AN ABSTRACT OF THE THESIS OF

The Kroll Process for the production of zirconium utilizes the reduction of zirconium tetrachloride with metallic magnesium. Control of the magnesium content of the final zirconium metal is essential, as residual magnesium adversely influences the properties of zirconium.

In this thesis a volumetric method has been presented for the determination of magnesium. An initial separation of the bulk of zirconium from magnesium was carried out by a rapid, batch ion exchange in hydrofluoric-hydrochloric acid solution. In this step 94% of the zirconium can be removed. The remainder was precipitated with ammonia in the presence of ammonium chloride. Magnesiu is determined in the filtrate by the complexometric titration with disodium ethylenediamine tetraacetate.

This method was applied to magnesium-zirconium mixtures containing from 1% to 0.1% magnesium. The lower level of 0.1% was established because the volume of versenate used in titration becomes too small for accurate determinations at concentrations lower than this.

DETERMINATION OF MAGNESIUM IN ZIRCONIUM
BASED ON ION EXCHANGE SEPARATION AND
TITRATION WITH VERSENE

by

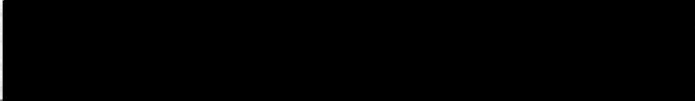RICHARD KENNETH METZLER

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
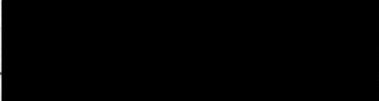degree of

MASTER OF SCIENCE

June 1954

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Date thesis is presented___May 10, 1954___

Typed by Evelyn Kanzelmeyer

ACKNOWLEDGMENT

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INTRODUCTION

Zirconium has currently been the subject of increased investigation in both the fields of fundamental and applied research. It is a material of notable interest in connection with nuclear studies because of its low neutron cross section and favorable high temperature properties. To cite only one of its many uses as a refractory material, zirconium dioxide lends itself well to the construction of combustion chambers for turbo-jet engines.

In these two very important uses of zirconium, a metal of highest purity must be produced. The Kroll Process for the production of zirconium utilizes the reduction of zirconium tetrachloride with metallic magnesium, and consequently results in a slight contamination of magnesium in the zirconium sponge. The control of the magnesium content is essential, as traces of magnesium adversely influence the properties of the refined metal. For this reason the precise determination of magnesium in concentrations as low as 0.01 percent is an analytical problem of practical and immediate interest.

The existing procedures for determination of magnesium can be classified under gravimetric, colorimetric or spectrophotometric, and volumetric methods. The

conventional gravimetric determination consists of precipitating magnesium ammonium phosphate which is ignited and weighed as magnesium pyrophosphate. An example of the spectrophotometric methods employs 8-hydroxyquinoline (11, pp.37-45) to precipitate the magnesium chelate. The precipitate is dissolved in dilute acid and ferric chloride is added. On addition, iron forms a dark green complex with 8-hydroxyquinoline which is suitable for a spectrophotometric determination. This method has been proposed for analysis of magnesium in zirconium (13, pp.13-15).

The magnesium 8-hydroxyquinoline precipitate can also be dissolved in acid and determined volumetrically (18, pp.656-657) based upon bromination of the quinoline nucleus. Another, and very convenient volumetric method is that of the versenate titration (3, pp.1640-1641). Here, the magnesium is determined by titration with the disodium salt of ethylenediamine tetraacetic acid. This reagent forms a strong, soluble chelate with magnesium, and makes possible a very rapid determination.

Usually magnesium is separated from zirconium before it is determined. Methods of separation that are applicable to this system are (1) precipitation, (2) solvent extraction, and (3) ion exchange. In separations the usual procedure is to remove the minor constituent by one of the above methods. However, the reagents that

affect a removal of magnesium from solution also remove zirconium. For this reason it is the zirconium that is removed from solution by these conventional procedures. An exception to this is ion exchange, which can be carried out by either cation exchange of magnesium or anion exchange of the fluoride complex of zirconium.

With respect to precipitation, zirconium may be separated with selenious acid as basic zirconium selenite (28, pp.211-212), or by cupferron (15, pp.348-349), which forms an insoluble chelate in acid solution. Another method, discussed by Venable (30, pp.121-125) furnishes a separation from a number of elements by use of ammonia. Solvent extraction of zirconium has been investigated by Connick and McVey (4, pp.3182-3191) in studies on extraction of the benzene soluble thenoyltrifluoroacetone chelate.

Kraus and Moore (12, pp.9-13), using an anion exchange resin, have separated complex ions of hafnium and zirconium in hydrochloric-hydrofluoric acid mixtures. A cation exchange of magnesium in hydrofluoric acid solution has been proposed by Freund and Lee (13, pp.17-24) for a separation of magnesium from zirconium.

Of these separation methods, the precipitation procedure is probably the least successful. It is inherently unsound, principally because of coprecipitation.

In the case of solvent extraction, the separation of the
major constituent is again not entirely a desirable pro-
cedure. On the other hand, ion exchange has been shown
to give greater recovery of magnesium and provides for a
feasible separation of the two metals.

The gravimetric method of analysis, used currently,
involves a separation of zirconium by a double precipi-
tation of the zirconium hydrous oxide with ammonia in the
presence of ammonium chloride. Magnesium is determined
in the filtrate by precipitation of magnesium ammonium
phosphate which is filtered off, ignited and weighed as
magnesium pyrophosphate. Since samples of zirconium of
from one to five grams are often taken for analysis, the
precipitation of this large quantity of the hydrous oxide
may lead to extensive coprecipitation of magnesium and
consequently a serious loss of the latter may be incurred.
In addition to this disadvantage, the final precipitation
of small amounts of magnesium ammonium phosphate is
notoriously slow.

The method of Freund and Lee (13, pp.35-39)
utilizing ion exchange has made possible the achievement
of greater accuracy in determining these low concentra-
tions of magnesium. This procedure involves running a
hydrofluoric acid solution of the zirconium-magnesium
mixture through a column of Dowex-50, a cation exchange

resin. Magnesium ion is exchanged on the resin and the zirconium, in the form of the anionic fluoride complex, passes through the column. After washing the column with water, the magnesium is eluted with acid. Magnesium is determined either by the phosphate gravimetric method or spectrophotometrically with 8-hydroxyquinoline. The latter method was used for samples containing less than 0.4 percent magnesium. Magnesium was determined within the range of 1.0 percent to 0.02 percent.

The column ion exchange separation eliminates the loss of magnesium through coprecipitation which is incurred in the separation using ammonium hydroxide. However, difficulties arise from this column ion exchange separation, in that large volumes of eluate and wash solutions are obtained. Also, it is difficult to obtain complete recovery of magnesium from the resin in a reasonable number of washings. The use of ion exchange columns is not always practicable for control work and is time consuming.

PROPOSED METHOD FOR DETERMINATION OF MAGNESIUM. The purpose of this work is to determine magnesium in zirconium by the versenate titration. The analysis will be attempted without separation from zirconium and a study will be made to establish the amount of zirconium that can be tolerated.

If it is found that zirconium should be removed, an ion exchange separation will be applied. In order to provide a more rapid method, it is proposed that an _anion_ exchange of zirconium in hydrofluoric acid be employed, utilizing a batch separation instead of the column method. By using this modification, magnesium remains in solution and there is no problem of recovery from the resin. For determination of magnesium, the versenate titration would still be applied, either in the presence of a small amount of zirconium remaining after batch separation, or after precipitation of residual zirconium with ammonia. This decision will depend upon the tolerance limit of zirconium in the versenate titration.

It is expected that this method will be both rapid and accurate, thus making it practicable for industrial control analysis.

THEORETICAL CONSIDERATIONS

THE VERSENE TITRATION OF MAGNESIUM. <u>Theoretical</u>
<u>basis for chelation reactions</u>. A metal combining with an
electron donor is said to form a complex, or coordination
compound. When the electron donor contains two or more
donor groups so that one or more rings are formed, the
resulting structure is said to be a chelate compound, and
the donor the chelating agent (16,p.1). Such structures
were first referred to as "molecular complexes" by Werner
(16,p.2) in 1891. This particular type of ring formation
was named "chelation" by Morgan and Drew (20,p.1457) and
the term applies to all types of ring systems with metals
and hydrogen, regardless of the nature of the chemical
bond involved (16,p.10).

The chelate compounds are of particular analytical
importance, since they have exceptionally high stability
and have found valuable application as reagents and metal
indicators. One of the most important chelating reagents
used today in analytical chemistry is the disodium salt
of ethylenediamine tetraacetic acid (16,p.2). In the
following discussion the sodium salt will be referred to
as versenate and the simple acid as EDTA. The structural
formula of the disodium salt is shown in Plate I.

HOOC—H₂C \
NaOOC—H₂C
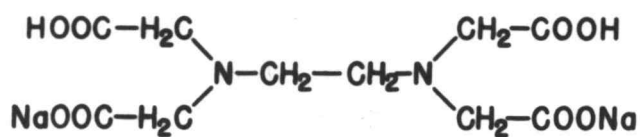
Disodium Ethylenediamine Tetraacetate
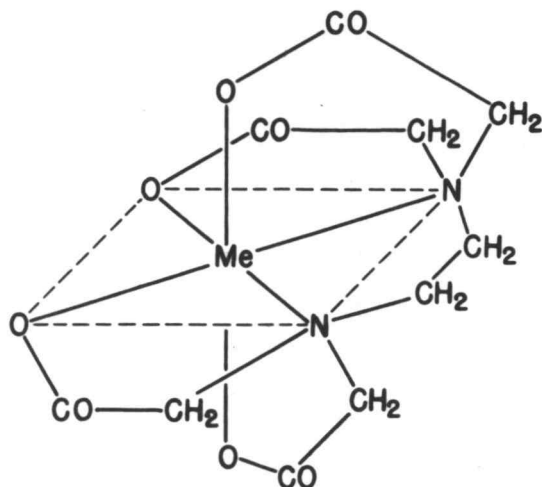
Metal Chelate of EDTA
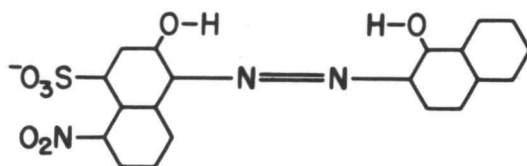
Eriochromeschwarz—T
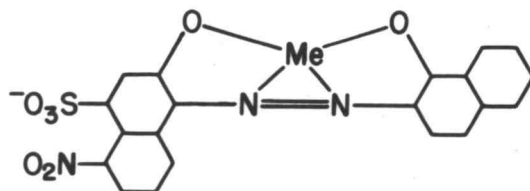
Metal Chelate of Eriochromeschwarz—T

PLATE I

It is not known definitely whether the alkali
earth metals have a coordination number of six or four
with EDTA. However, the former is preferred and the
proposed structure of the chelate assumes the chelating
agent to be hexadentate, having six donor groups (16,
p.14;pp.142-143). See Plate I.

The versene titration is based on the formation of
the magnesium chelate of EDTA. Similarly the end point
determination involves a chelate of magnesium and a dye.
Schwarzenbach (24,pp.1798-1804) first investigated the
alkaline earth chelates of EDTA and reported their
stability constants. The reaction of the partially
ionized EDTA, (H_2Y^{-2}) with a metal, (Me) may be summarized
as follows (16,p.41):

$$Me^{+2} + H_2Y^{-2} \rightleftharpoons MeY^{-2} + 2H^+$$
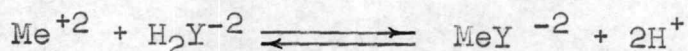
Chelation results in the release of protons from
EDTA as the stability constant of the chelate favors the
formation of MeY^{-2}. The first complexometric titra-
tions depended upon this release of hydrogen ions, as the
end point was determined by pH effects (27,pp.331-340).
Later, Schwarzenbach and Biedermann (25,pp.678-687)
studied alkaline earth complexes of the o,o'-dihydroxyazo
dyes (Eriochrome dyes) as visual indicators for these
titrations. One of these dyes, Eriochromeschwarz-T (F241),

was applied successfully to the versenate titration of magnesium. The structure of the dye and its metal chelate is given in Plate I (16,p.486).

The ability to detect the end point of the titration depends upon the formation of a wine-red chelate of the dye which is less stable than the magnesium chelate of EDTA (16,p.488). When versenate is added the dye dissociates according to the following equation:

$$\underset{\text{red}}{MgF^{-1}} + H^+ + Y^{-4} \rightleftharpoons \underset{\text{blue}}{HF^{-2}} + MgY^{-2}$$
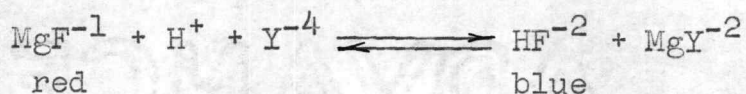
Y^{-4} represents EDTA in its completely dissociated form and HF^{-2} represents the ionized form of the dye. At pH 10 the equilibrium is far to the right and addition of sufficient versenate gives a sharp end point. An excellent discussion of chelate formation in titration processes is given in a review by Schwarzenbach (23, pp.141-156).

INTERFERENCE BY OTHER METAL IONS. Because versene is not a specific reagent for any one cation, metals such as Ca, Fe, Al, Ni, Cu, Mn, and Co often interfere with the titration. Calcium and manganese are titrated along with magnesium. However, conditions may be selected or cations removed so interference is usually not encountered (5,p.42). Banks (1,p.486) removed iron, aluminum and

copper by precipitation with ammonia, and manganese was removed by treating with bromine before ammonia was added. Small amounts of these interfering metals can be suppressed by complexing with certain reagents. Table I shows these metals and tolerable concentrations when complexed or suppressed. Hydroxylamine hydrochloride reduces iron to Fe^{++}, which does not interfere. Calcium, if present, can be determined by using another indicator, murexide (3,p.1640). This indicator titrates calcium only. Magnesium can be calculated from the difference between the murexide end point and the eriochromeschwarz-T end point. If the calcium concentration is greater than that of magnesium it is better to remove calcium by oxalate precipitation (31,p.379).

APPLICATIONS. The versenate titration has been applied to analysis of magnesium in limestone (3,pp.1640-1641). Banks (1,pp.484-488) determined magnesium in a concentration as low as 6 ppm, after removal of iron, aluminum, copper and manganese. The determination of calcium and magnesium water hardness is often performed by the versenate titration (5,pp.40-48). Diehl and Smith (14,pp.340-344) give a procedure for determination of total hardness within the range 0-2500 ppm $CaCO_3$. A colorimetric determination of magnesium based on the red color formed with eriochromeschwarz-T is given by Harvey,

TABLE I

REAGENTS THAT INHIBIT INTERFERENCE IN
THE MAGNESIUM TITRATION (5,p.46)

Metal Ion	Tolerance	Reagent
Al	over 20 ppm	sodium potassium tartrate
Cu	5 ppm	sodium diethyl dithiocarbamate
Cu	over 30 ppm	potassium cyanide
Co	over 20 ppm	potassium cyanide
Fe	15 ppm	sodium sulfide
Fe	20 ppm	hydroxylamine hydrochloride
Fe	over 30 ppm	potassium cyanide
Mn	2 ppm	sodium sulfide
Ni	over 20 ppm	potassium cyanide

Komarmy and Wyatt (10,pp.498-500). By this method mag-
nesium was determined between 12.7 and 2.5 ppm.

DETERMINATION OF MAGNESIUM IN THE PRESENCE OF
ZIRCONIUM. It would be desirable to determine magnesium
in the presence of zirconium. Since the titration is
carried out at pH 10, a complexing agent must be employed
to prevent precipitation of zirconium. The complexing
agent must form a stable complex in basic solution and
must not compete strongly for magnesium.

Haissinsky and Jeng-Tsong (9,pp.422-427) have investigated the stability of tartrate, citrate and oxalate complexes of zirconium in both alkaline hydroxides and in ammonia. Of these three complexing agents, tartrate is the best because the stability of the zirconium complexes increases in the following order: oxalate < citrate < tartrate. Tartrate is not precipitated at a metal concentration of seven millimoles (9,p.427), or about 64 milligrams of zirconium per 100 milliliters. The higher the tartrate concentration, the higher the pH can be raised without precipitating zirconium.

Tartrate appears to be a good complexing agent for zirconium in this case, but its effects on the magnesium versene complex need to be investigated. Monnier and Chouteau (19,pp.407-413) investigated magnesium tartrate complexes by electromigration measurements and demonstrated the presence of complexes in 0.1 M solutions of tartaric acid. Cannan and Kibrick (2,p.2319) showed by pH determinations that the magnesium tartrate complexes were relatively weak in tartaric acid buffer solutions. If magnesium tartrate does not precipitate, it would be expected to form a stronger complex in basic solution since more free tartrate ions would be available.

While investigating the precipitation of magnesium ammonium arsenate from an ammoniacal solution in the

presence of zirconium tartrate it was found that the
completeness of precipitation depended more upon the zir-
conium concentration than upon the tartrate concentration
(17,pp.11-12). Precipitation is practically complete from
solutions containing tartrate only. When zirconium is
present the recovery of magnesium decreases markedly with
an increasing zirconium to magnesium ratio (17,p.9). This
behavior is somewhat anomalous since zirconium ties up
much of the tartrate ion and decreased magnesium complex-
ing would be expected. The influence of high ionic
strength must be considered, and it may be that this fac-
tor contributes to incomplete precipitation.

Fritz and Ford (8,p.1641) have reported that at pH
2.8 the presence of zirconium causes an indistinct end
point in the titration of thorium with versenate. This
suggests either chelation of zirconium with versene, or
with eriochromeschwarz-T. The interference would be
expected to increase at the higher pH at which magnesium
is determined. The seriousness of zirconium influence
will depend upon the relative stabilities of the mag-
nesium and zirconium chelates involved.

One can readily see that the proposed system is
not a simple one, since three complexing agents and two
metals may be involved in any equilibria that are
established. It may be difficult to distinguish between

interacting or compensating factors, and direct effects.
An investigation of the problem is warranted for it is an
advantage to determine magnesium without complete separa-
tion of zirconium.

ION EXCHANGE SEPARATION. Development of ion
exchange. The phenomenon of ion exchange has been known
for almost a century, but has only found useful industrial
and experimental application in the past few decades (21,
p.1). A survey of the history of ion exchange resins,
their development, and applications, has been presented
by Tompkins (29,pp.32-33).

The wide application of anion exchange procedures
has been limited until comparatively recently, as the
available exchangers have been of the weak base type.
This type is confined to adsorption of anions in acid
solution and hence are restricted to operation in a narrow
pH range. The recent development of strongly basic anion
exchange resins such as Dowex 1 and Dowex 2 (14,p.1085)
has made possible adsorption of anions over a wide pH
range, and has led to a great many analytical applica-
tions. Wheaton and Bauman (32,p.1088) present an excel-
lent discussion of the properties of these resins,
developed by the Dow Chemical Company, Midland, Michigan.
Samuelson (22,pp.12-17;pp.23-26) has presented the
general considerations and fundamental properties of ion

exchange resins, together with the particular properties
of strongly basic anion exchanges in application to
analytical chemistry.

Separation of zirconium by ion exchange. The
specificity of anion exchange resins for negatively
charged ions suggests that they be used for exchange of
anionic complexes of metal ions. In addition, anion
exchange resins are particularly useful with metal ions
that hydrolyze in aqueous solution if not complexed (12,
p.9). This condition is typical of the aqueous chemistry
of zirconium. The main ionic species in aqueous solution
is ZrO^{++} (30,pp.32-33). Hydrolysis is increased by pro-
longed solution in water and water of hydration is
practically always present. Upon standing, colloidal dis-
persions result. Zirconium has a strong tendency to form
complex ions, and the fluoride complexes are exceptionally
stable. Connick and McVey (4,p.3190) report that in a
solution 8×10^{-3} molar in hydrofluoric acid, and 0.2
molar in perchloric acid, all but 0.0012 percent of the
zirconium is complexed.

Reference was made previously to the exchange of
fluoride complexes of zirconium with Dowex 1. Freund and
Miner (7,pp.565-567) used Dowex 1 to separate zirconium
from aluminum. Aluminum also forms fluoride complexes
but of differing stability so that conditions could be

selected in which only the zirconium was exchanged. The
success of this separation suggests that a similar prin-
ciple could be applied to the zirconium-magnesium separa-
tion using Dowex l.

The batch method of ion exchange. Ion exchange can
be carried out by column or batch equilibration. In the
introduction to this thesis it was pointed out that the
column method is capable of effecting a practically com-
plete separation of zirconium. It was also mentioned that
this method has certain disadvantages for the use of
multiple columns is not always practicable for control
work.

The batch method, which was chosen for this inves-
tigation, will not remove all the zirconium; however, it
has the advantages of taking a relatively short time to
separate the bulk of zirconium, and of keeping the volume
of solution to a minimum. A batch ion exchange separa-
tion is effected by merely shaking the mixture of the
resin and solution for the time necessary for equilibrium
to be established between the ions in solution and those
in the resin phase. The resin can be filtered from the
mixture by vacuum filtration.

If sufficient zirconium is removed by this pro-
cess, and if the remaining zirconium can be complexed
without interfering with the versene titration, further

separation would be unnecessary. On the other hand, if the residual zirconium must be removed, it could be precipitated with ammonia, since precipitation of the then smaller quantity of zirconium hydrous oxide would be expected to result in little or no coprecipitation.

EXPERIMENTAL

APPARATUS. Ion exchange. To prevent hydrofluoric acid from attacking glassware, the samples were prepared in polyethylene plastic beakers and equilibrated with Dowex 1 in polyethylene plastic bottles. A mechanical shaker was employed for equilibration. Separation of the resin after equilibration was accomplished by use of vacuum filtration, utilizing a 6 centimeter Büchner funnel and a 250 milliliter suction flask coated with paraffin.

Platinum dishes. To remove hydrofluoric acid, 6 centimeter platinum evaporating dishes were employed for fuming the samples. They were also used for solution of zirconium metal in hydrofluoric acid.

Burets. Versene titrations were initially carried out with a 50 milliliter buret. Later, for more precise work, a 10 milliliter micro buret calibrated in 0.02 milliliter was employed.

pH meter. The Beckman Model G pH meter was used to measure the pH of solutions before titration.

REAGENTS. Dowex 1, 200-400 mesh. This resin was supplied by the Bureau of Mines, Albany, Oregon. It was received in the moist form and was washed and regenerated with hydrochloric acid before using. The chloride form was used in all the experiments.

Magnesium metal. Grignard grade magnesium ribbon
was used. Before using it was washed successively with
dilute acid, water, acetone and water. It was dried at
110° centigrade. Standard magnesium solutions were pre-
pared by dissolving this metal in sufficient dilute
hydrochloric acid and diluting with distilled water.

Zirconium metal. Special ingot zirconium metal
was supplied by the Bureau of Mines, Albany, Oregon.

Zirconium oxychloride. Zirconium oxychloride was
used for initial investigations. It was prepared by
James Kanzelmeyer, Oregon State College, by dissolving
zirconium tetrachloride in water and crystallizing out
the oxychloride from an 8 normal hydrochloric acid solu-
tion. The composition was approximately that of the
hexahydrate, $ZrOCl_2 \cdot 6H_2O$.

Ethylenediamine tetraacetic acid. Eastman Chemi-
cal Company's white label grade was used. A 0.01 molar
solution of the disodium salt was prepared by dissolving
3.00 grams of the acid and 1.50 grams of sodium hydroxide
in distilled water and diluting to one liter.

Disodium ethylenediamine tetraacetate dihydrate.
The analytical reagent grade was supplied by the Bersworth
Chemical Company, Framingham, Massachusetts. A 0.01 molar
solution was prepared by dissolving 3.724 grams of the
dihydrate in distilled water and diluting to one liter.

Both of the versenate solutions were standardized against the magnesium solution which was taken as a primary standard.

Ammonia-ammonium chloride buffer solution. The buffer was prepared by dissolving 13.5 grams of ammonium chloride in 114 milliliters of concentrated ammonium hydroxide (28% NH_3) and diluting to 200 milliliters with distilled water.

Ammonium hydroxide. This was approximately twenty eight percent aqueous ammonia, as prepared at Oregon State College by saturation of distilled water with gaseous ammonia.

Eriochromeschwarz-T indicator. Eastman Chemical Company's white label reagent was used. A 0.4% solution was prepared by dissolving 200 milligrams in 50 milliliters of 100% methyl alcohol.

All other chemicals used were of reagent grade.

INITIAL INVESTIGATIONS. Versene titration of magnesium. Titrations on magnesium solutions alone were carried out to ascertain the feasibility of determining milligram quantities. The same conditions were applied as would be prevailing in the actual determination.

Procedure. Aliquots of standard magnesium solution containing 2.53, 1.90, 1.26, 0.63 and 0.32 milligrams of magnesium were placed in 150 milliliter beakers,

containing 10 milliliters of buffer solution. The volume was made up to 75 milliliters with distilled water and a pH of 10.0 was verified with the pH meter. After addition of 0.2 milliliter of indicator the solutions were titrated with 0.01 molar versenate using a 50 milliliter buret. The color change at the endpoint is from wine-red to a definite blue.

It was observed that endpoint perception was most successful by titrating under white fluorescent light and watching the change in color through the side of the beaker. Vigorous agitation of solution near the endpoint was found to be important as attainment of equilibrium is not instantaneous. A reagent blank gave zero titer.

Results of titration. See Table II for tabulated data. The volumes of titer used ranged from 9.83 to 1.27 milliliters and were reproducible within 0.03 milliliter. The maximum deviation from the theoretical, on any one sample, based on the titer obtained on the most concentrated solution, did not exceed 0.04 milliliter. This is well within the allowable error in this method, as 0.05 milliliter versenate is equivalent to only 0.01 milligram magnesium.

Effect of tartrate on the Versene Titration. Because tartrate was to be used to complex zirconium, the influence of sodium potassium tartrate, tartaric acid and

TABLE II

TITRATION OF MAGNESIUM

Milligrams magnesium	Theoretical versene titer	Experimental versene titer
2.53	9.82	9.83 9.82
1.90	7.36	7.38 7.40
1.26	4.91	4.90 4.93
0.63	2.46	2.50 2.50
0.32	1.23	1.26 1.27

ammonium tartrate were studied. It was kept in mind that tartrate may exhibit some complexing of magnesium. Also its presence results in increased ionic strength which has the effect of decreasing the stability of chelates.

Effect of sodium potassium tartrate alone on the titration. The first investigation involved titration of 7.5 milligrams of magnesium in the presence of sodium potassium tartrate, but no zirconium.

Concentrations of tartrate from 0 to 9.8 grams of $NaKC_4H_4O_6$ per 50 milliliters were employed. This was in anticipation of the tartrate needed to complex zirconium,

on the basis of a weight ratio of zirconium:tartaric acid
of 1:10.

It was found that above 3 grams of tartrate there
was serious increase in the volume of versenate used for
a constant quantity of magnesium. See Table III. Satis-
factory endpoint perception was achieved.

TABLE III

EFFECT OF SODIUM POTASSIUM TARTRATE
ON MAGNESIUM TITRATION

Grams of sodium potassium tartrate	Milliliters of versenate
0.0	30.18
2.8	30.30
7.0	30.85
8.4	31.40
9.8	31.70

These observations indicated two possible inter-
ferences. (1) Increased ionic strength may decrease
stability of the magnesium chelate; and (2) high concen-
tration of sodium and potassium may interfere, as alkali
metals form weak EDTA chelates.

Use of tartaric acid as a source of tartrate. To
help minimize effects (1) and (2) above, tartaric acid was
used in similar studies. The amount of tartaric acid
employed, 0 to 5 grams, paralleled the tartrate ion con-
centration used in the first investigation.

In this case no significant increase in volume of
versenate was obtained with increasing concentration of
tartrate between 0 and 4.5 grams. With five grams, how-
ever, some decrease was noted. Good, sharp endpoints were
obtained in all titrations.

The trend of this investigation was as expected;
that is, the ionic strength effects and alkali metals
effects seemed to be decreased. However, a possible com-
plexing of magnesium was indicated because at high
tartrate concentration the versene titer decreased.

Titrations utilizing ammonium tartrate. It seemed
feasible to investigate further the use of tartaric acid.
Since the acid is neutralized by addition of ammonia,
ammonium tartrate was employed. The first study involved
closer scrutiny of magnesium complexing.

Procedure. To achieve greater accuracy with
smaller volumes of titer which would eventually be used
for determination of magnesium, a 10 milliliter micro
buret was employed throughout the remainder of the work.
In preliminary investigations it was found that sharper

endpoints were obtained by a back titration. For this
reason, 10 milliliters of standard versenate was titrated
with standard magnesium solution. The rest of the pro-
cedure was the same as that given on pages 21 and 22.
The endpoint change is from blue to wine-red. Concen-
tration of ammonium tartrate was varied from 0 to 5 grams
per 80 milliliters.

Results of titrations. See Table IV for tabulated
data. The titer for zero tartrate was 8.28 milliliters.
A significant increase over this volume was observed at
0.6 gram of ammonium tartrate. It continued to increase
until at 5 grams it amounted to 0.5 milliliter. The plot
of milliliters magnesium solution versus millimoles of
ammonium tartrate in Figure 1 illustrates this trend.
The increase in magnesium titer corresponds to a decrease
in versenate in the direct titration. The trend in both
cases strongly indicates the formation of magnesium tar-
trate complexes at high tartrate concentration.

At this point the decision was to go on to investi-
gate the effects when zirconium was present.

Titration of magnesium in the presence of zir-
conium. These experiments were designed to study the
effect of zirconium:tartrate ratios on the back titration.
The following considerations were set forth: (1) It is
desired to employ a minimum amount of tartrate to complex

TABLE IV

INFLUENCE OF AMMONIUM TARTRATE
ON BACK TITRATION

Grams of ammonium tartrate	Magnesium titer (ml.).
0.0	8.28
0.62	8.33
1.25	8.41
2.50	8.60*
5.00	8.81*

* Fading endpoints were observed.

zirconium. (2) It must be known how much zirconium can be tolerated in the titration.

Procedure. In these experiments zirconium oxy-chloride was used as a source of pure zirconium. Reagents were added to a 150 milliliter beaker in the following order: 10 milliliters of standard versenate solution, ammonium tartrate, zirconium oxychloride solution, buffer solution and sufficient distilled water to adjust the volume to 80 milliliters at pH 10. The pH was checked with the pH meter. Directly before titration, 0.1 milli-liter of eriochromeschwarz-T indicator was added to the solutions and then they were titrated with standard magnesium solution.
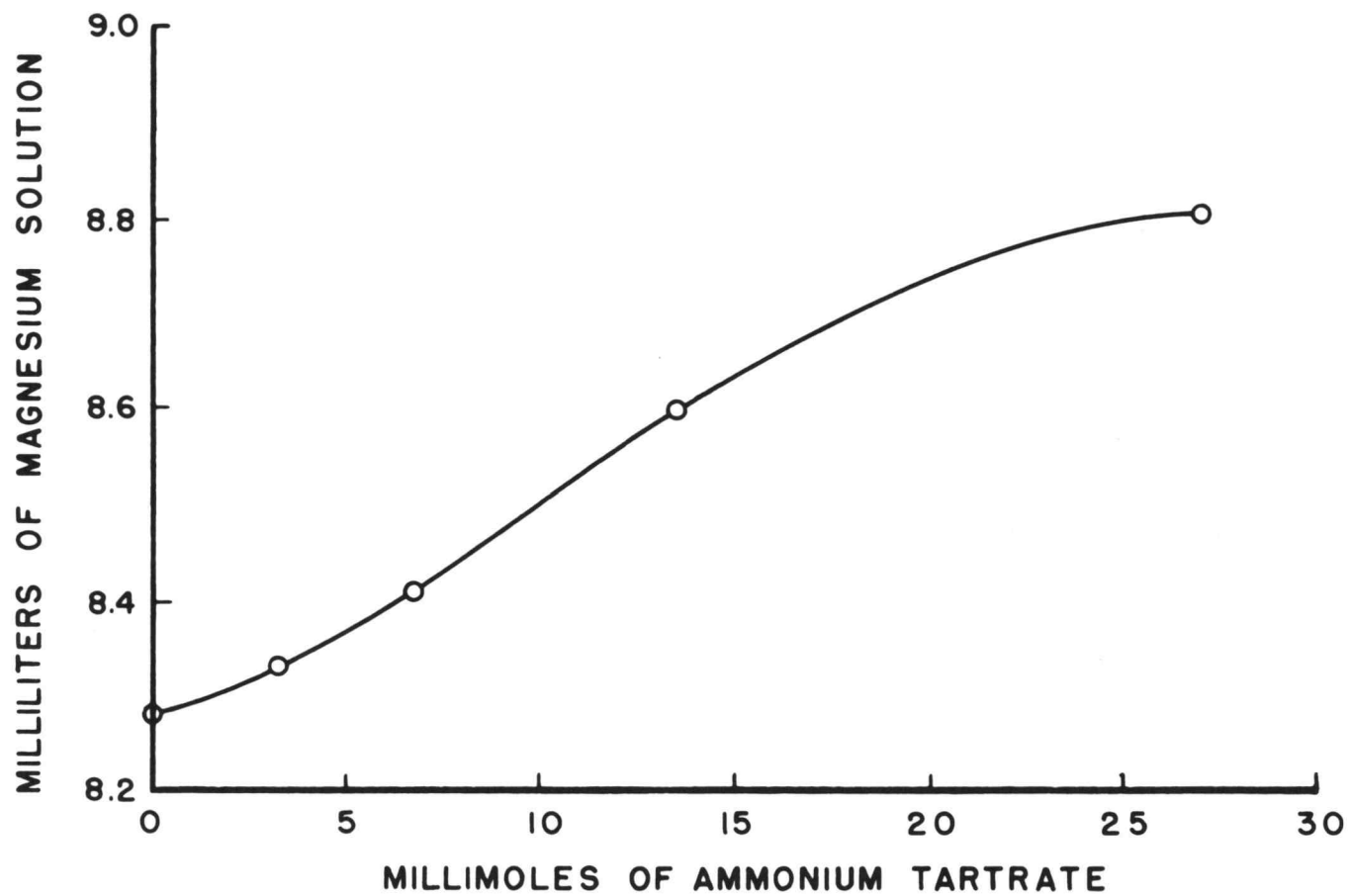
Figure I.   The Effect of Tartrate on the Versene   Titration

Results of titrations. The following trends were observed: (1) With high concentrations of tartrate the indicator had a tendency to fade out. Better results were obtained by adding it just before the endpoint was reached. (2) Uniformities in titration techniques were extremely important in reproducing results. (3) Results that agreed with the theoretical titer were obtained for solutions containing up to 150 milligrams of zirconium. Table V summarizes the data obtained.

TABLE V

TITRATIONS IN THE PRESENCE
OF ZIRCONIUM-TARTRATE

	Grams ammonium tartrate						
	0.63	1.25	2.50	5.0	7.5	10.0	20.0
Milli-grams Zr	Magnesium titer (ml.) (Average of two determinations)						
9.4	8.33	8.50	8.46				
18.8	7.66	8.06	8.46	7.56	8.50	8.50	
37.6	6.49	7.21	8.33	7.62	8.27	8.36	
75.3	5.58		7.77	7.50	8.55	8.36	
150.7				6.72	8.62	8.31	
301.4				6.66	7.46	3.57	5.36

The theoretical titer was 8.30 milliliters.

The acceptable titers, underlined in Table V, occurred at a weight ratio of tartaric acid:zirconium of 54:1 or greater. Extension of this concentration ratio to amounts of zirconium greater than 150 milligrams is not feasible as (1) high ionic strength decreases the stability of the chelates involved; (2) solubility of ammonium tartrate would be exceeded; and (3) the indicator fades seriously at high zirconium-tartrate concentration both upon addition and at the endpoint.

Conclusions on the use of tartrate to complex zirconium. Two general conclusions can be drawn on the observed effects of zirconium-tartrate complexing in the versenate titration: (1) Referring to Table V it was noticed that with constant zirconium and increasing tartrate the magnesium titer increases. This seems to indicate that tartrate complexes magnesium. It confirms the earlier observation of the same trend when no zirconium was present. (2) On the other hand, with constant tartrate, as zirconium increases the magnesium titer decreases. The lowering of free tartrate ion concentration may result in less magnesium complexing. This trend also may be interpreted to indicate that versene chelates with zirconium.

High tartrate concentration minimizes effect (2) above, but the proper amount of zirconium must be present

to balance the effect in (1). This is shown by the
influence of the tartrate:zirconium ratio on the magnesium
titer in Table V. It may be that a certain ratio simply
provides a balance between the two effects of magnesium-
tartrate complexation and zirconium-versene chelation.

The foregoing conclusions indicated that titration
of magnesium without separation of at least the bulk of
zirconium would be impossible. It was definitely decided
that the batch ion exchange separation would be necessary,
and that an attempt would be made to determine magnesium
without final separation of the residual zirconium.

Effect of Fluoride on Versene titration. Because
hydrofluoric acid is used in the separation procedure, it
was necessary to know the influence that fluoride might
exhibit in the titration and whether or not it would have
to be completely removed. It was calculated that 382
milligrams of fluoride ion would be present in the ali-
quot taken for analysis after separation.

Procedure. Ten milliliters of 0.01 molar versenate
was added to each of a series of solutions containing from
0 to 400 milligrams of fluoride. Baker's analyzed
ammonium fluoride was used. The solutions were buffered

to pH 10 and 0.1 milliliter of indicator added. They were
titrated with standard magnesium solution.

Results of titrations. See Table VI for tabulated
data. As the fluoride concentration was increased, a
marked decrease in the volume of titer was observed. Be-
yond 100 milligrams of fluoride the endpoint was difficult
to perceive as the indicator passed through a long range
of violet just before the end of the titration. After
reaching the endpoint, the indicator faded again to a
violet color. At 400 milligrams of fluoride the volume
of titer had decreased to 7.45 milliliters from an initial
titer of 8.20. The plot of milliliters magnesium solution
versus millimoles of ammonium fluoride in Figure 2
illustrates this trend.

An attempt to complex fluoride with boric acid was
unsuccessful, as even greater fading of the indicator was
observed, and there was no appreciable improvement in the
volume of titer used.

At a later date, another investigation utilizing a
direct titration of magnesium with versenate gave similar
results; that is, the volume of versenate increased with
increasing fluoride concentration and poor, indistinct
endpoints were obtained.

Conclusions on fluoride interference. It is evi-
dent that the presence of fluoride results in an error in

TABLE VI

EFFECT OF FLUORIDE ON BACK TITRATION

Milligrams of fluoride ion	Magnesium titer (ml.)
0	8.22 8.20
5	8.16 8.17
20	8.14 8.16
40	8.08 ----
100*	8.00 7.86
150	7.81 7.82
200	7.58 7.74
300	7.31 7.47
400	7.46 7.43

*Fading endpoints were obtained with fluoride concentrations greater than 100 milligrams.

titer and adversely effects the color change of the indicator. For this reason it was necessary to remove fluoride in later experiments by fuming with sulfuric acid.
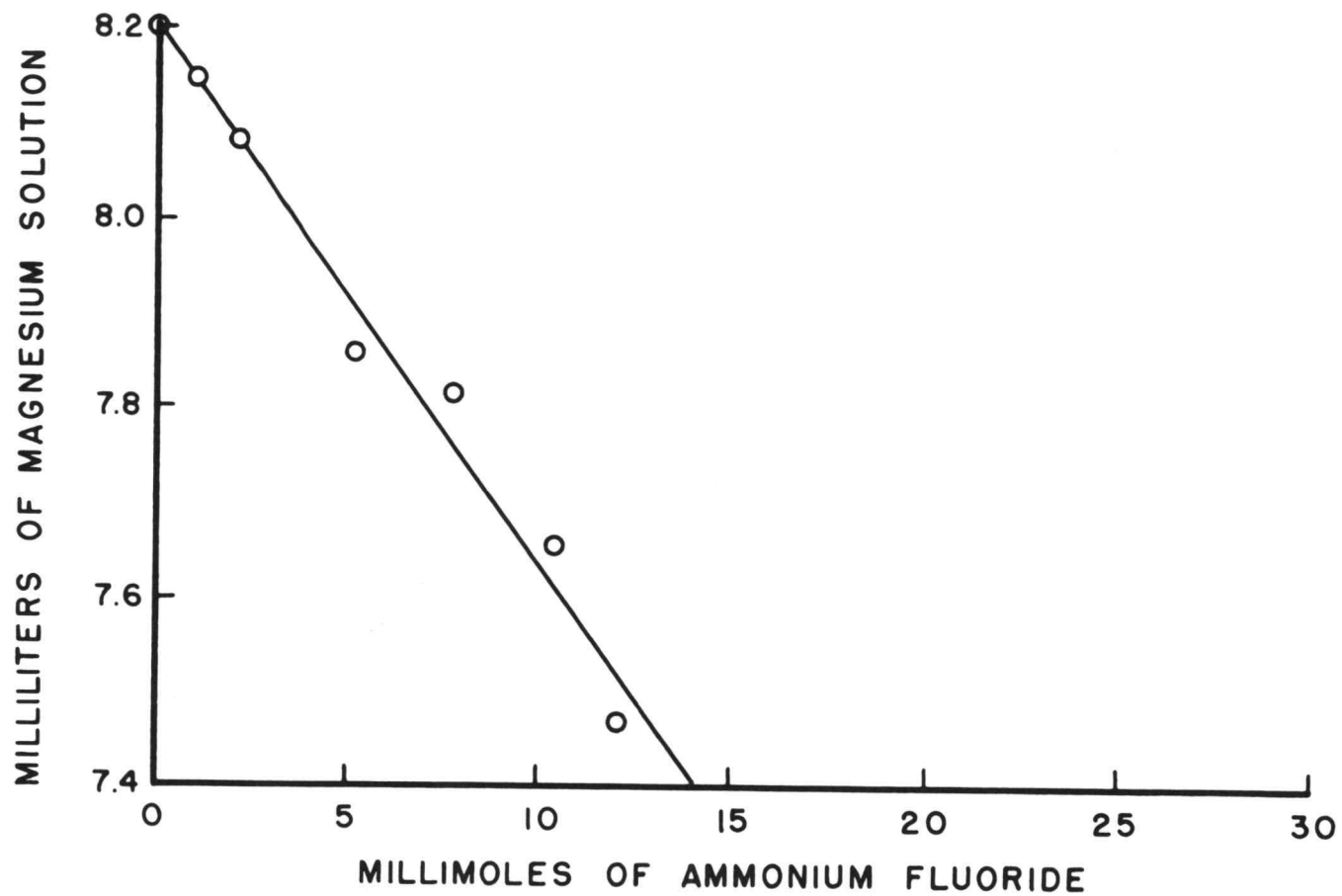
Figure 2. The Effect of Fluoride on the Versene Titration

The Extent of Aluminum interference. Aluminum is very often one of the trace impurities in zirconium. Because it is already known to produce fading of the indicator in versene titrations it was necessary to investigate the extent of this interference. Furthermore, in preliminary ion exchange investigations, it was indicated that aluminum was being introduced into the sample from the resin. This seemed to be a plausible explanation for the trouble observed, as aluminum oxide is used as a catalyst in the manufacture of the resin and the last traces of aluminum are difficult to remove.

Procedure. In this investigation, the procedure was identical with the fluoride experiments except that instead of ammonium fluoride, aluminum chloride was added in varying concentrations. The solutions contained from 0.5 to 5.0 milligrams of aluminum per 100 milliliters (5 to 50 ppm aluminum).

Results and conclusions on aluminum interference. All the solutions gave a serious decrease in titer with increasing aluminum concentration. At 27 ppm aluminum the titer had decreased from 8.10 to 2.70 milliliters. See Table VII. At 40 ppm aluminum the indicator turned red immediately upon adding. Attempts to complex aluminum with tartrate resulted in partial suppression of interference but led to serious fading of the indicator near

TABLE VII

ALUMINUM INTERFERENCE

ppm aluminum	Milliliters versenate
0.0	8.10
5.4	6.78
10.8	5.68
16.2	4.48
21.6	3.60
27.0	2.70
40.0	----*
54.0	----*
0.0**	7.50
16.0**	7.70
54.0**	6.42

* Solutions turned red immediately upon adding the indicator.
**Seven grams ammonium tartrate added.

the endpoint.

From these experiments it was concluded that the resin must be freed from aluminum and some provision must be made to remove aluminum if present in the zirconium metal.

ION EXCHANGE SEPARATION. Preparation of the Resin.
Dowex 1 was used in all experiments. Before use the resin
was treated with hydrochloric acid to remove aluminum.
During this washing process the very small resin particles
are removed which might otherwise remain suspended in
solutions following exchange.

Procedure. A slurry is made of the resin with 3
molar hydrochloric acid. It is stirred for about three
hours and then allowed to settle for thirty minutes.
Small resin particles remain suspended in the supernatent
liquid which is poured off. This procedure was repeated
eight times.

Finally the resin is filtered in a Büchner funnel
and washed with distilled water until only a slight amount
of chloride is present in the washings as indicated by
testing with silver nitrate solution. Excess water is
removed from the resin by vacuum filtration. The resin
is weighed in the moist form.

Exchange of Zirconium in HF-HCl solution. The
proper concentration of hydrofluoric acid and hydrochloric
acid is important for attainment of maximum exchange of
zirconium. The exchange of zirconium depends more
directly upon hydrofluoric acid since the anionic zir-
conium fluoride complexes are the species exchanged. The
amount of hydrofluoric acid used must be sufficient to

dissolve the zirconium sample and to give a slight excess in solution. An overall concentration of 0.8 molar is sufficient to obtain satisfactory exchange of one gram zirconium.

With a fixed concentration of hydrofluoric acid, as the hydrochloric acid increases, exchange decreases (7,p.565). On the other hand, if no hydrochloric acid is present the pH is not high enough to prevent hydrolysis of zirconium. Therefore the hydrochloric acid should be kept to a minimum, and the lowest practical limit is the concentration that will prevent hydrolysis from occurring. Freund and Miner found that 0.8 molar hydrofluoric acid and 0.06 molar hydrochloric acid gave the best conditions for exchange.

The capacity of the moist form of Dowex-1 is about 1 milliequivalent per milliliter of resin (about 0.7 gram) based on column exchange. One gram of zirconium, the size of sample taken for analysis, represents 11 milliequivalents. This means that about 8 grams of resin would be needed for a column exchange. Since batch exchange is less efficient, the quantity of resin used should be two or three times this amount.

Using 0.8 molar hydrofluoric acid and 0.06 molar hydrochloric acid, the weight of Dowex 1 was varied from 25 to 40 grams in a series of experiments to determine the

minimum weight of resin needed for satisfactory exchange.

Procedure - Preparation of solution. Samples of
one gram of zirconium metal were placed in plastic beakers
along with 50 milliliters of distilled water and 3 milli-
liters of 3 molar hydrochloric acid. The metal was dis-
solved by adding slowly 3 milliliters of 48% hydrofluoric
acid (27.6M). The solutions were made up to 100 milli-
liters in plastic bottles. Weights of 25, 30 and 40 grams
of Dowex-1 were added to the bottles.

Ion exchange. The bottles were shaken for 2 hours,
after which the resin was separated from the solution by
vacuum filtration.

Analysis. An aliquot of 25 milliliters was pipeted
into a platinum dish and 0.5 milliliter of concentrated
sulfuric acid was added. The solution was rapidly
evaporated over a Meker burner until bubbling occurred.
Further evaporation was carried out with extreme caution
to avoid spattering; then it was fumed to dryness. An
additional 0.5 milliliter of sulfuric acid was added and
again fumed to dryness. The fuming removes hydrofluoric
and hydrochloric acids. During the second fuming suffi-
cient concentrated nitric acid was added dropwise to
oxidize any organic matter that may have been introduced
by the resin. The residue was taken up in dilute sulfuric
acid (1:100), and the solution transferred to a 150

milliliter beaker. Zirconium was precipitated with ammonium hydroxide as the hydrous oxide. The precipitate is filtered off, ignited, and weighed as ZrO_2.

Results of exchange experiments. Thirty grams of resin gave a 1% increase over the separation achieved with 25 grams. Forty grams only showed an increase of 0.6% over the separation achieved with 30 grams. The data obtained for this experiment is tabulated in Table VIII. It was decided that 30 grams of resin would be used in the separation experiments, since 93% separation can be accomplished. This means that for a one gram sample about 18 milligrams of zirconium remain in the aliquot taken for analysis.

Study of equilibration time. The weight of resin required for exchange had been established by using a two hour equilibration period. It was necessary to determine the minimum time needed to obtain sufficient exchange, as one of the purposes for using this method was to minimize the time required for analysis.

Equilibration experiments were carried out with the same procedure that was described in the preceding section. Thirty grams of Dowex-1 were equilibrated with one gram of zirconium for periods of 5, 15, 30 and 60 minutes. After five minutes 94.7% separation was achieved and further equilibration did not lead to any significant

TABLE VIII

RELATIONSHIP BETWEEN PERCENT EXCHANGE
OF ZIRCONIUM AND WEIGHT OF DOWEX-1

Grams Dowex-1	Grams of zirconium Taken	Remaining	Percent Separation
25	0.2506	0.0198	92.1
30	0.2506	0.0169	93.3
40	0.2506	0.0153	93.9

increase. See Table IX for the data on this experiment.

TABLE IX

RELATIONSHIP OF EXCHANGE TIME
TO PERCENT EXCHANGE

Exchange time (minutes)	Grams of zirconium Taken	Remaining	Percent Separation
5	0.2509	0.0132	94.74
15	0.2505	0.0128	94.88
30	0.2522	0.0130	94.84
60	0.2514	0.0130	94.82

Regeneration of the resin. After the exchange
reactions, the resin was reclaimed and returned to its
normal chloride form. A slurry of the resin was made with
3 molar hydrochloric acid to remove the bulk of zirconium.

The resin was washed in a Buchner funnel with the acid until no precipitation of zirconium resulted on neutralization of the washing with ammonium hydroxide. The resin was washed with water until testing the washings with silver nitrate solution gave only a slight opalescence.

Recovery of Magnesium (Zirconium absent). An experiment was conducted to determine the efficiency with which magnesium could be recovered from an equilibration with the resin. Magnesium was determined by the versenate titration.

Procedure. Three solutions were prepared, each containing 6.0 milligrams of magnesium, 3 milliliters of 48% hydrofluoric acid and 3 milliliters of hydrochloric acid. The solutions were made up to 100 milliliters in plastic bottles and 30 grams of Dowex-1 was added to each. The ion exchange and fuming steps were carried out as described on page 39. It was unfortunate that an investigation of the minimum time for exchange had not been carried out at the time these experiments were conducted. The equilibration time was later established at 5 minutes, as mentioned above.

After fuming, the residue was taken up with distilled water and transferred to a 150 milliliter beaker. The solutions were buffered to pH 10 and 0.1 milliliter of indicator added. A back titration was employed in

which 10 milliliters of 0.01 molar versenate was added
and the excess versenate titrated with a standard mag-
nesium solution.

Results of titrations. Each aliquot taken for
analysis originally contained 1.50 milligrams of magnesium.
Results of the titrations are given in Table X. No ex-
planation was advanced at this time for the somewhat
greater recovery than the theoretical value, but it was
concluded that it would be possible to obtain an efficient
recovery of this quantity of magnesium.

TABLE X

RECOVERY OF MAGNESIUM FROM EQUILIBRATION
WITH DOWEX-1 (NO ZIRCONIUM PRESENT)

Milligrams taken	Magnesium recovered
1.50	1.51
1.50	1.57
1.50	1.56

Recovery of Magnesium in separations from Zirconium.
The next step was to study the recovery of magnesium in a
separation from zirconium and to determine the feasi-
bility of titrating magnesium in the presence of the small
quantity of zirconium left in solution. As an alternative,
the residual zirconium was precipitated with ammonia and
magnesium determined in the filtrate.

Procedure. The exchange solutions were made up to
contain one gram of zirconium and amounts of magnesium
from 10 to 2.5 milligrams, representing from 1% to 0.2%
magnesium. A blank, containing no magnesium, was also
included. Magnesium determinations were made in dupli-
cate. The exchange step and fuming were carried out as
described previously.

Analysis of magnesium in the presence of zirconium.
The residue obtained from fuming was dissolved in dilute
sulfuric acid. Since it was found by earlier studies
with tartrate that either 7 or 10 grams of ammonium tart-
rate would be needed to complex the zirconium present,
both of these quantities were employed. A back titration
was used for these analyses.

Analysis of magnesium after precipitation of
residual zirconium. An alternate procedure was employed
in which 3 grams of ammonium chloride was added to the
solution obtained from fuming and zirconium precipitated

by regulating the pH to 8 with 1:1 ammonium hydroxide.
At this pH any aluminum or iron present would also be
precipitated. The precipitate was filtered off and mag-
nesium determined in the combined filtrate and washings.
Since a large quantity of ammonium chloride was present
it was only necessary to add sufficient ammonium hydroxide
to buffer the solutions to pH 10. Both back titrations
and direct titrations were employed. An aliquot of the
blank, containing no magnesium, was analyzed along with
each concentration level.

Results of titrations in the presence of zirconium.
These analyses proved entirely unsuccessful, as the indi-
cator turned red immediately upon addition. Further
attempt of this procedure was abandoned.

Results of titrations after removal of zirconium.
The results of these analyses were more successful and
gave nearest agreement to the theoretical titers when the
direct titration was employed. No difficulty was en-
countered in determining the endpoint. The data for
direct titration compiled in Table XI show that when the
blank was not applied all the samples gave a higher value
than the theoretical. This trend was also observed in
the recovery of magnesium with no magnesium present.
See page 43. The blank determinations, recorded in Table
XII, are not all constant; however, the first two are

TABLE XI

RECOVERY OF MAGNESIUM
(No blank applied)

% Magnesium		Milligrams magnesium		Deviation from theoretical milligrams magnesium
Added	Found	Added	Recovered	
1.00	1.02	2.53	2.58	0.05
	1.03		2.59	0.06
0.75	0.80	1.90	2.02	0.12
	0.80		2.02	0.12
0.50	0.54	1.26	1.36	0.10
	0.55		1.37	0.11
0.25	0.30	0.63	0.76	0.13
	0.31		0.79	0.16

within the allowable titration error.

TABLE XII

BLANK DETERMINATIONS

Milliliters versenate	Equivalent milligrams magnesium
1.20	0.30
1.11*	0.28
0.96*	0.24
1.36*	0.34

* Fading endpoints were observed.

Application of the blank results in low values for each concentration level, with greater error than is encountered by not using a blank. The blank is on the order of one half the smallest quantity of magnesium determined, and presents an undesirable situation at low magnesium concentration. It was not known exactly what caused the blank but aluminum was suspected, especially since fading endpoints were observed on blanks.

As can be seen from Table XI, the deviation from the theoretical values was close to being constant. This suggests that a standard blank could be applied in which the deviation from theoretical for a known amount of magnesium would be applied to the other samples run at the same time. This type of blank determination would be expected to give more accurate results because fading endpoints would be avoided and a closer approximation of actual conditions could be accomplished.

Application of a standard blank. Solutions containing from 1% to 0.1% magnesium were analyzed according to the ion exchange and ammonia separation procedure as outlined above. A 0.5% level was used for the blank. It contained no zirconium. The difference between the theoretical and experimental versenate titers for the blank was subtracted from the titers obtained on all other samples.

The results of three separate runs, using the blank correction, are compiled in Table XIII. Good precision was obtained in any one concentration level for all three sets of determinations. In no case was the deviation from the mean greater than 0.01%. The deviation of the percent magnesium reported from the theoretical value was no greater than 0.01%.

The appearance of a very low blank of 0.03 and 0.02 milliliter of titer in the last two runs as compared to 0.35 milliliter in the first run was attributed to further washing of the resin after run number one. The resin was washed, in the manner described earlier, to remove aluminum that had possibly remained after previous washings and regeneration. The process was continued until the washings contained less than 3 ppm aluminum, as indicated by tests with aluminon reagent.

PROCEDURE FOR DETERMINATION OF MAGNESIUM IN ZIRCONIUM. One gram of zirconium is placed in a plastic beaker along with 50 milliliters of distilled water and 3 milliliters of 3 molar hydrochloric acid. Three milliliters of 4.8% hydrofluoric acid is added slowly and the solution made up to 100 milliliters in a plastic bottle.

Thirty grams of Dowex-1 (moist form) is added to the bottle and the mixture is shaken for 5 minutes, followed by vacuum filtration. An aliquot containing from

TABLE XIII

DETERMINATION OF MAGNESIUM IN ZIRCONIUM

Run No. 1

	Experimental titer	Theoretical titer	Difference
Blank:	5.18	4.83	0.35

Milligrams magnesium		% Magnesium			Deviation from the mean
Added	Found	Added	Found	Mean	
2.56	2.56	1.02	1.02	1.02	0.00
	2.57		1.03		0.01
	2.56		1.02		0.00
1.92	1.92	0.77	0.77	0.77	0.00
	1.91		0.76		0.01
	1.92		0.77		0.00
1.28	1.27	0.51	0.51	0.51	0.00
	1.28		0.51		0.00
	1.28		0.51		0.00
0.64	0.64	0.26	0.26	0.26	0.00
	0.65		0.26		0.00
	0.64		0.26		0.00
0.32	0.32	0.13	0.13	0.12	0.01
	0.31		0.12		0.00
	0.31		0.12		0.00

Run No. 2

	Experimental titer	Theoretical titer	Difference
Blank:	5.22	5.19	0.03

Added	Found	Added	Found	Mean	Deviation
1.92	1.92	0.77	0.77	0.77	0.00
	1.90		0.76		0.01
	1.94		0.78		0.01
1.28	1.26	0.51	0.50	0.50	0.00
	1.26		0.50		0.00
	1.27		0.51		0.01
0.64	0.62	0.26	0.25	0.25	0.00
	0.63		0.25		0.00
	0.63		0.25		0.00

TABLE XIII (Cont'd.)

Run No. 3

	Experimental titer	Theoretical titer	Difference
Blank:	5.20	5.18	0.02

Milligrams magnesium		% Magnesium			Deviation from the
Added	Found	Added	Found	Mean	mean
1.92	1.93	0.77	0.77	0.77	0.00
	1.94		0.78		0.01
	1.93		0.77		0.00
1.28	1.25	0.51	0.50	0.51	0.01
	1.28		0.51		0.00
	1.27		0.51		0.00
0.64	0.67	0.26	0.27	0.27	0.00
	0.66		0.26		0.01
	0.67		0.27		0.00
0.32	0.36	0.13	0.14	0.14	0.00
	0.35		0.14		0.00
	0.36		0.14		0.00

2.5 to 0.3 milligrams magnesium is evaporated and fumed down with two 0.5 milliliter portions of concentrated sulfuric acid. Nitric acid is added dropwise near the end of the fuming to oxidize organic matter.

The residue is taken up with 50 milliliters of 1:100 sulfuric acid in a 150 milliliter beaker. Three grams of ammonium chloride are added and the residual zirconium is precipitated with 1:1 ammonium hydroxide. Sufficient excess is added to regulate the pH to 8. The

precipitate is filtered off and washed with five, 5 milliliter portions of 2% ammonium chloride solution which has been regulated to pH 8 with ammonia. The filtrate and washings are combined and regulated to pH 10 by addition of concentrated ammonium hydroxide. A pH meter is used to determine the volume of ammonia needed for one sample, then if the solution volumes are equal, this quantity of ammonia can be added to the remaining samples without further varification of pH.

0.2 Milliliter of eriochromeschwarz-T indicator is added to each sample directly before titration. The samples are titrated with 0.01 molar versenate solution using a ten milliliter micro buret and stirring vigorously near the endpoint. The color changes from wine-red to a definite blue at the endpoint.

The volume of titer ranges from 10 to 1 milliliters for samples originally containing from 1% to 0.1% magnesium.

PLANS FOR FUTURE WORK

Application of the batch method ion exchange separation to the determination of magnesium within the range of from 0.1% to 0.01% should be investigated.

It is reasonable to believe that the spectrophotometric method utilizing 8-hydroxyquinoline could be employed for determination of magnesium.

SUMMARY

A volumetric method has been presented for the determination of magnesium in zirconium. The bulk of zirconium was separated by a rapid batch ion exchange in a hydrofluoric-hydrochloric acid solution using Dowex-1, and was followed by an ammonia precipitation of the remaining zirconium. Magnesium was determined by the complexometric titration with disodium ethylenediamine tetraacetate.

This method was applied to magnesium-zirconium mixtures containing from 1% to 0.1% magnesium. The lower concentration level of 0.1% was established because the volume of versenate used in titration becomes too small for accurate determinations at concentrations lower than this.

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