264. *The Comparison of Weak Neutron Fluxes by using Ethyl Iodide.*

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A quantitative study of the factors influencing the reproducibility of extractions of radioactive iodine from neutron-irradiated ethyl iodide has been made with a view to furnish a sensitive method of comparing weak neutron fluxes. Exchange rates between the radioactive species produced and the inactive ethyl iodide have been measured, and their bearing on the reproducibility is discussed. This method being used, the statistical error of the counts obtained from a weak neutron source was reduced from 14% for dysprosium oxide and indium detectors to 1%.

In comparing neutron fluxes it is desirable that the number of counts derived from them should be large and the statistical error small. To obtain a larger count use has been made of the fact that after ethyl iodide has been irradiated with neutrons a proportion of the radioactive iodine atoms produced can be extracted chemically together with a trace of carrier (Szilard and Chalmers, *Nature*, 1934, **134**, 462). This is because the recoil energies of the iodine atoms from the γ-rays emitted upon capture of the neutrons are greater than the chemical binding energies of the C–I bonds, and consequently the ethyl iodide dissociates, leaving some of the radioactive iodine combined in some new chemical species (Glückauf and Fay, *J.*, 1936, 390), some of which can be extracted conveniently by means of an aqueous solution. In this way the radioactive iodine atoms produced throughout a large volume of ethyl iodide can be concentrated under a β-ray counter as silver iodide, so that self absorption of the β-particles is negligible.

This paper presents a quantitative study of some of the factors influencing the reproducibility of such extractions in the case of ethyl iodide. Initially the reproducibility was less than $\pm 5\%$, but by following the corrections and technique suggested in the following sections the experimental error can be reduced to about $\pm 0{\cdot}5\%$.

EXPERIMENTAL.

For the purpose of testing the reproducibility of the extractions, the irradiations and extractions of the ethyl iodide were performed in a basement, the temperature of which was nearly constant, and where the diffuseness of the light greatly reduced the rate of iodine formation due to the photodecomposition of ethyl iodide. A large (500 millicurie radium–beryllium) source was housed in a cylinder of paraffin wax, on which stood the flask containing the ethyl iodide, which was first purified by shaking it with sodium sulphite solution, separating it, keeping it over calcium chloride, and finally filtering it. After irradiation the iodide was extracted in a separating funnel by shaking for a standard time (30 seconds) with dilute potassium iodide solution, the volume of which was about one-tenth of that of the ethyl iodide. The mixture was allowed to settle for a given time (2·5 minutes), and the denser ethyl iodide run off. It was found advisable to put a small constriction in the outlet of the separating funnel to ensure that droplets of the aqueous extract adhering to the walls were not dragged out with the ethyl iodide.

The aqueous extract, together with the washings from the funnel, was then poured into another separating funnel containing a little carbon tetrachloride. This was shaken to remove any ethyl iodide remaining, as this tends to hydrolyse in hot silver nitrate solution, producing more silver iodide; this is undesirable as it increases unnecessarily the self absorption of the silver iodide layer for the β-particles. The potassium iodide solution was then precipitated with a mixture of 10 c.c. each of 30% nitric acid and 0·5% silver nitrate solutions; it was found necessary to standardize this precipitation since under certain conditions the precipitated silver iodide tends to peptise.

When iodine was added to the ethyl iodide before irradiation, it was extracted with water containing enough sodium sulphite to reduce the iodine to iodide. It was found that a large excess of sodium sulphite was undesirable, as the aqueous extract tended to form an emulsion in the ethyl iodide; sodium hydrogen sulphite and sulphurous acid can also be used instead of sodium sulphite, but then the ethyl iodide tends to dissolve free sulphur dioxide, and has to be purified from it before the next irradiation by extraction with dilute sodium hydroxide solution.

The silver iodide was filtered through a small filter-paper (1 cm. diameter) held in a Gooch crucible, washed with 3% nitric acid, alcohol, and ether, and mounted in a holder which consisted of a brass plate having a central hole (1·1 cm. diameter) one side of which was closed by a piece of cellophane tape (weight 8·3 mg./cm.^{2}). The filter-paper was laid face downwards in the hole so that the silver iodide was in contact with the tape, and held in position by a small brass disc which fitted the hole tightly and was itself fixed by means of another piece of tape. The brass plate fitted a groove in a lead castle and was located so that the centre of the precipitate was under the centre of a G.E.C. " End-on " counter. The latter was held with the wire positive, the Geiger pulses obtained being amplified and passed into a Dynatron scaling unit. Readings were taken every minute, corrected for decay, for the paralysis time of the circuit, and for variation in counting conditions by means of an uranium oxide standard, and the mean of these taken. The errors given are the root-mean-square deviations of the counts obtained.

The reproducibility of the precipitation and measurement was checked by precipitating aliquots of a standard potassium iodide solution (containing radio-iodide ions) and measuring them, the counts obtained falling within the statistical error.

Self-absorption.—A rough " self-absorption " curve (of the β-particles in silver iodide) was obtained by diluting a solution of potassium iodide containing radio-iodide ions, taking aliquots, and precipitating after the addition of various known amounts of potassium iodide. The counts obtained (corrected to a given time) are shown in Table I; from these it appears that no correction for self-absorption was necessary providing that the weight of silver iodide was not greater than 56 mg./cm.², and that in this region there was little chance of errors due to unevenness of the precipitate.

TABLE I.

Run I.	AgI (mg.)/cm.².	Counts obtained.	*Run II.*	AgI (mg.)/cm.².	Counts obtained.
	16	15,500 ± 160		21	2540 ± 50
	38	15,600 ± 150		40	2500 ± 40
	54	15,500 ± 150		56	2570 ± 55
				98	2330 ± 60

Exchange between the Extractable ^{128}*I and Inactive Ethyl Iodide.*—It was found that exchange occurred at room temperature between the iodine in the extractable species and that in the bulk of the ethyl iodide. Since nearly all the iodine atoms in the latter were inactive, this meant that the rate at which the extractable radio-iodine disappeared was greater than could be accounted for by the decay constant alone, and consequently to correct the activity extracted for " saturation irradiation " (*i.e.*, the state when further irradiation did not result in a greater activity being obtained) the constants of the exchange reaction had to be determined (see later). The rate of exchange was measured by placing ethyl iodide (irradiated for a standard time at room temperature) in a thermostat at the desired temperature until thermal equilibrium was established. The ethyl iodide could then be extracted directly or, in the case of higher temperatures (where evaporation was liable to produce some error), cooled for a short standard time before extraction. The count obtained could then be considered as the activity at t (time) $= 0$; by varying the duration in the thermostat, the rate of exchange could be determined.

Efficiency of Extraction.—The efficiency of the extraction process for two reagents (potassium iodide solution, and the same solution containing a little sulphite) was obtained by making successive extractions of an irradiated sample of ethyl iodide; the activities obtained are given in Table II. The fact that the first extracts for both reagents are the same (within experimental error) can be explained by assuming that the amount of elementary iodine produced by the recoiling iodine atoms is small compared with the iodide present in the potassium iodide solution (when no sulphite is present). Exchange of the type $I^- + II^* \rightleftharpoons I^{*-} + I_2$ will then ensure that most of the radio-iodine atoms present will move into the aqueous layer (Roginsky and Gopstein, *Physikal. Z. Sowjetunion*, 1935, **7**, 672). It can be seen from Table II that more than one extraction is uneconomical, as in the time required for another extraction the first will have decayed by an amount greater than the activity gained.

The absolute efficiency (*i.e.*, the ratio of the radio-iodine extracted from the irradiated mixture to the total radio-iodine present as HI^*, I_2^*, and $C_2H_5I^*$, $C_2H_4I_2^*$, etc., produced by combination of the recoiling I^* with organic free radicals) was determined by measuring the activities of an unextracted and an extracted sample of ethyl iodide contained in a double-walled vessel. The inner wall of this was made of very thin glass permeable to some of the β-particles and was of such a diameter that it could be placed round a thin-walled cylindrical aluminium counter. The efficiencies observed (from one extraction only) are given in Table III. The significance of the increase in efficiency when the ethyl iodide contains iodine is discussed later.

TABLE II.

Extracting agent.	Extraction.	Activity (referred to a standard time).	Total activity.
KI (0·03%) solution	First	17,200 ± 380	18,300 ± 400
	Second	671 ± 15	
	Third	310 ± 9	
	Fourth	175 ± 6	
KI (0·03%) solution + Na_2SO_3	First	17,400 ± 500	18,100 ± 500
	Second	616 ± 15	
	Third	41 ± 5	
	Fourth	27 ± 3	

TABLE III.

Initial state of EtI.	Extracting agent.	Efficiency = ^{128}I extracted/^{128}I present before extraction.
0·005 g. I_2/l.	Na_2SO_3 soln.	0·657 ± 0·014 0·630 ± 0·010 mean = 0·643 ± 0·030
No I_2	KI soln.	0·589 ± 0·036 (calc.)

Comparison of Ethyl Iodide with Other Detectors.—Ethyl iodide has been compared with dysprosium and indium as a detector of weak neutron fluxes; the latter are often used owing to their large capture cross-sections for thermal neutrons. The source used was a 10-year old radon–beryllium tube (now a polonium–beryllium tube). The dysprosium was in the form of oxide supported by cellophane tape so that its weight was 40 mg./cm.² and its total area was 15 cm.². (This corresponded very roughly to the half-value thickness of dysprosium oxide for the absorption of the β-particles from the active isotope produced, *i.e.*, 50 mg./cm.².) The latter value was calculated from the absorption coefficient in aluminium (it being assumed that the mass-stopping power for β-particles of the same energy is a constant). The indium was a foil of area 13·5 cm.^{2} and thickness 0·05 cm. (360 mg./cm.^{2}) and was larger than the half-value thickness for the β- and γ-rays emitted by its active isotope (226 mg./cm.^{2}); this quantity was calculated directly by measuring the reduction in activity when a piece of inactive indium foil was placed between an active sample and the counter.

These detectors were irradiated to saturation by placing them round the source in a large bath of water (to slow down the neutrons) and were arranged to fit round a thin-walled (0·13 mm.) cylindrical aluminium counter, the background of which was 8·3 counts/minute in a lead castle 6 cm. thick. Table IV shows the counts obtained for saturation irradiation immediately after removal from the source.

The ethyl iodide irradiations were performed by holding the source at the centre of a round-bottomed soda-glass flask which was filled with ethyl iodide and iodine (0·01 g./l.) and suspended in a water tank; the counts given in Table IV are those obtained for saturation irradiation 25 minutes after removal from the source. The extraction and precipitation, etc., could be achieved comfortably in this time without the use of a centrifuge. Since the amount of radioactive silver iodide could be made as small as desired, the specimen was mounted in a hole in a brass plate 0·15 cm. thick, and supported at both ends with cellophane tape. By sliding this plate between two G.E.C. end-on counters mounted with their windows facing each other and about 0·3 cm. apart, the counts obtained were double those from the arrangement described above. The background of the counters (15·5 counts/minute in a lead castle 6 cm. thick) was approximately twice that due to a single counter, but since the percentage statistical error is given by $100\sqrt{N_e + N_b}/(N_e - N_b)$, where N_e is the number of counts due to the specimen and background, and N_b the number due to background only (for the same period), the statistical error given by this arrangement is $1/\sqrt{2}$ of that obtained using a single counter.

In Table IV the results given are for saturation irradiation; to attain a given degree of saturation, the time of irradiation for ethyl iodide is appreciably shorter than for the other detectors, a fact which may prove important when the neutron flux to be measured is of short duration.

Since iodine has a resonant absorption for 36 electron-volt neutrons, it is almost impossible to calculate the variation of the activity obtained with volume of the ethyl iodine when the neutron flux is not wholly thermal, and consequently some experimental figures for this are also included in Table IV.

TABLE IV.

(All detectors irradiated to saturation.)

Detector.		Counting time (mins.).	Total counts.	Counts due to back-ground.	Counts due to detector.	Statistical error, %.
Dy_2O_3 (2·5 hrs. half-life)		30	340	249	91 ± 24	26·3
		150	1,600	1245	355 ± 53	14·9
		300	3,020	2490	530 ± 74	14·0
In (54 mins. half-life)		30	391	249	142 ± 25	17·8
		120	1,344	995	349 ± 49	14·2
		150	1,623	1245	378 ± 53	14·2
	Litres.					
C_2H_5I (25 mins. half-life)	2·70	30	6,575	465	6,110 ± 84	1·37
	2·70	90	11,615	1395	10,220 ± 114	1·11
	1·65	30	6,115	465	5,650 ± 81	1·45
	1·10	30	5,320	465	4,855 ± 76	1·55
	0·51	30	3,590	465	3,125 ± 64	2·05
	0·32	30	2,170	465	1,705 ± 51	3·01

DISCUSSION.

Reproducibility.—By following the extraction process given above, two reproducible methods of extraction were developed. The first was to extract the irradiated ethyl iodide (containing no iodine) with dilute (0·03%) potassium iodide solution. The results given in Table V correspond to the activities obtained immediately after removal from the neutron source and are corrected to saturation irradiation. From the figures given, the experimental error was estimated to be about ±0·5%. When this method is used, care must be taken to remove all iodine, because the latter reduces the amount extracted owing to exchange with the potassium iodide in the extraction process and also alters the exchange-rate of the extractable radio-iodine with that in the ethyl iodide (see later). Sulphur dioxide and organic bases present in the ethyl iodide are also undesirable, for in the presence of these substances some of the radio-iodine appears on the walls of the irradiation flask, which must then be washed out. With ethyl iodide purified from these substances the amount of radio-iodine left on the walls is negligible (about 0·1—0·2%).

The second method uses a sodium sulphite extraction of an irradiated iodine–ethyl iodide solution. The activities (Table VI*a*) were obtained under the same irradiation conditions as those in Table V ; the significance of the increase in activity when iodine is added is discussed later. By using a set-up nearer the radium–beryllium source and reducing the volume of the ethyl iodide, the independence of the activity obtained with the variation of iodine concentration could be extended over a greater range.

TABLE V.

Counts/min. from KI extractions of pure EtI.	Counts/min. from KI extractions of pure EtI.	Counts/min. from KI extractions of pure EtI.
3633 $\pm$ 60	3630 $\pm$ 70	3685 $\pm$ 70
3701 $\pm$ 40	3675 $\pm$ 70	3775 $\pm$ 70
3703 $\pm$ 45	3809 $\pm$ 80	Mean 3701

TABLE VI.

(*a*)	I_2, g./l.	0·008	0·008	0·012	0·016
	Counts/min. ...	4150 $\pm$ 40	3910 $\pm$ 70	4050 $\pm$ 60	3950 $\pm$ 45
					Mean 4015
(*b*)	I_2, g./l.	0·200	0·080	0·020	
	Counts/min. ...	1670 $\pm$ 25	1681 $\pm$ 24	1661 $\pm$ 25	

Exchange.—Since effectively all the iodine atoms in the ethyl iodide after irradiation are inactive, the exchange rate (measured by the fall in activity of the extractable species) will be proportional to the number of radioactive extractable atoms in the ethyl iodide, *i.e.*, $dN/dt = -kN$ (N = number of " extractable " radioactive molecules). The rate of disappearance of extractable iodine atoms due to decay and exchange will be given by $dN/dt = -(\lambda + k)N$, where λ is the decay constant of ^{128}I, and if the activity extracted at $t = 0$ is N_0, and at time t is N_t, then $\ln (N_0/N_t) = (k + \lambda)t$. The results obtained at different temperatures are given in Table VII ; the errors in the values of k (the fraction exchanged per min., obtained by subtracting λ from the slopes of curves of $\log N_0/N_t$ against t) were estimated graphically. A trace of ethyl alcohol (normally removed in the drying process) added to the ethyl iodide did not alter the exchange rate at room temperature.

TABLE VII.

Temp.	Time (mins.).	Counts/min.	N_0/N_t.	k.
		(*a*) *No iodine present.*		
0°	0	1449 $\pm$ 10	—	0·0006 $\pm$ 0·0004
0	47	375 $\pm$ 8	3·86 $\pm$ 0·10	
0	92	107 $\pm$ 1·7	13·55 $\pm$ 0·27	
17	0	3700 $\pm$ 60	—	0·0025 $\pm$ 0·0005
17	31	1419 $\pm$ 30	2·61 $\pm$ 0·27	
17	70	449 $\pm$ 5·1	8·25 $\pm$ 0·20	
17	127	79 $\pm$ 1	48·25 $\pm$ 1·25	
42	0	1109 $\pm$ 15	—	0·0240 $\pm$ 0·0031
42	29	284 $\pm$ 3	3·90 $\pm$ 0·10	
42	60	54 $\pm$ 1	20·50 $\pm$ 0·70	
55	0	41·6 $\pm$ 1	—	0·1800 $\pm$ 0·0250
55	5	13·2 $\pm$ 1·5	3·16 $\pm$ 0·50	
55	10	5·02 $\pm$ 0·7	8·30 $\pm$ 1·50	
		(*b*) 0·01 *G. of iodine per l. of ethyl iodide.*		
0	0	2960 $\pm$ 30	—	0·0003 $\pm$ 0·0003
0	63	495 $\pm$ 5	5·99 $\pm$ 0·11	
0	117	108 $\pm$ 2	27·41 $\pm$ 0·81	
15	0	3960 $\pm$ 32	—	0·0009 $\pm$ 0·0003
15	79	404 $\pm$ 6	9·81 $\pm$ 0·21	
15	120	134 $\pm$ 2	29·55 $\pm$ 0·24	
41	0	2800 $\pm$ 19	—	0·0021 $\pm$ 0·0004
41	47	694 $\pm$ 7	4·03 $\pm$ 0·08	
41	109	111 $\pm$ 2·5	25·22 $\pm$ 0·78	
55	0	1945 $\pm$ 19	—	0·0041 $\pm$ 0·0003
55	48	415 $\pm$ 5	4·69 $\pm$ 0·11	
55	76	177 $\pm$ 4	10·96 $\pm$ 0·35	

By equating $k = \alpha \exp(-E/\boldsymbol{R}T)$, where α is a constant and E the heat of activation of the exchange, and plotting k against $1/T$, one obtains 19 $\pm$ 1 kcals./g.-mole for the heat of activation without iodine, and 7·8 $\pm$ 1·5 kcals./g.-mole in the presence of iodine. The former value is in good agreement with that obtained by McKay (*J. Amer. Chem. Soc.*, 1943, **65**, 702) for the exchange of iodide ions with ethyl iodide; this suggests that the exchange occurring in pure ethyl iodide is $HI^* + C_2H_5I \longrightarrow C_2H_5I^* + HI$. The mean values of α for the two exchanges are $4{\cdot}56 \times 10^{11}$ and $6{\cdot}46 \times 10^{2}$, respectively; the low value of the latter suggests that perhaps some additive complex of iodine with hydrogen iodide may be formed (*e.g.*, HI_3), in which event steric effects may reduce the exchange rate. An alternative explanation (that the exchange $HI^* + I_2 \rightleftharpoons HI + II^*$ occurs rapidly and is followed by exchange of the radio-iodine with ethyl iodide) can be excluded by Hull, Shifflett, and Lind's observation (*ibid.*, 1936, **58**, 535) that no exchange could be observed between iodine and ethyl iodide at 90°.

The importance of these exchanges on the reproducibility of the extractions can be seen from the following argument. Under the conditions of the experiments, the rate of formation of extractable radio-iodine is a constant, but the rate at which it effectively " decays " is proportional to the decay constant added to the exchange constant k. Assuming that the ethyl iodide is not irradiated long enough for " saturation irradiation " to occur, a correction of the form

$$\text{Activity at saturation} = \frac{\text{Activity immediately after removal from source (calc.)}}{1 - 2^{-t/\tau}}$$

where t = irradiation time, and τ = " effective " half-life, must be applied; τ is given by $\tau = (\ln 2)/(\lambda + k)$.

Although the conditions of irradiation were different from those under which the exchange curves were obtained (owing to γ-rays and free radicals produced by the capture of neutrons), these did not appear to affect (within experimental error) the exchange rate observed, since samples of ethyl iodide which had been irradiated to " half-saturation " (*i.e.*, so that the activity obtained was a half of that at " saturation ") when corrected as above gave activities within 1% of those obtained for " saturation-irradiation." Under very strong γ- or neutron-irradiation however, there might be an increased exchange, and then the above corrections would be invalidated (Williams, *J. Phys. Colloid Chem.*, 1948, **52**, 603).

From the exchange curves observed, it appears that a possible reason for the greater activity obtained when iodine is added to the ethyl iodide is that at saturation the equilibrium concentration (under constant irradiation conditions) will be greater since the exchange is much reduced. Using this reasoning, at saturation :

$$\begin{aligned}\text{number of `` extractable '' } I^* \text{ atoms produced/min.} &= -\ \text{number `` decaying ''}\\ &= -\ 3701\ (\lambda + k_1)\ (\text{No } I_2 \text{ present})\\ &= -\ N_1\ (\lambda + k_2)\ (I_2 \text{ present})\end{aligned}$$

where N is the activity expected from iodine–ethyl iodide solutions. (The number of counts due to the added iodine at the concentration used, 0·01 g. of iodine per l. of ethyl iodide, is very small compared to those due to the ethyl iodide, and can be neglected.) Substituting for k_1, k_2, and λ, N_1 is found to be 3915 ± 165, in fair agreement with the observed value (4015 ± 70). This means that the chief function of iodine is to inhibit the exchange, and not, as might have been expected, to increase the efficiency of the γ-recoil process by exchange of the type I^* (recoiling) $+ I_2 \longrightarrow II^* + I$, thus reducing the chance of recombination of the recoiling atom with a free radical; this is also substantiated by the fact that the activity extracted is independent of concentration of elementary iodine in the ethyl iodide.

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