

**THE ADSORPTION OF RADIOACTIVE
ISOTOPES ON PRECIPITATES**

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THESIS

**Presented to the Graduate Council of the
North Texas State College in Partial
Fulfillment of the Requirements**

For the Degree of

MASTER OF SCIENCE

By

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Denton, Texas

January, 1954

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CHAPTER I

INTRODUCTION

It is a well known fact that a determination in analytical chemistry may be made by volumetric methods if four conditions are met:¹

- 1) The reactions should quickly go to completion.
- 2) There should be only one reaction taking place.
- 3) There should be a marked change in some property of the solution at the stoichiometric point.
- 4) There should be an indicator available which will show the change at the stoichiometric point.

Most precipitation reactions fulfill the first three requirements, but very few indicators are available for most precipitation type reactions; as a result, there have been very few applications for volumetric precipitations in the field of quantitative analysis.

This thesis concerns the investigation of radioisotopes as indicators for precipitation reactions. As a precipitate forms in the presence of a radioisotope, adsorption may take place on its surface. If this adsorption changes markedly

¹W. C. Pierce and E. L. Haenisch, Quantitative Analysis, p. 292.

at the stoichiometric point it will be possible to use this variation as an indicator for the reaction.

Lottermoser² was the first to show that silver halide colloids acquire a positive charge when suspended in a solution containing an excess of silver ions, and that they acquire a negative charge when suspended in a solution containing an excess of halide ions. In order to explain this phenomenon the concept of the electric double layer was introduced by Verway, James, Ratner and others.³ If particles of solid silver iodide are brought in contact with a solution containing iodide ions, the coordination sphere of the silver ions at the interface will be completed by ions from the solution. As shown in Figure 1 the particles will acquire a negative charge and attract positive ions into the outer layers.

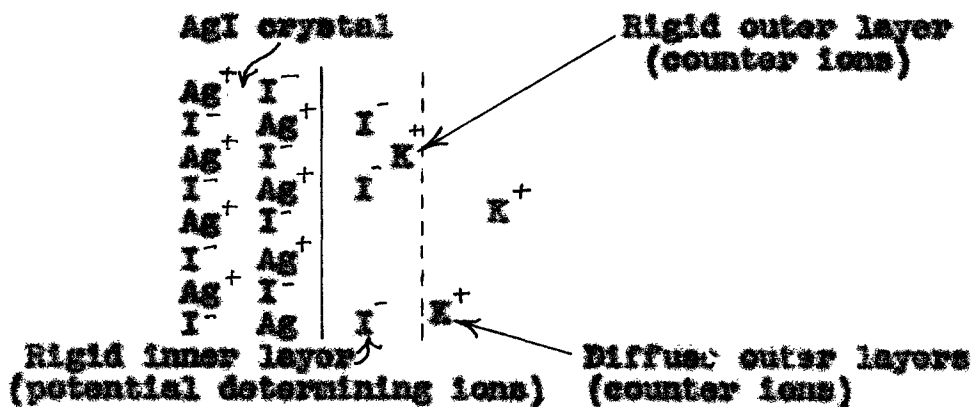


Fig. 1--Silver iodide sol in excess potassium iodide

²A. Lottermoser, J. prakt. Chem., 72, 39 (1905).

³A. C. Wahl and H. A. Benner, Radioactivity Applied to Chemistry, p. 124.

The iodide ions that are adsorbed on the surface of the silver iodide particle make up the inner portion of the double layer and are referred to as "potential determining ions." The outer portion of the double layer is made up of potassium ions which are referred to as "counter ions." According to H. Jenny⁴ the extent of the double layer is the order of several angstroms.

When this same precipitate is in contact with silver nitrate solutions, the iodide ions will complete their coordination spheres as shown in Figure 2. In this case the counter ions will be negatively charged.

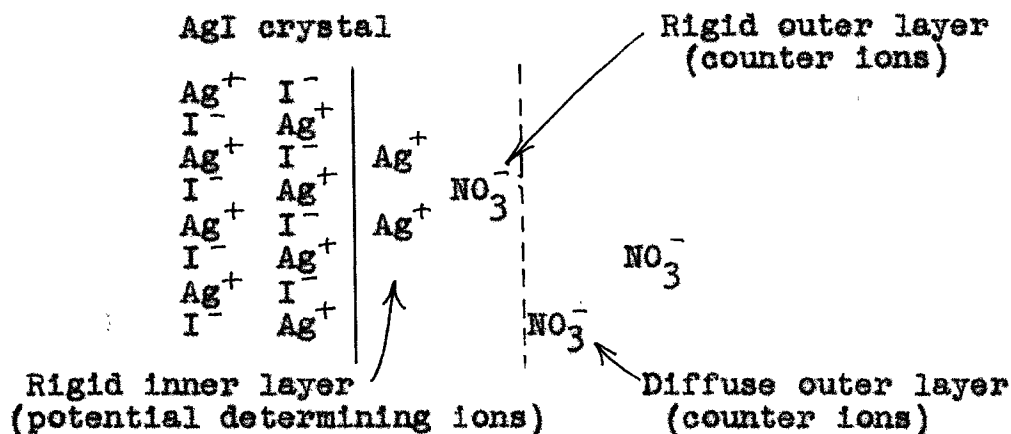


Fig. 2-- Silver iodide sol in excess silver nitrate

⁴A.C. Wahl and N. A. Bonner, op. cit., p. 125.

In order that an ion may be classed as potential determining, it must be able to fit into the crystal lattice of the precipitate. For example, bromide, chloride, and thiocyanate ions are potential determining ions for silver iodide. The phosphate ion is not, since its silver salt does not form mixed crystals with silver iodide.

The theory of the double layer qualitatively explains why a silver iodide precipitate separated from a solution containing an excess of potassium iodide is always contaminated with potassium iodide. If, on the other hand, there are other positive ions, such as sodium, in solution these would compete with the potassium ions for positions in the outer layer. When the silver iodide is separated from the solution it will be contaminated with sodium iodide as well as with potassium iodide. Adsorption of positive ions on negatively charged precipitates and adsorption of negative ions on positively charged precipitates can result through the rapid exchange between the ions in solution and the counter ions.⁵

Factors Affecting Adsorption of Ions on Precipitates

The two principal factors that determine the amount of adsorption that takes place when an ion is deposited on an ionic precipitate are:

⁵A. C. Wahl and N. A. Bonner, op. cit., p. 126.

- 1) The charge upon the precipitate.
- 2) The solubility of compounds formed from the ion that is coprecipitated and the ions of the precipitate.

Minor factors are:

- 3) Temperature.
- 4) The order of addition of the reagents.
- 5) The speed of the precipitation formation.
- 6) In some cases, digestion may affect the adsorption.⁶

Only the principal factors will be discussed.

Charge on the Precipitate

The charge on the precipitate is an important factor in determining the adsorption that takes place when an ion or radioactive tracer is deposited on an ionic precipitate according to Friedlander and Kennedy.⁷

Freshly formed precipitates with large surface areas may be capable of adsorbing radioelements effectively. 'Fajans rule' is of some importance for this type of carrying, but another important factor is the charge on the precipitate relative to the ionic charge of the tracer substance.

Important adsorption occurs only when these charges are of opposite sign; hence experimental factors affecting the surface charge of the precipitate strongly influence the carrying and this type is recognized by

⁶G. K. Schweitzer and I. B. Whitney, Radioactive Tracer Techniques, p. 125.

⁷G. Friedlander and J. W. Kennedy, Introduction to Radiochemistry, p. 265.

sensitivity to such factors as acidity, order of addition of reagents and physical state of subdivision of the precipitate.

Table 1⁸ illustrates the importance of an excess of the anion SO_4^- needed to produce the negative charge on the surface of CaSO_4 necessary for carrying cations.

TABLE 1
CARRYING OF THE ThB BY CaSO_4

Excess Ca^{++}	Excess SO_4^-	ThB carried
600% 10%	5% 900%	1.7% 5.2% 88.0% 98.0%

From this table it can be seen that when the Ca^{++} ion is in excess, very little of the ThB is carried by the CaSO_4 ; however, when the SO_4^- ion is in great excess, 88 to 98 per cent the ThB is carried by the CaSO_4 .

Solubility of Compounds Formed from the Ion That
Is Coprecipitated and the Ions of the Precipitate

The solubility factor affecting adsorption of ions or

⁸Ibid., p. 265.

radioactive isotopes on ionic precipitates appears to encompass other effects perhaps not readily apparent. They are:

- 1) Effects due to charge.
- 2) Effects due to polarization.
- 3) Effects due to size.
- 4) Effects due to hydration energy.⁹

To illustrate the role that the solubility factor plays in the adsorption phenomena, L. Imre¹⁰ investigated the adsorption of the ThX (Ra²²⁴), mesothorium 2 (Ac²²⁸) and thorium B (Pb²¹²) on the silver halides. He shook .0003 mole of Ag halide for several minutes at 0° C with 20 milliliters of solution which was .015 formal with respect to the halide concentration, 0.005 formal with respect to the hydrogen ion concentration and 0.03 formal with respect to the potassium ion concentration. The silver halides were then separated from the solution containing the various radioactive isotopes by means of filtration through a membrane and analyzed for their activity. The results are shown in Table 2.

⁹Wahl and Bonner, op. cit., p. 127.

¹⁰L. Imre, Phy. Chem. A 153, 127 (1931).

TABLE 2
 ADSORPTION OF ThB (Pb^{212}), $MesTh_2(Ac^{228})$,
 AND ThX (Ra^{224}) ON SILVER HALIDES

Silver Halide	% ThB Adsorbed	% $MesTh_2$ Adsorbed	% ThX Adsorbed
AgCl	62.2	4.26	0.45
AgBr	93.8	37.7	3.05
AgI	78.0	75.2	7.90

It can be seen that thorium X and mesothorium 2 are adsorbed to a smaller extent than thorium B. This is because thorium X and mesothorium 2 halides are soluble while thorium B halide is only slightly soluble. Also, it can be seen that mesothorium 2, which has a + 3 charge is adsorbed to a greater extent than thorium X which has only a + 2 charge. Another fact to be noted is that the fractions of mesothorium 2 and thorium X adsorbed vary directly as the solubility of their halide salt decreases. A partial explanation for this fact may be due to the greater polarization effect that Ac^{+++} and Ra^{++} have on the heavier halide ions.¹¹ This seems to be true, since the polarizability of a halide ion increases with the increase in size of the ion. Also, in part, there is an increase in polarizability due

¹¹Wahl and Bonner, op. cit., p. 129

to the large negative charge on the precipitate which results from the large adsorption of halide ions. This regularly is not observed for thorium B.

**Detection of Radioisotopes and Their Use As
Radioactive Indicators in A
Precipitation Type Reaction**

Radioisotopes may be detected by any device which is affected by their activity. The most common devices utilize a Geiger-Muller tube. In fact, the development of Geiger tube techniques and the availability of long-lived, artificially-produced radioactive elements has made possible the determination of the end point of a volumetric analysis by means of radioactivity measurements. Langer, in 1941, used radioactive phosphorus as a radioactive indicator in the titrations of magnesium and uranium with sodium phosphate and of phosphate with magnesium. These titrations all resulted in the formation of a precipitate, and a series of determinations was made of the solution activity during the course of the titrations. Since Langer's method was similar to the procedure involved in a conductometric or an amperometric type of titration, he chose to call his method a "radiometric titration" and in doing so, he described three different types of radiometric titration curves obtained when a fairly insoluble precipitate was formed. They were:

- 1) A titration curve, in which the substance to be

titrated was radioactive, and the reagent added was inactive.

- 2) A titration curve in which the substance to be titrated was inactive, and the reagent added was radioactive.
- 3) A titration curve in which both the substance to be titrated and the added reagent was radioactive.

In case 1, the activity of the solution decreased as the active substance was removed from solution by precipitation. After the equivalence point was reached, the activity became constant and nearly zero. The activity at this point was determined only by the solubility of the precipitate and the background of the detecting device. When the values of the measured activities were corrected to the original volume and plotted against milliliters of added titrant a sharp break in the curve resulted, indicating that the end point occurred at the intersection of the two straight lines. In case 2, the slope of the titration curve was at first constant. After the end point the radioactivity of the solution increased with further addition of the reagent. In case 3, the activity of the solution continued to decrease upon further addition of the reagent until the end point was reached, from this point the activity increased.

In this investigation, an attempt was made to determine the end point of a precipitation titration. In contrast to

Langer's method, the radioisotope was removed from the solution by adsorption on the precipitate. To insure that this removal was by adsorption the radioindicator was not isotopic with any of the ions of the precipitate. The activity of the solution was followed by means of a Geiger counter during the addition of the titrant.

CHAPTER II

EXPERIMENTAL PROCEDURE AND RESULTS

The apparatus used in this investigation was very similar in design to that used by Langer¹ in his radiometric titrations with radioactive phosphorus. Essentially, the apparatus consisted of:

- 1) A Geiger-Muller tube.
- 2) Counting rate meter or scaler.
- 3) Stirrer.

The Geiger-Muller tube had a wall thickness of approximately 30 mg/cm² and was operated on the Geiger plateau. While a counting rate meter was used for preliminary experiments, a scaler was used for more accurate counting. Either a magnetic stirrer or a hand stirrer was used to ensure uniform mixing of the titrant with the solution being titrated.

General Procedure

The general procedure used in this investigation was as follows:

A reagent was added from a burette into a beaker containing one of the materials to be titrated. As the titrant was

¹A. Langer, J. Phy. Chem., 45, pp. 639-40.

added a precipitate was formed in the presence of a radioactive isotope. This radioactive isotope was either in the burette or in the beaker containing the material being titrated. After the addition of a definite amount of the titrant, the solution was stirred thoroughly and contact was made with the Geiger-Muller dipping tube. This contact was made either by dipping the tube directly into the solution or by filtering the solution through a sintered glass filter stick into a glass envelope containing the dipping tube. After contact with the counting tube had been made, the solution was forced back into the beaker by use of air pressure. Then the sample was again drawn by vacuum into the glass envelope, and an interval of one minute was allowed to establish equilibrium before counting the activity of the solution. In the case of data taken with the counting rate meter, an average of a sufficient number of readings was taken to obtain a reliable counting value. When the scaler was used, a one minute counting interval of the solution was taken. After the titration was completed, a plot was made of the milliliters of titrant used against the activity of the solution. In some cases, the activities obtained were corrected to the original volume before being plotted. If any adsorption of the radioisotopes occurred on the precipitates, a break in the curve would be obtained, and it was hoped that this break would occur at the equivalence point.

Discussion of Results

In this investigation three radioisotopes were used. They were radium E (Bi^{210}), radioiodine (I^{131}), and radio-phosphorus (P^{32}).

Investigation with RaDEF

Dilution study of RaE.--Before using RaE as a possible radioactive indicator in a precipitation type titration a study was made in order to determine what effect dilution alone had on the activity of the radioisotope. Ten milliliters of RaDEF with a concentration of 10 mg/ml of lead was added to a test tube and a dipping Geiger-Muller tube was used to measure the activity of the solution. Again 10 milliliters of RaDEF with a concentration of 5 mg/ml was added to a test tube and the activity of the solution was determined in the same manner. This procedure was repeated with concentrations of 2.5 mg/ml, 1.25 mg/ml etc., always maintaining a constant volume of 10 milliliters. A plot was made of concentration against activity and the curve obtained is shown in Figure 3.

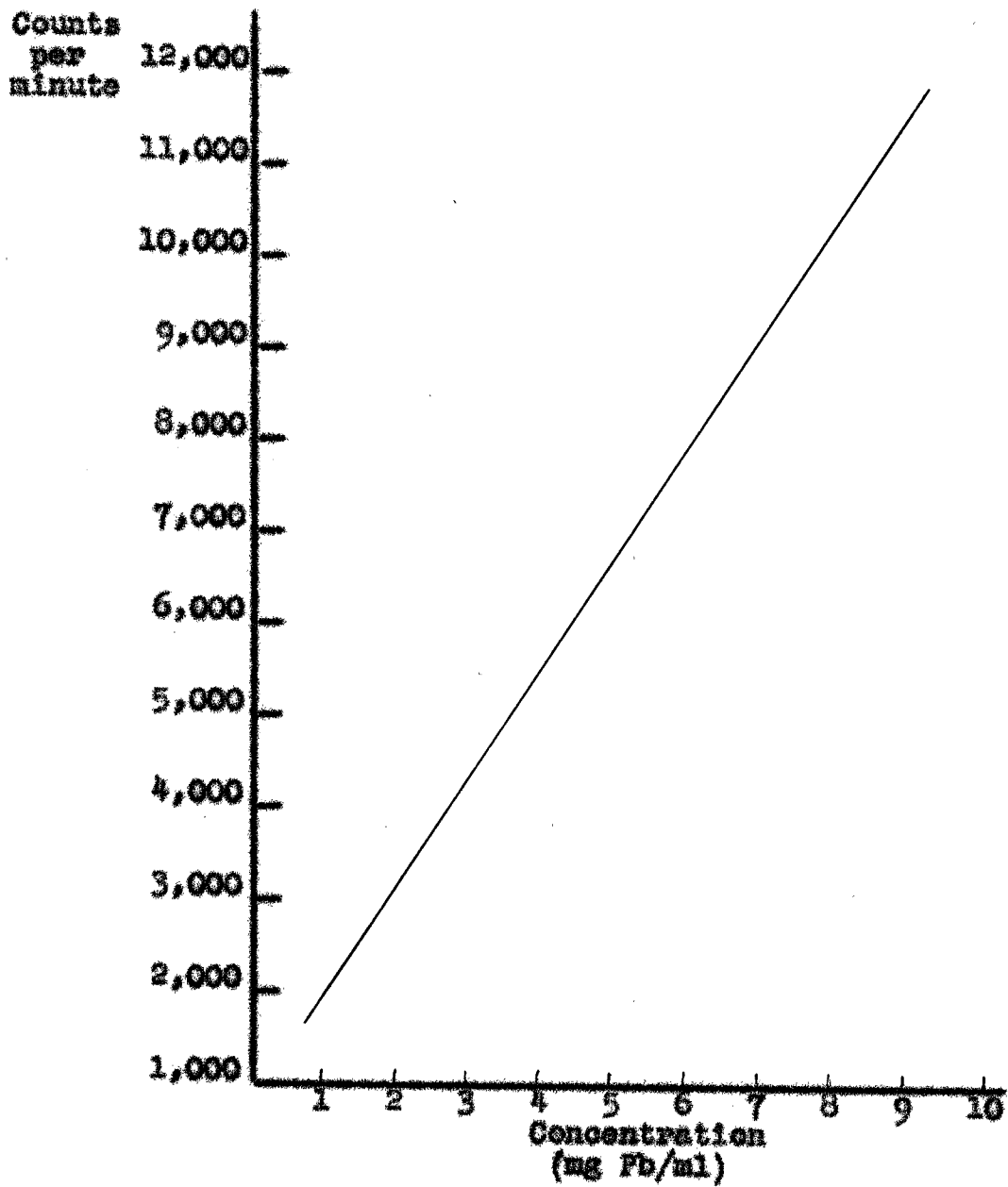


Fig. 3 --Dilution curve of RaDEF.

Precipitation with sodium sulphate.-- In this experiment 5 ml of RaDEF (10 mg/ml of Pb) was titrated with 8 ml Na_2SO_4 solution precipitating PbSO_4 . The titrant was added directly to a test tube and the counting tube immersed so as to reproduce the same degree of solution contact. A counting rate meter was used to follow the activity of RaE. The calculated equivalence point for this precipitation titration was 5 ml Na_2SO_4 solution. No great change in activity was shown at the equivalence point, however, as shown in Figure 4, Curve A.

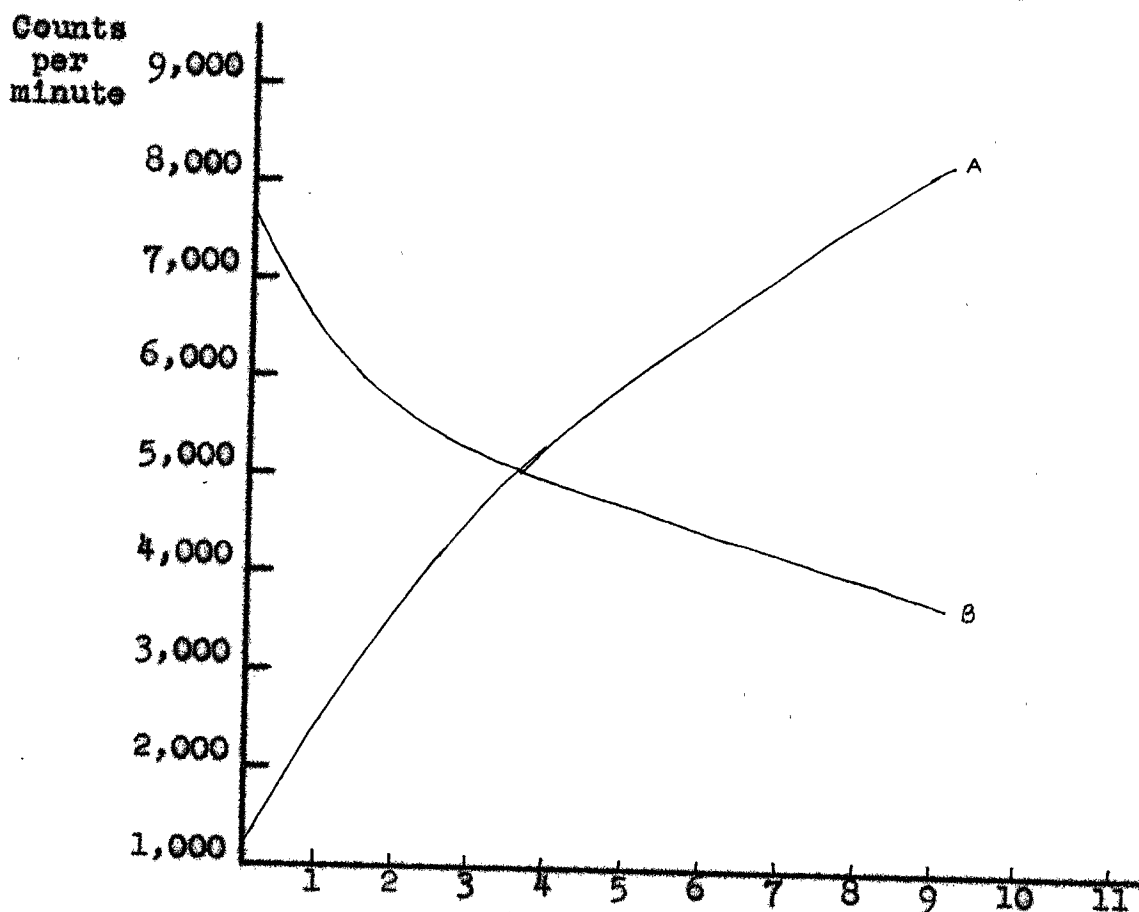


Fig. 4 --Precipitation titration curves of RaDEF with several reagents.

A. Na_2SO_4
B. KI

Precipitation with potassium iodide.-- Five milliliters of the RaDEF solution was titrated with 10 milliliters of KI solution (10 mg/ml) precipitating PbI_2 . In this procedure the titrant was added directly to the test tube containing the RaDEF and the counting tube immersed so as to reproduce the same degree of solution contact. A 64 scaler was used to follow the activity of the RaE solution throughout the titration. At the calculated equivalence point it was hoped there would be a sharp change in the activity of the RaE(Bi^{210}) but no such change in activity was observed, as seen in Figure 4, Curve B.

Precipitation of barium sulphate.-- The Na_2SO_4 solution was added to the RaDEF and $BaCl_2$ solutions in a beaker. The precipitate formed was filtered through a filter stick into a suction flask, and a definite volume of the supernatant liquid was transferred to a test tube, where a dipping Geiger tube was used to detect the activity of the solution. The dipping tube was connected to a 64 scaler. This experiment required considerable time because the $BaSO_4$ precipitate clogged the filter stick. This titration gave no better results.

Investigations with Radioiodine (I^{131})

Only one experiment was carried out with I^{131} . This was the titration of Na_2SO_4 with $BaCl_2$ in the presence of

I^{131} . It was found that beta particles emitted by the I^{131} could not be detected by the dipping Geiger tube in the presence of the I^{131} gamma rays. While the Geiger tube is more sensitive to beta rays, the actual counting volume of beta radiation is much smaller than that of the gamma radiation; hence practically all the counting observed was due to the gamma activity. It was also learned that the gamma activity remained essentially constant; and as a result it was not possible to follow the change in activity of the I^{131} throughout the course of the titration.

Investigations with Radiophosphorus (P^{32})

Water titration curve of P^{32} .-- Before using P^{32} as a radioactive indicator in a precipitation titration, a water titration curve was obtained. This curve was similar to the dilution curve obtained for $RadEP$. Ten milliliters of water containing 10λ of P^{32} stock solution (0.04 mc/ml) was placed in a burette. Thirty-five milliliters of water was added to a 150 ml beaker, and titrated with water from the burette. A plot was made of ml of water used against activity of the water solution corrected to the original volume (i.e., 35 ml) and a straight line was obtained as is seen in Figure 5.

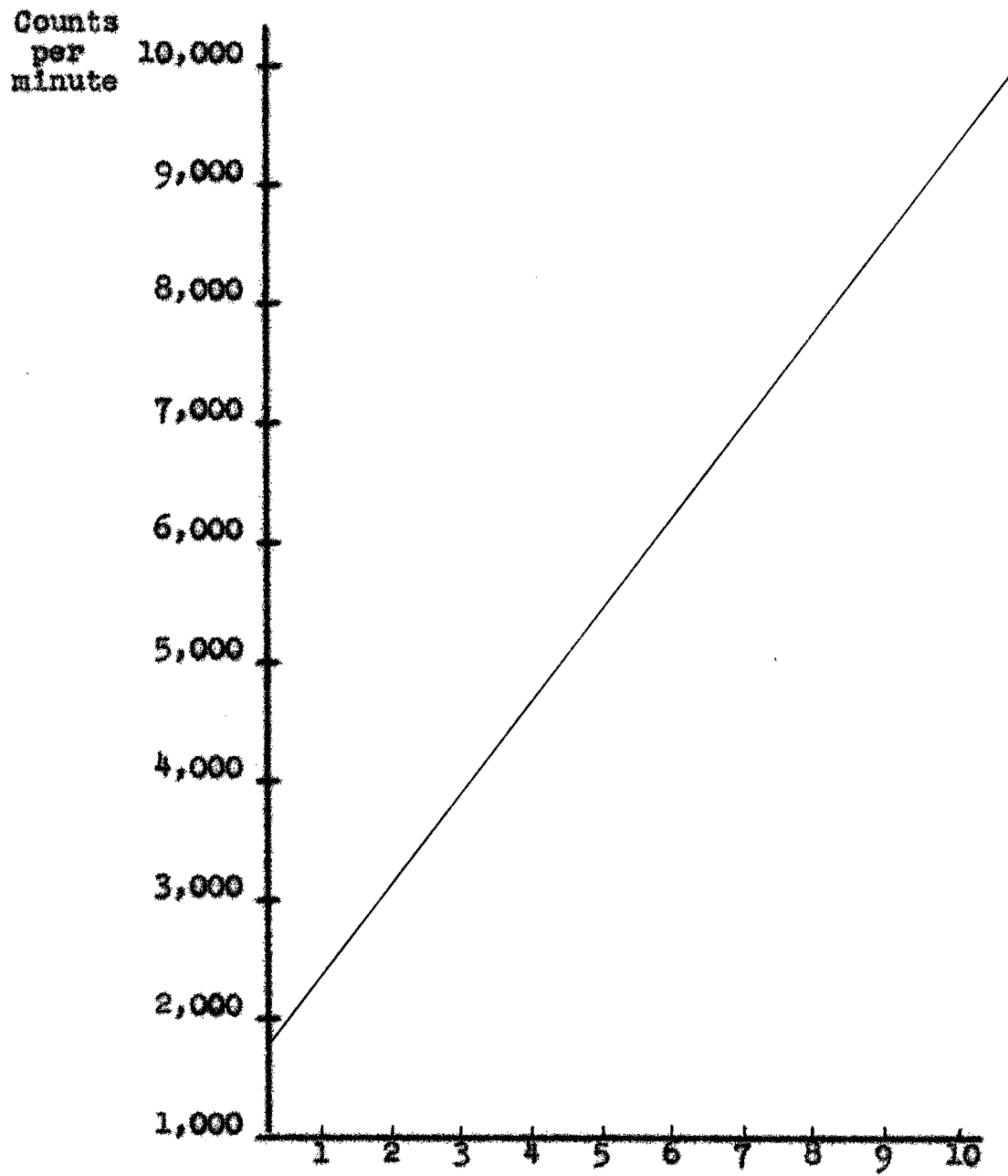


Fig. 5 --Water titration curve of p^{32} .

Precipitation of silver thiocyanate.-- Five ml of NH_4SCN solution (.037 mg/ml), 30 ml of distilled water, and 16.5 ml of 1:100 stock $\text{PO}_4^{=}$ solution were added to a 150 ml beaker. A volume of 6.5 ml of standard silver solution was added from a burette forming a precipitate of AgSCN . The calculated equivalence point for this titration would require 5.2 ml of Ag solution. At this point, hope was entertained that the radioactive P^{32} would be adsorbed on the AgSCN precipitate and show a sharp change in activity. No such results were observed, however; instead the curve obtained indicated no adsorption as shown in Figure 6A.

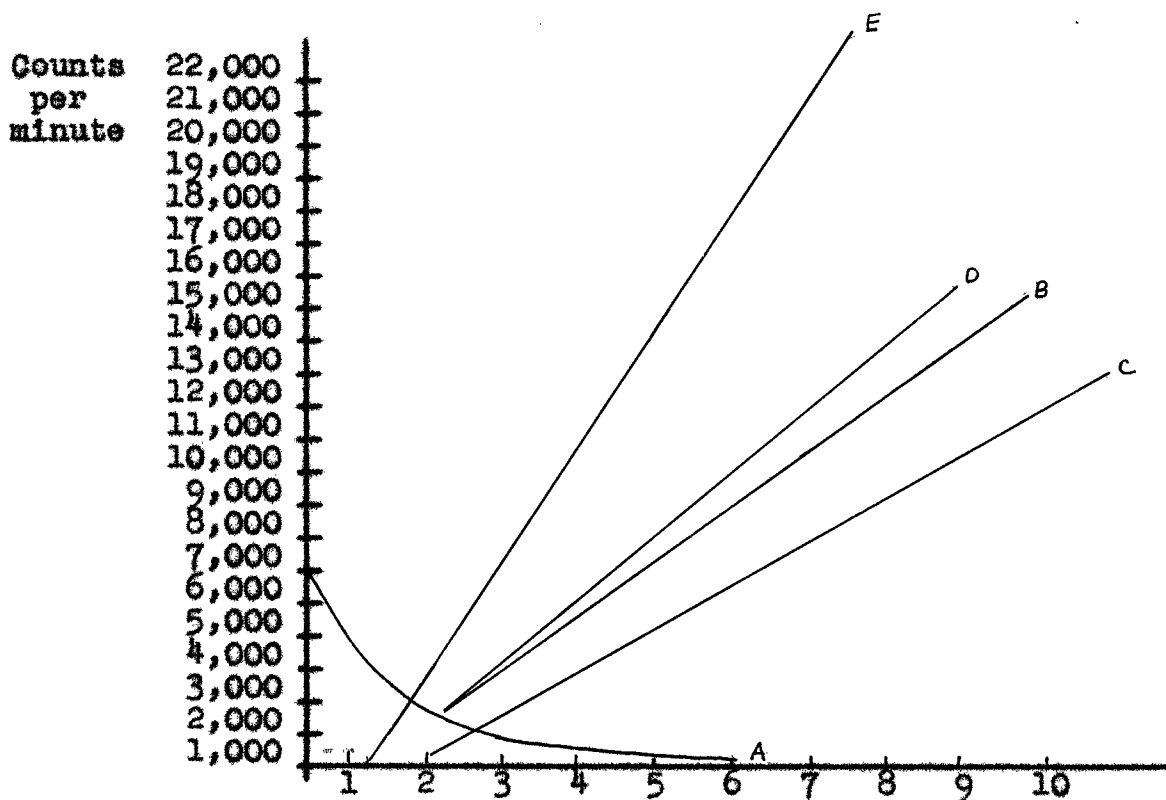


Fig. 6 --Precipitation titration curves using P^{32} .
 A. AgSCN C. AgSCN (pH=8) E. Ag_3AsO_4
 B. AgSCN (pH=1) D. Ag_2CrO_4

The activity of the P^{32} was followed with a decade ampliscaler using the 50 millivolt scale sensitivity and all activities obtained were corrected to the original volume.

In an effort to determine whether the pH of the silver solution was a factor influencing the possible adsorption of P^{32} on AgSCN precipitate, titrations of silver solution with NH_4SCN were carried out at pH values of 1 and 8. The pH value of 8 was obtained by buffering the standard silver solution with 7.5 M NH_4OH . It can be seen from Figures 6B and 6C that the pH of the standard silver solution had no influence on the adsorption of P^{32} since a straight line was obtained in both titrations. If any adsorption of P^{32} had occurred on the AgSCN precipitation, there would have been a break in the straight line obtained. Since no adsorption of P^{32} on the AgSCN was evident, further experiments with this precipitate were abandoned, and another precipitate was investigated.

Precipitation of silver chromate.--Ten milliliters of 0.1 N K_2CrO_4 solution containing 10 λ of radiophosphate stock solution was added to a burette. Five milliliters of 0.1 N $AgNO_3$ solution was added to 30 milliliters of water and this solution was titrated with a 0.1 N K_2CrO_4 solution forming a precipitate of Ag_2CrO_4 . When a plot was made of the milliliters of titrant used against the activity of the silver solution corrected to the original volume, a straight line was again obtained, as shown in Figure 6D.

Precipitation of silver arsenate.---Ten milliliters of 0.1 N Na_2HAsO_4 containing 20 λ of radiophosphate solution was added to a burette. Five milliliters of 0.1 N AgNO_3 solution was added to 30 milliliters of water and this solution was titrated with 0.1 N Na_2HAsO_4 solution forming a precipitate of Ag_3AsO_4 . A plot was made of the milliliters of titrant used against the activity of the silver solution corrected to the original volume. Again a straight line plot was obtained with no break. This curve is shown in Figure 6E.

CHAPTER III

SUMMARY OF RESULTS

Investigations with RaE were carried out because it was readily available. No adsorption of RaE on PbSO_4 was anticipated, however, since $\text{Bi}_2(\text{SO}_4)_3$ is soluble and probably could not be isomorphous with PbSO_4 because of a +3 charge. In the case of PbI_2 , and BiI_3 is insoluble but upon the addition of excess I, it forms soluble BiI_4^- . Although one might expect some adsorption of the RaE on PbI_2 with a subsequent removal in excess I, no adsorption was observed experimentally. This is not too surprising when one considers that BiI_3 does not meet the requirement of isomorphism - one of the two conditions necessary for adsorption. For the case of the BaSO_4 precipitate, it was hoped that RaE might be carried in the rigid outer layer by the high charge of Bi^{+++} . If a Geiger tube having a thinner wall were available, experiments could have been included work with Pb^{210} .

The choice of the P^{32} and I^{131} as radioisotopes to be investigated was also one of availability and economy. Since it is known that the $\text{PO}_4^{=}$ ion is not a potential determining one for silver halides, it was not too surprising that no adsorp-

tion occurred in the AgSCN precipitate. Although Ag_3PO_4 is insoluble, it is not likely that it would be isomorphic with AgSCN. Also, there is some question as to the ionic species which carries the P^{32} . This question arises because of the dependence of the concentration of the $\text{PO}_4^{=}$ ion on the hydrogen ion concentration. It was for this reason that two experiments were carried out at two different pH values, 1 and 8. Nevertheless, even at pH value of 8, little or no adsorption occurred. Since the $\text{CrO}_4^{=}$ ion is about the same size as the $\text{PO}_4^{=}$ ion, it seemed probable that they might fit into the same crystal lattice; hence experiments using Ag_2CrO_4 were tried but were not successful. The fact that adsorption did not take place might be due to the low pH value of the AgNO_3 solution which was found to be 4.5. At this pH the concentration of $\text{PO}_4^{=}$ must be very low. Attempts were made to buffer the AgNO_3 solution and raise the pH, but no successful buffers were found. Sodium bicarbonate, for example, precipitated Ag_2CO_3 before any pH change occurred while NH_4OH formed a soluble complex ion with the Ag^+ ion, and as a result Ag_2CrO_4 would not precipitate.

Realizing that $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ is isomorphic with the corresponding phosphorus compound, it was expected that definite coprecipitation or adsorption of P^{32} would occur with

a precipitate of Ag_3AsO_4 . The fact that adsorption was not observed was surprising and justifies further study of known isomorphous systems. Other suggestions for additional work would include:

- 1) The precipitation of AgSCN in the presence of I^{131} . Since it is known that SCN^- is a potential determining ion for AgI , it is likely that adsorption of I^{131} on AgSCN would occur.
- 2) The study of other buffer systems such as BO_3^{\equiv} with Ag_2CrO_4 in order that the pH and PO_4^{\equiv} ion concentration might be increased.
- 3) The investigation of other radioisotopes, especially those which will not complex with the H^+ ion. One such isotope might be radioactive silver.
- 4) The use of I^{131} might be investigated again, being sure that the precipitate formed is removed from the counting region of the tube and that adequate shielding from gamma background is used.

One difficulty which prevents the general use of radioisotopic adsorption as an indicating mechanism in precipitation reactions is the fact that the carrier-free materials are readily adsorbed on the glass surface of the dipping Geiger tube and on the glassware used. Some attempts to minimize this were made by treating glass surfaces with Desicote, a silicone compound, but the results were not successful.

Another way to minimize this adsorption might be to try a lower solution activity. This would also allow detection of much lower adsorptions if they occurred, because of more favorable statistics.

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