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RADIATION STABILITY STUDIES

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RADIATION STABILITY STUDIES

Part I Aqueous Ethylenediamine Tetraacetate and Acetate Solutions

R E Blanco and A H Kibbey

Part II Beckman Glass Electrodes

J. H Pannell

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Abstract

The initial decomposition rate in aqueous solution of ethylenediamine tetraacetate ion exposed to a 3000-curie Co^{60} source was 0 62 millimole per watt-hour of absorbed energy The decomposition of acetate ion under similar conditions was not measured quantitatively, but it was apparently low It was concluded that ethylenediamine tetraacetate is entirely satisfactory for use in separating fission products in the presence of moderately low activity levels, but at higher levels, approaching 0 04 watt-hr per gram of solution, acetate is preferable

Standard-size Beckman type glass electrodes in a solution containing 0 36 curie of Ce^{144}-Pr^{144} activity per milliliter, corresponding to calculated total irradiations of 1 2 x 10^7 to 5 2 x 10^7 rep, had useful lives of two to eight days It was concluded that any of the electrodes tested could be used with assurance for several hours at a radiation level of approximately 1 curie/ml

Part I AQUEOUS ETHYLENEDIAMINE TETRAACETATE AND ACETATE SOLUTIONS

Introduction

Ethylenediamine tetraacetic acid, a chelating agent sold under the trade name "Versene," has proved to be a valuable reagent for the separation of fission products at low radiation levels The present study was undertaken in an attempt to determine the radiation stability of this material The study included experiments on the effect of the rate of irradiation and the presence of metallic ions The relative radiation stability of the simpler acetate ion was also evaluated in terms of usefulness for fission product separations at high radiation levels

Experimental

Sodium Ethylenediamine Tetraacetate A 3000-curie Co^{60} source was used as the source of radiation All the sample tubes surrounding the source were fabricated of brass tubing having a 1/32-in wall thickness, the proximity to the source determining the intensity of the radiation received The radiation energy in each tube was calibrated by quantitative determination of the amount of ceric ion reduced in aqueous solution within a given time at any particular point in the radiation field

Samples, 40 to 50 ml in volume, of solution were placed in glass-stoppered pyrex bottles equipped with an air inlet and gas vent, and the entire apparatus was lowered into one of the brass tubes for irradiation

In order to maintain the oxygen content of the sample solutions in equilibrium with the atmosphere, water-saturated air was bubbled through them continuously during the irradiation The irradiated solutions were filtered through Whatman No 42 filter paper, and samples of both the original solution and filtrate were analyzed for pH, and for cation, nitrite, and ethylenediamine tetraacetic acid concentrations A Beckman model G pH meter was used for the pH determinations Barium, strontium, and cerium were determined by radiochemical methods, and lead was determined polarographically The ethylenediamine tetraacetic acid determinations were made by slight modifications of a standard spectrophotometric method [1] The experiments were carried out on systems made

(1) The Versenes, Technical Bull No 2, Bersworth Chemical Company, Framingham, Mass

up to simulate conditions that might be encountered during radiochemical separations

The first experiment was done on a simulated process solution of the composition

Ethylenediamine tetraacetate ion	0 065 M
Ba^{++}	0 0009 M
Sr^{++}	0 0016 M
Pb^{++}	0 03 M
Diethanolglycine	0 018 M

NO_3^- (total Kjeldahl nitrogen minus nitrogen in ethylenediamine tetraacetate)	0 31 M
Na^+ (total)	0 48 M
Ba^{140}, Sr^{90}, Ce^{144}	Tracer amounts
Initial pH	6 2 to 6 3

Three samples of the solution were irradiated at a rate of 2 18 x 10^{-3} watt per gram of solution for 24, 66 5, and 72 hr , corresponding to total energy absorptions of 0 052, 0 145, and 0 157 watt-hr per gram of solution, respectively The first and third samples were made 0 1 M in sodium bromide before the irradiation, since bromide ion had been suggested[2] as a possible agent for protection against radiation damage

(2) C J Hochanadel, J Phys Chem , 56, 587 (1952)

In the second experiment a similar solution was used except that the initial nitrate and sodium concentrations were only 0 16 and 0 33 M, respectively A sample of this solution was irradiated for a total of 840 hr at a rate of 8 40 x 10^{-4} watt per gram of solution, and samples were analyzed at intervals

Following the irradiations, the solutions were analyzed for nitrite in order to determine whether nitrite was formed in irradiation of barium nitrate solutions, as has been reported for irradiation of solid barium nitrate [3]

(3) A O Allen and J A Ghormley, J Chem Phys , 15, 208 (1947)

Determinations of pH were also made because it was thought that decomposition of the sodium ethylenediamine tetraactate might result in an increase in pH owing to the formation of amines and weak acids

Control runs were made on two aliquots from a sodium ethylenediamine tetraacetate sodium nitrate system at irradiation rates of 2 18 x 10^{-3} and 8 40 x 10^{-4} watt per gram of solution, respectively, to determine the rate of the solvent decomposition in the absence of any catalytic effects caused by ions other than sodium or nitrate The solution was sampled at intervals during the irradiation The composition of the solution, which had an initial pH of 6 3, was

Ethylenediamine tetraacetate ion	0 065 M
NO_3^-	0 1 M
Na^+	0 33 M

Sodium Acetate The relative radiation stability of acetate solutions to irradiation from the 3000-curie Co^{60} source at rates of 2 18 x 10^{-3} and 1 74 x 10^{-3} watt per gram of solution was determined on two aliquots of a solution of initial pH 5 00 The composition was

Sodium acetate	0 49 M
Ba^{++}	0 0029 M
Sr^{++}	0 0046 M
Pb^{++}	0 072 M
NO_3^-	0 26 M
Ba^{140}, Sr^{90}, Ce^{144}	Tracer amounts

The irradiated solutions were filtered and the filtrate was analyzed for pH and for nitrite, lead, barium, and strontium concentrations The acetate concentration was not determined In experiments using three aliquots of a similar solution, the effects of corrosion products on the stability of the acetate system were studied by making the samples 0 0018 M in ferric ion, 0 00033 M in chromic ion, and 0 00058 M in nickelous ion The initial pH of the solution in these experiments was 4 92

Results

Sodium Ethylenediamine Tetraacetate The data obtained from the irradiation of the sodium ethylenediamine tetraacetate sodium nitrate control solution (see Fig 1) indicated that the organic compound was decomposed initially at a rate of 0 69 millimole/watt-hr in a field of 8 40 x 10^{-4} watt per gram of solution, and at 0 55 millimole/watt-hr in a field of 2 18 x 10^{-3} watt per gram of solution The small difference between these values cannot be considered significant since some fluctuations in the experimental conditions probably occurred, particularly in the oxygen content of the solutions The pH of the solutions rose from 6 3 to the range of 8 5-9 0 at a rate of approximately 0 05 pH unit per milliwatt-hour per gram of solution and then remained constant The pH increased rapidly from 6 6 to 8 25 in the initial stages of irradiation at a rate similar to that noted in the control experiment and thereafter increased gradually to a final value of 9

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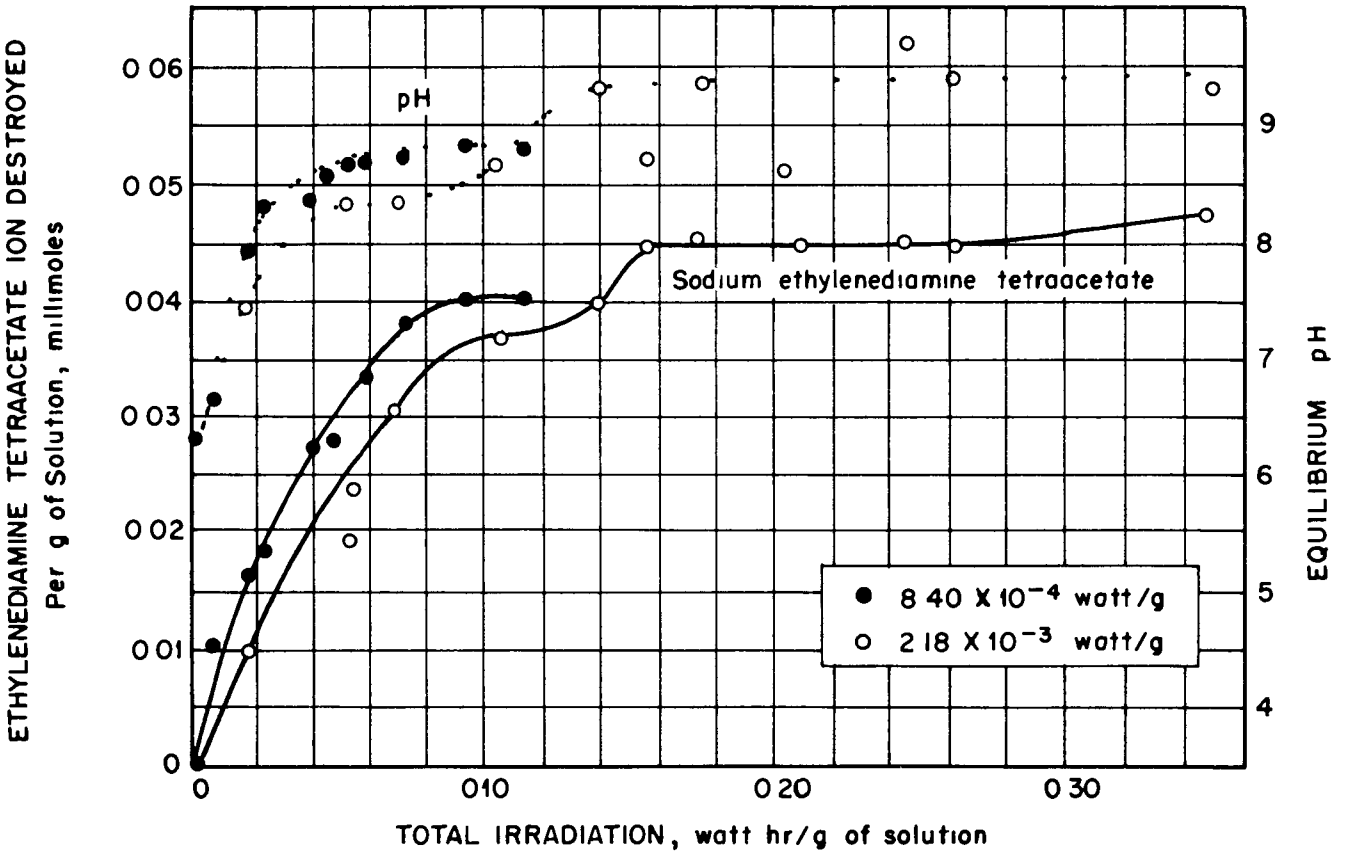

Fig 1 DECOMPOSITION OF SODIUM ETHYLENEDIAMINE TETRAACETATE UNDER IRRADIATION IN THE ABSENCE OF CATIONS OTHER THAN SODIUM

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In the first experiment (see Table I) in which the irradiation rate was 2 18 x 10^{-3} watt per gram of solution, 56, 74 8, and 42% of the barium, strontium, and cerium, respectively, had precipitated at the end of the 66 5-hr irradiation period The total energy absorbed by this sample was equivalent to 0 145 watt-hr per gram of solution Other effects on the solution were an increase in pH from 6 3 to 8 5, a rise in nitrite concentration from zero to 0 13 M, and a color change from water-white to yellow It was also found that 34% more acid was required to decrease the pH of the irradiated solution from 10 8 to 6 3 than was necessary for the original solution This would indicate the formation of additional weak acid and amino groups as decomposition products The irradiation data of the two aliquots of this solution, to which sodium bromide had been added, indicated that bromide ion was ineffective as a protective agent in preventing the irradiation decomposition of sodium ethylenediamine tetraacetate

In the second experiment, sodium ethylenediamine tetraacetate was initially destroyed at a rate of 0 62 millimole/watt-hr in a field of 8 40 x 10^{-4} watt per gram of solution (see Fig 2) After an irradiation of 0 2 watt-hr per gram, the concentration of the sodium ethylenediamine tetraacetate had decreased by approximately 60%, and its apparent rate of decomposition had approached zero It has not been determined as yet if the organic decomposition products are selectively oxidized in the later stages of irradiation and thus protect the original compound, or if the decomposition products absorb in the same spectrophotometric range as the original compound and are mistaken

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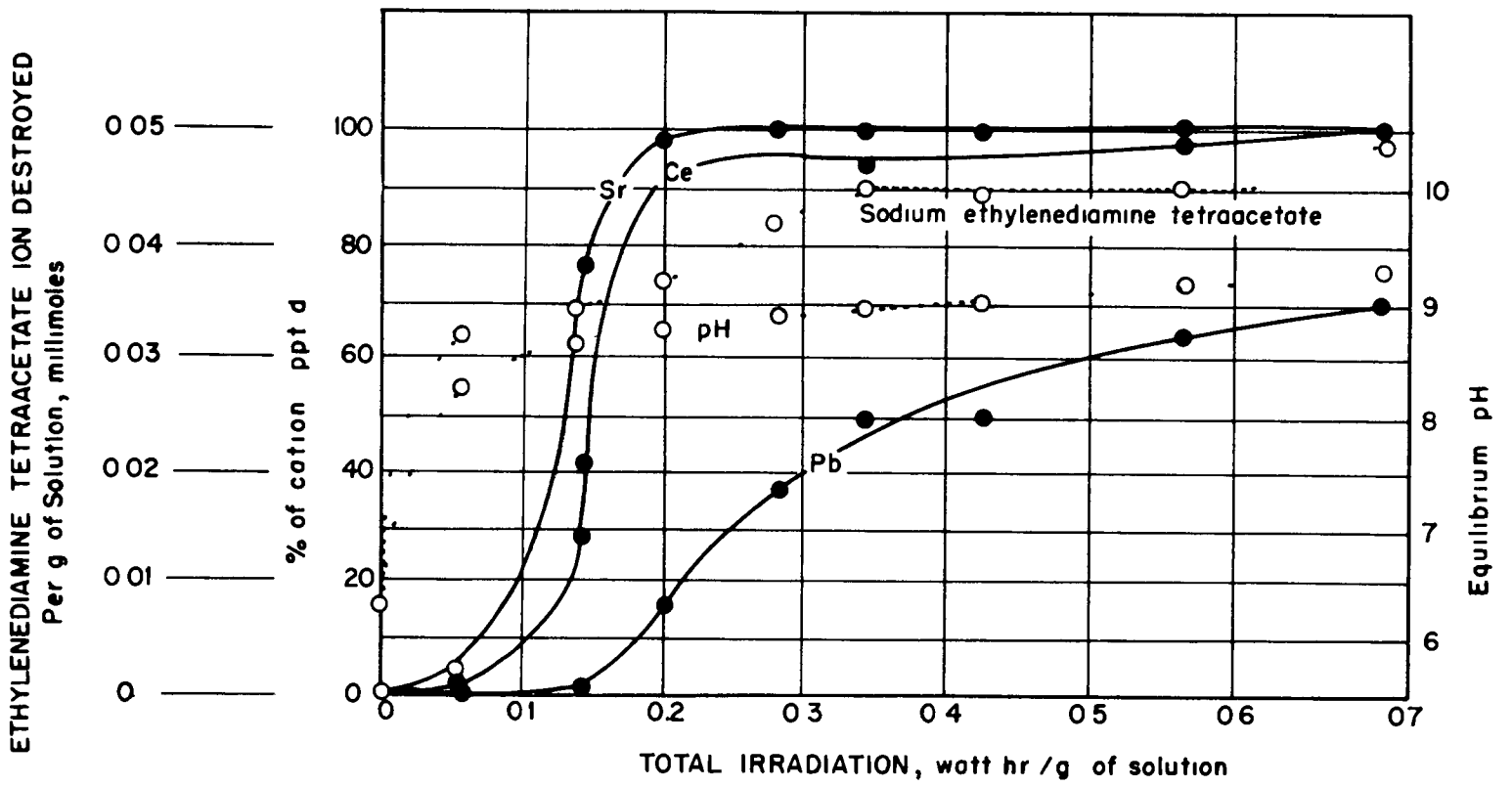

Fig 2 RADIATION STABILITY OF ETHYLENEDIAMINE TETRAACETATE UNDER IRRADIATION AT A RATE OF 8 40 X 10^{-4} WATT/GRAM IN THE PRESENCE OF CATIONS, PRECIPITATION OF CATIONS DURING THE IRRADIATION,

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Table I

Radiation Stability of Simulated Sodium Ethylenediamine Tetraacetate and Sodium Acetate Process Solutions

Irradiation rate = 2.18×10^{-3} watt/g.

Aliquot No	Irradiation time, hr	Total irradiation, watt-hr per g of solution	pH		NO_2^- formed, M	% of total precipitated			
			Initial	Final		Ba	Sr	Ce	Pb
1st Sodium Ethylenediamine Tetraacetate Experiment									
1*	24	0 052	6 11	8 05	0 02	0	0 74	NA**	NA**
2	66 5	0 145	6.24	8 50	0 12	56	74 8	42	NA
3*	72	0 157	6 24	8 53	0 12	98 4	98 4	99 5	NA
Sodium Acetate Experiment:									
1	24	0 052	5 00	5 08	0.0048	0	0	0	0
2***	24	0 052	4 92	5 00	0 0045	0	NA**	NA	0
3***	47	0 102	4 92	5 03	0 0087	0	NA	NA	0
4	72 5***	0 158****	5 00	5 18	0 0114	0	0	0	0
5***	74	0 161	4 92	5 13	0 0072	0	0	0	0

*Contained sodium bromide
**No analysis made
***Contained iron, nickel, and chromium
****Actually irradiated 91 hr at 1 74 x 10^{-3} watt per gram of solution, corrected to correspond with other data

for it in analysis The pH increased rapidly from 6 3 to 8 25 in the initial stages of irradiation at a rate similar to that noted in the control experiment and thereafter increased gradually to a final value of 9

After a total energy absorption of 0 2 watt-hour per gram of solution, the strontium was quantitatively precipitated Cerium determinations were not made in this range, but the results (see Fig 2) show that with a total radiation of 0 15 to 0 35 watt-hr per gram of solution, 95% of the cerium is precipitated The cerium percipitation curve was drawn to follow the strontium curve Lead was the last cation to precipitate, and at a total energy absorption of 0 70 watt-hour per gram of solution, only about 70% of it had precipitated

The retarded lead precipitation may be ascribed to any of several factors (1) the lead forms a stronger complex with ethylenediamine tetraacetate than the alkaline earth or rare earth ions and is therefore selectively complexed by the ethylenediamine tetraacetate remaining in solution (2) some of the organic decomposition products may form soluble lead complexes, or (3) lead, being amphoteric, become more soluble as the pH increases Again, the most rapid rise in pH, that is, from 6 3 to 8 25, occurred during the initial stages of irradiation, the pH then increased gradually to a final value of 9 over the range of energy absorption of 0 06 to 0 70 watt-hr per gram of solution The greatest rate of decomposition of ethylenediamine tetraacetate, 0 62 millimole/watt-hr , was coincindental with the first large increase in pH (see Fig 2)

In the absence of cations other than sodium, sodium ethylenediamine tetraacetate decomposed at a rate of 0 69 millimole/watt-hr in an irradiation field of 8 40 x 10^{-4} watt/g and at 0 55 millimole/watt-hr in a field of 2 18 x 10^{-3} watt/g The average of these two values, 0 62 millimole/watt-hr , is the same as the value obtained in the presence of cations other than sodium The slight differences in the decomposition rates from run to run may be accounted for by the variations in oxygen content caused by fluctuations in the flow of moist air through the samples rather than by differences in the irradiation rates

Sodium Acetate In the acetate series of runs no increase in nitrite concentration and no barium, strontium, cerium, or lead precipitation was observed at a total energy absorption of 0 16 watt-hr per gram of solution A slight rise in pH was noted (see Table I), but since the irradiated solution was not analyzed for acetate, it is not known whether this small increase in pH indicated that (1) acetate is more stable to radiation than ethylenediamine tetraacetate, or (2) the high concentration of acetate buffer prevents a large change in pH In addition, the organic salts of the cations, or their hydroxides and carbonates in the case of lead and cerium, would be less likely to precipitate at pH 5 0 than in the range 6 0 to 8 0 The presence of ferric, chromic, and nickelous ions in the system had no noticeable effect on the radiation stability of acetate

Part II. BECKMAN GLASS ELECTRODES

J H Pannell

Introduction

In many applications using complexing agents for fission product separations, it is necessary to adjust the pH of the solution The accuracy of pH determinations at high levels of radiation has been questionable in the past because of the meager information available concerning the dependability of the electrodes under these conditions In an effort to better evaluate the usefulness of pH electrodes in such high radiation fields, experiments were carried out with standard-size Beckman glass electrodes, using as a radiation source a solution of Ce^{144}-Pr^{144} with an activity of 0 36 curie/ml

Experimental

The electrodes tested were standard size, types 8990, 1190-80, and 290-1 Under process conditions the reference electrode could be connected by means of a salt bridge and thus not subjected to the full intensity of the radiation This principle was employed in these experiments by using a saturated KCl salt bridge terminating in a Leeds and Northrup junction (Corning 881 sealed into the tipe of a pyrex tube)

The irradiation was carried out in a pyrex vessel designed for remote manipulation of the radioactive solution, standard buffer solutions, and wash water The solutions were drawn into the vessel by suction and discharged

by gravity (see Fig 3) Since the pyrex vessel eventually became darkened and opaque from the radioactivity, liquid-level adjustments were observed through a 4-in thickness of lucite Electrodes and measuring equipment were interconnected by 25-ft leads

A solution containing 0 36 curie of Ce^{144}-Pr^{144} activity per milliliter was chosen as the irradiation source because of low intensity of γ radiation in its decay scheme[4] (Fig 4) From the diagram it is evident that the more

(4) B H Ketelle, Oak Ridge National Laboratory, unpublished data

penetrating β radiation originated with the 17 5-min Pr^{144} rather than with the 275-day Ce^{144} The maximum range[5] of the β radiation from Pr^{144} decay is

(5) W H Burgus, L Winsberg, J A Seider, and W Rubinson, in "Radiochemical Studies The Fission Products," National Nuclear Energy Series, Division IV, Vol 9, Paper 184, p 1195, esp p 1197, McGraw-Hill Book Company, Inc , New York (1951)

1 5 g /cm ^{2} aluminum or 1 5 cm of water As the radial depth of solution surrounding the electrode was about 1 1 cm , it effectively approached an infinitely thick source (Calculation of the dose is given below)

Initial experiments were carried out with a Beckman model H pH meter connected to a 10-mv Brown recorder, but excessive drift in the pH meter made the results difficult to interpret This instrument was later replaced

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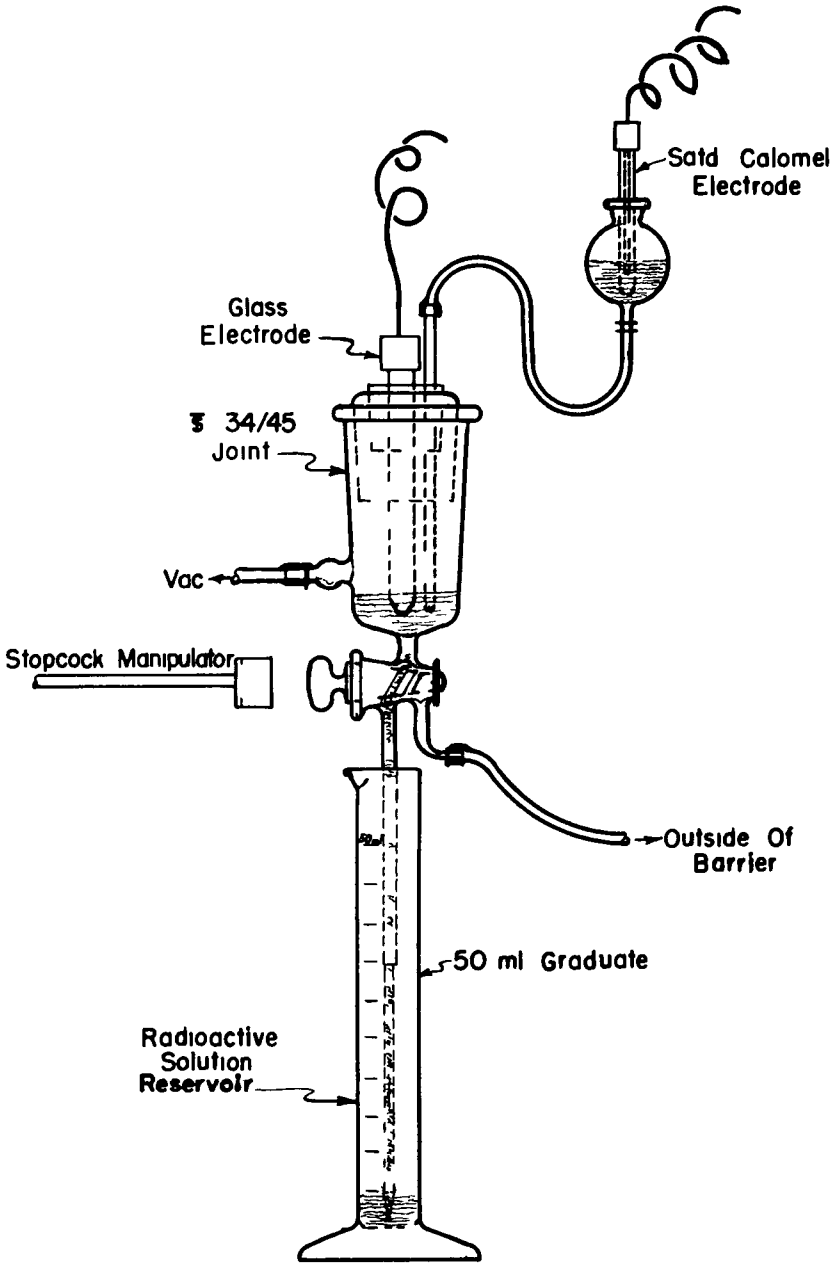

APPARATUS FOR REMOTE IRRADIATION OF GLASS ELECTRODES

Figure 3

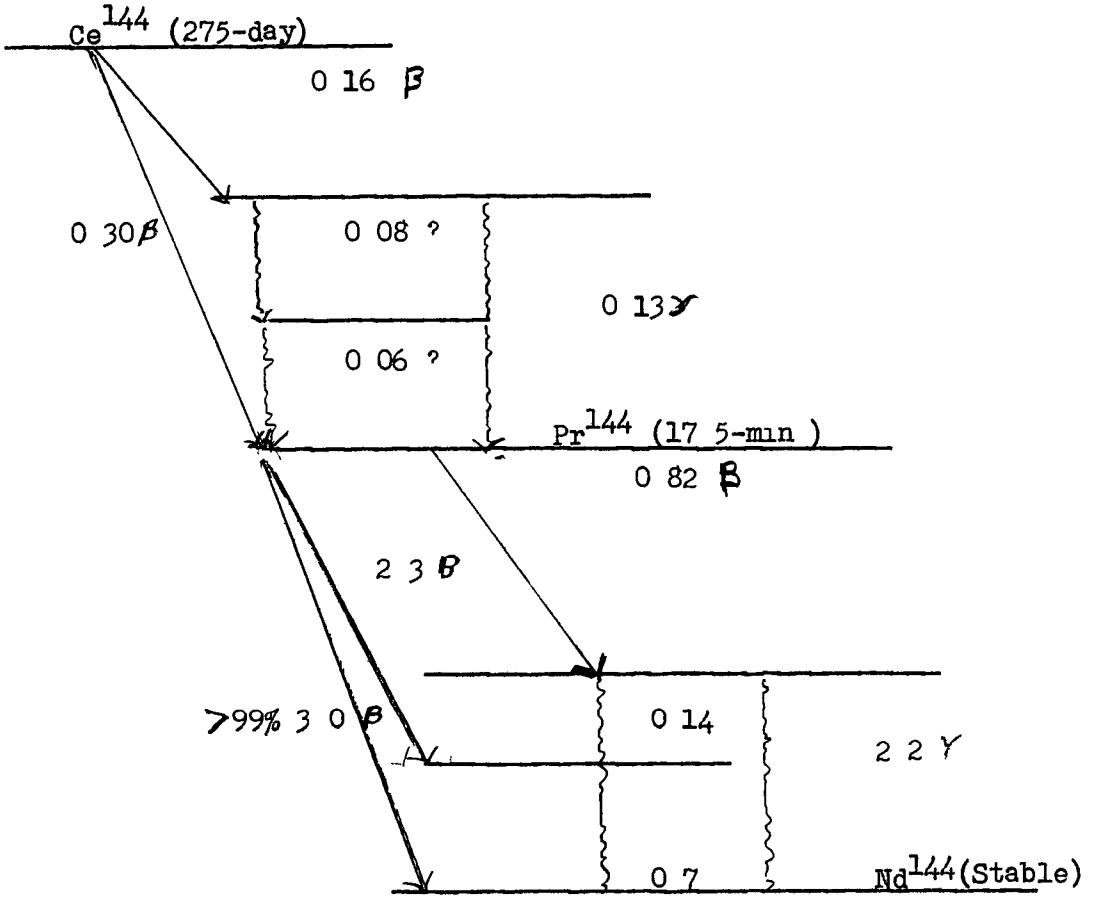

Fig 4
Decay Scheme of Ce144
(Energy units, Mev)

with a Beckman model RX electrometer The printed chart, however, could not be considered a valid indication of the condition and behavior of the glass electrode, since such uncontrollable variables as self-generated heat and radiation decomposition, inherent in the unbuffered solution itself, caused a decrease in volume with a corresponding rise in pH Therefore periodic checks with standard buffer solutions of pH 2 00 or 4 00 were made in order to verify proper functioning of the electrodes

Results

The first electrode tested was an older Beckman electrode similar to model 8990, but of unknown type and history After 44 hr of exposure, corresponding to 1 2 x 10^7 equivalent roentgens of irradiation, it showed a drop in emf of 0 10 volt in about 1 hr , thereafter giving a moderately steady, but erroneous, reading for an additional 36 hr , at which point exposure was stopped After thorough and prolonged cleaning in acid, the electrode still gave excessively high pH readings in buffer solutions of pH 2 0 and 7 0 Its d-c resistance, however, was 200 megohms, the same as before being irradiated

The second and third electrodes tested were Beckman type 1190-80, an improved general-purpose model of sturdy construction Electrode No 2 performed exceptionally well for eight days in the solution at pH 1 0 but then exhibited a sudden increase of emf corresponding to a pH of 0 0, after which it indicated gradually a still lower pH After being cleaned it continued to indicate hydrogen ion concentrations too high by 1 5 pH units at pH 4 00 and 7 00 Soaking in 0 1 N HCl was without beneficial results

Electrode No 3 was also satisfactory, and after operating continuously for three days gave a reading within 0 15 of the true pH (2 00) on buffer solutions Exposure of this electrode was stopped after six days

The fourth electrode to be tested was a Beckman type 290-1 with a drawn-down tip Use of such an electrode may reduce the dosage received by 0 1 N HCl contained within it, if this should appear desirable This electrode performed satisfactorily for four days

The data of Fig 5 show that long-period drifts sometimes occurred but were eventually followed by steady readings After standardization, the electrodes appeared to be sluggish in attaining their final potential, regardless of previous exposure This effect may have been due to partial dehydration of the glass electrode by an unknown concentration of salts in the cerium solution The upward pH trend measured by electrode No 3 was not anticipated, but its real nature is shown by the fact that correct readings were given with buffered standards Hence, it was the solution, not the electrode, that was changing This fact was confirmed when electrode No 3 was replaced A summary of the results is given in Table II

Table II

Stability of Beckman Glass Electrodes Under Irradiation

Electrode No.	Beckman type	Total exposure, rep	Exposure at which failure occurred, rep
1	8990	$2\ 2 \times 10^7$	$1\ 2 \times 10^7$
2	1190-80	$5\ 8 \times 10^7$	$5\ 2 \times 10^7$
3	1190-80	$3\ 9 \times 10^7$	___
4	290-1	$3\ 4 \times 10^7$	___

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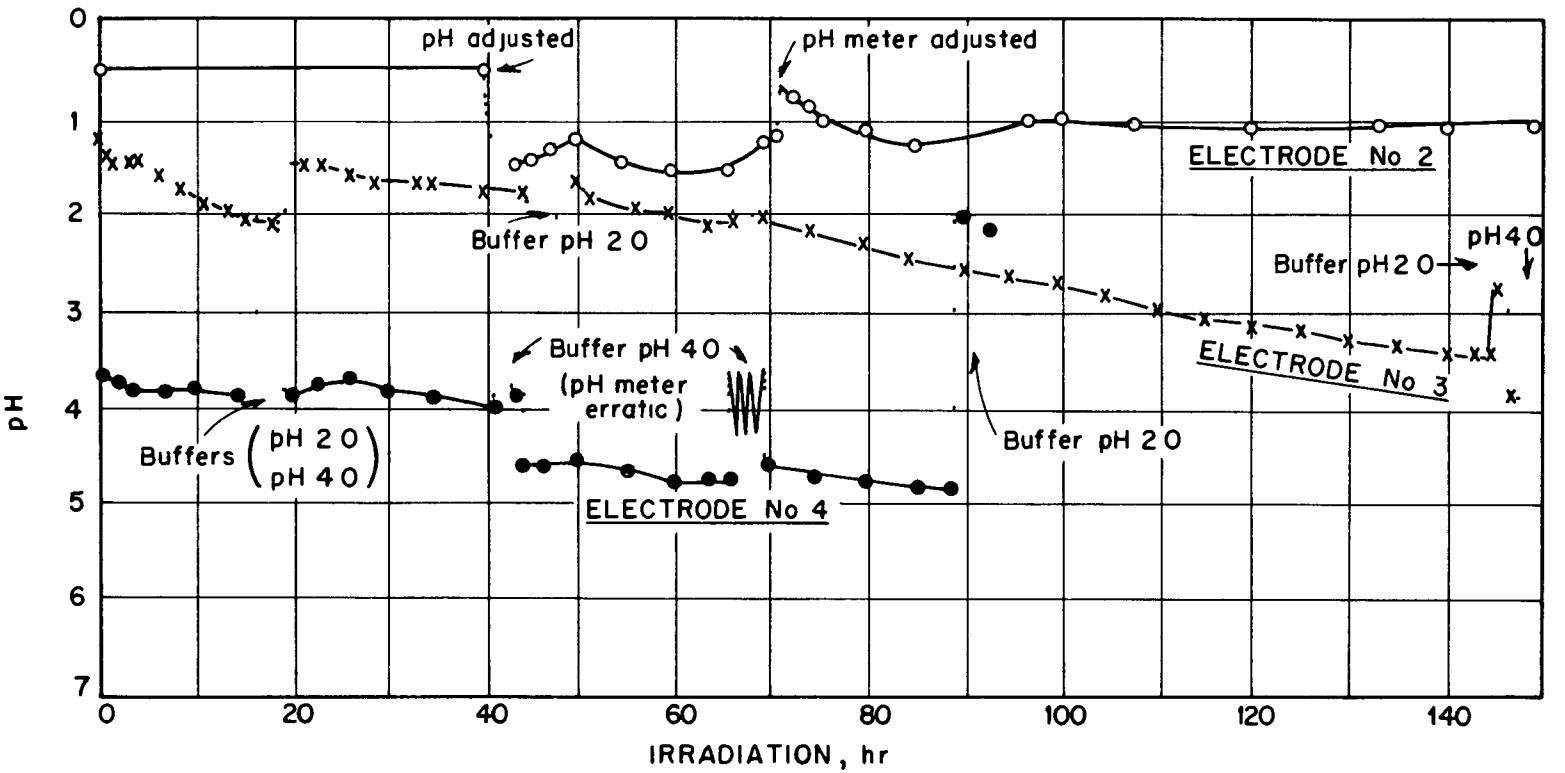

Fig 5 APPARENT pH vs TIME OF EXPOSURE FOR THREE GLASS ELECTRODES IN A SOLUTION CONTAINING 0 36 CURIE OF Ce^{144} - Pr^{144} PER MILLILITER

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Calculations

A rough approximation to the dose of radiation received by electrodes of standard size may be calculated by assuming the submerged portion to approximate a hemisphere 0 6 cm in radius The average energy[6] of the predominant β radiation from Pr^{144}, $\bar{E}_\beta$, is 0 41 x 3 0 = 1 25 Mev, for Ce^{144}, $\bar{E}_\beta$ = 0 30 x

(6) D Marinelli et al, Revs. Modern Phys, 19, 25 (1947)

x 0 30 = 0 09 Mev Since for an infinitely thick source the effective source thickness is directly proportional to $\bar{E}_\beta$, it is clear that radiation from Ce^{144} accounts for only about 8% of that impinging on the electrode

Application of the formula for μ, the absorption coefficient,

$$\mu = \frac{22}{E_{max}^{4/3}},$$

gives μ = 5.0 cm ^{2}/g for the 3 0-Mev β particles The mean thickness of water through which the radiation must travel can be calculated from the formula

$$t_{mean} = \frac{1}{\mu} \ln \frac{\mu t}{1 - e^{-\mu t}}$$

knowing that the maximum range is 1 5 g /cm ^{2}, [7] where t, the effective source thickness, is 1 5 This gives t_{mean} = 0 40 cm, corresponding to 27% of the maximum range Hence, if uniform loss of energy is assumed, the average β energy incident on the electrode may be considered to be 0 73 x $\bar{E}_\beta$ = 0 95 Mev

(7) A F Ried, "Detection and Measurement of Radioactive Tracers," pp 83-108, symposium by D W Wilson, A O C Nier, and S P Reimann, "Preparation and Measurement of Isotopic Tracers," J W Edwards, Ann Arbor, Mich (1946)

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