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An Investigation Of The Feasibility Of Making Radiometric Titrations Of Precipitation Reactions

Harold Elmore Hammerstrom

University of the Pacific

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AN INVESTIGATION OF THE FEASIBILITY OF MAKING RADIOMETRIC TITRATIONS OF PRECIPITATION REACTIONS

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A Dissertation
Presented to
The Faculty of the Department of Chemistry
University of the Pacific

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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

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by
Harold Elmore Hammerstrom
June 9, 1968
This dissertation, written and submitted by

Harold Elmore Hammerstrom

is approved for recommendation to the
Graduate Council, University of the Pacific.

Department Chairman or Dean:

Dated June 5, 1967

Dissertation Committee:

Dated June 5, 1967
ABSTRACT OF DISSERTATION

The purpose of the present work was to (1) determine the feasibility of performing radiometric titrations using low activity radioisotopes and inexpensive equipment; (2) develop a workable procedure for performing radiometric titrations in the classroom; and (3) assemble the basic radioactive concepts needed so the content could be used in a chemistry course of study.

The limited work done previously with radiometric titrations has used solutions of high specific activity and relatively large volumes of solution. The use of high activity radioisotopes creates problems of radioisotope procurement, shielding, handling and disposal. The use of high activity radioisotopes required special training and licensing. This imposed a severe limitation on the number of persons that could perform radiometric titrations. Thus to make this technique available to a large number of classroom teachers and other similarly qualified persons, it was imperative that a procedure be devised that would allow radiometric titrations to be performed using low activity, license free radioisotopes.

The low activity of the license free radioisotopes necessitated the deliniation of the physical conditions that could best utilize the limited activity of the solution. The amount of radioisotope used was determined as an amount low enough to simplify or eliminate the problems of procurement, shielding, handling and disposal but yet have a sufficient count rate to enable precise and accurate results.

A physical setup was devised that met the desired criteria. Using this setup, the feasibility of radiometric titrations was determined for precipitation reactions using, as the indicator, one or more of the following radioisotopes: Ca-45; I-125; I-131; Ag-110; Cl-36; W-185; Tl-204; and S-35.

The isotopes selected allowed deliniation of systems having wide variation of emission type and energies. Thus in addition to the systems deliniated, this allows the prediction of the usefulness of isotopes for other systems than those investigated.

The systems using Ca-45, S-35, and Tl-204 were found capable of giving very good results.

A field study was conducted in which a total of sixty-two students performed a radiometric titration. Their average results agreed almost exactly with the accepted value. Their average deviations were of the same order of magnitude as the accuracy reported in many studies using radioisotopes of high activity.

The effects of complexation and pH dependence was also studied for some of the systems. The affect on the titration curve shape agrees well with the theoretical predictions.

Therefore, in addition to the deliniation of new systems for radiometric titrations, this study provided a method of teaching radioactive concepts in a manner that allows safe student participation. Student participation not only allows the teaching of radioactive concepts, the techniques of radioactive solution handling and disposals, and an analytical method, but also allows ready observation of the factors affecting solubility.
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PREFACE

The literature of radioactivity is so vast that it could be thought that all areas would soon be completely surveyed. However, the area of radioactivity seems of the fission reaction type in that as research answers one question it also finds that several new questions have been raised.

Since 1934, when I. Curie and F. Joliot announced that boron and aluminum could be made radioactive by bombardment with the alpha rays from polonium, artificially produced radioisotopes have been studied extensively. The number of artificial radioisotopes produced has had an almost unbelievable growth. Many of these isotopes are now available commercially. Thus, with greater selection and availability of isotopes, it is possible for research to be conducted at small educational institutions that previously would have lacked the facilities. This availability of low activity isotopes will also allow the development of new course content related to radioactivity and these isotopes will be utilized in lecture demonstrations and laboratory work as suitable content and methods are developed.

Radioisotopes have been used in many studies involving reaction mechanisms, exchange rates, kinetics, complexing and analysis. The present work deals with the use of radioisotopes in analysis and the content has been planned
to be useful to teachers of radioactivity in undergraduate courses. A small part of the study is concerned with the effect of pH and complexing on precipitation reactions.

The author wishes to express gratitude and sincere appreciation for the many helpful suggestions and encouragement given by Dr. Herschel Frye and the following members of the Dissertation Committee: Dr. Richard Dodge, Dr. Floyd Helton, Dr. Neil Lark, and Dr. Calvin Potts.

A special recognition must go to Dr. Emerson Cobb, who initiated this doctoral program and was most helpful in arranging for financial support from the National Science Foundation and a University of the Pacific Teaching Fellowship.

Continuation of this program would have been impossible without the encouragement and understanding of my wife, Florence, who deserves my utmost appreciation for her needed support.

Stockton, California
June 9, 1968

H.E. Hammerstrom
CHAPTER I
INTRODUCTION

Radiometric titrations are titrations in which a radiotracer is used as an indicator to follow the changes taking place between two phases in equilibrium. The kind of changes that may be followed include precipitation, complexation and redox reactions. Most of the work done thus far has been in the investigation of precipitation reactions.

A radiometric titration, for a precipitation reaction, should have the following characteristics: (1) the solubility of the precipitating species must be so low that the amount remaining in solution is negligible as compared to the amount precipitated; (2) a radioisotope must be available that is isotopic with one of the ions to be precipitated; and (3) the strength of the radioisotope solution should be negligible compared with the nonactive isotope to be analyzed.

For an analysis using radiometric titrations an active solution may be titrated with an inactive solution; an inactive solution titrated with an active solution; or both solutions may be active. The method used most often involves the titration of an active solution with an inactive solution. For this situation a radioactive species, isotopic with the ion to be precipitated, is added to the solution to be analyzed. The amount of radioisotope
added is in accordance with the amount required to give a reasonably high count rate. Increments of a standard solution are then added and the count rate of the solution determined. Since the precipitate formed will include a corresponding portion of radioactive species, this will cause the count rate of the solution to decrease up to the equivalence point. A graph of the counts per minute plotted against the volume of titrant added will allow two straight lines to be drawn. The point of intersection of the lines determines the equivalence point.

Radiometric titration is one method of using radioisotopes in analysis. Radiometric analysis is the term used to indicate an analysis in which radioisotopes are used in the process. Most radiometric analysis requires a determination of the specific activity of the unknown solution containing the radioactive substance. This solution is then used to form a new compound of the species to be determined. This new compound is then isolated by filtration or extraction and the quantity of the compound formed is determined by measuring the amount of activity of this new derivative.

Obviously this short summary of Radiometric Analysis leaves many questions unanswered for those not familiar with this technique. Because the composition of the material to be analyzed is somewhat in doubt, how does one select the
best radioactive reagent to add that will
(1) form a derivative with, and only with, the substance to be determined,
(2) react completely in the desired direction to include all of the substance to be analyzed in the new derivative
(3) form a derivative that is capable of being completely removed from the excess radioactive reagent?

Once the new derivative has been separated, questions arise as to the best method for counting. If the derivative is a solid and is to be counted dry, in a planchet, what is the method of transfer to the planchet? What method of drying is best? What method is used to spread out the solid uniformly? Is the sample thickness a factor to consider? Will a chunky precipitate count the same as a powdered precipitate?

These and other considerations make this method overwhelming to those not actively working in this area. For those trained in this area Radiometric Analysis can be a powerful tool for analysis of either anions or cations. Removal of these can be through chelation and derivatives can be formed with organic compounds. The method can be extended to multiple unknowns if suitable means of separation can be found. There are times when it is not possible to separate the new derivative at 100 percent yield. For this situation the analytical method, known as Dilution
Analysis is often used. A specific type of Dilution Analysis, often called Isotopic Derivative Dilution Analysis may be explained as follows: Suppose a solution contains a small amount of X and a large amount of Y; it is desired to determine the amount of X, and it is known that X cannot be removed from the solution in 100 percent yield. To this solution a suitable radioactive species is added to form a new derivative of X. Excess radioactive material of the same composition as the new derivative of X is added to the solution. This derivative is now separated and counted. This allows the radioactive proportion to be determined, and by comparing with the nonradioactive compound calculation of the original species is possible.

Isotopic Derivative Dilution Analysis, is limited by the problem of complete removal of radioactive contaminants during the separation and purification. A variation of this method, called Isotopic Dilution Analysis eliminates the step to form a derivative.

Isotopic Dilution Analysis is a clever and powerful method of analysis. It is economical since the amount of radioisotope needed is low. Preferably the amount of radioactive material should not exceed the weight of the unknown since this weight is subtracted from the total weight. Too large an amount of labeled material will exaggerate the statistical variation arising in counting the samples. This
is then a restriction because the analyst must have a reasonable knowledge of the possible concentration of the compound to be analyzed.

In industry where routine analysis of this type is done the process becomes mechanical. However, the beginner in the area would find that many problems would arise in the application of the generalized procedure to a specific example. There would be problems regarding the separation scheme that would yield the desired material; likewise, problems regarding the amount of radioactive material to add would arise because the labeled material was added in the same form as the compound to be separated. This means that this material must be available commercially or synthesized. Although the number and type of labeled materials available commercially are increasing, this will still be a significant restriction to the method for years to come.

Methods of analysis are also being developed which depend on the specific radiation absorbing characteristics of each element. Thus it may be possible to calculate the ratios of the different elements in a sample by measuring its ability to stop beta rays. This is possible when only a few elements are present and they differ considerably in atomic weight. A Nuclear Science Study Guide (1964) mentions that the hydrogen content in hydrocarbon is
measured in this manner and since boron absorbs neutrons so very efficiently, this allows a means of measuring the boron content in a sample.

In educational institutes the uses of isotopes will undoubtedly continue to increase. Counting equipment is becoming more readily available. The number and types of radioisotopes available have increased. With the increased availability of isotopes that may be possessed without special U.S. Atomic Energy Commission license, many individuals and institutions are now able to work with radioisotopes.

Work with radioisotopes in the past has been restricted by lack of equipment, restriction on or unavailability of isotopes, and unfamiliarity with isotopic techniques by many teachers and/or chemists. The past years have seen the increasing availability of equipment and isotopes; indeed the availability of isotopes has had a remarkable growth. A tremendous number of radioisotopes has been developed allowing a wide selection for the investigator. In addition, the number of labeled compounds has grown rapidly.

The recent availability of license-free radioisotopes should have had great potential in encouraging research with isotopes, and should have increased the teacher's potential for teaching in a needed area. This potential has not
nearly been realized. The reason is that the field of radioactivity has been advanced rapidly by a relatively few workers specializing in this area. However, a large number of teachers and chemists have either not had the time or the opportunity to keep abreast of all developments. The result of this unfamiliarity on the part of teachers with radioisotope techniques has resulted in most graduates in chemistry receiving little or no training in this area.

This omission in training chemists will not be corrected without the development of content and techniques to help the teacher.

I. THE PROBLEM

Statement of the Problem. The purpose of this study was (1) determine the feasibility of Radiometric Titrations using low activity radioisotopes and inexpensive equipment; (2) develop a workable procedure for performing Radiometric Titrations in the classroom; and (3) assemble the information needed so the content could be used in a chemistry course of study. The intent was to organize and develop an area that would be used to give increased depth and unity to the isolated facts of radioactivity that have usually been presented to undergraduate college chemistry students. The content could be presented as lectures, as lecture demonstrations or as laboratory exercises.
The teaching of the theory and techniques of Radio-
metric Titrations would include the following content:

1. A workable procedure for following the progress of a precipitation reaction
2. Some knowledge of which low activity isotopes can be used in this method
3. Some knowledge of the quantity of isotopes needed to give a reasonable count rate and hence reasonably consistent and reproducible curves
4. Some knowledge of the type of sample holder that gives the best results
5. Techniques in the safe handling of isotopes
6. Some knowledge of the strengths of reagents that can be titrated accurately
7. The effects of change of pH on the curve where the pH affects the solubility
8. The effect of complexation on a titration curve
9. The difference in solubility where titrations are made of mixtures such as mixed halides titrated with silver nitrate
10. Some knowledge of the type of equipment found most useful in this method
11. Some knowledge of how the type and energy of emission affects the result
12. Information on how the statistical nature of
radioactive emissions determines the count time and/or accuracy

13. A greater understanding of and appreciation for the factors involved in equilibrium of aqueous solutions.

The area of radiometric titrations was selected for this problem in preference to the more sophisticated Radiometric Analysis and Dilution Analysis procedures because the changes in the equilibrium of a system can be more readily observed by the former method and therefore it is more adaptable as a teaching tool.

The problem selected was to experimentally develop content to extend the usual material given on radioactivity to undergraduate students. This information will be useful experimentally only to the extent of availability of equipment and chemicals. To assure the optimum possibility that adequate equipment and chemicals would be available, the problem was limited to use of inexpensive equipment and chemicals that are easily available. Figure I, Page 10, shows a sketch of the G-M counter and sample holder used for this experimental work.

The basic instrument selected for this problem was the Lionel 455 Scaler Ratemeter. The Lionel 455 is a combination count-ratemeter and scaler, specifically designed to provide an accurate measurement of radioactivity for industrial, school and medical laboratories. Since this is
A. GM counter and sample holder

1. GM tube
2. Sample holder (planchet)
3. Plastic sample slide holder
4. Lucite tube mount and sample holder.

B. Full size cross section view of sample holder geometry.
one of the most inexpensive scaler-ratemeter instruments available, all individuals having access to a similar or better G-M counter could perform similar experiments in this area. This instrument is of the type given to participants of Reactor and Radioisotope Institutes sponsored by the Atomic Energy Commission. Therefore, this instrument has been available for some time to many chemistry, physics and biology teachers.

The isotopes used were purchased in quantities representing the maximum activity that could be purchased, as an unsealed source, without a specific license. This choice was made specifically so as to make the isotopes available to the largest number of potential users.

Previous investigators in this field were apparently interested in Radiometric Titrations as an analytical tool and in attempting to secure very precise results the instruments have been more sophisticated and the isotope activity higher. Therefore, a part of this problem has been to determine if reasonably precise results could be obtained by this method, using low activity isotopes and inexpensive equipment.

Chapter II consists of a resume of the historical development of Radiometric Titrations, Chapter III gives the background concepts pertaining to Radiometric Titrations, Chapter IV specifically characterizes the equipment and
chemicals used, Chapter V discusses the experimental method, Chapter VI describes the results and gives an interpretation of the data, Chapter VII presents the results of the field study, and Chapter VIII summarizes the important findings and conclusions of this study.
CHAPTER II

THE DEVELOPMENT OF RADIOMETRIC TITRATION

Radiometric Titration started with the work of Alois Langer in 1941. Langer called the method Radiometric Titration because of the similarity to conductometric or amperometric titration. Langer's discussion of Radiometric Titration indicated the possibility of three curve types: the titration of an active solution with an inactive reagent would give a decreased count rate that levels off at the equivalence point, titration of a nonactive solution with an active reagent would give a low count rate up to the endpoint at which time the count rate would increase and titration of an active solution with an active reagent would cause a decrease in count rate up to the equivalence point followed by an increase of count rate after the endpoint.

Langer used radioactive phosphorous as the endpoint indicator to determine barium, lead and thorium. Solutions containing 50 mg. Ba/50 ml. (Solutions 2.0 molar in both ammonium chloride and ammonium hydroxide) were titrated with 0.5 to 1 milliliter portions of 0.1 molar radioactive phosphate.

The basic instrument used by Langer was a Geiger counter. The sample holder was large enough to hold a fifty milliliter sample, reagents to provide the best
experimental conditions for the reaction and the titrant required to complete the reaction. A buret was mounted over the sample holder, and with each phosphate increment added, the solution was mechanically stirred and some of the solution drawn up around the G-M tube for counting. The liquid was drawn up through a glass tube having a sintered glass filter to prevent solid from entering. The accuracy reported was ± two percent.

The sintered glass filter used by Langer was reported to be easily clogged with precipitate, hence making it somewhat difficult to draw up the liquid for counting.

World War II stopped work in the area of Radiometric Titration until the late 1940's.

In 1950, Langer reported that by using a procedure and apparatus similar to that he used in 1941, argentometric titrations could be performed using radioactive silver as the indicator. Some work was also done in attempting to find the endpoint by using only two points on one branch of the titration curve.

By use of the same method as Langer, I.P. Alimarin (1956) determined cobalt by titration with potassium hexacyanoferrate (II) solution. Cobalt-60 was the radioisotope used in this determination.

Korenman et. al. (1956) used diammoniummercury (II) thiocyanate and potassium hexacyanoferrate (II) to determine
the concentration of zinc and copper. For this radiometric titration, a small quantity of Zn-65 was added to the zinc salt solution, standard potassium hexacyanoferrate (II) was added, the solution was centrifuged, and the activity of the filtrate was determined radiometrically. When copper and zinc were both present, the copper precipitated first with no changes in the solution activity. This allowed the determination of both metals without intermediate filtration to remove the copper.

To determine zinc with diammoniummercury (II) thiocyanate, Korenman et. al. added mercury-203 to the standard diammoniummercury (II) thiocyanate solution and the endpoint was determined when the filtrate first became radioactive. Using an alternate procedure to determine zinc, some zinc-65 was added to the salt solution of zinc, and increments of standard diammoniummercury (II) thiocyanate solution added until the endpoint when the radioactivity of the filtrate had decreased to zero. This last method can be modified by adding a radioisotope such as cobalt-60 to the solution of zinc salt. Titrating with potassium hexacyanoferrate (II) will cause coprecipitation of the cobalt and zinc and the endpoint was determined when the count rate dropped to zero. This method extended the use of Radiometric Titration to elements for which highly active isotopes are unobtainable or too expensive, if the elements to be
determined can be coprecipitated with or before the radioisotope that is added.

Alimarin (1956) reported that methods of coprecipitation are useful for the isolation from a solution of various ions that are present in very small concentrations.

The years from about 1950 to 1956 were a time for exploration of the possible ways in which radioisotopes could be utilized in solving various theoretical and applied problems of analytical chemistry. With the simultaneous development and improvement of such related areas as Isotopic Dilution Analysis, Radiometric Analysis, and Radiometric Titrations, it is understandable that some conflict might arise in terminology. Some studies have been named using the terms Radiometric Titrations, whereas they are actually Radiometric Analysis.

Alimarin, the most prominent Russian investigator utilizing Radiometric Titration, helped resolve this notation conflict by the publication of the theoretical principles of Radiometric Titrations in 1957.

The main principles discussed by him emphasized the following conclusions: (a) the use of radioisotopes in analytical chemistry permits the developing of methods of radiometric titration, by precipitation or by extraction of the elements being determined, (b) the radioisotope is either added during radiometric titration, or the titration
is carried out with the aid of a reagent containing the isotope, (c) the equivalent parts can be determined graphically or computed on the basis of two titration points, and (d) there is the possibility of simultaneous determinations of two elements providing there are either differences in the solubility of the derivatives formed or if isomorphism takes place.

Alimarin represented the Soviet Union at the International Conference for Peaceful Uses of Atomic Energy held in Geneva in 1955. Comments made at this conference stressed the value of using radioisotopes in analytical chemistry. Alimarin also discussed the importance of radioisotopes in the study of the behavior of substances present in solutions, the use of tracers in qualitative and quantitative work, the value of tracers in coprecipitation studies, the results of complexation studies, the area of exchange reactions, the determination of precipitate solubility.

Willard (1956) reported that the application of radioisotopes in chemical research and analysis were among the most important scientific benefits to mankind from the development of atomic energy. This report based the usefulness of radioisotopes on three features; (1) they furnish "tagged" atoms which make it possible to study in detail reactions and reaction steps which were previously unobservable; (2) they can often be detected from their radiations with much
greater sensitivity than the same element can be detected by other means; (3) they can serve as efficient and economical sources of ionizing radiation for use in the study of radiation. The ready availability of many radioisotopes with specific activities of $10^4$ disintegrations per microgram or higher was cited as a reason for their extreme usefulness. The wide variety of radiation characteristics made it possible to choose radioisotopes to suit specialized needs in studies of exchange reactions, free radical identification, complex molecules, polymerization, intermolecular exchange, and analytical applications.

According to Meinke (1958), the period from late 1955 to late 1957 showed a large expansion in use of isotopes. Several of the major reasons for this increase were believed to be (1) interest fostered by the International Conference on the Peaceful Uses of Atomic Energy held in Geneva in 1955 and (2) the recent declassification in the United States of a large amount of information on analytical procedures using radioisotopes.

Meinke noted that in the United States considerable impetus had been given to the use of small amounts of labeled material in analytical procedures by the decision of the United States Atomic Energy Commission to make available microcurie amounts of most radioisotopes license-free. The more general acceptance of the microcuries amounts of
radioisotope lead Meinke to speculate that the average analytical chemist may have shied away from tracer techniques because of the danger and cost. Other reasons that may contribute are "ignorance of the possibilities and perhaps a sense of conservatism." The increased number of publications shows more interest and the techniques are becoming more varied. The range of useful techniques has been widened; however, Meinke (1958) felt that some of the techniques, though extending the overall concepts will "remain laboratory curiosities of use only to the group that developed them."

A variation of techniques compared with most Radiometric Titrations was reported by Yatsimirskii and Roslyakova (1958) in the titration of solutions with complex compounds of cobalt-60. The suggested method of radiometric titration with $\text{Co}^{60}(\text{NH}_3)_6\text{Cl}_3$ was to add about one milliliter or less of the unknown sulfate or phosphate solution to a series of centrifuge tubes. The solution was diluted with water so the final volume in all the tubes was the same and was from two to three milliliters. A one tenth molar solution of $\text{Co}^{60}(\text{NH}_3)_6\text{Cl}_3$ was then added to each tube in increasing increments ranging from 0.2 to 1.4 milliliters. The solutions were stirred, and centrifuged and then two tenths milliliter from each tube was placed on filter paper, allowed to dry and the radioactivity determined. Phosphate and sulfate
were determined by this method with an accuracy of ± two percent.

Duncan and Thomas (1958) at the Proceedings of the Australian Atomic Energy Symposium of 1958 described the technique of radiometric titrations and presented the experimental results of titrations such as Ag\textsubscript{110}NO\textsubscript{3} titrated against potassium thiocyanide, potassium chloride, and thiocyanatopentaaminecobalt (III) thiocyanide; Co\textsubscript{60}Cl\textsubscript{2} titrated against sodium tungstate and Na\textsubscript{2}W\textsuperscript{185}O\textsubscript{4} and nickel and lead titrated against dithizone in the presence of Co\textsubscript{60}Cl\textsubscript{2}. The method used was claimed to form the basis of a new technique for determining the solubility products of insoluble salts.

A study by Straub and Csapo (1961) used silver-110 to successfully titrate oxalate and cyanide, but they claimed the method would not work with vanadates.

Eristovic et. al. (1959) found that radiometric titrations of a cobalt sulfate solution containing cobalt-60, with a solution of potassium hexacyanoferrate (II), showed that with low concentration of reagents the composition of the precipitate at the equivalence point was K\textsubscript{4}Co\textsubscript{10}[Fe(CN)\textsubscript{6}]\textsubscript{6} and on this basis a method was developed to analyze small amounts of cobalt.

The radiometric titration method of Yatsemirskii and Roslyakov (1958) mentioned previously has many similarities
to a radiometric determination described by Laszlo Adam. Adam (1962) analyzed a sample containing 20-600 milligrams of phosphorous as phosphate ion by the following procedure. The sample of phosphate was divided into four portions of less than fifty milliliters each. To each portion, equal volumes of Na$_2$HP$_3^{20}$O$_4$ containing one microcurie of phosphorous was added. Precipitation was caused by adding magnesium ammonium phosphate or barium phosphate in varying amounts, all less than stoichiometric amount, of the corresponding precipitating agent to each aliquot. Each volume was adjusted to 100 milliliters and when the precipitate had settled, ten milliliters of each liquid was withdrawn and the count rate determined. The count rate of a blank was also determined.

A similar procedure was described in which the phosphate was precipitated with various excesses of cobalt chloride tagged with cobalt-60. The counts per unit of time (including the blank) were plotted versus the milliliters of precipitating agent. Extrapolation to zero counts gave the amount of precipitating reagent required for the complete precipitation of the phosphate by direct means. Having at least two points in the 1000-5000 count per minute range was considered essential for obtaining good results. By using the points from the blank and one precipitation, the amount of P$_2$O$_5$ was calculated from the
formulas:  
\[ X = \frac{AZ_b}{Z_b - Z} \]  
(tagging the material being determined)  
or  
\[ X = \frac{A(Z_b - Z)}{Z_b} \]  
(tagging the precipitating agent)  

where A is the milligrams of P\textsubscript{2}O\textsubscript{5} equivalent to the precipitating agent, Z\textsubscript{b} is the count rate for the blank, and Z is the count rate of the liquid from the sample. The errors of the calculated and graphical solution were ± 5 and ± 3 percent respectively.

Bebesel and Sirbu (1960) claimed improvement in the method of Langer with Ag\textsuperscript{110} by radiometric determination of titer and graphical estimation of the endpoint. The procedure followed was to add small aliquots of KIO\textsubscript{3} solution to a 0.01 molar silver nitrate solution having a specific activity of approximately three thousand counts per minute per milliliter of solution. After each addition, the solution was centrifuged and an aliquot of the clear solution was siphoned into a spiral surrounding a cylindrical counter to determine the count rate. The aliquot was then returned to the solution and the process continued. From the count rates determined, two straight lines were constructed which were extrapolated to intersect at the equivalence point. Cyanide, oxalate and sulfamides were titrated with the standardized silver nitrate solution by the same procedure. The
relative errors for some species were given as "less than 0.9 percent for 0.3 milligrams of cyanide, 0.9 percent for 0.3 - 5.3 milligrams of oxalate, less than 0.7 percent for 1.5 - 7.5 milligrams of sulfathiazole, and less than 0.8 percent for 1.5 percent talazole."

The method was found applicable to titration in the nonisotopic phase such as a radiometric titration of lead with standard potassium chromate. The principle is explained that if the solubility products $P_{AB}$ and $P_{CB}$ differ by at least 2-3 orders of magnitude, the cation $A^{+m}$ can be titrated with $B^{-n}$ in the presence of the cation $C^{+m}$, tagged with tracer $C^*$. The activity of the solution will remain constant during the precipitation of $AB$ and decrease only when $CB$ starts to precipitate. The equivalence point can be determined graphically. The accuracy was claimed to be 0.13-1.4 percent for 21-0.5 milligrams of lead.

Another variation of radiometric titration was reported by Galateanu et. al. (1960). This procedure was initiated by the precipitation of $\text{AgIO}_3$ in a solution containing silver-110 at a pH of 10.0. EDTA was then added until a reasonable number of counts was found for a portion of the filtrate. The pH was then adjusted back to ten and counts on the filtrate determined. Knowledge of the count rate decrease allowed the amount of zinc and copper complexed by the EDTA to be determined. The results of
determining the amount of copper in brass and bronze was described as fair.

While the number of investigations in the area of radiometric titrations per year was still small at this time, it can be seen interest had increased and various techniques had evolved.

A review of the fundamental developments in analysis by Leddicotte (1962) noted that many existing analysis problems are now being solved through the use of radioisotopes. In this reviewer's opinion, radiometric analysis methods involving either isotope dilution with radioactive tracers, labeled reagents for use in chemical techniques such as titrations, or the use of radioactive tracers for procedure development have much use in analytical chemistry. This review mentions radiometric titrations and isotope dilution analysis as useful analytical methods.

This indicates that radiometric titration is being recognized as a valid analytical technique.

The reporting of one type of radiometric titration leads to other investigators validating the results, refining the method, or extending the knowledge in this area by other means.

The area of complexation was extended by Casey and Robb (1963) in titration of the hexachloroplatinate (IV) ion. The hexachloroplatinate (IV) ion was determined in the
presence of tetrachloroplatinate (II) ion by the precipitation of cesium (I) hexachloroplatinate (IV) with cesium chloride containing cesium-137. The count rates for the supernatent solutions from a series of increasing volumes of platinum solution, all adjusted to the same final volume were determined. The data obtained allowed the cesium hexachloroplatinate (IV) to be determined.

In 1963, Chernyi et. al. studied the method of precipitation in nonaqueous solutions by use of radiometric titration techniques. A summary of the findings of this study, as reported by Mary Elvira Weeks¹, is as follows:

The radiation intensity of tracer atoms is not dependent on the solvent, is linear with concn. and provides great sensitivity. Org. acids and salts can be titrated in MeOH, acetone, and dioxane-MeOH mixts, with Ag-110 as the tracer. Use of a nonaq. solvent in which the pptd. is less soluble than in H₂O increases the accuracy of the analysis; the solvent should have a low dielectric constant. Certain salts, org. acids and salts of quaternary ammonium bases that can be pptd, as difficulty sol. Ag salts were studied. The intensity of the radiation of Ag-110 from an aliquot of the soln. is first measured. The titration is performed in sep. portions contn equal amounts of the component to be titrated and varying amts. of the titrant, the vol. being kept constant by addn. of pure solvent: Dioxane is added to MeOH to lower the dielec. constant; MeOH is added to acetone to increase the soly. of the titrant. The salts NaOAc and NaOBz and Ca butyrate in MeOH can be titrated by the radiometric method. The titration of acetic, butyric, valeric, and caproic acids is improved by the use of MeOH-dioxane mixts. Halide salts of quaternary ammonium bases are titrated in

acetone, MeCoEt, and MeOH-acetone mixts. The curve obtained by radiometric titration in acetone, of a mixt. of salts having a common anion, KBr+(C6H5)2NBr, is a combination of the titration and complex-formation curves.

A rather extensive review of the uses of radioactive tracers by Reynolds and Leddicotte (1963) lists the systems determined by radiometric titration.

A publication, entitled "Radiometric Titration: New Possibilities" by Braun (1964) stated that "the indication of the equivalent point of reactions used in volumetric analysis using radioisotopes, has been used up to the present only in the case of precipitation reactions and the formation of complexes extractable with organic solvents." This publication describes the extension of radiometric titrations to formation reactions in aqueous solutions and to redox reactions. According to the theoretical considerations described, radiometric titration can be used in all cases of volumetric reactions and also in all radiometric titrations by precipitation formation.

Burger (1964) developed a new method for the determination of trace amounts of chloride (one to ten micrograms per milliliter). This method was based on the dependence of the solubility of silver chloride on the concentration of chloride ions already in solution. The solubility of silver chloride was determined using a solubility column filled with silver chloride labeled with silver-110. The
activity of a series of solutions of varying chloride concentrations to which silver chloride is added is determined by the use of the solubility column. Since the count rate is related to the amount of silver chloride that dissolved, a solubility curve can be plotted for various concentrations of chloride ion. Once this solubility curve is determined, analysis can be made by adding silver chloride to an unknown solution, allowing equilibrium to be established, determining the specific activity and relating the specific activity to the solubility curve.

The method used to determine the solubility curve is essentially the same as that used in some radiometric titrations. Once the solubility curve is established, the method is actually radiometric analysis. This method worked well for chloride concentrations between $10^{-3}$ to $10^{-5}$ moles per liter. For chloride concentrations greater than $10^{-3}$ moles per liter, the method was quite satisfactory.

The concentration ranges here seem indicative of a difference in the methods. Radiometric titrations using precipitation reactions appear more usable with the higher concentrations, whereas radiometric methods are more often used for quite low concentrations.

Braun (1964) applied the radiocomplexometric method of titration to indirect and back titrations. In making indirect titrations, the component to be determined is
separated as a precipitate, whose other component, on being dissolved, can be directly titrated with EDTA. Tunstate and sodium ions were titrated by this method using solid $\text{Ag}^{110}\text{IO}_3$ as the indicator.

Braun and Koroos (1964) discussed radiometric titrations at the Symposium on Radiochemical Methods of Analysis held in Salsburg, Austria in 1964. The systems discussed included titration using radioactive standard solution and titration of labeled components using inactive standard solutions. An interesting method has been developed whereby indication by radioactive amalgams was used in redox titration. The indicator was liquid amalgam labeled with zinc-65 or cadmium-115. The titration was made using an oxidizing agent as the titrant. After the total amount of reducing agent was oxidized, the oxidizing agent reacts with the amalgam and an equivalent amount of the Zn-65 or Cd-115 ion appears in the solution. As the ions appear a break occurs in the titration curve. Another new development mentioned was the use of a circulating system titration apparatus using precipitate membranes.

An article by Illoszewics et. al. (1966) indicated that the three main types of radiometric titrations are based on precipitation, complexation and redox reactions. The type used most commonly is the titration based on precipitation reactions.
Most of the work in this area has been and is being done in Russia and Hungary and the literature is difficult to obtain.

No reference has been found for attempt to introduce radiometric titrations into college chemistry courses. In view of the use of radioisotopes in analytical work, this appears to be a discrepancy that needs to be corrected.

This study is an attempt to aid college teachers in meeting this need.
CHAPTER III

BACKGROUND CONCEPTS PERTAINING TO RADIOMETRIC TITRATIONS

A survey, conducted as a part of this study, of some representative undergraduate textbooks (see appendix) revealed that only the General Chemistry textbooks include a section on radioactivity. The discussion of radioactivity in these textbooks present primarily elementary factual data with little attempt at either depth or completeness. The concepts discussed are primarily in the area of nuclear chemistry in that emphasis is on the reactions of nuclei and the properties of the resulting species. Little or no information is given on radiochemistry which deals with the techniques or theory of usage or to the techniques of handling radioactive materials. Nuclear chemistry and radiochemistry are so interdependent for radiometric titrations and related areas that a complete discussion must include both.

Chapter II of this dissertation discusses previous work in the area of radiometric titrations. This content is primarily radiochemistry in nature since the discussion centers on the chemical species being titrated, the radioisotope used, and the manner of manipulation of the reagents.

The basic nuclear chemistry concepts that should be understood in connection with radiometric titrations include
the nature and types of radioactive emissions, theory of emission detection, radioisotope production and characteristics, decay modes, specific activity and the statistical nature of radioactivity.

Radioactive decay is energetically possible when the atomic mass resulting is lighter than the starting atomic mass. This mass difference determines the maximum decay energy that may be released.

Radioactive emission occurs due to a nuclear structure that is unstable because it either has too many neutrons and protons or the ratio of the neutrons to protons is unfavorable. The former situation is found with the higher atomic weight elements and is often responsible for alpha emission. An unfavorable neutron ratio may be corrected by some form of beta decay. A low neutron to proton ratio may be corrected by positron emission or electron capture whereas a high neutron to proton ratio may be corrected by negatron emission.

Beta decay may occur in several ways, all of which change the atomic number but maintain the same atomic mass number.

Negatron emission, the most common type of beta decay, occurs in nuclei that contain an excess number of neutrons for stability. Since the mass difference for a given nuclide undergoing beta emission should be a constant
value, one might expect the energy of betas from a given nuclide to have the same energy. However, the beta particles from a given radioactive species are emitted with a continuous energy distribution ranging from zero up to a maximum value. This energy difference is due to the simultaneous emission of a second particle (called a neutrino) which accepts the energy not retained by the beta. This distribution of energy is important in radiometric titrations of precipitation reactions since the increased thickness of solution through which the emissions from the precipitate must pass for detection causes a decrease of count rate that can be used for the end-point determination.

Positron emission occurs when proton rich nuclei change a proton to a neutron, a positron, and a neutrino and thereby decrease the atomic number of the nuclei by one.

A positron is the antiparticle of a negatron and has a positive charge. The production of a positron requires 1.02 Mev of energy, twice the rest-mass energy of the electron. The joining of a positron and negatron will cause these species to be destroyed and the 1.02 Mev of energy reappears as two gamma rays.

The third type of beta decay is electron capture. This occurs when neutron deficient nuclides take up an extranuclear electron. This electron is usually taken up from the K shell since quantum-mechanical wave functions of the
K electrons have larger amplitudes at the nucleus than those of the L, M etc. electrons. This beta decay mode is the only mode possible for a neutron-deficient nuclide when the decay energy (the mass difference between the decaying and product atoms) is less than 2 mc². The electron-capture process is more difficult to observe than negatron or positron emission because no detectable nuclear radiation is emitted except in cases where the product nuclei are left in excited states and gamma rays are emitted.

Friedlander, Kennedy and Miller (1964) describe three types of gamma emission. One uncommon type of gamma transition involves the creation and emission of a positron-negatron pair. Another type involves electromagnetic interaction between the nucleus and an extranuclear electron with the electron being ejected from the atom. The internal conversion electron emitted by this process could be detected by the method used in this research provided the energy acquired is at least 0.1 Mev. The most common type of gamma emission is simply the emission of electromagnetic radiation to allow a nucleus in an excited energy state to go to a lower, more stable energy state. The energy released in making this transition may be lost as a single unit or the ground state may be reached by a stepwise path whereby the energy has been released as several smaller units. Therefore, the gamma rays emitted are either monoenergetic or
else there is a spectrum made up of a limited number of discrete groups having definite energies.

This study was concerned primarily with beta emission and to a lesser extent with gamma emission. This choice is a natural result of the nature of the emissions, the types of emission given off by the available isotopes and limitations of the detection equipment used. The G-M counter used is incapable of detecting alpha particles and the gamma rays are detected with perhaps only one percent efficiency. Beta particles, however, may be detected with about a twenty-five percent efficiency. Therefore, beta emission is the most useful for this technique.

The inability to count alpha emissions is not serious since the isotopes available without a specific license are practically all beta and/or gamma emittors. Of sixty-seven isotopes available for purchase from General Radioisotope Processing Corporation without a special license, only polonium-210 is listed as a 100 percent alpha emittor. The maximum activity of the polonium-210 sample available, however is 0.1 microcurie and therefore it would be too weak to make a good indicator even if it could be detected. Two other isotopes, radium-226 and uranium-238 are listed as complex alpha, beta, gamma emittors and again are available only as solutions with very low activities. The remaining isotopes available from the above Company are beta and/or
gamma emitters so most low activity radioisotopes available are of the desired emission type.

Beta emitters were also selected for use because of their counting characteristics. Counting differences are caused by the physical characteristics of the different types of emission. In general, this difference is due to emission size and velocity. Alpha particles, having greater charge and having a low velocity will undergo a large number of collisions per unit of distance traveled. Beta particles with a smaller charge and having a much higher velocity will undergo fewer collisions per unit of distance traveled. The specific ionization for an alpha particle is more, therefore, than the specific ionization of a beta particle of comparable energy.

A gamma ray may pass through a Geiger-Muller tube undetected, whereas an alpha particle will not travel far enough to enter the counting tube. Most beta particles have sufficient range to enter the Geiger tube and a high enough specific ionization to be detected when they do enter.

All detection methods depend on interaction of the nuclear radiation with matter to produce ions. For each ion pair formed the radioactive emission loses about 35 ev. The behavior of ion-pairs in an electrical field has received considerable study. Glasstone (1958) discusses this behavior by considering a gas filled container having two parallel
electrodes. The electrodes are connected to a power source so the voltage across the electrodes can be varied from zero to a voltage high enough to permit a spark to pass between the electrodes. At a low potential any radioactive emission that enters may cause ionization and the applied potential will cause the ions to migrate to the electrodes. The amount of charge collected at the electrodes can be measured. The magnitude of the charge collected will depend on the number of primary ion pairs produced and the voltage across the electrodes.

Figure II shows the general type of results for the number of ion pairs collected (pulse size) at various voltages. At low voltage some of the ions may combine so the pulse size is less than would be expected from the ion pairs produced. However, as the voltage is increased less recombination takes place and in the saturation region all of the ion pairs produced are retained and contribute to the pulse size. An additional voltage increase above the saturation range causes the ions to acquire enough velocity, in migrating to the electrodes, that they may produce some secondary ionization. A voltage increase over this proportional range, therefore, results in a multiplication of the primary ionization that is proportional to the increased voltage.

The Geiger region utilized in this study uses a
FIGURE II

VARIATION WITH APPLIED VOLTAGE OF PULSE SIZE DUE TO AN IONIZING PARTICLE
higher voltage than the proportional region. At this higher voltage photoionization begins in which process the intense ionization produced by a single primary electron is spread the entire length of the anode. This causes interaction with other primary ionizations and destroys proportionality of response. The negative charge collected on the anode will cause a sheath of positive ions to form which has the effect of reducing the voltage gradient below the value necessary for ion multiplication. This leaves the Geiger counter insensitive and it must recover before another ionizing event can be counted. This dead time will restrict its use to count rates of perhaps 40,000 or less counts per minute. A later section describes the method used in this study to determine the maximum count rate that could be used for the specified G-M counter.

The artificially produced radioisotopes used in this are listed in Table I together with some pertinent data. Note that the emphasis has been on using beta emitters. To prepare radioisotopes that are beta emitters, Glasstone (1958) discusses the \((d,p)\), \((n,p)\), \((n,\alpha)\), \((n,\gamma)\) and \((\gamma,p)\) as possible processes. All of these processes increase the neutron to proton ration. The \((n,\gamma)\) process is easily accomplished in a nuclear reactor. The ease of this reaction, compared to other possibilities, explains why most of the available radioisotopes are beta emitters.
<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life</th>
<th>Main type of Emission</th>
<th>Energy of Emission (Mev)</th>
<th>Sample Activity and Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-45</td>
<td>165.1 days</td>
<td>Beta</td>
<td>0.254</td>
<td>10 microcuries CaCl₂ in HCl</td>
</tr>
<tr>
<td>Cl-36</td>
<td>3.08 x 10⁵ years</td>
<td>Beta</td>
<td>0.714</td>
<td>1 microcurie HCl</td>
</tr>
<tr>
<td>I-125</td>
<td>57.4 days</td>
<td>Gamma</td>
<td>0.0354</td>
<td>1 microcurie NaI in NaOH</td>
</tr>
<tr>
<td>I-131</td>
<td>8.05 days</td>
<td>Beta, Gamma</td>
<td>0.608, 0.335, 0.364</td>
<td>10 microcurie NaI in basic sodium sulfate</td>
</tr>
<tr>
<td>Ag-110</td>
<td>249 days</td>
<td>Beta, Gamma</td>
<td>0.087, 0.530, 0.656, 0.884</td>
<td>1 microcurie AgNO₃ in HNO₃</td>
</tr>
<tr>
<td>S-35</td>
<td>89.0 days</td>
<td>Beta</td>
<td>0.167</td>
<td>50 microcurie H₂SO₄ in HCl</td>
</tr>
<tr>
<td>Tl-204</td>
<td>3.57 years</td>
<td>Beta</td>
<td>0.77</td>
<td>50 microcurie TlNO₃ in HNO₃</td>
</tr>
<tr>
<td>W-185</td>
<td>75.8 days</td>
<td>Beta</td>
<td>0.428</td>
<td>10 microcurie Tungstate in NH₄OH and K₂CO₃</td>
</tr>
</tbody>
</table>

The above information was obtained from the 1965 Catalog for Radioisotopes from: General Radioisotope Processing Corporation, 3000 San Ramon Valley Boulevard, San Ramon, California 94583
To determine the starting nuclide from which a specific radioisotope might be prepared, it is convenient to refer to a Chart of the Nuclides of the type published by the Knolls Atomic Power Laboratory.

FIGURE III

DISPLACEMENTS CAUSED BY NUCLEAR BOMBARDMENT REACTIONS

\[
\begin{array}{|c|c|}
\hline
\text{Original Nucleus} & \frac{(d,p)}{Z} \frac{(n,\gamma)}{N+1} \\
\hline
Z & N \\
\hline
\text{(\gamma,p)} & \frac{(n,p)}{Z-1} \\
N-1 & Z-1 \\
\hline
\text{(n,\alpha)} & \frac{(n,\alpha)}{Z-2} \\
N-3 & N \\
\hline
\end{array}
\]

\(\alpha = \text{alpha}\)
\(d = \text{deuteron}\)
\(p = \text{proton}\)
\(n = \text{neutron}\)
\(\gamma = \text{gamma}\)
\(Z = \text{at. no.}\)
\(N = \text{no. of neutrons}\)

For the production of Cl-36, the reactions K-39, (n,\alpha)Cl-36, Cl-35 (d,p) Cl-36, Cl-35 (n,\gamma) Cl-36, Ar-37 (\gamma,p) Cl-36 are all theoretical possibilities. The actual process selected will depend on a number of factors such as availability and properties of the beginning substance and the efficiency of the activation process.

For Cl-36 production the (\gamma,p) reaction would be a
poor choice since Ar-37 has a half-life of only 34.3 days and therefore is not readily available. The most logical choice in terms of availability of the starting nuclide and efficiency of the activation process is the Cl-35 \((n,\gamma)\) Cl-36 reaction since this utilizes the most common stable isotope of chlorine. The chance of effective collision is also better with a neutron than with a particle such as a deuterion since the electrically neutral neutron is not subjected to electrostatic repulsion as it approaches an atomic nucleus. In fact, as the neutron approaches the nucleus, attractive forces will begin to operate to aid in capturing the neutron.

The type of activation particle used is also of importance when the activated nuclide is to be isolated. If the product nuclide is isotopic with the starting nuclide, chemical separation of the active atoms from the inactive atoms may not be feasible, or even possible and the radioactive solution is used without any separation.

In cases where the product nuclide is changed to a different atomic species, the different properties of the nuclides may allow chemical separation. However, the amount of radioisotope produced is usually quite small and often the usual analytical methods may fail. To make the separation possible, it is common to add some inactive material, isotopic with the radioactive nuclide produces, to act as
carrier. This allows the desired radioisotope to be separated but does add to the total chemical concentration of the radioisotope solution. This actual concentration must be determined and considered in making radiometric titrations. Ideally, the radiometric indicator should be of such activity and concentration that the initial count rate of the solution to be titrated is from 20,000 to 35,000 counts per minute, and the actual concentration of the radioisotope is too low to cause precipitation to take place. It was necessary, therefore, for the success of this study, to determine if radioisotopes were available that have a low total concentration so as to not severely restrict the analysis concentration range and at the same time had an activity high enough to give the desired count rate.

For radioisotope solutions having a low activity compared to the total concentration, the actual concentration must be determined so endpoint correction calculations can be made.

The activity of the five milliliter samples, purchased for this study, varied from one to fifty microcuries. A curie is defined as $3.7 \times 10^{10}$ disintegrations per second. The disintegration rate expressed in curies measures only the number of disintegrations per second and gives no information concerning the type of radiation, emission energy or decay scheme.
Strominger (1958) and others have compiled a table of the properties of many isotopes. A decay scheme such as represented by Ca-45 is of the simplest type.

**FIGURE IV**

DECAY SCHEME FOR CALCIUM-45

Ca-45 (164 d)

Ca-45 → Sc-45

Calcium simply emits a negatron and the energy lost would be the same for all disintegrations. The decay scheme for I-131, by contrast, is complex as is shown in the figure below:

**FIGURE V**

DECAY SCHEME FOR IODINE-131

I-131 (6.1 d)

0.7% 9.3% 87.2% 2.8% 0.722

Xe-131 2 x 10^{-11}s 0.637

Xe-131m 12d 0.364

4.8 x 10^{-10}s 0.164

Xe-131 0.080

Xe-131 0.000
With a five milliliter sample of either calcium-45 or iodine-131, one would have the same number of disintegrations per unit of time since both have a ten microcurie activity. It does not necessarily follow, however, that under the same conditions one would obtain the same count rate from two similar sized samples since many factors such as type and energy of emission enter in. Knowledge of the sample activity can be used in determining the minimum volume of radioisotope needed to obtain a count rate. Since a curie is $3.7 \times 10^{10}$ disintegrations per second, it can be calculated that ten microcuries would give $2.2 \times 10^7$ disintegrations per minute. If the counting conditions allow ten percent of the counts to be determined, this would give $2.2 \times 10^6$ counts per minute. For illustrative purposes, if it is assumed that $1 \times 10^4$ counts per minute are needed, the amount of solution required would be:

$$\frac{1 \times 10^4 \text{ cpm required}}{2.2 \times 10^6 \text{ cpm total}} \times 5 \text{ ml.} = 2.3 \times 10^{-2} \text{ ml.} = 23 \text{ lambda}$$

A knowledge of the count rate is important because radioactive disintegrations are statistical in nature. This means that the number of counts may not be the same even if the sample is counted under the same conditions for the same time interval. A calculation of the standard deviation allows one to determine the amount of deviation that could be expected. The percent of deviation will be lessened by
increased count rates and/or increased count time. In practice, where the observation time is short compared with the half-life, Friedlander, Kennedy and Miller (1964) give the formula for finding the standard deviation as:

\[ \sigma = \sqrt{M} \quad \text{or} \quad \sigma = \sqrt{\frac{Mt}{t}} \]

where \( M \) is the number of counts per minute and \( t \) is the time in minutes.

With the counts per minute \((1 \times 10^4)\) required in the above example, a count time of one minute would give a standard deviation of:

\[ \sigma = \sqrt{10,000} = 100 \]

The count rate would be expressed as \(10,000 \pm 100\) and the standard deviation would not be expected to be greater than one percent. The standard deviation can be decreased by using a longer count time. A count time of one hundred minutes giving a total of \(1 \times 10^6\) counts would give a standard deviation as follows:

\[ \sigma = \sqrt{\frac{1 \times 10^6}{1 \times 10^2}} = 10 \]

The count rate would now be expressed as \(10,000 \pm 10\). The deviation is now one tenth of one percent.

Loevinger and Berman (1951) made a study of statistical error due to background and sample fluctuations. Since a sample is not counted directly, but is counted in the presence of a background of counts characteristic of the
counting device and its environment, they found that the standard deviation obtained by the above formula is actually an estimate that may deviate from the true value by as much as ten percent. For strong samples the background variations can be neglected. However, for weaker samples to insure the standard deviation being within the desired precision requires a count time approximately ten percent longer than calculated.

The concepts in this chapter were selected as the basic background information needed by college teachers planning to use radiometric titration as a teaching tool. The inclusion of these concepts allows this dissertation to be a self-contained teaching unit.
CHAPTER IV

EQUIPMENT AND CHEMICALS

I. INSTRUMENTATION

The basic instrument, used to obtain the data in this investigation, was the Lionel 455 Scaler-Ratemeter. This instrument was developed and manufactured in accordance with United States Atomic Energy Commission specifications to provide an accurate measurement of radioactivity for industrial, school, university and medical laboratories.

The Lionel 455 Scaler-Ratemeter provides five basic circuit functions. The main function of each circuit is summarized briefly in the following paragraphs. For detailed information, the Instruction and Maintenance Manual for this instrument should be consulted.

The input amplifier and discriminator circuit accepts only those input pulses whose magnitude is above a minimum pulse height. This minimum pulse height may be adjusted by the sensitivity control. The discriminator has a range from 0.25 to 5.0 volts. This circuit insures equal pulse height acceptance for all other circuits.

The ratemeter circuit converts the pulse input signal to a D.C. voltage which is monitored to cause a meter deflection proportional to the count rate. Three ratemeter ranges are provided: 50,000, 5,000 and 500 pulses per minute.
The scaler section indicates the total pulse count during a given time interval. The scaler consists of eight identical binary stages in cascade. Count indication is made by neon lamps connected to the binary output plates of each stage. On each binary stage an electrical pulse cuts off the other half. The output pulse from the last binary stage is used to trigger the tube that drives the mechanical register.

The five digit mechanical register is an extension of the electronic scaler. The total count capacity of the register is 256 times 99999. A timer measures the elapsed time in increments of one hundredth of a minute on a five digit mechanical register. This allows a count time up to 999.99 minutes. The timer is actuated by the count-stop switch located on the front panel of the instrument. A mechanical reset button for the timer provides simultaneous resetting of the electronic scaler and count register.

The audio circuit provides an audible click for each pulse.

The high voltage supply is designed to deliver a regulated output voltage over the range of 400 to 1250 volts. Line (90-130v, A.C.) and load regulation can be expected to exceed 0.2 percent. The high voltage supply cannot be turned on unless the low voltage supply has been turned on, and a thirty second time delay has been actuated.
II. THE GEIGER-MULLER TUBE

The experimental work was done using an end-window G-M tube of the type LIA 7618. The mica end-window has a rating of 1.4 to 2.0 milligrams per square centimeter. This is a halogen filled, self-quenching type G-M tube which, because of the very thin end-window, offers high sensitivity with low background for use in beta and gamma detection. These tubes are designed to operate between 860-940 volts with a normal of 900 volts. This is the voltage at which each ionizing event is spread along the entire length of the anode. The resolving time for the Lionel 455 is listed in The Instruction Manual as 200 microseconds. The resolving time limits the measurable count rate to a maximum value which can be calculated by assuming the pulses are equally spaced. Experimentally the maximum count rate has a lower value since the pulses entering before the tube clears will not be counted. The maximum experimental count rate that can be determined with reasonable accuracy is about thirty thousand counts per minute.

The G-M tube contains halogen gas to prevent secondary emission of electrons. As the positive ions reach the cathode, there is a possibility that secondary electrons might be emitted from the surface and trigger a new discharge that would be independent of the source of radiation being measured. This type of discharge can be avoided by
use of an external quench circuit or by use of self-quenching G-M tubes. Polyatomic gases seem to be effective in preventing secondary emission because they may dissipate energy by predissociation. They may also quench metastable states of the argon atoms. Many organic additives used for quenching are consumed by use. However, mixtures containing halogens as the quench gas do not seem to deteriorate with use.

A thin walled G-M tube, type FCDA 6993, was used in connection with this study primarily for monitoring purposes. This tube is designed for use in detecting beta and gamma emissions. It is enclosed in a hand probe with a revolving shield which allows a maximum exposure of up to 120 degrees of cylindrical surface for entry of beta radiation. A coaxial cable of approximately sixty inches in length, connected to the probe assembly, makes this a convenient and versatile means of monitoring the experimental work area and equipment for possible contamination.

III. ACCESSORY EQUIPMENT

The end-window G-M tube was fastened for use in a lucite tube mount which contains variable positions for holding a plastic sample slide holder and/or an absorber slide holder. The sample holder has a circular recess in the center to hold a planchet. A discussion on back-scattering
by Friedlander and Kennedy (1956) mentions that electrons are scattered much more than heavy particles. A very significant fraction of a number of electrons striking a material may be reflected with single and multiple scattering processes. The reflected intensity increases as the reflector thickness increases until saturation is achieved with a reflector thickness about one third of the range of the electrons. The amount of scattering has been found to increase as the atomic number of the reflector increases. Energetic betas scattered from lead are found only slightly reduced in energy, whereas those back-scattered from low atomic number materials are of low energy. This means that a lucite sample holder will be more effective in reducing back-scattering than would a holder made of material of high atomic number. This back-scattering reduction is most desirable since in the measurement of beta activities, samples should be mounted in such a way that the back-scattering from the mount is either negligible or constant from sample to sample.

Aluminum and lead absorbers were available and were used in determining counter characteristics. The aluminum absorbers consisted of one each of the following weights per square centimeter; 10, 20, 40, 50, 100, 150, 250 and 350 milligrams. Four lead absorbers were available having densities of 100, 200, 300 and 400 milligrams per square
Lambda pipets were used to measure the solution for titration and to add the aliquots of titrating reagent. The most commonly used sizes were 25, 50 and 500 lambda. The lambda pipets should be the best quality available since only properly designed pipets have the very narrow tapered end to allow the ready release of the last small drop.

An Accropet pipet control was used to fill and empty the lambda pipets. By means of a knurled knob, the Accropet will accept and hold a pipet. Rotation of a second knob at the top of the Accropet creates a partial vacuum in the pipet causing it to fill. Reversing the rotation causes the liquid to be released. This allowed small amounts of solution to be transferred safely and accurately.

V. SAMPLE HOLDERS

Containers used as sample holders were of four basic types: (1) glass bottles of approximately twenty milliliters capacity, having a diameter of twenty-five millimeters and a depth of fifty-six millimeters; (2) shell vials with a diameter of twelve millimeters and a depth of sixty millimeters; (3) plastic bottle caps having a diameter of twenty-six millimeters and a depth of eleven millimeters; and (4) nylon planchets having a diameter of twenty-four millimeters.
and a depth of six millimeters. The nylon planchets are made by Atomic Products Corporation and are advertised to be capable of eliminating back-scattering.

VI. CHEMICALS

The nonradioactive chemicals used in this study were selected from reagents that usually would be available to a chemistry teacher or could be easily obtained. Most of the chemicals used were Fisher Certified Reagent grade, although 99.57 percent pure sodium chloride, 100.19 percent pure sodium oxalate and 99.98 percent pure sodium carbonate reagents were purchased from Thorn Smith, Chemist. These analyzed samples are used as standards in many Quantitative Analysis courses and therefore are usually available.

The radioisotopes were obtained from the General Radioisotope Processing Corporation. These radioisotopes are available in five milliliter solutions in one ounce pyrex bottles with sealed plastic caps. The label on the bottle is imprinted with the yellow and magenta radioactivity warning label, radioisotope name and number, type of solution, calibration, date of calibration and activity. The catalog price for both long-lived radioisotopes (35 days or more) and short-lived isotopes (14.3 days or less) includes a calibration within ten percent of the activity ordered. More precise calibrations could have been obtained at extra cost. This company does not calibrate radioisotopes.
more precisely than three percent since there are too many unknowns for greater precision.

The radioisotopes can be easily obtained by teachers since all radioisotopes used in this study are available with a general license.
CHAPTER V

EXPERIMENTAL PROCEDURE

The experimental procedure for this study was developed to serve as a teaching tool for undergraduate chemistry students. The steps of a titration, therefore, serve to emphasize specific ideas in addition to allowing the analysis of some chemical species. The determination of an unknown offers an opportunity not only to give the student an understanding of radioisotope techniques, but also to give increased understanding in other areas.

Radiometric titrations based on precipitation reactions dictate that the titrant must be fairly concentrated and capable of causing essentially complete precipitation of the chemical species to be determined.

The initial phase of the analysis is, therefore, a literature search to find a reagent that will meet the above requirements. The literature search should also determine the best conditions for this precipitation and this information used in making up the solution to be titrated. Meaningful use of handbooks and other literature aids give a student valuable training in library usage and for this study should give an increased understanding of solubility principles.

During the selection and preparation of the titrant,
the Geiger counter would be allowed to warm up and the background count rate determined.

The samples are prepared, either working in a plastic tray lined with absorbent toweling or over Saran wrap covered with absorbent toweling. This is done to allow easy and complete cleanup to be effected in case a small amount of radioisotope is accidentally spilled. All of the steps of the titrations are conducted not only to follow safe practices, but also that the student might be safety conscious in radioisotope use.

The sample was made up to contain about one milliliter of solution in a two milliliter plastic planchet. The use of a two milliliter plastic planchet allows the count rate for a given sample to be high compared with a larger amount of solution mounted a greater distance from the Geiger-Muller tube.

The solution was made up to give the best known medium for fostering complete precipitation. This provides a student with practice in predicting the overall interaction of reagents in a solution.

The reagents used to make up the solution are added using lambda pipets, the control of which is effected using an Accropet. This permits the reagent to be transferred safely and accurately.

As a sample is being titrated, an estimate of the
count rate can be obtained by a glance at the scaler and register readings at the end of the first minute. The approximation formula for the standard deviation ($\sigma$) is used to estimate the time required to give the desired precision. For example, if the count total is 1000 for the first minute and a precision of about one percent is desired, the value of sigma would be ten. The values substituted into the equation give: $\sqrt{\frac{1000X}{X}} = 10$ and solving, $X = 10$ minutes.

The above method of determining count time should give the student increased understanding of statistics and the statistical nature of radioactivity. The relationship between specific activity and count time is well illustrated by this method.

After counting for the calculated time, the count rate is recorded and an aliquot portion of the titrating reagent is added. To aid in obtaining complete solution transfer from the pipet to the solution, the last portion of a drop was touched against the tip of a stirring rod that was drawn out to a thickness of about one millimeter. This stirring rod was then used to stir the solution to allow a uniform distribution of the precipitate.

The sample would be counted using the method described above and the process continued until four or five aliquots have been added past the equivalence point.

There is usually sufficient time during the count
times to plot the count rate graphically. The volume of
titrating reagent added is plotted along the abscissa and
the counts per minute along the ordinate. The break in the
curve indicates the equivalence point and allows the strength
and amount of material in the sample to be calculated. This
step can provide student training in methods of handling
data, analysis of curve shape factors and chemical calcula-
tions.
CHAPTER VI

EXPERIMENTAL RESULTS

The curve for the titration of a radioactive solution with a nonradioactive reagent was determined experimentally by Langer (1941) to be of the type shown in Figure VI on page 60. The experimental values, used to plot this curve, were obtained from chemical systems having the following characteristics: the approximately fifty milliliter solution to be titrated was about five percent as strong as the titrating solution; about 0.3 millicurie of radioisotope was used as the indicator; 0.5 to 1 milliliter increments of titrating solution were added each time; and the counts per minute were found experimentally as about 2000 or less with a background of about 100 counts per minute. The amount of reagent to be titrated should be sufficiently strong so the addition of the required amount of radioactive isotope does not change the concentration appreciably. The high activity of the radioisotopes made procurement more restricted, required shielding, was expensive, and made disposal difficult.

This study was conducted to determine the feasibility of this type of titration in an educational situation. The problems relating to procurement, shielding, handling and solution disposal can be largely eliminated if low activity radioisotopes are used. However, use of low activity
TYPICAL TITRATION CURVE OF AN ACTIVE SOLUTION TITRATED WITH A NONACTIVE SOLUTION

COUNTS PER MINUTE

VOLUME OF TITRANT
solution in which the activity is reduced by a factor of $10^3$ or more, will require a different physical setup than used for the high activity solutions.

The chemical system determined to give comparable results to the work done involving high activity solutions was determined to have the following characteristics: the 1 to 1.5 milliliter solution to be titrated was about 10-15 percent as strong as the titrating reagent; about 0.25 microcurie of radioisotope was used as the indicator; 10 to 25 lambda increments of titrating reagent were added each time; and the counts per minute were found to be 30,000 or less initially with a background of 20 or less counts per minute. Ideally, the amount of indicator required would not change the concentration appreciably. In practice, this was found for half of the systems investigated.

The approximate curve that can be expected from a titration of this type can be calculated from the equation:

$$ cpm = \left[ \frac{cpm}{\text{perm}} \right]_0 \left[ 1 - \frac{\mu\text{eq.}B}{\mu\text{eq.}A} + \frac{C_A}{\mu\text{eq.}A} \right] $$

where:

- $cpm$ = counts per minute
- $\left[ \frac{cpm}{\text{perm}} \right]_0$ = initial count rate of the solution
- $\mu\text{eq.}B$ = the amount of titrant (B) added in microequivalents
- $\mu\text{eq.}A$ = the amount of substance to be titrated in microequivalents
\( C_A \) = the microequivalents of A that remain in solution rather than precipitating.

This equation is valid up to the equivalence point. After this point only the last term in the parenthesis is valid and therefore the first two terms would be ignored.

This equation requires that the precipitate formed will be under sufficient solution so no emissions reach the G-M tube from this source.

A variance is caused if precipitate is held on the surface of the solution. This precipitate will cause the count rate to be somewhat high all along the curve and this is most apparent if the addition of the first increment of titrant produces very little precipitate other than that on the surface. After this point, the curve follows that of the calculated curve.

Assuming the solution depth is sufficient to stop emissions from the precipitate from being counted, the count rate beyond the endpoint is determined primarily by the solubility of the precipitate.

To obtain a high count rate with a small amount of low activity radioisotope required a physical setup that could detect a maximum number of emissions. This lead eventually to the titrations being done in a two milliliter plastic planchet and the increments for the titration being added by use of a lambda pipet. To utilize the maximum count rate, the
solution was counted in the presence of any precipitate that had formed. This introduces factors that may influence the curve shape.

Factors that cause the curve shape to depart from the theoretical curve include: the dilution effect of any solution added; the position of the precipitate relative to the counter; and the nature and energy of the emissions.

The addition of water to a sample will cause the count rate to decrease. Langer (1941) made a correction for the count rate using the correction factor \( \frac{V + U}{V} \) where \( V \) is the original volume and \( U \) is the volume added. With a 20:1 ratio between the sample being titrated and the titrating reagent and no effect from the precipitate, the correction would seem theoretically acceptable.

However, the experimental results of this study show that, with the conditions of geometry required, the decrease of count rate of a solution is not always linear. The use of larger volumes (necessitating larger containers) gave a much faster initial count rate decrease than the use of small volumes. This was expected since the new average distance through which the betas must pass will prevent a longer range of low energy betas from emerging with sufficient energy to enter the Geiger-Muller tube. The count rate is affected with addition to the small volume, but only a short range of the lower energy betas will be stopped. The inverse
square law is also more effective in maintaining the higher count rate for the system where some reagent is added to a small amount of solution positioned close to the G-M tube.

The overall percentage decrease was also found to be larger for large volumes. A comparison between the count rates of a given initial volume and the count rates as water in multiples of the initial volume were added is shown in Table II on this page.

**TABLE II**

A COMPARISON OF COUNT RATE DECREASE WITH THE ADDITION OF WATER TO DIFFERENT VOLUMES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Volume</th>
<th>Total Volume of Water Added</th>
<th>Counts/Minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 Milliliter</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 Milliliter</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 Milliliters</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 Milliliters</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 Milliliters</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7 Milliliters</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>200 Lambda</td>
<td>6100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 Lambda</td>
<td>5600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400 Lambda</td>
<td>5000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600 Lambda</td>
<td>4600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000 Lambda</td>
<td>3900</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1400 Lambda</td>
<td>3200</td>
<td></td>
</tr>
</tbody>
</table>
The general values tabulated in Table II indicate several factors that had to be considered for this type of titration. The point just mentioned, that the addition of water alone gave various curve possibilities, was important in selecting the starting volume. For Sample A, before dilution, direct titration would show a very fast initial decrease and then a gradual leveling off. This would be caused primarily by the solution added and to a small extent by the precipitation effect. The exact effect of each contributing factor would be impossible to determine and this initial part of the curve would not help in determining the final end point. Several techniques were used to minimize this dilution effect and allow the major change of count rate to be due to the precipitation occurring. Reference to Table II, page 64, indicates the drop in count rate for Sample A was fairly linear after the addition of two milliliters of water and that the count rate decrease was not changing by large amounts. The addition of 600 lambda of Sample B was sufficient to cause a nearly linear count rate decrease. This dilution effect was determined for each type of titration and care taken that sufficient sample was present to offset the initial fast decrease. The best way to offset the dilution decrease is to use a reagent for the titration that is considerably stronger than the solution to be titrated. For example, if the initial chloride ion concentration of a
one milliliter solution was one tenth normal, the amount of one normal silver nitrate solution required to reach the equivalence point would be 0.1 milliliter. From Table II, one would predict the dilution effect would cause a decrease of about seventeen counts per minute. Since the actual decrease would have been from about 4250 to about 100 counts per minute, the effect of the dilution would be much less than one percent.

Sample A was counted in a twenty milliliter glass bottle with a top opening diameter of eighteen millimeters and a distance from the bottom of the sample to the G-M tube of fifty-seven millimeters. By contrast, the plastic planchet has a diameter of twenty-three millimeters and the distance from the bottom of the sample to the G-M tube is seven millimeters. Comparison of differences of count rate reveals that it is only by keeping the sample size small that it is possible to get reasonable count rates from low activity radioisotopes. This also shows the increased utilization of the available emissions and helps explain how it is possible to obtain reasonable results from such low activities.

The description of sample containers, used for the experimental data, is listed in Chapter IV. A number of types were tested to determine the solution thickness needed to give a sufficient count rate decrease. The
verification that small volumes allow a sharp decrease in count rate was most fortunate since this allowed small plastic planchets to be used. This allowed the maximum count rate to be obtained from a given activity and thus reduced the amount of indicator required.

The minimum volume that can be determined is determined partially by the thickness of the solution being titrated. The count rate decrease during titration is due, not only to the increased average distance of the radioisotope in the precipitate, but also to the absorption of the betas by the increased solution thickness through which the betas must pass to be detected. It is therefore desirable to know the relationship between beta energy and absorption in water. This allows the selection of a solution thickness that will absorb most of the betas from the precipitate formed.

Figure VII, page 68, shows the range versus energy curve for beta absorption in water. For Tl-204, the most energetic beta emitter used, the minimum solution thickness should be about 1.7 mm. In the small plastic planchets, this would require an initial volume of about 650 lambdaas of solution. For beta emitters of lesser energy the volume could be reduced.

However, since all of the precipitate does not form under the surface at the minimum distance, it is better to
FIGURE VII
RANGE VERSUS ENERGY CURVE FOR BETA ABSORPTION IN WATER

Mev.

0.8

0.6

0.4

0.2

Thickness of water (mm)
use a solution thickness greater than the calculated minimum distance. For the Tl-204, the minimum solution thickness would require about 650 lambdas of solution. The use of 1000 lambdas of solution is more desirable since there is more assurance than most of the precipitate will be under sufficient solution to stop most of the beta emissions.

Satisfactory radiometric titrations can be performed with 0.1 normal or greater chloride solutions. Since the Cl-36 sample is 1.02 normal, use of one hundred lambda in a milliliter of total solution will give the minimum concentration required. Chlorine-36 can therefore, be titrated directly. Due to this overall chloride concentration, the most accurate titrations will be found for concentrations considerably above the minimum value.

This situation in which the activity is low in comparison to the total concentration restricts the concentration range that can be titrated and the results are less accurate. This situation was found with Cl-36, I-125, I-131 and Ag-110. The concentrations of Ca-45, S-35, Tl-204 and W-185 were too low to give precipitation under the experimental conditions. Therefore, sufficient indicator could be added to give a high count rate without limiting the concentration range.

The theoretical curve and the actual experimental curve appeared quite different for certain systems. Figure VIII, page 70, indicates that small amounts of titrant added
FIGURE VIII

RELATIONSHIP BETWEEN CURVE SHAPE AND CONCENTRATION

CURVE A

CURVE B

EQUVALENCE POINT

COUNTS PER MINUTE

VOLUME OF TITRANT
Initially will often cause a count rate increase rather than decrease even though precipitation is occurring. This is caused by some of the precipitate remaining suspended on the surface of the solution. This decreases the average distance of some of the radioactive species and causes the count rate to increase. As additional titrating reagent was added, the small amount of precipitate held on the surface reached a maximum which gradually decreased until at or near the endpoint little or no precipitate remained suspended. Therefore, after the addition of some amount of titrant, this amount determined by the specific system, the count rate due to the suspended precipitate decreased. All of the precipitate that falls to the bottom will cause a count rate decrease.

Examination of Figure VIII indicates the curve possibilities that may be found depending on the concentration of the solution being titrated. For extremely weak solutions, the equivalence point may fall on the ascending portion of the curve. This occurs when the amount of precipitate that may be held by surface tension may be a large portion of the total precipitate formed. The precipitate held by surface tension is normally a very thin layer so if a sufficient amount of precipitate has formed on the bottom, normal crystal growth will eventually cause all the precipitate to be on the bottom. However, where the amounts of precipitate are about
equal, the time required for this equilibrium to be achieved is much too long to make this a feasible titration and this must be considered below the acceptable concentration range.

The dotted line A represents the type of break found for a more concentrated solution. If sufficient points can be obtained along the region of count rate decrease, and a definite break results, the values will be quite accurate. The much longer linear decrease, before the break for solid line B, would be expected to give better results than the previous break since the slope of the line can be determined more accurately. This indicates that the stronger solutions can be determined most accurately and this was experimentally verified.

The type of curve represented by A has a count rate advantage over curve B. All of the points up to and including line A represent quite high count rates. This high count rate allows the points to be more statistically valid than would be true for the points on line B unless much longer count times are followed here.

The titration of a very concentrated solution with a concentrated reagent was found to give a final solution that has precipitate in such large amounts that it doesn't form a layer on the bottom but the precipitate extends throughout the solution. A very small amount of titrating reagent added initially again increases the count rate. However, a small
addition of the titrating reagent as compared with the amount required at the endpoint will have caused the solution to become thick with precipitate. This causes an abnormally large count rate decrease since much of the radioactive species in the liquid will be absorbed or scattered by the solid located near the top of the solution. The addition of more titrant continues to decrease the count rate. All points on the curve will be somewhat abnormal. For extreme cases, the slope may become so shallow that the endpoint cannot be determined exactly. Figure IX, page 74, represents the type of curve found with many very concentrated solutions. A ten fold dilution of these concentrated solutions is normally sufficient to give a more ideal curve and a much sharper endpoint.

In the analysis of an unknown solution, time may be saved by a preliminary run using short count times. The point at which precipitation ceases gives a general indication of the endpoint. The amount of precipitation formed and the preliminary titration curve will give added information. This information should be revealing enough so a titration can now be run in such a manner that perhaps eight or ten increments of titrant will be added before the endpoint and four or more points can be determined beyond the endpoint. A graphical plotting of the data as the titration progresses will indicate when sufficient points have been
FIGURE IX

TYPICAL CURVE FOR VERY CONCENTRATED REACTANTS

COUNTS PER MINUTE

VOLUME OF TITRANT

POSSIBLE EQUIVALENCE POINT
accumulated beyond the endpoint.

With some of these more generally applicable ideas in mind, more exact analysis of specific experimental results may now be discussed.

The strength of iodine-131 was determined, by direct titration with one molar silver nitrate solution, to be a 0.0443 molar solution of potassium iodide. The strength of each new sample of I-131 would have to be determined since it does add significantly to the total iodide concentration. An advantage of a weak titratable indicator such as I-131 is the assurance that all iodide of a sample will precipitate since the indicator alone is strong enough to cause precipitation. Since the I-131 strength is quite low, it was possible to obtain results within about one percent of the calculated values for concentrations of iodide ion as low as 0.01 normal. This strength was considered the lower limit of iodide that could be titrated reasonably accurately by this method. Figure X, page 76, shows a representative curve for this type of titration. This shows that the curve is very similar to the theoretical curve shown on page 60. The endpoint is sharp and the results are capable of an accuracy of one percent or better.

The 8.05 day half-life of I-131 may be advantageous or not, depending on the planned experimentation. If the experimentation is to be completed within a week or so, this
TITRATION CURVE TYPICAL FOR THE TITRATION OF 1000 LAMBDA OF 0.106 N KI (ACTIVITY OF I-131 OF 0.05 MICROCURIES) WITH 1.00 N AgNO₃.
isotope may be a good choice. However, if it is desired to use small amounts of a radioisotope periodically over several months, some other choice would be recommended. Longer lived isotopes also have the advantage that they can be ordered ahead of time to make sure they are available when needed. Short-lived radioisotopes are made on special order and in addition to the restriction on being readily available the short-lived special order radioisotopes are more expensive.

A short-lived radioisotope does have an advantage for beginning students in that if a spill should occur, the amount of activity that cannot be cleaned up immediately will soon be gone. For example, an unusually large amount of I-131 used as an indicator would be 250 lambda (0.5 microcurie) of solution. From an initial disintegration rate of about 20,000 counts per second, the count rate would drop to about fifteen counts per minute in four months.

The titration of an iodide solution using Cl-36 as the indicator works best if the iodide concentration is at least four times greater than the chloride ion concentration. Since silver iodide will precipitate first, the count rate should remain essentially constant until silver chloride precipitation begins. Each additional increment of silver nitrate solution should cause a steady count rate decrease until the chloride ion has been removed by precipitation.
When the iodide ion concentration exceeded the chloride ion concentration by eight times or more, the expected curve was approximated experimentally. The low chloride ion concentration caused a very fast count rate drop during the chloride precipitation. This gave sharp breaks to the curve allowing the iodide and chloride ion endpoints to be readily determined.

As the ratio of iodide to chloride ion decreased, the experimental results show the count rate dropped an increasing amount over the iodide precipitation range. This is believed due to the simultaneous precipitation of some silver chloride as the silver nitrate was added. With a lower iodide ion concentration the time required to replace the precipitated chloride ions with iodide became longer. This lack of complete equilibrium caused the points near the iodide equivalence point to be somewhat erratic. Figure XI, page 79, shows a typical curve for the titration of a solution containing several times as much iodide ion as chloride ion when Cl-36 is the indicator.

Inspection of the curve shows that the count rate decreases with the first increment of titrant added. This further confirms the conclusion drawn previously that a small amount of radioactive solid supported by surface tension will increase the count rate. Here the precipitate held on the surface is nonradioactive and hence will not
FIGURE XI

TITRATION CURVE TYPICAL OF THE TITRATION OF A SOLUTION CONTAINING BOTH IODIDE AND CHLORIDE IONS WITH SILVER NITRATE
increase the rate.

It was found impractical to allow sufficient time for complete equilibrium to be established if the only ion to be analyzed was the iodide ion. It was faster to obtain the endpoint break for the silver chloride precipitation and then subtract the known amount of chloride ion.

With a high ratio of iodide to chloride ion, the experimental values usually agreed within one percent of the calculated values.

Hein and McFarland (1956) worked out an experiment designed to illustrate to a class in Radiometric Tracer Techniques the potentialities of radioisotopes as an analytical tool. They used 0.3 millicuries of silver-110 having a specific activity of 100-300 millicuries per gram. It seemed worthwhile to determine the potential use of the low activity silver-110 to obtain comparative results.

Most of the activities for the available low activity radioisotopes range from one to fifty microcuries. The five milliliter solution of low activity silver-110 has a maximum activity of one microcurie. Of this activity, only the 0.53 Mev betas, which make up thirty-five percent of the disintegrations, will be detected readily by the counter. This makes the effective activity of the silver-110 sample about 0.35 microcurie. This activity placed in a physical setup comparable to that used by Hein and McFarland (1956) would
yield a count rate of about one count per minute. Use of a two milliliter plastic planchet, as done in this study, enable count rates up to 500 counts per minute to be realized from a 0.1 microcurie sample. This requires a count time of about twenty minutes and longer per increment added to give results that should be within one percent of the accepted value. Thus, reasonably exact results can be obtained only by using quite long count times. This means that as an analytical tool this system will either be time consuming or will lack accuracy. It can be used in a teaching situation to illustrate the theory involved.

The Ag-110 solution was determined experimentally to be 0.184 normal. This limits the concentrations of silver solutions, in which Ag-110 can be used as an indicator, to about one tenth normal or greater.

The main value of the experimental delineation of the Ag-110 system was to set forth and verify the expected results. An understanding of this phase of the study should aid a teacher in proper isotope selection based on knowledge of concentration, activity, and emission type and energy.

Very few one hundred percent gamma emitters are available and for those that are the usual maximum activity is one microcurie. Since only a small percentage of the gamma emissions entering the G-M tube are detected, this should reduce the count rate potential of a one hundred percent
gamma emitter to a value even lower than that obtained for a mixed beta and gamma emitter such as silver-110.

This count rate decrease was verified using iodine-125 which doesn't emit any betas. Initial count rates of about 200 counts per minute can be obtained from a solution made up of 500 lambda (0.1 microcurie) of I-125 in a total of 1.2 milliliters of solution. To obtain results that are statistically valid within one percent would require count times of fifty minutes or longer.

These results allow some approximate calculations to be made for the activity of iodine-125 that would give a high enough count rate to assure a minimum of statistical variation. The calculated activity for optimum count rates would be about fifty microcuries. Quite good results should be possible with ten microcurie samples.

It is concluded that one hundred percent gamma emitters, in which the overall concentration is such that the amount of activity must be limited to 0.1 microcurie, should not be used for titrations in which the end result is expected to be very accurate.

Since nearly every beta entering the G-M tube will be counted, one hundred percent beta emitters should give the best results for a given sample activity.

This phase of the problem was explored using Cl-36 in which the activity of the five milliliter sample was one
microcurie.

One tenth of a microcurie of Cl-36 in 1.2 milliliters of solution is capable of giving about 2000 counts per minute. This reduced the initial count time to five minutes to obtain statistical results that could be expected to fall within one percent of the accepted value. This time reduction allows titrations to be conducted within a reasonable time interval.

Ideally, to keep the count time short, the initial count rate for the radiometric titrations would be near the maximum count rate that could be accurately determined by the counter used. A four microcurie sample of Tl-204 was allowed to dry up in a plastic plachet and this source was used to determine the maximum count rate for the counter used in this study. This activity was sufficient to flood the counter when placed near the G-M tube. By determining the count rates at various distances and plotting the results graphically, the maximum count rate that could be considered reasonably accurate was found to be about thirty thousand.

Since the count rate decreases through the titration, the last increments added will require the longer count time. Hence, timewise, this is the most critical region. For Cl-36 the count rate is very near background at the equivalence point and quite accurate results can be obtained by determination of just those points required to allow extrapolation
to zero. Chloride solutions 0.1 normal or stronger can be titrated quite accurately.

In most of the experimentation, the active chloride solution was titrated with nonactive silver nitrate giving a curve similar to Figure VI. This trend can be reversed by titration of a nonactive silver nitrate solution with an active chloride solution. The chloride solution contained 0.05 microcurie of Cl-36 per milliliter. The curve for this titration is shown in Figure XII, page 85. The count rate for this type of titration starts with a count rate very near background, increases very slowly up to the equivalence point and then rises sharply. Titration in this direction usually gave a very sharp break. Since the first increments of titrating reagent will give count rates near background, it is most imperative for this type of titration that a preliminary titration be run to determine the approximate endpoint. This allows a second titration to be performed in which a small number of carefully selected points are used to determine the slope of each portion of the curve. The accuracy obtained by this method gave results that were normally within two percent of the calculated value.

Combination curves are also possible. This involves the titration of a radioactive solution with a radioactive solution. This type of titration was predicted possible by Langer (1941). The system used was a sodium chloride solution
FIGURE XII

TYPICAL RADIOMETRIC TITRATION CURVE FOR A NON-ACTIVE SOLUTION TITRATED WITH A RADIOACTIVE SOLUTION

COUNTS PER MINUTE

VOLUME OF TITRANT

EQUIVALENCE POINT
containing Cl-36 titrated with a silver nitrate solution containing Ag-110. The predicted curve was a decrease of count rate to the equivalence point followed by an increase beyond this point. Since comparable activities yield more detectable emissions for the Cl-36, it was expected that the count rate following the endpoint would be much less than the count rate decrease along the chloride portion of the curve. All of the predicted trends were supported by the experimental results. The experimental curve is shown in Figure XIII, page 87.

The experimental values obtained using two radioisotopes deviated close to two percent of the calculated values. The simpler systems have given greater accuracy and reproducibility.

Calcium-45 was used in the titration of oxalate, molybdate and carbonate solutions. This radioisotope has quite ideal characteristics in terms of half-life, specific activity and type of emission. The much weaker beta emission decreased the count rate considerably from its potential value. A 0.2 microcurie sample of Ca-45, diluted to one milliliter will give about three hundred counts per minute. This gives some indication of how the lower energy betas will be absorbed compared with high energy betas.

The experimental curves, resulting from titrating calcium (II) solutions that contain Ca-45 with a molybdate
FIGURE XIII

TYPICAL RADIOMETRIC TITRATION CURVE FOR RADIOACTIVE CHLORIDE SOLUTION (CONTAINING Cl-36) WITH RADIOACTIVE SILVER (CONTAINING Ag-110) SOLUTION
solution show the curve characteristics represented in Figure VIII, page 70, and Figure IX, page 74. Titration of solutions of about 0.6 molar or stronger calcium chloride solutions gave curves most closely resembling Figure IX, page 74. Solutions of about 0.4 molar gave results close to the theoretical curve, shown in Figure VI, page 60. Solutions 0.1 molar or less gave too little precipitate to go beyond the ascending part of the curve as shown in Figure VIII, page 70.

The medium strength calcium (II) solutions gave results within one percent of the calculated values. Extremes of strength become less accurate due to curve limitations.

Since the titration method used in this study depends on the precipitate being insoluble, the nature of the solution being titrated had to be carefully considered. The calcium-45 solution available comes as a solution of calcium chloride in hydrochloric acid. Since calcium molybdate is acid soluble, it is necessary to make the solution basic before titration.

A series of titrations were performed to determine the exact amount of variation that would be found with pH dependant solutions. In each case 920 lambda samples of 0.438 molar calcium chloride solution, with a specific activity of 0.2 microcuries of Ca-45, was titrated with
1.138 molar sodium molybdate. A tabulation of the results is listed in Table III below:

**TABLE III**

**TITRATION RESULTS OF pH DEPENDENT SOLUTIONS**

<table>
<thead>
<tr>
<th>Milliliters of 4 M NaOH added</th>
<th>Approximate Initial pH</th>
<th>Approximate Final pH</th>
<th>Exp. Endpoint</th>
<th>Calc. Endpoint</th>
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<td>2</td>
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</table>

A literature search failed to give a value for the constant of ionization of molybdic acid. It is simply listed as being very insoluble. The solubility product constant for calcium molybdate is given as $1 \times 10^{-7}$. Therefore, under acidic conditions some molybdic acid would form since this is the least soluble and the count rate would not drop as much or over as long a range as when the molybdate precipitates only with the calcium under basic conditions. The student could calculate that the constant of ionization for the molybdic acid would be $1 \times 10^{-17}$ or less using the equation: $H_2MoO_4 = 2H^+ + MoO_4^{2-}$.

Some precipitation occurred in all of the above titrations. Accurate results were obtained with excess base. The solution became slightly more acidic as the titration proceeded so if the amount of base added was just enough to
make the solution basic, the solution changed from basic to acidic during the titration. This caused a slightly premature endpoint. With no neutralization at all, the acidic conditions caused the experimental endpoint to be much lower than the calculated endpoint.

This series makes an excellent teaching exercise to emphasize the necessity of examining all factors of a solution that may effect the desired point. The study of radiometric titrations will teach the student much about solubility characteristics.

Calcium-45 was also used as the radioisotope for the titration of calcium chloride solutions with sodium oxalate. A saturated solution of sodium oxalate is 0.276 molar at twenty degrees. To insure complete solubility, the actual strength of sodium oxalate prepared was 0.155 molar. The best experimental results had been obtained by adding non-radioactive reagents to the radioactive solution. It had also proven best to have the titrating reagent considerably stronger than the solution to be analyzed. Analysis of this criteria indicates that all desirable requirements can not be realized in titrating calcium chloride (containing Ca-45) with 0.155 molar sodium oxalate unless it is possible to titrate extremely weak solutions of calcium chloride.

To determine the feasibility of titrating a radioactive solution with a nonactive solution, a 525 lambda
solution of 0.193 molar calcium chloride (contains 0.2 microcurie Ca-45) was titrated with 0.121 molar sodium oxalate solution. The expected curve shape was realized, but the curve was not abrupt. This was expected since the endpoint required 837 lambda of sodium oxalate solution. Since a comparatively large volume was required, however, the endpoint can be a little indefinite and still give an experimental result comparable to the calculated value. This titration gave results such that the deviation was usually less than one percent.

A reversal of titration direction minimizes the dilution effect, but titration with an active solution has variations due to the different amounts of radioisotope present as the titration progresses.

One thousand lambda solutions of 0.155 and 0.0155 molar sodium oxalate were titrated with a 0.505 molar calcium chloride solution having an activity of one microcurie of Ca-45 per milliliter.

The curve for the 0.155 molar sodium oxalate solution gave results within one percent of the accepted value. The weaker solution required so little titrant (28.2 lambda) at the equivalence point that a small deviation was sufficient to cause a relatively large percentage deviation. The expected curve did occur, but the quantities were too low for accurate results. A ten fold dilution of the titrant
and an increase in titrant activity gave results that were normally within two percent. Since the quantities of reagents used for a titration were becoming so small, this was considered as the lowest feasible concentration to delineate.

The titration of a nonactive solution with an active solution had now been performed for several systems. The experimental results indicated this method was a little less accurate than the titration of an active solution. In addition to the poorer accuracy, this method was less preferred because less benefit was derived from the radioisotope and the titration time was longer.

Calcium-45 was used in the titration of carbonate solutions. Since most carbonate solutions have a quite limited solubility, the calcium solution should be the stronger solution. However, this required that the inactive carbonate solution be titrated with the active calcium solution. Speculation of a way to obtain the maximum benefit from each controlling factor led to consideration of the possible result of adding calcium-45 to the sodium carbonate solution and then titrating with calcium chloride solution. This manner of titration depended on uniformity of sample so the addition of a drop of calcium chloride would form calcium carbonate involving primarily the calcium ions added. Some calcium-45 ions should also be precipitated in the small
region involving precipitation. Therefore, assuming a comparable proportion of the remaining calcium-45 ions would precipitate each time, a trend should be established that would allow the correct endpoint to be determined. The experimental results proved the above assumptions valid.

Sodium carbonate solutions of 0.144 to 0.504 molar, having a Ca-45 activity of 0.2 microcurie, were titrated with calcium chloride solutions. The deviation from the accepted value was less than one percent. The lower concentration level for reasonable accuracy was determined as about 0.05 molar for the carbonate solutions. The curve shape follows Figure VIII, curve B.

All of the count rates remained considerably above background throughout the titration. This indicated that some calcium-45 remained in the final solution beyond the equivalence point. This made the titration even more attractive since the count time at the equivalence point need not be extremely long for statistically valid count rate determination.

No literature reference of this variation of method has been found. However, this method should work well for other titration possibilities in which the radioisotope concentrations are sufficiently low to achieve complete solubility in the solution to be titrated.

Sulfur-35 was used as the indicator for a reaction in
which the precipitate was barium sulfate. The indicator was obtained as a solution of radioactive sulfuric acid in hydrochloric acid. This required neutralization prior to titration since barium sulfate is acid soluble. This system gave results within one percent of the accepted value with sulfate solution concentrations ranging from one hundredth to one molar. This was a wider range than had been found feasible for any other system studied. This system was also less sensitive to the dilution effect. The better results were still obtained when the titrant strength was several times that of the strength of the solution being titrated. However, good results were obtained even when the titrant was the weaker solution. The amount of sulfate ion determined in these weak solutions was calculated as about $4.37 \times 10^{-4}$ grams.

To confirm the conclusions drawn for the acid soluble nature of the calcium compounds, basic solutions of $0.994$ molar sodium sulfate (activity of $S-35$ of one microcurie) titrated with $0.574$ molar barium chloride were found capable of giving results within one percent. By contrast, the titration of a solution made up exactly the same, but left acidic, gave results with about an eighty percent deviation from the calculated result. In a teaching situation, these large variations of experimental endpoint can show dramatically the pH dependence of many precipitation reactions.
Thallium-204 was used as the indicator for the titration of thallium (I) solutions with potassium iodide. The precipitate was thallium iodide.

The activity (0.5 microcurie) and high energy of emission caused an initial count rate of about 30,000 counts per minute. This count rate decreased steadily, as the titration progressed, to about 1000 counts per minute at the equivalence point. This high count rate allowed statistical results within one percent to be realized with count times from about one to ten minutes and allowed a complete titration to be performed in less than two hours.

The experimental curve for this system was found to agree almost exactly with the theoretical curve as shown by Figure VI, page 60.

The range of thallium (I) acetate concentrations that were found feasible for radiometric titration, was about one hundredth molar and greater.

This system was used in the field study conducted as a part of this research. The nearly ideal curve shape, relatively high precision, and lack of sensitivity to pH changes, made this an ideal system with which to begin teaching the theory of radioactivity and to provide training in the use and manipulation of radioisotopes.

Both the solution activity and energy of beta emission is less for W-185 than for Tl-204. In addition, most
tungstates are quite insoluble. A saturated solution of sodium tungstate, one of the more soluble tungstates, is about 0.25 molar. This concentration was near the lower limit determined feasible for this type of titration. The experimental work done previously indicated that the curve shape would be similar to curve A of Figure VIII. These predictions were supported by the experimental results. Therefore, this system has a very short range of concentrations that may be titrated by this method.

The principal value of the experimental determination of the titration possibilities of this system was to verify previously predicted trends. In addition, this titration could be used in a teaching situation to show the type of solution and radioisotope characteristics required to give a curve such as indicated by curve A of Figure VIII, page 70.

This study was devoted to precipitation reactions. The effect of pH has been pointed out several times. For teaching purposes, the complete study of solubility must consider, not only pH, but also possible complexation effects.

The system involving the titration of a chloride solution with silver nitrate will give a typical curve. The effect of complexing agents on this curve was experimentally determined using the ammine and cyano ligands. A comparison of the curves obtained with or without ammonium hydroxide
The concentration of ammonium hydroxide required to prevent precipitation at the equivalence point was calculated as 3.19 molar. In the titration of this system some precipitate formed with each increment of silver nitrate added. A small amount of stirring was sufficient to achieve equilibrium and redissolve the precipitate. The precipitate held on the surface dissolved quite slowly and acted over most of the titration in causing an increased count rate. The last part of the curve shows a slight decrease. This was caused primarily by the dilution effect since the amount of precipitate left undissolved beyond the endpoint was extremely small. This indicates that the excess ammonium hydroxide remaining beyond the equivalence point was still effective in preventing most of the possible silver chloride precipitation from occurring. This type of experiment has much potential in teaching equilibrium concepts.

To determine the complexing effect of cyanide, sufficient potassium cyanide was added to furnish two cyanide ions for each silver ion present at the equivalence point.

Figure XV, page 99, shows the titration curves for a chloride solution titrated in the presence or absence of cyanide ion.

It was observed, during this titration, that no precipitation remained in the solution when fifty lambda of
FIGURE XIV

COMPARISON OF CURVE SHAPE WHEN A RADIOACTIVE CHLORIDE SOLUTION IS TITRATED WITH NONACTIVE SILVER SOLUTION IN THE PRESENCE OR ABSENCE OF AMMONIUM HYDROXIDE

AMMONIUM HYDROXIDE PRESENT

AMMONIUM HYDROXIDE ABSENT

COUNTS PER MINUTE

VOLUME OF TITRANT

100 200 300 400
FIGURE XV

COMPARISON OF CURVE SHAPE WHEN A RADIOACTIVE CHLORIDE SOLUTION IS TITRATED WITH NONACTIVE SILVER SOLUTION IN THE PRESENCE OR ABSENCE OF CYANIDE IONS

CYANIDE PRESENT

CYANIDE NOT PRESENT

VOLUME OF TITRANT

50 100 150
silver nitrate had been added. With sixty lambda of silver nitrate added, a very small amount of precipitate remained in solution. Only a small amount of precipitate increase was then noted until about 180 lambda of silver nitrate had been added, at which point additional precipitate formed for each increment added and the count rate decreased much more rapidly.

It is known that in aqueous solutions containing silver ion, an increase of cyanide ion concentration brings about the successive formation of \([Ag(CN)_2]^-\), \([Ag(CN)_3]^-\), and \([Ag(CN)_4]^-\) and that the tricyano complex exists over a wide range of concentration.

It is of interest to note that, while the cyanide ion concentration was at least four times greater than the silver concentration, no precipitation remained. Over the ranges with the cyanide ion concentration two and three times the silver ion concentration only a very small amount of precipitate formed. Little change in count rate occurred until the cyanide to silver ion ratio was nearly one to one. At this point, a rather rapid decrease in count rate resulted from each increment added. This would imply that the silver ion was held as molecular silver cyanide prior to the precipitation of silver chloride. Therefore, in addition to obtaining comparison curves to note the complexing effect, some indication of the effect of concentration ratios of the
species making up the complex seems evident.

The findings of this investigation and the method developed offer a fresh approach to the teaching of the concepts of radioactivity. The use of low activity radioisotopes makes it possible to safely integrate the study of radioactivity and the study of solubility equilibrium. The radioactive effect allows additional information to be learned about solubility factors such as pH and complexation. The use of radioisotopes in solutions allows much to be learned about the nature and use of radioisotopes. With proper use, this should be a most powerful teaching tool.
CHAPTER VII

RADIOMETRIC TITRATION FIELD STUDY

This research was conducted to determine the feasibility of radiometric titrations using radioisotopes of low activity. The author believes that the most meaningful laboratory experiences of a student are those in which the exercises are realistic and purposeful. The area of radiometric titrations offers the teacher an opportunity to provide the student with exercises that not only allow the student to learn radioactive concepts and techniques, but also emphasize one of the many uses for radioisotopes. The use of low activity radioisotopes allows a learning situation in which students having relativity limited training in this area can work safely.

The author has also noted from past experience that students seem to expect science experiments to yield quite exact results and they respond best to experiments that will yield reasonably accurate and reproducible results. It was therefore most desirable that the method used in determining the status of radiometric titrations could be used by students and that they could expect to obtain reasonably accurate values.

A field study was conducted to determine how well this technique could be followed by students and teachers
and to determine the precision of the experimental equivalence point.

The chemical system used in this field study was a solution of thallous acetate titrated with potassium iodide. The radioisotope used as the indicator was thallium-204. This radioisotope was selected because the system is one that meets quite well the criteria considered desirable for radiometric titrations and some of this radioisotope was still available from previous experimentation.

The unknown to be determined was the normal strength of the thallous acetate solution. Tables IV-A through IV-C list under "value obtained" the normal strengths of the thallous acetate solutions as determined by the participating students. The column entitled "accepted value" represents the actual normal strength of the solution being analyzed.

The students participating in this field study fall primarily into two categories; undergraduate and graduate students.

The six participating graduate students were the students in the Instrumental Analysis class of the University of the Pacific during the second summer session of 1966. All of these graduate students are college chemistry teachers.

The undergraduate students represent the following classes: The General Chemistry class of the University of
the Pacific during the second summer session 1966; and the General Chemistry and Quantitative Analysis classes of the fall semester 1966 at Northwestern College, Orange City, Iowa.

The results of the radiometric titrations are listed in Tables IV-A through IV-C, pages 105-107.

The actual experimental results obtained by one of the students are recorded on page 126. These results indicate typical count rates and count times used during a titration and the graph of the results indicates the type of curve obtained.

The poorest average results of a class was found for the teachers doing the graduate work. Observation of these students while they were performing the titration and personal consultations with each individual indicated reasons for this.

The graduate students worked as though they were pressed for time and some failed to take sufficient time to insure that the addition of each potassium iodide increment was exact. This type of error could be easily remedied. However, another important factor is manual dexterity and physical characteristics. The younger students, in general, mastered the transfer of lambda quantities of reagent much quicker than the older students. Much of the deviation of experimental results is believed due to improper transfer.
### GROUP I
(General Chemistry Class, Second Summer Session 1966, Univ. of the Pacific)

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<th>Student</th>
<th>Major</th>
<th>Lambda KI Used</th>
<th>Value Obtained</th>
<th>Accepted Value</th>
<th>% Deviation</th>
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Average Value

(4D Correction)

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* Student Major Key
1. Biology
2. Chemistry
3. Chemistry, Graduate Student
4. Mathematics
5. Pharmacy
6. Pre-Engineering
7. Pre-Medicine
8. Pre-Nursing
9. Miscellaneous Areas (Includes Fashion Buying, History, Psychology, and Undecided)
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(General Chemistry Class, Fall semester 1966, Northwestern College)

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<tr>
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<td>0.172N</td>
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GROUP III (continued)

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<tr>
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<th>Value Obtained</th>
<th>Accepted Value</th>
<th>% Deviation</th>
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<tr>
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<td>0.172 N</td>
<td>1.16</td>
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<td>140</td>
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<td>0.172 N</td>
<td>0.00</td>
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<td>0.172 N</td>
<td>2.32</td>
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<tr>
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<td>0.168 N</td>
<td>0.172 N</td>
<td>2.32</td>
</tr>
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<td>58</td>
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</table>

Average Value: 142 (4D Correction) 0.174 N 0.172 N (4D Correction) 1.64

GROUP IV
(Quantitative Analysis Class, Fall Semester 1966, Northwestern College)

<table>
<thead>
<tr>
<th>Student</th>
<th>Major</th>
<th>Lambda KI Used</th>
<th>Value Obtained</th>
<th>Accepted Value</th>
<th>% Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
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<td>140</td>
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<td>0.172 N</td>
<td>0.00</td>
</tr>
<tr>
<td>61</td>
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<td>0.172 N</td>
<td>0.00</td>
</tr>
<tr>
<td>62</td>
<td>2</td>
<td>142</td>
<td>0.174 N</td>
<td>0.172 N</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Average Value: 141 0.173 N 0.172 N 0.39
techniques at the beginning of a titration when the process is being learned. Several of the graduate students indicated having some difficulty in seeing the meniscus in the lambda pipet and their results turned out to be quite poor.

Two strengths of thallous acetate were titrated by the various groups. The results obtained at the University of the Pacific involved the titration of 1500 lambda of 0.159 normal thallous acetate with 1.220 normal potassium iodide. The Northwestern College results involved the titration of 1000 lambda of 0.172 normal thallous acetate with 1.220 normal potassium iodide.

The amount of solution titrated at Northwestern was reduced since it was found that using the two milliliter planchets to near capacity created a situation in which an occasional student would spill a small amount of the solution being titrated. This slight spillage was retained by the planchet holder and fortunately is most likely to occur near the end of the titration. Therefore, this did not appear to be an appreciable factor on the endpoint determination. It did, however, complicate cleanup procedures and in order to avoid this and also to determine what kind of results could be obtained using a lesser quantity, the titrations at Northwestern involved 1000 lambda of a slightly stronger thallous acetate solution. This amount utilized about sixty-five percent of the planchet capacity as
compared with about ninety-two percent of the planchet capacity used previously.

It was desirable to see how this reduction of total volume would affect the accuracy of the experimental value. The expectation was that the accuracy would be poorer and this was found to be correct when comparing groups of similar background. The average deviation of the general chemistry class using an initial volume of 1500 lambda was 0.63 percent as compared with an average value of 1.64 percent for those using an initial volume of 1000 lambda.

The above value of 1.64 represents a corrected value from 2.64 percent. Examination of the percent of deviation for Group III reveals two very large deviations. Discussion with the students at the end of these analysis and analysis of the titration data lead to the conclusion that the students had failed to add one of the increments early in the titration. If this was the situation, both of these titrations would be invalid and the results should not be used. This omission can also be justified by use of the 4D rule. By omitting these two values, the corrected value is 1.64 percent.

For Group IV, a short practice session was devoted to lambda pipet control and solution transfer techniques prior to the actual titrations. This group had the smallest average deviation of any group. Although this group was too
small for the results to be statistically significant, this seems to indicate that a trial run prior to the actual titration would improve the results.

The average results achieved agreed well with the accepted results. This is shown by the following comparisons.

<table>
<thead>
<tr>
<th>Group</th>
<th>Average Result</th>
<th>Accepted Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.161</td>
<td>0.159</td>
</tr>
<tr>
<td>II</td>
<td>0.162</td>
<td>0.159</td>
</tr>
<tr>
<td>III</td>
<td>0.172</td>
<td>0.172</td>
</tr>
<tr>
<td>IV</td>
<td>0.173</td>
<td>0.172</td>
</tr>
</tbody>
</table>

These results were obtained by inexperienced individuals performing one titration each. Therefore, it must be concluded that this method will give quite accurate and reproducible results and that it can be performed quite well after a minimum of instruction.
CHAPTER VIII

SUMMARY AND CONCLUSIONS

This study was conducted to determine the feasibility of performing Radiometric Titrations using low activity, license-free radioisotopes. Radiometric titrations using low activity radioisotopes was found feasible. However, as with the titrations using high activity radioisotopes, the method has definite limitations. There are limitations in the number of reactions that give precipitates that are sufficiently insoluble. For some reactions that meet this criterion, the required radioisotope may not be available. In some cases the required radioisotope may be available, but lack the necessary activity. The titration is based on the formation of an insoluble precipitate. In some instances it may be difficult to find compounds that are soluble enough to give solutions of the desired strength for optimum titration conditions. This may impose a severe limitation on the concentration range that may be titrated.

Despite these restrictions, when conditions are properly selected radiometric titration allows accurate results to be obtained.

The use of low activity license-free radioisotopes was considered most important because they are available to so many chemists and chemistry teachers not licensed to use
the high activity radioisotopes. Further advantages of using the low activity radioisotopes, are lower cost, less danger in handling and less difficulty in disposal.

Previous investigations of Radiometric Titrations, conducted by other investigators, had used radioisotopes with typical activities of 100 millicuries per gram or more. The use of 0.3 millicuries was sufficient, in a study by Hein and McFarland (1956) to give a count rate of 1000 counts per minute.

The low activity radioisotopes are available in five milliliter samples having activities ranging typically from one to fifty microcurie. Based on the volume and cost of the sample, it was considered quite important to limit the volume of the radioactive sample used in a titration to less than 0.1 milliliters. This limited the sample activity from 0.02 to 1.0 microcurie. This low amount of activity, compared with the approximately 300 microcuries used by previous investigators, necessitated a completely different method of titration be devised if count rates sufficiently high for statistical validity were to be realized.

The titration method that proved successful utilized the following principles: The amount of titrant was limited to about one milliliter; the solution was counted in a two milliliter nylon planchet set very close to an end-window G-M tube; and the solution was not removed from the
precipitate for counting.

This experimental setup allowed count rates from 30,000 to 1000 counts per minute to be obtained over the titration range when using 0.5 microcuries of Tl-204 as the indicator. The upper range could have been extended. However, since this represented the upper level of count rate that could be accurately determined by the Geiger Counter used, additional activity would have been detrimental because the initial titration points would have been meaningless. The less active radioisotopes were capable of giving count rates from 2000 counts per minute to near background over the titration range.

This study has delineated the quantity of radioisotope required to give an adequate count rate for good counting statistics, when performed under the specified experimental conditions. This delineation was made for the eight radioisotopes used in this study. These results are considered important in aiding teachers or chemists, unfamiliar with radiometric titrations, in proper radioisotope selection.

The systems delineated, using radiometric titration techniques, included the use of radioisotopes emitting 100 percent betas, 100 percent gammas, and mixtures of betas and gammas. In addition, the energy of emissions ranged from 0.0274 to 0.77 MeV and the specific activity of the
original samples ranged from 1 to 50 microcuries. The experimental results prove the best indicators, using this method, will be the 100 percent beta emitters having the highest energy of emission and the highest specific activity.

Less important factors to consider in radioisotope selection are half-life and solution strength. The best indicators will be low in total solution strength and high in specific activity. A radioisotope with a short half-life would theoretically meet these conditions better than one having a long half-life. It was found experimentally that high total concentration was found with both the radioisotopes having very long and very short half-lives. The best results were obtained with the radioisotopes having half-lives from 75.8 days to 3.57 years.

A number of factors such as the solubility characteristics of the compound to be precipitated, specific activity and concentration of the radioisotopes, and physical limitations of accurately adding extremely small volumes of solution determine the concentration range that can be titrated with reasonable accuracy.

Feasible concentration ranges have been experimentally determined for systems in which the precipitate is silver chloride, silver iodide, calcium molybdate, calcium oxalate, calcium carbonate, barium sulfate, thallium (I) iodide and magnesium tungstate. A knowledge of the feasible
concentration ranges for these systems also provides information for the predictions of concentration ranges that could be titrated for other systems. Analysis of the curve shape characteristics for a solution about three tenth molar allows a prediction to be made regarding the minimum concentration capable of being titrated.

The amount of deviation between experimental and other calculated values, either predicted or experimentally determined by other investigators using the radiometric titration method was found most often to be around one percent. Some references claim the results are within two percent. All of the systems of this study that use monoenergetic beta emission were found capable of giving results within this range even though the specific activity was low.

This method depends on essentially complete insolubility if accurate results are to be obtained. The effect of pH on solubility was determined for the systems studied. For precipitates insoluble in acid (or base) the pH did not change the experimental results. For precipitates that are soluble in acid (or base) variation in pH will change the experimental value considerably. The exact amount of change will be dependent on the pH change. A small amount of reagent added, therefore, was found capable of introducing large deviations if the pH shifted sufficiently to give a solution in which the precipitate was soluble. Titration
of an acidic solution, in which the desired precipitate is acid soluble, causes the experimental end-point to give a value that is too low as compared with the actual value.

The effect of adding reagents that caused complexing was also determined. With a high concentration of the complexing reagent present, precipitation does not take place readily. This causes the end-point to fall much later than the calculated end-point.

The sequential analysis of two species in a solution was found to be possible using this method. The best results were obtained when the concentration of the ion, giving the least soluble precipitate, exceeded the concentration of the other ion by a factor of at least four.

A section was included on radioactive concepts and theory. The theory and factual content were selected to extend the course material normally presented to undergraduate chemistry students. Therefore, the inclusion of a limited discussion of the theoretical aspects of radioactivity and its detection makes this a self-contained unit that can be used to enrich the teaching of radioactivity.

No reference has been found of a radiometric titration conducted by placing in the titrant a radioisotope of the same species as the titrating reagent. This variation seems unique to this study and appears to have some advantage over the usual method. This may be a worthwhile area
for further investigation.

The field study, conducted as a part of this research, proved that the radiometric titration method developed in this study is capable of giving fairly precise and accurate results. The results were obtained by students performing the experiment for the first time after a minimum of instruction. Familiarity with the method should allow a greater precision to be realized. This may be an area that could be investigated in a future study.

The student response was most gratifying. Many students indicated having an initial feeling of apprehension and fear when asked to perform a radiometric titration. This fear of working with radioactive solutions was soon dispelled and the students worked eagerly and confidently. In addition to the many facets of radioactivity theory, Geiger counter operation, techniques of handling radioactive solutions, solubility principles, statistical nature of radioactive disintegration, and other related ideas taught the undergraduate students as a part of this titration, the students asked many other related questions. Quite a number of the students suggested modifications of procedure that seemed capable of simplifying or improving the technique. With the degree of interest shown, the author feels this area has great potential as a teaching tool.

To teach an area effectively requires stimulation of
interest, active participation by the student and meaningful content. The results of and response to the field study prove that the teaching of radioactivity concepts built around radiometric titrations provides these vital requirements most adequately.
BIBLIOGRAPHY

A. BOOKS


B. PERIODICALS


C. OTHER PUBLICATIONS


D. BOOKS USEFUL FOR ADDITIONAL REFERENCE


APPENDIX
THE FOLLOWING UNDERGRADUATE TEXTBOOKS WERE EXAMINED TO DETERMINE THE RADIOACTIVE CONCEPTS NORMALLY PRESENTED TO UNDERGRADUATE STUDENTS.

A. GENERAL CHEMISTRY


B. QUANTITATIVE ANALYSIS


C. ORGANIC


D. PHYSICAL CHEMISTRY


DIRECTIONS FOR A RADIOMETRIC TITRATION

The following directions were used for the radiometric field study.

1. Turn the Geiger counter on and allow about ten minutes for warm up.

2. Determine the background count rate with the plastic planchet in counting position.

3. Pipet fifty lambda of Tl-204 into a plastic planchet.

4. Rinse the pipet used in step three in distilled water and place it in soap solution in preparation for complete washing.

5. Using a 500 lambda pipet, add 1500 (or 1000) lambda of the unknown thallium (I) acetate solution to the planchet.

6. Determine the count rate of the sample. Count long enough to give one percent statistical deviation or less.

7. Add a 25 lambda increment of the standard (1.1 to 1.3 M) potassium iodide solution, stir to achieve uniformity and determine the count rate.

8. Repeat step seven until past the endpoint 4-5 increments.

9. The titration curve points are plotted as time permits. The intersection of the straight lines obtained from using the points before and after the endpoint determine the experimental endpoint. This endpoint value is then used to calculate the strength of the unknown solution.

Note: Leave the plastic planchet on the plastic shelf all through the titration. It is safer and easier to remove and replace the entire shelf assembly each time more titrant is added.
1500Å TiC₂H₃O₂(Tl-204) titrated with 1.22N KI

Actual results obtained by a student.

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<th>Count Time</th>
<th>Reagent</th>
<th>c/min.</th>
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</thead>
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<td>3</td>
<td>Sample</td>
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</table>

\[(1500Å)(x) = (197Å)(1.22N)\]
\[x = 0.160N\]
SUPPLIERS OF LOW LEVEL RADIOISOTOPES

1. Oak Ridge Atom Industries, Inc.
   Educational Products Division
   500 Elza Drive, Dept. 2E C, P.O. Box 429
   Oak Ridge, Tennessee

2. General Radioisotope Processing Corporation
   3000 San Ramon Valley Boulevard
   San Ramon, California 94583

3. Nuclear-Chicago Corporation
   333 East Howard Avenue
   Des Plaines, Illinois