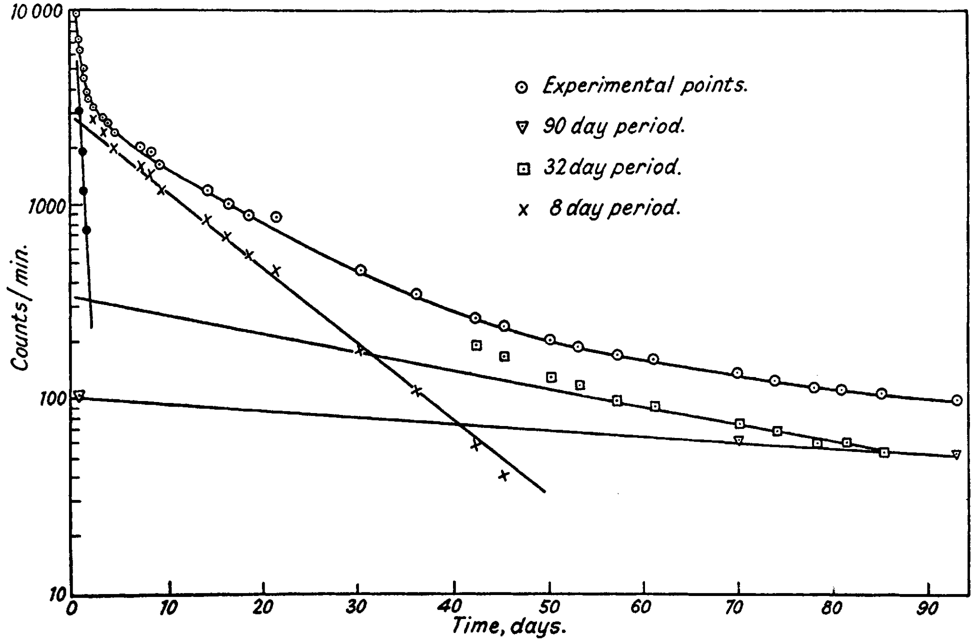
* In our experiments the rate of decomposition of hydrogen peroxide was constant during 24 hours and a function only of the concentration of the catalyst. This technique seems convenient for research on catalysis.

information about the yield or purity of product is given in any of these papers. In processing tellurium irradiated in the low-energy Harwell pile (G.L.E.E.P.), until recently the only pile in operation in this country, we found the yield of radio-iodine by this method to be about 60% unless distillation was continued until fuming of the distilland occurred, the remainder of the iodine then distilling off. This distillation rate is shown in Table I (excess of oxalic acid column), in which the activity of successive fractions of 10 ml. is reported.

FIG. I.



Decay curve of irradiated tellurium.

TABLE I.

Rate of distillation of ^{131}I *from tellurium.*

	Excess of oxalic acid.		Minimum of oxalic acid.	
Fraction no.	Volume, ml.	Counts/sec. in 0·05 ml.	Volume, ml.	Counts/sec. in 0·05 ml.
1	10·9	1570	10·3	3620
2	14·1	275	10·2	513
3	8·8	75	17·0	390
4	10·0	31	12·6	79
5	13·5	21	9·1	45
6	12·0	18	11·8	25
7	14·7	16	16·8	13
8	15·8	14	15·0	12
9	11·7	1600	11·8	11
10	13·4	174	—	—

Oxalic acid and, in the later stages of the distillation, formic acid distilled in amounts which, with the low activity of the tellurium available from G.L.E.E.P., rendered the product unsuitable for medical use without further purification. The distillate may be purified by oxidation with alkaline and acid permanganate, back-titration with oxalic acid, and redistillation. To avoid distillation of the oxalic acid and the necessity for this purification, the minimum amount of oxalic acid required was determined; this was found to be the amount required to reduce the excess of chromic oxide and to reduce about one-third of the tellurate to tellurite. When this minimum amount of oxalic acid is used, no organic acids distil off with the iodine, and, moreover, almost all the iodine distils off in the first fractions (Table I).

TABLE II.

Rate of distillation of H^{131}I *from 5% sulphuric acid with and without oxidation by nitric acid.*

Fraction no.*	Without nitric acid; counts/sec. in 0·05 ml.	With nitric acid; counts/sec. in 0·05 ml.
1	0·8	931
2	0·8	228
3	0·8	118
4	0·8	39
5	0·8	44
6	0·8	37
7	0·9	21
8	0·8	18
9	0·8	14
10	0·8	12
11	1·1	8·2
12	1·3	5·7
13	1·6	3·9
14	1·8	2·9
15	3·3	1·8
16	214·2	1·5
17	213	1·3
18	24·5	1·3
19	22·7	0·8

* Each fraction = 10 ml.

This inhibitive effect of oxalic acid was confirmed in simplified systems. Table II shows the rate of distillation of ^{131}I from hydriodic acid in 5% sulphuric acid. It will be seen that the ^{131}I distils off only when the sulphuric acid is concentrated to about 20%. Addition of carrier hydriodic acid in this experiment has confirmed the presence of iodine in the distillate. The oxidation of the carrier-free H^{131}I by a trace of nitric acid in 5% sulphuric acid results in immediate distillation of ^{131}I. Oxidation of the ^{131}I with acid permanganate or dichromate takes the iodine to a higher oxidation level, and no distillation of iodine is observed in weak acid. Reduction of the permanganate or dichromate solution with the minimum amount of oxalic acid results in immediate distillation of the iodine, whereas the presence of excess of oxalic acid partly inhibits the distillation until the acid is concentrated to about 50% (Table III).

TABLE III.

Rate of distillation of ^{131}I *from* HIO$_3$ *reduced with minimum or excess of oxalic acid.*

Fraction no.	Minimum of oxalic acid; counts/sec. in 0·05 ml.	Excess of oxalic acid; counts/sec. in 0·05 ml.
1	402	486
2	180	72
3	124	25
4	124	29
5	104	28
6	94	27
7	76	23
8	70	17
9	60	12
10	44	7
11	34	5
12	28	4
13	26	4
14	26	4
15	12	5
16	12	11
17	6	52
18	2	184
19	1·4	352
20	1·2	95

These experiments show that carrier-free radio-iodine behaves like iodine in macroscopic quantities in that it distils readily as iodine, but not as hydriodic or iodic acid. This was worth confirmation as curious results have often been reported with carrier-free radio-elements. It would appear, therefore, that the effect of an excess of oxalic acid is to convert some (up to 50%) of the ^{131}I into hydriodic acid. This might occur by direct interaction of oxalic acid with iodine, or by interaction of oxalic and sulphuric acid with formation of sulphur dioxide. The latter interpretation is favoured as we have been unable to detect iodide after heating iodine and oxalic acid in aqueous solution, although a trace has been detected in the presence of 5% sulphuric acid. This would explain why distillation is inhibited in the presence of undissolved tellurium, which would also liberate sulphur dioxide with hot sulphuric acid.

In large-scale production of radio-iodine from irradiated tellurium, both the yield and the distillation rate are somewhat variable when an excess of oxalic acid is used, but on all occasions some ^{131}I remains in the distilland until fuming begins. With the minimum amount of oxalic acid, however, 90% of the ^{131}I is obtained in the first fraction, no organic acids distil, and there is no evolution of carbon dioxide during distillation, which, when an excess of oxalic acid is used, carries appreciable quantities of ^{131}I through the receiver, necessitating the use of extra traps.

The yield is obtained by measurements on *ca.* 1 mg. of the active tellurium, and on an aliquot of the final solution : since the two measurements are made under identical conditions, corrections for geometry, counter efficiency, absorption in air, counter window, etc., need not be made, as they cancel when the ratio is determined. A small correction might be required for self-absorption in the tellurium. By adopting the decay scheme of Metzger and Deutsch (*Physical Rev.*, 1948, **74**, 1640) and using an interpolated value for the absorption coefficient of the softer β-ray, it is easily shown that the correction to the yield on this account is much less than 1%.

EXPERIMENTAL.

The following method is recommended for processing 50 g. of irradiated tellurium. 200 G. of potassium dichromate or 136 g. of chromium trioxide, are placed in a 3-l. flask, followed by the tellurium, so as to avoid possible caking if precipitated tellurium is used. 1 L. of 50% (by volume) sulphuric acid is added. Cautious warming to *ca.* 80° initiates a vigorous reaction. If tellurium ground in a mortar from a lump of cast metal is used, the reaction does not normally get out of hand, but if precipitated tellurium is used water-cooling may be required. After the reaction has subsided, the mixture is heated under reflux for *ca.* 2 hours to ensure complete dissolution, as radio-iodine does not distil if any tellurium remains undissolved. 118 G. of oxalic acid dihydrate are added to the cold solution, and reaction is effected by cautious warming. On completion of the reduction, 200 ml. of distillate are collected in 1 ml. of N-sodium hydroxide containing a trace of sodium sulphite. The mixture is then evaporated to a suitable volume and made up to a suitable pH.

Experiments with this method scaled down for 10 g. of tellurium and with gradual addition of the oxalic acid showed that distillation of iodine is possible when 23·3—23·6 g. of oxalic acid dihydrate have been added (equiv. to 116·5—118 g. for 50 g. of tellurium).

The acidity of the distillate is shown in the following results obtained in experiments using 10 g. of tellurium :

	(*a*) 23·3 g. of oxalic acid.		(*b*) 51·5 g. of oxalic acid.	
Fraction no.	Volume, ml.	N-NaOH, ml.	Volume, ml.	N-NaOH, ml.
1	8·8	0	11·2	0·20
2	9·5	0	9·5	0·22
3	11·0	0	10·8	0·65
4	9·9	0	10·0	0·80
5	9·8	0·10	13·0	1·40
6	9·5	0·25	12·2	1·75
7	9·2	0·30	16·4	3·10
8	10·3	0·40	8·2	1·50
9	13·3	0·65	—	—

The extra acidity when an excess of oxalic acid is used is due to oxalic and formic acid and carbon dioxide.

Spectroscopic examination of the distillate revealed no impurities; the concentration of tellurium or chromium is not more than 50γ in the 200 ml. of distillate.

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