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M. H. Kurbatov, FuChun Yu, and J. D. Kurbatov

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Target Chemistry of Cesium; Isolation of Ba^{133,134}

M. H. KURBATOV, FU-CHUN YU, AND J. D. KURBATOV
The Ohio State University, Columbus 10, Ohio
(Received July 28, 1947)

Barium (Ba^{133,134}) obtained by dn and $d2n$ reactions of spectroscopically pure cesium chloride was separated in quantities of $<1\times10^{-9}$ gram without addition of common barium. The procedure studied involves adsorption of barium on hydrous ferric oxide under conditions at which cesium ions remain in solution. The effect of (a) pH of solution and (b) varying quantities of ferric hydrous oxide on the fraction of Ba adsorbed from solution containing $<10^{-9}$ g Ba, keeping other factors constant, showed that the fraction of Ba adsorbed, $y=k[Z(X-X_0)]^\lambda$, Z being the quantity of adsorbent (from 1×10^{-5} to 3×10^{-4} g atom Fe); X, the OH$^-$ concentration in solution (from 3×10^{-9} to 3×10^{-6}); X_0, the critical concentration of OH$^-$ necessary to maintain the adsorbent in the solid state. When pH was kept constant the value of λ for $y=k'Z^\lambda$ was found to be 0.35, and when the quantity of adsorbent was constant the λ for $y=k''(X-X_0)^\lambda$ was 0.33. The fact that the two experimental slopes were so nearly the same in spite of certain variations in experimental conditions is taken as support for two assumptions made in the derivation of the expression *viz.*, (1) the fraction of barium adsorbed from a very dilute solution depends on the quantity of adsorptive centers in the solid phase and (2) the quantity of adsorptive centers in the solid phase available for barium adsorption is proportional to the OH$^-$ concentration in solution, other factors being constant. Adsorption procedure is described.

INTRODUCTION

IN previous work it has been shown that absorbents such as hydrous ferric oxide will remove part of such divalent ions as strontium, barium, and radium from their solutions at any feasible low concentration if experimental conditions are appropriate.[1,2]

Consequently it was suggested that chemisorption might be applied first, to isolation, without carriers, of minute quantities of radioactive and stable species produced by nuclear transmutations, from elements of different atomic number and, second, to determination of quantities as low as 1×10^{-11} g atom, that is, quantities less than those measurable by the most sensitive previously known schemes.[3]

The adsorption of divalent ions on hydrous ferric oxide is influenced by such variables as pH, salt concentration, quantities of adsorbent and adsorbate, volume of liquid phase, temperature and duration of adsorption. However, the dependence of adsorption of divalent ions in extreme dilution on the above variables is insufficiently known especially for purposes of isolation, without carriers, of species produced by nuclear transmutations.

In the present work a scheme for isolation of Ba^{133,134} (produced by activation of cesium with 10.5-Mev deuterons) in quantities of less than 10^{-9} g has been studied with reference to its dependence on hydrogen ion concentration and quantity of adsorbent.

PROCEDURE

Ba^{133,134} as the chlorides were separated (as described later in this paper) in quantities of less than 10^{-11} g atom from the target material; the

[1] J. D. Kurbatov, J. L. Kulp, and Edward Mack, Jr., J. Am. Chem. Soc. 67, 1923 (1945).
[2] M. H. Kurbatov and J. D. Kurbatov, J. Am. Chem. Soc. 69, 438 (1947).
[3] M. H. Kurbatov and J. D. Kurbatov, Phys. Rev. 71, 466 (1947).

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TABLE I.

Fe g atom./exp.	0.1 N HCl ml	Water ml	1 N NH₄OH ml	0.1 N NH₄OH ml
6×10^{-4}	0.0	23.0	1.50	5.55
1×10^{-4}	16.7	6.3	1.60	5.90
1×10^{-5}	19.7	3.3	1.65	5.40

target being spectroscopically pure cesium chloride and the holder platinum. The purity of tracer (Ba[133] as chloride*) was confirmed by (1) evaporation of the whole tracer in a micro beaker and weighing, with the result that no weight could be detected to 10^{-6} g (10^{-8} g atom) and (2) by adsorption procedure indicating less than 10^{-9} g atom Ba. That is, 40 percent of the tracer solution was added to 1×10^{-5} g atom Fe, the solution titrated to pH 8, and the fraction adsorbed found to be 25 percent. Then ten percent of the residual solution after adsorption (7.5 percent of the total) was added to a fresh portion of iron and volume and pH adjusted as before. The second portion adsorbed was the same fraction, i.e., 25 percent, indicating the original concentration was in the region in which the fraction adsorbed is independent of concentration.[2]

The quantity of tracer used in individual adsorption experiments did not exceed 1×10^{-4} of the total tracer obtained after bombardment, that is not more than 10^{-13} g atom Ba. Also the bombarded target was spectroscopically pure cesium chloride so it contained less than 10^{-6} g barium per 0.1 g of activated material and this in turn was diluted to less than 10^{-10} g (or 10^{-12} g atom). Considering a maximum of 2000 counts used per adsorption experiment with a counter efficiency of 9 percent the amount of radioactive Ba[133] was of the order of 10^{-14} g atom.

The purity of the tracer with reference to radioactivity was verified by following its disintegration on an electrometer. The curve obtained corresponded to Ba[133] ($T = 38.8$ hours) and was the same as that obtained from a sample purified with stable barium carrier added.

For the adsorption studies on the effect of pH and quantity of adsorbent, in addition to the purified tracer solution just described, solutions of stable barium chloride, ferric chloride, hydro-

* Ba[134] is stable.

chloric acid and ammonia, were required. Spectroscopically pure barium chloride was diluted to 1×10^{-11} g atom/ml in $0.01N$ hydrochloric acid. Since the spectroscopic analysis indicated no impurities present to the extent of 10^{-5} g/g barium, the diluted barium could not contain more than 10^{-15} g atom/ml of impurities from the barium chloride. The water used in preparing all solutions was triple distilled and checked by pH measurement. The ferric chloride used as source of adsorbent was purified by repeated precipitation of the hydrous oxide at low pH, under which conditions divalent impurities are removed in solution.

The ammonia solutions used in titrating the samples were prepared by ammonia gas transfer from concentrated solutions into triple-distilled water in a closed vessel.

For the individual adsorption determinations under a given set of conditions a series of samples was made up of stable barium, tracer, and ferric chloride. The required volumes of these solutions having been transferred into outside ground weighting bottles, water or hydrochloric acid or both were added to adjust salt concentration and volume. Then the samples were rapidly titrated with ammonia to the predetermined pH and samples closed and set aside to allow adsorbent to settle. After a given time interval, portions of solution were removed by pipette, these portions evaporated in 4-cm Petri dishes, and the activity measured on a G-M counter.

More specifically, in the case of the determination of pH effect the factors which were held

TABLE II. Effect of amount of hydrous ferric oxide on adsorption of barium.

Constant factors: Temp. $= 25° \pm 1°$; total Ba $= 1 \times 10^{-11}$ g atom, pH $= 8.01 \pm 0.01$; NH₄Cl conc. $= 5.4 \times 10^{-2}$ N; Vol. $= 32.3 - 34.4$ ml.

Total Fe in g atom	Ba adsorbed in 4 hours g atom $\times 10^{-12}$	Total Ba left in sample after 10 ml sol'n. removed g atom $\times 10^{-12}$	Ba adsorbed after total of 23 hours g atom $\times 10^{-12}$
1×10^{-5}	2.41	7.71	4.42
2×10^{-5}	2.88	7.87	5.51
3×10^{-5}	3.40	7.96	5.67
6×10^{-5}	4.37	8.29	6.84
1×10^{-4}	5.92	8.82	7.61
2×10^{-4}	6.85	9.11	8.40
3×10^{-4}	7.95	9.37	8.98
6×10^{-4}	9.20	9.76	9.61

constant are shown in Table II. Each sample was made up with 1-ml barium chloride solution containing 1×10^{-11} g atom Ba in 0.01 N HCl, 1 ml FeCl$_3$ solution containing 1×10^{-4} g atom Fe, 1-ml tracer in 0.01 N HCl and 5 ml of water. Then each was titrated to a different pH using both 0.1 N and 0.01 N NH$_4$OH, so that the final volumes were all within the range of 12 to 13 ml.

In the case of the experiments using different quantities of adsorbent, the samples were made up with each containing 1 ml of barium chloride solution having 1×10^{-11} g atom Ba in 0.01 N HCl, 1 ml of tracer in 0.01 N HCl, and 1 ml ferric chloride solution containing the various quantities of iron shown in Table I. Since the varying quantities of ferric chloride meant varying amounts of acid from hydrolysis, the more dilute iron solution had acid added to compensate for the greater acidity in the more concentrated iron solutions and varying amounts of water were added to maintain constant final volume. All then were titrated to the same pH.

Typical samples were as shown in Table I.

DEPENDENCE OF ADSORPTION OF BARIUM IN EXTREME DILUTION ON HYDROGEN ION CONCENTRATION AND QUANTITY OF ADSORBENT

The adsorption of divalent ions on a given quantity of hydrous ferric oxide may be looked upon as competitive with all positive ions present in solution. With very dilute solutions of divalent ion the change in hydrogen ion concentration in solution—resulting from an adsorption—would not be measurable. However, as the pH of the solution is changed by the addition of an appropriate reagent it would be expected that the amount of adsorption would be inversely related to the hydrogen ion or directly related to the hydroxyl ion concentration in solution.

If we assume that (1) the fraction of barium adsorbed (y) depends only upon the quantity of adsorptive centers in the solid phase when other factors such as salt concentration, temperature, volume, and duration of adsorption are held constant (in dilution below 10^{-10} g atom/ml the fraction adsorbed is known to be experimentally independent of total barium) and (2) the available quantity of adsorptive centers (S) in the solid phase for a given quantity of Fe (Z) is
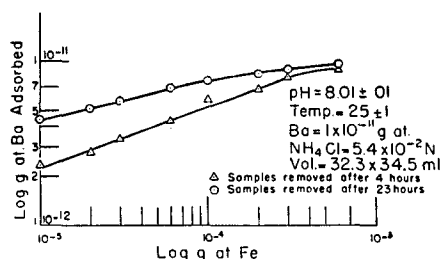

FIG. 1. Effect of amount of hydrous ferric oxide on adsorption of barium.

inversely proportional to hydrogen ion concentration, or directly proportional to the hydroxyl ion concentration in solution, that is,

$$S/Z = C[\text{OH}^-],$$

where C is a proportionality constant; then since both S and Z refer to the solid phase the effective [OH$^-$] is that above a critical value at which the solid phase can be maintained. This critical [OH$^-$] is designated X_0 and the higher [OH$^-$] as X so the above expression becomes

$$S = KZ(X - X_0).$$

If a fraction y of barium is adsorbed in the presence of a quantity S of adsorptive centers in the solid phase, then an increase of S by dS would give rise, according to (1), to a proportionate increase in y by dy. Therefore,

$$\frac{dy}{y} = k' \frac{dS}{S}.$$

Integration gives

$$\ln y = \lambda \ln[Z(X - X_0)] + \text{const.},$$

TABLE III. Effect of pH on adsorption of barium ion by hydrous ferric oxide.

Constant factors: Temp., 25°±1°; total Ba, 1×10^{-11} g atom; Fe, 1×10^{-4} g atom; NH$_4$Cl conc., 2.5×10^{-2} N; Vol., 13.3±0.3 ml. Duration of adsorption ~3¼ hours.

pH	Activity in 5 ml of solution	Tracer in exp.	Ba adsorbed
	Counts/min.	Counts/min.	g atom $\times 10^{12}$
5.48	303	878	1.02
6.00	290	882	1.45
6.53	259	884	2.32
6.89	239	858	2.79
7.48	166.5	853	4.82
7.98	114.5	880	6.61
8.45	26.8	856	9.15

and

$$y = k[Z(X - X_0)]^\lambda.$$

From this expression it follows that a log-log plot of adsorbed barium against total iron present when pH and other factors are constant should give a straight line.

EXPERIMENTAL RESULTS

The effect of varying the quantity of adsorbent while keeping the pH, total barium, salt, volume, and duration of adsorption constant is shown in Table II and Fig. 1.

The range of iron quantities which could be used readily was rather limited. The lower limit was an amount which would settle well under the conditions used and the upper limit an amount which would introduce acid in quantity not too much in excess of that used in the other series of experiments (to keep salt concentration comparable). As a check on the results obtained for a four-hour interval a second portion was removed from each sample twenty-three hours after the titration.

Within the range of iron quantities from 1×10^{-5} to 3×10^{-4} g atom Fe the log-log plot of adsorbed barium vs. iron is an experimentally straight line, in agreement with the equation, but above this range the curve breaks. Extrapolation of the straight line would indicate 100 percent adsorption by 5.5×10^{-4} g atom of Fe but 6×10^{-4} g atom Fe does not adsorb all the barium even at the longer time interval.

The curve at 23 hours verifies the fact that the curve at 4 hours is not a straight line throughout and that the range of iron quantities which gives a straight line is dependent on duration of adsorption in addition to other factors mentioned.** In addition, from comparison of the two curves on Fig. 1, it can be seen that (with extreme dilutions

of barium and limited quantities of hydrous ferric oxide) the adsorption occurs sufficiently slowly to show its dependence on time. Equilibrium is not established in a period of a few hours.

In Table III and Fig. 2 may be seen the result of changing the pH of the solution on barium adsorption when the total barium, iron, salt, volume, and duration of adsorption were kept constant. The log-log plot is an experimentally straight line over the range of pH values used (pH 5.5 to 8.5).

Extrapolation of this curve indicates that at pH 3.3 ($2 \times 10^{-11}[OH^-]$), the region in which iron precipitates, the amount of adsorption would be two percent, however, since the iron does not settle well enough at this pH for accurate measurements, the deviation from a straight line was not established. On the other end of the curve extrapolation indicates 100 percent adsorption at 3.5×10^{-6} $[OH^-]$ or pH 8.56 and this is experimentally not observed. An explanation of this is the time factor. So the application of the equation for pH effect must be considered as limited to about the range of $[OH^-]$ studied. It is to be noted that the value of X_0 (2×10^{-11}) becomes insignificant in this range.

The slope of the straight line part of the curve of the "iron effect" is 0.35 while that of the "pH effect" curve is 0.33. Considering the differences in volume and some experimental variations in salt concentrations and time intervals, the similarity in slopes is taken as supporting the assumptions made in the derivation of the equation.

TARGET CHEMISTRY OF CESIUM ACTIVATED WITH DEUTERONS

The bombarded cesium chloride was allowed to stand for several hours for disintegration of the radioactive chlorine.
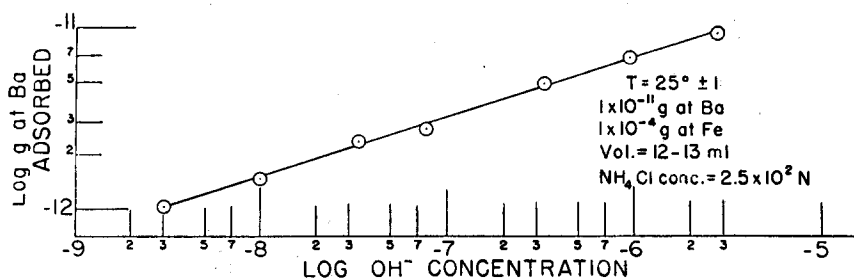

FIG. 2.

Plot labels: Log g at Ba ADSORBED (vertical axis); LOG OH⁻ CONCENTRATION (horizontal axis). Annotations: T = 25° ± 1; 1×10^{-11} g at Ba; 1×10^{-4} g at Fe; Vol. = 12–13 ml; NH_4Cl conc. = 2.5×10^2 N

** The short half-life of the tracer required study of adsorption over short time intervals.

The target material was then washed from the platinum holder with triple-distilled water, dissolved in hydrochloric acid ($pH \sim 2$) and filtered through analytical paper. The impurities insoluble in hydrochloric acid were rejected (see Fig. 3). To the acid filtrate was added 1×10^{-3} g atom iron as ferric chloride and the solution titrated with ammonia to pH 10. The filtrate from this was rejected.

The precipitate containing 91.5 percent of the active barium was dissolved in acid and the procedure repeated twice.

The additional loss of 1.8 percent of active barium was less than previously lost because of lower salt concentration and volume.

Potassium, activated by deuterons, was purified by similar adsorption procedure, and ~ 300 counts added to the barium[133,134] as a tracer for monovalent ions (Cs) that might be present in the barium solution.

The adsorption procedure with hydrous ferric oxide was carried out again.

Finally the iron was precipitated at pH 5.4, and the filtrate containing 83.1 percent of the initial barium activity was freed from salt by sublimation, dissolved in 0.01 N HCl, filtered, the operation repeated, the sample weighed and found to contain no weighable material.

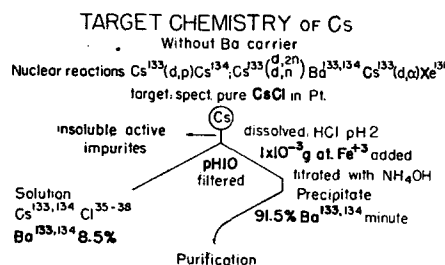The active material was dissolved in 0.01 N HCl and diluted 10^4 times for use as tracer. It is
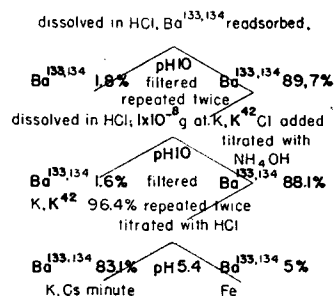

FIG. 3a.

FIG. 3b.

assumed that the tracer contained minute quantities of potassium and cesium.