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NOTE TO USERS

ANALYSIS OF BERYLLIUM-ALUMINUM MIXTURES

AND PROPERTIES OF COMPLEXES INVOLVED

by

Homer Virgil Meek

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I. INTRODUCTION

Some 293 publications concerning the analytical
chemistry of beryllium, or of analytical interest, have
appeared during the 152 years which have elapsed since
the discovery of beryllium by Vauquelin in the year
1798. The rather recent increased academic and indus-
trial interest in the chemistry of beryllium is shown
by the fact that of these 293 articles, 194 have
appeared during the years 1929-49 inclusive. The rather
unique and useful properties which are imparted to other
metals by the presence of relatively very small amounts
of beryllium account for part of this interest. Most of
the remainder is probably due to its use in fluorescent
lights and similar devices, in the fabrication of
crucibles, and in applications of interest in nuclear
studies.

It was felt that there was considerable need of a
method of determining small amounts of beryllium without
the use of a spectrograph. The purpose of this work was
to develop such a method and in so doing to contribute
as much as possible to the understanding of the chemical

behavior of aqueous beryllium solutions. The most
appealing mode of attack was the spectrophotometric
method since, in general, it is highly sensitive to low
concentrations of materials and does afford a means of
examining systems with a minimum of disturbance to them.
Usually the determination of metallic substances in
solution by the spectrophotometric method involves the
use of materials capable of forming soluble complexes
with the metallic ions. It was hoped that in his
studies the author could successfully identify any such
complex and determine the degree of its stability. It
was further hoped that any method developed would require
the use of only such materials and equipment as are
available in the ordinary modern chemical laboratory.

Of all the elements beryllium is probably most
closely resembled by aluminum in its aqueous chemistry.
The author deliberately set as his goal the determina-
tion, without preliminary separation, of small quantities
of beryllium in the presence of very large quantities of
aluminum, hoping that in so doing the probability of
interference by foreign ions would be minimized and the
general value of the method be thus enhanced.

Throughout this work the author has attempted to interpret his experimental data on the premise, or indeed the theorem, that the simplest explanation of natural phenomena is the best explanation, so long as it is consistent with all the known experimental facts and not in disagreement with accepted theory.

II. REVIEW OF THE LITERATURE

A. General

The chemistry and literature of beryllium previous
to 1908 was adequately reviewed by Parsons (1) in his
excellent book, "The Chemistry and Literature of Beryl-
lium". In his preface to this book he warned future
workers in the field as follows:

> Especially is it desired to call atten-
> tion to the fact that a large proportion of
> its accredited compounds are in reality but
> indefinite solid solutions. This condition
> of the literature of beryllium is due to the
> abnormal extent to which its hydroxide is
> soluble in solutions of its normal salts,
> giving rise to solids of almost any degree of
> basicity or to solutions with decreased
> osmotic effects. Accordingly, results of
> analysis, freezing points, etc., give little
> evidence of the true nature of its compounds,
> unless accompanied by proved definiteness of
> composition, a proof too often omitted through-
> out the whole field of inorganic chemistry,
> but nowhere more than in studying beryllium
> and its compounds.

Parsons (1) listed a very large number of the
normal compounds of beryllium, presumably all that had
been prepared or claimed up to 1908, and the general
manner in which they were prepared together with their

properties, if known. He particularly emphasized the necessity for anhydrous conditions or at least, very strongly acid conditions, for the preparation of the normal salts. Neither normal beryllium nitrite nor carbonate was known but the possibility of their preparation under anhydrous conditions was suggested. Perhaps the most interesting of the normal compounds of beryllium is the acetylacetonate, $Be(C_5H_7O_2)_2$, which was carefully studied by Parsons (2) in connection with his determination of the atomic weight of beryllium. This material sublimes easily, hence is readily purified and is hydrolyzed slowly by cold water, rapidly by hot water and strong acids, to give acetyl acetone and beryllium hydroxide. In many respects its behavior resembles that of basic beryllium acetate and its homologs.

Parsons (1) also listed a large number of double salts of beryllium, a very few acid salts, and a considerable number of basic compounds of beryllium. Of these, the most interesting are the basic beryllium acetate, $Be_4O(C_2H_3O_2)_6$, used by Parsons (2) in his studies of the atomic weight of beryllium, and its

homologs. These substances are definitely crystalline
in character, sublime readily, hydrolyse in contact
with water, and must be prepared under anhydrous condi-
tions.

A complete bibliography of the analytical chemis-
try of beryllium was compiled by Banks, McClure, and
Meek (3) in 1948. In Section XI of this work the pres-
ent author has listed a supplement to this bibliography
including those articles abstracted by Chemical Abstracts
through January 10 of 1950.

Since the comprehensive work of Parsons, Frommes
(4) rather critically reviewed the literature of the
detection and determination of beryllium without con-
tributing anything new to the subject. Gadeau (5) some-
what less extensively reviewed the general analytical
chemistry of beryllium, and concluded that the precipi-
tation of beryllium as beryllium ammonium phosphate,
$BeNH_4PO_4$, and subsequent ignition to the pyrophosphate,
$Be_2P_2O_7$, constituted the best method of determining
this element.

It was of interest to note that in his excellent
book concerning oxidation potentials Latimer (6) saw

fit to list the following equilibria involving various species of beryllium in aqueous solution:

$$2 \, Be^{++} + H_2O \rightleftharpoons Be_2O^{++} + 2H^+ \qquad K = 4 \times 10^{-7}$$

$$Be_2O \, (OH)_2 \rightleftharpoons Be_2O^{++} + 2OH^- \qquad K = 4 \times 10^{-19}$$

$$Be_2O(OH)_2 + H_2O \rightleftharpoons 2Be^{++} + 4OH^- \qquad K = 1 \times 10^{-40}$$

$$H_2Be_2O_3(s) \rightleftharpoons 2H^+ + Be_2O_3^= \qquad K = 7.3 \times 10^{-30}$$

$$H_2BeO_2(I) \rightleftharpoons 2H^+ + BeO_2^= \qquad K = 2.8 \times 10^{-30}$$

$$H_2BeO_2(II) \rightleftharpoons 2H^+ + BeO_2^= \qquad K = 1.4 \times 10^{-30}$$
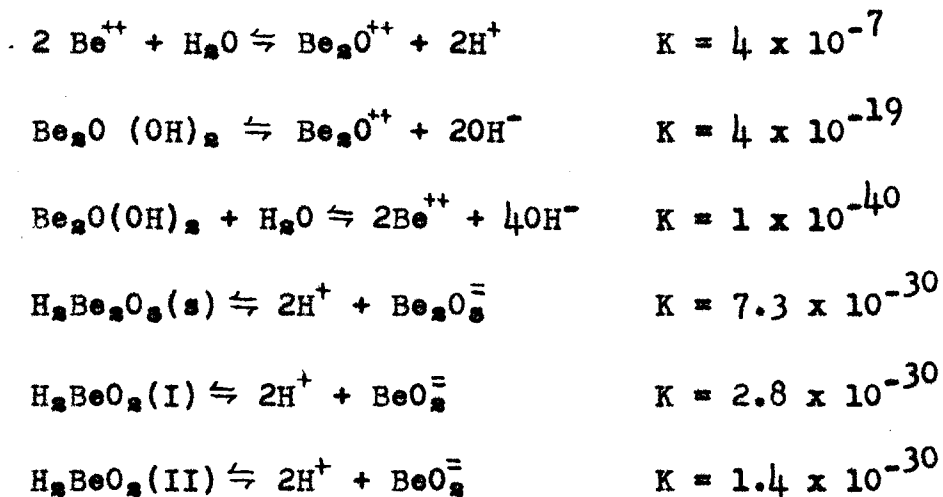
The present author did not desire to question the reality of these equilibria but reproduced them here only to emphasize the fact that very probably in them lie the reasons for the wide disagreements regarding the aqueous chemistry of beryllium. There are doubtlessly equilibria involved other than those listed above. Each of the hydrated beryllium oxide species, H_2BeO_2 and $H_2Be_2O_3$, may be capable of ionizing stepwise, twice as acids and twice as bases, to give even more beryllium species in solution. The determination of the actual conditions with regard to temperature, pH, and concentration which lead to the creation of each of these species in even

approximately known ratios would contribute to the understanding of the chemical behavior of aqueous solutions of beryllium as no other study has done.

It was of interest to note the distribution of the analytical methods published since 1909 relative to the general analytical methods employed. The methods used were virtually completely restricted to five types. These types are the gravimetric, volumetric, fluorimetric, colorimetric, and spectrographic methods. The frequency, with respect to these types during the period 1909 to 1950 were 70, 13, 12, 26, and 34, respectively. Before 1925 the gravimetric methods were virtually the only ones in general use although some volumetric analyses had also been carried out. After this time the fluorimetric, colorimetric, and spectrographic methods became more popular mainly because they generally require less time and involve less intricate manipulation.

It was felt that a brief discussion of the chemical principles upon which these methods depend would be desirable. Accordingly the two short sections below were written.

B. Gravimetric Methods

Parsons (1) favored above all other methods the determination of beryllium as the oxide. The main problem has always been to completely separate beryllium from iron and aluminum. Parsons accomplished this by first precipitating all three as a mixture of the hydrated oxides and then redissolving in a minimum amount of hydrochloric acid. After oxidizing the iron with a little nitric acid he concentrated the solution by evaporation, nearly neutralized with ammonia, and then poured the solution into a hot solution of sodium bicarbonate and brought the whole to a boil. Under these conditions the beryllium hydroxide dissolved leaving iron and aluminum as a precipitate. A second precipitation on the redissolved precipitate was carried out, if necessary. The beryllium in the filtrate was usually doubly precipitated with ammonia (to insure removal of any sodium contamination), filtered, and ignited to the oxide for weighing.

In the opinion of this author the above separation depended upon the relative acidity of the hydrated oxides

of aluminum, iron and beryllium, that of beryllium
presumably being the more acidic. The function of the
hot sodium bicarbonate solution was essentially that
of a buffer to keep the solution at the optimum pH for
the separation. Various other materials, mostly salts,
have been used to serve essentially the same purpose
as the bicarbonate in the above work. Beryllium oxide
was invariably chosen as the final form of weighing in
these cases. Quite recently Duval and Duval (7)
studied the ignition of compounds of beryllium for
gravimetric analytical determination. They indicated
that the hydroxide could be ignited to the oxide at a
temperature of 951°C. but preferred the ignition of
beryllium ammonium phosphate, $BeNH_4PO_4$, to the pyro-
phosphate, $Be_2P_2O_7$. Neither amorphous beryllium sul-
fate nor crystalline beryllium sulfate were found
satisfactory. Moser and Singer (8) were the first to
recommend the gravimetric determination of beryllium by
precipitation as beryllium ammonium phosphate and igni-
tion to the pyrophosphate for weighing. They also
recommended precipitation of insoluble beryllium tannate
and subsequent ignition to the oxide for weighing.

Probably the most satisfactory method of separating beryllium from iron and aluminum is that described by Kolthoff and Sandell (9) which involves the precipitation of iron and aluminum by 8-hydroxyquinoline and subsequent precipitation of beryllium in the filtrate by ammonia.

C. Other Methods

Fischer (10) developed a volumetric method for titrating rather small amounts of beryllium with a standard solution of quinalizarin, 1,2,5,8-tetrahydroxyanthraquinone, which evidently was quite satisfactory. He also described a colorimetric method based on the same reagent which gave a blue color, actually a precipitate in some cases, in alkaline solutions of beryllium.

Evans (11) developed a variation of an earlier volumetric method of Bleyer and Moorman (12). The general principle in the latter was to use the acid liberated from the hydrolysis of salts of strong acids and beryllium to liberate iodine from a mixture

of potassium iodide and potassium iodate which was sub-
sequently titrated with sodium thiosulfate. In the
former, sodium arsenite was used to titrate the iodine.
Obviously in both these cases a preliminary separation
was required.

A very sensitive qualitative test for beryllium
was devised by Zermatten (13) which depended upon the
fluorescence of beryllium in alkaline solutions of
morin, 3,5,7,2',4'-pentahydroxy flavone. Sandell (14)
investigated the reaction further and extended the
limit of detection from 0.01 parts per million in day
light to 0.001 parts per million in the presence of
ultraviolet radiation. He also used this method in
determining beryllium in silicate rocks (15) making it
quantitative by comparison with standards. More
recently White and Lowe (16) found that 1-amino-4-
hydroxyanthraquinone in alkaline solution fluoresces in
the presence of beryllium. The sensitivity was some-
what less than that of morin but interferences were
fewer than those of either morin or quinalizarin. Other
materials which have been shown to have color or to
fluoresce in the presence of beryllium are 1,4-dihy-
droxyathraquinone-2-sulfuric acid (17, p. 10),

1,4-dihydroxyanthraquinone (17, p. 16), p-nitrobenze-
neazoorcinol (18), and others. Only Fischer (10) was
found to give the ratio of complexing body to complexed
body; he claimed the ratio of quinalizarin to beryllium
to be 2:1.

Many spectrographic methods of analyses have been
developed and reported for the determination of beryl-
lium in various materials. These methods are not of a
chemical nature and were not of interest in the present
work.

III. INSTRUMENTS EMPLOYED

A Cary automatic recording photoelectric spectrophotometer, Model 12, was used for most of the work involving the scanning of solutions at varying wave length. This instrument is manufactured by the Applied Physics Corporation of Pasadena, California, and is designed particularly for use in the ultraviolet region of the spectrum but may also be used in the visible region. It is equipped with a double-prism monochromator in order to obtain high dispersion and minimize scattered radiation. The light beam is chopped at 90 cps., and the radiation receiver is a photo-multiplier tube. The output of the photomultiplier is fed through an electronic amplifier to a recorder which automatically plots optical density of solutions under examination as a function of wave length. Widely differing scanning speeds are made possible by changing the gear ratio between the drive shaft of the motor and the prism table which it rotates. This varies the length of the wave length coordinate on the recorder when the recorder is rotating at constant speed. A further variation in coordinates is made possible by

changing the gear ratios in the driving mechanism of the recorder itself. The instrument is equipped with a so-called "multipot" control to permit unmatched cells to be effectively "matched" throughout the visible and untraviolet regions of the spectrum. The instrument is extremely useful for the rapid determinations of absorption spectra. It should also be very convenient for kinetic studies involving spectrophotometrically determinable substances because one could obtain a continuous recording of time versus concentration for such a system.

Some of the spectrophotometric scanning of solutions and virtually all of the constant wave length work was done by means of the Beckman photoelectric quartz spectrophotometer, Model DU. The instrument has been in use for several years and its versatility and usefulness are well-known. It is particularly convenient for constant wave length spectrophotometry and is very widely used in routine analysis in modern laboratories.

Beckman pH meters were used exclusively in the present work wherever the determination of the pH was

demanded. Three different models were used, depending upon the accuracy desired and the models which were available. For most work of a routine nature where the magnitude of the pH was not very critical either the Beckman Model H-2 or Model M pH meters were used. Where greater accuracy was required the Beckman Model G meter was used. The pH of alkaline solutions of appreciable sodium ion concentration were determined either by using the conventional glass electrodes and the appropriate sodium ion corrections supplied by the manufacturer or by using the special Type E glass electrodes together with the corrections similarly supplied.

IV. MATERIALS

A. Beryllium Basic Acetate

Beryllium basic acetate, $Be_4O(C_2H_3O_2)_6$, was dis-
covered in 1901 by Urbain and Lacombe (19) who studied
it and described its properties. It was chosen as our
primary standard, or near primary standard, source of
beryllium because it is rather easy to prepare and
purify and affords properties desirable enough for it
to have been used by Parsons (2) in 1904 for the
determination of the atomic weight of beryllium. It
may be readily recrystallized from chloroform or from
glacial acetic acid. Parsons (1, p. 63) gave its
melting point as 283°-284°C. and boiling point as
330°-331°C. and claimed that it sublimed without decom-
position. Lacombe (20) prepared the basic formate,
acetate, propionate, isobutyrate, butyrate, and iso-
valerianate, all of the same type as the basic acetate,
by the action of the anhydrous acids in excess on the
carbonate and subsequent sublimation under diminished
pressure. Thus the basic acetate is only one member of
a series of very unique and interesting chemical

compounds seemingly peculiar to beryllium alone.

In the preparation of the basic acetate by this author 1133 g. of crude beryllium hydroxide from a commercial source was placed in a 32-liter Pyrex glass jar and dissolved in the minimum amount of reagent-grade concentrated hydrochloric acid required to give a clear solution. The beryllium was then precipitated, probably as a mixture of hydroxide and basic carbonate, by the addition of a saturated solution of ammonium carbonate. The ammonium carbonate was added continuously over a period of several hours with vigorous mechanical stirring. The optimum amount of carbonate to be used was determined by sampling the supernatant liquor and adding to it small portions of hydrochloric acid or saturated ammonium carbonate solution. The point where the addition of a little of the carbonate solution or of the hydrochloric acid failed to give a precipitate in the supernatant liquid was taken as the optimum condition. The precipitate was then allowed to settle and the mother liquor separated by filtration through a large inverted Beuchner funnel containing a filter paper. Vacuum was applied to the funnel

until no noticeable amount of mother liquor was being withdrawn. The filtrate did give a slight positive test for beryllium with the addition of ammonium carbonate, and this small amount of beryllium was precipitated, filtered, and combined with the bulk of the precipitate in the large container. The precipitated beryllium was then washed twice with 5-liter portions of 1 per cent ammonium carbonate solution and vigorous mechanical stirring over a period of two hours for each washing. Each wash solution was removed in the same manner as the original mother liquor. The filter-dry precipitate was then transferred to a 22-liter ground-glass joint, round-bottom, Pyrex distillation flask and dried under the maximum reduced pressure supplied by a water aspirator. To assist in the drying, heat was supplied to the system by means of a hemispherical Glascol heating mantle placed about the lower half of the flask and four 250-watt reflector drying lamps directed symmetrically at the upper half of the flask. Heat and vacuum were applied until the mass of material assumed the appearance of a dry, free-flowing white powder.

A large excess of reagent-grade glacial acetic
acid was then added to the "dry" powder and the whole
heated by means of the mantle and infrared lamps to
give a clear solution. Acetic acid and water were
then removed by distillation, without rectification,
until the vapor temperature reached 112°C. At this
point considerable precipitation had occurred. The
entire mass was allowed to cool over a period of one
day and was filtered by decantation. The crystals
were again dried as before to give any easy-pouring,
presumably dry, mass of beryllium basic acetate. The
yield at this point was 2741 g. of crude basic acetate
equivalent to 102 per cent of the theoretical.

A sublimation apparatus was designed and con-
structed, the principal features of which were a 5-
liter round bottom Pyrex distillation flask equipped
with a single 45/50 ℉ female ground-glass joint and
heated by a fully spherical Glascol mantle, a Pyrex
glass goose-neck equipped at one end with a 45/50 ℉
male ground-glass joint and at the other with 71/60 ℉
ground glass, male joint, and an 8 x 125 cm. Pyrex
glass condensing tube equipped at one end with a

71/60 $\overline{5}$ female ground glass joint and drawn down to a
9 mm. tube at the other end. The crude basic acetate
was introduced into the 5-liter flask and the goose-
neck and condensing tube attached in the proper order.
The goose-neck was covered with asbestos paper, wound
with nichrome heating wire to which was connected a
variac, and the whole insulated with about a one inch
layer of 85 per cent Magnesia pipe insulation. The
flask and goose-neck were both equipped with thermometer
wells. The small end of the condensing tube was packed
with a little glass wool and connected through a water
cooled Friedrichs condenser and a dry ice-acetone
cooled vapor trap to a vacuum pump. The basic acetate
was sublimed at the minimum temperature possible at a
pressure of 1-5 mm. as indicated by a mercury manometer.
The temperature of the vapor in the flask and in the
goose-neck were kept as nearly as possible equal by
appropriate adjustment of the variacs. Excessive
accumulation of sublimate in the entrance of the con-
densing tube was eliminated by playing the heat from a
pair of 250-watt reflector drying lamps on this portion
of the tube. The first sublimation yielded approxi-
mately 1700 g. of sublimate and gave about 100 g. of

grey residue. The sublimate itself was somewhat grey, indicating that some decomposition had occurred. A second sublimation was performed in a similar manner and again an appreciable tan colored residue of about 12 g. was obtained. Again, the sublimate was a rather unattractive grey in appearance. It was felt that the infrared lamps may have contributed to thermal decomposition of the sublimate in the head of the tube. The product of the second sublimation was recrystallized from reagent-grade glacial acetic acid, dried as before, and sublimed a third time. On this occasion the heating lamps were not used but the nichrome heating wire was wound about the first few inches of the condensing tube. In addition the whole apparatus was swept by a very slow stream of nitrogen. The nitrogen was scrubbed through alkaline pyrogallol and dried with anhydrous magnesium perchlorate before being introduced through a ground-glass jointed tube into the bottom of the sublimation flask. The rate of nitrogen passage was regulated by means of a screw clamp, through a bubble counter, to about one bubble per second. This time the main part of the sublimation was carried out at a pressure of 1.5 mm. of mercury and at a vapor temperature

of about 240°-250°C. It seemed almost certain that the heat lamps had contributed to the previous decomposition because on this occasion a pure white sublimate was obtained and a residue of less than 1.0 g. remained in the flask. Further, the time required for this sublimation was less than one-third that required in the two previous sublimations. Approximately 1200 g. of the third sublimate was obtained which represented about a 45 per cent yield of material, considered to be pure beryllium basic acetate. This material was placed in a large crystallization dish and stored over anhydrous magnesium perchlorate in a vacuum desiccator.

Six samples of the beryllium basic acetate prepared above were analysed gravimetrically by decomposing with a large excess of concentrated reagent-grade nitric acid in covered 500 ml. Erlenmeyer flasks and igniting to constant weight as the oxide in platinum dishes. The results of these gravimetric analyses are summarized in Table 1. The corrected wt. beryllium oxide, BeO, represents the final apparent weight in air versus brass weights, of the residues, corrected for nonvolatile material in the nitric acid. This

TABLE 1

Gravimetric Analysis of Beryllium Basic Acetate

Sample No.	Weight sample in grams	Vol. concentrated HNO_3 used	Corrected wt. BeO in grams	Per cent by weight, BeO
1	1.2793	50.0	0.3164	24.73
2	3.2790	50.0	0.8065	24.60
3	3.9988	50.0	0.9815	24.55
4	2.5193	120.0	0.6205	24.63
5	2.8617	120.0	0.7073	24.72
6*	4.3054	120.0	1.0540	-----

Average, 1-5 inclusive = 24.65% BeO; Theoretical = 24.63% BeO

* No. 6 was discarded because of known loss by "bumping" in HNO_3 treatment.

correction amounted to 0.0008 g. per 100 ml. of acid.
Both the beryllium basic acetate and the ignited beryl-
lium oxide gained weight in air very rapidly and at
least part of the rather poor duplication of results is
assignable to this cause. However, the analysis did
indicate that substantially pure beryllium basic acetate
had been prepared.

The ignited residue from sample 1, Table 1, was
submitted to Dr. V. A. Fassel of the Spectrographic
Group at the Ames Laboratory of the Atomic Energy
Commission for spectrographic analysis. His analysis
in parts per million calculated on the basic acetate
basis were: manganese, 1.2; magnesium, 22; silicon,
42; iron, 25; calcium, 30; aluminum, 6. Other elements
were not detected. Mr. Anton B. Carlson obtained 48
parts per million silicon on the basic acetate basis
using a chemical method of analysis and this was seen
to agree quite well with the spectrographic result.
Although the relative amounts of contaminants listed
above are quite small it is probable that even they are
mostly assignable to the nitric acid used in the analy-
sis. At any rate the spectrographic analysis substan-
tiated the gravimetric analysis in indicating that

quite pure beryllium basic acetate had been prepared.

Beryllium stock solutions Nos. 1 and 2 were
prepared by dissolving known weights of the basic
acetate in a considerable excess of reagent-grade
concentrated sulfuric acid, fuming, and diluting to
known volumes in volumetric flasks. Beryllium stock
solution No. 1 was prepared as a 0.0645 M solution and
beryllium stock solution No. 2 as a 0.1039 M solution.
For the most part any beryllium solutions used in sub-
sequent work was obtained directly from one of these
two stock solutions by measuring the proper volume
from a pipet or buret. Where other procedures were
used the manner in which such solutions were prepared
was clearly indicated.

B. Sulfosalicylic Acid

After having established qualitatively that a
rather stable complex was formed in aqueous solution
between beryllium and sulfosalicylic acid it was of

interest to examine somewhat critically the nature of
the sulfosalicylic acid available commercially before
proceeding with a more fundamental study of the com-
plex. Among the points of interest was the question
of whether or not the commercially available material
consisted essentially of only one of the possible
isomers and, if it did not, was this fact of importance
in the complex formation with beryllium. Numerous
recrystallizations from water of commercial samples
of sulfosalicylic acid gave material of excellent appear-
ance but no correlation was apparent between melting
point and purity as evidenced titrimetrically, by the
appearance of the crystals, and by the color of the
aqueous solutions. Nor was such correlation found
among various preparations of exhaustively desiccated
material. This was not particularly surprising since
sulfonic acids in general are not well suited for melt-
ing point characterization. Rae (21) compared the
melting points of seven different commercial samples of
dried sulfosalicylic acid and found that three melted
at 110°-111°C. and four melted in the range 120°-124°C.
The results of the determination of water content,
degree of purity by titration, test for iron, comparison

of the color of 50 per cent aqueous solution, deter-
mination of sulfate and of free salicylic acid failed to
disclose to him a reasonable relationship among these
properties and the two groups of melting points.
Horkeimer (22) pointed out that the undried product
melts at 105-8°C., but when heated slowly it does not
melt up to 200°C. The present author found the latter
to be the case also. More recently Schulze (23)
claimed that melting points variously reported for this
acid depended on the water content and that the dihy-
drate, $C_6H_3(OH)(CO_2H)SO_3H \cdot 2H_2O$, melts at 108-13°C.
Our conclusions were that the melting point of sulfo-
salicylic acid, taken with only ordinary care and using
only conventional apparatus, was not a reliable or
satisfactory criterion of purity.

Meldrum and Shah (24) developed a method of pre-
paring sulfosalicylic acid which they claimed was
better than previously reported methods and proved
that, of the several possible isomers of the mono-sulfo-
nation of salicylic acid, the one which they obtained
was really the 5-sulfosalicylic acid. The proof of
structure was made by brominating an aqueous solution

of the acid to give the monobrominated product and
subsequently hydrolysing with superheated steam to
give the monobrominated salicylic acid. That this was
really the 3-bromosalicylic acid was confirmed by com-
parisons with known 3-bromosalicylic acid. Thus, it
was concluded that the original sulfonic acid must have
been the 5-sulfosalicylic acid.

Several preparations of sulfosalicylic acid were
made by the method of Meldrum and Shah (24). Their
method consisted simply of a low temperature (ca. 75°C.)
sulfonation of salicylic acid with sulfuric acid con-
taining 3 per cent sulfur trioxide. The product
crystallized out on cooling, was filtered on glass
cloth, and recrystallized from distilled water. For
the purposes of this work the sulfosalicylic acid was
recrystallized twice more from distilled water to give
a very white product of excellent crystalline appearance.

It was decided to then make comparisons in three
important respects between this synthetic sulfosali-
cylic acid and that obtained from two commercial
sources. The first respect was the nature of the curves
obtained by plotting the pH of solutions of the acids

of equal molarity versus ml. of standard alkali
throughout the course of potentiometric titrations
using the glass electrode. The second was the nature
of spectral absorptions obtained when solutions of the
acids of equal molarity and pH were scanned using the
Cary recording spectrophotometer. The third was the
nature of spectral absorptions obtained when equal
molar solutions of the acids containing equal quanti-
ties of beryllium and adjusted to the optimum pH of
the beryllium-sulfosalicylate complex were scanned
using the Cary recording spectrophotometer. These com-
parisons were made, see Figures 1 and 2 respectively,
and from the extreme similarity in all respects it was
concluded that either in all cases we were dealing
with the 5-sulfosalicylic acid or, if not, at least
the behaviors were the same as though we were, and
hence for our purposes the choice of the source of the
acid would be immaterial. We chose to still refer to
the acid simply as "sulfosalicylic" acid, thereby making
no claim as to the identity of it with respect to
isomerism. It was strongly felt, however, that in
reality we were in all cases using the same isomer,
5-sulfosalicylic acid.
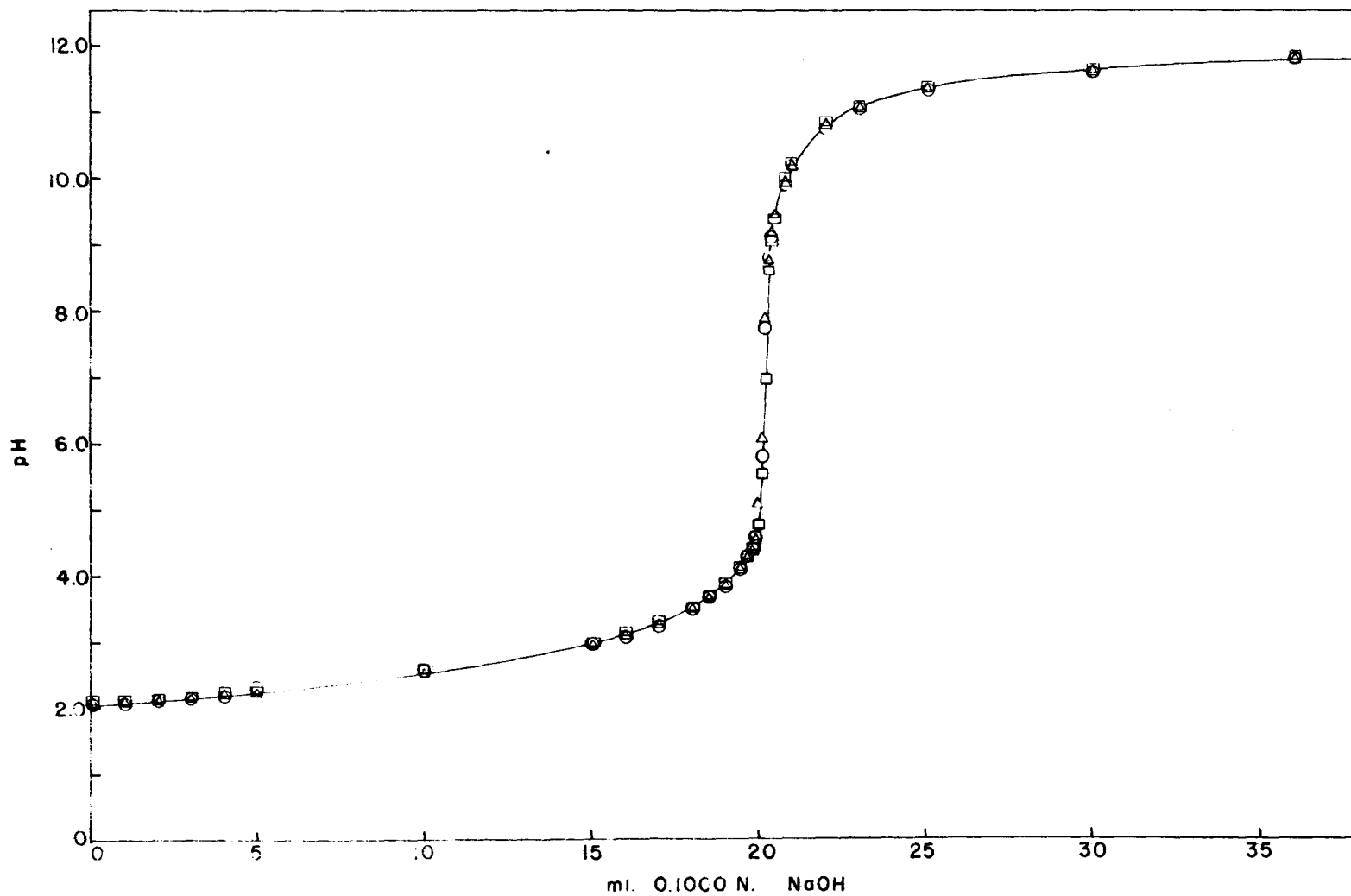
Figure 1. —— Potentiometric titration of sulfosalicylic acids using the Beckman Glass Electrode pH Meter (Model H-2). △ , acid synthesized by the method of Meldrum and Shah; □, commercial acid, 1; ○ , commercial acid, 2.
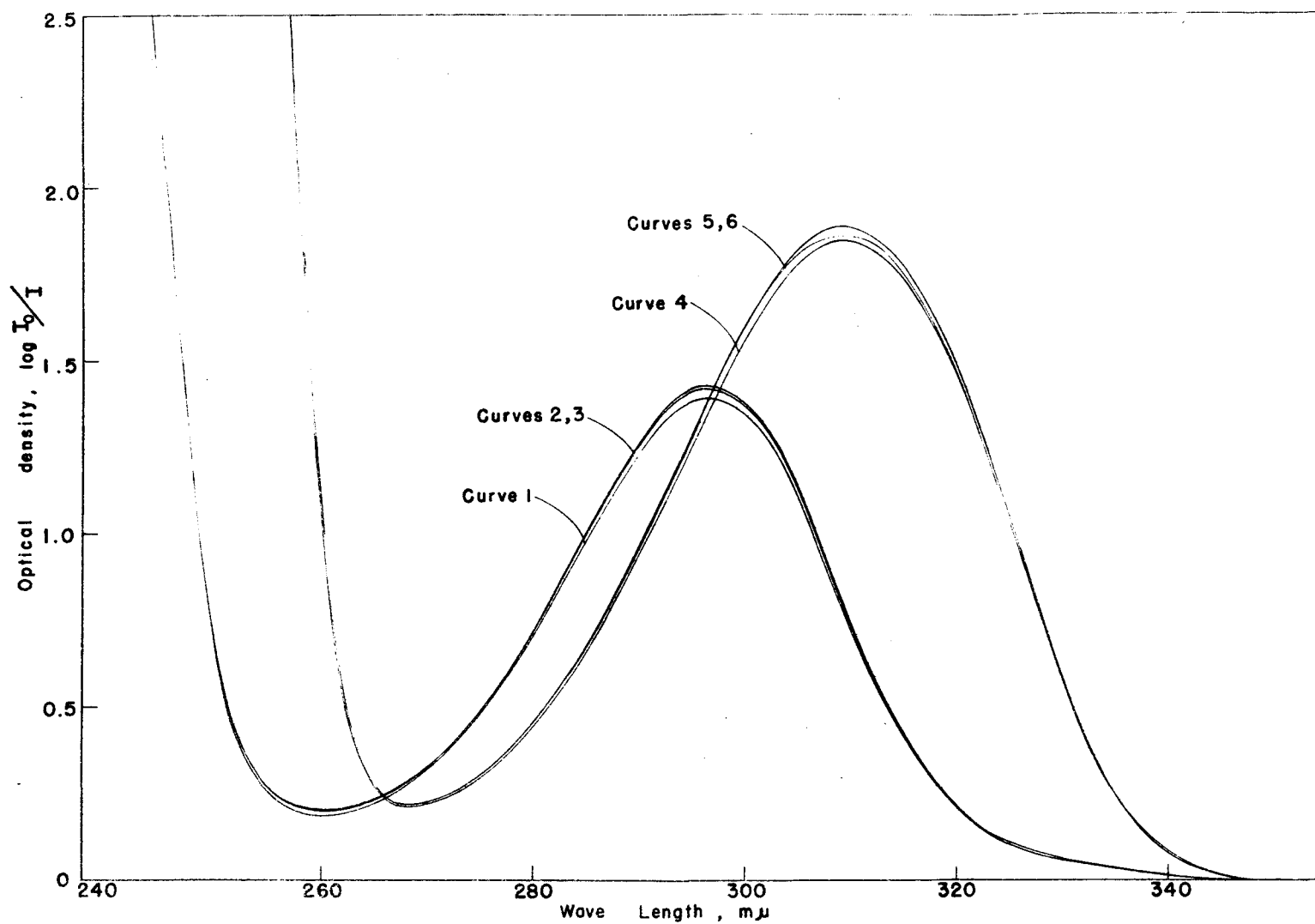
Figure 2. — Absorption spectra of 5.00×10^{-4} M sulfosalicylic acids and of 5.00×10^{-4} M sulfosalicylic acids 2.50×10^{-4} M in $BeSO_4$ using the Cary instrument ; curve 1, synthetic acid, pH 10.38; curve 2, commercial acid 1, pH 10.42; curve 3, commercial acid 2, pH 10.39; curve 4, synthetic acid plus beryllium, pH 10.30; curve 5, commercial acid 1 plus beryllium, pH 10.26; curve 6, commercial acid 2 plus beryllium, pH 10.28.

For the purposes of this work stock solutions
of sulfosalicylic acid were prepared from time to time
by weighing the approximate quantity desired of the
dihydrate directly from the reagent bottle and dilut-
ing to an appropriate volume. The actual acid concen-
trations were then established either by titrating
potentiometrically with standard alkali using a glass
electrode instrument or by simple titration with
standard alkali using methyl red-phenolphthalein
mixed indicator. In the latter case the end-point was
taken as the point midway between the appearance of
the yellow methyl red color and the first orange color
imparted to the solution by the phenolphthalein. This
point had been checked using a glass electrode instru-
ment and had been found to correspond identically with
the end point observed potentiometrically. Actually
no great difference is noted using either of the
indicators alone because sulfosalicylic is really a
very strong acid (25). Actual solutions used in the
studies were then prepared as needed by suitable dilu-
tion of these stock solutions in the conventional manner.

C. Aluminum

Obviously it was quite critical in this work to have available a comparatively large stock of very pure aluminum. Beryllium could not be tolerated in quantities greater than a few parts per million and it was important that the iron content of the material be at an absolute minimum because of the fact that ferric iron, and possibly ferrous iron, forms very stable complexes with sulfosalicylate in both acid and alkaline solution (26).

In the preliminary tests for aluminum interference reagent-grade aluminum salt hydrates notably aluminum sulfate octa-deca-hydrate, $Al_2(SO_4)_3 \cdot 18H_2O$, and the ammonium alum, $NH_4Al(SO_4)_2 \cdot 12H_2O$, proved to be very convenient sources of aluminum. Stock solutions of the approximate concentration desired were prepared by simply weighing out the proper amount of hydrate, dissolving it in distilled water, acidifying slightly with reagent-grade sulfuric acid, and diluting to the proper volume in a volumetric flask. When studies other than those of a preliminary nature were undertaken the

aluminum stock solutions were analysed for aluminum gravimetrically by the method of Willard and Tang (27). This method involves the precipitation of the aluminum as the basic succinate and subsequent ignition to the oxide for weighing. The proper volumes of the stock solution were then measured from a buret or pipet to give the desired weights of aluminum.

Later it became necessary to prepare special aluminum solutions and the methods employed and sources of the material were described in detail under Section VI G.

D. N,N,N',N'-tetrakis-(carboxymethyl)-
         ethylenediamine

N,N,N',N'-tetrakis-(carboxymethyl)-ethylene-diamine, $[CH_2N(CH_2COOH)_2]_2$, in the last few years has received considerable attention because of the fact that under the proper conditions it forms complexes with a large number of metal ions in aqueous solution. The free acid and aqueous solutions of its sodium salts have been variously referred to in the technical literature and commercially as ethylenediaminetetra-acetic acid, ethylenediaminotetraacetic acid,

ethylenebis-(iminodiacetic) acid, Trilon B, Sequestrene
AA, and Versene. For the most part in this work the
author refers to this compound as ethylenediaminetetra-
acetic acid as a matter of convenience with the under-
standing that what really is intended is the compound,
$\underline{/}CH_2N(CH_2COOH)_2\underline{7}_2$, specifically described as N,N,N',N'-
tetrakis-(carboxymethyl)-ethylenediamine.

Ender (28), pointed out that it was possible to
prevent soap precipitation due to water hardness and
to redissolve lime soaps when deposited on textile
fibers by using Trilon A or Trilon B, two commercial
water softeners, the composition of neither of which
was given. Later, Bird and Malloy (29) studied the
prevention of dull shades due to the presence of iron
in the dye bath, when dyeing with chrome dyes, using
Trilon B as one of their complexing agents. At this
time the authors wrongly considered Trilon B to be
essentially trimethylamine-α, α', α''-tricarboxylic acid.
Shortly thereafter Bird (30) gave experimental evidence
to show that Trilon B is, in reality, the sodium salt
of ethylenebis-(iminodiacetic) acid and that Trilon A
is the sodium salt of α, α', α''-trimethylamine tricarboxylic

acid. He also pointed out that Trilon B gives a much
better protection from iron to iron-sensitive mordant
dyes on wool than does Trilon A. Presumably this
would mean that Trilon B was a better complexing agent
for iron than Trilon A, at least under the conditions
of the dyeing.

Pfeiffer and Simons (31) showed that Trilon B
could be used instead of glue to complex heavy metals,
particularly copper, in the Raschig method for making
hydrazine from ammonia and sodium hypochlorite. In
the absence of glue, or Trilon B, hydrazine and
chloroamine react to give nitrogen and ammonium chloride,
the reaction presumably being catalyzed by copper and
other heavy metals. Trilon A failed to prevent this
reaction. Earlier Pfeiffer and Offermann (32) had
studied the calcium and copper complex salts of Trilon
A and Trilon B. They claimed that it was possible to
prepare a solid sodium salt of copperethylenebisnitril-
odiacetic acid which is composed of green crystals with
a light bluish tinge and contains four molecules of
water of crystallization. They also claimed that it
was possible to prepare a derivative still richer in

copper by replacing the sodium in this salt by copper
to give blue-violet crystals with four molecules of
water of crystallization. Only this last copper, not
that originally coordinated between two carboxyl
groups and the two nitrogen atoms, was capable of being
precipitated by alkali. The potassium salts of both
calcium- and magnesiumethylene-bisnitrilodiacetic acid
were also prepared.

Perhaps the most nearly complete study of
ethylenediaminetetraacetic acid has been included in
a series of papers by Schwarzenbach et al. entitled
"Complexons". Schwarzenbach and Ackermann (33)
reported approximate ionization constants for the four
carboxylic hydrogens of ethylenediaminetetraacetic
acid (H_4A) and indicated that lithium and potassium
form trivalent complexes, $(LiA)^{\equiv}$ and $(NaA)^{\equiv}$ with it.
They further claimed that calcium, magnesium,
strontium, and barium form intermediate complexes of
the type $(M\ HA)^{-}$ and a more stable type $(MA)^{\equiv}$.
Schwarzenbach, Biedermann, and Bangerter (34) then
developed titrimetric methods for the hardness of
water which depended on the complexing ability of this

reagent. Two general methods involving ethylenedia-
minetetraacetic acid, H_4A, were developed. In the
first, solutions of the metals were titrated with a
standard disodium salt, Na_2H_2A, in alkaline solution
using ammonium purpureate as indicator. This indica-
tor forms a red violet complex with calcium and the
color becomes blue violet when the solution is depleted
of calcium ions by the addition of the disodium salt,
Na_2H_2A. The second method was dependent upon the
titration of the acid liberated by the disodium salt
addition to solutions of the metals using a suitable
acid-base indicator to recognize the end point. This
method was not applicable in the presence of magnesium
nor did it give an accuracy comparable to that of the
first method. Later, Schwarzenbach and Biedermann (35)
elaborated on the second method and indicated that
either the dipotassium salt, $K_2(H_2A)$, or the tripotas-
sium salt, $K_3(HA)$, could be used with the formation of
two or one hydrogen ions respectively. They preferred
to use the dipotassium salt. Solutions of the salts
of cadmium, cobalt, copper, iron, mercury, manganese,
nickel, lead, zinc, cerium, lanthanum were determinable.
Aluminum, trivalent iron, and trivalent chromium caused

some difficulty, presumably because of the formation
of hydroxo complexes. Still later, Biedermann and
Schwarzenbach (36) elaborated even further on the
titrimetric methods giving more explicit details and
emphasizing the use of an indicator, Eriochromschwarz
T, which changed color with the disappearance of the
metal ion, rather than acid-base indicators or poten-
tiometric indication of the end-point.

Schwarzenbach and Ackermann (37) then examined
the effect of varying n from 2 to 5 in the structure
$(HO_2CCH_2)_2N(CH_2)_nN(CH_2CO_2H)_2$ on the pK-values and on
the stability of the alkaline earth complexes. The
values of pK_1, and pK_2 are little affected by this var-
iation but pK_3 and pK_4 change from 6.2 to 9.5 and 10.3
to 10.6, respectively, by increasing n from 2 to 5.
The stability of alkaline earth complexes, $(MHA)^-$,
vary but little with n but the stability of complexes
$(MA)^-$ decrease sharply as n is increased. Complexes
M_2A were not found when n is 2 or 3 but were found
when n is 3 or 4. Calcium complexes were found to be
always more stable than those of barium or strontium
but less stable than those of magnesium when n = 4 or

5 and more stable than magnesium when n = 2 or 3.

Finally, in this series thus far, Schwarzenbach (38) studied a large number of the cobalt complexes of ethylenediaminetetraacetic acid both in solution and as solid crystalline derivatives and showed that substituents such as Br^-, OH^-, and NO_2^- could be attached to the central atom.

The most recent method of preparation for ethylenediaminetetraacetic acid has been described by Smith, Bullock, Bersworth, and Martell (39). The overall reaction is represented by

$$H_2NCH_2CH_2NH_2 + 4NaCN + 4CH_2O + 4H_2O = \angle(NaO_2CH_2)_2NCH_2\angle_2 + 4NH_3.$$
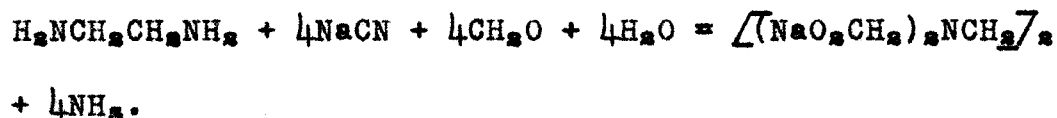
By keeping the temperature low and using excesses of NaCN and CH_2O yields as high as 96 per cent on the ethylenediamine basis were realized. This method is probably to be preferred over other earlier methods of preparation.

In the present work it was found convenient to obtain the ethylenediaminetetraacetic acid commercially

either as the solid free acid or as a solution of the
sodium salt and subject it to a purification process.
The purification was performed by the very slow addi-
tion, with stirring, of reagent-grade sulfuric acid
to the solution of the sodium salt. The sulfuric acid
addition was continued until the solution attained a
pH of approximately 2.8, which was the pH given by
Bird (30) for a saturated solution of the acid. Under
these conditions virtually all of the free acid precip-
itated as a dense, white precipitate. The precipitate
was then filtered in a large Beuchner funnel and
washed with hot distilled water. This material melted
at about 235°C. which is considerably below the value
of 241°C. reported for the pure acid by Bird (30). It
was found that simple digestion on a steam bath of
this impure acid in a large volume of distilled water
over a period of about 24 hours gave material which on
filtering, washing with hot distilled water, and dry-
ing, melted consistently at 245-6°C. This material
appeared to be very pure, gave clear, water white,
solutions on treatment with alkali solutions, and
proved to be very satisfactory for our work. It was
suspected that only traces of occluded or adsorbed

sulfuric acid may have accounted for the low melting
points and rather low temperature discoloration of
the crude free acid during melting point determina-
tions.

In general, stock solutions of the sodium salt
of the acid, prepared in the manner described above,
were made by slowly adding a solution of reagent-grade
sodium hydroxide of a convenient normality directly
to the proper quantity of the weighed free acid. A
final pH of about 9.0 was usually chosen for the stock
solutions. Such solutions were then used as a com-
plexant whenever the need arose for it in the subse-
quent work.

E. Miscellaneous

In general, throughout this work, only the best
available reagent-grade chemicals, as indicated on
the manufacturers' labels, were used. Particular atten-
tion was paid to the reagent-grade sodium hydroxide
used because it was frequently present in relatively
large amounts in the final solutions under spectro-

photometric examination. One particular lot of sodium
hydroxide was chosen for use throughout the study mainly
because it contained only a very small amount of iron,
less than ten parts per million, as indicated by the
manufacturer's analysis. Wherever qualitative tests on
various lots of reagents by accepted methods revealed
appreciable amounts of contaminants other lots were
tested until material of acceptable quality was dis-
covered.

V. METHODS

A. Job's Method of Continuous Variations

In a quite extensive work Job (40) developed a
method of determining the ratio of complexing to com-
plexed bodies in so-called "imperfect complexes" in
solutions. By an "imperfect complex" he evidently
meant a complex which was appreciably dissociated into
its simple constituents, as evidenced by the measure-
ment of some property of the solution, such as the
concentration of the complex itself or the concentra-
tion of either or both of its simple constituents.
He distinguished these "imperfect complexes" which,
as he claimed, are in mobile equilibrium in solution
with their simple constituents, from the "perfect
complexes" which are "practically stable". The pres-
ent author believes that these differences are matters
of degree, rather than kind, but these features are
not of importance to the work at hand.

Job limited his methods of examination of solu-
tions of complexes to the physicochemical methods for

obvious reasons. Further he divided the methods into two groups. The first comprised those cases where one could directly measure either the concentration of the complex itself or the concentrations of its products of decomposition. Examples of ways in which such measurements were carried out in successful studies were the determination of the solubility of silver chloride in concentrated ammonia solutions to give a measure of the silver ammine concentration, colorimetric or spectrophotometric examination of colored complexes to determine their concentration, the determination of cell potentials to measure metallic ion concentrations, and vapor pressure measurements to determine concentrations of ammonia and similar substances. The second method was somewhat more general in principle. He considered the formation of a complex by mixing solutions in the same solvent of two simple constituents A and B and varied the relative amounts of A and B in the final mixture. When this was done it was shown that quite frequently some physical property of the solution passed through a maximum, or minimum, for a particular ratio of A to B. Job referred to this particular composition of the mixture as the "maximum composition".

He gave a mathematical proof that the necessary and sufficient conditions for which the "maximum composition" does not vary with changing concentration of the two simple solutions are that these two solutions be equimolar and that the sum of the number of moles of the two simple substances be constant. Under these conditions only does the "maximum composition" correspond to the proportion of the two constituents which react to form the complex. He further indicated that "maximum composition" depends together on the concentrations of the two original solutions and the equilibrium constant, K, for the complex. He then showed that once the formula for the complex was known, it was possible to measure the stability of it. He thus chose to study in two different parts the formation of a complex by the mixing of the two simple solutions. The first, the study of the mixing of equal molar solutions to determine the formula of the complex. The second, the study of non-equimolar mixtures to determine its stability.

The mathematical treatment of Job applied strictly only to those situations in which a single

complex was formed. He warned that by studying only
one concentration series it was possible to arrive at
an erroneous conclusion regarding the identity of the
complex and recommended that series of widely differ-
ing concentrations be examined. This was only reason-
able because it is often possible for more than one
complex to be formed and in very dilute solutions only
one of these complexes may be of importance; in more
concentrated solutions a different complex may be the
important one.

In Job's treatment he mixed volumes of the
simple constituents of equal molarity in such a way
that, assuming additivity of volumes, the volumes of
the final solutions were constant. Not always is this
convenient because frequently the adjustment of a
factor such as pH, after mixing, is required. The
same effect as keeping the sum of the volumes of the
two simple equimolar solutions constant is produced
by keeping the sum of the number of moles of the two
simple constituents constant and diluting to a con-
stant volume in each case. This last method was the
one adopted by the present author in his studies.

Relative to the property measured in determining the identity of the complex Job considered three different cases.

In Case 1 the property was independent of the two simple constituents and was uniquely determined by the concentration of the complex. In this case a plot of the property versus the composition passed through a maximum (or minimum) at the "maximum composition" itself.

Case 2 was the situation in which the measured property depended together on the complex and its components, but was additive with respect to its simple constituents. In this case the plot of the measured property, corrected for the simple constituents assuming their additivity, gave a maximum or minimum at the "maximum composition" itself.

In Case 3 the measured property depended in a more complicated manner on the concentration of the compounds. In this case it was not possible to determine the "maximum composition" unless the nature of the more complicated dependence of the measured

property on the concentration of contributing compounds was accurately known.

Case 2 was the situation under study by the present author and the methods used in determining the dissociation constant of the complex were somewhat different than those used by Job.

Job concluded that in practice the "method of continuous variations" should be restricted to the cases in which the chosen property was practically independent of the simple constituents or at least more or less additive with respect to them. He successfully applied his method to the examination of halide complexes of cadmium and mercury, the alkaline trihalides and the ammonia and amine complexes of silver, copper, and thallium, to discover their identity and to evaluate their instability constants. It was of interest to note that the equilibrium constants which he determined were not true equilibrium constants in the usual modern sense but "molar" equilibrium constants; that is, pseudo constants represented by molar concentrations rather than activities. This fact becomes of importance when we consider that Job in

summary declared that all of his reasoning rested on three hypotheses:

1. The two simple constituents have, in solution, a well determined molecular formula; that is to say that there is no equilibrium between two polymers, between one substance and its products of dissociation, etc.

2. There is formed a single complex.

3. The law of mass action is applicable to the reaction studies. Experiment alone can confirm or disprove this hypothesis. In particular, two conditions are indispensible so that the results can be considered as certain:

    a. Generally for all equimolar mixtures, within the concentration limits, the "maximum composition" must remain the same.

    b. For non-equimolar mixtures, the value of the equilibrium constant

must remain the same within the
conditions as far as possible.

This last condition, today, seems somewhat super-
fluous because an equilibrium constant is truly a con-
stant. By changing concentration one would certainly
be changing the ionic strength and the molar equili-
brium constant of Job could only be a constant under
these conditions when the magnitudes of activity coef-
ficients cancelled in the true equilibrium constant
expression itself. Of course it would also have been
possible to have been working under such conditions of
ionic strength that the changes in it would not have
been experimentally detectable.

Vosburgh and Cooper (41) reviewed the theory of
Job's method of continuous variations and extended it
to cases in which more than one compound is formed
from a given pair of components. Along with Job they
recommended the use of the spectrophotometric method
because it frequently happens that each of the com-
plexes, as well as the components, have spectrophoto-
metric properties which differ. They included theo-
retical derivation of a nature somewhat similar to that

of Job but considerably simpler. Their theoretical
treatment indicated that if two or more compounds can
be formed from simple components, A and B, the value
of the "maximum composition" at which the measured
property is a maximum should vary with the wave length.
If only one complex is formed, the "maximum composition"
should not vary with the wave length provided that the
extinction coefficient of the complex differs from
that of the reactants. It should then be possible to
determine whether more than one compound is formed by
the use of several wave lengths. If different "maxi-
mum compositions" are found with different wave lengths
it is an indication of the presence of more than one
complex.

Vosburgh and Cooper further indicated that
activity coefficients should be included in the equili-
brium expressions and hence that constant ionic strength
should be maintained. According to their reasoning the
activity coefficients, if constant, have no more effect
on the composition of the maximum than the equilibrium
constant. They made no effort to determine the magni-
tudes of equilibrium constants but only the identity

of the complexes. They studied the acid chromate and dichromate ions, the complex ions formed by nickel ion with o-phenanthroline and with ethylenediamine and the complex ions of copper and ammonia. Their theoretical treatment was substantiated by the systems investigated.

Later Gould and Vosburgh (42) studied the systems ferric iron and thiocyannate, ferrous iron and o-phenanthroline, nickel and dithio-oxalate, copper and aminoacetate, and nickel and aminoacetate. These systems gave satisfactory results when treated by the same method as employed by Vosburgh and Cooper (41). One additional contribution was made with respect to theory in the work of Gould and Vosburgh (42). They showed mathematically that if in addition to the complex under study, a second equilibrium involving the metallic ion in question is present, there is yet no change in the maximum composition, so long as the second complexing agent is present in constant concentration. Such a second complexing agent in the opinion of the present author might well be hydroxyl ion, and so long as pH is kept constant no interference in the determination of the maximum composition should then be observed.

Crouthamel, Meek, Martin, and Banks (43) made a spectrophotometric study of dilute aqueous periodate solutions which, although not made by means of Job's method, did employ methods of interest relative to Job's method. By observing the nature of the variation of the absorption spectrum in the ultraviolet region, of solutions of periodate as a function of pH they were able to evaluate the three dissociation constants of periodic acid which are of importance in dilute aqueous solution. These dissociation constants were all three substantiated by non-spectrophotometric methods. It was of interest to note that they succeeded in this endeavor by assigning for each region of pH through which there was virtually no change in the absorption spectra, an essentially constant concentration of absorbing species of ion. Departures from constancy of absorption spectra was taken to indicate the creation of appreciable quantities of new species of absorbing ions. The region and rate of change of absorption spectra with respect to pH uniquely established the magnitude and nature, respectively, of the dissociation constants of the acid. The present author mentions this now only to emphasize a rather

obvious general technique of interpreting absorption spectra.

B. Ionic Strength Considerations

The importance of the effects of ionic strength on the study of equilibria was realized. In addition to the importance of ionic strength mentioned by previous authors (41, 42) with respect to the determination of the maximum composition it was intended to use the control of ionic strength in quite another connection. It is a well-known fact that, according to the Debye-Huckel limiting law (44, pp. 410, 412) the activity coefficients of substances in solution approach unity as the ionic strengths of the solutions of these substances approach zero. By evaluating molar concentrations of materials involved in an equilibrium at various known ionic strengths it is then possible to extrapolate to zero ionic strength where activities and molarities become identical, to obtain the true thermodynamic equilibrium constants (44, pp. 421-424).

VI. EXPERIMENTAL

A. Search for a Suitable Complexing Agent

It was felt that a study of a new beryllium complex rather than complexes already described would make the maximum contribution to the literature. Particularly was it apparent that the ultraviolet region of the spectrum had been neglected in previous methods. The possibilities of success in this relatively unexplored region were immediately recognized and the search was begun with the hope that these possibilities might be fruitfully utilized.

In general when a metallic substance is complexed by a complexing agent there is appreciable alteration of the nature of the absorption spectra of both the complexed and complexing materials. Harrison, Lord, and Loofbourow (45, p. 420) remark that "the absorption maximum associated with a particular group is, in general, shifted toward longer wave lengths (lower frequencies) when a substituent is linked to the group; this effect is increased with increasing

atomic weight of the substituents". It was this
effect that the present writer used as a criterion of
complex formation.

Mellor (46, p. 217) stated that citric acid
hinders the precipitation of beryllium ammonium phos-
phate, $BeNH_4PO_4$, if much aluminum is present. This
fact suggested the possibility of complex formation
between beryllium and citric acid but examination of
the spectra of citric acid solutions and citric acid
solutions containing beryllium failed to disclose any
appreciable change in spectra due to the presence of
beryllium. Examination was made in acid solutions of
pH 3.54 with a large excess of citric acid using the
Beckman instrument. In alkaline solutions, even with
a large excess of citric acid, precipitation of beryl-
lium occurred, and decantation of the supernatant
liquid gave absorption of essentially the same char-
acter as that of the citrate solution.

Fortune and Mellon (47) stated that below a pH
of 3.0 beryllium was complexed by o-phenanthroline.
This claim was examined exhaustively using o-phenan-
throline (1,10-phenanthroline) from a commercial

source, purified by recrystallization from a mixture
of ethanol and water as suggested by Smith and
Richter (48, p. 10). With the mole ratio of
o-phenanthroline to beryllium adjusted to 3 to 1
there was absolutely no spectrophotometric evidence
of complexation of beryllium by o-phenanthroline at
pH values of 1.02, 1.36, 1.76, 3.15, and 11.3 when
such solutions were scanned using both the Beckman
and the Cary spectrophotometers. Had complexation
occurred one would have expected an appreciable differ-
ence in the absorption spectra of the solutions of the
o-phenanthroline and the solutions of o-phenanthroline
of the same concentration and pH, which contained
beryllium.

It was virtually by accident that the sulfosali-
cylate complex of beryllium was discovered. Sulfo-
salicylic acid was being used in the same laboratory
for an entirely different purpose when the present
author decided to test it as a complexing agent for
beryllium. It was immediately observed that an excess
of sulfosalicylate prevented the precipitation of
beryllium as the hydrated oxide and that beryllium

appreciably altered the absorption spectra of solutions of salfosalicylate. The detailed discussion of the qualitative nature of the spectrophotometric properties of the complex follows in the next section.

B. Qualitative Nature of the Beryllium-Sulfosalicylate Complex

The general character of the ultraviolet absorption spectra of solutions of sulfosalicylate and of solutions of the beryllium-sulfosalicylate complex is shown in Figure 2. These solutions were scanned on the Cary instrument in 1.000 cm. quartz cells using distilled water as a reference solution. The solutions were adjusted by means of sodium hydroxide to the optimum pH which gave the greatest displacement of the absorption maximum for constant beryllium concentration. This optimum pH was established by comparing the scanning curves of solutions of sulfosalicylic acid alone at various pH values with those of sulfosalicylic acid containing beryllium at various pH values. Figure 3 shows how the absorption spectra of solutions 5.00×10^{-4} M in sulfosalicylic acid varies
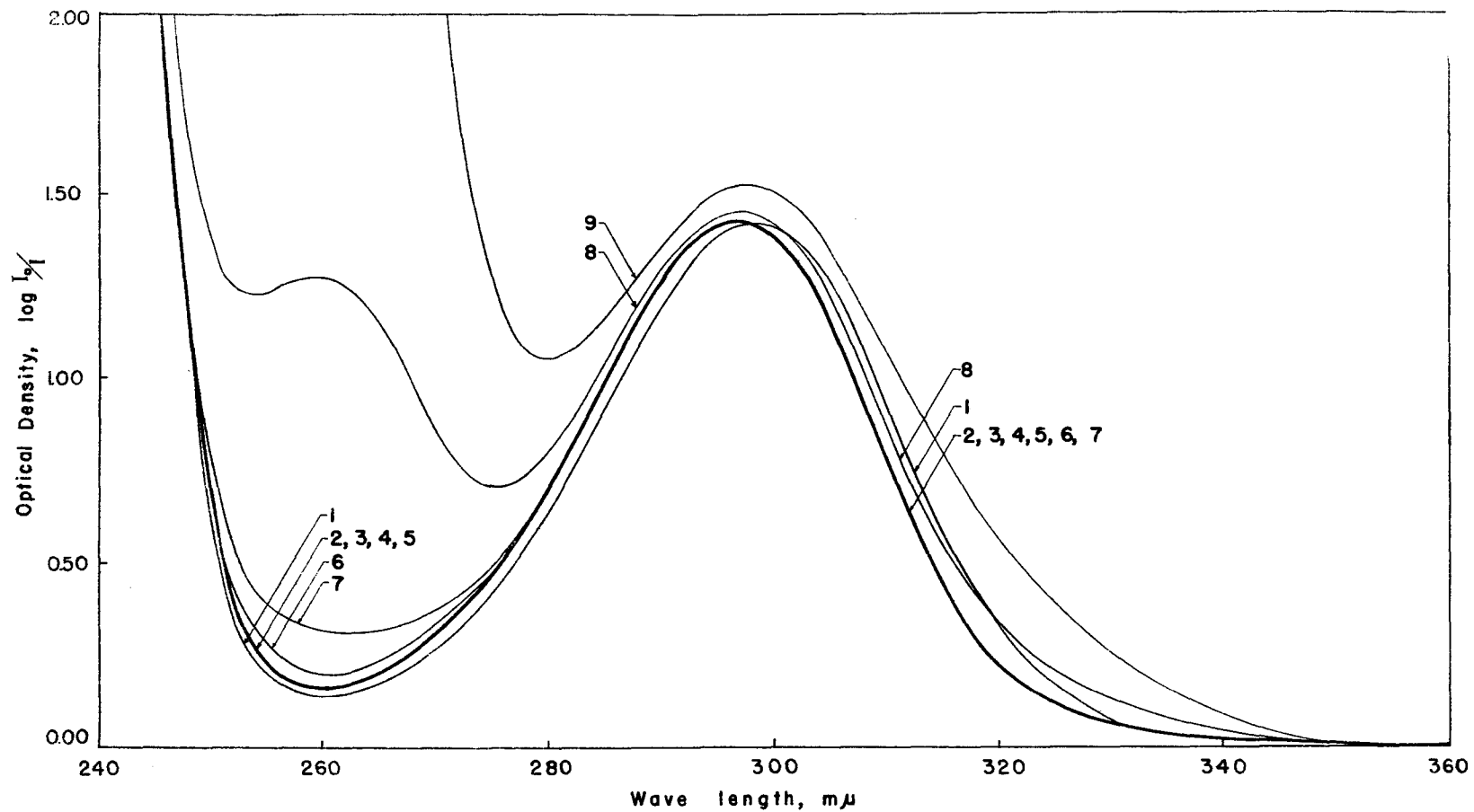
Figure 3.— Scannings of solutions 5.00×10^{-4}M in sulfosalicylic acid at various pH values as adjusted with sodium hydroxide and using the Cary instrument; Curve 1, pH 3.30; Curve 2, pH 4.52; Curve 3, pH 6.05; Curve 4, pH 7.60; Curve 5, pH 8.55; Curve 6, pH 10.20; Curve 7, pH 10.8; Curve 8, pH 11.7; Curve 9, pH 12.2

with pH as adjusted by sodium hydroxide using distilled
water as the reference solution. It can be readily
seen that the spectra for sulfosalicylate in the absence
of beryllium remain essentially constant in the pH
range from about 5.0 to almost 11.0. The present
author attributed this constancy of spectra to essen-
tially one sulfosalicylate species, that of the doubly
negatively charged sulfosalicylate ion, $C_6H_3SO_3OHCO_2^=$,
formed by the removal of the two protons from the
sulfonic acid group and the carboxyl group of the
sulfosalicylic acid molecule. Examination of Figure
1 indicates that virtually all of the sulfosalicylic
acid is neutralized as a dibasic acid at a pH of ca.
5.0. At somewhat lower pH values, see Figure 3, curve
1, appreciable quantities of a singly negatively
charged sulfosalicylate species were believed to be
present since the absorption maximum which occurs at
about 296.5 mu. for the doubly negatively charged
species is appreciably displaced toward the longer wave
lengths. Presumably this singly negatively charged
species would be the one in which the proton of the
carboxyl group is still intact. At pH values higher
than about 10.5 a severe alteration of the absorption

spectrum begins to occur, particularly in the wave
length range of 245 mu. to 280 mu., and to a somewhat
smaller extent on the long wave length side of the
absorption maximum. This effect was presumed to be
due to the attack of the hydroxylic hydrogen atom
adjacent to the carboxyl group by the increased mass
action effects of strongly proton-seeking hydroxyl
ions. At any rate it could be safely said that above a
pH of ca. 10.5 a deep-seated change begins to occur in
the nature of the molecular species contributing to the
absorption. For the purposes of this work the cardinal
fact of interest was that there is a broad range of
nearly 6.0 pH units over which no noticeable change
in spectrophotometric properties occurs at wave lengths
longer than ca. 280 mu. This meant that any changes in
absorption of sulfosalicylate solutions containing
beryllium over this range of pH and wave length which
was brought about by changing pH could be logically
attributed to properties peculiar to the beryllium
species involved or to the beryllium sulfosalicylate
complex (or complexes) itself.

Figure 4 shows a similar examination of solutions

5.00×10^{-4} M in sulfosalicylate and 2.50×10^{-4} M in beryllium sulfate. It was noted that all of the solutions containing beryllium have their absorption maxima displaced to the long wave length side of the maximum characteristic of the doubly negative sulfosalicylate ion as indicated in curves 2 to 7 inclusive in Figure 3. It was further noted that in very alkaline solutions, curve 9, Figure 4, a species of material of high molecular extinction coefficient on the long wave length side of the sulfosalicylate absorption maximum must have been destroyed because an actual decrease in optical density was observed there.

By taking the absorption curve characteristic of the doubly negative sulfosalicylate ion as a reference and reading the differences in optical density between it and those solutions containing beryllium which were near the optimum pH for maximum displacement of the absorption curve toward the long wave length end of the spectrum it was found that ca. 317.0 mμ.was the wave length which gave the maximum increase in optical density for a given quantity of beryllium. This process of determining the optimum wave length was
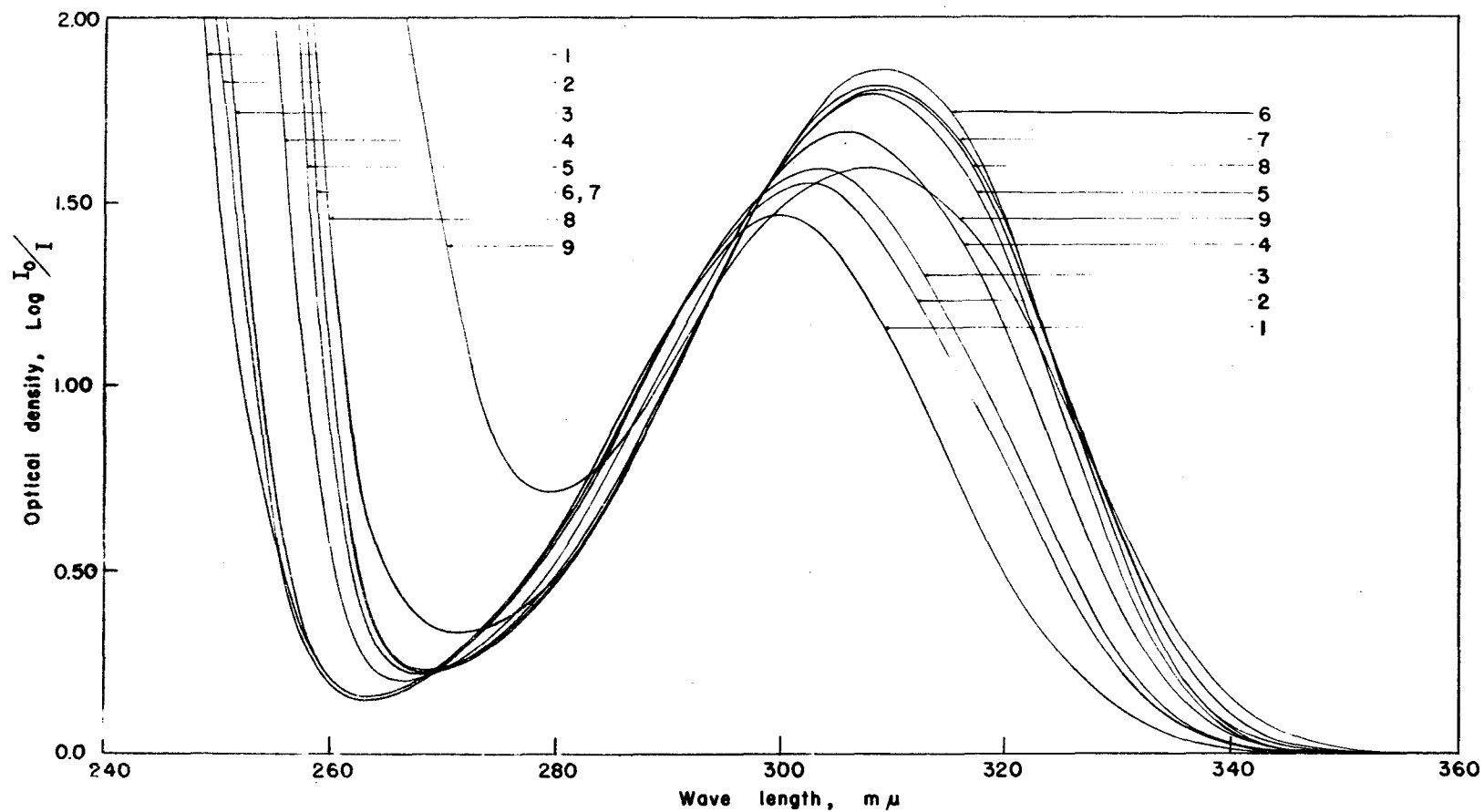
Figure 4 —— Scannings of solutions 5.00×10^{-4} M in sulfosalicylic acid and 2.50×10 M^{-4} in beryllium sulfate at various pH values as adjusted with sodium hydroxide and using the Cary instrument; Curve 1, pH 3.15; Curve 2, pH 4.25; Curve 3, pH 5.67; Curve 4, pH 7.35; Curve 5, pH 8.05; Curve 6, pH 8.83; Curve 7, pH 9.82; Curve 8, pH 11.5; Curve 9, pH 12.2.

repeated several times under considerably different conditions of pH and with various ratios of sulfosalicylate to beryllium and in all cases it was found that ca. 317.0 mu. was the optimum wave length. This wave length was then adopted as the best one to use in the study of the various aspects of the complex.

Figure 5 was constructed by reading the optical densities at 317.0 mu. of each of the curves in Figures 3 and 4 and plotting them versus pH. It adequately describes the critical nature of pH in the formation of the complex (curve 2, Figure 5) and emphasizes the constancy of the optical density at 317.0 mu. of solutions containing only sulfosalicylate through the pH range 5 to 11 (curve 1, Figure 5).

The plateau in curve 2, Figure 5, in the pH range of ca. 9.0 to 11.0 was attributed by this author to the presence of some species of beryllium-sulfosalicylate complex in essentially constant concentration throughout the plateau. At lower pH values it was felt that increasing the pH brought about the formation of some beryllium species of an unknown nature which was most easily complexed by sulfosalicylate
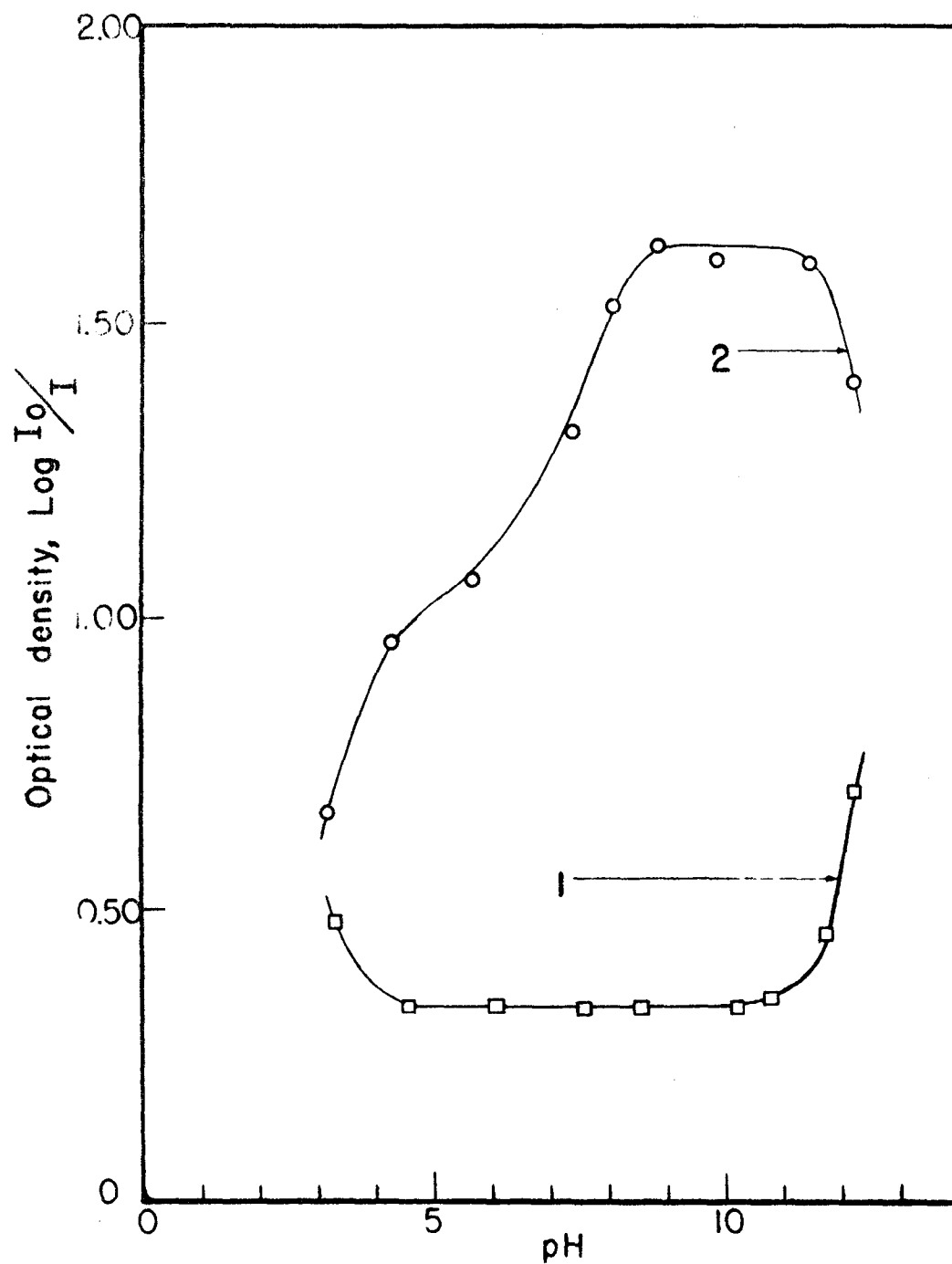
Figure 5—Optical densities at 317.0 mμ as
functions of pH taken from Figures 3 and 4;
☐ curve 1, 5.00×10⁻⁴ M in sulfosalicylic acid;
○ curve 2, 5.00 × 10⁻⁴ M in sulfosalicylic
acid and 2.50 × 10⁻⁴ M in berylium sulfate.

and that throughout the plateau beryllium was present
essentially only in the form of the sulfosalicylate
complex and in the form of the beryllium species most
easily complexed by sulfosalicylate. It was further
believed that at higher pH, destruction of the complex
was brought about by the formation of a new, more
stable beryllium species, possibly beryllate, $BeO_2^=$,
or diberyllate, $Be_2O_3^=$.

It should be emphasized that the solutions from
which the data for Figures 3, 4, and 5 were taken were
not buffered in any way except by what natural buffer-
ing action was supplied by the beryllium sulfate, the
sulfosalicylate, and the excess sulfuric acid introduced
from the beryllium stock solution. Thus it would have
been possible for appreciable changes in pH to have
occurred by absorption of carbon dioxide from the air
during the manipulation required by the spectrophoto-
metric measurements, particularly in those solutions
near a pH of 7.0. It should be further remarked that
ionic strength was not held constant throughout the
range of pH studied in these solutions.

C. Application of the Method of Job

After it had been discovered that sulfosali-
cylate complexed beryllium it was at once desirable
to determine the nature of the complex in so far as
it was possible. The use of the method of Job was at
once recognized as a promising means of determining
the ratio of sulfosalicylate to beryllium in the com-
plex. Obviously it was necessary to keep the pH in
the optimum range as indicated in Figure 5 and indeed,
for the sake of complete duplication, to keep it
essentially constant. The necessity of keeping ionic
strength constant has already been mentioned. Actually
the ionic strength cannot be kept absolutely constant
in such a study because the concentration of the com-
plex varies throughout the range of ratios of mixed
simple components. This may well create species (com-
plexes) of new ionic charge, and since ionic strength,
μ, is defined (44, p. 400) as half the sum of the terms
obtained by multiplying the molality of each ion pres-
ent in the solution by the square of its valence (molar-
ity may be substituted for molality (44, p. 411) in
the case of dilute aqueous solutions) there may well

be changes in ionic strength except in very special
cases. However, in the case of quite dilute solutions
of reacting substances such changes can be made to be
relatively small by adding a comparitively large, con-
stant, amount of an "inert" electrolyte. In the present
work the electrolyte chosen was purified ethylenediamine-
tetraacetic acid; it served not only the purpose of
keeping ionic strength constant (at constant pH) but
facilitated the adjustment of pH by its buffering
action. It was further hoped that this acid might
prevent the actual precipitation of a solid hydrated
beryllium oxide phase in those solutions in which the
ratio of beryllium to sulfosalicylate was high but
such did not prove to be the case. Preliminary investi-
gation had not indicated that ethylenediaminetetraacetic
acid would complex beryllium but mass action effects of
large excesses of the acid and quite small concentra-
tions might have prevented actual precipitation had
there been even a very slight tendency for complexation.

Table 2 indicates the composition and pH of the
solutions used in the determination of the ratio of
sulfosalicylate to beryllium in the beryllium-sulfosali-
cylate complex. The ethylenediaminetetraacetic acid,

TABLE 2

Content of Solutions for Applying Job's Method

Solution No.	2.00×10^{-2} M ethylenediaminetetraacetic acid, ml.	1.00×10^{-2} M beryllium sulfate, ml.	1.00×10^{-2} M sulfosalicylic acid, ml.	Final volume, ml.	pH
1	100.0	0.00	10.00	200.0	10.49
2	100.0	2.00	8.00	200.0	10.43
3	100.0	2.50	7.50	200.0	10.45
4	100.0	3.00	7.00	200.0	10.45
5	100.0	3.50	6.50	200.0	10.44
6	100.0	4.00	6.00	200.0	10.45
7	100.0	4.50	5.50	200.0	10.42
8	100.0	5.00	5.00	200.0	10.42
9	100.0	7.00	3.00	200.0	10.41
10	100.0	9.00	1.00	200.0	10.39
11	100.0	10.00	0.00	200.0	10.37

beryllium sulfate (prepared by dilution from beryllium stock solution No. 2), and sulfosalicylic acid solutions were pipetted directly into 250-ml. beakers and diluted to approximately 150 ml. with distilled water. The pH of each solution was then adjusted by means of dilute reagent-grade sodium hydroxide to ca. 10.45 as indicated by the Beckman pH meter (Model H-2) while stirring by means of a magnetic stirrer. The solutions were then transferred to 200 ml. volumetric flasks and diluted to 200.0 ml. with distilled water of pH ca. 10.45. Solutions 6 to 10 inclusive developed a visible precipitate, presumably beryllium hydroxide, on standing. This probably accounted for the slightly low pH values observed for these solutions. The solutions were allowed to stand over night and the pH recorded in Table 2 was determined on the following day. Figure 6 shows the ultraviolet absorption spectra obtained from these solutions using the Cary recording spectrophometer. Solutions 6 to 11 inclusive were decanted from above the slight precipitates for scanning purposes. The solutions were examined in 1.000 cm. quartz cells using distilled water as the reference solution.
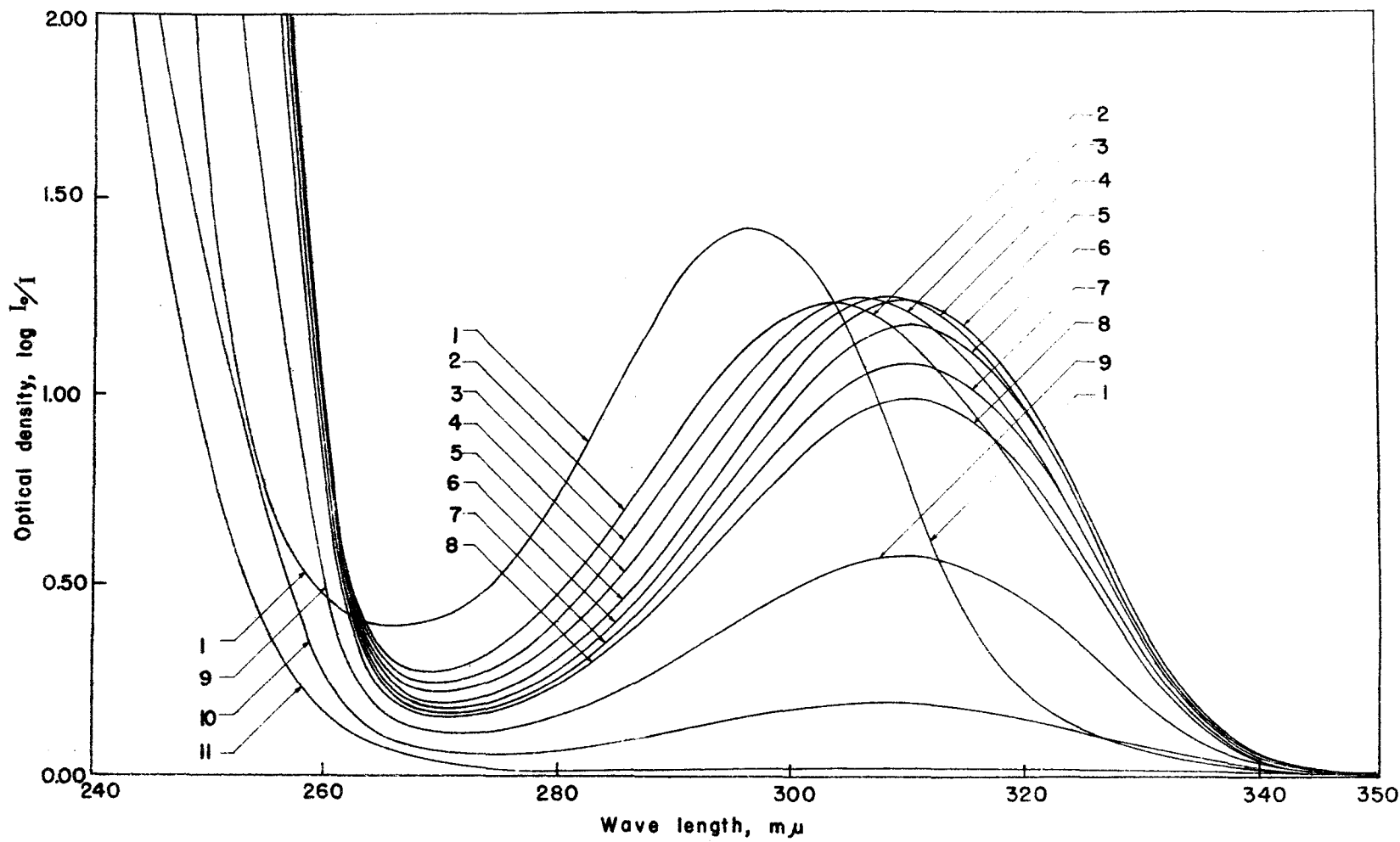
Figure 6— Scannings of solutions corresponding to Table 2 using the Cary instrument. The numbers assigned to the curves correspond to the numbers of the solutions in Table 2.

TABLE 3

Optical Densities at Various Wave Lengths, Taken from Figure 6

Solution No.	Optical densities at wave lengths of				
	280.0 mu.	290.0 mu.	300.0 mu.	310.0 mu.	317.0 mu.
1	0.740	1.280	1.385	0.770	0.340
2	0.467	0.883	1.215	1.135	0.900
3	0.407	0.795	1.165	1.215	1.025
4	0.350	0.715	1.110	1.248	1.095
5	0.308	0.640	1.040	1.240	1.120
6	0.275	0.575	0.975	1.180	1.075
7	0.255	0.535	0.890	1.080	0.982
8	0.232	0.490	0.812	0.988	0.902
9	0.152	0.304	0.485	0.572	0.520
10	0.063	0.116	0.170	0.183	0.164
11	0.010	0.010	0.008	0.010	0.008

Table 3 lists the observed optical densities
from Figure 6 for each of the solutions at 280.0,
290.0, 300.0, 310.0, and 317.0 mu.

It was necessary to assume that solutions of
beryllium sulfate do not absorb light in the spectral
region of interest at a pH of ca. 10.4. This assump-
tion could not be checked experimentally because at
a pH of 10.4 a solid hydrated beryllium oxide phase
is precipitated. However, acidic solutions of beryl-
lium do not absorb in this region and it was considered
reasonable to believe that beryllium species other
than that in complex form, would not absorb. A dis-
persed solid phase would, of course, absorb light
throughout the ultraviolet region of the spectrum.
It was assumed that the doubly negative sulfosalicylate
ion was the only absorbing species of ion in these
solutions other than the beryllium sulfosalicylate
complex (or complexes) itself. Along with Job (40) and
the others (41, 42) linearity in the degree of absorp-
tion by the component (sulfosalicylate) as though not
complexed was assumed. It was only necessary to multi-
ply the optical density values for solution No. 1,

TABLE 4

Corrected Optical Density Values at Various
Wave Lengths

Solution No.	Corrected optical density values at wave lengths of				
	280.0 mu.	290.0 mu.	300.0 mu.	310.0 mu.	317.0 mu.
1	0.000	0.000	0.000	0.000	0.000
2	-0.125	-0.141	0.107	0.519	0.628
3	-0.148	-0.165	0.126	0.637	0.770
4	-0.168	-0.181	0.140	0.709	0.857
5	-0.173	-0.192	0.140	0.739	0.899
6	-0.169	-0.193	0.144	0.718	0.871
7	-0.152	-0.169	0.128	0.656	0.795
8	-0.138	-0.150	0.119	0.603	0.732
9	-0.070	-0.080	0.069	0.341	0.418
10	-0.011	-0.012	0.031	0.106	0.130
11	0.010	0.010	0.008	0.010	0.008
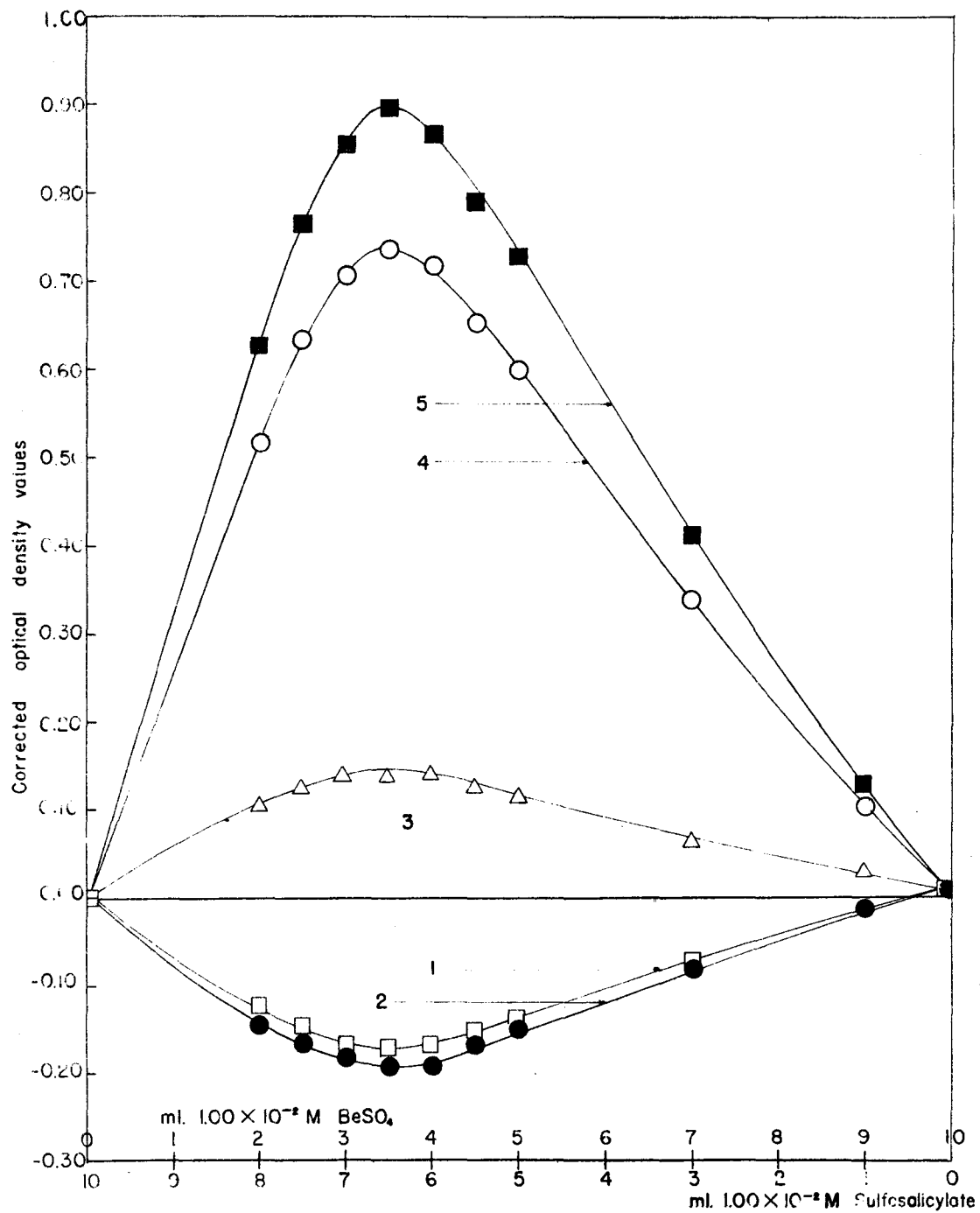
Figure 7— Corrected optical densities for various wave lengths from Table 4 as a function of the composition of solutions in Table 2 to indicate the composition maximum of the sulfosalicylate complex of beryllium ; curve I, 280.0 mμ ; curve 2, 290.0 mμ ; curve 3, 300.0 mμ ; curve 4, 310.0 mμ ; curve 5, 317.0 mμ.

Table 3, at each wave length by the volume in ml. of
the sulfosalicylate solution used in each of the other
solutions divided by 10.0 to obtain the correction for
the linear absorption due to the sulfosalicylate. For
instance in the case of solution No. 2 at 280.0 mμ.:

$$\text{optical density correction} = \frac{8.00}{10.00} \times 0.740 = .592$$

$$\text{corrected optical density} = 0.467 - 0.592 = -0.125$$

In the case of solution No. 7 at 317.0 mμ.:

$$\text{optical density correction} = \frac{5.50}{10.00} \times 0.340 = 0.187$$

$$\text{corrected optical density} = 0.982 - 0.187 = 0.795$$

Each of the optical density values in Table 3 were
corrected in the manner indicated in the above two
examples to give the corrected optical density values
listed in Table 4. In Figure 7 the corrected optical
density values from Table 4 were plotted versus the
number of ml. of beryllium sulfate and sulfosalicylate
present in each solution to give the maximum composition
as was done by Job (40) and the others (41, 42). It
should be noted that in Table 2 the molarities of the

sulfosalicylate solution and beryllium sulfate solu-
tion added were equal. Hence the ratios of the ml. of
each used in the preparation of the final solutions
were identical with the ratios of their molar concen-
trations.

Figure 7 clearly indicates that the maximum com-
position for the beryllium sulfosalicylate complex
occurs at the point where the ratio of the molarity of
sulfosalicylate to beryllium is ca. 0.66 to 0.34, or
1.94 to 1.00. This was taken to mean that two mole-
cules of sulfosalicylate combine with one atom of beryl-
lium to form the beryllium-sulfosalicylate complex.

The fact that the application of Job's method
showed that the ratio of sulfosalicylate to beryllium
was 2 to 1 in the complex was not surprising. Pauling
(49, p. 178) indicated that beryllium is capable of
forming tetrahedral covalent bonds and the fact that it
might do so in complex formation in solution would not
be unexpected.

The constancy of the maximum composition at var-
ious wave lengths as indicated by the curves in Figure

7 was taken to mean that essentially only one complex is formed (41), that in which the ratio of sulfosalicylate to beryllium is 2 to 1.

The present author feels that almost certainly the beryllium atom is coordinated between an oxygen atom of the carboxyl group and the oxygen atom of the hydroxyl group in each of two sulfosalicylate ions. Whether or not the proton of each of the hydroxyl groups in the complex remained intact at the optimum pH for the formation of the complex was somewhat conjectural. One would expect that coordination of the electron pair of the hydroxylic oxygen atom to the beryllium would weaken the hydrogen-oxygen bond of that hydroxyl group appreciably. In other words this hydroxyl group should become more "acidic" by such coordination. It was then recalled that a radical change in the ultraviolet absorption spectra of solutions of sulfosalicylic acid alone did appear with increasing hydroxyl in concentration at a pH just below 11.0 (see Figure 3). This change had been attributed to the removal of the hydroxylic hydrogen atom by hydroxyl ions in solutions of pH greater than ca. 10.8.

Such an attack would be expected to create in solution

a triply negative sulfosalicylate ion, $C_6H_3SO_3OCO_2^{\equiv}$.

Now if this was the case in such solutions then one

would expect that coordination of beryllium by sulfo-

salicylate in the manner described above would lead to

the formation of a stronger acid than was present

before. Indeed, then, it was only reasonable to sus-

pect that since the optimum pH for the complex was in

the region just below 11.0 (roughly 9.0 to 11.0 in pH)

this optimum pH range might be the result of the com-

plete removal of these hydroxylic protons to form the

beryllium-sulfosalicylate complex ion, $Be(C_6H_3SO_3OCO_2)_2^{\equiv}$.

This species of complex then, in constant concentration,

was believed to be responsible for the plateau between

a pH of 9.0 and 11.0 in the plot of optical density at

317.0 mμ. versus pH in curve 2, Figure 5.

D. Titration of Beryllium Basic Acetate

In order to test experimentally the postulates

presented at the end of the preceding section regarding

whether or not the hydroxylic protons of the sulfosali-

cylate molecules in the complex remained intact at the

optimum pH for the formation of the complex a titri-
metric method for beryllium basic acetate, $Be_4O(C_2H_3O_2)_6$,
was devised. One would expect that if beryllium basic
acetate were weighed into a solution containing an
appreciable excess of sulfosalicylic acid, which was
adjusted to the optimum pH for the formation of the
complex, the beryllium basic acetate might dissolve and
the amount of acid or base liberated in the formation
of the complex be determinable titrimetrically. By our
previous reasoning one of the following two reactions
would be expected to describe stoichiometrically the
process of complex formation in the pH range, 9.0 to 11.0.

(Equation 1) $Be_4O(C_2H_3O_2)_6 + 8Na_2C_6H_3SO_3OHCO_2 + 2HCl =$
$4Na_2Be(C_6H_3OHCO_2)_2 + 6NaC_2H_3O_2 + 2NaCl + H_2O$.

(Equation 2) $Be_4(C_2H_3O_2)_6 + 8Na_2C_6H_3OHCO_2 + 6NaOH =$
$4Na_4Be(C_6H_3OCO_2)_2 + 6NaC_2H_3O_2 + 7H_2O$.
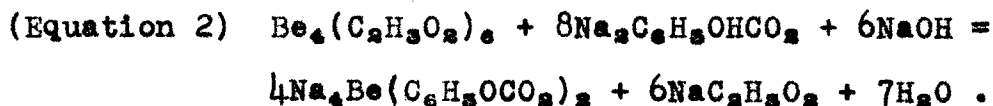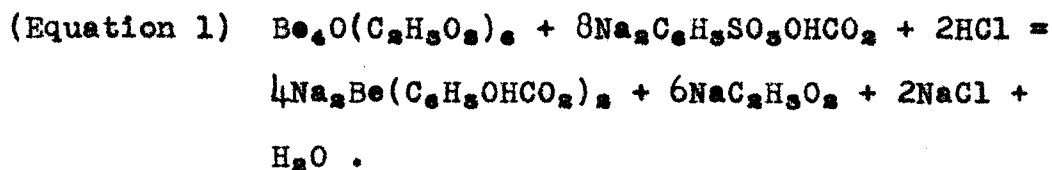
Equation 2 was believed to be the more probable one for
reasons discussed near the end of the preceeding sec-
tion. It should be noted that Equation 1 predicts
that if the hydroxylic hydrogen atoms are retained, the

equivalent weight of beryllium basic acetate is one-
half its molecular weight with acid (hydrochloric acid
in Equation 1) being required to readjust the solution
of sulfosalicylate to its original pH. Equation 2, on
the other hand predicts that if the hydroxylic hydrogen
atoms are removed, the equivalent weight of beryllium
basic acetate is one-sixth its molecular weight with
alkali (sodium hydroxide in Equation 2) being required
to readjust the solution of sulfosalicylate to its
original pH.

Preliminary qualitative tests indicated that
beryllium basic acetate dissolved very, very slowly
in solutions of sulfosalicylic acid at their natural
pH. The introduction of samples of beryllium basic
acetate into solutions of sulfosalicylic acid which
had been adjusted to a pH of ca. 10.6 with sodium
hydroxide resulted in the lowering of the pH to about
5.5 indicating that some dissolution had occurred and
that Equation 2 was probably the correct one. (Equa-
tion 1 predicts that the dissolution of beryllium
basic acetate by solutions of sulfosalicylate would
lead to an increase in hydroxyl ion concentration,
hence a higher pH.)

For obvious reasons it was felt that the addition of sodium hydroxide in excess to the sulfosalicylate solutions would appreciably hasten the process of the dissolution of beryllium basic acetate.

A 0.50M solution of disodium sulfosalicylate, $Na_2C_6H_3OHCO_2$, was prepared by neutralizing the proper weighed quantity of the free acid with sodium hydroxide and diluting in a volumetric flask. The pH of this solution was 10.6. Exactly 50.0 ml. portions of this solution were pipetted into each of three 150 ml. Fluorethene beakers. To each of these solutions was added by a buret 40.0 ml. of 0.1049N potassium hydroxide. One of these solutions was preserved as a blank and into each of the other two solutions an accurately weighed quantity of anhydrous beryllium basic acetate was weighed from a ground-glass stoppered weighing bottle. The quantities of materials used are summarized in Table 5. The mole ratio of the sulfosalicylate to beryllium in the solutions was calculated to be about 7 to 1. The beakers were tightly stoppered with clean rubber stoppers and stirred magnetically until dissolution was complete as indicated by the solutions being

entirely devoid of suspended material. This process
required a stirring period of approximately 14 hours
for each of the two samples. All three solutions
were then titrated potentiometrically with 0.1032N
hydrochloric acid using magnetic stirring and the

TABLE 5

Solutions for the Titration of
Beryllium Basic Acetate

Solu-tion No.	0.5M Sulfo-salicylate, ml.	Excess 0.1049N KOH added, ml.	Wt. anhydrous $Be_4O(C_2H_3O_2)_6$,g.
Blank	50.0	40.0	------
1	50.0	40.0	0.3437
2	50.0	40.0	0.3766

Beckman pH meter (Model H-2) calibrated at a pH of
10.00. The volumes of titrating solution used and the
corresponding pH values observed are recorded in Table
6. Figure 8 shows the plots of the potentiometric
titration data taken from Table 6. The volumes of
0.1032N hydrochloric acid required to titrate each of

TABLE 6

Potentiometric Titration of Solutions
from Table 5

Blank solution ml. 0.1032N		Solution No. 1 ml. 0.1032N		Solution No. 2 ml. 0.1032N	
HCl	pH	HCl	pH	HCl	pH
0.0	11.05	0.0	10.62	0.0	10.48
10.0	10.97	5.0	10.47	5.0	10.32
30.0	10.84	8.0	10.37	9.0	10.07
50.0	10.54	12.0	10.18	12.2	9.73
57.0	10.33	15.35	9.88	13.0	9.60
59.5	10.20	16.0	9.79	14.0	9.42
61.5	10.07	17.0	9.65	14.5	9.27
63.1	9.97	18.0	9.45	15.0	9.13
64.4	9.82	18.6	9.28	15.3	9.00
66.0	9.62	19.0	9.15	15.5	8.90
67.2	9.35	19.2	9.06	16.1	8.43
68.0	9.07	19.3	9.00		
68.6	8.66	19.5	8.90		
69.0	7.90	19.7	8.75		
69.1	7.50	20.0	8.45		
69.2	7.17				
69.3	6.90				
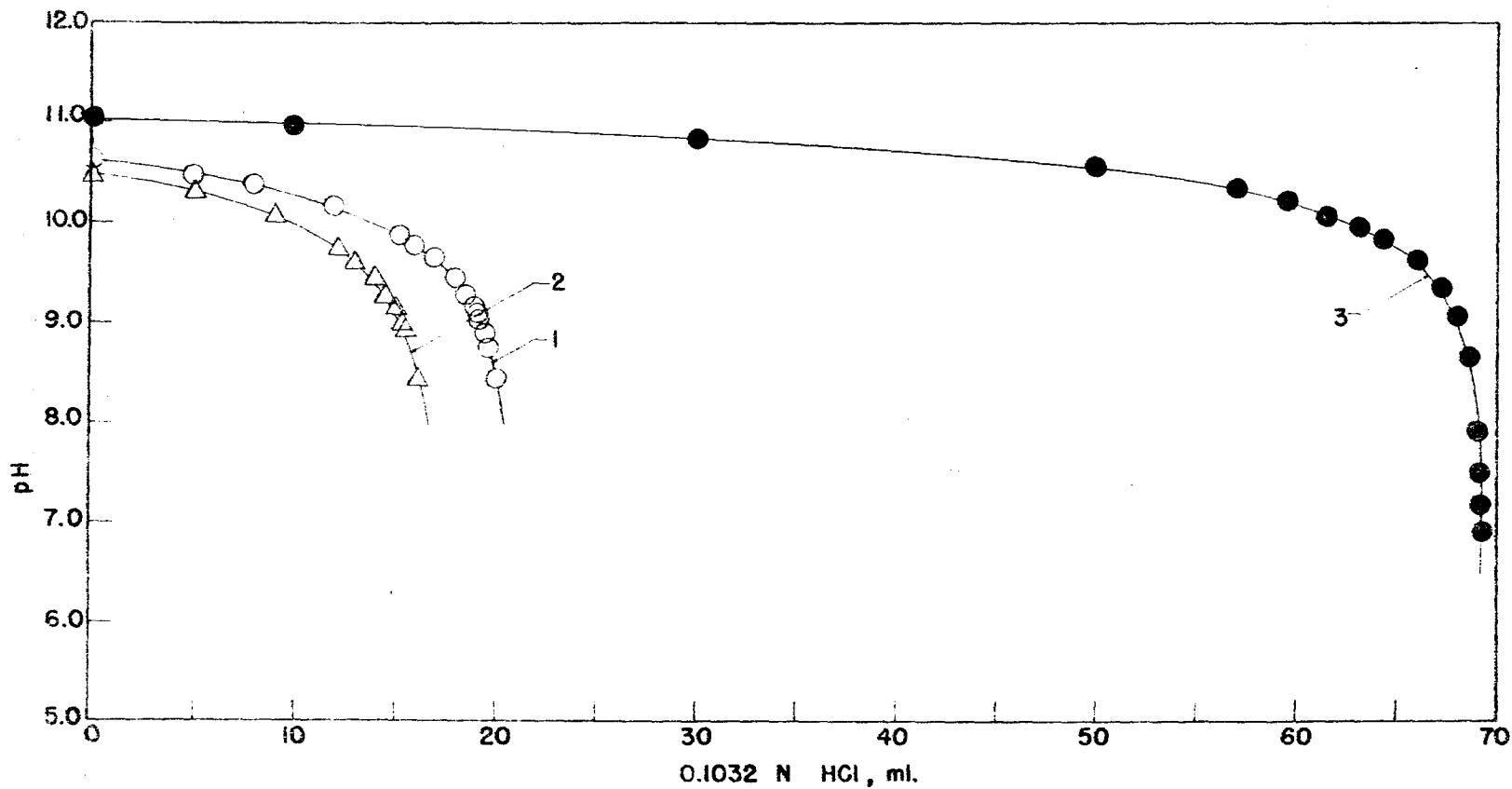
Figure 8——— Potentiometric titration curves for beryllium basic acetate complexed by sulfosalicylate in the presence of excess alkali using the data from Table 6; Curve 1, solution 1, Table 5; Curve 2, solution 2, Table 5; Curve 3, blank solution, Table 5.

the solutions to pH values of 10.0, 9.5, 9.0, and 8.5
were read from Figure 8. The differences between the
volumes required for the titration of samples and those
required to titrate the blank to each of these pH
values was assumed to be a measure of the acid libera-
ted by the complexation of beryllium basic acetate by
sulfosalicylate. In Table 7 was listed the number of
ml. of the 0.1032N hydrochloric acid required to
titrate each of the solutions to the various pH values
indicated. For each sample the corresponding apparent
per cent beryllium basic acetate at the various pH
values is listed, assuming that Equation 2 properly
describes the stoichiometry of the reaction. The fol-
lowing equation explains the calculations used to obtain
the apparent per cent beryllium basic acetate.

$$\frac{(V_B - V_S) \times 0.1032 \times 0.06772 \times 100}{G} = \text{per cent apparent}$$

$$Be_4O(C_2H_3O_2)_6.$$

where: V_B = number of ml. 0.1032N hydrochloric acid
required to titrate the blank solution to
each of the pH values.

TABLE 7

Results of Titrating Beryllium Basic Acetate

	Blank solution	Solution 1		Solution 2	
pH	0.1032N HCl ml.	0.1032N HCl ml.	app. % $Be_4O(C_2H_3O_2)_6$	0.1032N HCl ml.	app. % $Be_4O(C_2H_3O_2)_6$
10.0	62.50	14.10	98.42	9.80	97.80
9.5	66.60	17.80	99.23	13.60	98.35
9.0	68.12	19.30	99.30	15.30	98.02
8.5	68.68	19.96	99.07	16.00	97.76

V_S = number of ml. 0.1032N hydrochloric acid required to titrate the sample solutions to each of the pH values.

0.06772 = milliequivalent weight of beryllium basic acetate indicated by Equation 2.

G = g. beryllium basic acetate taken in each case.

After the completion of the titration of each of the samples the solutions were restoppered and allowed to stand for 6 hours. At the end of this time no appreciable change in pH had occurred, indicating that equilibrium had been attained.

The results of the calculations for apparent per cent beryllium basic acetate summarized in Table 7, assuming the applicability of Equation 2, virtually assured the fact that this equation was the correct one. A pH of 9.0 to 9.5 was evidently the optimum pH for the end point. At higher pH values the slopes of the curves in Figure 8 were too small to permit accurate measurements of the volumes and at lower pH values the complex apparently was somewhat destroyed.

The present author was unable to write any reasonable reactions other than that described in Equation 2 to account for stoichiometry indicated in Table 7. It was thus felt that almost certainly, the complex present in maximum concentrations between a pH of 9.0 and 11.0 was the complex with the two hydroxylic protons removed. This means that the beryllium-sulfosalicylate complex most probably bears a negative charge of 4. The identity of the complex was thus concluded to be $Be(C_6H_3SO_3OCO_2)_2^{\equiv}$, which for simplicity's sake was chosen to be written as $Be(SS)_2^{\equiv}$. Structurally it was felt that the complex is best represented by the structure
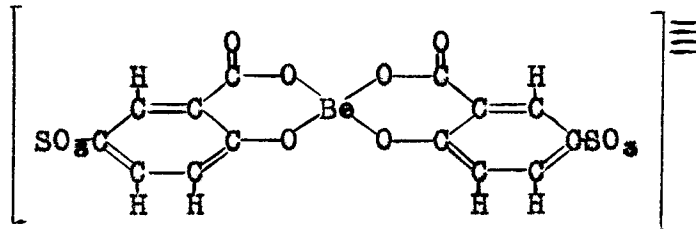
with each pair of coplanar rings being oriented at least approximately at right angles to each other and the four bonds from the beryllium atom to the oxygen atoms being directed, at least in an approximate manner,

toward the corners of a tetrahedron with the beryllium atom in the center. It is of interest to note that such a structure predicts the capability of the existence of optical isomers. However this fact was not of importance in the present work because so far as was known the conditions were always such that only racemic mixtures would be obtained; that is, no asymmetric conditions of preparation were knowingly imposed.

E. Instability Constant of the Beryllium-Sulfosalicylate Complex

After the nature of beryllium-sulfosalicylate complex ion, $Be(SS)_2^{\equiv}$, had been established insofar as was possible by Job's method (Section VI, C) and by the titrimetric method (Section VI, D) it was at once desirable to determine the degree of instability of the complex ion, $Be(SS)_2^{\equiv}$. It was believed that the dissociation of the ion at constant pH could be best represented by an equilibrium such as that represented in Equation 3,

(Equation 3) $$Be(SS)_2^{\equiv} \xrightarrow{H+} Be_x + 2HSS^{=}.$$
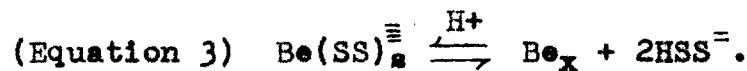
in which Be_x is a species of beryllium ion of an
unknown nature and $HSS^=$ is the simple doubly-negative
sulfosalicylate ion with the hydroxylic proton intact.
Such a representation as Equation 3 makes no claim with
regard to the beryllium species, Be_x, formed by the
dissociation of the complex although it is almost
certain that the beryllium species would involve
hydroxyl ions. It was firmly believed that the simple
sulfosalicylate ion, $HSS^=$, possesses its hydroxylic
proton intact on the right hand side of Equation 3.
Finally, it was believed that Equation 3 as written,
adequately describes the dissociation of the complex
at constant pH and at the pH of maximum complex forma-
tion.

It was already known that the beryllium-sulfo-
salicylate complex has a much higher molecular
extinction coefficient at 317.0 mµ. than does the
simple sulfosalicylate ion, $HSS^=$. It was obvious that
if solutions of the complex were prepared at widely
differing concentrations, then the fractions of the com-
plex dissociated in each of these solutions should also
vary widely, the more dilute solutions being dissociated

to the greater extent. For the difference in this
fractional dissociation to be observable in the
measurement of the optical densities at 317.0 mμ. it
was necessary, not only that there be an appreciable
difference between the molecular extinction coefficients
of the complex and the simple sulfosalicylate ion, but
that the equilibrium constant for Equation 3 be large
enough for appreciable quantities of the free sulfosa-
licylate ion to be present in solution under the
experimental conditions.

It was finally decided to use solutions in which
the mole ratio of sulfosalicylate to beryllium was 2
to 1. A preliminary solution was prepared with just
this ratio of sulfosalicylate to beryllium at a pH of
10.5 and allowed to stand for two days. No cloudiness
or precipitation was observed and it was concluded that
the complex was stable enough to permit the use of
solutions in which the ratio of sulfosalicylate to
beryllium was just 2 to 1 for spectrophotometric exam-
ination.

A stock solution of the complex was prepared by
mixing 35.00 ml. of 1.00×10^{-2} M sulfosalicylic acid,

17.50 ml. of 1.00×10^{-2} M beryllium sulfate prepared
from beryllium stock solution No. 2, and 250. ml. of
2.00×10^{-2} M ethylenediaminetetraacetic acid. The pH
of this solution was adjusted to approximately 10.4
with sodium hydroxide and the whole diluted to exactly
500.0 ml. This gave a solution 3.50×10^{-4} M in the com-
plex (disregarding dissociation) and 1.00×10^{-2} M in
ethylenediaminetetraacetic acid. The ethylenediamine-
tetraacetic acid was added to serve the dual purpose
of keeping the ionic strength constant and buffering
the solution. Various dilutions were made from this
solution for spectrophotometric examination as indicated
in Table 8. The solutions were allowed to stand for 18
hours and were then scanned on the Cary instrument at
$25 \pm 1°C$. in 1.000 cm. silica cells versus distilled
water to give the absorption spectra shown in Figure 9.
It was of interest to note qualitatively that the
absorption maxima shifted from about 310.0 mμ. in the
most concentrated solution to about 300.0 mμ. for the
most dilute solution indicating that absorption due
to the simple sulfosalicylate ion, HSS^-, did play an
increasingly important part in the absorption with
increased dilution. This fact increased the prospect

of being able to evaluate the equilibrium constant.

The final composition of the solutions prepared as indicated in Table 8 together with the observed optical densities at 317.0 mμ. as read from Figure 9 are summarized in Table 9.

A contributing reason for using ethylenediamine-tetraacetic acid in the solutions in Tables 8 and 9 was that it had already been decided at the time this work was done to use that acid in eliminating aluminum interference. It was not possible to make an accurate calculation for ionic strength, μ, in these solutions because the activities of the ions were not known. Even though this was known to be true it was felt that the experiment should be done because it closely approximated the general conditions later imposed during the actual analytical determination of beryllium in the presence of aluminum. An approximation of the ionic strength, μ, of the solutions in Table 9 was made using the ionization constants for ethylenediamine-tetraacetic acid reported by Schwarzenbach and Ackermann (33). Representing ethylenediaminetetraacetic acid as H_4A we have approximately in dilute solution that

TABLE 8

Beryllium Sulfosalicylate Solutions for Examination
of Dilution Effects

Solution No.	3.50×10^{-4} M Complex added ml.	2.00×10^{-2} M Ethylenediamine-tetraacetic acid added, ml.	Final volume, ml.	pH (Beckman Model G)
1	200.0	----	200.0	10.35
2	150.0	25.0	200.0	10.34
3	100.0	50.0	200.0	10.37
4	50.0	75.0	200.0	10.38
5	25.0	87.5	200.0	10.39
6	10.0	95.0	200.0	10.37
7	5.0	97.5	200.0	10.43
8	4.0	98.0	200.0	10.42
9	3.0	98.5	200.0	10.44
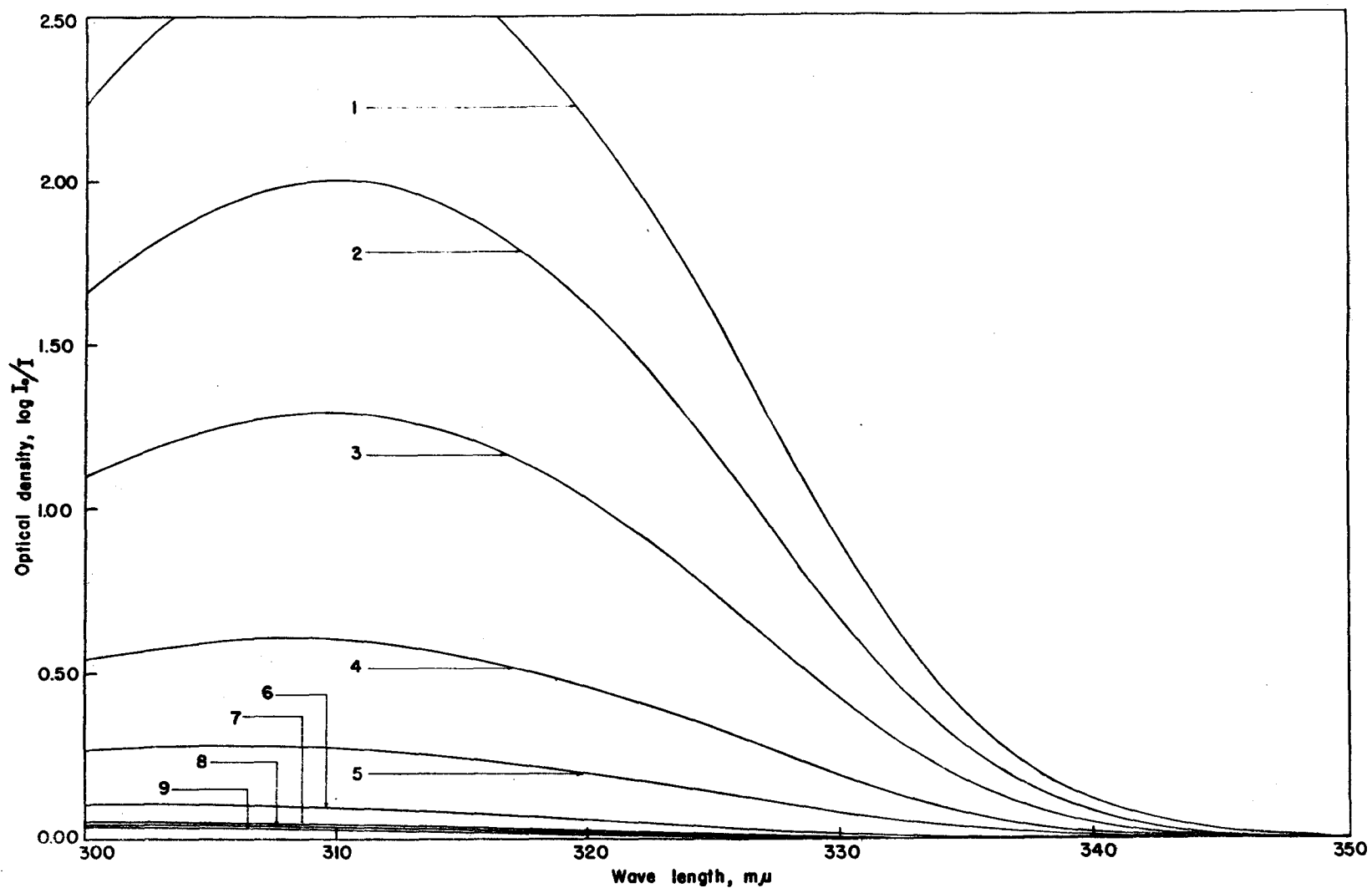
Figure 9— Absorption spectra of solutions of the beryllium sulfosalicylate complex prepared as indicated in Table 8. using the Cary instrument ; curves 1,2,3, 4, 5, 6, 7, 8, and 9 correspond to solutions 1, 2,3, 4, 5, 6, 7, 8, and 9 respectively in Tables 8 and 9.

TABLE 9

Composition of Solutions Corresponding to Figure 9

Solution No.	Ethylenediamine-tetraacetic acid molarity	Total beryllium molarity	Total sul-fosalicylate molarity	Observed optical density at 317.0 mμ.
1	1.00×10^{-2}	3.50×10^{-4}	7.00×10^{-4}	2.450
2	1.00×10^{-2}	2.625×10^{-4}	5.25×10^{-4}	1.806
3	1.00×10^{-2}	1.75×10^{-4}	3.50×10^{-4}	1.157
4	1.00×10^{-2}	8.75×10^{-5}	1.75×10^{-4}	0.520
5	1.00×10^{-2}	4.37×10^{-5}	8.74×10^{-5}	0.226
6	1.00×10^{-2}	1.75×10^{-5}	3.50×10^{-5}	0.070
7	1.00×10^{-2}	8.75×10^{-6}	1.75×10^{-5}	0.029
8	1.00×10^{-2}	7.00×10^{-6}	1.40×10^{-5}	0.022
9	1.00×10^{-2}	5.25×10^{-6}	1.05×10^{-5}	0.014

$$K_1 = \frac{(H+)(H_3A^-)}{(H_4A)} \quad ; \quad K_2 = \frac{(H+)(H_2A^=)}{(H_3A^-)}$$

$$K_3 = \frac{(H+)(HA^{\equiv})}{(H_2A^=)} \quad ; \quad K_4 = \frac{(H+)(A^{\equiv})}{(HA^{\equiv})} \; .$$

Solving each expression for the respective anion
species and summing to give the total molarity, M, of
all the species involving the ethylenediaminetetraacetic
acid we have

(Equation 4) $\quad M = x + \dfrac{K_1 x}{(H+)} + \dfrac{K_1 K_2 x}{(H+)^2} + \dfrac{K_1 K_2 K_3 x}{(H+)^3} + \dfrac{K_1 K_2 K_3 K_4 x}{(H+)^4}$

where $x = \underline{/H_4A/}$. In the solutions under consideration
the pH was very close to 10.4 and M was 1.00×10^{-2}.
Schwarzenbach and Ackermann reported that $K_1 = 10^{-1.996}$,
$K_2 = 10^{-2.672}$, $K_3 = 10^{-6.161}$, and $K_4 = 10^{-10.262}$. Sub-
stituting these values in Equation 4 gives $x = 1.795 \times 10^{-23} M$.
This gives $\underline{/HA^{\equiv}/} = 4.2 \times 10^{-3}$ and $\underline{/A^{\equiv}/} = 5.8 \times 10^{-3}$ as the
only anions of the acid present in appreciable amounts.
Now

(Equation 5) $\quad \mu = \frac{1}{2} \sum (M_i z_i^2)$

where μ is the ionic strength, M_i is the molarity of
the ith ion and z_i is its charge, the summation to be

made for all charged species in the solution. In the solutions under consideration the contribution of the sulfate ions, complex ions, hydrogen ions, free beryllium ions, and free sulfosalicylate ions to the ionic strength were all small compared to the contributions of the sodium ion concentration, $[Na^+]$ = 3.6×10^{-2}, the triple negative acid ion, $[HA^\equiv]$ = 4.2×10^{-3}, and the tetra-negative acid ion, $[A^\equiv]$ = 5.8×10^{-3}. Applying Equation 5 to these three ions we have μ = 0.078, approximately. Such a calculation gives only a very rough approximation of the ionic strengths of the solutions under consideration.

It was desirable to use the optical density values from Table 9 as an index of the magnitude of the instability of the complex ion described by Equation 3. The equilibrium constant describing Equation 3 may be written as in Equation 6.

(Equation 6) $K = \dfrac{a_{Be_x} \times a^2_{HSS^\equiv}}{a_{Be(SS)^\equiv_2}}$.

In Equation 6 the terms on the right side of the equation denote the activities of the subscripted ions. Equation 6 may also be written as

(Equation 7) $K = \dfrac{(Be_x)\ (HSS^=)^2}{(Be(SS)^{\equiv}_2)} \times \dfrac{\gamma_{Be_x} \times \gamma^2_{HSS^=}}{\gamma_{Be(SS)^{\equiv}_2}}$

where the symbols, γ, are the activity coefficients
of each of the subscripted ions. Now rearranging
Equation 7 we may write that

(Equation 8) $\dfrac{\gamma_{Be(SS)^{\equiv}_2}}{\gamma_{Be_x} \times \gamma^2_{HSS^=}} \times K = K' = \dfrac{(Be_x)\ (HSS^=)^2}{(Be(SS)^{\equiv}_2)}$.

At constant ionic strength, μ, the term, K', should
truly be a constant because at constant ionic strength
the activity coefficients should be constant. (Note:
the development and terminology from Equations 6 to 8
inclusive is common to almost all standard texts in
elementary physical chemistry.)

It was assumed that only two species of beryl-
lium were present in the solutions, the complex ion,
$Be(SS)^{\equiv}_2$, and the unknown species, Be_x. It was further
assumed that only two species of ions contributed to
the absorption of light at 317.0 mμ., these being the
complex ion, $Be(SS)^{\equiv}_2$, and the free sulfosalicylate
ion, $HSS^=$. On the basis of this last assumption it
was possible to write Equation 9.

(Equation 9) $D = 1(E_1M_1 + E_2M_2)$

where D is the optical density ($\log I_o/I$), 1 is the thickness of the sample cells in cm. (1.000 cm. for all work done with the Cary instrument; 0.998 cm. for the Beckman instrument), E_1 and E_2 are the molecular extinction coefficients for the free sulfosalicylate ion, $HSS^{=}$, and the complex ion, $Be(SS)_2^{\equiv}$, respectively, and M_1 and M_2 the respective molarities of these last-named ions.

The molecular extinction coefficient, M_1, of the simple sulfosalicylate ion was readily calculated from the optical density at 317.0 mμ. observed for solution 1, curve 1, Figure 6, containing only the simple sulfosalicylate ion, $HSS^{=}$. For this solution

$$D = 0.340 = M_1E_1 = (1.000)(5 \times 10^{-4})(E_1)$$

or

$$E_1 = 680.$$

The molecular extinction coefficient, E_2, for the complex ion was not so readily calculated because for obvious reasons it was not possible to prepare

solutions containing only this absorbing species.
However it was possible to estimate E_2 from the
optical density of solutions in which there were
appreciable excesses of sulfosalicylate over the
stoichiometric amount required for complexation of
the beryllium. Such a solution was solution No. 3,
curve 3, Figure 6, for which the optical density
observed at 317.0 mμ. was 1.025 and the sulfosalicylate
was present in a 50 per cent excess. Assuming that all
the beryllium was in the form of the complex, $Be(SS)_2^{\equiv}$,
we have that

$$1.025 = (1.000) (1.25 \times 10^{-4})E_2 - (1.000) (1.25 \times 10^{-4})$$
$$(680)$$

or

$$E_2 = 7.52 \times 10^3.$$

A similar calculation for solution No. 2 of the same
series, in which the sulfosalicylate was present in 100
per cent excess shows $E_2 = 7.64 \times 10^3$. It was felt that
the latter value was probably the more nearly correct
one because it would be more nearly true that the beryl-
lium was all in the form of the complex where the

sulfosalicylate was present in the greater excess. It was believed that even the value for E_2 of 7.64×10^4 was probably a little too low because under no circumstances could the beryllium be absolutely all present in the form of the complex. The final value for E_2 was determined by successive approximations using Equations 8 and 9 as follows:

Let x = molarity of species Be_x in each solution of Table 9.

then $M-x$ = molarity of complex species, $Be(SS)_2^{\equiv}$ in each solution, where M equals total beryllium molarity.

and $2x$ = molarity of free sulfosalicylate in each solution.

Substitution of these terms in Equations 8 and 9 give Equations 8' and 9', respectively.

(Equation 8') $K' = \dfrac{(x)\,(2x)^2}{(M-x)}$.

(Equation 9') $K = 1/\overline{E_1}\ (2x) - E_2\ (M-x)\overline{)}7$.

Only the first five solutions in Table 9 were

examined in determining the value of E_a because only they had values of optical density not subject to great relative error. For each solution Equation 9' was solved for x, assuming E_a to be $7.64x10^4$. The values for x, 2x, and (M-x) thus obtained were then substituted in Equation 8' to give values for K'. The value for E_a of $7.64x10^4$ did give nearly constant values for K' for each of the five solutions, but E_a was adjusted by successive approximations to give a more nearly constant value for K' in each of the solutions. A sample calculation for solution No. 1, Table 9, with E_a equal to $7.64x10^4$, shows that from Equation 9'

$$2.450 = 1.000 \ (680 \ (2x) - 7.64x10^3 \ (3.50x10^{-4}-x))$$
$$\text{that } x = 3.567x10^{-5}.$$

Substitution in Equation 8' gives K' = $5.78x10^{-10}$.

A summary of the various values for K' obtained with the original and final E_a values selected is shown in Table 10. Actually K' was not very sensitive to variations in E_a and because of other uncertainties involved it was not justifiable to establish very

accurately the optimum value for E_2. The final values
selected for E_2 and K' were 7.70×10^3 and 7.80×10^{-10}
respectively.

TABLE 10

Approximation of K' and E_2

Solution No.	$K' \times 10^{10}$ for E_2 equal to 7.64×10^3	$K' \times 10^{10}$ for E_2 equal to 7.70×10^3
1	5.78	7.34
2	5.55	6.82
3	6.44	7.53
4	8.28	9.08
5	7.67	8.17
K' (Average) = 6.74×10^{-10}		K' (Average) = 7.80×10^{-10}

Having approximated E_2 and K' it was then possi-
ble to reverse the calculations just completed to give
calculated values for optical densities which should be
observed at 317.0 mμ. for various molarities of sulfo-
salicylate and beryllium at the molar ratio of 2 to 1.
This was done assuming E_1 is 680, E_2 is 7.70×10^3, and

K' is 7.80×10^{-10} for the various concentrations of beryllium indicated in Table 11. The observed optical densities at the known concentrations from Table 9 were plotted versus total beryllium molarity in Figure

TABLE 11

Observed and Calculated Optical Density Values
at 317.0 mμ. for Solutions of the Beryllium-
Sulfosalicylate Complex

Total beryllium molarity	Calculated optical density at 317.0 mμ.	Observed optical density at 317.0 mμ.
2.00×10^{-6}	0.003	0.004
5.00×10^{-5}	0.269	0.265
1.00×10^{-4}	0.615	0.610
2.00×10^{-4}	1.340	1.345
3.00×10^{-4}	2.075	2.080

10 and the optical densities corresponding to the concentrations listed in Table 11 were read from this curve. These observed optical densities were placed in Table 11 for comparison purposes. Agreement was quite good,
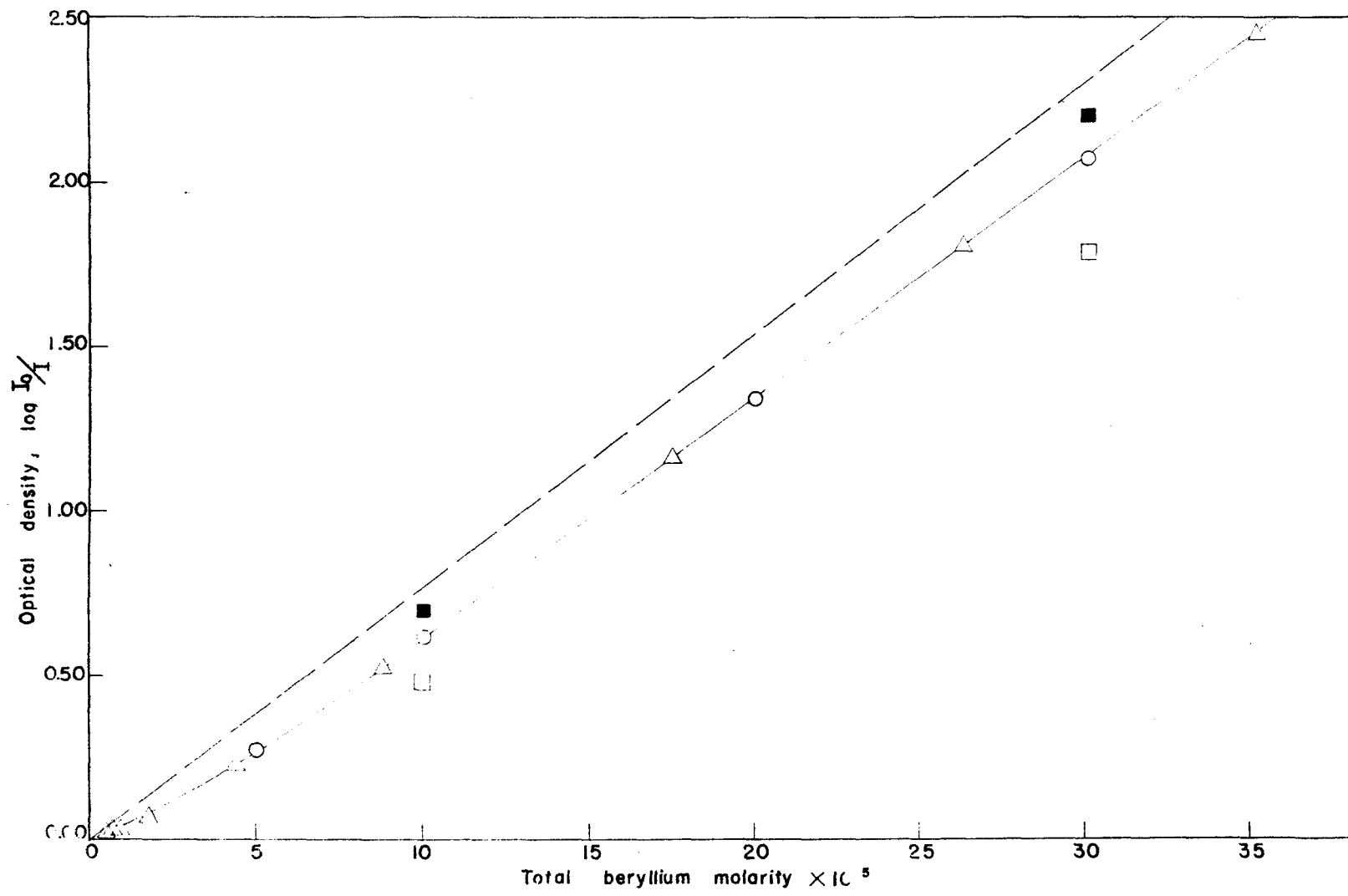
Figure 10 —— Calculated and observed optical densities at 317.0 mμ for solutions of the beryllium sulfo-salicylate complex from data in Tables 9 and 11 ; broken line, theoretical, assuming no dissociation ; O , calculated points ; △ , experimental points ; □ , calculated , assuming K' 10 times larger than observed ; ■ , calculated , assuming K' $\frac{1}{10}$ as large as observed.

as was expected. In Figure 10 a straight broken line
was drawn indicating the optical densities which should
be observed were the complex not at all dissociated
and that E_2 is 7.70×10^3. Also in Figure 10 was indica-
ted two pairs of points, one above and one below the
experimental curve, which would be observed if K'
were 1/10 as large and 10 times as large respectively,
as was actually observed, assuming E_1 and E_2 to be the
same as actually observed.

It was of interest to test the applicability of
the constants E_1, E_2, and K' to situations other than
those in which sulfosalicylate and beryllium were
mixed in the ratio of 2 to 1. Solution 2, curve 2,
Figure 6, in which the mole ratio of sulfosalicylate
to beryllium was 4 to 1 showed an optical density of
0.900 at 317.0 mμ. Application of Equations 8' and 9'
gave a calculated optical density of 0.895 which
differs by only 0.005 optical density units from the
value observed. A similar calculation for solution 3
of the same series in which the mole ratio of sulfo-
salicylate to beryllium was 3 to 1 gave a calculated
optical density value of 1.016 as compared to the

experimental value of 1.025. These comparisons were believed to lend substantial confirmation of the truth of the calculated magnitudes of the constants.

A further comparison was made with solutions in which insufficient sulfosalicylate was present to prevent the precipitation of a solid hydrated beryllium oxide phase. Under these conditions it was expected that the unknown beryllium species, Be_x, should be present in constant concentrations. Solutions 7, 8, and 9 in Figure 6 contained a visible solid phase. Assuming the calculated values for E_1, E_a, K', the measured optical densities and knowing the total sulfosalicylate concentration, it was then easy to solve for the molar concentrations of Be_x by Equations 8 and 9. Solutions 7, 8, and 9 gave values for (Be_x) of $1.67x10^{-4}$, $2.14x10^{-4}$, and $1.56x10^{-4}$ respectively. It was believed that these molarities were of a nearly enough constant nature to feel that they, too, constituted good evidence for the accuracy of the values previously calculated for E_1, E_a, and K'.

It was of interest to know just how stable the

solutions of the beryllium-sulfosalicylate complex
are on long standing. Solutions Nos. 2, 3, and 6
from Table 9 were examined at 317.0 mµ. on the Cary
instrument 53 days after the readings in Table 9 were
taken. The optical density values obtained were
1.793, 1.145, and 0.210 as compared with values of
1.806, 1.157, and 0.226, respectively, which were
read 53 days earlier. It was concluded that the
complex was very stable with respect to effects of
aging.

It was considered advisable to repeat the deter-
mination of E_1, E_2, and K' from a series of solutions
in which the ionic strength was more accurately known.
Accordingly a fresh solution of complex, $1.00x10^{-3}M$
in beryllium from beryllium stock solution No. 2, and
$2.00x10^{-3}M$ in sulfosalicylate was prepared. The
various dilutions of this stock solution, the amounts
of sodium perchlorate used in controlling the ionic
strength, and the pH values of the final solutions used
in the study are shown in Table 12.

Figure 11 shows the ultraviolet absorption
spectra versus distilled water as reference solution
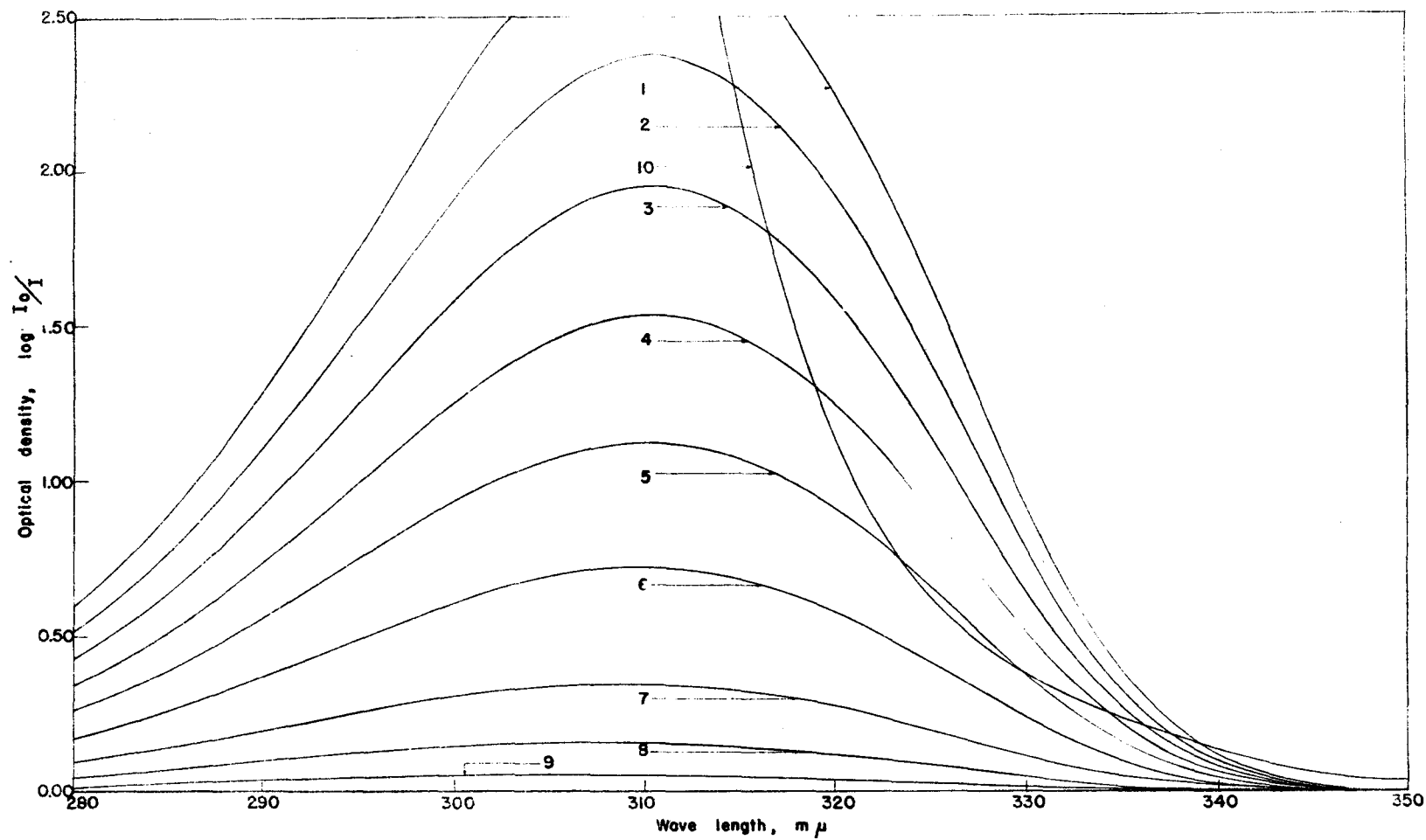
Figure II ——— Absorption Spectra of sciutions cf the beryllium—sulfosalicylate complex prepared as indicated in Table 12, using the Cory instrument ; curves 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 correspond to solutions 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 respectively in Table 12. Temperature, 26 ± 1° C.

TABLE 12

Composition of Solutions Used in the Determination of K' With
the Ionic Strength Controlled by the Use of Sodium Perchlorate

Solution No.	Complex solution 1.00×10^{-3}M added, ml.	Sodium perchlorate 0.625M added, ml.	Final volume, ml.	pH (by Beckman Model H-2 instrument)
1	70.0	25.0	200.0	10.39
2	60.0	25.0	200.0	10.40
3	50.0	25.0	200.0	10.37
4	40.0	25.0	200.0	10.35
5	30.0	25.0	200.0	10.52
6	20.0	25.0	200.0	10.45
7	10.0	25.0	200.0	10.37
8	5.0	25.0	200.0	10.40
9	2.0	25.0	200.0	10.34
10	5.00 ml. 0.0995M sulfosalicy-lic acid added instead of complex solution.	25.0	200.0	10.40

for the solutions prepared as described in Table 12.

The optical density at 317.0 mμ. of solution No. 10,

Table 12, was used to calculate the molecular

extinction coefficient, E_1, of the free sulfosalicylate

ion, $HSS^=$. E_1 was found to be 691 in this case as

compared to 680 in the previous set of solutions. The

molar extinction coefficient, E_2, of the complex and

the molar equilibrium constant, K', for its dissocia-

tion were found in exactly the same manner as before.

They were determined to be 7.75×10^3 and 2.63×10^{-10}

as compared to the previously obtained values of

7.70×10^3 and 7.80×10^{-10} for E_2 and K', respectively.

Differences in the corresponding values between the

two sets of solutions were attributed to errors in

the preparation of solutions, other mechanical errors,

slight differences in temperature, differences in

ionic strength, and any slight interference caused by

the presence of ethylenediaminetetraacetic acid in

the first series. Table 13 shows the observed optical

densities at 317.0 mμ. and the approximated values

for K' for each solution. The molarity of sodium

perchlorate, $NaClO_4$, in these solutions was 0.0781,

hence the ionic strength was also very nearly 0.0781

TABLE 13

Observed and Calculated Data Corresponding
to Solutions in Table 12 Which Gave Absorption
Spectra Shown in Figure 11

Solution No.	Total beryllium molarity	Optical density at 317.0 mμ.	Approximated values for $K' \times 10^{10}$
1	3.50×10^{-4}	2.517*	3.65
2	3.00×10^{-4}	2.160	2.54
3	2.50×10^{-4}	1.790	2.20
4	2.00×10^{-4}	1.407	2.57
5	1.50×10^{-4}	1.030	2.87
6	1.00×10^{-4}	0.657	3.11
7	5.00×10^{-5}	0.304	2.50
8	2.50×10^{-5}	0.133	2.28
9	1.00×10^{-6}	0.042	1.56

* Estimated from Figure 11; recording pen went off scale
on Cary instrument.

because the ionic strength of a uniunivalent electrolyte is equal to its molarity. The maximum contribution to the ionic strength by the excess sulfuric acid present in the beryllium stock solution, the sulfate ions originally associated with the beryllium, and the complex itself was calculated to be less than 5 per cent of the ionic strength due to sodium perchlorate in even the most concentrated solution of the complex.

Only the K' values for solutions Nos. 2 and 7 inclusive were used in getting the average value for K' because it was believed that these solutions were subject to the best relative accuracy in the measurement of optical density.

Table 14 shows the comparison between calculated and observed optical density values at 317.0 mμ. and at various selected molarities of beryllium assuming E_1 is 691, E_a is 7.75×10^3 and K' is 2.63×10^{-10}. Figure 12 graphically makes the same sort of comparison. The straight broken line indicates the optical density values which would have been observed had no dissociation of the complex occurred. Again,
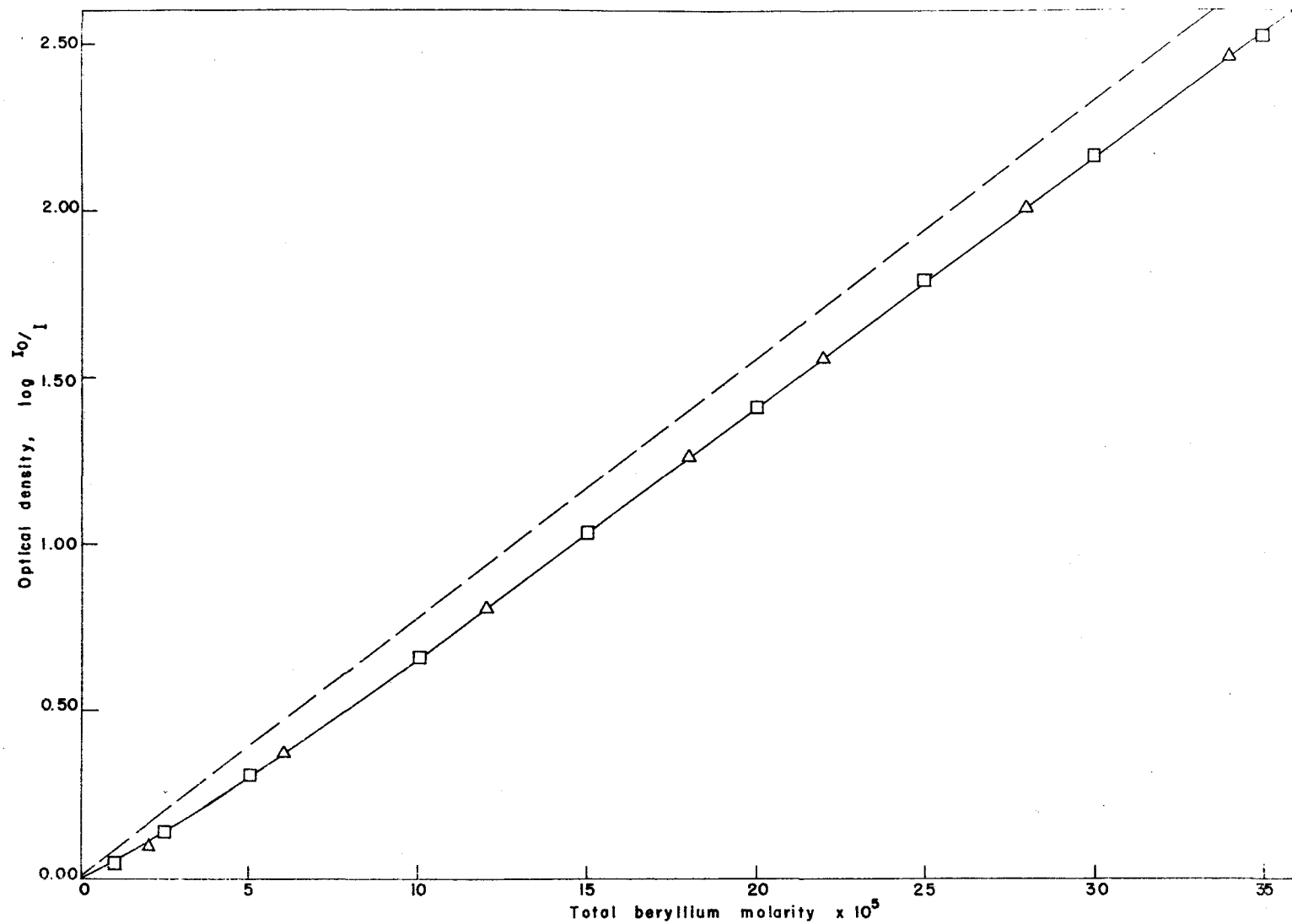
Figure 12— Calculated and observed optical densities at 317.0 mμ for solutions of the beryllium—sulfosalicylate complex from data in Tables 12 and 13; broken line, theoretical, assuming no dissociation; △ , calculated points; ☐ , experimental point

excellent agreement between calculated and experimental optical densities was obtained throughout the concentration range.

TABLE 14

Comparison of Calculated Optical Density
Values at 317.0 mµ. with Observed Values from
Figure 12 at Selected Beryllium Concentrations

Total beryllium molarity x10^{-4}	Observed optical density at 317.0 mµ.	Calculated optical density at 317.0 mµ.
0.20	0.100	0.098
0.60	0.372	0.373
1.20	0.806	0.810
1.80	1.260	1.256
2.20	1.560	1.555
2.80	2.008	2.007
3.40	2.450	2.460

It was believed that by keeping the concentrations of beryllium and sulfosalicylate constant (and in the molar ratio of 1 to 2) and adding ever decreasing amounts of sodium perchlorate to reduce the ionic

strength it would be possible to evaluate the true
equilibrium constant by extrapolation to zero ionic
strength. Under these circumstances it became neces-
sary to know quite accurately the amount of sulfuric
acid present in excess in the beryllium sulfate stock
solution.

The total sulfate was determined volumetrically
by the method described by Peabody and Fisher (50)
in which sulfate is titrated with standard barium
chloride solution to the equivalence point recognized
by the use of the sodium salt of tetrahydroxyquinone
("THQ") as an external indicator. The barium chloride
was standardized versus standard sulfuric acid solu-
tion. Beryllium stock solution No. 2 was found to be
0.1597M in sulfate by this method. Free sulfuric acid
was also titrated potentiometrically using standard
sodium hydroxide and the Beckman Model H-2 pH meter.
The solution was found to be 0.0529M in free sulfuric
acid by this means and by adding this value to the
known beryllium sulfate molarity of 0.1039, a value
of 0.1568 was obtained for the total sulfate molarity.
The average of the values, 0.1582, was taken as very
closely representing the true sulfate molarity of

beryllium stock solution No. 2.

It was convenient to use for this study the same stock solution of complex as was used in Table 12. This solution was prepared as 1.00×10^{-3}M in beryllium, 2.00×10^{-3}M in sulfosalicylate, and (on the basis of the total sulfate analysis) 1.52×10^{-3}M in sulfate ion. Two series of solutions, of different, constant complex concentration were prepared for spectrophometric examination. The composition of these two series of solutions is summarized in Table 15.

In order to calculate the ionic strengths of these solutions it was necessary to make some approximations. After a preliminary examination of the data for these solutions it was estimated that the complex, $Be(SS)_a^{\overline{=}}$, was about 15 per cent dissociated ($K' \sim 1.4 \times 10^{-9}$) in Series I through the range where the contribution of the complex ion and its products of dissociation to the ionic strength was most important. The same degree of dissociation was assumed in the solutions of higher ionic strength, as adjusted by sodium perchlorate, realizing that this was not quite true, but knowing that the relative effect of the degree of

TABLE 15

Composition of Solutions for the Study of K'
as a Function of the Ionic Strength

Solution No.	Complex solution 1.00×10^{-3}M added, ml.	Sodium perchlorate 0.625M added, ml.	Final volume, ml.	pH (by Beckman Model H-2 instrument)	Calculated ionic strength, $\mu \times 10^2$
Series I					
1	60.0	50.0	200.0	10.42	16.04
2	60.0	30.0	200.0	10.40	9.82
3	60.0	20.0	200.0	10.40	6.69
4	60.0	10.0	200.0	10.40	3.57
5	60.0	5.0	200.0	10.40	2.01
6	60.0	0.0	200.0	10.42	0.44
Series II					
1	30.0	50.0	200.0	10.39	15.82
2	30.0	30.0	200.0	10.38	9.60
3	30.0	20.0	200.0	10.37	6.47

TABLE 15 (continued)

Solu-tion No.	Complex solution 1.00×10^{-3}M added, ml.	Sodium perchlorate 0.625M added, ml.	Final volume, ml.	pH (by Beckman Model H-2 instrument)	Calculated ionic strength, $\mu \times 10^2$
4	30.0	10.0	200.0	10.42	3.35
5	30.0	5.0	200.0	10.42	1.78
6	30.0	0.0	200.0	10.42	0.22

dissociation of the complex on the ionic strength in these cases was small. An outline of the calculation of the ionic strength for solution No. 6, series I, Table 15, is as follows:

$$[SO_4^=] \qquad = 4.56 \times 10^{-4}$$

$$[OH^-] \qquad = 2.51 \times 10^{-4}$$

$$[HSS^=] \qquad = 9.0 \times 10^{-5}$$

$$[Be_x] \text{ not considered} \qquad \text{----}$$

$$[Be(SS)_2^=] \qquad = 2.55 \times 10^{-4}$$

$$[Na^+] \qquad = 2.36 \times 10^{-3}$$

then by definition, from Equation 5

$$\mu = \tfrac{1}{2}\,(18.24 \times 10^{-4} + 2.51 \times 10^{-4} + 3.60 \times 10^{-4} + 40.8 \times 10^{-4} +$$

$$23.63 \times 10^{-4})$$

or $\mu = 0.44 \times 10^{-2}$.

In the other solutions of Series I the molarity of sodium perchlorate present was simply added to the value obtained above for solution No. 6, series I. Series II was treated in an exactly analogous manner to obtain the ionic strengths.

The solutions prepared as indicated in Table
15 were scanned on the Cary instrument at temperatures
of $25 \pm 1°C$. and $30 \pm 1°C$. versus distilled water as
a reference solution. The instrument was not
thermostatted hence it was necessary to control the
temperature in the room to achieve the desired temper-
atures. A thermometer was kept in the sample com-
partment and its indicated temperature compared fre-
quently with that of the room. No appreciable differ-
ences in temperature were observed. The optical den-
sities observed at each of the two temperatures for
each of the two series of solutions are shown in Table
16. The change in concentration brought about by a
$5°C$. difference in temperature would theoretically be
only slightly more than 1 part per 1000. This change
was considered to be insignificant for the present
work hence no corrections of this type were made. It
was of interest to note that the optical density values
at $30°C$. were appreciably smaller than the correspond-
ing values at $25°C$. for the same solutions. This was
the very effect expected because one would predict
that at higher temperatures the complex would be disso-
ciated to a greater extent and this would, of course,

TABLE 16

Optical Densities at 317.0 mμ. of Solutions
Prepared as Indicated in Table 15

Solution No.	Total beryllium molarity x10^4	Optical density at 317.0 mμ. 25 ± 1°C.	Optical density at 317.0 mμ. 30 ± 1°C.
Series I			
1	3.00	2.169	2.144
2	3.00	2.144	2.138
3	3.00	2.150	2.132
4	3.00	2.125	2.123
5	3.00	2.120	2.096
6	3.00	2.043	2.018
Series II			
1	1.50	1.030	1.005
2	1.50	1.032	1.008
3	1.50	1.032	1.001
4	1.50	1.013	0.981
5	1.50	0.992	0.960
6	1.50	0.951	0.919

lead to a lower optical density.

It was assumed that the previously determined values for E_1 of 691, and E_2 of 7.75×10^3, applied to these solutions. This was considered reasonable because these were the values of E_1 and E_2 which had been determined on solutions prepared from the same stock solution of complex and in the presence of sodium perchlorate.

For each solution and temperature in Table 16 values of K' were calculated by substituting the known values into Equations 9' and 8' respectively. Table 17 summarizes the values of K' obtained for each solution at the two temperatures and lists the calculated square roots of ionic strengths for each solution.

Figure 13 is the plot of the values of K' from Table 17 versus the square root of the ionic strength for each of the two temperatures. Since at zero ionic strength the activity coefficient term in Equation 8 becomes equal to 1 it is obvious that at zero ionic strength K and K' become identical. The curves describing K' as a function of the square root of ionic strength in

TABLE 17

Calculated Values of K' for Solutions Described
in Tables 15 and 16

Solution No.	Calculated value of K' x 10^{10} at 25 ± 1°C.	Calculated value of K' x 10^{10} at 30 ± 1°C.	$\sqrt{u}$
Series I			
1	2.14	3.37	0.401
2	3.37	3.76	0.313
3	3.05	4.16	0.259
4	4.61	4.76	0.189
5	4.99	7.07	0.142
6	13.60	17.79	0.066
Series II			
1	2.74	4.75	0.398
2	2.62	4.51	0.310
3	2.62	5.20	0.254
4	4.05	7.53	0.183
5	6.18	10.77	0.133
6	12.41	19.94	0.047

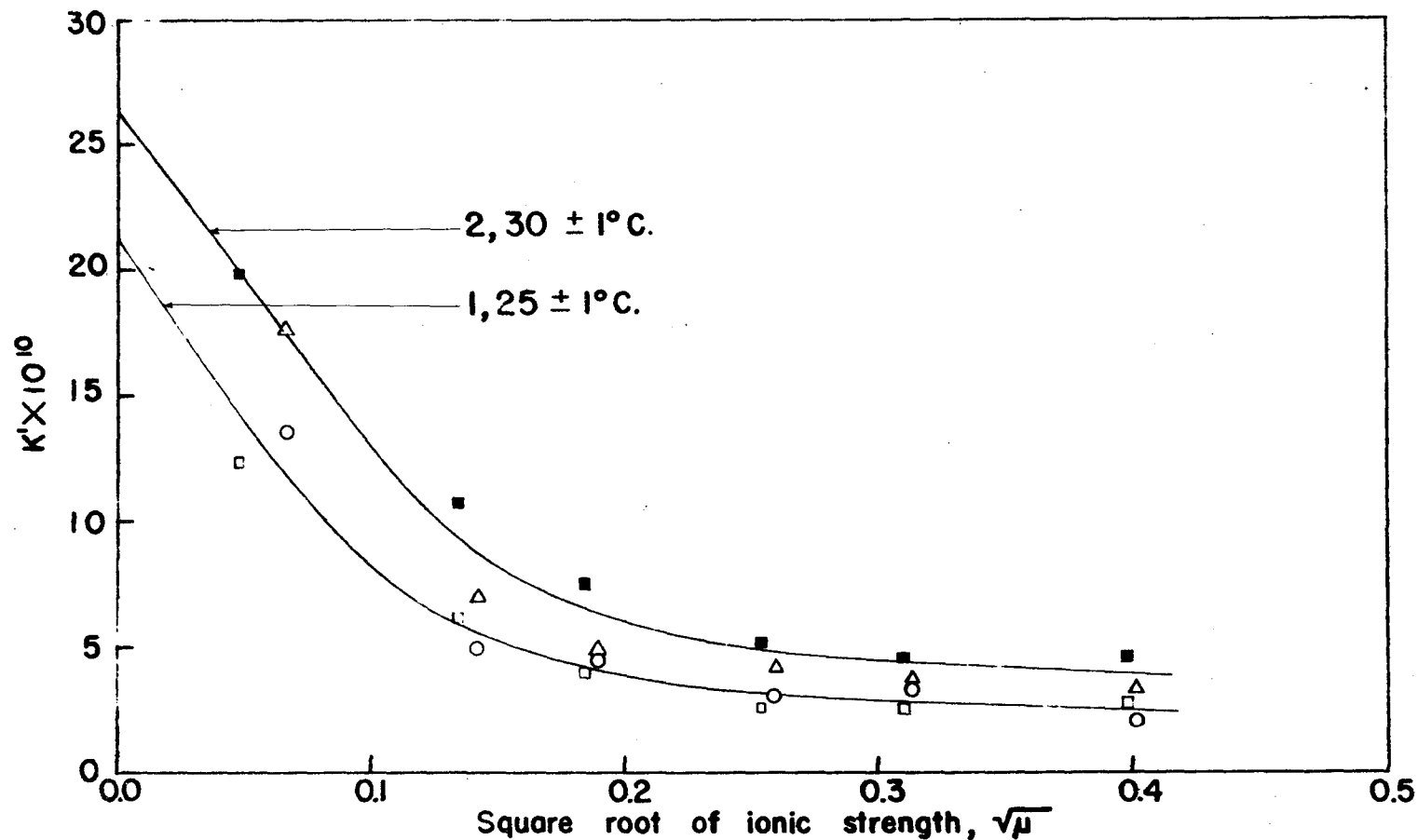Figure 13——Extrapolation of Curves obtained by plotting K' as a function of the square root of ionic strength from data in Table 17 to obtain the true equilibrium constants for the beryllium sulfosalicylate complex at $25 \pm 1°C$ and at $30 \pm 1°C$; Curve 1, 25°C; O, values from solutions of Series I; □, values from solutions of Series II; Curve 2, 3C°C; △, values from solutions of Series I; ■, values from solutions of Series II.

Figure 13 were extrapolated to zero ionic strength to obtain the values for the true equilibrium constant at the two temperatures. At $25 \pm 1°C$. the value obtained for K was about 2.1×10^{-9}. At $30 \pm 1°C$. the value obtained for K was about 2.6×10^{-9}.

It was remembered that the ionic strengths were not accurately known for the points nearest zero ionic strength so it should be stated that there may be considerable relative error in values reported for the true equilibrium constants.

It was of interest to note that very real differences in K' were obtained for a temperature difference of only $5°$. If this difference could be attributed to only the temperature coefficient of the equilibrium under consideration it suggested that a fairly accurate value for the temperature coefficient of the equilibrium constant would be determinable by investigating a range of temperature of only 20 or 30 degrees.

F. Quantitative Effects of pH

It was of interest to examine more closely the effects of pH on solutions of the beryllium-sulfosalicylate complex. The nature of the change in absorption spectra as a function of pH at constant ionic strength was a study which was hoped would indicate the dependence of the concentration of the complex ion on pH.

A fresh 3.00×10^{-3}M stock solution of the complex was prepared by mixing 93.02 ml. of 0.0645M beryllium sulfate from stock solution No. 1 and 114.9 ml. of 0.1044M sulfosalicylic acid. A series of solutions at various pH values was prepared as indicated in Table 18. Ionic strength was kept essentially constant by the addition of 20.0 ml. of 1.00M sodium perchlorate. A series of solutions containing only sulfosalicylate, but of the same total concentration of sulfosalicylate as that in the complex solutions, was prepared as indicated in Table 19. The pH of both sets of solutions was adjusted with sodium hydroxide and measured with Beckman Model G pH meter calibrated at a pH of 4.00 for the acid solutions

TABLE 18

Beryllium-Sulfosalicylate Solutions Used in the
Study of the Quantitative Effects of pH at
Constant Ionic Strength

Solution No.	3.00×10^{-3} M Complex added, ml.	1.00 M Sodium perchlorate added, ml.	Final volume, ml.	Corrected pH (Beckman Model G instrument)
1	20.0	20.0	200.0	1.53
2	20.0	20.0	200.0	2.65
3	20.0	20.0	200.0	3.78
4	20.0	20.0	200.0	4.80
5	20.0	20.0	200.0	6.50
6	20.0	20.0	200.0	6.94
7	20.0	20.0	200.0	7.39
8	20.0	20.0	200.0	7.96
9	20.0	20.0	200.0	8.08
10	20.0	20.0	200.0	8.08

TABLE 18 (continued)

Solution No.	3.00×10^{-3} M Complex added, ml.	1.00 M Sodium perchlorate added, ml.	Final volume, ml.	Corrected pH (Beckman Model G instrument)
11	20.0	20.0	200.0	9.44
12	20.0	20.0	200.0	9.68
13	20.0	20.0	200.0	10.08
14	20.0	20.0	200.0	10.27
15	20.0	20.0	200.0	10.48
16	20.0	20.0	200.0	10.58
17	20.0	20.0	200.0	10.79

TABLE 19

Solutions of Sulfosalicylate Used in the Study of the
Quantitative Effects of pH at Constant Ionic Strength

Solution No.	6.00×10^{-3} M Sulfosalicylate added, ml.	1.00 M Sodium perchlorate added, ml.	Final volume, ml.	Corrected pH (Beckman Model G instrument)
1	20.0	20.0	200.0	1.53
2	20.0	20.0	200.0	2.77
3	20.0	20.0	200.0	3.80
4	20.0	20.0	200.0	5.32
5	20.0	20.0	200.0	8.24
6	20.0	20.0	200.0	9.28
7	20.0	20.0	200.0	9.68
8	20.0	20.0	200.0	10.07
9	20.0	20.0	200.0	10.78

and at a pH of 10.00 for the alkaline solutions. In the alkaline region measurements were made with both the conventional glass electrode and the Type E electrode, the sodium ion correction being made in each case and the average of the values thus obtained taken as best representing the true pH of the solutions. In no cases were differences of more than 0.2 pH unit obtained with the two different electrodes.

The solutions from Tables 18 and 19 were all scanned on the Cary instrument using 1.00 cm. cells and a distilled water reference solution. The temperature was $25 \pm 1°C$. The optical densities observed at 317.0 mμ. for the two series of solutions are recorded in Table 20. The plot of the optical densities for each set of solutions as a function of pH is shown in Figure 14. At a pH of 1.53 it was obvious that the absorption spectra indicated no complex formation. However, at a pH of ca. 2.5 complex formation began to be appreciable and continued to increase with increasing pH (curve 1) up to a pH of ca. 8.5 where it evidently reached a maximum concentration. Above a pH of ca. 10.6 this maximum concentration of complex began to be destroyed, presumably due to the formation

TABLE 20

Optical Densities at 317.0 mμ. by the Cary Instrument
for Solutions Described in Tables 18 and 19

Table 18 solution No.	Total beryllium, $M \times 10^4$	Optical density at 317.0 mμ.	Table 19 solution No.	Total sulfosalicylate, $M \times 10^4$	Optical density at 317.0 mμ.
1	3.00	0.850	1	6.00	0.850
2	3.00	0.678	2	6.00	0.562
3	3.00	0.977	3	6.00	0.423
4	3.00	1.258	4	6.00	0.404
5	3.00	1.808	5	6.00	0.402
6	3.00	1.908	6	6.00	0.400
7	3.00	2.102	7	6.00	0.400
8	3.00	2.178	8	6.00	0.410
9	3.00	2.140	9	6.00	0.450
10	3.00	2.160			
11	3.00	2.184			

TABLE 20 (continued)

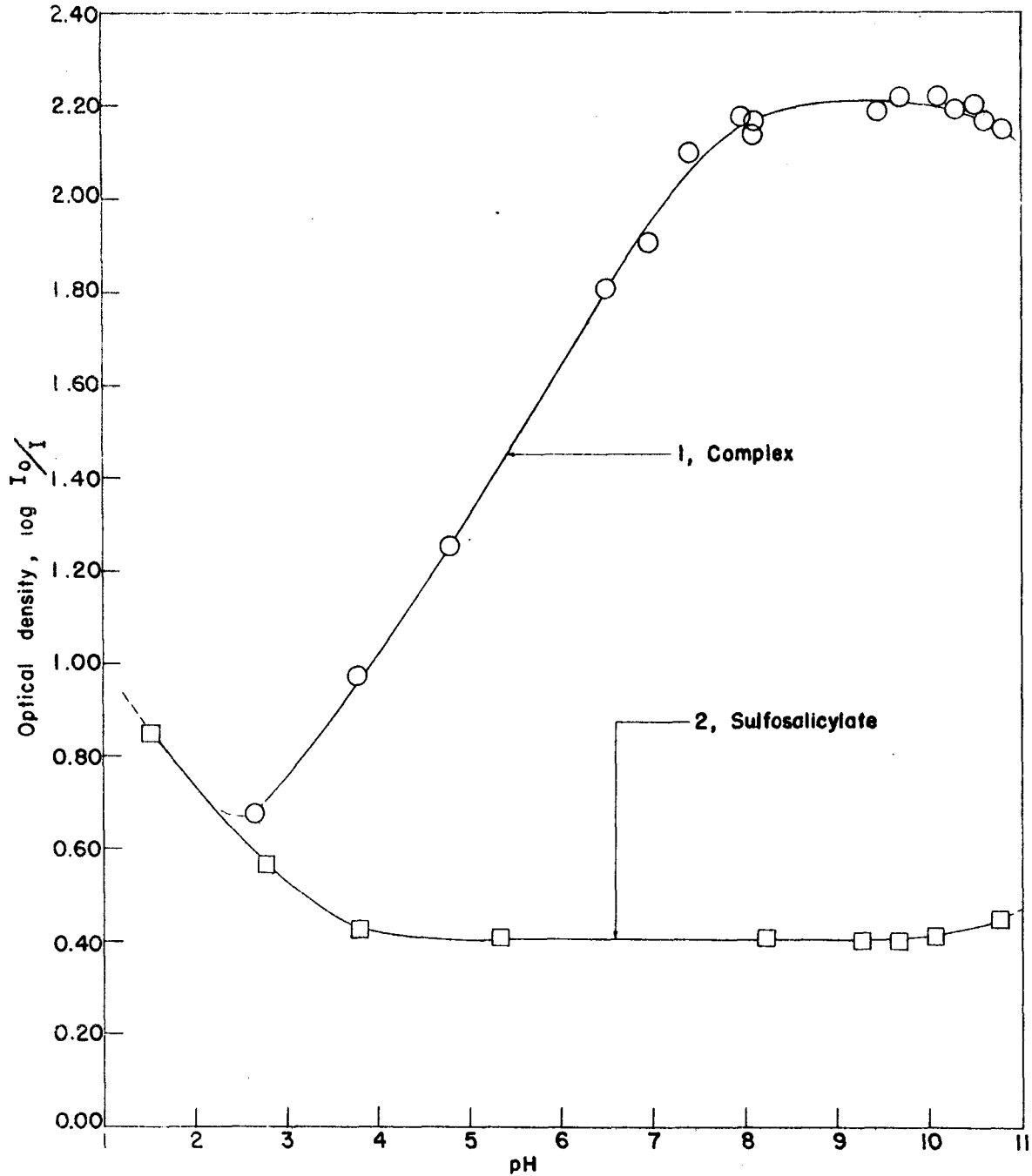| Table 18 solution No.	Total beryllium, $M \times 10^4$	Optical density at 317.0 mμ.	Table 19 solution No.	Total sulfosalicylate, $M \times 10^4$	Optical density at 317.0 mμ.
12	3.00	2.220			
13	3.00	2.220			
14	3.00	2.190			
15	3.00	2.200			
16	3.00	2.165			
17	3.00	2.152			

Figure 14 —— Variation with pH of the optical density at 317.0 mμ of solutions 6✕10⁻³ M in sulfosalicylate (Curve 2) and 3✕10⁻⁴ M (total) in the beryllium — sulfosalicylate complex (Curve 1) ; ○, experimental points from Tables 18 and 20 ; ☐ , experimental points from Tables 19 and 20.

of appreciable quantities of a new species of beryl-
lium. It should be remembered that these ranges of
pH were obtained for a constant ionic strength of
0.10 and the particular concentrations of beryllium
and sulfosalicylate used in these solutions; concen-
trations appreciably different from these would be
expected to give curves somewhat different in char-
acter than those in Figure 14 because of contributions
of the equilibria that are involved. The nature of
curve 1, Figure 14, between a pH of 3 and 8 was quite
smooth in contrast to the nature of curve 2, Figure
5, but it must be remembered that the former was
determined at constant ionic strength and at very care-
fully determined pH values, while the latter was
determined at an appreciably different concentration
of complex with no attempt made to keep the ionic
strength constant and only moderate care used in the
adjustment and measurement of pH. However, the general
appearances of the curves in Figures 14 and 5 were
quite similar.

It was hoped that it might be possible to
explain the slope of curve 1, Figure 14, between the
pH where no complex was present and the pH where

complex formation was at a maximum. A number of
factors may contribute to the slope of this curve.
It would be expected that due to the rather complica-
ted amphoteric nature of beryllium more than one
species of beryllium ion would be present in apprecia-
ble quantities through such a broad range of pH even
in the absence of sulfosalicylate. In the presence
of sulfosalicylate there is the additional complicating
possibility that more than one beryllium-sulfosali-
cylate complex ion may be present in appreciable con-
centrations through this range of pH. Examples of
such complexes theoretically capable of existence
are, the one in which one of the hydroxylic protons
remains intact, $Be(HSS)(SS)^{=}$, the one in which both
hydroxylic protons remain intact, $Be(HSS)_2^{=}$, and the
one which was believed to be present alone through
the optimum pH range, $Be(SS)_2^{\equiv}$. Conceivably other
sulfosalicylate complexes might also exist.

A wide variety of attempts were made to explain
the slope of curve 1, Figure 14, but no satisfactory
explanation was found. It was believed that too
little was known about the species of ions present

along the sloping part of the curve to make any
reasonable assumptions regarding it. In fact, the
free sulfosalicylate ion, $HSS^=$, was the only species
which could be predicted with a good degree of
assurance.

From the analytical standpoint it was neces-
sary to determine the importance of the adjustment of
pH in those solutions in which the determination of
the optical density of solutions containing beryllium
and sulfosalicylate was to be taken as the criterion
of beryllium concentration.

In practice it is common to add an excess,
usually large, of the complexing agent so that due to
mass action effects, the metal ion being determined
is essentially all in the form of the complex. When
this is done the plot of the optical density versus
concentration of the metal usually gives a straight
line and Beer's Law is then said to apply to the
system. If the complex has a large dissociation con-
stant then it sometimes becomes impossible to add
sufficient of the complexing agent to force all the
metallic ions into the form of the complex,

particularly for the higher concentrations of the

metal. Hence at higher concentrations of the metal

lower optical density values are observed than would

otherwise be true and the curve of optical density

versus concentration of metal drops off with increas-

ing metal concentration. Under these conditions

Beer's Law is said to not apply to the system. This

is only one of several possible reasons for apparent

deviations from Beer's Law. In the most nearly pure

sense it is doubtful if there are any real deviations

from Beer's Law.

In the case of the beryllium-sulfosalicylate

complex it is not possible to add very large excesses

of sulfosalicylate for moderate concentrations of

beryllium because sulfosalicylate does absorb some-

what at the wave length of interest, 317.0 mu. It

was thus somewhat arbitrary to decide on just what

concentration of sulfosalicylate to choose in establish-

ing a method of analysis. If solutions are read versus

distilled water as a reference solution it frequently

happens that the excess of reagent contributes such a

large fraction of the observed optical density that

there is an appreciable sacrifice of sensitivity,
particularly for low beryllium concentrations. An
alternative method is to use the solution of the
reagent itself as a reference solution, in which case
it is necessary to widen the slit of the spectrophoto-
meter to permit radiation of sufficient intensity to
pass through the reference solution. The latter
method was chosen in the present work. The best
operating range for the Beckman spectrophotometer
appeared to be from about 0.0 to slightly over 1.0
optical density units and the sulfosalicylate concen-
tration chosen was calculated to give optical density
readings in this region with an appreciable excess of
sulfosalicylate present over that required by the
stoichiometry of the formation of the complex. The
total concentration of sulfosalicylate chosen to be
present in the final volume of solution was 5.00×10^{-4}M.
This was all entirely arbitrary.

For the reasons given above the final total
concentration of sulfosalicylate was chosen as
5.00×10^{-4}M. It was for this concentration that exami-
nation of the limits of pH adjustment for the actual

determination of beryllium were made. Solutions of
the composition and pH shown in Table 21 were prepared
as indicated, the pH being adjusted by means of dilute
reagent-grade sodium hydroxide solution. The pH
values were determined using the Beckman Model M
instrument equipped with a special Type E electrode
to minimize sodium ion errors. The reference solu-
tion from Table 21 was used as a blank to give the
optical density values at 317.0 mμ. on the Beckman
instrument. Four concentrations of beryllium were
examined, 1.00×10^{-5}M, 1.00×10^{-4}M, 2.00×10^{-4}, and
2.50×10^{-4}M, so that most of the determinable range
was included. Figure 15 graphically represents the
dependence of observed optical density on the pH. So
long as the pH was between 9.2 and 10.8 the optical
densities remained within 0.01 optical density units
of each other, except in the case of the most dilute
beryllium solution. In the case of very dilute beryl-
lium solutions the pH should be adjusted to between
9.2 and 10.5 to give a range of no more than 0.01
optical density units. In general, for the best
duplication it would be advisable to keep the solutions
as near the same pH as possible but departures of no

TABLE 21

Effect of pH on Observed Optical Densities of Solutions
of Beryllium as a Function of the Excess of Sulfo-
salicylate (Beckman Spectrophotometer)

Solution	1.00×10^{-2}M sulfosali-cylic acid, ml.	1.00×10^{-3}M beryllium sulfate, ml.	Final volume, ml.	Corrected pH (Beckman Model M instrument)	Optical density at 317.0 mμ.
Reference	10.0	----	200.0	9.87	-----
I 1	10.0	2.00	200.0	9.28	0.067
I 2	10.0	2.00	200.0	9.70	0.068
I 3	10.0	2.00	200.0	10.34	0.075
I 4	10.0	2.00	200.0	10.82	0.081
I 5	10.0	2.00	200.0	11.15	0.098
II 1	10.0	20.0	200.0	9.42	0.620
II 2	10.0	20.0	200.0	9.62	0.632
II 3	10.0	20.0	200.0	10.12	0.628

TABLE 21 (continued)

| Solu-tion	1.00×10^{-2} M sulfosali-cylic acid, ml.	1.00×10^{-3} M beryllium sulfate, ml.	Final volume, ml.	Corrected pH (Beckman Model M instrument)	Optical density at 317.0 mµ.
II 4	10.0	20.0	200.0	10.67	0.632
II 5	10.0	20.0	200.0	11.20	0.640
III 1	10.0	40.0	200.0	9.22	1.145
III 2	10.0	40.0	200.0	9.75	1.145
III 3	10.0	40.0	200.0	10.40	1.155
III 4	10.0	40.0	200.0	10.77	1.150
III 5	10.0	40.0	200.0	11.17	1.115
IV 1	10.0	50.0	200.0	9.36	1.295
IV 2	10.0	50.0	200.0	9.88	1.290
IV 3	10.0	50.0	200.0	10.33	1.300
IV 4	10.0	50.0	200.0	10.78	1.290
IV 5	10.0	50.0	200.0	11.13	1.280
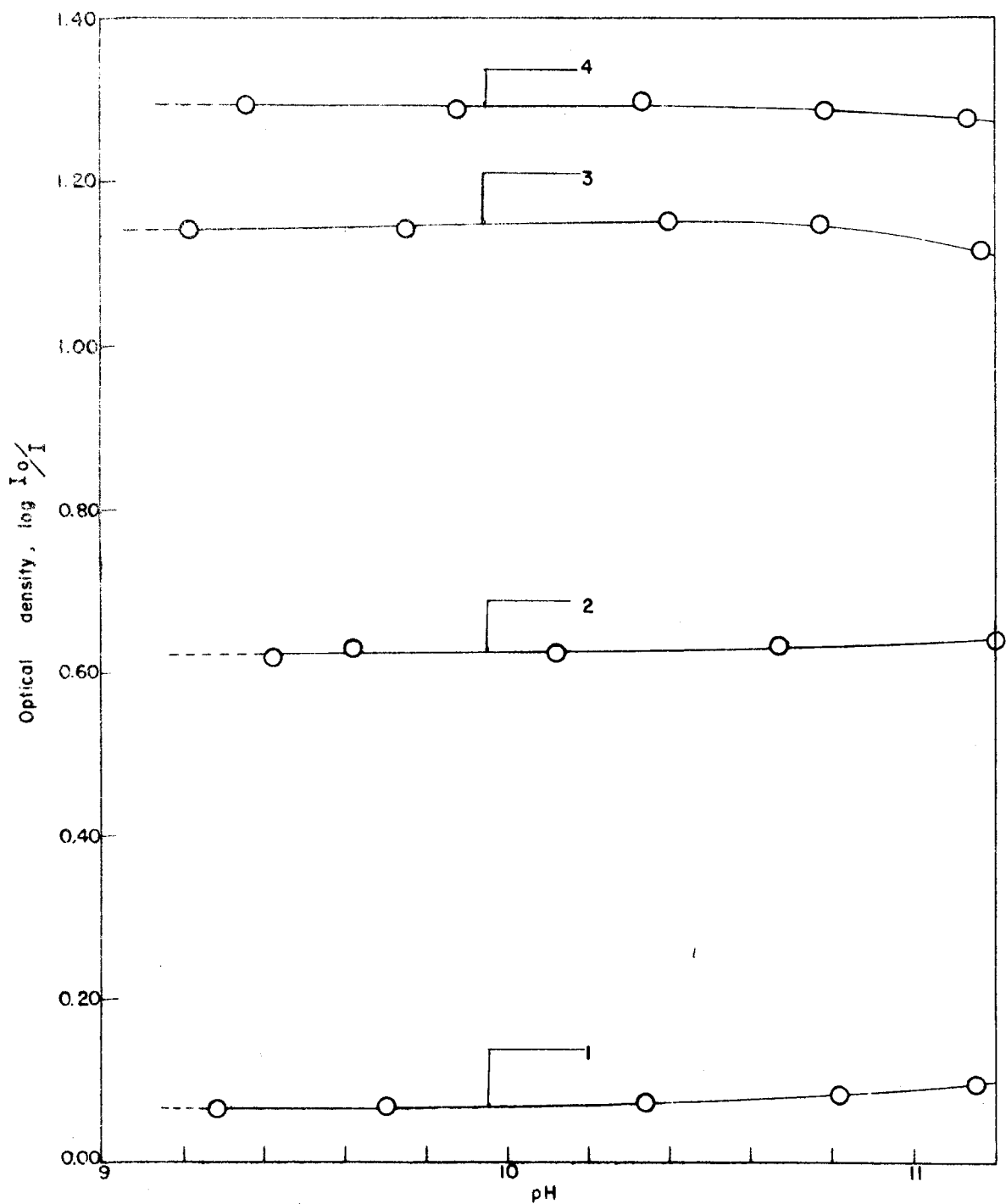
Figure 15 —— Effect of pH on observed optical densities at constant sulfosalicylate concentration for various beryllium concentrations as described in Table 21 and using the Beckman instrument ; Curve 1, 1.00×10^{-5} M beryllium ; Curve 2, 1.00×10^{-4} M beryllium ; Curve 3, 2.00×10^{-4} M beryllium ; Curve 4, 2.50×10^{-4} M beryllium.

more than $\pm$ 0.005 optical density units were observed
for the ranges indicated above.

G. Elimination of Aluminum Interference

It was hoped that it would be possible to deter-
mine small amounts of beryllium in the presence of
quite large amounts of aluminum by measuring the
absorption of the beryllium-sulfosalicylate complex
at 317.0 mμ. Qualitatively both sulfosalicylic acid
and ethylenediaminetetraacetic acid, when present in
sufficient excess, prevent the precipitation of
aluminum as the hydrated oxide. Sulfosalicylic acid
prevents the precipitation of beryllium as the
hydrated oxide even when the mole ratio of sulfosali-
cylic acid to beryllium is only 2 to 1 but qualitatively,
at least, ethylenediaminetetraacetic acid does not pre-
vent the precipitation of beryllium as the hydrated
oxide. The possibility of using the ethylenediamine-
tetraacetic acid to prevent aluminum interference in
the sulfosalicylate method for beryllium was at once
apparent. It was hoped that the aluminum complex with

ethylenediaminetetraacetic acid would be quite stable
compared to aluminum complex with sulfosalicylate and
that no appreciable absorption by this complex would
occur at 317.0 mμ.

It was necessary to adopt a systematic procedure
of analysis using specified amounts of aluminum and
other reagents to accommodate some chosen range of
beryllium concentration. After some preliminary work
it was somewhat arbitrarily decided to standardize
upon the use of 0.2000 g. of aluminum, 50.0 ml. of
0.50M ethylenediaminetetraacetic acid, 10.0 ml. of
$1.00x10^{-2}$M sulfosalicylic acid and a final volume of
200.0 ml. for the spectrophotometric examination.
Under these conditions the mole ratio of ethylene-
diaminetetraacetic acid to aluminum is approximately
3.4 to 1.0 and amounts of beryllium up to about 0.45
mg. are determinable. This much beryllium is equiva-
lent to approximately 0.22 per cent beryllium on the
aluminum basis. With $9.0x10^{-3}$ mg. of beryllium an
optical density change of about 0.034 is observed;
this is equivalent to approximately 0.0045 per cent
beryllium in aluminum. Other conditions could have

been chosen to accommodate other concentrations of
beryllium in aluminum but the ones chosen were considered
to cover a very useful range.

It was necessary to complex the aluminum for at
least two reasons. In the absence of a suitable com-
plexing agent the aluminum simply precipitates at the
pH demanded by the analysis because sulfosalicylate is
used in very small amounts relative to the aluminum
concentration. This precipitation could not be toler-
ated. The fact that aluminum is complexed by sulfo-
salicylate alters the spectral properties of the solu-
tions at the wave length of interest and makes the
elimination, or at least the minimization, of aluminum
complexation by sulfosalicylate necessary.

A series of solutions involving the various
materials of interest was prepared as described in
Table 22. In this case a filtered solution of concen-
trated reagent-grade ammonium hydroxide was used to
adjust the pH of the solutions. The reasons for this
were that, in general, solutions of ammonium hydroxide
are somewhat more nearly pure than those of the
hydroxides of the alkali metals and further that the

TABLE 22

Composition of Solutions for Spectrophotometric Examination
in Attempt to Eliminate Aluminum Interference by
Ethylenediaminetetraacetic Acid

Solu-tion No.	0.2287M Aluminum sulfate added, ml.	1.00×10^{-3}M Beryllium sulfate added, ml.	0.50M Ethyl-enediamine-tetraacetic acid, ml.	1.00×10^{-2}M Sulfosali-cylic acid, ml.	Final volume, ml.	pH (Beck-man Model H-2) instrument
1	----	----	50.0	----	200.0	10.05
2	32.4	----	50.0	----	200.0	10.04
3	----	----	50.0	10.0	200.0	10.07
4	32.4	----	50.0	10.0	200.0	10.06
5	----	25.0	50.0	10.0	200.0	10.08
6	32.4	25.0	50.0	10.0	200.0	10.08
7	----	----	----	10.0	200.0	10.28
8	----	25.0	----	10.0	200.0	10.20

pH is more conveniently adjusted with the ammonia
solutions particularly when ethylenediaminetetraace-
tic acid is present to supply its buffering action.
After their preparation the solutions described in
Table 22 were scanned on the Cary instrument at a
temperature of 25 ± 1°C. using 1.000 cm. quartz cells
and a distilled water reference solution. The absorp-
tion spectra obtained are shown in Figure 16. Curve
1, Figure 16, shows that solutions 0.125M in ethylene-
diaminetetraacetic acid at a pH of 10.05 absorb only
in amounts of about 0.01 optical density units in the
wave length range of 290 to 350 mμ. At 317.0 mμ. the
optical density was 0.009. Curve 2, Figure 16, shows
that solutions 0.125M in ethylenediaminetetraacetic
acid and containing 0.200 g. of aluminum per 200.0 ml.
of solution at a pH of 10.04 also absorb only in
amounts of about 0.01 optical density units over the
same range of wave length. At 317.0 mμ. the optical
density was 0.012. Quite obviously the aluminum-
ethylenediaminetetraacetate complex does not absorb at,
or near, 317.0 mμ., the wave length of interest.

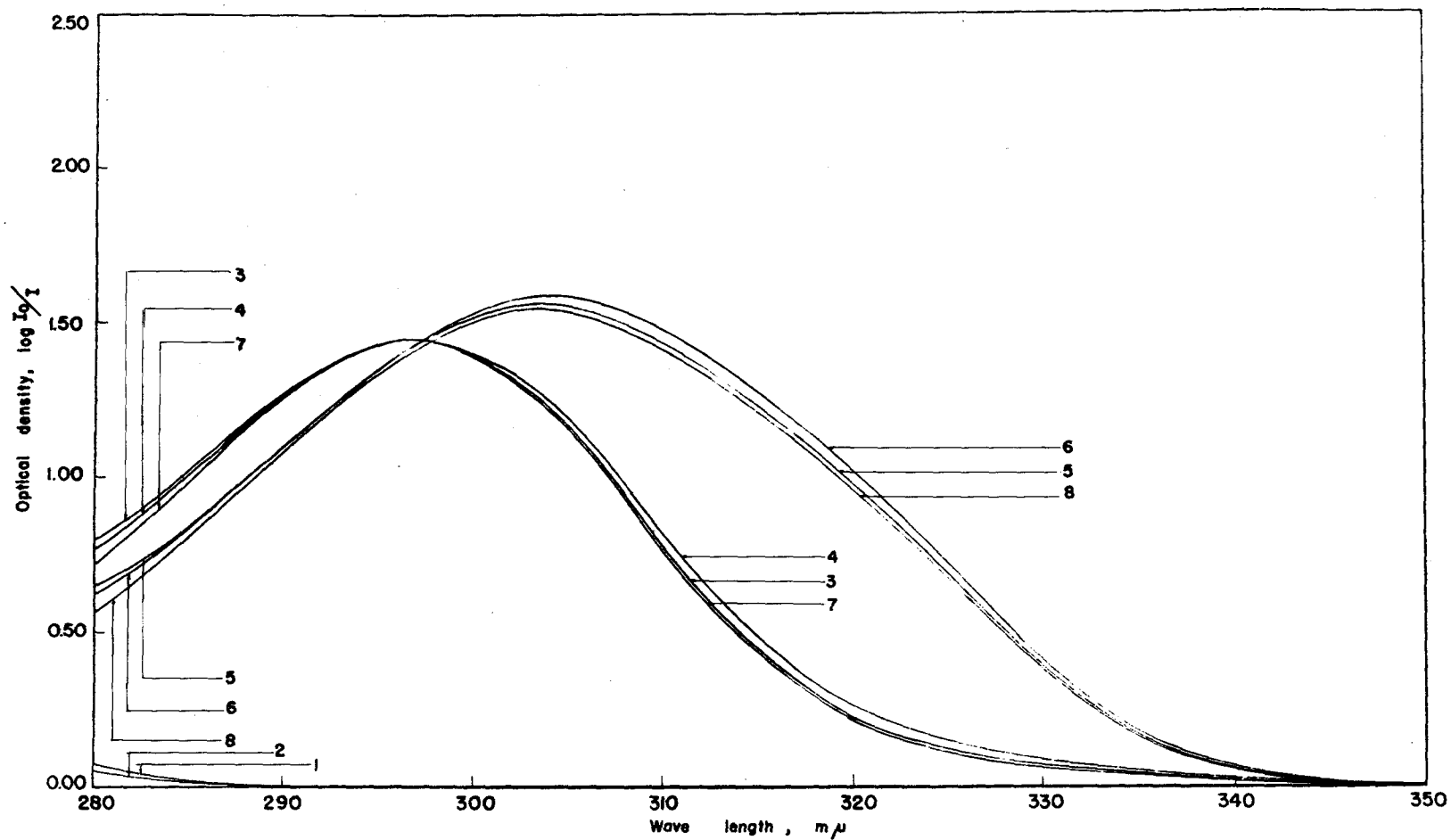Curve 3, Figure 16, shows the absorption due to

Figure 16 — Absorption spectra of various solutions prepared as described in Table 22 using the Cary instrument and a distilled water reference solution ; Curves 1,2,3,4,5,6,7, and 8 correspond to solutions 1,2,3,4,5,6,7, and 8 respectively, in Table 22.

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a solution 0.125M in ethylenediaminetetraacetic acid and 5.00×10^{-4}M in sulfosalicylic acid at a pH of 10.07. At 317.0 mμ. the optical density was 0.341. Curve 7, Figure 16, which represents absorption due to a solution 5.00×10^{-4}M in sulfosalicylic acid at a pH of 10.28, was virtually identical with curve 3 and differed from it by no more than 0.010 optical density units anywhere in the wave length range from 290 to 350 mμ. The optical density observed at 317.0 mμ. for curve 7 was 0.338 as compared with 0.341 for curve 3. This comparison showed that the presence of ethylenediaminetetraacetic acid did not appreciably interfere with the characteristic absorption of sulfosalicylate solutions at or near 317.0 mμ., the wave length of interest.

Curve 4, Figure 16, shows the absorption of a solution 5.00×10^{-4}M in sulfosalicylic acid, 0.125M in ethylenediaminetetraacetic acid, and containing 0.2000 g. of aluminum at a pH of 10.06. This curve does differ appreciably, 0.045 optical density units, from curve 3 and this difference was presumed to be due to the fact that aluminum, or an aluminum solution

contaminant, was complexed by sulfosalicylate and did cause this much interference. This phenomenon was later examined in more detail. The optical density observed for curve 4 at 317.0 mμ. was 0.386.

Curves 5, 6, and 8, Figure 16, show the changes in optical density brought about when solutions exactly similar to solutions Nos. 3, 4, and 7 respectively, Table 22, are made 1.25×10^{-4} in beryllium. The optical densities at 317.0 mμ. for curves 5, 6, and 8 were 1.133, 1.178, and 1.122. These represented increases in optical densities over those of solutions Nos. 3, 4, and 7, of 0.792, 0.792, and 0.784 respectively. It was thus shown that the increase in optical density for the constant amount of beryllium added was essentially the same in the presence of aluminum and ethylenediaminetetraacetic acid as it was in their absence. The reason for the observed increase in optical density due to the presence of aluminum, even when complexed by an excess of ethylenediaminetetra-acetic acid, remained to be determined.

It was known that ferric iron formed a quite stable complex with sulfosalicylate (26) hence the

choice of the aluminum source was made with particular care with respect to iron content. A series of reagent-grade aluminum salt hydrates were examined colorimetrically with sulfosalicylate. The one which contained the least amount of iron, as indicated by the color with sulfosalicylate, was chosen as the source of aluminum. However, the use of this material still gave an interference similar to that shown in Figure 16, i.e., the presence of 0.2000 g. of aluminum gave from 0.03 to .06 optical density units higher readings, depending on the beryllium concentration, than corresponding samples containing no aluminum. Aluminum chosen from various reagent salt hydrates did give slightly varying degrees of interference, but always the interference was in the direction of higher optical densities. It was noted that those samples of aluminum which did contain more iron, as indicated colorimetrically, did give more interference, that is, the degree of interference at least increased with increasing iron contamination. This fact suggested that it was quite possible that iron was causing the high optical density readings in all cases.

Accordingly a solution of the most nearly possible iron-free material was prepared. This material was a commercially purchased bottle of the ammonium alum, $Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$, and appeared to be much more nearly free of iron than the other reagent-grade aluminum salts tested. A small amount of hydrated aluminum oxide was precipitated from the solution by the addition of reagent grade ammonium hydroxide. It was hoped that by so-doing most of the small amount of iron present would be precipitated with the aluminum and thus be effectively removed from solution. The solution was filtered and the filtrate acidified by the addition of a little sulfuric acid. On standing, a very large fraction of the original alum crystallized from solution, so much that a prohibitively large volume of the remaining solution would have been required to give 0.200 g. of aluminum. It was presumed that the common-ion effect of the addition of the ammonium hydroxide in the precipitation process and subsequent acidification with sulfuric acid had reduced the solubility of the alum to far below its normal solubility in water. This solution was discarded.

A second sample of the alum was ignited in a
large Vycor beaker over a Meker burner to drive off
a large portion of the ammonia and sulfuric acid.
The residue was then leached with hot distilled water
and the solution filtered. A little of the aluminum
was again precipitated as before, except sodium
hydroxide was used as precipitant, and the solution
was again filtered. Attempts to use this solution
as the source of aluminum in testing for interferance
in the beryllium determination showed that in all
cases a precipitate was obtained in the final solution
regardless of how much ethylenediaminetetraacetic acid
was used in complexing the aluminum. Finally, it was
discovered that by boiling the acidified stock solu-
tion of aluminum, a precipitate was formed. Presum-
ably a colloidal dispersion of aluminum oxide had
been formed in the original ignition treatment and
this had been coagulated by the treatment used in the
preparation of the solutions for spectrophotometric
examination.

The entire stock solution was boiled for several
hours and the solution again filtered. This solution

gave no precipitate when used in testing for aluminum interference. Colorimetric determination of iron by the use of o-phenanthroline indicated that less than half as much iron per g. of aluminum was present in this solution as was present in solutions of the original alum. It was believed that this solution could not possibly contain sufficient iron to give appreciable interference in the determination of beryllium by the sulfosalicylate method, or at worst that the observed interference should be markedly reduced. The aluminum stock solution was standardized gravimetrically by the basic succinate method of Willard and Tang (27) and found to contain 0.006167 g. aluminum per ml. at 24°C. It was thus necessary to use 32.43 ml. of this stock solution to obtain 0.2000 g. of aluminum.

Table 23 lists the composition of various solutions prepared to test the interference of aluminum using the aluminum stock solution just described. The pH was adjusted with reagent grade sodium hydroxide and was measured using the Beckman Model H-2 pH meter, the proper sodium ion corrections being made.

The optical densities were read on the Beckman instrument at 317.0 mμ. using 0.998 cm. cells and the blank solution as a reference.

The beryllium concentration for each solution in Table 23 was converted to parts per million beryllium on the aluminum basis. In Figure 17 is plotted the observed optical densities from Table 23 versus parts per million beryllium on the basis of a 0.2000 g. sample of beryllium. It was obvious that those solutions containing aluminum were appreciably higher in optical density than the ones in which no aluminum was present. It was of further interest to note that the increase in optical density due to the presence of aluminum became smaller with increasing beryllium concentration. This is the effect that one would expect from mass action considerations.

It was now considered almost certain that aluminum itself, not a contaminant, was causing the increase in optical density values. However, to confirm this fact a sample of pure aluminum metal, kindly supplied by Mr. J. R. Churchill of the Aluminum Company of America, was dissolved in dilute reagent-

TABLE 23

Composition of Solutions Used in Testing for Aluminum
Interference at Various Beryllium Concentrations

Solu-tion No.	1.00×10^{-2}M Beryllium sulfate, ml.	0.2287M Alumi-num sul-fate, ml.	0.50M Ethyl-enediamine-tetraacetic acid, ml.	1.00×10^{-2}M Sulfosali-cylic acid, ml.	Final volume, ml.	Final pH.	Optical density at 317.0 mμ.
Blank	0.00	-----	50.0	10.00	200.0	10.50	-----
1	0.10	32.43	50.0	10.00	200.0	10.35	0.084
2	0.10	-----	50.0	10.00	200.0	10.56	0.034
3	0.30	32.43	50.0	10.00	200.0	10.39	0.147
4	0.30	-----	50.0	10.00	200.0	10.62	0.102
5	0.50	32.43	50.0	10.00	200.0	10.36	0.208
6	0.50	-----	50.0	10.00	200.0	10.65	0.165
7	1.00	32.43	50.0	10.00	200.0	10.35	0.368
8	1.00	-----	50.0	10.00	200.0	10.65	0.328
9	2.00	32.43	50.0	10.00	200.0	10.43	0.668

TABLE 23 (continued)

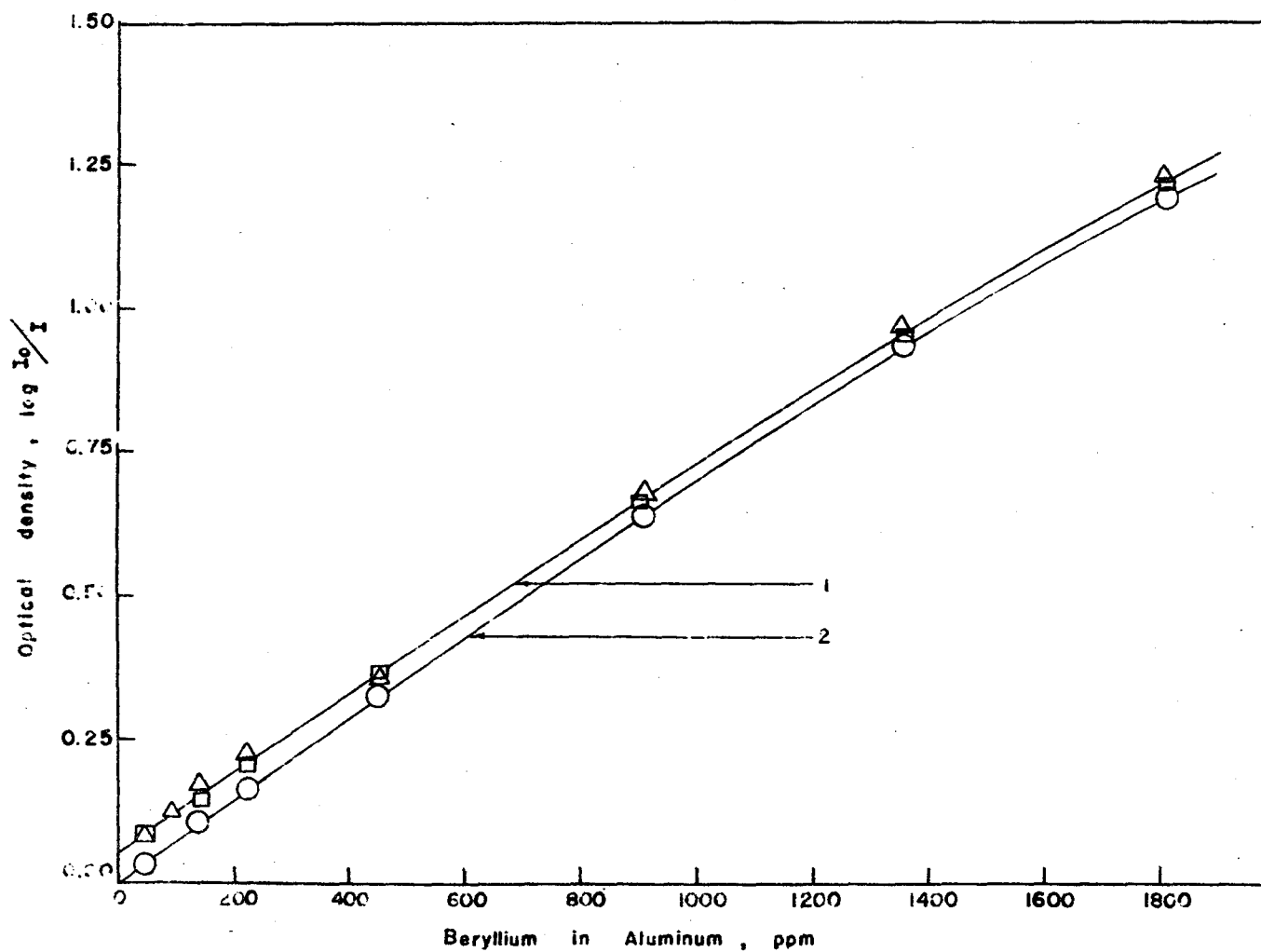| Solution No.	1.00×10^{-2}M Beryllium sulfate, ml.	0.2287M Aluminum sulfate, ml.	0.50M Ethylenediaminetetraacetic acid, ml.	1.00×10^{-2}M Sulfosalicylic acid, ml.	Final volume, ml.	Final pH.	Optical density at 317.0 mµ.
10	2.00	-----	50.0	10.00	200.0	10.60	0.642
11	3.00	32.43	50.0	10.00	200.0	10.36	0.956
12	3.00	-----	50.0	10.00	200.0	10.60	0.938
13	4.00	32.43	50.0	10.00	200.0	10.34	1.22
14	4.00	-----	50.0	10.00	200.0	10.58	1.19

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Figure 17 —— Optical densities observed at 317.0 mμ using the Beckman instrument for various concentrations of beryllium as indicated in Table 23; □, Curve 1, 0.2000 g purified aluminum present; ○, Curve 2, no aluminum present; △, 0.2000g aluminum from Aluminum Company of America.

grade sulfuric acid, and examined in a manner similar
to that of the solutions in Table 23. The optical
density values for this aluminum are shown in Figure
17 and correspond quite closely to the values observed
for the purified aluminum solution prepared by the
author. It was then considered certain that the rather
small increases in optical density values were due to
aluminum itself. It should be remarked that the
aluminum obtained from Mr. Churchill did give slightly
higher values than the purified aluminum solution
prepared by the author. A possible reason for this
may have been that a little aluminum oxide may have
been colloidally dispersed in the former during the
dissolution of the metal and thus caused slightly
high readings; a faint turbidity did develop on long
standing in the solutions prepared for spectrophoto-
metric examination.

It should be added that Mr. Churchill indicated
that the aluminum metal supplied by him was the most
nearly pure aluminum metal currently available. The
spectrographic impurities in the metal reported by
Mr. Churchill were: copper, 0.0004 per cent; iron,

0.0006 per cent; silicon, 0.0016 per cent; manganese, 0.001 per cent; magnesium, 0.0012 per cent; sodium, 0.0005 per cent; beryllium, not detected. The author believed that this metal adequately met the purity specifications required for confirming the nature of the aluminum interference.

Although the aluminum interference was not completely removed by complexation with ethylenediamine-tetraacetic acid it was reduced to a very small amount. At most, under the conditions stipulated, the interference was ca. 0.05 optical density units. In order to eliminate errors due to the presence of aluminum it is only necessary to add approximately the same amount of aluminum to the beryllium standards. A difference of 20 per cent in the aluminum content should bring about only ca. 0.01 difference in the optical density observed. For the most accurate work, particularly in very low beryllium concentrations, the aluminum content of samples and standards should be more nearly equivalent. As a matter of convenience actual beryllium concentrations in solution, rather than parts per million beryllium on the aluminum basis, may be

plotted along the abscissa in Figure 17.

H. Interferences

It was of interest to establish the amount of interference which diverse ions would produce in the determination of beryllium in aluminum by the proposed sulfosalicylate method. It had been decided that the recommended procedure would use 0.2000 g. of aluminum and it was arbitrarily decided that tests for interferences by various cations would be made at two concentrations of beryllium, one moderately low and the other moderately high, with 2.0 milligrams, or 1.0 per cent, of the contaminating cation present.

The contaminating cations chosen were those of sodium, potassium, copper, magnesium, calcium, zinc, strontium, cadmium, barium, aluminum, lanthanum, cerium, titanium, zirconium and hafnium together, tin, lead, arsenic, antimony, chromium, manganese, iron, cobalt, and nickel. It was somewhat superfluous to include sodium and aluminum because these had

been exhaustively examined but they were included in
the tests. In general, a 1.00M stock solution of each
of the contaminating ions was prepared and a volume-
tric dilution of each of these stock solutions was
made to give solutions containing 0.0010 g. per ml.
of each of the cations desired. In each case 2.00
ml. of each of the latter solutions was added to each
of the sample solutions of beryllium and aluminum to
give the equivalent of 1.0 per cent of the contami-
nating cation on the aluminum basis. The sources
chosen for the cations were not primary standard, in
most cases, but were definite crystalline compounds
of reagent-grade purity. The 1.00M solutions were
prepared by weighing the proper quantity of the com-
pound, without drying, to give 250.0 ml. of the
1.00M solution, dissolving in water or appropriate
acid or alkali, and diluting to 250.0 ml. The rela-
tive errors brought about by the choice of cation
sources and methods of preparation of the solutions
were not considered important for the type of study
proposed. The source and method of preparation of
each stock solution is described below.

Sodium. The source was reagent-grade sodium chloride and the solution was prepared by dissolution in distilled water.

Potassium. The source was reagent-grade potassium chloride and the solution was prepared by dissolution in distilled water.

Copper. The source was reagent-grade copper sulfate pentahydrate and the solution was prepared by dissolution in distilled water.

Magnesium. The source was, dried, reagent-grade magnesium sulfate and the solution was prepared by dissolution in distilled water.

Calcium. The source was reagent-grade calcium carbonate and the solution was prepared by dissolving in a slight excess of reagent-grade hydrochloric acid and diluting with distilled water.

Zinc. The source was pure zinc wire (99.99
per cent) which was dissolved in a
slight excess of reagent-grade
hydrochloric acid and diluted with
distilled water.

Strontium. The source was reagent-grade
strontium chloride hexahydrate and
the solution was prepared by disso-
lution in distilled water.

Cadmium. The source was reagent-grade cad-
mium chloride with $2\frac{1}{2}$ molecules of
water of crystallization. The
solution was prepared by dissolu-
tion in distilled water.

Barium. The source was reagent-grade barium
chloride and the solution was pre-
pared by dissolution in distilled
water.

Aluminum. A previously prepared 1.00M solu-
tion was used. This solution had
been prepared from reagent-grade

aluminum sulfate octadecahydrate and
had been analysed gravimetrically
by the basic succinate method.

Lanthanum. The source was not reagent-grade
in character but was the best com-
mercially available lanthanum oxide.
The solution was prepared by dis-
solving the oxide in a slight excess
of reagent-grade hydrochloric acid
and diluting with distilled water.

Cerium. The source was a reference purity
grade of ammonium hexanitratocerate.
The solution was prepared by dis-
solving the salt in distilled water
containing 10.0 ml. of concentrated
reagent-grade nitric acid.

Titanium. The source was pure titanium metal.
The solution was prepared by dis-
solving an unknown amount of the
metal in a mixture of hydrogen per-
oxide and reagent-grade sulfuric

acid. The solution obtained
(not all of the weighed quantity
of the metal was dissolved) was
filtered, diluted with distilled
water and analysed gravimetrically
by the cupferron method of Smith
(51, p. 34).

Zirconium and hafnium. The source was sub-
limed zirconium tetrachloride con-
taining approximately 1.2 per cent
hafnium tetrachloride. The solu-
tion was prepared by dissolution in
dilute reagent-grade hydrochloric
acid. This solution was used only
in the low beryllium concentration
test. For the high beryllium con-
centration test a solution was pre-
pared from zirconyl chloride octa-
hydrate, containing approximately the
same amount of hafnium as in the for-
mer case, by dissolution in dilute
reagent-grade hydrochloric acid.

This source of zirconium was
known to contain only ca. 10 parts
per million iron on the zirconium
basis.

Tin. The source was reagent-grade mossy
tin and the solution was prepared
by dissolution in reagent-grade
sulfuric acid. No effort was made
to keep the tin in the stannous
form so that in the final tests
both stannous and stannic tin were
doubtlessly present.

Lead. The source was test lead and the solu-
tion was prepared by dissolution in
reagent-grade nitric acid.

Arsenic. The source was reagent-grade
arsenous oxide and the solution was
prepared by dissolution in reagent-
grade sodium hydroxide.

Antimony. The source was reagent-grade anti-
monous oxide and the solution was

prepared by dissolution in
reagent-grade hydrochloric acid.

Chromium. The source was reagent-grade
chromic chloride hexahydrate and the
solution was prepared by dissolu-
tion in distilled water.

Manganese. The source was pure electro-
lytic manganese and the solution
was prepared by dissolution in
reagent-grade hydrochloric acid.
Consequently the oxidation state of
the manganese was +2.

Iron. The source was reagent-grade iron
wire and the solution was prepared
by dissolution in reagent-grade sul-
furic acid. The iron was oxidized
to the +3 state by the dropwise addi-
tion of reagent-grade nitric acid to
the hot solution.

Cobalt. The source was reagent-grade cobalt
nitrate hexahydrate and the solution

was prepared by dissolution in distilled water.

Nickel. The sourse was reagent-grade nickel nitrate and the solution was prepared by dissolution in distilled water.

Appropriate dilutions of each of these stock solutions of contaminating cations were made such that 1.00 mg. of the cation was contained in each ml. of diluted solution. By adding 2.00 ml. of each solution to the solutions containing 0.2000 g. of aluminum, contamination to the extent of approximately 1.0 per cent was brought about.

Interferences were first tested for a beryllium concentration of 90.2 parts per million on the aluminum basis, or 0.0090 per cent beryllium in aluminum. To each solution listed in Table 24, except the blank solution and two control solutions, was added 2.00 mg. of contaminating ion, 0.2000 g. of aluminum, 2.00 ml. of 1.00×10^{-3} M beryllium sulfate, 10.00 ml. of 1.00×10^{-2} M sulfosalicylic acid, and 50.0 ml.

of 0.50M sodium ethylenediaminetetraacetate. For convenience in tabulation these quantities were not listed in Table 24. The pH in each solution was adjusted with filtered concentrated reagent-grade ammonium hydroxide, and in each case the final volume was adjusted to 200.0 ml. Table 24 lists the contaminant, the approximate number of ml. ammonium hydroxide used, the final pH, the observed optical density at 317.0 mμ. using the Beckman instrument, parts per million beryllium found, and pertinent remarks for each solution. The beryllium, contaminating ion, and aluminum additions were not made to the blank solution. Only the contaminating ion addition was omitted from the two control solutions.

Figure 18 graphically illustrates the degree of interference brought about by each contaminating ion using the optical density value of the two control solutions as a reference line. It should be noted the optical density of 0.112 observed for the control solutions in Table 24 compares very favorably with the corresponding optical density of 0.115 noted for the same beryllium concentration in Figure 17. In the latter case sodium hydroxide was used in

TABLE 24

Cation Interferences in the Sulfosalicylate Method for
Beryllium in Aluminum;

Lower Beryllium Range

Solution	Contaminating ion	Conc. amm. hydroxide, ml.	Corrected pH (Beckman Model G)	Optical density at 317.0 mμ.	Beryllium found, ppm.	Remarks
Blank	---	3.0	10.05	-----	---	
Control 1	---	8.3	10.08	0.111	(90.2)*	
Control 2	---	8.7	10.10	0.112	(90.2)*	
1	Na^+	9.0	10.12	0.115	92	
2	K^+	9.0	10.10	0.114	91	
3	Cu^{++}	7.0	9.98	0.160	155	slt. blue color
4	Mg^{++}	8.0	10.06	0.112	90	
5	Ca^{++}	10.0	10.10	0.112	90	
6	Zn^{++}	10.0	10.08	0.112	90	
7	Sr^{++}	10.0	10.08	0.115	92	

TABLE 24 (continued)

Solution	Contaminating ion	Conc. amm. hydroxide, ml.	Corrected pH (Beckman Model G)	Optical density at 317.0 mμ.	Beryllium found, ppm.	Remarks
8	Cd^{++}	10.0	10.10	0.113	90	
9	Ba^{++}	10.0	10.09	0.114	91	
10	Al^{+++}	11.0	10.05	0.109	88	
11	La^{+++}	10.0	10.01	0.108	87	
12	Ce^{++++}	11.0	10.06	0.266	300	slt. yellowish turbidity
13	Ti^{++++}	9.0	9.96	0.108	87	
14	Zr^{++++}, Hf^{++++}	8.0	10.09	0.143	130	
15	Sn^{++}, Sn^{++++}	10.0	10.06	0.130	115	slt. white turbidity
16	Pb^{++}	11.0	10.13	0.117	95	
17	As^{+++}	9.0	10.06	0.112	90	
18	Sb^{+++}	11.0	10.09	0.115	92	

TABLE 24 (continued)

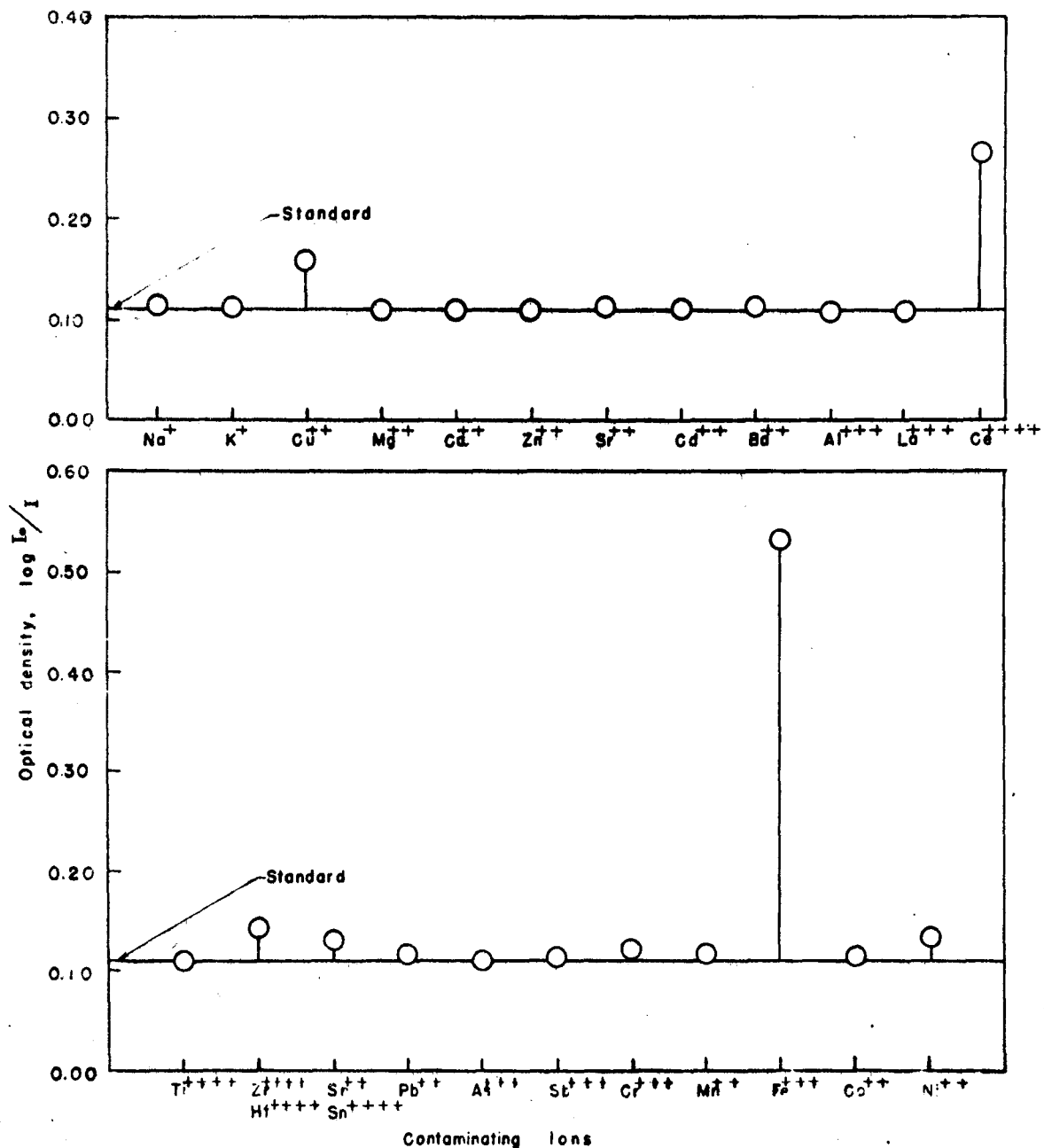| Solution	Contaminating ion	Conc. amm. hydroxide, ml.	Corrected pH (Beckman Model G)	Optical density at 317.0 mμ.	Beryllium found, ppm.	Remarks
19	Cr^{+++}	9.0	10.04	0.122	102	slt. violet color
20	Mn^{++}	11.0	10.14	0.119	100	
21	Fe^{+++}	9.0	10.02	0.532	690	slt. yellow color
22	Co^{++}	10.0	10.06	0.116	93	slt. pink color
23	Ni^{++}	10.0	10.05	0.134		

* Beryllium, taken

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Figure 18——— Relative interferences brought about in the sulfosalicylate method for beryllium in cluminum by the presence of 1.0 per cent of each of the indicated contaminating ions as determined using the Beckman spectrcphotonicter; low beryllium range; data from Table 24.

adjusting the pH; in the former, ammonium hydroxide was used.

After a period of 48 hours had elapsed the solutions which contained the cerium, zirconium-hafnium, and tin contaminants contained slight, definite coagulated precipitates. These solutions were decanted and re-examined on the Beckman instrument. A noticeable reduction in the degree of interference was brought about by the coagulation. The optical density values observed on the decanted solutions were respectively 0.131, 0.124, and 0.116. Comparison of these values with the standard value of 0.112 indicated that the interferences were almost completely eliminated.

An exactly similar set of solutions was prepared to test the interferences at a much higher beryllium concentration. The amount of beryllium used was 30.0 ml. of $1.00 \times 10^{-3} M$ beryllium sulfate, or the equivalent of 0.135 per cent beryllium on the aluminum basis. Table 25 lists the data corresponding to this set of solutions at the higher beryllium concentration. Figure 19, in a manner similar to Figure 18, graphically

TABLE 25

Cation Interferences in the Sulfosalicylate Method for
Beryllium in Aluminum;

Higher Beryllium Range

Solution	Contam-inating ion	Conc. amm. hydroxide, ml.	Corrected pH (Beckman Model G)	Optical density at 317.0 mμ.	Beryllium found, ppm.	Remarks
Blank	---	10.0	10.40	-----	----	
Control 1	---	16.0	10.38	0.985	(1353)*	
Control 2	---	16.0	10.37	0.984	(1353)*	
1	Na$^+$	16.0	10.36	0.984	1350	
2	K$^+$	16.0	10.40	0.984	1350	
3	Cu^{++}	17.0	10.43	1.04	1440	lt. blue color
4	Mg^{++}	17.0	10.40	0.990	1360	
5	Ca^{++}	17.0	10.40	0.990	1360	
6	Zn^{++}	17.0	10.43	0.986	1350	
7	Sr^{++}	17.0	10.35	0.992	1360	

TABLE 25 (continued)

Solution	Contaminating ion	Conc. amm. hydroxide, ml.	Corrected pH (Beckman Model G)	Optical density at 317.0 mµ.	Beryllium found, ppm.	Remarks
8	Cd^{++}	17.0	10.41	0.985	1350	
9	Ba^{++}	17.0	10.43	0.985	1350	
10	Al^{+++}	17.0	10.41	0.988	1360	
11	La^{+++}	17.0	10.43	0.988	1360	
12	Ce^{++++}	17.0	10.41	1.17	1660	Yellow opalesence
13	Ti^{++++}	17.0	10.39	0.984	1350	
14	Zr^{++++}, Hf^{++++}	17.0	10.39	0.880	1180	White opalesence
15	Sn^{++}, Sn^{++++}	17.0	10.38	0.984	1350	Slt. white opalesence
16	Pb^{++}	17.0	10.41	0.984	1350	
17	As^{+++}	17.0	10.40	0.993	1360	
18	Sb^{+++}	17.0	10.38	0.983	1350	

TABLE 25 (continued)

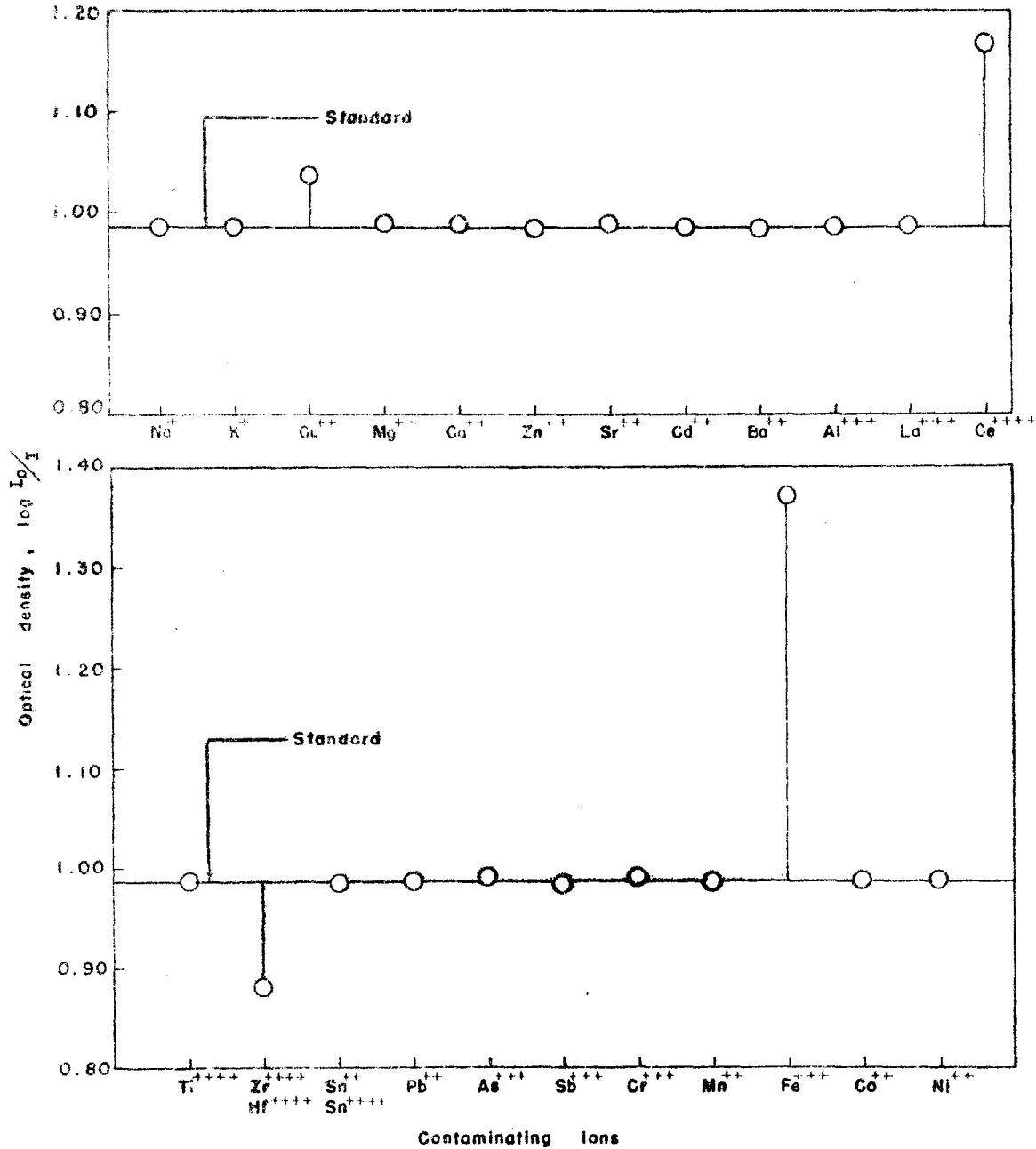| Solution	Contam-inating ion	Conc. amm. hydroxide, ml.	Corrected pH (Beckman Model G)	Optical density at 317.0 mμ.	Beryllium found, ppm.	Remarks
19	Cr^{+++}	17.0	10.42	0.990	1360	Lt. blue color
20	Mn^{++}	17.0	10.42	0.985	1350	
21	Fe^{+++}	17.0	10.44	1.37	2000+	Lt. yellow color
22	Co^{++}	17.0	10.44	0.988	1360	
23	Ni^{++}	17.0	10.44	0.988	1360	Lt. pink color

* Beryllium, taken

Figure 19 —— Relative interferences brought about in the sulfosalicylate method for beryllium in aluminum by the presence of 1.0 per cent of each of the indicated contaminating ions as determined using the Beckman spectrophotometer ; high beryllium range ; data from Table 25.

illustrates the degree of interference brought about
by each contaminating ion, using the optical density
value of the two control solutions as a reference
line.

It was indicated earlier that a different source
of zirconium was used in the higher beryllium range
than in the lower one. In the case of the higher
beryllium range there immediately was formed a slight
precipitate; this effect was not observed in the
lower beryllium range. In the lower beryllium range
a positive error was brought about by the presence
of zirconium whereas in the higher beryllium range a
negative error was introduced. It was suspected that
in the former case a finely dispersed solid phase of
hydrated oxide or basic salt caused the higher
absorption and that in the latter case the immediate
precipitation process occluded, adsorbed, or other-
wise removed beryllium from the solution. In both
cases long standing virtually eliminated the interfer-
ence.

In this case, as before, a small amount of pre-
cipitate collected in the bottom of the flasks

containing the cerium, zirconium-hafnium, and tin
contaminants. These solutions were re-examined by
decantation 5 days after their preparation. The
optical densities observed for them at this time were
0.982, 0.973, and 972, respectively. The departures
from the standard value of 0.985 were small enough to
be considered insignificant for the range of concentra-
tion of beryllium used.

Of the cations examined only cupric copper and
ferric iron offered serious interference in the high
beryllium range, if we consider the fact that allowing
the solutions to stand for a long period virtually
eliminated the errors due to cerium, zirconium-hafnium,
and tin. In the lower beryllium range, without an
aging period, appreciable relative interference was
brought about by copper, cerium, zirconium-hafnium,
and ferric iron. Much less relative interference was
observed for tin, chromium, manganese, and nickel. Of
the interferences, that of copper and iron were con-
sidered the most important because they are more common
in character, particularly iron. The interference by
copper was not considered a serious problem because

its interference could certainly be eliminated by removing the copper by electrodeposition (52). The interference by iron could very probably be removed by electrodeposition at the mercury cathode (53) or by the separation of ferric chloride from beryllium by extraction with amyl acetate or diethyl ether (54). The extraction of iron by β,β'-dichloroethyl ether was described by Axelrod and Swift (55) and it appeared that the hydrochloric acid concentration was perhaps less critical in this method than in the others, provided that the hydrochloric acid concentration was greater than 7 formal. This method was essentially the one used in removing the iron interference in the present work.

Duplicate samples for the same two previous concentrations of beryllium examined were prepared as indicated in Table 26, along with a blank solution and two standards, one for each of the beryllium concentrations. For solutions Nos. 1, 2, 3, and 4, the iron, beryllium, and aluminum solutions were added to 250 ml. beakers. Three drops of concentrated reagent-grade nitric acid were added to each to insure

TABLE 26

Solutions Used in the Removal of Iron by Extraction
with β,β'-dichloroethyl Ether

Solution No.	Iron added mg.	1.00×10^{-3}M Beryllium sulfate ml.	Alu-minum added g.	1.00×10^{-2}M Sulfosali-cylic acid ml.	0.50M Ethyl-enediamine-tetraacetic acid ml.	Final volume, ml.	Corrected pH (Beck-man Model H-2)
Blank	----	----	------	10.00	50.0	200.0	10.19
Control 1	----	30.0	0.2000	10.00	50.0	200.0	10.25
Control 2	----	2.00	0.2000	10.00	50.0	200.0	10.22
1	2.00	30.0	0.2000	10.00	50.0	200.0	9.98
2	2.00	30.0	0.2000	10.00	50.0	200.0	10.07
3	2.00	2.00	0.2000	10.00	50.0	200.0	9.98
4	2.00	2.00	0.2000	10.00	50.0	200.0	9.95

the complete oxidation of the iron to the trivalent
state. To each solution was added approximately 30.0
ml. of concentrated reagent-grade hydrochloric acid
and the solutions evaporated to near dryness on a hot
plate. To each solution was added 40.0 ml. of concen-
trated reagent-grade hydrochloric acid and 10 ml. of
distilled water. Each solution was then extracted
with three 25-ml. portions of freshly distilled β,β'-
dichloroethyl ether, observing the usual extraction
techniques. Each solution was again evaporated to
near dryness, to avoid the necessity of later
neutralizing an excessive amount of acid, and the
solutions each diluted to about 125 ml. with distilled
water. The sulfosalicylate and ethylenediaminetetra-
acetic acid solutions were then added in the amounts
indicated in Table 26. All the solutions in Table 26
were then adjusted to the final pH indicated, using
filtered reagent-grade ammonium hydroxide, and the
volumes made up to 200.0 ml. The solutions were then
examined on the Beckman instrument at 317.0 mμ. using
the blank solution as a reference. Table 27 indicates
the observed optical density and corresponding parts
per million beryllium on the aluminum basis which were

obtained. It was concluded that the β,β'-dichloro-
ethyl ether extraction successfully removed from the
iron interference.

TABLE 27

Beryllium Analysis After Removal of Iron with β,β'-
dichloroethyl Ether; Solution Numbers Correspond to
Table 26

Solution	Observed optical density	Beryllium taken, ppm.	Beryllium found, ppm.
Control 1	0.998	1350	1350
Control 2	0.114	90.2	90
1	0.992	1350	1360
2	0.996	1350	1370
3	0.122	90.2	100
4	0.118	90.2	95

An attempt was made to determine beryllium in
thorium in the same manner as the determination of
beryllium in aluminum was carried out. The attempt
was not successful. Qualitatively the results indica-
ted that thorium was complexed slightly by both

sulfosalicylate and ethylenediaminetetraacetate, because a very large mole ratio of either of these reagents did prevent the precipitation of thorium at a pH of 11.0. It appeared that the ethylenediamine-tetraacetate complex of thorium was not stable enough to prevent a large interference by the sulfosalicylate complex of thorium. When the thorium concentration was of the same order of magnitude as the beryllium concentration no appreciable interference was observed.

Essentially the same results as those with thorium were obtained when the same technique was attempted for the determination of beryllium in lanthanum. However, lanthanum interference was considerably less than that of corresponding concentrations of thorium.

It had already been shown that large amounts of perchlorate, chloride, and sulfate did not interfere in the proposed method for thorium because wide differences in the concentrations of these anions led to no appreciable differences in observed optical densities when sodium perchlorate was used to control ionic strength, when hydrochloric acid was used in

large amounts in the iron extraction, and when a wide
variation in sulfate concentration was brought about
by the presence of excess sulfuric acid in the alumi-
num stock solutions. It was of interest to examine
any interference brought about by the presence of
nitrate, acetate, phosphate, and fluoride ions. Table
28 indicates the identity and quantity of contaminating
anion and the observed analyses obtained in their
presence. The preparation of solutions for spectro-
photometric examination was essentially the same as
that used in the determination of cation interferences.
The solutions were examined on the Beckman instrument
as before.

Table 28 indicates that fluoride, in the amount
used, offered no interference. However, a crystalline
precipitate, probably ammonium fluoride, was noted.
Acetic acid interferred very slightly. Large inter-
ferences were brought about by the presence of 1.0 ml.
of reagent-grade nitric acid and by 1.0 ml. of reagent-
grade phosphoric acid.

It was of interest to examine the optical density
at 317.0 mμ. of a solution containing only nitrate.

TABLE 28

Anion Interferences in the Sulfosalicylate Method for
Beryllium in Aluminum;

Lower Beryllium Range

Solution No.	Nature and amount of anion contaminant	Observed optical density at 317.0 mµ.	Beryllium taken, ppm.	Beryllium found, ppm.
Blank	---	-----	----	---
Control	---	0.115	90.2	92
1	1 ml. conc. reag. grade nitric acid.	0.437	90.2	550
2	1 ml. reag. grade glacial acetic acid.	0.124	90.2	105
3	1 ml. reag. grade syrupy phosphoric acid.	0.065	90.2	20
4	1 g. reag. grade sodium fluoride	0.115	90.2	92

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Accordingly 1.0 ml. of concentrated reagent-grade nitric acid was diluted to 200.0 ml. and the optical density read at 317.0 mμ. The value observed was 0.325. This value, added to that of the standard, 0.115, gives a total 0.340, which is almost identical with the value of 0.337 obtained for the beryllium solution containing nitric acid.

It was concluded that nitrate and phosphate must be absent in the proposed determination of beryllium.

Nitrate ion was present in several of the cation solutions used in testing interferences. Calculation of the actual interferences which would be brought about by such nitrate ion concentrations as were used, revealed that in all cases an error of less than 0.010 optical density units would be observed.

A summary of the directions to be followed in the proposed procedure for beryllium in aluminum in the range of approximately 0.002 per cent beryllium to 0.23 per cent follows:

Obtain the aluminum and beryllium in the form of the sulfuric, perchloric, or hydrochloric acid solution

in a volume of about 100 ml. The solution should
contain 0.2000 ± 0.0200 g. of aluminum. The excess
of acid should be kept as small as conveniently pos-
sible to minimize the amount of base required for
neutralization. Add to the solution 10.0 ml. of
approximately 1.00×10^{-2}M reagent-grade sulfosalicylic
acid and 50.0 ml. of approximately 0.50M ammonium
ethylenediaminetetraacetate of a pH about 8.0 or 9.0.
Very accurate measurement of the volume of the latter
solution is not required. Unless the ethylenediamine-
tetraacetic acid used is quite pure as indicated by
melting point and ability to form a clear, water-
white, sodium or ammonium salt solution it should be
purified by recrystallization as described in Section
IV, D. Adjust the pH of the solution to between 9.2
and 10.8 with filtered, concentrated reagent-grade
ammonium hydroxide. Dilute the solution to exactly
200.0 ml. with distilled water and measure the optical
density at 317.0 mµ. versus a reference solution pre-
pared in exactly the same manner as the sample solu-
tion, omitting the sample. The final pH of this solu-
tion should not be greater than about 10.5. Read the
corresponding beryllium concentration from a calibration

curve prepared by using known amounts of beryllium
and 0.2000 ± 0.0200 g. of pure aluminum. For conven-
ience, parts per million beryllium may be plotted
versus optical density and the same sample size
always used, or actual beryllium concentration may be
plotted versus optical density and the per cent
beryllium in the sample calculated therefrom. For the
most accurate work it is best to keep the pH of the
sample solutions and standards as nearly the same as
possible. This is not inconvenient because of the
buffering action supplied by the ethylenediamine-
tetraacetic acid in the pH range of interest. A pH
of 10.0 is convenient.

Sodium hydroxide may be substituted for ammonium
hydroxide but in general sodium hydroxide solutions
are not as free of contamination as are ammonium
hydroxide solutions. Too, the use of sodium hydroxide
does not permit the ease of pH adjustment that ammon-
ium hydroxide affords.

It should be emphasized that by choosing various
sample sizes, final volumes, etc., it should be pos-
sible to accommodate much different ranges of beryllium

concentration than was described above.

In the above method, under the most favorable conditions, an optical density of 0.010 is observed for a beryllium concentration in aluminum of about 0.0015 per cent. In general, of course, large relative errors would be observed for such concentrations.

In the absence of aluminum the ethylenediamine-tetraacetic acid need not be used. However, this acid does effectively complex a large number of metallic ions at the pH range of interest and may profitably be used where this complexation is desirable.

VII. SUMMARY

1. A new spectrophtometric method for the determination of beryllium was described. The method depends upon the increased absorption at 317.0 mμ. which is brought about by the addition of beryllium to solutions of sulfosalicylic acid in the pH range of 9.2 to 10.8.

2. It was shown that sulfosalicylic acid from commercial sources is either the isomer, 5-sulfosalicylic acid, or, at least for the purpose of complex formation with beryllium, the behavior is the same as that of 5-sulfosalicylic acid.

3. The method of continuous variations, developed by Job, was used to show that the mole ratio of sulfosalicylate to beryllium in the complex is 2 to 1. By the constancy of the maximum composition at various wave lengths it was shown that only the one complex is present in appreciable quantities at the optimum pH.

4. An alkalimetric titration of pure beryllium

basic acetate, $Be_4O(C_2H_3O_2)_6$, in solutions containing a large excess of sulfosalicylate, was employed to show that at the optimum pH of complex formation, both of the hydroxylic hydrogen atoms of the sulfosalicylate ions are removed in the formation of the complex. The formula for the complex ion is therefore best represented as $Be(C_6H_3SO_3OCO_2)_2^{\equiv}$. Qualitative theoretical justification for this formulation was presented.

5. The equilibrium constant for the dissociation of the complex ion, $Be(C_6H_3SO_3OCO_2)_2^{\equiv}$, into simple sulfosalicylate ions, $C_6H_3SO_3OHCO_2^{\equiv}$, and an unknown beryllium species, Be_x, at the optimum pH was shown to be equal to approximately 2.1×10^{-9} at $25 \pm 1°C$.

6. The spectrophotometric determination of very small amounts of beryllium in aluminum by means of the sulfosalicylate complex was successfully carried out. The aluminum interference was eliminated by the complexation of the aluminum with ethylenediaminetetraacetic acid. A method of analysis for beryllium in aluminum was proposed. In this method

a solution containing 0.2000 ± 0.0200 g. of aluminum
is used and concentrations of beryllium in aluminum
up to 0.23 per cent are determinable. Under the most
favorable conditions concentrations as low as 0.0015
per cent beryllium in aluminum should be detectable.
The relative errors for such low beryllium concentra-
tions is quite great. It was indicated that by
varying the sample size, extent of dilution, etc.,
widely differing ranges of concentrations of beryl-
lium in aluminum might be accommodated.

7. Interferences brought about in the proposed
method by the presence of 1.0 per cent of each of a
number of cations were established for relatively low
and relatively high concentrations of beryllium in
aluminum. In the lower beryllium concentration
large interferences were found for cupric copper,
ceric cerium, and ferric iron. Much smaller relative
errors were found for stannous-stannic tin, zirconium
and hafnium, chromic chromium, manganous manganese,
divalent cobalt, and divalent nickel. The interfer-
ences due to the chromium, manganese, and cobalt were
small enough to be neglected. In the higher beryl-
lium range appreciable interferences were observed

for only cupric copper, ceric cerium, zirconium and
hafnium, and ferric iron. No interference at either
beryllium concentration was noted for sodium, potas-
sium, magnesium, calcium, zinc, strontium, cadmium,
barium, lanthanum, titanic titanium, plumbous lead,
arsenous arsenic and antimonous antimony.

8. The interference in the proposed method
due to iron was successfully eliminated by extraction
of the ferric chloride with β,β'-dichloroethyl ether.

9. It was shown that relatively large quanti-
ties of perchlorate, chloride, fluoride, and sulfate
ions do not interfere in the proposed method.
Acetate ion interferes very slightly and phosphate
and nitrate ions must not be present in appreciable
quantities.

VIII. SUGGESTIONS FOR FUTURE WORK

The results of the investigations described in the preceding sections indicated the possibility, and in some cases the necessity, of other related researches. These are most conveniently listed point-wise.

1. In the opinion of the author the most needed study relative to the aqueous chemistry of beryllium is that of the accurate determination of the solubility of hydrated beryllium oxide as a function of pH. Such a study could probably best be made by using a convenient radioactive isotope of beryllium and a radiation counting technique to determine the concentrations of beryllium in solution. After such a study it should then be possible to describe the solubilities thus obtained by means of the proper equilibrium constants and thus make intelligent predictions with regard to the important beryllium species

present in solution over particular
ranges of pH. This information should
then assist materially in the explanation
of such phenomena as the character of
curve 1, Figure 14.

2. In order to contribute further to the
understanding of curve 1, Figure 14, it
would be desirable to investigate Job's
method of continuous variations at suitable
points over the pH range of interest to
establish whether or not more than one
beryllium-sulfosalicylate complex is of
importance under these conditions. This
information would be absolutely necessary
to properly account for the observed values
of optical density.

3. Relative to curve 2, Figure 14, it was sus-
pected that a singly negative species of
sulfosalicylate ion, H_2SS^-, with the car-
boxylic hydrogen atom intact, was respon-
sible for the observed increased optical
density values at 317.0 mu. below a pH of

ca. 4.0. This fact suggests that it might
be possible to determine at least the
second ionization constant of sulfosali-
cylic acid by means of a method similar to
that used by Crouthamel, Meek, Martin,
and Banks (43) to determine the ionization
constants of periodic acid. Such a method
appears to have excellent possibility of
quantitative success where Okahara (25)
met with no more than qualitative success.

4. The author believes that the use of the
ultraviolet region of the spectrum for the
spectrophotometric determination of metals
has been unnecessarily neglected. An
extremely large number of colorimetric
methods of analysis for metals are in use
today which depend only on the fact that
suitable complexes of the metals conven-
iently absorb light in the visible region
of the spectrum. With the present-day
universal availability and use of ultra-
violet spectrophotometric equipment it is

only reasonable to believe that the ultra-
violet region of the spectrum may just as
fruitfully lend itself to the quantitative
determination of metals. Fundamentally
the techniques involved are no different
than those used in the ordinary spectro-
photometry of the visible region of the
spectrum.

5. The use of beryllium basic acetate in
Section VI, D, was somewhat inconvenient
because of the length of time required for
its dissolution. Pure, soluble, beryl-
lium salts, such as the sulfate, perchlor-
ate, chloride, etc., would be expected to
be titratable more quickly and conveniently.
Even in the presence of an excess of acid
and various other metallic ions a suitable
volumetric method of determining beryllium
might be developed.

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X. ACKNOWLEDGMENTS

XI. APPENDIX

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