micron diameter, or 5×10^{-9} lumen. The unit is small, rugged, and self-contained, incorporating suitable circuits for checking the operation of the vacuum tube, the condition of the phototube and the smoke cell, the scaling circuits and the batteries.

Penetration measurements with this instrument are self-consistent, and agree well with those obtained with instruments developed elsewhere during the last four years. The instrument can be calibrated to measure smoke concentrations. It is applicable to a wide range of uses in colloidal chemistry and photometry.

Evanston, Illinois Received July 22, 1946

[Contribution from the Ohio State University]

Absorption Isotherm for Determination of Barium in Quantities as Low as 10^{-10} Gram Atom

By M. H. Kurbatov and J. D. Kurbatov

Introduction

There is an excellent method for the determination of small quantities of radioactive atoms using coincident counting technique.[1] However, the determination of *stable* nuclei in such small quantities as those formed during activation processes and accompanying radioactive nuclei is not known. Specifically, the determination of stable isotopes in quantities below one microgram is the object of the present work.

Quantities of the divalent ions of barium, strontium, and some others, which lie beyond the range of usual analytical methods are readily adsorbed from solution by hydrous oxides in amounts varying with concentration of divalent ions. So it is plausible to suggest using the adsorption isotherm as a means of determining unknown quantities, with the limitation that the reference isotherm for a given ion should be obtained with a slope which is not unity for only then is the fraction adsorbed a measure of concentration.

Various hydrous oxides which may be prepared in solutions and maintained without change in adsorptive surface area during experiments, can be offered as adsorbents.

Since some information was previously obtained on adsorption of barium (mainly in conventional quantities) on hydrous ferric oxide, this combination of adsorbate and adsorbent was chosen for study at very low concentrations.[2]

Experimental

Chemisorption of quantities of less than one microgram is relatively easily measured using radioactive tracers. Thus the proposed method is dependent, first, on the existence of radioactive isotopes of divalent elements with appropriate half-life and radiation intensity, and second on preparation of a tracer of high specific activity so that the weight of an isotope added as a tracer, is negligible compared to the amount of inactive ion being traced. Therefore a parent material differing in atomic number from the tracer element is the more advantageous for such a study.

The radioactive isotope, Ba^{133}, of half-life 38.8 hours was selected as tracer. It was separated without carrier after deuteron bombardment of spectroscopically pure cesium chloride. The target chemistry is described elsewhere.[2] The purified Ba^{133} in the form of chloride was diluted with 0.01 *N* hydrochloric acid 1×10^4 times and one ml. of tracer was used per experiment. Since the bombarded cesium chloride cannot contain more than 1×10^{-6} g. of barium, the one ml. of tracer can have no more than 1×10^{-10} g. of common barium. On the other hand, the quantity of radioactive Ba^{133} per experiment was less than 1×10^{-12} g., since it produced on an average 2,000 counts with a counter efficiency of about 16%.

The data described later were obtained with a high rate counter having an electronic recorder which allows reading the number of discharges on neon lamps instead of a dial recorder. Consequently the fluctuation and correction due to the dead interval of the dial recorder was eliminated.[3]

The resolving time of the Geiger–Mueller counter used did not exceed 1×10^{-4} sec. Therefore variations in the experimental data due to the resolving time of the counter was less than 1% cent in the range of activities measured.[4]

In addition, the counter data given in the following tables are mean values obtained from decay curves for each individual sample. Thus the final figures presented are averages corrected against fluctuations.

The chemisorption procedure consists in first establishing a reference isotherm with known concentrations of barium under a given set of conditions and then carrying out the adsorption of an unknown quantity under identical conditions, determining the fraction adsorbed and using it to read the unknown value from the isotherm.

The reference isotherm is established as follows:

(a) A series of barium chloride solutions of known concentrations, (from 10^{-8} to 10^{-11} g. atoms per ml.) is made up by repeated dilution with hydrochloric acid, usually 0.01 *N* and not less than 0.001 *N*, of an analyzed solution of barium chloride. (b) A tracer solution is is made in dilute hydrochloric acid 0.01–0.001 *N*, so that one ml. of solution contains adequate activity for accurate measurement of a portion of the solution after absorption and after several days of disintegration. (c) A ferric chloride solution of known concentration (usually 1×10^{-5} g. atom of iron per ml. of solution) is freshly prepared in dilute hydrochloric acid such that one or two ml. of this solution contain the amount of iron to be used in each adsorption experiment.

It has been shown that even extremely dilute solutions of barium in 0.01 *N* hydrochloric acid, in new glass vessels, maintain experimentally constant molarity for the duration of an experiment. Freshly redistilled water checked by *p*H was used for the experiments.

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(1) L. G. Elliott and M. Deutsch, *Phys. Rev.*, **64**, 321 (1943).

(2) J. D. Kurbatov, J. L. Kulp and Edward Mack, This Journal, **67**, 1923 (1945); other references in this paper.

(3) L. I. Schiff, *Phys. Rev.*, **50**, 88 (1936).

(4) J. D. Kurbatov and H. B. Mann, *ibid.*, **68**, 40 (1945); J. D. Kurbatov and G. K. Groetzinger, *ibid.*, **69**, 253 (1945).

The samples for adsorption are prepared by introducing known quantities of (a) the stable barium solutions, (b) the tracer solution and (c) the ferric chloride solution into tall-form (outside ground) weighing bottles. In order to adjust salt concentration and volume of samples as desired, hydrochloric acid or water is sometimes added to each sample of a series. Thus, the series of adsorption samples have experimentally constant iron, acidity and volume. The samples are then titrated rapidly with ammonia to the selected *p*H and set aside to allow the iron to settle. (If a sample is overtitrated it is discarded, not back titrated, because the increased amount of barium adsorbed at the higher *p*H is not desorbed rapidly and also the final volume and salt concentration are not comparable to other samples.)

After the precipitated iron with the adsorbed barium settles, a portion of the supernatant liquid is pipetted, the period between the completion of the titration and sampling being the same for all samples. The samples pipetted (usually 5 or 10 ml. of a total of 10 or 30 ml., respectively) are then evaporated to dryness in Petri dishes and their activities measured on a Geiger-Mueller counter.

The total activity and barium left in solution is then calculated and the amount of adsorbed barium obtained by difference. The validity of this determination of adsorption by difference has been checked repeatedly by measurement of the activity of the redissolved iron—in which case the recovery is 100 ± 2%.

A typical set of experimental conditions for determining an isotherm are those for the isotherm at *p*H 8 with ammonium chloride concentration of 1.14×10^{-2} *N*.

Each of six samples contained: 1 ml. of stable barium chloride solution (sample 1, 1×10^{-6} g. atoms of barium; sample 2, 1×10^{-7} g. atoms of barium; . . . sample 6, 1×10^{-11} g. atoms of barium; all in 0.01 *N* HCl); 1 ml. of ferric chloride solution (1×10^{-5} g. atoms of iron in 0.01 *N* hydrochloric acid); 1 ml. barium tracer (as barium chloride in 0.01 *N* hydrochloric acid); 5 ml. of 0.01 *N* hydrochloric acid; 8 ml. total volume before titrating.

These samples were titrated using first 1.1 ml. of 0.1 *N* ammonium hydroxide and the titration finished at once using about 1.5 ml. of 0.01 *N* ammonium hydroxide to bring the solution to *p*H 8. The samples were then closed and allowed to stand fifteen minutes to settle. When opened, 5 ml. of clear solution was pipetted, evaporated and activity measured. After pipetting the *p*H of samples was checked.

Experimental Results

When the quantity of adsorbent, hydrous ferric oxide, is as low as 1 or 2×10^{-5} g. atoms of iron and the *p*H is 8, the ratio of adsorbed barium to total barium increases with dilution until the total quantity of barium is 1×10^{-9} g. atoms. With more dilute solutions the adsorption ratio becomes experimentally constant, that is, the adsorption approaches Henry's law.

Table I, parts A and B, gives the data on adsorption of barium at *p*H 8 using two different quantities of adsorbent and different salt concentrations.

With similar volumes of liquid phase and identical temperature and *p*H the change in quantity of adsorbent from 1 to 2×10^{-5} g. atoms of iron is experimentally insufficient to lower the order of magnitude of barium concentration at which Henry's law begins to apply.

The two isotherms, Fig. 1, are experimentally parallel.

TABLE I

ADSORPTION OF BARIUM ON HYDROUS FERRIC OXIDE AT *p*H 8 AND 25°

Total g. at. Ba	Total activity, counts/min.	Activity in soln. after adsorp., counts/min.	% Ba adsorbed
Part A: Fe = 1×10^{-5} g. atom; final vol. = 10.60 to 11.2 ml.; NH_4Cl concn. = 1.14×10^{-2} *N*			
1.00×10^{-6}	1030	960	6.8
1.00×10^{-7}	1025	830	19.0
1.00×10^{-8}	1020	737	27.7 (?)
1.00×10^{-9}	1020	774	24.1
1.00×10^{-10}	1000	753	24.7
1.00×10^{-11}	1015	762	24.9
Part B: Fe = 2×10^{-5} g. atom; final vol. = 11.25 to 11.35 ml.; NH_4Cl concn. = 6.03×10^{-3} *N*			
1.00×10^{-7}	1040	751	27.9
1.00×10^{-8}	1070	651	39.2
1.00×10^{-9}	1075	618	42.6
1.00×10^{-10}	1065	621	42.2
1.00×10^{-11}	1050	624	41.8
1.00×10^{-12}	1055	607	42.5
Part C: Fe = 6×10^{-5} g. atom; final vol. = 33.45 to 33.50 ml.; NH_4Cl concn. = 6×10^{-3} *N*			
3.00×10^{-8}	1035	650	37.2
3.00×10^{-9}	1030	620	39.8
3.00×10^{-10}	1025	568	44.6
3.00×10^{-11}	1025	560	45.4

Decreasing the amount of adsorbent below 1×10^{-5} g. atoms of iron magnifies experimental errors when using the technique described. Contrary to this, the simultaneous increase of adsorbent and volume of liquid phase, decreases errors and also allows an extension of the determination of barium to 3×10^{-10} g. atom (Part C, Table I).

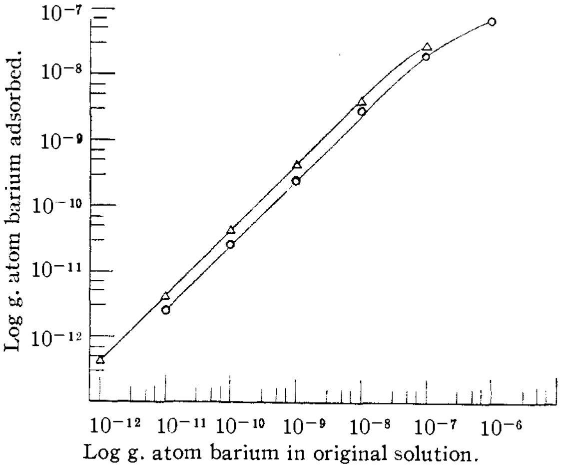

Fig. 1.—Adsorption isotherm of barium: *p*H 8.0; temp., 25°; ○, Fe = 1×10^{-5} g. atom; △, Fe = 2×10^{-5} g. atom.

Another approach to an extension of the region of concentrations of barium in which the isotherm has a slope less than unity, is the lowering of *p*H. In Table II are given the results of adsorption of barium at *p*H 7.5.

Table II

Adsorption of Barium on Hydrous Ferric Oxide at pH 7.5 and 25°

Fe = 1 × 10^{-5} g. atm.; final vol. = 10.6 to 11.2 ml.; NH_4Cl concn. = 1.06 × 10^{-2} N.

Total g. atom Ba	Total activity, counts/min.	Activ. in soln. after adsorption, counts/min.	% Ba adsorbed
1.99 × 10^{-6}	620	608	4.2
5.98 × 10^{-7}	615	572	7.0
1.99 × 10^{-7}	700	643	8.2
5.98 × 10^{-8}	730	658	9.8
1.99 × 10^{-8}	710	633	10.9
1.99 × 10^{-9}	708	625	11.7
1.00 × 10^{-9}	705	621	11.9
1.00 × 10^{-10}	770	646	16.1
1.99 × 10^{-11}	995	830	16.5
1.00 × 10^{-12}	766	641	16.3

Comparing the above results with those given in Part A, Table I, it may be seen that the decrease in pH allows extension of the determination of barium to 1 × 10^{-10} g. atom. The isotherm at pH, 7.5 is given in Fig. 2.

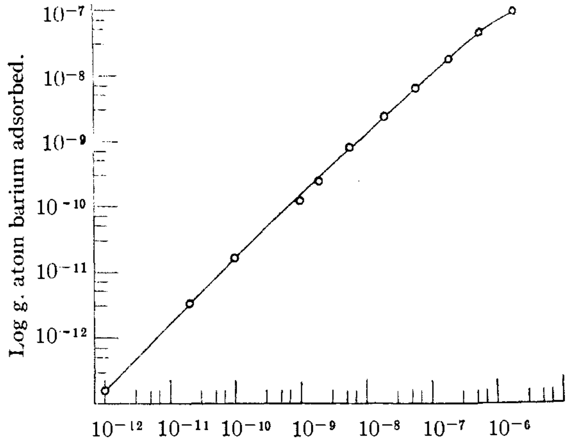

Fig. 2.—Adsorption isotherm of barium: pH 7.5; temp., 25°; Fe = 1 × 10^{-5} g. atom.

A significant factor affecting the dilution at which the adsorption ratio becomes constant is the salt concentration, a minimum of salt being advantageous. Table III shows that a two and a half fold increase of salt concentration with 10^{-9} to 10^{-11} g. atom of barium, results in a constant fraction adsorbed at the higher salt concentration while with the lower concentration of salt the fraction adsorbed varies to 1 × 10^{-10} g. atom of barium even at pH 8.

Table III

Effect of Salt on Adsorption of Barium on Hydrous Ferric Oxide

pH = 8; T = 25°; Fe = 1 × 10^{-5} g. atom.; final volume = 10.5 to 11.0 ml.

Total g. at. Ba	NH_4Cl 4.4 × 10^{-3} N % Ba adsorbed	NH_4Cl 1.14 × 10^{-2} N % Ba adsorbed
1.00 × 10^{-9}	24.3	24.1
1.00 × 10^{-10}	26.1	24.7
1.00 × 10^{-11}	26.6	24.9

In Fig. 3 the effect of pH is shown at two salt concentrations with other factors constant, the volume being about 33 ml. In the narrow range of pH selected the semilog plots of hydrogen ion concentration $vs.$ fraction of barium adsorbed are not parallel. That is, the effect of change in salt is greater in the lower pH region.

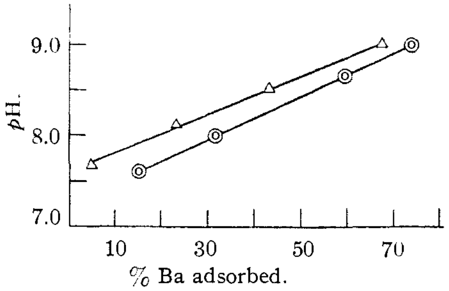

Fig. 3.—Effect of pH on adsorption of barium at two salt concentrations: total Ba = 1 × 10^{-11} g. at.; Fe = 2 × 10^{-5} g. at.; ◎, NH_4Cl = 3.8 × 10^{-3} N; △, NH_4Cl = 3.3 × 10^{-2} N.

In Fig. 4, the upper curve of Fig. 3 is compared with that obtained with one-third the concentration of salt (instead of one-tenth as in Fig. 3) with an additional change in the volume and amount of adsorbent. Again the difference in amount of adsorption under the two sets of conditions is greater in the lower pH range.

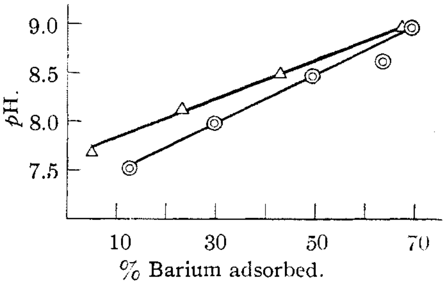

Fig. 4.—Effect of pH on adsorption of barium: ◎, Fe = 1 × 10^{-5} g. atom; vol., 10 ml. NH_4Cl = 1.1 × 10^{-2} N; △, Fe = 2 × 10^{-5} g. atom; vol., 33 ml. NH_4Cl = 3.3 × 10^{-2} N.

These figures (3 and 4) indicate that at the lower pH there is greater sensitivity to other factors and the procedure requires over-all more precise control.

Acknowledgment.—It is a great pleasure to express our indebtedness to Professor Edward Mack, Jr., for his interest and support in this research. The grant in aid obtained from the Alumni Foundation of The Ohio State University is deeply appreciated by the authors.

Summary

The data presented show that an adsorption isotherm for barium on hydrous ferric oxide can

be obtained with a slope less than unity for quantities of barium as low as 10^{-10} g. atom, and can therefore be used for analysis of barium chloride solutions containing amounts of barium down to that order of magnitude.

However, the experimental procedure involves some difficulties since it requires constant *p*H, volume and salt concentration for a whole series of samples in addition to specific techniques in chemical manipulation with the small quantities of adsorbent and adsorbate indicated. It necessitates that all Geiger counter measurements be carried out over a sufficient interval of time to obtain mean values of each individual determination from the decay curve. In this way fluctuation of background, change in sensitivity of Geiger–Mueller tubes and variations due to geometry of samples are eliminated. A single measurement of tracer for a given experiment is insufficient for the required exactness.

Some of the conditions which are desirable using the techniques described are as follows:

(a) ***p*H.**—A *p*H of not greater than 8 and preferably as low as 7.5 (or possibly even less if a corresponding increase in adsorbent were used) is favorable.

(b) **Salt.**—The ammonium chloride concentration should be kept as low as is possible considering the acidity necessary for stability of the original dilute barium, tracer and iron solutions.

(c) **Volume.**—Total final volume (after titration) of less than 10 ml. is not to be desired and a volume of around 30 ml. seems to result in increased accuracy (as compared to 10 ml.) in manipulation. This larger volume also makes possible lower salt concentrations.

(d) **Quantity of Adsorbent.**—One or 2×10^{-5} g. atom of iron as hydrous oxide is sufficient for 10-ml. samples and as high as 6×10^{-5} g. atom of iron have been used for 30-ml. samples. Quantities below 1×10^{-5} g. atom of iron do not settle well so cause errors in adsorbent pipetted with solution. A quantity of the order of 6×10^{-5} g. atom of iron (other conditions being as above) results in adsorption of 40% or more leaving only 60% or less in solution and since it is the activity of a portion of the solution which is measured, the accuracy of the measurements decreases rapidly beyond this ratio. Therefore quantities of from 1 to 6×10^{-5} g. atom of iron, with other conditions as described, are suggested.

Columbus, Ohio Received July 5, 1946

[Contribution from the School of Chemistry of the University of Minnesota]

The Mechanism of Emulsion Polymerizations. II. The Effect of Oxygen on the Emulsion Polymerization of Styrene[1]

By I. M. Kolthoff and W. J. Dale

Recently Barnes[1a] has interpreted the dualistic role of oxygen in the catalyst-free photo- and thermo-polymerizations, and also the catalyzed thermal polymerizations of vinyl compounds. Under such conditions an induction period is found during which the oxygen reacts with one or more constituents of the system with formation of peroxides. The peroxide acts as a "catalyst" at the end of the induction period. When the initial system contains a "catalyst" in addition to oxygen, the "catalyst" also produces free radicals which react with oxygen. Under these conditions the oxygen acts like a typical inhibitor. The extent to which it exerts a catalytic effect after the polymerization begins may be expected to depend on the ratio of the amount of "catalyst" and oxygen present in the system.

The present paper deals with the induction period caused by oxygen in the emulsion polymerization of styrene. Previously[2] it has been shown that oxygen acts like a typical inhibitor with persulfate as "catalyst." In unpublished work the authors in coöperation with D. R. May devised a method by which the disappearance of oxygen during the induction period in the emulsion polymerization of styrene could be measured with the aid of a rotating platinum micro-wire electrode. It was shown in this way that "normal" polymerization of styrene does not start until the oxygen has practically disappeared. Thus the oxygen acts like a typical inhibitor which is being used up during the induction period.

In the same study it was also shown polarographically that at the end of the induction period only traces of alcohol soluble peroxides were present, the amount of peroxides being only a minor fraction of the amount of oxygen consumed during the induction period.

In the present paper and subsequent papers we confine ourselves to a study of the various factors which affect the induction period caused by oxygen in the emulsion polymerization of styrene. The interpretation of the experiments yields interesting information in regard to the kinetics and locus of the activation of styrene molecules in emulsion polymerization.

We have shown previously[2] that with the use

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[1a] C. E. Barnes, This Journal, **67**, 217 (1945).

[2] I. M. Kolthoff and W. J. Dale, *ibid.*, **67**, 1672 (1945).