BENZOYLACETONE AS A POLAROGRAPHIC REAGENT FOR BERYLLIUM

BENZOYLACETONE AS A POLAROGRAPHIC

REAGENT FOR BERYLLIUM

By

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SCOPE AND CONTENTS: Of several potential reagents for the
indirect polarographic determination of beryllium, benzoyl-
acetone was found to be the most attractive. A study of the
relevant properties of this reagent and of the characteris-
tics of its reaction with beryllium led to the development
of a new method for the determination of beryllium with good
precision at concentrations as low as 10 p.p.m. and with
reasonable precision even at 2 p.p.m. Less than 0.5 mg. of
beryllium is required.

The method, when preceded by an appropriate mercury-
cathode separation, is applicable to the determination of
beryllium in copper-base alloys. The application of the
method was extended to aluminium-base alloys by the develop-
ment of an ion-exchange procedure for the separation, with
at least 95% efficiency, of beryllium from relatively high
concentrations of aluminium.

A similar method is applicable to the determination
of aluminium, in concentrations down to about 20 p.p.m.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The primary purpose of this work was to devise and develop a sensitive polarographic method for the quantitative determination of beryllium, with particular reference to the determination of this element in copper-base alloys. Attention was also given to a new polarographic method for the determination of aluminium and to an ion-exchange separation of beryllium and aluminium.

I   Metallurgical Interest in Beryllium

Although some thirty beryllium minerals are known, only beryl (a double silicate of aluminium) is at present of industrial significance as a source of beryllium. A few of the more important beryllium minerals which are considered as potential sources of beryllium are: euclase (another double silicate of aluminium), chrysoberyl (an aluminate), phenacite (a beryllium orthosilicate), beryllonite (a beryllium sodium phosphate), and hambergite (a borate).

Since Vauquelin's discovery of beryllium in beryl in 1797, the compounds and alloys of beryllium have been found to possess many unique properties. These have won for this element, particularly in recent years, increasing application and widespread interest.

Beryllium is the only low-density metal with a high melting point (1285°C.). The metal has high electrical conductivity and fair strength, but poor ductility. Owing to its low atomic number, beryllium has a high permeability to x-rays — a permeability about 17 times that of

1

aluminium. This property, coupled with its strength and high melting point, makes it ideally suited for the windows of x-ray tubes and has made possible the use of longer wave-length x-rays in, for example, x-ray therapy and in the x-ray study of low-density metals.

By far the greatest use of beryllium metal is in the nuclear field. Because beryllium has a low neutron-capture cross-section and a high neutron-scatter cross-section, it is effective as a moderator or reflector in nuclear reactors. Beryllium is also used in a convenient and portable neutron source: a mixture of metallic beryllium and an alpha-particle emitter, such as a compound of radium or polonium, yields neutrons by the reaction:

$$_{4}Be^{9} + {}_{2}He^{4} \longrightarrow {}_{6}C^{12} + {}_{0}n^{1}$$

Before the development of beryllium-copper alloys, to which reference will be made presently, the principal use of beryllium was as the oxide, in the manufacture of refractory crucibles. Other beryllium compounds are used in the making of glass of high permeability to ultra-violet radiation, and in the fabrication of Welsbach gas mantles.

The most important beryllium alloys at present are the ternary beryllium-copper-nickel and beryllium-copper-cobalt alloys. They usually contain 1.90-2.00% beryllium and 0.50% (maximum) nickel or cobalt. These alloys are soft and ductile and are well suited for machining or other fabrication. They may also be hardened by suitable heat treatment. Some less common beryllium-copper alloys contain about 0.25% iron. Beryllium is the hardening agent; the nickel, cobalt and iron merely serve to refine the grain size.

The unique properties of beryllium-copper alloys have led to a great variety of industrial applications. In the electrical field, the high electrical and thermal conductivities of beryllium-copper, coupled with its strength and unusual resistance to fatigue and impact even at elevated temperatures, makes these alloys valuable for high-strength, current-carrying springs, welding electrodes, and circuit-breaker parts. Heat-treated, beryllium-hardened copper vibrator springs are said " to exhibit no measureable change in physical or electrical properties after being heavily stressed at the rate of 230 times a second, and subjected to severe temperature changes during a total of two billion vibrations" (171). Alloys of copper with approximately 2% beryllium do not spark when struck. This makes them suitable for hand-tools in applications where sparking might well be serious, such as around explosives, in gas plants, or in petroleum refineries.

In such specialized fields as the fabrication of springs, diaphragms and Bourdon gauges for precision instruments, beryllium-copper is preferred because of its freedom from elastic drift as well as its resistance to corrosion. Among casting applications, the making of heavy-duty brake and clutch drums, gears, and molds in the plastics industry are of interest.

Beryllium-aluminium alloys employed at present contain less than 1% beryllium and are used in the production of cylinder heads for air-cooled engines and for shutter leaves in aircraft cameras. Now that powder metallurgy is becoming highly developed, certain alloying problems, which today limit the ratio of beryllium to aluminium, may be overcome; this in turn, may lead to a renewed interest in beryllium-

rich beryllium-aluminium alloys.

Beryllium when alloyed with magnesium, in concentrations even as low as 0.005%, greatly reduces the flammability of magnesium and retards its oxidation at the melting point (162). Beryllium also increases the resistance of magnesium-base alloys to corrosion by salt water. "Hydronalium", an aluminium-magnesium-beryllium alloy containing low concentrations of manganese, titanium and silicon, has been used in air-cooled cylinder heads in Germany.

Beryllium-nickel alloys have no outstanding properties such as the high electrical conductivity of beryllium-copper alloys. The addition of 2% of beryllium to nickel, with subsequent annealing and cold-working, however, yields alloys of very high tensile strength; these have been used for high-temperature springs and special parts in instruments.

Excellent books, dealing with the methods of production of beryllium and its applications have been published in recent years (168, 203).

II   Methods for the Determination of Beryllium

Most of the methods for the determination of beryllium come under one or other of the headings: gravimetric, fluorimetric, absorptiometric, titrimetric and spectrochemical. The choice of method usually depends on the quantity of beryllium and on the nature and concentration of the other elements present. If the quantity of sample is not limited, a separational procedure may isolate sufficient quantities of beryllium to allow any of the methods to be used.

Gravimetric Methods: Gravimetric methods of analysis for beryllium may
conveniently be subdivided into two classes: those in which beryllium
is eventually ignited and weighed as the oxide, and those in which ber-
yllium is weighed in another form.

Beryllium is commonly determined gravimetrically by precipitat-
ing the hydrous oxide by means of aqueous ammonia followed by ignition
to the oxide (15,67,68,79). West (199) and Ostroumov et al. (139,140)
precipitated the hydrous oxide by means of α-picoline; they claimed that
aqueous ammonia (and pyridine) precipitate the hydrous oxide of beryll-
um incompletely. Cottin (49), who precipitated the hydrous oxide with
sodium hydroxide, potassium hydroxide and aqueous ammonia, preferred
sodium hydroxide, with the pH not lower than 7.2, and a ratio of ten
hydroxyl ions to one beryllium ion, for precipitation of beryllium from
pure salts. Akiyama (13) studied several determinations and, of those
concerned with the hydrous oxide, recommended four, namely: the ammonium
hydroxide, sodium hydroxide, ammonium acetate and sodium thiosulfate
methods. Ammonium carbonate (which precipitates beryllium as a basic
beryllium carbonate) and hydrazine carbonate (10,87) have been proposed
as precipitants for beryllium. The hydrazine carbonate method has an
advantage over the methods using aqueous ammonia (9) or ammonium carbon-
ate in that the precipitate is less slimy and less soluble in a slight
excess of precipitant. Ethylamine (10,15) benzylamine and triethanola-
mine (161) have also been used to precipitate the hydrous oxide of ber-
yllium. Brewer (36) precipitated the hydrous oxide in the presence of
ethylenediaminetetraacetate-ion, which eliminated the interference of
aluminium. Basic beryllium carbonate, which is converted to the hydrous

oxide of beryllium upon heating, is precipitated by ethylamine carbonate (11,15).

Reagents that precipitate beryllium in a form other than the hydrous oxide but which is eventually ignited to beryllium oxide are: Tannin (67,68,126,135,163), ammonium benzoate (17), guanidine carbonate (76,88,89), hexamethylenetetramine (12,14), acetyl chloride (which precipitates beryllium in a manner similar to the precipitation of aluminium chloride hexahydrate by the same reagent) (124). Dupuis (57) with the aid of a thermobalance, has made a critical study of the various precipitants which have been proposed for beryllium. He has tabulated the minimum temperatures to which the precipitates must be ignited to convert the hydrous oxides into weighable beryllium oxide.

Other gravimetric determinations are those in which beryllium is weighed in a form other than beryllium oxide. Eight-hydroxyquinoline (28,67,68,95,113,129,161,193) and, later, 8-hydroxyquinaldine have been investigated as precipitants for beryllium. Phillips et al. (148) reported that beryllium is only partially precipitated by 8-hydroxyquinaldine when techniques recommended for 8-hydroxyquinoline are used. Motojima (127), however, made a more detailed study of the precipitation of beryllium by means of 8-hydroxyquinaldine, and believes it to be the best precipitant for beryllium developed so far. The final step in his procedure consists of weighing the precipitated compound as beryllium 8-hydroxyquinaldinate. The pyrophosphate method has been used extensively (8,15,53,68,105,164); Duval and Duval (59) indicated their preference for this method after studying, with a thermobalance, the pyrolysis of the hydrous oxide, crystalline sulfate, amorphous sulfate and

ammonium phosphate of beryllium. A gravimetric determination of beryllium as barium fluoroberyllate (58,166), has met with some success. More recently, the use of 2-hydroxy-1-naphthaldehyde (78) and hexa-amminocobalt chloride (149) have been introduced as precipitants for beryllium.

Fluorimetric Methods: The list of reagents that form fluorescing compounds with beryllium is steadily growing. One of these, morin (30,94,110, 158,190,191,196), which reacts with beryllium at pH values greater than 11, has been claimed to be the most sensitive reagent for beryllium thus far developed (182). Quinizarin (40,41,65,66,131,134), alkannin (75,183,186, 187,188), 1-amino-4-hydroxyanthraquinone (41,201), cochineal (74,75), 1,8-dihydroxyanthraquinone (201,215), 2-(o-hydroxyphenyl)benzothiazole (81,82,210,211), and 8-hydroxyquinaldine (128), amongst others, have been proposed as fluorimetric reagents.

A serious difficulty encountered with all these reagents, however, is the rapid decrease in fluorescence after the reactants are mixed. Freshly prepared alkaline stannite solution has been used to stabilize the fluorescence in some instances (94,110).

Absorptiometric Methods: Many methods have been reported, for almost any dye which may be used for the absorptiometric determination of aluminium may be adapted for use with beryllium.

Among the reagents which have been recommended for either the detection (197) or the quantitative estimation of beryllium, or both, are the following: acetylacetone (1), alizarin sulfonic acid (23), Aluminon (103, 115,122,205), Alumocresone, an improved reagent of the Aluminon type (106), Arsenazo (108), Beryllone I & II (116), Chromeazurol S (176,206), curcumin (96,179,180), eriochrome cyanine R (181,135), 8-hydroxyquinoline (121),

Mitsui Fast Mordant Blue B (70), Naphthazarin (92), Naphthochrome Green
G or Naphthochrome Azurine 2B (18), Naphthochrome Green 3 (54), p-nitro-
benzeneazoorcinol (50,52,101,138,150,172,204), oxyquinones in general
(153), quinalizarin (64,96,117,168), Resorcinol (189), salicylic acid
(3), Solochrome cyanine (207), sulfosalicylic acid (120), Sunchromine
Fast Blue MB Nisshin (70) and Thoron (2,4,5,6,7). Most of these rea-
gents, however, are highly unselective (182).

Sundarasan and Sankar Das (173) used an indirect method in which
beryllium was precipitated as beryllium ammonium phosphate. The phos-
phorus was then converted into phosphomolybdic acid. As little as 2
p.p.m. of beryllium-ion can, it is claimed, be determined by this meth-
od.

Titrimetric Methods: Bleyer and Moorman (32) suggested the first titri-
metric method for beryllium. It differed little from the following two
methods.

Ivanov's method (86) consists of adding an excess of a solution
containing sodium thiosulfate (known amount), potassium iodide, and po-
tassium iodate to a solution of a beryllium salt. The beryllium salt
is readily hydrolyzed; the overall reaction is given by the equation:

$$3Be^{++} + IO_3^- + 5I^- + 3H_2O + 6S_2O_3^= \longrightarrow 3Be(OH)_2 + 3S_4O_6^= + 6I^-$$
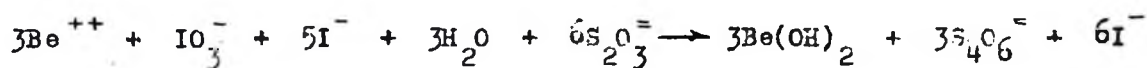
The excess thiosulfate is then determined iodimetrically. Evans (62)
proposed an alternative but closely similar method in which a measured
excess of hydrochloric acid is added to a solution, neutral to thymol-
phthalein, containing the "hydroxide" of beryllium. Potassium iodate
and potassium iodide are then added, iodine is liberated, and this is
titrated with a standard solution of sodium arsenite. Novoselova and

Vorob'eva (136) and Suseela (174) have applied variations of this technique to the determination of beryllium. Other methods involving the hydrolysis of beryllium salts have also been reported (42,43,216).

Sankar Das and Athavale (160) published a method involving precipitation of beryllium as beryllium ammonium phosphate (60) in the presence of ethylenediaminetetraacetate-ion, the dissolution of the precipitate in dilute perchloric acid, and the titration of the liberated phosphate with standard bismuthyl perchlorate. Brenner (35) determined beryllium by a microtitration procedure based on titration with a standard solution of Diamond Black F.

A relatively rapid titrimetric method similar to the Craig method for aluminium has also been applied to beryllium (119). The chemistry of the method is briefly as follows. Beryllium is precipitated as the "hydroxide" and excess sodium fluoride is added, converting the "hydroxide" to the weakly ionized beryllium fluoride and liberating hydroxyl ions. The alkalinity so produced is determined by titration with standard acid. Other titrimetric methods have also been reported (21,147, 212,213,214).

Spectrochemical Methods: The sensitivity of the spectral lines of beryllium, especially the lines at 2348.6 Å and 3131 Å, make spectrochemical analysis a very useful method for the determination of trace concentrations of beryllium. Many papers having to do with the spectrochemical determination of beryllium, especially in low concentrations as in air and urine, have been published (29,44,63,146,164,169,170). The papers cited are a few of the most recent ones. As with other spectrochemical procedures, this method of determination decreases in usefulness as the

concentration of beryllium in the sample increases.

Other Methods: Under this heading there may be cited a potentiometric method (177), a non-destructive photodisintegration method (71) which exploits the γ,n reaction, a determination using radioactive iron (31), and one using radioactive phosphorus (20) and a possible conductimetric titration making use of the soluble, slightly dissociated compound beryllium forms with oxalate-ion (194). Thus far no polarographic method appears to have been developed, although Kostromin (104) has suggested a possible amperometric determination using m- and p-nitrophenylazoresorcinol. The pronouncedly negative value of the half-wave potential of beryllium militates against the development of a useful direct polarographic method for the determination of this element.

A review of the analytical chemistry of beryllium by Vinci (192), an extensive bibliography of the analytical chemistry of beryllium by Banks et al. (27), and a critical study of some twenty reagents for beryllium by Wenger et al. (198) are most useful to the chemist concerned with the analytical chemistry of beryllium.

<u>111</u>   Methods for the Separation of Beryllium and Aluminium

The thirteen methods for the separation of beryllium and aluminium best known in 1921 are discussed by Britton (37). He also described experiments which were performed to ascertain the best conditions for precipitating the hydrous oxide of beryllium by sodium hydroxide without precipitating the hydrous oxide of aluminium, studies which were initiated by numerous earlier workers. Moser and Niessner (125), in a critical review of methods known before 1927, concluded, however,

that none of the methods discussed by Britton was of analytical value.
They offered another one, based on the different behaviour of beryllium
and aluminium when tannin is added to a solution containing considerable
ammonium acetate. According to these workers, under these conditions
aluminium is precipitated quantitatively but beryllium remains in solu-
tion. Dewar and Gardiner (55), however, after a re-examination of
Britton's method, concluded that the criticisms of Moser and Niessner
were not entirely justified, and that the procedure described by Britton
is excellent provided that the concentration of aluminium is not greatly
in excess of that of beryllium. They also claimed that even if the con-
centration of aluminium is originally much greater than that of beryll-
ium, this method is a good one if some beryllium is added to adjust the
relative proportions of the two ions.

Before the 8-hydroxyquinoline method (vide infra) was introduced,
the extraction procedure of Parsons (143), using sodium hydrogen carbon-
ate, was for long considered to be the only useful method for separating
aluminium and beryllium. This method is based on the solubility of the
hydrous oxide of beryllium in a boiling solution of sodium hydrogen car-
bonate and the relative insolubility of the hydrous oxide of aluminium
in this medium. Separation of beryllium from a preponderance of alumin-
ium has been effected by the method of Gooch and Havens (69) in which
aluminium is precipitated as aluminium chloride hexahydrate from a con-
contrated solution of hydrochloric acid and ethyl ether saturated with
hydrogen chloride. Residual small amounts of aluminium can then be re-
moved by other means, such as by the very important 8-hydroxyquinoline

method of Kolthoff and Sandell (96,97). The combination of these me-
thods (the Havens-8-hydroxyquinoline method) was successfully used by
Churchill, Bridges and Lee (45).

Brewer's (36) separation of beryllium from aluminium and other
elements is based on the fact that the beryllium complex with ethylene-
diaminetetraacetic acid is decomposed by aqueous ammonia whereas other
elements form more stable complexes (152). Miller (123) precipitated
the hydrous oxide of beryllium in the presence of complex tartrates.
Aluminium forms a complex tartrate which prevents its precipitation as
the hydrous oxide. In 1949 Coppins (48), using a method similar to
that of Britton, showed that when a solution, containing sodium beryll-
ate and sodium aluminate in dilute sodium hydroxide is neutralized with
hydrochloric acid, the hydrous oxide of beryllium precipitates before
that of aluminium. Kolthoff et al. (98) proposed ammonium benzoate as
a reagent for the separation. Beryllium was found to be coprecipitated
but much less so than when aqueous ammonia was used. Osborn and
Jewsbury (137) showed that no coprecipitation of beryllium occurs if
the pH is carefully controlled within the range 3.5-4.0. Glassman (73)
found that when slightly acidic solutions of beryllium and aluminium
salts are treated with an excess of sodium thiosulfate solution and hea-
ted to boiling, aluminium is completely precipitated as the hydrous ox-
ide whereas beryllium remains in solution.

Sastri et al. (161) studied p-chloroaniline, acridine, trieth-
anolamine, benzylamine and 8-hydroxyquinoline as reagents for the sepa-
ration. Guanidine carbonate (89), sodium carbonate (209) and tannin
(135,163) also have been employed. Arnal (22) suggested calcium ferro-

cyanide, which was found to precipitate aluminium but not beryllium. Methods that depend on the differences in the volatility of the basic acetates of aluminium and beryllium have been reported (16,72). Ruml (155) separated beryllium from aluminium in a mineral by leaching out the complex fluoride of beryllium after having fused the mineral with sodium fluoride. Aluminium is left in the melt.

Qvadrat and Svejda (154) showed that of the reagents sodium hydrogen carbonate, ethylamine, 8-hydroxyquinoline and guanidine carbonate, 8-hydroxyquinoline was the most reliable for separating aluminium and beryllium. Otsuku (141) also favoured the use of this reagent. He found, however, that the sodium hydrogen carbonate method of Parsons (143) gave equally good results.

It should be noted that most of the separations referred to above are based on differential precipitations and are therefore prone to difficulties arising from coprecipitation.

Various extraction methods employing acetylacetone (19), butyric acid (20), amyl alcohol (38), ethylenediaminetetraacetic acid (200), ethyl ether (25), and chloroform (46) have been investigated. Paper strip chromatography, using methyl ethyl ketone as a carrier (109), has also been applied to the separation of beryllium and aluminium.

Honda (83,84) separated lithium, beryllium and aluminium using a cation-exchange resin by taking advantage of the difference in adsorptive properties of the ions, arising from their differing charge. After the cations are adsorbed on the resin, lithium is desorbed with 0.1 N hydrochloric acid, beryllium with 0.025 N calcium chloride, and aluminium with 4 M hydrochloric acid. Takihana (91), using a resin of the

phenolsulfonic acid type, separated beryllium and aluminium by using 0.005 M calcium chloride solution as the elutriant. Ryabchikov and Buktiarov (156) succeeded in separating beryllium from aluminium and iron also by using a cation-exchange resin. Their method was based on the relative stabilities of the oxalates. By converting aluminium and iron into oxalates at pH 4.4, the aluminium and iron are fixed as complex ions which are not adsorbed on a cation-exchange resin. Beryllium, which does not form a complex ion under these conditions, is retained on the resin and can be later eluted. Another ion-exchange method that has been proposed for the separation of beryllium from aluminium, iron, titanium, calcium and phosphate ion (132) involves the preferential adsorption of beryllium on a cation-exchange resin after complexing the other ions with ethylenediaminetetraacetic acid and hydrogen peroxide.

If either beryllium or aluminium, or both, are to be determined by a polarographic method after separation, then the introduction of complexing anions or interfering cations, as in the aforementioned separations, is highly undesirable. A cation-exchange method depending on selective elution, whereby only hydronium ions and non-complexing anions are introduced, would avoid complications in later analytical work. Such a method was developed in the course of the present study.

EXPERIMENTAL

The present investigation, has been concerned mainly with the study of potential reagents for a polarographic determination of beryllium, and with the development of a method based on the most promising one. Some attention has also been given to the application of this method to aluminium. Study has also been given to the problem of separating aluminium and beryllium, and of removing from copper-beryllium alloys the elements that would interfere in the determination of beryllium by the proposed method. This work is set forth below. Section II, it may be noted, is set down primarily for purposes of record; the work dealt with in that section was not fruitful.

I   Apparatus and Materials

(a)   Apparatus

Some of the polarographic measurements were made using a Tinsley model V722 /13 pen-recording polarograph (Tinsley Industrial Instruments, London, England), and others using a Sargent model XX pen-recording polarograph (E. H. Sargent and Co., Chicago, U.S.A.). The capillary for the dropping mercury electrode was a length of marine barometer tubing (E. H. Sargent and Co.). The polarographic cell was either a conventional H-type cell (114), in which electrolytic contact to the saturated calomel reference cell is made through a potassium chloride-agar bridge, or an Heyrovsky cell (20-ml. capacity) supplied by E. H. Sargent and Co.. All polarographic measurements were made at 25.00° ± 0.05°C.

15

Measurements of pH were made with a Beckman model G pH meter (Beckman Instruments Inc., South Pasadena, U.S.A.) in conjunction with a G-1190-50 glass electrode. Readings were not corrected for sodium-ion.

Ion-exchange experiments were done with an ion-exchange column similar to the one described by Larrabee (112). The column was prepared as follows: the resin was slurried in water in a beaker, washed into the column and allowed to settle to form the desired size of bed. This bed was kept in place at the top and bottom by wads of glass wool that had been previously washed with carbon tetrachloride and water. The resin was then washed with 50 ml. each of 10 M and 4 M hydrochloric acid and then with 50 ml. of distilled water. These washings removed the yellow colour which a new resin usually imparts to concentrated hydrochloric acid. Regeneration of resin was accomplished by washing with 3-4 M hydrochloric acid until the effluent gave negative tests for ions which had been previously adsorbed; then 50 ml. of 0.1 M hydrochloric acid was put through the column.

Mercury-cathode separations were made with the cell described by Graham, Hitchen and Maxwell (77). A Fisher A.C. Model Electrophotometer was used for absorptiometric determinations.

(b) Reagents

These were as follows:

Chemical	Source and Grade
Acetic acid (glacial)	C. I. L., C.P. reagent
Acetone	Mallinckrodt, N.F. grade
Acetylacetone	British Drug Houses, certified chemical

Chemical	Source and Grade
Alizarin Red S	National Aniline Division of Allied Chemical and Dye Corporation
Aluminium (rod)	Johnson, Matthey and Co., Ltd. (minimum purity reported as 99.99% Al.)
Aluminium sulfate	General Chemical Company, reagent grade
1-Amino-4-hydroxyanthraquinone	Eastman Kodak, practical
Aurintricarboxylic acid	Eastman Kodak, practical
Beryllium chloride (anhydrous)	Amend Drug and Chemical Co.
Beryllium (flake)	Johnson Matthey and Co., Ltd. (Their spectrographic analysis is reported as follows: 99.5% Be, 0.40% Al, 0.055% Fe, plus traces of other elements.)
Benzoylacetone	(a) Eastman Kodak, white label (b) Matheson, Coleman and Bell
Chromeazurol S	Delta Chemical Works, Inc.
Curcumin	Eastman Kodak, white label
1,8-Dihydroxyanthraquinone	Eastman Kodak, practical
1,4-Dihydroxy-2-anthraquinone (sodium salt)	Eastman Kodak, practical
Dipicrylamine	Eastman Kodak, white label
Dowex resin (50W x 8 and 50W x 12)	Dow Chemical of Canada, Ltd.
Ethyl alcohol (95%)	Gooderham and Worts, Toronto

Chemical	Source and Grade
Gelatin	Eastman Kodak, purified pigskin
Hydrochloric acid	C. I. L., analyzed grade
Lithium hydroxide	Merck and Co., Ltd., reagent grade
Mercury	Purified by bubbling for at least three hours in 10-15% nitric acid, then washed twice with tap water and once with distilled water, then dried, filtered, and distilled three times *in vacuo*
Methyl Red	British Drug Houses, Analar
Morin	Eastman Kodak, blue label
Naphthachrome Azurine 2B	Ciba Co., Ltd.
Naphthachrome Green G	Ciba Co., Ltd.
Naphthazarin	Delta Chemical Works, Inc.
Nitrogen	Canadian Liquid Air Company, further purified by bubbling through an alkaline solution of potassium pyrogallate
Pontachrome Blue Black R	Eastman Kodak, practical
4-(p-Nitrophenylazo)orcinol	Eastman Kodak, yellow label
Quinalizarin	(a) British Drug Houses, spot test reagent (b) Fisher Scientific Co., C.P. reagent

Chemical	Source and Grade
Quinizarin sulfonic acid	British Drug Houses, indicator grade
Sulfosalicylic acid	Merck and Co., Ltd.

All other reagents were analyzed grade.

The benzoylacetone used in the experiments was purified by one or other of the following methods :

(1)✶ Ten grams of benzoylacetone (Matheson Coleman and Bell grade) was distilled, under a pressure of 5-10 cm. of mercury. The recorded boiling point at this pressure was 142-143°C. The melting point of the product, a white crystalline one, was 57.5-58°C.

(2)✶ Five grams of benzoylacetone (Eastman Organic Chemicals, white label) was dissolved in a minimum amount of hot (70°C.) ethyl alcohol (95%) in an Erlenmeyer flask and placed on a steam cone. Boiling water was then added till the solution was almost turbid. The flask was then removed from the steam cone and allowed to cool slowly to room temperature. The mixture was filtered and the resultant crop of crystals was recrystallized in a similar manner. The overall yield was 70%. The melting point was 57.5-58°C.

p-Dioxane was purified by distilling a reagent grade product (Eastern Chemicals Corporation) from sodium. The fraction that distilled over at 99-101°C. was collected. The yield was 90%.

(c) Solutions

The gelatin dispersion was prepared by dispersing one gram of

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✶ In all experiments involving the use of benzoylacetone, the method of purification of the reagent used in that particular experiment is referred to by the number (1) or (2) following the name.

gelatin in 100 ml. of cold water, allowing this to stand for one-half
hour, then heating to approximately 70°C. and finally allowing the
dispersion to cool. This solution was stable for about three days if
it was kept in a refrigerator.

Stock solutions used in the ion-exchange work were prepared as
follows: Aluminium rod was dissolved in 50 ml. of 6 M sulfuric acid
and then diluted to one liter with water. The final aluminium concen-
tration was 561.3 mg. per liter. Aliquot portions of this stock solu-
tion were used in experiments $\overline{I}$ to $\overline{V}$. Another solution of aluminium
was prepared by dissolving aluminium sulfate 18-hydrate (66.6 g.) in
one liter of water. Aliquot portions of this solution were used in
experiments $\overline{VI}$ to $\overline{IX}$. Beryllium solutions were prepared by dissolving
beryllium flake in slightly more than a minimum quantity of approxi-
mately 6 M sulfuric acid and then diluting the solution with water to
give the required beryllium concentration.

Exception to this method of preparing stock beryllium solution
is found in the section "Possible Polarographic Reagents for Beryllium
other than Benzoylacetone". In experiments under this heading, stock
solutions were prepared by dissolving anhydrous beryllium chloride in
water.

The observed molting point of beryllium benzoylacetonate pre-
pared in the course of this investigation (208°C.) approached that of
209-211°C. reported in the literature (33,39).

<u>11</u>   Possible Polarographic Reagents for Beryllium

other than Benzoylacetone

A substantial number of reagents other than benzoylacetone
were investigated to ascertain their possible usefulness in an indi-
rect polarographic determination of beryllium. As is indicated below,
some of these were given only cursory examination and others were in-
vestigated in some detail. Only one of the reagents dealt with in
this section, however, appears to be promising for use in a polaro-
graphic method for beryllium.

Reagents to which some, though little, attention was given
were: Alizarol Azurine F.C.A., alizarinsulfonic acid, aluminon, 1-
amino-4-hydroxyanthraquinone, 1,8-dihydroxyanthraquinone, naphthazarin,
Naphthochrome Azurine 2B, Naphthochrome Green G and sulfosalicylic
acid. In almost all cases the polarographic results with these rea-
gents were such as to discourage further investigation. In some cases
poor waves were obtained, in others no waves at all were found. These
observations did not even encourage purification of those reagents
whose purity was questionable. For these reasons, amongst others,
these substances were not investigated in any detail.

Because preliminary experiments offered some encouragement,
further exploratory work was carried out with each of the following
reagents: (a) acetylacetone, (b) Chromeazurol S, (c) dipicrylamine,
(d) 4-(p-nitrobenzeneazo)orcinol, (e) quinalizarin and (f) quinizarin-
2-sulfonic acid.

21

(a) Acetylacetone (1,99)

In a 0.1 M solution of lithium chloride, acetylacetone (or an impurity in it) gave a well defined wave at a half-wave potential of about -1.9 volts (versus the quiet mercury pool electrode). After the solution had stood for some twenty hours the diffusion current had decreased by 60-70%. In a 0.1 N solution of ammonium chloride two waves were observed at half-wave potentials of approximately -1.9 and -2.1 volts. These waves, though not entirely unmeasureable, were not analytically attractive. The only wave on the polarogram obtained from an aqueous solution of acetylacetone in 0.01 M hydrochloric acid and 0.1 M potassium chloride was one due to hydrogen.

It was decided, in view of the vastly better wave forms given by other organic compounds that were under study, to discontinue work with acetylacetone.

(b) Chromeazurol S (178,208)

Aqueous solutions of Chromeazurol S buffered at pH 6.1 and 7.4 with citrate and acetate buffers, respectively, produced two-step reductions, the waves of which were not very exciting. Aqueous solutions of the reagent using lithium chloride as a supporting electrolyte also showed very little promise. On one occasion a solution of Chromeazurol S buffered at pH 5.5 with sodium acetate gave very poor waves but at a later date, another solution apparently similarly prepared, gave quite measureable waves. This discrepancy was not resolved for a more serious objection was noticed. During the removal of dissolved oxygen by bubbling nitrogen through a solution of Chromeazurol S containing beryllium, a fairly stable foam was formed. This

necessitated a considerable decrease in the rate of bubbling with, consequently, an increase in the time needed for the removal of oxygen. Moreover, a blue precipitate was observed in the foam.

Altogether, this reagent was not promising and studies with it were discontinued.

(c) Dipicrylamine (99,142,195)

Preliminary experiments showed that solutions of dipicrylamine in an acetate medium were very stable and that they gave a well-defined polarographic wave in acetate buffers at pH values of about 5 to 6. It was also observed that beryllium is precipitated by solutions of dipicrylamine at pH values of about 5 to 6. Most of the subsequent work, however, unfortunately revealed a series of complicating problems. These are briefly outlined below.

The calibration curve obtained by plotting the concentration of dipicrylamine (using an acetate buffer at pH 4.5 ± 0.04) against the diffusion current, though smooth, was not a linear one. It was found that the precipitation of beryllium dipicrylaminate is very slow, especially so when the concentration of beryllium is low. The technique of scratching the inner side of the vessel with a glass rod to induce precipitation yielded a modest improvement. It soon became evident that the pH in the precipitation process is very critical: below a pH value of 5 the reagent, at the concentrations used, itself began to precipitate, and above a pH of about 5.7 to 6, beryllium, in the concentrations used (less than 50 mg./l.), began to precipitate as the hydrous oxide. Increasing the alcohol content of the dipicrylamine solution lowered the pH value at which precipitation of dipicryl-

amine would occur but it also increased very significantly the solubil-
ity of the beryllium dipicrylaminate. Furthermore, it was exceedingly
difficult to reproduce results even under what appeared to be identical
conditions of precipitation and polarography. Precipitation of ber-
yllium was also never found to be quantitative, even at the pH values
approaching those that would precipitate the hydrous oxide of beryll-
ium.

In view of these and other disadvantages it was decided that
the study of this reagent be abandoned in favour of a more suitable
reagent for beryllium.

(d)   4-(p-Nitrobenzeneazo)orcinol (50,52,101,138,150,172,204)

In solutions, buffered with tartrate at pH values of 11, 11.5,
12.1 and 12.3, and containing gelatin as a maximum suppressor, quite
measureable and reproducible two-step reductions were obtained. Addi-
tions of beryllium to these solutions did not bring about a change in
diffusion current. Conditions almost identical to those used in absorp-
tiometric studies by Pollock (150) and Osborn (138) were also tried,
but with unsuccessful results. Changing the buffer system to borate
did not yield any encouraging effects.

This work suggested that the absorptiometric method for beryll-
ium using p-nitrobenzeneazoorcinol cannot readily be adapted to a po-
larographic method.

(e)   Quinalizarin (56,90,206)

Experiments with quinalizarin in buffered alkaline solution
showed that this compound can be polarographically reduced. The wave,
however, is relatively poorly defined: the uncertainty in the measure-

ment of a given wave is about ± 3%. Solutions prepared from recrystallized quinalizarin (recrystallized from nitrobenzene, ethanol or acetic acid) or with quinalizarin purified by sublimation in vacuo, yielded waves that were little improved.

Quinalizarin is noticeably unstable in borate and tartrate buffers, this instability being greater the higher the pH. As much as a 50% reduction of diffusion current in 24 hours was found in some cases. Furthermore, in strongly alkaline solution, a fading of the colour of the beryllium complex in solution occurs at the rate of approximately 10% every 30 minutes (90). The storing of alkaline solutions of quinalizarin in the dark did not produce a significant increase in stability.

Another serious objection to the use of quinalizarin is the very pronounced dependence of its diffusion current on pH. For example, in the pH range 11.2 to 12.1 the diffusion current for a given concentration of quinalizarin varied by about 20%.

In acid media (sulfuric acid, acetic acid or hydrochloric acid) waves were also obtained but a similar deterioration in wave slope and diffusion current with time was found.

Because of these characteristics, work with quinalizarin was discontinued.

(f) Quinizarin-2-sulfonic acid (51,35,167)

The effect of pH (between the values 3.6 and 12.1) on the wave form and diffusion current was investigated using various buffer systems. This work can be summarized as follows: the wave form degenerates at the higher pH values; the diffusion current increases as the

pH value increases; a serious instability was observed at the higher
pH values; however, satisfactory stability for a period of 2 hours was
found at a pH value of about 7 (an 8% reduction in diffusion current
was noted after 20 hours' standing even when the solution was stored
in the dark); in the pH range 6.3 to 7.3 the diffusion current of a
0.04% solution of reagent in an ammonium acetate buffer was constant;
the diffusion current of a solution of the reagent in an ammonium ace-
tate buffer at pH 7.1 is a linear function of concentration up to a
concentration of 0.04%; the ammonium acetate-dye system at pH 7.1 gives
a wave that is as good as, or better than, waves given at other pH val-
ues.

Qualitative tests with the dye and various concentrations of
beryllium with the mixed solutions at pH values of 5, 7 and 12 showed
a striking colour gradation only in the solutions with a pH value of
7.1. Polarographic tests on all these solutions showed little or no
reduction in diffusion current (when beryllium was present) except on
those solutions whose pH value was 7.1.

Preliminary experiments indicated that quinizarin-2-sulfonic
acid and beryllium probably react in the ratio of two moles quinizarin-
2-sulfonic acid to one mole beryllium at a pH value of 7.1.

This reagent is quite promising and more work with it (possibly
using a histidine monohydrochloride buffer system and applying gentle
heat to increase the rate of reaction (51)) is recommended.

III   Benzoylacetone as a Polarographic Reagent for Beryllium

The preceding Section (II) is concerned with reagents whose study did not prove fruitful for the development of a polarographic method for the determination of beryllium. The present Section deals with another reagent - benzoylacetone - whose study proved much more rewarding.

The work set forth on the next several pages has to do with properties of benzoylacetone, and with characteristics of the reaction between benzoylacetone and beryllium, that seemed relevant to the development of a method for the determination of beryllium using this organic reagent. Among the matters considered are factors that influence the polarographic wave given by benzoylacetone; the stability of solutions of benzoylacetone; the rate, completeness, and stoichiometry of the precipitation of beryllium by benzoylacetone; and calibration procedures for the method that was developed from these studies.

(a) Polarography of Benzoylacetone

Benzoylacetone has previously been shown to be polarographically reducible (102,151,175,176), although no analytical use has been made of this fact. Experiments in this laboratory have shown that the wave given in acid media (pH about 1) is the one most easily measured and is on other accounts the one best suited to analytical work.

(1) Effect of pH. Solutions of benzoylacetone of pH values in the range 0.60-1.85 containing a constant concentration of benzoylacetone

27

No 2*$(2.1 \times 10^{-4}$ M), sodium acetate $(5.0 \pm 0.5 \times 10^{-2}$ M), and ethyl alcohol (15% by volume), were prepared using 18 M sulfuric acid for the pH adjustment. The polarography of these solutions showed that the wave form and diffusion current were virtually independent of pH over the range studied. The half-wave potential, however, shifted to slightly more negative values with increasing pH.

Another experiment was carried out using aliquot portions of a solution saturated with benzoylacetone No 1 and containing sodium acetate $(0.10 \pm 0.01$ M). This time the desired pH values were obtained by adjustment with 12 M hydrochloric acid. These solutions did not contain any alcohol. The observations were similar to those of the first experiment. The only major difference was that the half-wave potential was slightly less negative with these solutions. Again, the half-wave potential became more negative with decreasing acidity of the solutions.

In a similar experiment from which, again, alcohol was excluded, it was found that benzoylacetone No 2 $(2.1 \times 10^{-3}$ M) in solutions 1.75 M in acetic acid, whose pH values were adjusted with 18 M sulfuric acid, gave a constant diffusion current in the pH range 0.7 to 1.4. At slightly higher pH values (2.1), however, the diffusion current showed a decrease (about 3%).

The measured half-wave potential (versus S.C.E.) of benzoylacetone in a 1.75 M solution of acetic acid whose pH was adjusted to 1.0 with 18 M sulfuric acid was -0.89 volts. In chloride media the

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*See footnote in Section 1 (d), page 19, for an explanation of the number.

half-wave potential is somewhat less negative, being about -0.7 volts.

A typical polarographic wave for benzoylacetone, obtained at pH 1.0, is shown in Figure 1. From this it is seen that the wave form is excellent.

(ii) Effect of Ethyl Alcohol. Because benzoylacetone is not very soluble in water, ethyl alcohol was used to facilitate the dissolution of the reagent. It was therefore considered necessary to investigate the effect of alcohol on the polarographic wave (though later developments showed this not to have been necessary).

Solutions containing similar concentrations of benzoylacetone No 2 (about 5×10^{-4} to 10×10^{-4} M) and sodium acetate (0.10 ± 0.01 M) and varying concentrations of ethyl alcohol (up to 50 by volume) were polarographed after the pH of each solution had been adjusted to 1.00 ± 0.01 with 12 M hydrochloric acid. The results, given in Table $\overline{I}$, show that there is an almost linear decrease in diffusion current with increase in alcohol concentration up to about 35 alcohol by volume. Above this, the wave form degenerates quite rapidly and at an alcohol

TABLE $\overline{I}$

Effect of Ethyl Alcohol on Diffusion Current of Benzoylacetone

Alcohol (by volume)	Wave Height (mm.*)	Viscosity(η) (centipoises)	$\sqrt{\eta}$	$i_d \eta^{1/2}$
0	169	0.89	0.94	159
12.4	143	1.32	1.15	164
24.1	122	1.82	1.35	165
35.2	108	2.18	1.48	160

*Average of readings on 6-8 polarograms. In all of these and succeeding measurements the average deviation is about 0.4 mm.
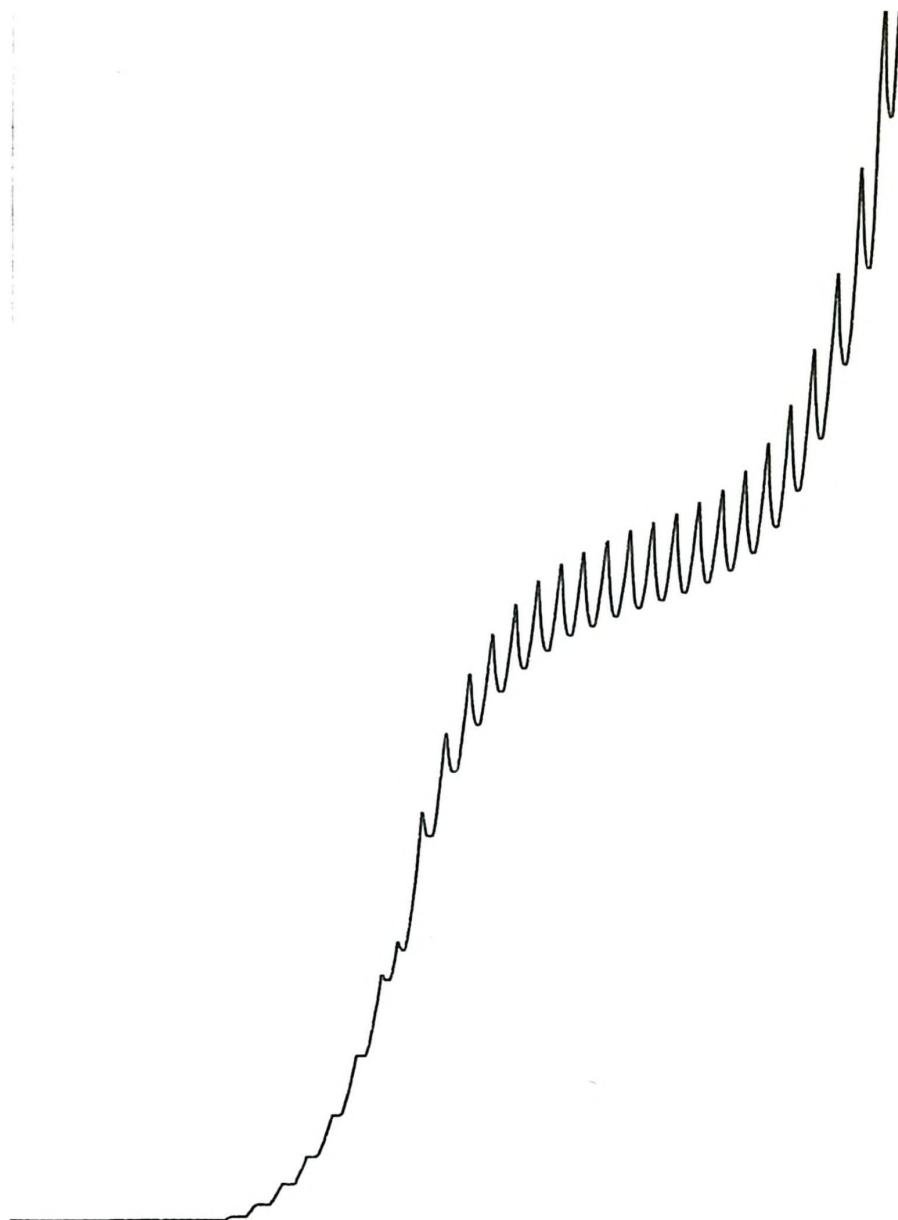
FIGURE 1

A Typical Polarogram of Benzoylacetone

concentration of 50%, the distortion in the waves make their precise measurement impossible. The relevance of the last three columns of Table $\underline{I}$ will be dealt with later (page 67).

(iii) Effect of Chloride, Nitrate and Sulfate Ions. In the early stages of experimentation, the choice of an acid that could most advantageously be used to lower the pH of a solution of benzoylacetone had to be considered. Although many possibilities were open, only the three most common inorganic acids were investigated. The experiment took the following form:

The pH of 50-ml. portions of solutions, 6.2×10^{-4} M in benzoylacetone No 1, 0.09 ± 0.01 M in sodium acetate, and containing 9.5% ethyl alcohol (by volume), were adjusted to 1.00 ± 0.01 with 12 M hydrochloric acid, 16 M nitric acid or 18 M sulfuric acid just prior to polarography in each case. The wave form was not influenced by the acid used. Table $\underline{II}$ shows the effect of these acids on the diffusion current and half-wave potential of benzoylacetone.

TABLE $\underline{II}$

Effect of Certain Anions on Polarographic Characteristics

of Benzoylacetone

Acid used to Adjust pH	E (volts*)	Wave Height (mm.±)
HCl	-1.05	53.5
HNO$_3$	-1.35	53.7
H$_2$SO$_4$	-1.35	52.7

* Versus quiet mercury pool electrode.
± Average of readings on 6-8 polarograms.

(iv) <u>Effect of Acetate-Ion</u>. In early experiments, sodium acetate had served both as a buffering component and as a supporting electrolyte. In order that succeeding experiments (following the observation that sodium acetate was not really needed) in which sodium acetate was not present not be invalidated, the following experiments were deemed necessary.

The concentration of sodium acetate in solutions containing a constant concentration of benzoylacetone No 2 ($1S.6 \times 10^{-4}$ M) and of ethyl alcohol (9.5% by volume) was varied between zero and 0.15 M. The pH for polarography was adjusted to 0.83 ± 0.02 by adding 1 ml. of 18 M sulfuric acid. The results, given in Table $\overline{111}$, show that the diffusion current is independent of the concentration of acetate-ion, at least for concentrations of this ion up to 0.15 M.

<div align="center">

TABLE $\overline{111}$

<u>Effect of Acetate-Ion on the Diffusion Current</u>

<u>of Benzoylacetone</u>

</div>

Concentration of Acetate-Ion (M)	Wave Height (mm.*)
0.000	142.5
0.001	140.6
0.005	139.9
0.015	140.8
0.050	139.7
0.150	139.9

* Average of readings on 6-8 polarograms.

The effect of higher concentrations of acetate-ion on the diffusion current of benzoylacetone, containing neither ethyl alcohol nor sodium-ion, was also studied. A decrease in wave height (89.5 to 70.2 mm.) was observed for increasing concentrations of acetate ion (0.05 to 4.43 M). In a solution containing acetate-ion in a concentration of 8.75 M the wave was so poorly defined that it was unmeasureable.

(v) Stability of Benzoylacetone Solutions. A solution of 95% ethyl alcohol (by volume) 61 X 10^{-4} M in benzoylacetone No 1, was stored in a volumetric flask at room temperature. At intervals, some days apart, 10-ml. aliquot portions were withdrawn and diluted to 100 ml. with a 0.1 M sodium acetate solution. The pH of each sample withdrawn was adjusted to 1.00 ± 0.02 with 12 M hydrochloric acid, and the solution was polarographed. The data, recorded in Table IV, show that the diffusion current remained constant, within the precision of measurement.

TABLE IV

Stability of Benzoylacetone Solutions

Time (days)	Wave Height (mm.[*])
1	52.7
7	53.1
10	52.4
30	52.5
60	52.8

[*] Average of readings on 6-8 polarograms.

In another experiment, the pH value of a stock solution consisting of benzoylacetone No 1 (6.1×10^{-4} M), sodium acetate (0.09 M) and 9.5% ethyl alcohol (by volume), was adjusted to 5.0 ± 0.1. Portions were periodically withdrawn, the pH was adjusted to 1.00 ± 0.01 with 12 M hydrochloric acid, and then the solution was polarographed. The wave height values were constant, at least for 10 days.

Further indications of the stability of benzoylacetone is afforded by data recorded elsewhere: in Figure 3 (page 37) and Table VI (page 43).

(vi) <u>Diffusion Current of Benzoylacetone as a Function of its Concentration</u>. A calibration curve (Figure 2) was obtained for 9.5% (by volume) alcoholic solutions of benzoylacetone No 2 in concentrations up to 17×10^{-4} M. The concentration of sodium acetate in these solutions varied from 0.01 to 0.05 M, but earlier work (Table III) had shown that such variation would not affect the diffusion current of benzoylacetone. The pH value for polarography (0.90 ± 0.05) was obtained by adjusting the acidity of each solution with 18 M sulfuric acid. As is seen from Figure 2, a straight line was obtained which, when extrapolated, goes through the origin.

It was found that for concentrations of benzoylacetone below about 3×10^{-4} M the base line of the wave is not horizontal; this makes measurement more difficult and less precise. For polarographic work a concentration of reagent above this value is therefore recommended.

(b) Precipitation of Beryllium with Benzoylacetone

(i) <u>Rate of Precipitation</u>. An experiment designed to gain information
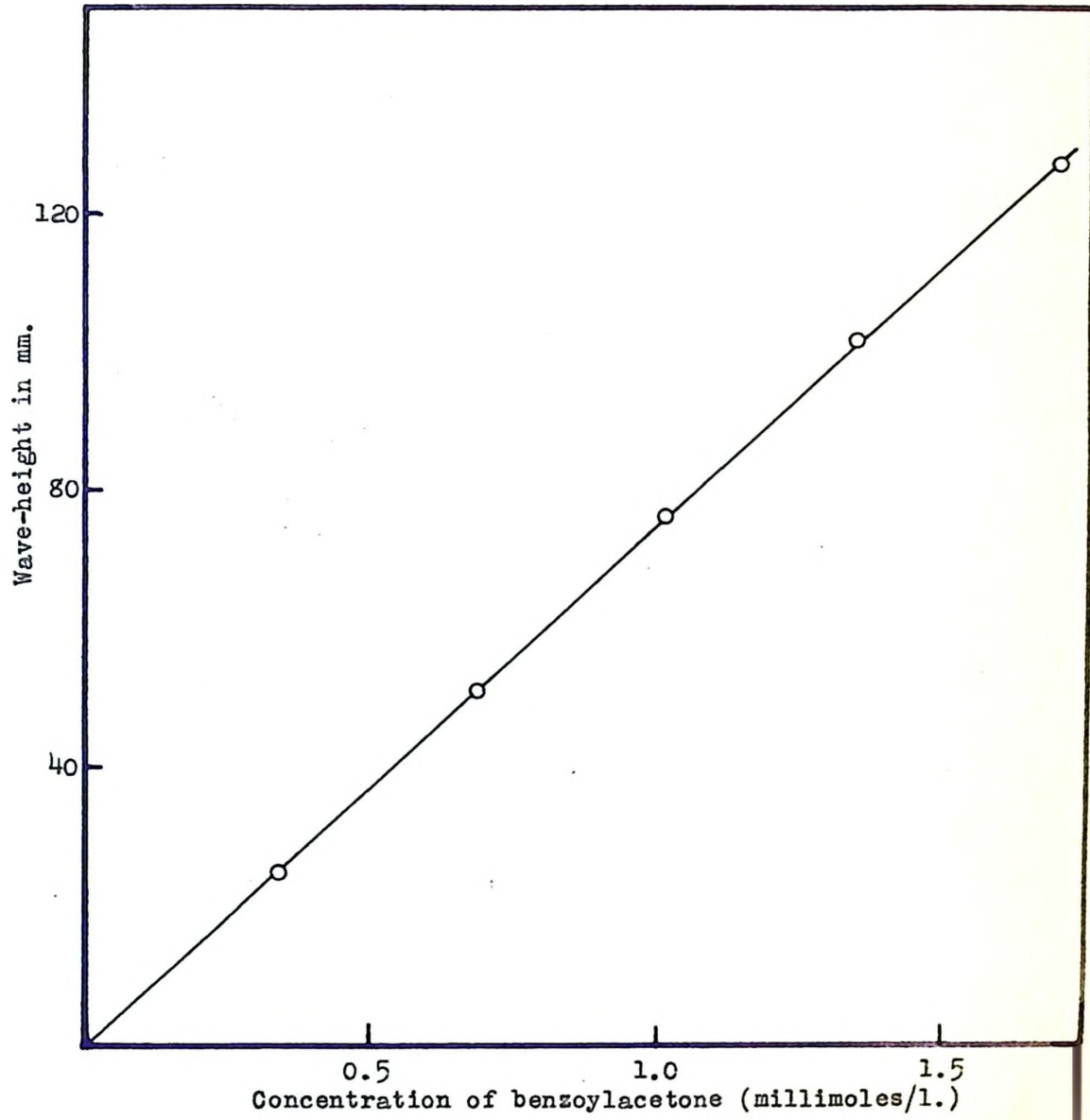
FIGURE 2

Calibration Curve

about the rate of precipitation of benzoylacetone by beryllium was per-
formed as follows: To 125 ml. of a solution containing ethyl alcohol
(19% by volume), benzoylacetone No 2, and sodium acetate (0.10 ± 0.01 M),
there was added an equal volume of a solution containing beryllium-ion
so that the concentration (before precipitation) of benzoylacetone was
about 20 X 10^{-4} M and that of beryllium was about 5 X 10^{-4} M. The pH
was then adjusted to 6.0 ± 0.1 using both sulfuric acid and a sodium
hydroxide solution. After various intervals of time 30-ml. portions
of the supernatant solution were removed by filtering through Whatman
No 42 filter paper. The pH values of the filtrates were then adjusted
to 1.00 ± 0.02 with 18 M sulfuric acid and the solutions polarographed.
The results show that precipitation is complete in one hour.

A similar experiment was carried out using a lower concentra-
tion of beryllium (about 2 X 10^{-4} M) and substantially the same concen-
tration of benzoylacetone No 2. In this instance, too, precipitation
was found to be complete within one hour.

The results of both these experiments are plotted in Figure _
in which the "open" symbols refer to the control solutions (to which
no beryllium was added, but which otherwise were treated similarly).

(ii) Completeness of Precipitation of Beryllium Benzoylacetonate as a
Function of pH. To solutions of beryllium were added solutions of
benzoylacetone No 2 so that the concentrations of beryllium and benzo-
ylacetone after mixing, but before reaction, were 4.9 X 10^{-4} M and
about 18 X 10^{-4} M, respectively. The final solution in every case also
contained 9.5% alcohol (by volume) as well as sodium acetate (0.05 to
0.08 M). The pH values of these solutions after mixing were adjusted
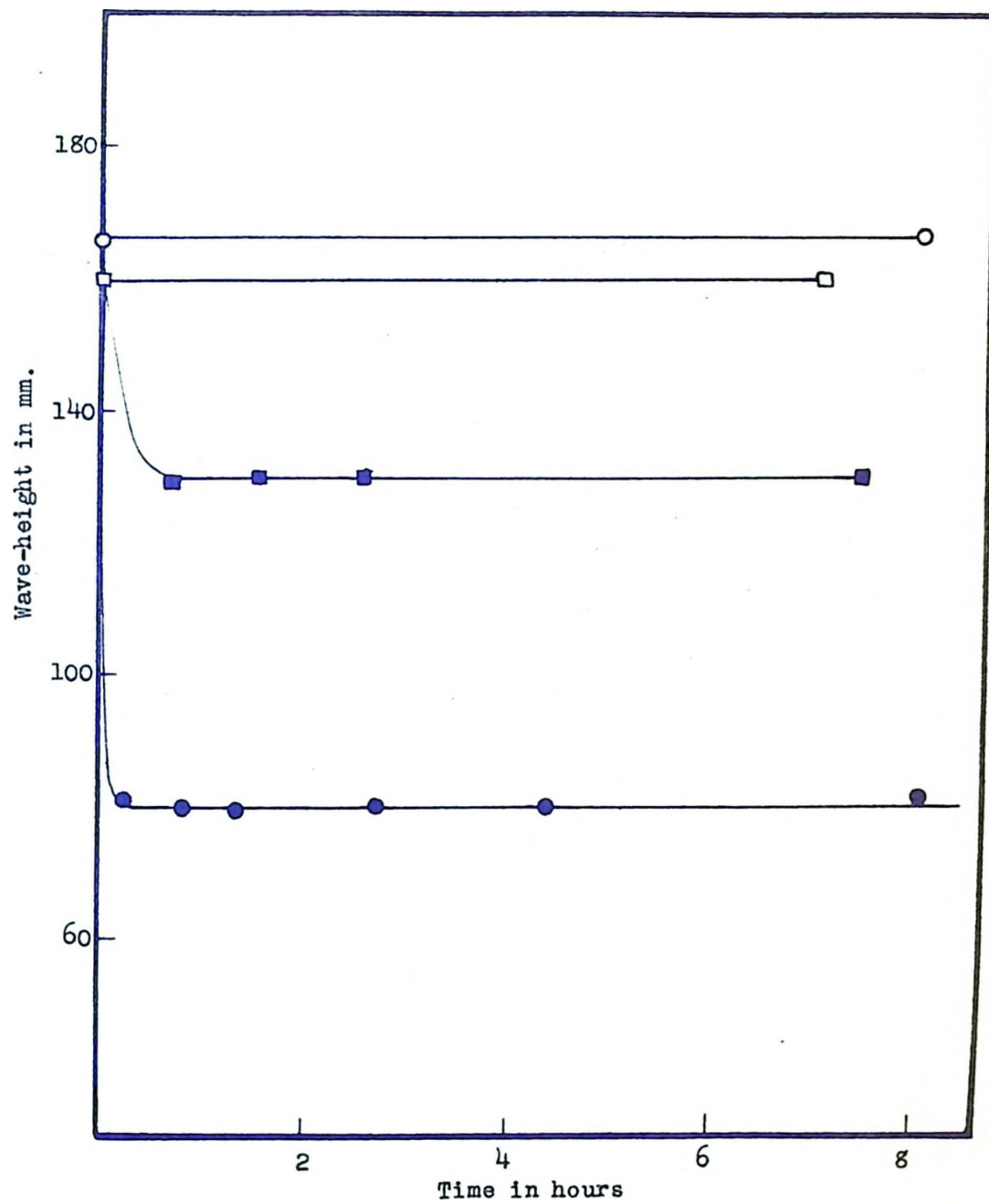
FIGURE 3

Rate of Precipitation of Beryllium Benzoylacetonate

with either sulfuric acid or sodium hydroxide. All were diluted to the
same volume with water. The reaction mixtures were then allowed to
stand 2-6 hours and then filtered through Whatman No 42 filter paper.
The pH of each of the supernatant solutions was adjusted to 1.0 ± 0.1
with 18 M sulfuric acid, and then the solutions were polarographed.

The results of the experiment, shown in Figure 4, indicate that
no precipitation occurs at pH values below 2.9.

When those reaction mixtures and controls whose pH values were
above 8 were allowed to stand for from 12 to 20 hours, a decrease in
diffusion current was noted. (There is, of course, no necessity for
such long standing periods.) The data of Figure 4 suggest further that
precipitation is complete at a pH value of about 5.1 and that precipi-
tation is constant over a range of at least 2 pH units. At pH values
higher than 11, no precipitation takes place.

(iii) Completeness of Precipitation of Beryllium Benzoylacetonate. In
attempting to determine polarographically the extent of precipitation
of beryllium benzoylacetonate the following assumptions were made: that
purified benzoylacetone could be used as a primary standard; that two
moles of benzoylacetone react with one of beryllium (24); that the pres-
ence of aluminium (0.40% of the beryllium metal used in making the stock
solution is aluminium) may be nullified by considering in the calcula-
tion that one mole of aluminium reacts with three moles of benzoylace-
tone. That this last assumption is correct was shown in later work
(page 49).

The calibration curve given earlier, (Figure 2) was used. A
resumé of the method is as follows: To a known volume of a solution of
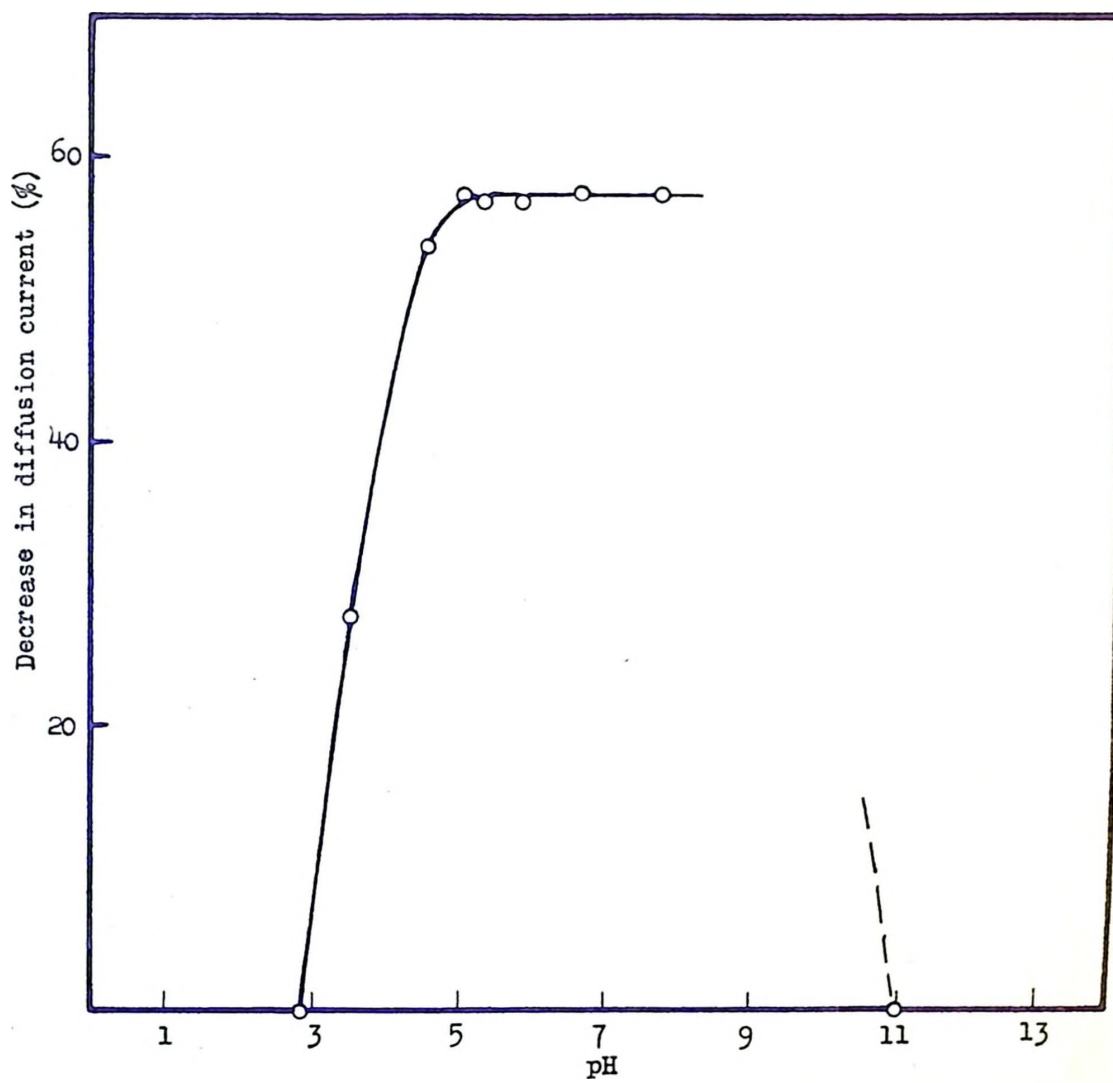
FIGURE 4

Precipitation of Beryllium Benzoylacetonate as a Function of pH

known concentration of benzoylacetone, there was added an equal volume
of a solution of beryllium of known concentration. The concentration
of benzoylacetone remaining in the solution was calculated, assuming a
stoichiometry of 2:1. This concentration was compared with that found
experimentally (Table $\overline{V}$). Alternately, using the same data, but assum-
ing complete precipitation, the stoichiometry of the reaction can be
calculated (Table $\overline{V}$).

The procedure in greater detail follows: To a 100-ml. portion of
benzoylacetone solution of accurately known concentration containing
19% ethyl alcohol (by volume) and sodium acetate (0.04 M), was added
100 ml. of a beryllium solution of accurately known concentration. Con-
centration data are implied by the data of Table $\overline{V}$. The pH value was
adjusted appropriately using varying concentrations of a sodium hydrox-
ide solution. The mixture was allowed to stand at room temperature for
two hours and then filtered through a medium porosity fritted glass cru-
cible directly into a 250-ml. volumetric flask, washed 4-5 times with
ice-cold water (with the wash liquid being allowed to drain into the
flask) and then the filtrate and washings were made up to volume with
water and ethyl alcohol to give a final concentration of 9.5% ethyl al-
cohol. Sulfuric acid (18 M) was added to the filtrate for pH adjustment
(0.90 ± 0.05) and the dilution factors were noted. The solution was
then polarographed.

The results of two such experiments, (given in Table $\overline{V}$), indi-
cate that the precipitation is quantitative, within experimental error,
if the precipitate requires two moles of benzoylacetone for every mole
of beryllium. Conversely, by assuming that the precipitation is 100%,

the data indicate that the stoichiometry is 2:1.

A difficulty encountered in attempting to dry benzoylacetone to constant weight for the preparation of the standard solution suggested that this substance sublimes fairly readily. That this is actually so was shown by heating a small quantity of benzoylacetone in a flask placed on a jacket heater. The temperature was carefully controlled at 45° ± 2°C. for about 30 hours, at the end of which time a sublimate had collected on the inside of the water-cooled condenser attached to the mouth of the flask. A further indication of the volatility of the compound was obtained by heating a quantity of benzoylacetone No 2 in an

TABLE $\overline{V}$

Precipitation of Beryllium with Benzoylacetone (BzAc)

	Experiment $\overline{I}$	Experiment $\overline{11}$
pH of precipitation	5.25 ± 0.02	6.0 ± 0.1
Moles of beryllium taken *	6.67×10^{-5}	14.93×10^{-5}
Moles of BzAc available **	37.59×10^{-5}	37.57×10^{-5}
Calculated moles of BzAc remaining after precipitation (assuming 2:1 stoichiometry for BzAc:Be)	24.25×10^{-5}	7.71×10^{-5}
Moles of BzAc remaining (as determined polarographically)	23.95×10^{-5}	7.50×10^{-5}
Accordingly: per cent precipitation found	101.3	102.8
or, moles of BzAc reacting per mole of Be (assuming 100% precipitation)	2.04	2.01

* The grams of beryllium metal dissolved in the solution was 6.038×10^{-4} (6.699×10^{-5} moles, calculated as Be) but 0.4% of it is aluminium. A similar correction is made in Experiment $\overline{11}$.

** The moles of benzoylacetone used in Experiment $\overline{I}$ was 37.62×10^{-5}, but the aluminium present requires 0.03×10^{-5} moles. A similar correction is made in Experiment $\overline{11}$.

unstoppered weighing bottle at 45°C. and weighing the bottle at regular
intervals. Over a period of 3 1/2 days, the weight loss was 0.004% per
hour. The weighing of samples of this reagent for the preparation of
standard solutions should therefore always be done with a minimum of
delay; the weighed sample should be immediately, thereafter, dissolved
and the solution transferred to a stoppered flask.

(iv)   Dissolution of Beryllium Benzoylacetonate. In preliminary ex-
periments having to do with the choice of a good solvent for beryllium
benzoylacetonate, and one that would not have adverse effects on the
polarography of benzoylacetone, it was found that acetic acid or acetone
or p-dioxane could conceivably be used. These three solvents are
treated separately below.

The beryllium benzoylacetonate used in these experiments was
prepared by mixing equivalent quantities of beryllium and benzoylace-
tone, so that the final solution contained 9.5% ethyl alcohol (by vol-
ume). The pH was then adjusted to 6.0 with solutions of sodium hydrox-
ide. After the reaction mixture had stood for 2 hours, it was filtered,
the precipitate was washed several times with ice-cold water, and then
dried at 100°C.

Several experiments, using various concentrations of acetic acid
(4.4 M to 17.5 M) at various temperatures showed that, as expected, the
rate of dissolution increased with the concentration of acid and with
the temperature. The magnitude of the effects of concentration of acid
and of temperature, together with conditions imposed by, or rendered
desireable by, the nature of the method of analysis being developed in-
dicated that a concentration of acetic acid of about 8.8 M was very

suitable. A reasonable volume of this acid will dissolve the amount of beryllium benzoylacetonate expected in a determination in about 15 minutes at 65°C. and in about 2 minutes at 100°C.

This having been decided on, at least tentatively, experiments were performed with solutions of benzoylacetone in 8.8 M acetic acid in which the solutions were subjected to much more severe conditions (as regards time and temperature of heating) than would be met in an actual analysis. The results, shown in Table $\overline{VI}$, indicate that no decomposition of benzoylacetone need be feared during the dissolution procedure.

TABLE $\overline{VI}$

Stability of BzAc in Solutions of Acetic Acid

Conditions imposed on the solutions (BzAc No 2: 15.4×10^{-4} M; Acetic acid: 8.8 M)	Wave-height[*] (mm.)
Solution was polarographed immediately	98.2
Solution allowed to stand at room temperature for 4 hours before being polarographed	99.1
Solution allowed to stand at 100°C. for 4 hours before being polarographed	97.3
Solution allowed to stand at 60°C. for 5 hours before being polarographed	98.3

[*] Average of readings on 6-8 polarograms. Each solution, before being polarographed, was diluted with an equal volume of water and the pH of the solution adjusted to ~1.0 with 18 M sulfuric acid.

An aqueous solution of acetone is a very good solvent for beryllium benzoylacetonate, too; however, the volatility of acetone would be a serious disadvantage, for the diffusion current corresponding to a given concentration of benzoylacetone was found to be noticeably dependent (in a linear fashion) on the concentration of acetone in the solution. This effect, dealt with in the Discussion, is almost certainly

related to changes in the viscosity of the medium. The difficulty of maintaining a constant concentration of acetone in the solution being polarographed dictated the rejection of aqueous acetone as a solvent for beryllium benzoylacetonate.

An aqueous solution of p-dioxane (about 40% p-dioxane) is also an acceptable solvent for beryllium benzoylacetonate, but here again the diffusion current corresponding to a given concentration of benzoylacetone is dependent on the concentration of p-dioxane in the solution (changing about 1% for a change of 1% in the concentration of p-dioxane, at least in the concentration range 40-55%). This, together with the high concentration of p-dioxane required, led to the rejection of this solvent in favour of acetic acid.

(v) Calibration Curves for the Determination of Beryllium by means of Benzoylacetone. The experiments reported earlier, and other experiments, give reason to believe that beryllium can be determined by means of benzoylacetone in either of two ways: a known amount of benzoylacetone may be added to the beryllium solution, the beryllium precipitated quantitatively under appropriate conditions, and then the excess benzoylacetone determined polarographically; or an excess of benzoylacetone may be added to the beryllium solution, the precipitated beryllium benzoylacetonate filtered off, washed, and dissolved, and then the released benzoylacetone (which is equivalent to the beryllium) determined polarographically. Either method of course requires a calibration curve in which the polarographic diffusion current of benzoylacetone is related to its concentration. The methods used to obtain the calibration curves are set forth in what follows.

The calibration curve for the method in which the amount of excess benzoylacetone is assessed is considered first. Known volumes of a beryllium solution of known concentration were added to alcoholic solutions of benzoylacetone No 2 containing sodium acetate. The pH of each solution was then adjusted to 6.0 ± 0.1 with solutions of sodium hydroxide. The solutions after mixing, and before reaction, contained sodium acetate (0.04-0.06 M), alcohol (9.5 by volume), benzoylacetone (18.3×10^{-4} M) and beryllium (up to 6.6×10^{-4} M). After allowing each reaction mixture to stand at room temperature for 3-6 hours, it was filtered through Whatman No 42 filter paper. The pH of the filtrate was adjusted to 1.00 ± 0.01 with 18 M sulfuric acid, the solution was brought to volume with water, and then polarographed. A plot of the diffusion current given by the benzoylacetone in the supernatant liquid versus the concentration of beryllium in the original solution was essentially a linear one.

The calibration curve for the other method, in which the precip itated beryllium benzoylacetonate is dissolved and its content of ben-zoylacetone assessed, was obtained as follows. To 50-ml. portions of a solution (19% ethyl alcohol) of benzoylacetone No 2, there was added 50 ml. of solutions of beryllium of such concentrations that, after mixing, the solutions had the following beryllium concentrations: 1.5, 3.0, 4.5, 6.0, 7.5, 9.0 and 10.5 mg./l. (1.7×10^{-4} to 11.7×10^{-4} M). The pH values of these solutions varied from 1.8 to 2.6. No precipitation was observed in any of the solutions. The pH values were then adjusted to 6.5-7.2 by the addition, drop by drop, with stirring, of solutions of

sodium hydroxide; three solutions of widely varying concentration were used, the most concentrated being used first. The concentration of ethyl alcohol was not appreciably changed by this operation. Each mixture was then allowed to stand for 4 hours before filtering with suction through medium-porosity fritted glass crucibles. Each precipitate was then washed with cold water (about 5°C.), the filtrate and washings being discarded. The crucible and its contents were then placed in a beaker (on the steam plate) containing 50 ml. of hot (75°C.) 8.75 M acetic acid measured by a pipet. Dissolution of the beryllium benzoyl-acetonate took place within 30 minutes. The solution was then transferred quantitatively, with water as the wash solution, to a 250-ml. flask and made to volume with water. A 50-ml. portion was then withdrawn; 0.3 ml. of 18 M sulfuric acid added to adjust the pH to 1.00 ± 0.02, and then a portion of the solution was polarographed.

The results are plotted in Figure 5, from which it is seen that the data fit very well a straight line that, as it should, passes through the origin. The first two points (at the low concentrations of 3 and 6 milligrams of beryllium per litre) are a bit, though only a bit, off the line; this is accounted for by the fact that the corresponding polarograms had sloping base lines (in contrast to perfectly horizontal base lines on the polarograms for all the other points).

(c) Recommended Method for the Determination of Beryllium with Benzoyl-acetone

On the basis of the foregoing work, the following method for the determination of beryllium by means of benzoylacetone is proposed.
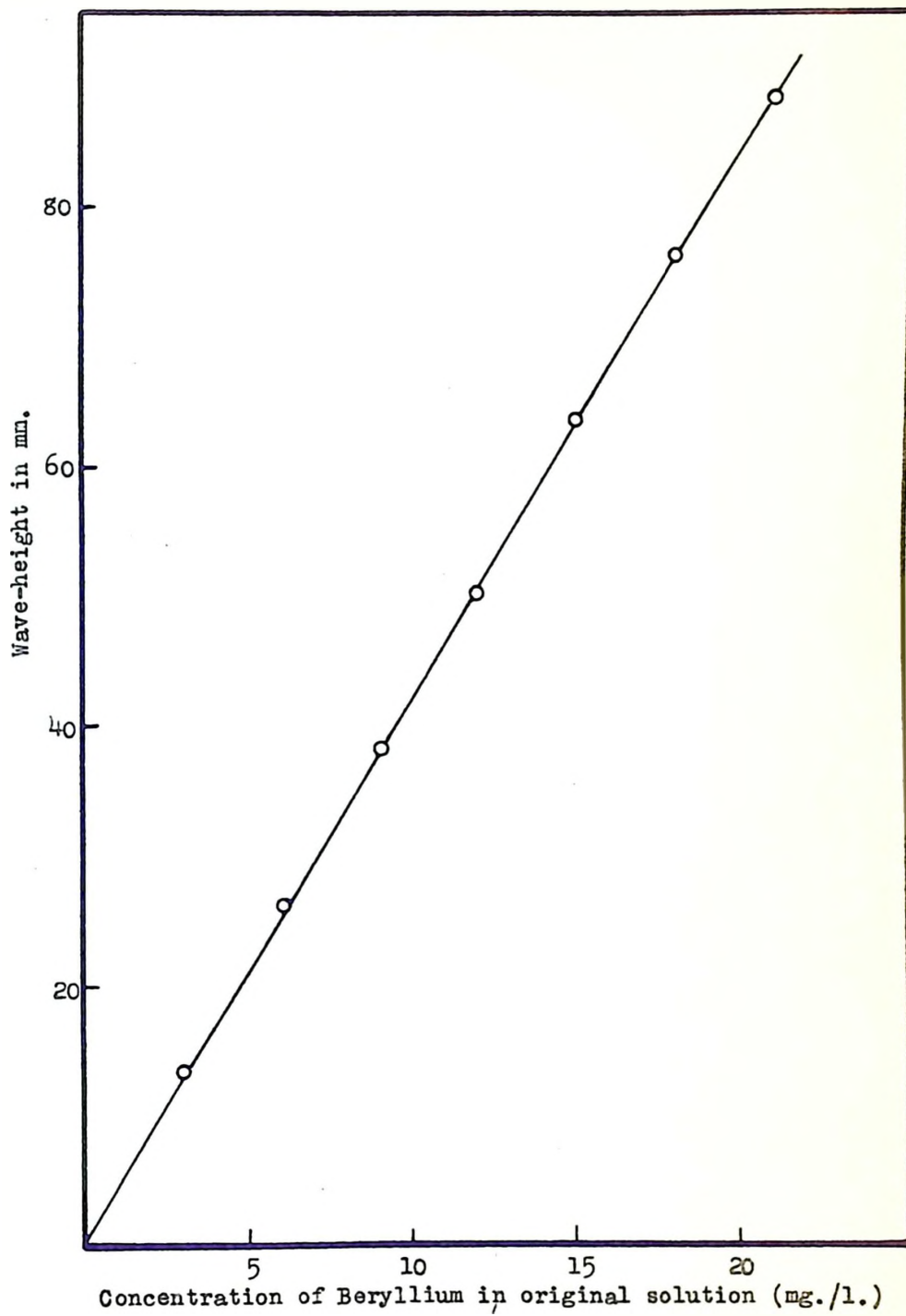
FIGURE 5

Calibration Curve

To 50 ml. of a solution containing less than one milligram of beryllium, and preferably about half a milligram, at a pH of 3 or below, add 50 ml. of a 0.09% solution of benzoylacetone in aqueous ethyl alcohol containing 19% (by volume) alcohol. Adjust the pH of the solution to between 5.5 and 7.5 by adding, drop by drop with stirring, solutions of sodium hydroxide of varying concentration; (start with a solution about 1 M and finish the adjustment with solutions of about 0.1 M and 0.01 M). Allow the mixture to stand at room temperature for 2 hours. Then filter the precipitate through a medium fritted glass crucible and wash 3 or 4 times with cold water (at about 5°C.). Next, dissolve the precipitate by immersing the crucible in a beaker containing 50 ml. (added by a pipet) of hot (75°C.) 8.75 M acetic acid. When dissolution of the precipitate is complete (which requires about 30 minutes) transfer the solution quantitatively with water to a 250-ml. volumetric flask and make up the solution to volume with water. After mixing the solution, transfer a 50-ml. portion of it to a graduated cylinder, and add 0.3 ml. of 18 M sulfuric acid. Decant a portion of this solution into a polarographic cell, bubble with purified nitrogen for 15 minutes and then polarograph the solution.

Record 6-8 polarographic waves for the reduction step of benzoylacetone, calculate the average wave-height, and assess the corresponding concentration of beryllium by reference to a calibration curve (such as that of Figure 5) constructed on the basis of experiments carried out in the same way using solutions of known beryllium content.

<u>IV</u>   Benzoylacetone as a Polarographic Reagent for Aluminium

The experiments that are described in this section have to do with the usefulness of benzoylacetone as a polarographic reagent for aluminium. They are concerned with the rate of precipitation of aluminium benzoylacetonate, the appropriate range of pH values for its precipitation, and with a possible analytical method for aluminium based on the use of benzoylacetone.

(a) Rate of Precipitation of Aluminium Benzoylacetonate

The rate of precipitation was studied in 3 solutions of 3 different pH ranges, over a period of at least 22 hours. The general procedure (the method of pH adjustment, alcohol content, filtration, etc.) and method for polarographing the supernatant liquid was as given in Section <u>111</u> (b) (i) (page 34). There was, however, no sodium acetate

TABLE <u>V11</u>

<u>Data Relating to Figure 6</u>

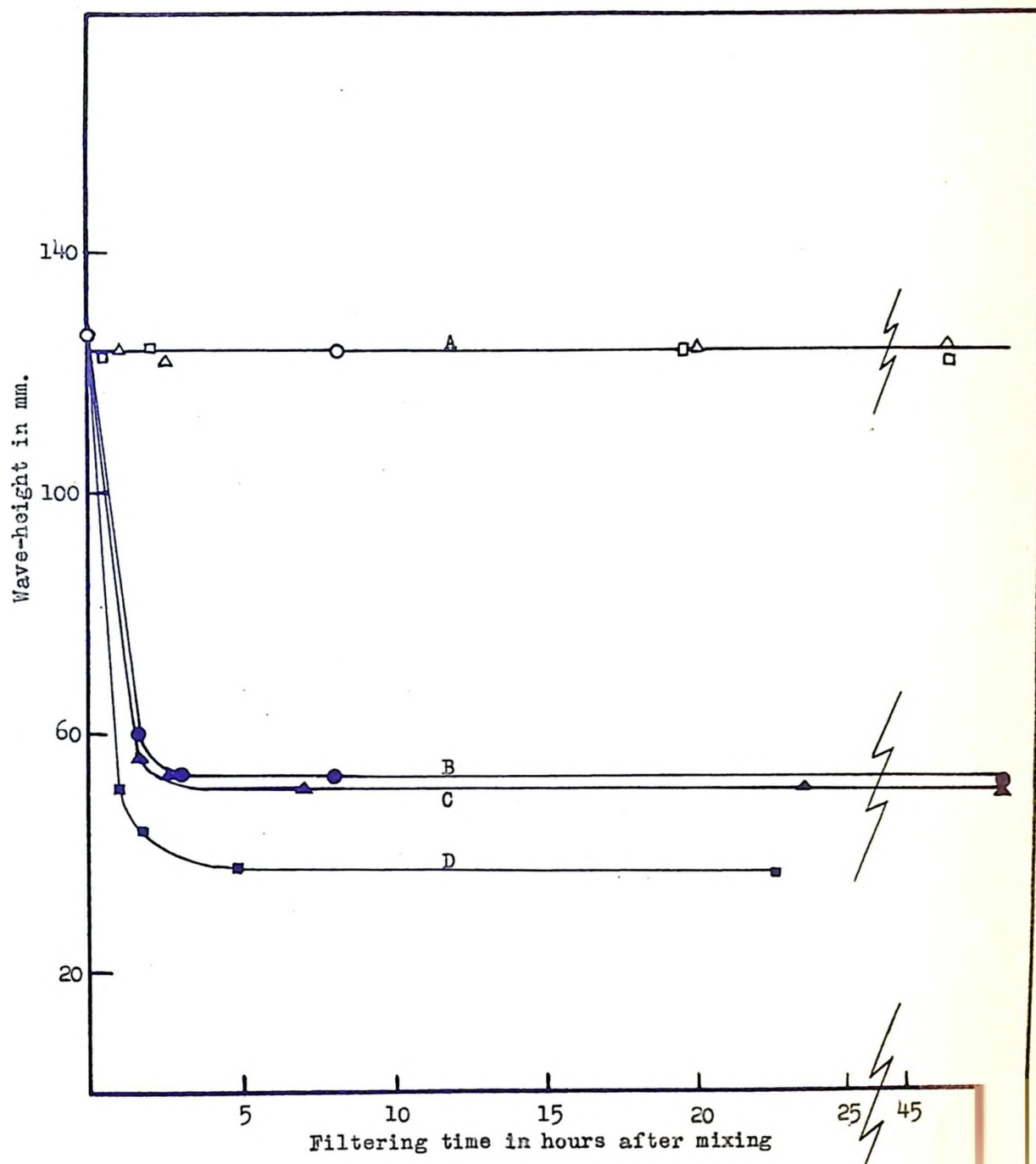| Concentration of Aluminium (after mixing)	pH	Coding in Figure 6
nil	5.9	(Curve A)
nil	6.5-7.1	(Curve A)
nil	7.7-7.8	(Curve A)
3.6×10^{-4} M	5.8-6.0	(Curve B)
3.6×10^{-4} M	6.5-7.0	(Curve C)
4.3×10^{-4} M	7.5-8.0	(Curve D)

49

FIGURE 6

Rate of Precipitation of Aluminium Benzoylacetonate

in either the precipitating or the polarographic media. Experiments
with control solutions, which contained no aluminium, showed that no
decomposition of the reagent occurred under the conditions of the ex-
periment. The benzoylacetone concentration, after mixing and before
reaction, was ~19.8 $\times$ 10^{-4} M. The aluminium concentrations and tho pH
ranges for the experiments are given in Table VII.

The results, plotted in Figure 6, show that the reaction be-
tween benzoylacetone and aluminium, although less rapid than that be-
tween benzoylacetone and beryllium (Figure 3), is under the conditions
of the experiment essentially complete within 5 hours.

(b)   Completeness of Precipitation of Aluminium Benzoylacetonate as a
Function of pH

The solutions of benzoylacetone and of aluminium used for this
work were the same as those for the experiments reported in the pre-
vious section.

After the mixing of the solutions and the adjustment of the pH
in the usual manner, the reaction mixtures were allowed to stand for
from 4 to 6 hours at room temperature before filtering. To 50 ml. of
the filtrate in each case there was added 0.5 ml. of 18 N sulfuric acid
to bring the pH, for polarography, within the range 0.80-1.00. The
concentration of ethyl alcohol during both precipitation and polaro-
graphy was 9.5% (by volume). The concentrations of benzoylacetone and
aluminium, after mixing but before reaction, were 19.8 $\times$ 10^{-4} M and
3.7 $\times$ 10^{-4} M, respectively.

The data, which are plotted in Figure 7, indicate that there
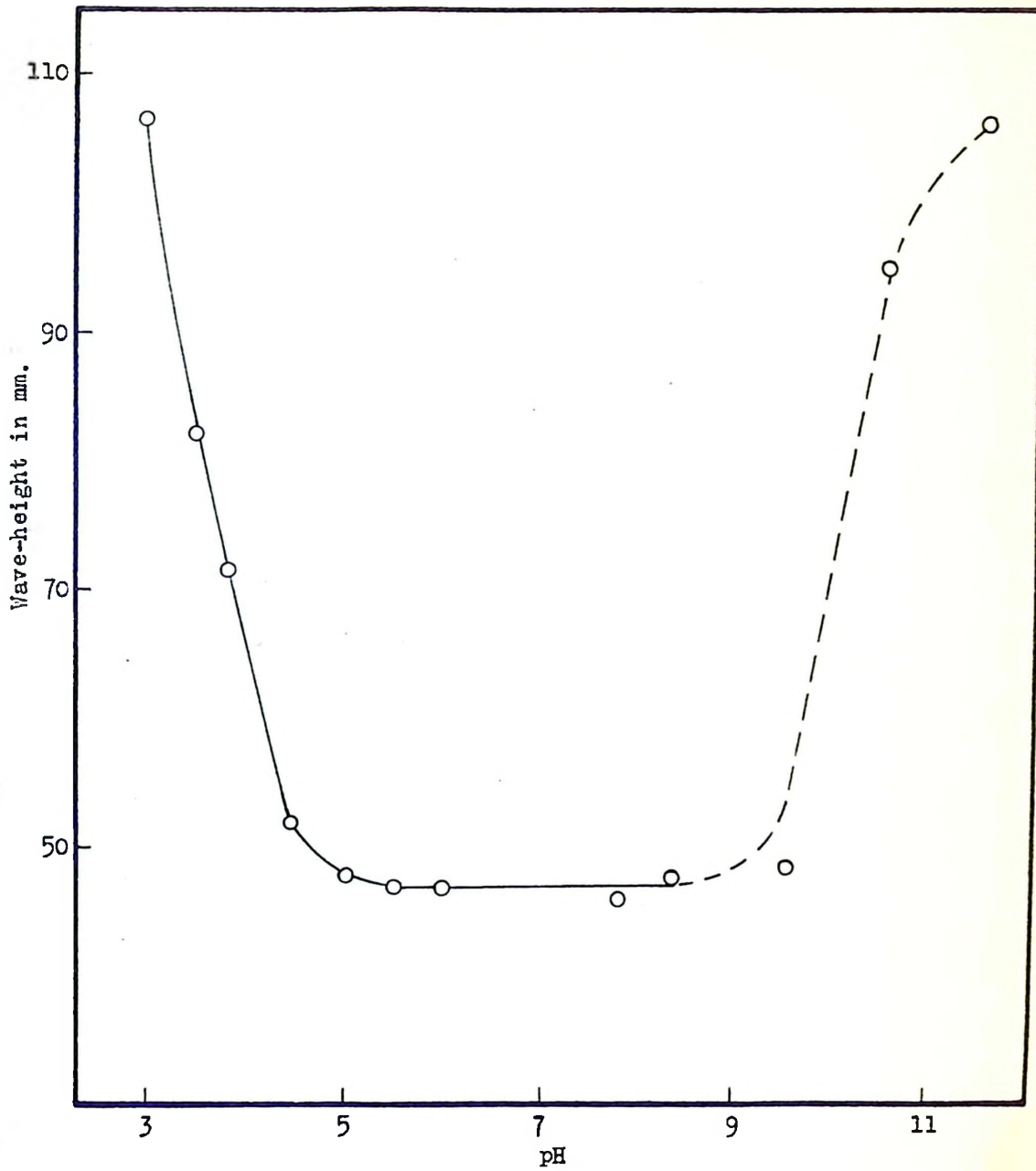is a reasonably wide range of pH values (5.5 to 7.5) over which precip-

FIGURE 7

Precipitation of Aluminium Benzoylacetonate as a Function of pH

itation may usefully be carried out. Above a pH value of about 11 ben-
zoylacetone fails to precipitate any aluminium.

The reduction in the magnitude of the diffusion current, cal-
culated from the known amount of aluminium taken on the assumption
that 3 moles of benzoylacetone react with every mole of aluminium pres-
ent, was 56.2%; the reduction found experimentally, over the pH range
5.5 to 7.5, was 56.6%. Thus the precipitation was quantitative over
this range of pH values.

(c) Calibration Curve for the Determination of Aluminium with Benzo-
ylacetone (by Dissolution of Aluminium Benzoylacetonate)

To 50-ml. portions of 50×10^{-4} N benzoylacetone No 2 in 19%
ethyl alcohol were added equal volumes of aluminium solutions of vary-
ing concentrations (7.5 to 37.5 mg./l.). The pH values of the solutions
(initially 1.5 to 2.0) were then adjusted to within the range 7.2-7.6
with solutions of sodium hydroxide of varying concentrations. Four
hours later the solutions were filtered through medium-porosity fritted
glass crucibles with suction, and washed 4 times with ice-cold water.
Each precipitate was then dissolved in a 50-ml. portion of hot (75°C.)
8.75 M acetic acid, measured by a pipet. (The dissolution process,
aided by the breaking up of the compact crystalline precipitate which
formed upon immersion of the crucible and contents in the acetic acid,
required about one hour.) Each solution was then transferred quanti-
tatively to a 250-ml. flask and diluted to volume with water. The pH
value of a 50-ml. portion of the resulting solution was adjusted for
polarography to about 1.0 by adding 0.3 ml. of 18 N sulfuric acid. The
polarographic results showed that the diffusion current of the benzoyl-

acetone obtained by dissolving the precipitates is directly proportional to the concentration of aluminium in the original solution, at least over the range of concentrations studied (7.5 to 37.5 ng./l.). The calibration curve was, in fact, an excellent one.

(d) Recommended Method for the Determination of Aluminium with Benzoylacetone

The method recommended for the determination of aluminium with benzoylacetone is the same in principle, and much the same in detail, as that for the determination of beryllium using the same reagent (Section III (c)).

The original solution should contain about 1 mg. of aluminium (instead of about 0.5 mg. of beryllium). The precipitate of aluminium benzoylacetonate is coagulated, and given time to precipitate completely, by allowing it to stand at room temperature for 5 hours instead of 2; the precipitate is dissolved in a manner similar to that used in the procedure for beryllium except that this process requires that the aluminium precipitate should be broken with a stirring rod and the dissolution time may be twice as long.

The amount of aluminium in the solution is assessed by reference to a calibration curve obtained in a similar manner with solutions of known aluminium content.

$\underline{V}$ Determination of Beryllium in Copper-Base Alloys using Benzoylacetone

(a)   Removal of Interfering Ions

Since copper reacts readily with benzoylacetone (80,130), it must be separated from beryllium before the latter element can be determined as the benzoylacetonate. Experiments on synthetic-alloy solutions (corresponding in their metal-ion content to the composition of copper-base alloys), using a mercury cathode electrolysis cell (77,118), indicated that interference from copper as well as other ions (e.g., iron) could be completely eliminated by this separational tool.

To determine the effect of time of electrolysis on the removal of interfering ions, aliquot portions of a synthetic-alloy solution (see Table $\overline{VIII}$) were electrolyzed and then analyzed for their beryllium content as follows:

Fifty ml. of the synthetic-alloy solution, to which was added one ml. of 18 M sulfuric acid and 50 ml. of water, was placed in an electrolysis vessel of the type used by Graham, Hitchen and Maxwell (77). A cell potential of 12-13 volts produced an average current of about 8 amp., corresponding to a current density of about 0.27 amp./cm.^{2} During electrolysis the current was maintained above 6.5 but below 9.5 amp. (corresponding to a current density of 0.23-0.33 amp./cm.^{2}) by very small additions of sulfuric acid. After a recorded time interval, the electrolyte was quantitatively removed from the vessel and diluted to 250 ml. Fifty ml. of this solution was used in the subsequent analysis for beryllium using the method described in Section $\overline{III}$ (c) (page 46).

TABLE VIII

Composition of Synthetic-Alloy Solution

Element	Source of ion	% of total metal ions present	Millimoles of metal ion in a 50-ml. sample
Cu	$Cu(NO_3)_2 \cdot 3H_2O$	89.0	0.420
Zn	$Zn(NO_3)_2 \cdot 6H_2O$	3.0	0.139
Ag	$AgNO_3$	2.0	0.0056
Ni	$Ni(NO_3)_2 \cdot 6H_2O$	1.5	0.0076
Co	$Co(NO_3)_2 \cdot 6H_2O$	1.5	0.0076
Fe	$Fe(NO_3)_2 \cdot 9H_2O$	1.0	0.0054
Pb	$Pb(NO_3)_2$	0.02	0.00003
Be	Stock sol'n.*	2.0	0.0667

*The stock solution of beryllium was prepared by dissolving 150.0 mg. of flake beryllium in 10 ml. of 15 M nitric acid containing 5 drops of 18 M sulfuric acid, and then diluting the solution to 500 ml.

A control solution containing beryllium as the only metal ion was analyzed for beryllium in the same manner though it was not electrolyzed.

The results, shown in Table IX, indicate that after an electrolysis time of 60 minutes the removal of interfering ions could be considered complete. Unduly short electrolysis periods leave in the solution copper (which precipitates with benzoylacetone, giving high results for beryllium); electrolysis periods sufficiently long to eliminate this source of error, but still less than an hour, give slightly low results for beryllium (see Discussion).

(b) Recommended Method for the Polarographic Determination of Beryllium in Copper-Base Alloys

Dissolve 0.25 g. of a sample of the alloy in 25 ml. of hot 3 M nitric acid and dilute the solution to 250 ml. with water. Put 150 ml. of this solution in the mercury-cathode electrolysis cell, and pass a current, using a current density of about 0.3 amp./cm.^{2}, for 60-70 minutes. (During the electrolysis the current density may be maintained

by small additions of sulfuric acid.) Removo the electrolyte quantita-
tively, wash out the cell with water, and dilute the electrolyzed solu-
tion and washing to 250 ml. with water in a volumetric flask. Analyzo
a 50-ml. aliquot of this solution for beryllium as recommended in Sec-
tion <u>111</u> (c) (page 46).

The preceding method applies to alloys containing about 2% ber-
yllium. For alloys containing a somewhat higher concentration of ber-
yllium (greater than 2.5%, say) or a lower one (less than 1.5%, say),
a proportionately smaller or larger sample should be used. This means
that with the electrolysis cell used, the analysis is conveniently per-
formed with only about 0.5 milligrams of beryllium.

TABLE <u>IX</u>

Electrolytic Removal of Interferences from a Beryllium-Copper

Synthetic Alloy Solution

(Beryllium control solution yielded a wave-height of 69.0 mm.)

Time of Electrolysis (min.)	Wave-height (mm.)
8	75.1
12	64.9
27	64.8
40	64.2
50	67.1
58	69.2
67	68.5
75	69.3

TABLE X

Summary of Experiments on the Ion-exchange Separation

of Beryllium and Aluminium

| Expt. No.	Resin	Column (cm.×cm.²)	Ml. of sol'n. passed through column	Mg. of Be in solution	Mg. of Al in solution	Weight ratio Be/Al	pH of solution	Molar conc. of elutriant (HCl)	Flow rate (cm.min.)	Ml. of eluate before Be was detected	Ml. of eluate after which Be was no longer detected	Ml. of eluate before Al was detected
I	Dowex 50W×8 50-100 mesh in hydrogen form	16×0.79	300	5.0 ± 0.1	14.0 ± 0.1	5/14	1.2	0.30	4-5	200	1200	not detected after 1800 ml.
II	"	9×0.79	300	"	"	"	"	0.50	"	less than 10	400	600
III	"	"	500	45.0 ± 0.1	"	45/14	0.9	"	"	"	"	550
IV	"	24×0.79	600	1.00±0.01	100 ± 1.0	1/100	0.95	"	4.5	50	"	450
V	"	"	500	0.25±0.01	50 ± 1.0	1/200	1.0	"	"	300	500	900
VI	"	40×0.79	800	1.00±0.02	200 ± 1.0	"	1.8-1.9	"	4.0	"	400	500
VII	Dowex 50W×12 100-200 mesh in hydrogen form	45×0.79	80	"	"	"	"	"	2.5	"	1000	not detected after 1600 ml.
VIII	"	"	100	0.95±0.01	"	"	"	0.70	"	100	450	500
IX	" (different column)	"	"	"	nil	-	1.5	"	"	-	just detected after 1800 ml.	-

59
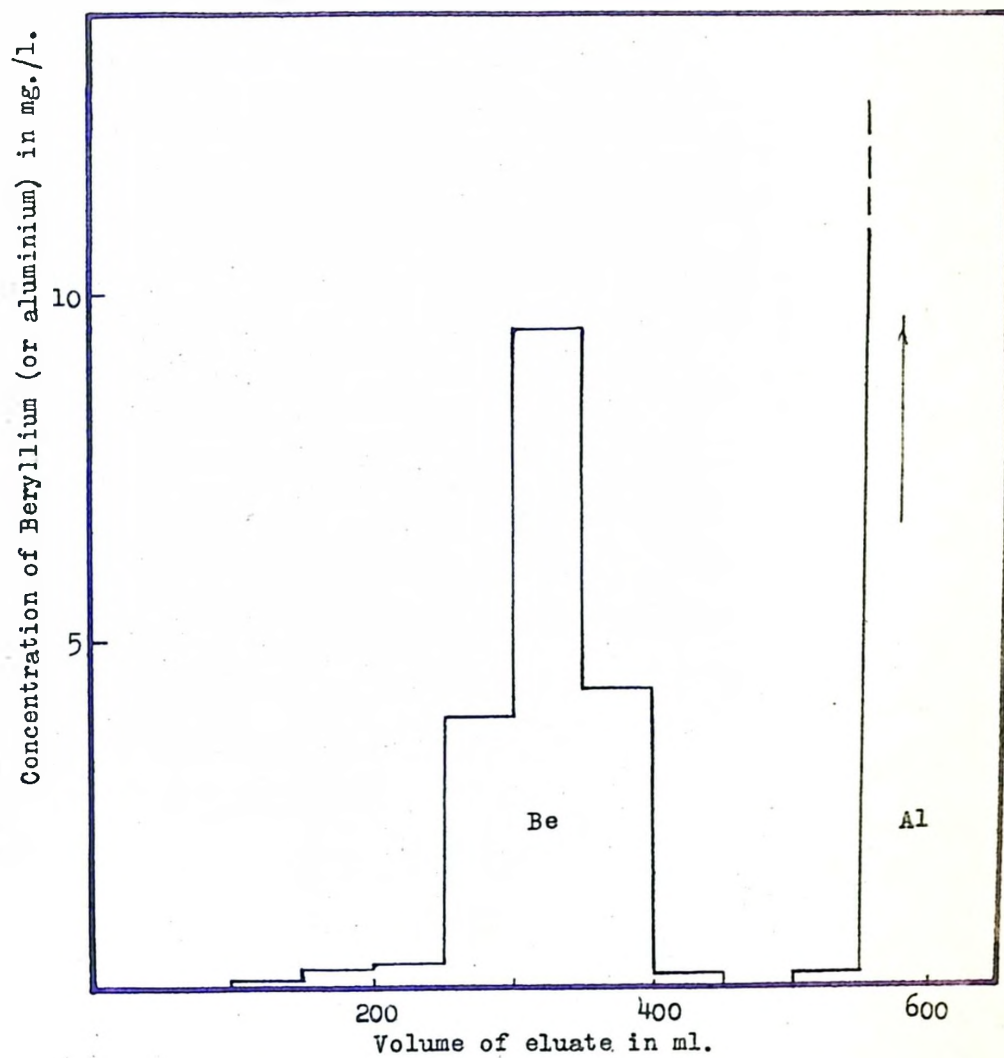
FIGURE 8

Elution Curve for Beryllium and Aluminium

found. No aluminium was detected in the eluate, (using the fluorimet-
ric Pontachrome Blue Black R test (34,202)), before 500 ml. of elutri-
ant had been passed through the column and no beryllium was detected
(using the fluorimetric morin test (159)) after 450 ml. of elutriant
had been passed through.

By this procedure, then, one milligram of beryllium was sepa-
rated (with an efficiency of at least 95%) from 200 times as much al-
uminium.

Experiment IX was performed as follows: A solution (100 ml.
at a pH value of about 1.5 and containing 0.95 ± 0.10 mg. of beryllium
was passed through a column having the same dimensions and containing
the same type of resin as the column used in Experiment VIII. The
sorbed beryllium was then eluted with 600 ml. of 0.70 ± 0.02 M hydro-
chloric acid followed by 175 ml. of 1.5 M hydrochloric acid. The 1.5
M acid was passed through the column to determine if this higher con-
centration of acid would elute any beryllium that had remained on the
column after the elution with 600 ml. of 0.70 ± 0.02 M hydrochloric
acid. The morin test (159) for beryllium was only very slightly posi-
tive after 550 ml. of 0.70 M hydrochloric acid had been passed through
the column (in comparison with a negative test in the preceding experi-
ment). Absorptiometric data, using a Fisher AC model Electrophotometer,
showed that elution with 25 ml. of 1.5 M hydrochloric acid removed an
additional 0.029 ± 0.001 mg. of beryllium. (No more beryllium was elu-
ted after this). This corresponds to 3.1 ± 0.2% of the beryllium that
was initially put into the column. This experiment confirmed the data
from Experiment VIII: the separation of beryllium from aluminium by

this procedure is not a perfect one - though its efficiency is 97-98%.
This cannot be considered unsatisfactory when it is borne in mind that
the separation is concerned with two analytically similar ions, and
that the desired ion is being separated from a solution that initially
contained the interfering ion in relatively massive concentration
(200:1).

Nelson and Kraus, in anion-exchange studies on the separation
of beryllium and magnesium through their citrate complexes (133), also
noted a similar effect on changing the elutriant; the recovery of a
"tailing" fraction that the first elutriant did not remove from the
column.

DISCUSSION

In general, direct polarographic methods (in which the polaro-
graphic wave arising from the reduction of the ion sought is measured)
are to be preferred to indirect methods (in which the wave arising from
the reduction of some substance equivalent in concentration to the ion
sought is measured). In specific cases, however, a direct method may be
impossible, or at least somewhat unattractive on account of the rigid
control of conditions that may be necessary. This situation arises
when the ion sought has a relatively very negative half-wave potential,
as a result of which the desired wave does not appear before the dis-
charge (reduction) of hydrogen ion or other cation of the supporting
electrolyte, or else is merged with waves arising from these other re-
ductions. Such a state of affairs exists, for example, in the polaro-
graphy of thorium, zirconium, beryllium, and aluminium. The difficul-
ties are not necessarily insuperable, as work with aluminium in this
laboratory has shown, but the restrictions imposed by the nature of the
system make a direct polarographic method for such elements, if it can
be evolved at all, of rather more confined utility than is desirable.

Beryllium can yield a polarographic wave, albeit an ill-defined
one at a very negative half-wave potential, as was demonstrated by
Kemula and Michalski (93) in 1933. The wave coalesced with that for
aluminium, as might be expected. Later, Lamontagne (111) concluded that
beryllium cannot be directly determined polarographically. In the early
stages of the present study, some investigations strengthened this view.
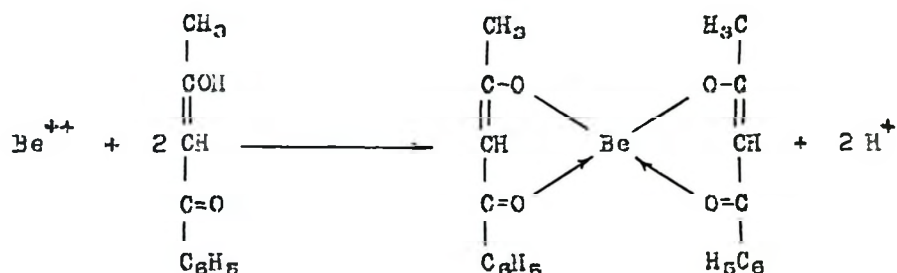
63

Attention was accordingly directed toward the development of an indirect method for the polarographic determination of beryllium. To the best of the author's knowledge, no polarographic method of any kind for the determination of beryllium has been reported in the literature, although an amperometric determination has been suggested very recently (104).

In the course of this work some 15 substances were considered as possible reagents for use in an indirect polarographic method for the determination of beryllium. Some of these substances were given very cursory attention, for that was sufficient to rule them out from serious consideration; others, such as dipicrylamine and quinizarin-2-sulfonic acid, were given a considerable amount of study because of the promise they showed until substantial undesirable characteristics of the reactions were revealed. (It is deemed unnecessary to consider here the work with these rejected reagents or the reasons for their rejection; details are to be found in the Experimental section.) Most attention was given to benzoylacetone and with this reagent a very satisfactory method for the determination of beryllium, in concentrations as low as a few parts per million, was developed. The method depends on the quantitative precipitation of beryllium benzoylacetonate under controlled conditions, followed by the dissolution of the washed precipitate and then the polarographic determination of the released benzoylacetone. In passing, it should be mentioned that quinizarin-2-sulfonic acid, despite certain undesirable reaction characteristics, showed promise in preliminary studies sufficient to justify the recommendation that a more detailed examination of its reaction with beryllium be made.

The development of the method for the determination of beryllium

by means of benzoylacetone required investigations in two general areas:
the characteristics of the reaction of beryllium with benzoylacetone,
and aspects of the polarography of benzoylacetone.

The work reported in this thesis has shown that under appropriate conditions benzoylacetone is a quantitative precipitant for beryllium and that two moles of the organic reagent are required for every mole of beryllium. Beryllium likely reacts with benzoylacetone in the enol form as follows (33):

$$
\text{Be}^{++} + 2 \quad
\begin{array}{c}
CH_3 \\ | \\ COH \\ \| \\ CH \\ | \\ C=O \\ | \\ C_6H_5
\end{array}
\longrightarrow
\begin{array}{c}
CH_3 \\ | \\ C-O \\ \| \\ CH \\ | \\ C=O \\ | \\ C_6H_5
\end{array}
\text{Be}
\begin{array}{c}
H_3C \\ | \\ O-C \\ \| \\ CH \\ | \\ O=C \\ | \\ H_5C_6
\end{array}
+ 2 \text{ H}^+
$$

As would be expected, if the pH of the solution is unduly low, precipitation is incomplete or does not occur at all. If the pH is too high, precipitation as the benzoylacetonate is likewise incomplete, probably because of the formation of beryllate-ion. Thus, from solutions containing about 50 mg. of beryllium per liter of solution and a substantial excess of benzoylacetone, the beryllium can be precipitated quantitatively, as the benzoylacetonate, within the pH range from 5.1 to something over 7. The recommended value of the pH for precipitation is 6.5 ± 1.0. No difficulty need be encountered in maintaining the pH at such a value.

Experiments having to do with the rate of precipitation disclosed the need for allowing about an hour (at room temperature) for the precipitation to become "complete". Such a digestion period also serves

to improve the physical properties of the precipitate and so is beneficial with respect to the subsequent filtering and washing procedures. The digestion period prolongs the over-all time required for the completion of a determination but does not consume any of the operator's time, for the digestion requires no attention.

After the beryllium benzoylacetonate has been precipitated, filtered, and washed, the remaining steps are the dissolution of the precipitate (to yield a solution in which beryllium and benzoylacetone are present in equivalent quantities) and the polarographic determination, under appropriate conditions, of the benzoylacetone in the resultant solution. Acetone, p-dioxane, and acetic acid were studied as solvents for beryllium benzoylacetonate but, for reasons mentioned in the Experimental section, the choice fell upon acetic acid. This solvent was studied at various concentrations and under various conditions of temperature, with convenient and satisfactory conditions for its use being found. Experiments with benzoylacetone and acetic acid under more severe conditions than would be met in an actual analysis showed that no decomposition of benzoylacetone resulted from the action of the acetic acid.

The remaining aspects of the method for the polarographic determination of beryllium by means of benzoylacetone have to do with the polarography of benzoylacetone. As early as 1936 benzoylacetone was shown to be reducible at the mercury cathode (175,176). Again, in 1948, Portillo and Varela (151) showed this compound to be reducible in 20% ethanol, at a pH of 6. Korshunov et. al. (102) measured the reduction potential of benzoylacetone in various buffers, and reported that the

diffusion current is independent of pH at pH values of less than 5 and decreases linearly to zero when the pH is increased to 12.

In the present work it was found that the most easily measured polarographic wave, and the one most satisfactory for analytical work on other grounds, was that given by benzoylacetone in an acid solution of pH about one. This wave is an excellent one (Figure 1). In solutions containing sodium acetate (which would be present from the sodium hydroxide used for adjusting the pH during the precipitation of the beryllium and the acetic acid used for dissolving the beryllium benzoylacetonate) and ethanol (which would be present because the benzoylacetone reagent solution contained ethanol), it was found that the diffusion current of benzoylacetone was independent of pH over the range 0.60-1.85, which result is in limited accord with the findings of Korshunov et al. (102) mentioned above. The wave form was likewise independent of pH over this range, although the half-wave potential became slightly more negative with increasing pH. The elimination of alcohol from the solutions did not qualitatively affect the observations nor did it matter whether the adjustment of the pH was done with sulfuric acid or hydrochloric acid.

If ethanol is to be present in the solution, however, its concentration must be controlled, because the value of the diffusion current is dependent on the concentration of alcohol (Table I, page 29). The decrease in the diffusion current of benzoylacetone with increasing concentration of ethanol in the solution can be accounted for by the changing viscosity of the solution and the effect of this on the diffusion coefficient of the benzoylacetone. The Ilkovic equation, a funda-

mental one in polarography, is:

$$i_d = 607 \, n \, D^{1/2} \, C \, m^{2/3} \, t^{1/6}$$

i_d = diffusion current (microamperes)

n = number of faradays consumed per mole of substance reduced

D = diffusion coefficient of the reducible ion ($cm.^2$/sec.)

C = concentration of reducible ion (millimoles/liter)

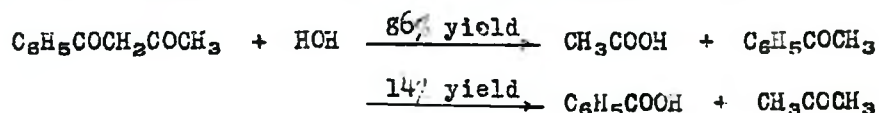m = rate of flow of mercury (mg./sec.)

t = drop time (sec.)

Other factors being constant (and they were in the experiments being considered), the diffusion current, i_d, is directly proportional to $D^{1/2}$. By the Stokes-Einstein relation for diffusing particles that are large compared to the solvent molecules, D is inversely proportional to η, where η is the viscosity coefficient of the medium. Hence, if the change in the diffusion current given by a constant concentration of benzoylacetone with changing alcohol content of the solution is due to change in the viscosity of the medium, it would be expected that the quantity $i_d^{1/2}$ would be a constant (100). That this is substantially true is shown by the values in the last column of Table I. In a similar fashion the change in the diffusion current given by a fixed concentration of benzoylacetone with changing concentration of acetone in the solution (in experiments concerned with the choice of a suitable solvent for beryllium benzoylacetonate) can be largely accounted for. Other factors may, too, of course be involved. For example, the wave form may be changing slightly with changing concentration of alcohol or acetone, thus making the measured wave-height not truly indicative of the diffusion current and, contrary to the assumptions made above, a change in

the viscosity of the solution will also have some effect on the drop time, t (61).

Although changes in the concentration of acetate in the solution have no significant effect on the diffusion current given by a fixed concentration of benzoylacetone when the (stoichiometric) acetate concentration is less than 0.15 M, higher concentrations of acetate do measurably affect the diffusion current, decreasing the value of it. Since the concentration of acetate in the procedure, as finally developed, is greater than 0.15 M, the concentration must be controlled, and the acetic acid used to dissolve the beryllium benzoylacetonate is, accordingly, measured by a pipet.

Several experiments showed that benzoylacetone solutions were stable for at least several days, under the conditions that would be encountered in the proposed analytical method. Evidence of decomposition of benzoylacetone was found, however, as mentioned in the Experimental section, when solutions of pH value 8 or higher were examined 12-20 hours after their preparation. This has no relevance to the proposed method, for such long standing periods and so high a pH are not required, but it is worth noting that this observation is consistent with some findings of Kutz and Adkins (107). These workers showed that when benzoylacetone is heated in a 0.1 M solution of sodium hydroxide at 60°C. for 24 hours the following transformation occurs:

$$C_6H_5COCH_2COCH_3 + HOH \xrightarrow{\text{86\% yield}} CH_3COOH + C_6H_5COCH_3$$
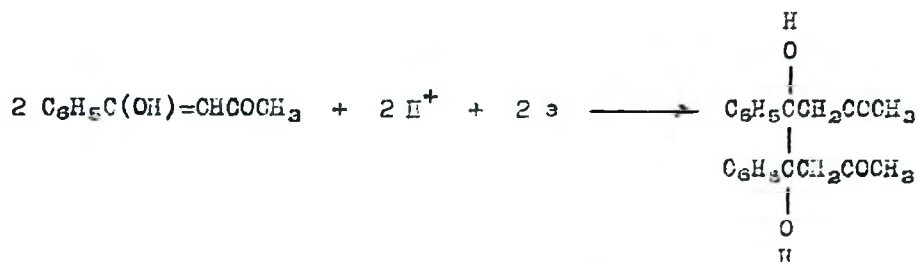$$\xrightarrow{\text{14\% yield}} C_6H_5COOH + CH_3COCH_3$$

The diffusion current given by benzoylacetone was found to be strictly a linear function of its concentration, the pH, alcohol and

acetate concentration, and other relevant factors being controlled within the easily-met limits that earlier experimentation had prescribed. A linear calibration curve was established (Figure 2) using concentrations of benzoylacetone up to about 2×10^{-3} M. The curve very properly extrapolated through the origin. For concentrations of the organic compound below about 3×10^{-4} M, the base line of the polarographic wave is not horizontal, and this fact causes the method to have a reduced precision below this concentration level.

The details of the method, as finally developed after the aforementioned and other experiments had pointed the way, are set forth in the Experimental section (page 46). The results are of good precision for concentrations of beryllium, in the original solution, down to 10 p.p.m. (1.1×10^{-3} M) and have reasonable precision at a concentration as low as 2 p.p.m. (2.2×10^{-4} M). The absolute amount of beryllium required for an analysis is less than 0.5 mg. The method is thus a sensitive one.

To the best of the author's knowledge, the course of the polarographic reduction of benzoylacetone in acid media is not known. The mechanism of this polarographic reduction would be a study in itself and, interesting though this might be, it is not essential to the present investigation. Nonetheless the following notes on the subject are offered.
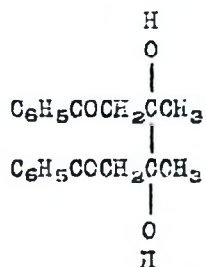
By analogy with the work reported by Pasternak (144) one may deduce the following possible reduction:

$$2\ C_6H_5C(OH)=CHCOCH_3\ +\ 2\ H^+\ +\ 2\ e\ \longrightarrow\ \overset{\overset{\displaystyle H}{\overset{\displaystyle |}{\overset{\displaystyle O}{|}}}}{\underset{\underset{\displaystyle H}{\underset{\displaystyle |}{\underset{\displaystyle O}{|}}}}{\underset{C_6H_5CCH_2COCH_3}{C_6H_5CCH_2CCCH_3}}}$$
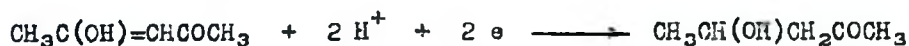
The chemical properties of benzoylacetone have, on the other hand, led some workers to adopt the alternative structural formula for the enol form of benzoylacetone (184):

$$C_6H_5COCH=C(OH)CH_3$$

which, if substituted for its isomer in the above plausible reduction, would give rise to the following corresponding pinacol:

$$\overset{\overset{\displaystyle H}{\overset{\displaystyle |}{\overset{\displaystyle O}{|}}}}{\underset{\underset{\displaystyle H}{\underset{\displaystyle |}{\underset{\displaystyle O}{|}}}}{\underset{C_6H_5COCH_2CCH_3}{C_6H_5COCH_2CCH_3}}}$$

If, however, the reduction is analogous to that of the enol form of acetylacetone (165):

$$CH_3C(OH)=CHCOCH_3\ +\ 2\ H^+\ +\ 2\ e\ \longrightarrow\ CH_3CH(OH)CH_2COCH_3$$

then the reduction of benzoylacetone would be as follows:

$$C_6H_5C(OH)=CHCOCH_3\ +\ 2\ H^+\ +\ 2\ e\ \longrightarrow\ C_6H_5CH(OH)CH_2COCH_3$$

or

$$C_6H_5COCH=C(OH)CH_3\ +\ 2\ H^+\ +\ 2\ e\ \longrightarrow\ C_6H_5COCH_2CH(OH)CH_3$$

The present work appears to constitute not only the first polarographic method for beryllium but also the first analytical exploitation

of the polarographic reducibility of benzoylacetone. This is not to say, however, that benzoylacetone has not been used for inorganic analytical purposes previously: it has been the basis of a gravimetric determination of copper (130). Workers (33,47) who prepared the beryllium derivative of benzoylacetone made no mention of its suitability for the determination of beryllium. The present study, it is hoped, clearly shows it to be a very useful one.

In the Introduction it was pointed out that one of the most important metallurgical applications of beryllium is in beryllium-copper alloys, alloys that have an interesting combination of useful properties. The method for the determination of beryllium developed in this work is not directly applicable to the determination of beryllium in this type of alloy for, as has just been mentioned, copper precipitates with benzoylacetone. A simple mercury-cathode electrolysis procedure has been found, however, to separate quantitatively the copper and any other interfering elements from a solution of a beryllium-copper alloy, and thereafter the method can be applied, with a precision of $\pm 1\%$. The electrolytic separational procedure requires about one hour in elapsed time, but the analyst is largely free to do other work throughout this time. With very short electrolysis times, the results of the analysis, calculated as beryllium, are high - presumably this is due to incomplete removal of the copper; with somewhat longer electrolysis times, the results are somewhat low - possibly this is due to the effective loss of benzoylacetone (with resultant incomplete precipitation of beryllium) by virtue of the presence of soluble but stable complexes of benzoylacetone with one or more of the alloying constituents

other than beryllium. With electrolysis times of one hour or longer (for the weight of sample recommended) the results are correct (Table IX).

In this work attention has also been given to benzoylacetone as a precipitant and polarographic reagent for aluminium. The rate of reaction of benzoylacetone with aluminium is less rapid than with beryllium, about five hours being required for "complete" precipitation, under the conditions of the experiments. The pH range for useful precipitation is similar to that for beryllium, being about 5.5 to 7.5. The aluminium precipitates as the tri-benzoylacetonate. No precipitation occurs at pH values above 11, due in all probability to the formation of soluble aluminate ions.

On the basis of these findings, a polarographic method similar to that developed for beryllium has been tested with solutions of aluminium ranging in concentration up to about 40 mg./l. (40 p.p.m.). The calibration curve was an excellent one, and there is reason to believe that determinations of aluminium can be made by this method with good precision on solutions containing this element in concentrations at least as low as 20 p.p.m. By contrast, good precision for the method for beryllium is claimed, as noted above, at concentrations down to 10 p.p.m. But, on a molar basis, 20 p.p.m. for aluminium is of course a lower concentration than 10 p.p.m. for beryllium.

In view of the general similarity in the analytical behaviour of aluminium and beryllium, it is by no means surprising that both these elements quantitatively precipitate benzoylacetone, and over about the same pH range. This fact, however, naturally precludes the use of the

method for the determination of beryllium in the presence of aluminium
and vice versa. (Musante (130), incidentally, also reported the inter-
ference of aluminium in his benzoylacetonate determination of copper.)

With a view to making the benzoylacetone method for beryllium
developed in this work applicable to substances containing both beryll-
ium and aluminium (such as certain beryllium-aluminium alloys) some
study was given to a possible ion-exchange separation of beryllium and
aluminium. A satisfactory procedure has been developed, though it i
not the first ion-exchange procedure that has been proposed for the
separation of these two elements. The method recommended has the advan-
tage over some that have been published in that no complexing agents
(which would be objectionable in the later determinative procedure) are
introduced into the solution. The method is simple and efficient: it
is able to separate one milligram of beryllium from 200 times as much
aluminium, with a recovery of better than 95% of the beryllium. These
relative amounts of beryllium and aluminium correspond to what might be
encountered in a beryllium-aluminium alloy. Thus there is good reason
to believe that this separational technique will permit the newly devel-
oped polarographic method to be applied to the determination of beryll-
ium in aluminium alloys just as the mercury-cathode electrolytic separa-
tion permits it to be applied to the determination of beryllium in
copper alloys.

Benzoylacetone reacts with more ions than those of copper, ber-
yllium, and aluminium. Several chelates of benzoylacetone have in fact
been prepared (33,47,130). Selectivity of action is of course a virtue
in an organic reagent, but if lack of selectivity in a reagent were a

paramount consideration then 8-hydroxyquinoline (8-quinolinol), a highly unselective reagent, would never have acquired the important role it has in inorganic quantitative analysis. The development of preferential sequestering agents (such as ethylenediaminetetraacetic acid) and the development of effective and simple separational procedures (such as controlled potential electrolysis and ion-exchange techniques) have combined to make less important than was thought a few years ago the lack of a single truly specific organic reagent and the fewness of even reasonably selective ones.

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