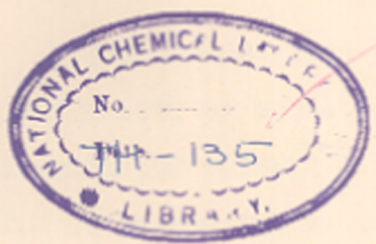


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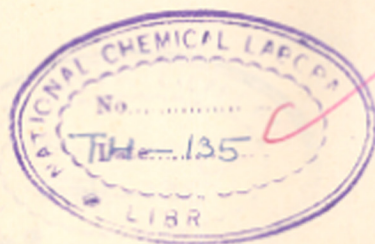
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GRAVIMETRIC DETERMINATION OF BERYLLIUM AND
ITS SEPARATION FROM OTHER ELEMENTS USING
ORGANIC REAGENTS

A THESIS SUBMITTED TO
THE UNIVERSITY OF POONA FOR THE DEGREE
OF MASTER OF SCIENCE IN CHEMISTRY
(PARTLY BY PAPERS AND PARTLY BY RESEARCH)

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CHAPTER : I

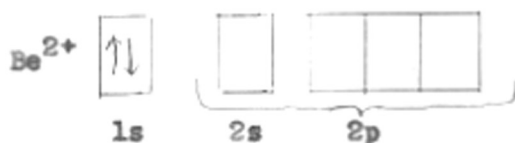
GENERAL INTRODUCTION

Chemistry and bonding in beryllium compounds

Beryllium with an atomic number four and atomic weight 9.013 (chemical scale)¹ lies in the first short period of the periodic table and heads Group IIA which includes magnesium, calcium, strontium, barium and radium.

The electron configuration of the gaseous beryllium atom is $1s^2 2s^2$. Beryllium has an outer shell of two 2s electrons, characteristic of the elements of this family and possesses an inert gas core of electrons. The configuration of the simple cation Be^{2+} is $1s^2$. Although usually considered as ionic, the bonds formed by beryllium in many compounds have considerable covalent character as, indeed, would be expected from the high electronegativity of beryllium². The Be^{2+} possesses high charge to radius ratio (Z/r) of 6.45. This high value would itself indicate that beryllium compounds possess marked covalent character. In fact in all compounds² whose structure has been determined, there appears to be substantial covalent character in the bonding. The value 6.45 may be compared with (Z/r) ratios of 1.67, 6.00, 3.07 and 2.02 for the Li^+ , Al^{3+} , Mg^{2+} and Ca^{2+} ions respectively. These values reflect both the chemical similarity of beryllium and aluminium and the sharp difference between the properties of beryllium and those of the other alkaline earth elements³. The difference between beryllium and the other alkaline earth elements is also reflected in the ionization potentials of the neutral atoms.

Beryllium forms a wide range of complex compounds in which it accepts a share in two extra lone pairs of electrons to form four tetrahedral sp^3 bonds. Such bonds have considerable polarity, $\overset{\delta+}{\text{Be}}-\overset{\delta-}{\text{X}}$, and beryllium complexes have an ionic character.



available for sp^3 hybridization.

Unlike the other alkaline earth elements and zinc, beryllium cannot expand its co-ordination number to six. This is due to the small size of beryllium atom and inaccessibility of the 3d orbitals which are required for sp^3d^2 hybridization.

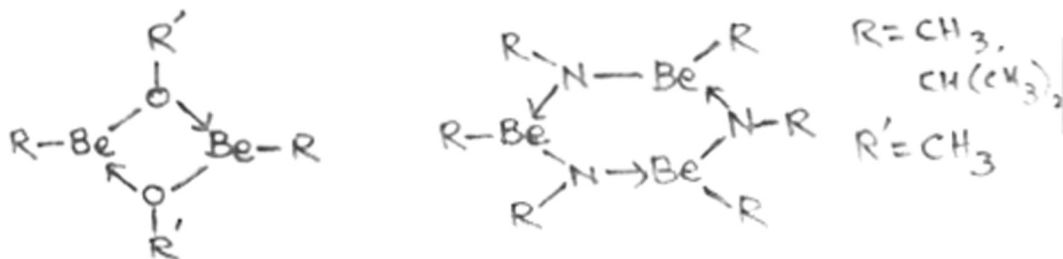
Theoretically it should be possible for beryllium atom to form tetrahedral, trigonal planar, and linear structures by employing sp^3 , sp^2 and sp hybrid orbitals, ^{respectively.} In the $1s^2 2s^2$ state beryllium, like helium, is zero valent, but it can form covalent bonds by the promotion of one 2s electron to the 2p level which results in two linear hybrid sp bonds. Although three and two coordinate beryllium compounds are known under special condition, beryllium prefers four coordination. Thus beryllium chloride, BeCl_2 , and dimethyl beryllium, $\text{Be}(\text{CH}_3)_2$, all are polymeric species⁴. X-ray diffraction⁵ studies show the presence of chains of beryllium atoms with bridging atoms or molecules such as chlorine or methyl groups. Although the structure of dimethyl beryllium, $\text{Be}(\text{CH}_3)_2$, is consistent with

four coordination, the theoretical interpretation is more difficult because the bridging groups are saturated and the methyl groups are usually considered monovalent. In an attempt to overcome this difficulty, a new type of bond - three centred bond was postulated⁶. A three centred bond involves the overlap of three orbitals to form a molecular orbital which can contain a maximum of two electrons. In this view, the theoretical interpretation of bonding in polymer compounds consists of three centred bond formed by overlap of two orbitals from adjacent beryllium atoms and an orbital from chlorine or methyl carbon atom. The electron density, in such a bond, is not along the internuclear distance and accordingly the 'bond angle', determined experimentally, is not necessarily directly related to the hybridization schemes.

The coordination number in ionic compounds is predominantly governed by the radius rule. Compounds of beryllium which are essentially covalent bound gaint molecules, show predominantly a coordination number four. Although compounds of beryllium with coordination number greater than four have not been identified, compounds with lower coordination number are known. Dialkyl beryllium compounds react with trimethylamine to form an adduct of type $R_2Be:N(CH_3)_3$ ⁷, a monomeric compound. Three coordinated compounds of beryllium can also be prepared by reacting the dialkyl compounds with alcohols liberating hydrocarbon⁸.



These dimeric and trimeric beryllium compounds possess a cage-like structure formed by coordinate covalent linkage through donor atoms as shown below.



There are very few examples of beryllium compounds existing at room temperature in which beryllium is two coordinated with sp linear bond. $\text{Be}(\text{CMe}_3)_2$, $\text{Be}(\text{CBu}_3)_2$ and silazane, $\text{Be}[\text{N}(\text{SiMe}_3)_2]_2$ belong to this class⁹. Beryllium chloride which is a polymeric solid, gives monomeric vapor at 750°C . However, the structure of monomeric halide shows interesting features that are not totally understood. The i.r. spectra of molecular species BeX_2 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) isolated in an inert matrix indicate that these compounds are linear¹⁰.

The difference between the first and second ionization potentials for beryllium might suggest the possibility of univalent beryllium. However, there is some evidence for Be^+ in fused chloride melt¹¹, but no compound has yet been isolated. During electrolysis of aqueous solution using beryllium anode, the dissolution of beryllium from anode suggest Be^+ , an intermediate but subsequent work showed that disintegration of the metal occurs during dissolution so that the apparent

effect is one of the metal going into solution in unipositive state. The anode sludge, a mixture of Be and $\text{Be}(\text{OH})_2$ has been considered to be due to disproportionation of Be^+ but photomicrography indicates that the beryllium in the sludge is due merely to spallation of the anode¹². Recent mass spectral studies on beryllium β -diketonate complexes have revealed the existence of monovalent beryllium chelates¹³. TGA studies on bis(4-chloro-2,5-dimethoxyacetoacetanilidato)-beryllium(II) also suggest the formation of univalent beryllium species¹⁴.

The oxide carboxylates, $\text{Be}_4\text{O}(\text{RCOO})_6$, form one of the most important groups of compounds in beryllium chemistry, the best known member being the oxide acetate which was first made by Urbain and Lacombe¹⁵. The oxide carboxylates are non-electrolytes, soluble in organic solvents such as chloroform or benzene and can usually be sublimed or distilled without decomposition.

Beryllium also forms some nitrogen complexes. The tetraamine, $[\text{Be}(\overset{\sim}{\text{N}}\text{H}_3)_4]\text{Cl}_2$, is very stable thermally but is rapidly decomposed by water, an indication that oxygen is a stronger donor to beryllium than is nitrogen. Beryllium phthalocyanine complexes represent one of the few instances in which beryllium forms a stable complex containing only beryllium nitrogen bonds¹⁶. X-ray analysis has shown beryllium phthalocyanine possesses a planar structure similar to other

phthalocyanines¹⁷. The geometry of the molecule forces the beryllium to adopt a planar configuration in contrast to its normal tetrahedral arrangement. That such a configuration is unstable is shown by the fact that beryllium-phthalocyanine forms a dihydrate when presumably two of the nitrogen-beryllium bonds in the phthalocyanine are broken and replaced by bonds between beryllium and the water molecules. Such an arrangement allows the beryllium to adopt a tetrahedral configuration.

Compounds containing beryllium-nitrogen multiple bonds have attracted much interest recently¹⁸. Structural studies on the aminoderivatives $[\text{Be}(\text{NMe}_2)_2]_3$ ¹⁹, $\text{MBe}(\text{NH}_2)_3$, ($\text{M}=\text{K}$ or Rb)²⁰ and $\text{Be}[\text{N}(\text{SiMe}_3)_2]_2$ ⁹ have shown their amino groups to be attached to their coordinatively unsaturated beryllium atoms by short Be-N bonds, indicative of $\text{N} \Rightarrow \text{Be}$ dative π -bonding. X-ray crystal analysis of bis(di-*t*-butyl methylene-amino) beryllium dimer $[\text{Be}(\text{N}:\text{C}^t\text{Bu}_2)_2]_2$ prepared from the ketimine $\text{Bu}_2\text{C}^t\text{:NH}$ and diisopropyl beryllium, shows that it adopts a structure containing both bridging and terminal methylene-amino groups, the latter attached to 3-coordinate metal atoms by Be-N bonds only 150 pm long, the shortest yet reported for a solid beryllium-nitrogen compound²¹.

Analytical chemistry of beryllium

The most important beryllium mineral is beryl, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$, which often occurs as large hexagonal prisms. Beryllium is made by electrolysis of the fused chloride but the extraction from ores is complicated²². Other ores of beryllium are phenacite, Be_2SiO_4 , chrysoberyl, BeAl_2O_4 , bentrandite, $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$, berylite, $\text{BaBe}_2\text{Si}_2\text{O}_7$ and helvine $(\text{MnFeZn})_3\text{Be}_6\text{Si}_4\text{O}_{24}\text{S}_2$.

Gravimetric methods

There is a general lack of precise, accurate and specific methods for the gravimetric determination of beryllium involving the use of organic precipitants. Beryllium estimation involves its precipitation as beryllium ammonium phosphate, $\text{Be}(\text{NH}_4)\text{PO}_4 \cdot x\text{H}_2\text{O}$ or beryllium hydroxide and subsequently weighing it as pyrophosphate, $\text{Be}_2\text{P}_2\text{O}_7$, or beryllium oxide, BeO , respectively. These procedures require careful separation of beryllium from both anions and cations that would otherwise interfere. The difficulties of ensuring these separations without loss of beryllium are reported²³.

Beryllium hydroxide is precipitated by ammonia from neutral or weakly acid solutions in the presence of ammonium salts²⁴⁻³⁷. Ammonium salts suppress peptization of beryllium hydroxide and reduce its adsorptive capacity. Precipitates formed in hot solutions are more compact and are easy to filter.

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The ammonia solution should be free from carbon dioxide and a large excess of the precipitant should be avoided as beryllium hydroxide dissolves in excess of ammonia^{24,38}. The precipitation of beryllium by ammonia is also conducted in the presence of alkali metals and in the presence of metals which form hydroxides that are not precipitated from solutions containing ammonium salt in excess (calcium, magnesium, manganese) and elements which form soluble ammoniates (zinc, nickel, cobalt). However, the adsorption of bivalent metals by the precipitated beryllium hydroxide is so strong that two or three reprecipitations are needed to achieve a satisfactory separation. The weighing form is the oxide, which is obtained by igniting the hydroxide at 1000°C.

Morachevskii and Novikov^{39,40} studied coprecipitation of small amounts of a number of elements with beryllium hydroxide by radiochemical methods. Rare earths are found to be precipitated with beryllium hydroxide and occludes cadmium at pH 7-8⁴¹. In order to improve the separation of beryllium from mixtures of bivalent metals, organic bases which are weaker than ammonia have been used. α -Picoline^{33,34} is found to precipitate beryllium in presence of elements such as manganese, cobalt, nickel, zinc, magnesium, calcium, strontium, barium, etc. The hydroxyl ion concentration in solution produced by α -picoline is sufficient to precipitate beryllium

quantitatively, but not sufficient for the precipitation of magnesium, calcium, barium, strontium, at the same time forming soluble complexes with zinc, manganese, nickel and cobalt.

The best separation of beryllium as hydroxide in the presence of foreign elements is said to be achieved with the aid of disodium salt of EDTA at pH 9.5-~~to~~ 9.8⁴². Under these conditions most of the accompanying elements, usually present, remain in solution. According to Pribil^{43,44} better separation of beryllium as hydroxide from major amounts of interfering elements, in the presence of disodium salt of EDTA, is achieved by a second precipitation of beryllium hydroxide by an excess of ammonia in the cold. With this method, it is reported that beryllium could be separated from aluminium, ferric iron, nickel, cobalt, manganese, chromium, zinc and copper. Titanium, antimony, uranium and bismuth are precipitated along with beryllium⁴³. The separation of titanium and uranium from beryllium by ion-exchange or titanium hydroxide precipitation from a solution of carbonate complex of beryllium after masking uranium with oxalate has also been reported⁴⁵.

Beryllium is quantitatively precipitated at pH 5.2 as crystalline beryllium ammonium phosphate, $\text{Be}(\text{NH}_4)\text{PO}_4$, and igniting the washed precipitate, beryllium is determined as beryllium pyrophosphate ($\text{Be}_2\text{P}_2\text{O}_7$)⁴⁶. This method has been subjected to criticism²³ because of specific pH conditions

and the presence of a specific excess of diammonium hydrogen phosphate. Furthermore, the precipitate does not have the ideal composition indicated by the formula $\text{Be}(\text{NH}_4)\text{PO}_4$. However, acceptable results have been obtained by Smythe and Whitten⁴⁷ adopting phosphate method as a gravimetric method for beryllium. The advantages claimed are the favourable conversion factor ($\text{Be}_2\text{P}_2\text{O}_7 : \text{BeO} = 1:0.2606$), and the absence of interference from phosphate, present in many beryllium ores. Under the right conditions the phosphate precipitate is granular and when this is achieved there is a reduced tendency towards the occlusion of impurities. Airoidi⁴⁸ in a review of the method, recommends using the disodium salt of EDTA, but this has been found unsatisfactory because the final precipitate may be contaminated with sodium and glassy appearance to the pyrophosphate residue which tends to adhere to the platinum dish used for the ignition. Other workers⁴⁹ consider that the conversion of beryllium ammonium phosphate into pyrophosphate is quantitative only if the ignition is conducted at 1000°C for several hours. Separations from aluminium, iron, chromium, manganese, zinc, cobalt, nickel, copper, lead, vanadium, molybdenum and alkaline earth metals have been reported by double precipitation of beryllium ammonium phosphate, $\text{Be}(\text{NH}_4)\text{PO}_4 \cdot x\text{H}_2\text{O}$.⁵¹ Chromium was found to remain in solution as the complex only when heated. Use of disodium salt of EDTA to mask magnesium, calcium, iron, aluminium, copper, nickel

and other ions have also been reported⁴⁶. Use of disodium salt of EDTA and hydrogen peroxide has been reported in the separation of titanium from beryllium⁵⁰. Other procedures for the separation of titanium from beryllium are also given in the literature^{52,53}.

The precipitation of beryllium by hydrazine and guanidine carbonate⁵⁴⁻⁵⁷ has no advantage over the method mentioned above, and is very seldom used in analytical practice.

Pirtea and Constantinescu^{58,59} adopted a new method, for the gravimetric determination of beryllium, which is based on the formation of a sparingly soluble compound between beryllium carbonate complex and hexaminecobaltic chloride, $[\text{Co}(\text{NH}_3)_6]_2[\text{Be}_4\text{O}(\text{CO}_3)_6] \cdot x\text{H}_2\text{O}$, and weighed as such. With careful drying, this method gave satisfactory results with pure beryllium solutions, but application to ores analysis gave low results for beryllium⁶⁰.

Moser and Singer²⁴ recommended tannin precipitation for minute quantities of beryllium from slightly alkaline medium. Tannin forms a voluminous insoluble adsorption complex, which is easily filtered, washed and finally ignited to oxide. Schoeller and Webb⁶¹ used tannin to precipitate beryllium from alkaline medium and to separate it from aluminium, iron, chromium, thorium and vanadium ions from a weakly acid solution.

Beryllium is quantitatively precipitated as the crystalline beryllium ammonium arsenate, $(\text{BeNH}_4\text{AsO}_4)$, of constant composition from acetate solution at pH 5.2. The beryllium content is determined by titrating the arsenate iodometrically⁶².

The chelate complexes formed by beryllium with organic reagents include many which are insoluble in water. Many organic compounds of beryllium have large molecular weights and can be used as weighing forms. Unfortunately, the organic reagents which are suitable for gravimetric determination of beryllium are not selective; selectivity can, however, often be attained by masking the interfering elements with disodium salt of EDTA, since the precipitation of beryllium is quantitative under these conditions.

Przheval'skii and Moiseeva⁶³ studied a number of compounds of beryllium with β -diketones derived from acetylacetone and showed that some of them can be used as the weighable forms in the gravimetric determination of beryllium. 2,2-Dimethylhexanedione-3,5 and 3-acetylhexanone-2 have been recommended for the gravimetric determination of beryllium⁶⁴. Das and Banerjee⁶⁵ introduced acetoacetanilide as a gravimetric reagent for beryllium but found that this chelated compound and the reagent have marked solubility in hot water leading to the experimental error of 1-3%⁶⁶. Benzoylacetone⁶⁷ was used at pH 8.8-10.5 to precipitate beryllium in presence of

ammonium carbonate. The disadvantage is that the complex itself dissolves in alcohol when washed to remove the excess of the reagent leading to an error. Das and Banerjee⁶⁸ proposed cupferron as a gravimetric reagent for beryllium. The drawbacks of this method are that the precipitate of beryllium cupferronate is soluble on heating, and the excess reagent is carbonized on heating. N-Benzoylphenylhydroxylamine⁶⁹, which is an analog of cupferron, precipitates beryllium at pH 4.6-8.0. The complex is insoluble in water, stable to heat, and can be used as a weighing form $\text{Be}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_2$, after drying at 110°C . The maximum error reported is 2%. Aluminium and iron are precipitated by N-benzoylphenylhydroxylamine at pH 4 and titanium at pH 1. In the presence of disodium salt of EDTA at pH 5-6, titanium, vanadium, niobium, molybdenum, tin, uranium, aluminium and iron are precipitated together with beryllium⁷⁰.

Motojima⁷¹ was the first to use 8-hydroxyquinoline as a gravimetric reagent for beryllium and the composition of the precipitate was proposed to be $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$. This was not studied in detail. A methyl derivative of 8-hydroxyquinoline, 8-hydroxyquinaldine⁷², was found to form sparingly soluble chelate having composition $\text{Be}(\text{C}_{10}\text{H}_8\text{NO})_2 \cdot 2\text{H}_2\text{O}$ at pH 7.8-9.2. This could be dehydrated at 110°C to anhydrous beryllium complex $\text{Be}(\text{C}_{10}\text{H}_8\text{NO})_2$. However, iron, magnesium, copper, manganese, nickel, titanium,

zinc, cadmium, chromium, cobalt and silver interfere in the estimation of beryllium. The accuracy of the determination is upto 1%. A modified method for gravimetric determination of beryllium with 2-methyl-8-quinolinol has been reported recently⁷³.

Ammonium cinnamate was used by Dema⁷⁴, Ostrotamov^{75,76} to precipitate beryllium from weakly acid solutions to form a basic salt $C_6H_5.CH = CHCOO-BeOH$. The precipitate is non-stoichiometric when obtained at pH 5.6-6.5. Beryllium is precipitated in the pH range 3.5 to 5.0 depending upon the concentration of beryllium and preferable to ignite to BeO .

2-Hydroxy-1-naphthoic aldehyde⁷⁷ was used for the gravimetric determination of beryllium. A large excess of the ligand was found to be necessary for the complete precipitation of beryllium. Benzoyl acetanilide⁷⁸ was used in the gravimetric determination by Das et al. and the interfering elements magnesium and iron(III) were masked with disodium salt of EDTA and tartaric acid respectively. The precipitation was carried out at pH 6.0 - 7.8 and the complex formed had a ratio of metal to ligand = 1:2 and could be dried to constant weight at 105°C.

Recently Singh and Kumar⁷⁹ have used bis-Salicylaldehyde-ethylenediamine (Salen), a schiff base, for the gravimetric determination of beryllium at pH 7.5 - 8.5, in presence of

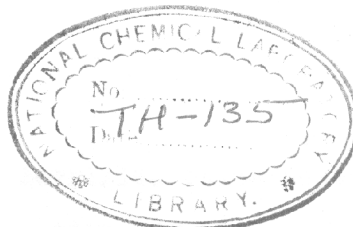
sodium potassium tartarate. The beryllium compound has a composition $C_{16}H_{14}N_2O_2Be \cdot 2H_2O$. The beryllium compound is reported to be insoluble in all common organic solvents.

Das and Chakraborti⁸⁰ have reported N-benzoyl-o-tolyl hydroxylamine as a gravimetric reagent for beryllium. The complex was weighed directly as $Be(C_{14}H_{12}O_2N_2)_2$ which was precipitated from solution at pH 6.3 - 8.7. Foreign impurities were masked with disodium salt of EDTA. The authors have claimed this ligand as the only suitable analytical reagent for beryllium with small conversion factor (0.01952) than any reagent reported so far.

Spectrophotometric and fluorimetric methods

Although a large number of spectrophotometric and fluorimetric methods for beryllium have been reported in literature,⁸¹⁻¹¹⁹ a review of these methods is not attempted since this thesis is mainly concerned with the gravimetric determination of beryllium. However, a few reagents commonly used are mentioned here. Zenia⁸² (p-nitrobenzeneazo-orcinol), acetylacetone⁸⁶, beryllon^{83,84} and Chrome Azurol S^{109,119} are the most important reagents. Beryllon seems to be the most satisfactory absorptiometric reagent. It gives a magenta to violet colour with beryllium(II) in strong alkaline medium. Diazo reagents of interest, such as, the Fast Sulphan Black F⁸⁵ have also been proposed for the determination of beryllium

in presence of fluoride, nitrate and salicylate ions. Flavones¹²⁰⁻¹²⁹, hydroxyanthraquinones^{130,131}, 8-hydroxyquinoline^{92,132-136} give fluorescent reaction with beryllium. Morin^{120,123,129} (3,5,7,2',4'-pentahydroxyflavone) gives yellowish-green fluorescence with beryllium in an alkaline medium at pH > 11. Careful control of conditions of temperature, reagent concentrations, etc. give a detection limit of 0.004 µg. of beryllium. However, the method is not specific and many elements interfere. Sill and his coworkers¹²⁹ assigned beryllium-morin complex, a composition corresponding to 1:1 while others^{127,128} gave a ratio of 3:2. A disadvantage of the method is the instability of the alkaline solution of morin in ^{to} atmospheric oxygen¹²⁰. The primary cause of the instability is ascribed to the catalytic oxidation, by traces of copper present in the distilled water and the reagent¹³⁰.



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Uses of beryllium 3,137-139

One of the largest uses of beryllium metal is in nuclear reactors as a moderator to lessen the speed of fission neutrons and as a reflector to reduce leakage of neutrons from the reactor core. Beryllium is useful in nuclear applications because of its relatively high neutron scattering cross section, low neutron absorption cross section and low atomic weight.

Another large scale use of beryllium is in the manufacture of beryllium bronze which has high tensile strength and a capacity for being hardened by heat treatment. A small but important use of beryllium is in sheet or foil form as window material in X-ray tube. Copper-beryllium alloys are non-sparking and tools made from these alloys are employed for work in areas where inflammable solids or explosive gases are present. This alloy is also used in making of springs, diaphragms, dies and electrode materials. Beryllium improves the corrosion and oxidation resistance of nickel, aluminium and magnesium base alloys. Recently beryllium-aluminium alloys have become important.

Beryllium oxide is used in the manufacture of high temperature refractory material and high quality electrical ~~pro~~celains such as air-craft ^{spark-} plugs and ultrahigh-frequency radar insulators. High thermal conductivity of BeO and its high frequency electrical insulation properties find application

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in electrical and electronic fields. Beryllium oxide coated graphite crucibles are used where exceptionally high purity or reactive metals are being melted. Several salts of beryllium find uses in fabrication of incandescent gas mantles, glasses with a high permeability to UV, fluxes, coating and catalyst in organic chemical reactions.

Health hazards caused by beryllium and its compounds

The report of Weber and Engelhardt¹⁴⁰ in 1933 describes the first occasion on which the incidence of disturbing respiratory conditions, bronchitis and bronchiolitis, was observed in beryllium workers. The hazardous nature of beryllium became more prominent during second World War.

The chief hazards of working with beryllium or its compounds such as beryllium fluoride, beryllium oxide, beryllium hydroxide, sulphate, chloride, etc. is the inhalation of the material as dust, smoke or aerosols. All simple beryllium compounds appear to be dangerous. The mineral beryl is not considered hazardous because no information appears to be available concerning the toxicity of beryl, although beryllium silicate phosphors are reported to be toxic. Inhalation of these solids lead to pneumonitis, a chronic disease of the lung tissue. Beryllium fluoride inhalation is reported to cause bronchitis¹⁴¹. Beryllium diseases have also been detected among the workers undertaking manual work and exposing to dust containing beryllium oxide etc. Contact

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dermatitis has also been reported as arising from the exposure to beryllium containing dusts and fumes. Contacts of body cuts and wounds with soluble beryllium compounds may lead to the production of ulcers which persist until the beryllium is removed. Many details of symptoms of beryllium diseases have been reported^{142,143}.

The handling of beryllium solution is considered much less hazardous than dry powder compounds. Various precautionary measures, such as cleaning of working benches, glass-ware on each day, cleaning of fume cupboard, reagent bottles periodically reduced the chances of the beryllium disease.

The maximum permissible concentration of beryllium in air contamination, as described by U.S. Atomic Energy Commission and American Industrial Hygiene Association¹⁴³, in laboratory should not exceed $2 \mu\text{g Be/m}^3$ as an average over an eight hours day and no person should be exposed to concentration greater than $25 \mu\text{g Be/m}^3$ even for very short time. Carefully built laboratory which has efficient ventilation and which can handle 500 g. of the beryllium containing sample at a time showed 0 - $0.2 \mu\text{g Be/m}^3$ air contamination over a long period.

The present thesis deals with two new organic precipitants, (a) 4-chloro-2,5-dimethoxyacetoacetanilide and (b) sodium oxinate as possible gravimetric reagents for the estimation of beryllium(II) and its separation from interfering elements. Although a few organic chelating agents, for instance,

β -diketones, 8-quinolinol etc. have been proposed recently, as precipitants for beryllium(II) in solution, these on closer scrutiny, as reported in the present thesis, have been found to be neither precise nor specific. The results obtained with various other organic reagents reported in literature for the gravimetric estimation of beryllium(II) from (a) solutions, (b) in ores (beryl) and (c) in alloys (copper-beryllium alloy) have been presented for comparison, along with those obtained with the two new reagents and the relative merits (or otherwise) of these reagents are discussed.

CHAPTER : II

4-CHLORO-2,5-DIMETHOXYACETOACETANILIDE AS A
GRAVIMETRIC REAGENT FOR BERYLLIUM(II) AND
COPPER(II)

Abstract

4-Chloro-2,5-dimethoxyacetoacetanilide, has been found to precipitate Be(II) and Cu(II) ions from solutions, quantitatively in the pH range 5.8 - 6.5 and at slightly higher pHs. The precipitated complexes, having the compositions, $\text{Be}(\text{C}_{12}\text{H}_{13}\text{O}_4\text{NCl})_2$ and $\text{Cu}(\text{C}_{12}\text{H}_{13}\text{O}_4\text{NCl})_2$ are stable and can be weighed directly after drying at $115^\circ\text{-}20^\circ\text{C}$. A method for the estimation of these metal ions, using 4-chloro-2,5-dimethoxyacetoacetanilide as a precipitant has been described. Beryllium(II) in presence of aluminium(III) and iron(III) and copper(II) in presence of aluminium(III), cadmium(II) and zinc(II) can be precipitated from solutions by masking the foreign ions with disodium salt of EDTA or ammonium fluoride. I.R., T.G.A. and D.T.A. data for the beryllium and copper complexes are also presented.

Introduction

Only recently organic precipitating agents for the gravimetric determination of beryllium have been proposed^{65,69}. These reagents form precipitates of definite composition with beryllium so that the precipitates can be weighed directly after drying to constant weight. Although beryllium(II) ion does not react with ligand, such as, ethylenediaminetetraacetic acid⁶⁹, with β -diketones, it forms stable chelates. Ligands containing 1,3-diketo group have been employed as reagents for beryllium(II) and zirconium(IV) in extraction procedures^{144,145} and for the determination of copper(II)¹⁴⁶. Thenoyl trifluoroacetone, a substituted β -diketone, was investigated as a complexing agent for the separation and purification of various metallic ions^{147,148}. Since only a few β -diketones were investigated as analytical reagents, particularly for beryllium, 4-chloro-2,5-dimethoxyacetanilide was examined as a possible organic precipitant for beryllium(II) as well as copper(II) and their separations from other metal ions. The results of our investigation are presented in this Chapter.

Experimental

Beryllium stock solution was prepared from beryllium nitrate trihydrate, $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or from beryllium hydroxide (Fluka AG., Chemische Fabrik, Buchs, S.G.). The latter was dissolved in nitric acid or hydrochloric acid and was diluted with water. The beryllium content was determined by (a) hydroxide method¹⁴⁹ and (b) by the pyrophosphate method⁴⁶. Copper sulphate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (ANALAR) was dissolved in water with a few drops of sulphuric acid. The metal content was determined volumetrically¹⁵⁰. All the other reagents used were of A.R. grade.

Preparation of 4-chloro-2,5-dimethoxyacetoacetanilide

4-Chloro-2,5-dimethoxyacetoacetanilide was prepared essentially following a procedure similar to the one described for the synthesis of acetoacet-o-chloroanilide¹⁵¹.

To 200 ml. of xylene (C.P. grade distilled, b.p. 137-38°C), in a 500 ml. flask fitted with a fractionating column and a receiver, was added 0.2 g. of triethanolamine in 10 ml. of absolute alcohol and the solution was refluxed for 1 hr. To the boiling xylene solution 13 g. (~13 ml.) of ethylacetoacetate ester (0.1 mole, b.p. 180°C.) was added and the solution was refluxed for 2 hrs. During refluxing ~10 ml. of alcohol was distilled. 18.75 g. of 4-chloro-2,5-dimethoxyaniline (0.1 mole) in 100 ml. xylene was added

and the mixture was further refluxed for about 2 hr. The liberated alcohol was removed by distillation. A major portion of xylene (~250 ml.) was distilled out by raising the temperature to 137°-38°C. and the solution was cooled to ~10°C. The solid product obtained was collected on a filter under suction and washed with small portions of xylene till it was free from any colour. The product was dried at 70°-80°C and was purified by recrystallization from benzene or chloroform. Yield of the white crystalline product, 90%, m.p., 122°-3°C. Anal. Found: C, 53.60; H, 5.07; N, 5.74; Cl, 13.1%. Required for C₁₂H₁₄O₄NCl: C, 53.04; H, 5.19; N, 5.16; Cl, 13.05%. The characteristic absorption bands (cm⁻¹) in the infrared spectrum of 4-chloro-2,5-dimethoxyacetanilide in Nujol are given below. 3310 (m, bonded NH), 1710 (vs, C=O Str.), 1650 (vs, Amide I), 1600 (s, C=C Str.) 1520 (s, Amide II), 1340 (m, Amide III). (Fig.I). P.M.R. (CDCl₃), τ = 7.75 (CH₃), 3.3 (>CH₂), 6.2. (-OCH₃), 6.17 (-OCH₃), 5 (=CH), 3.5 (3H), 1.67(2H), 0.93 (NH), -3.5 (OH) (disappeared on D₂O exchange). M⁺, 271. Required for C₁₂H₁₄O₄NCl: M⁺ 271.

Reagent solution:

1 g. of 4-chloro-2,5-dimethoxyacetanilide was dissolved in 50 ml. of hot alcohol and was diluted with water to 100 ml. The hot clear (filtered if necessary)

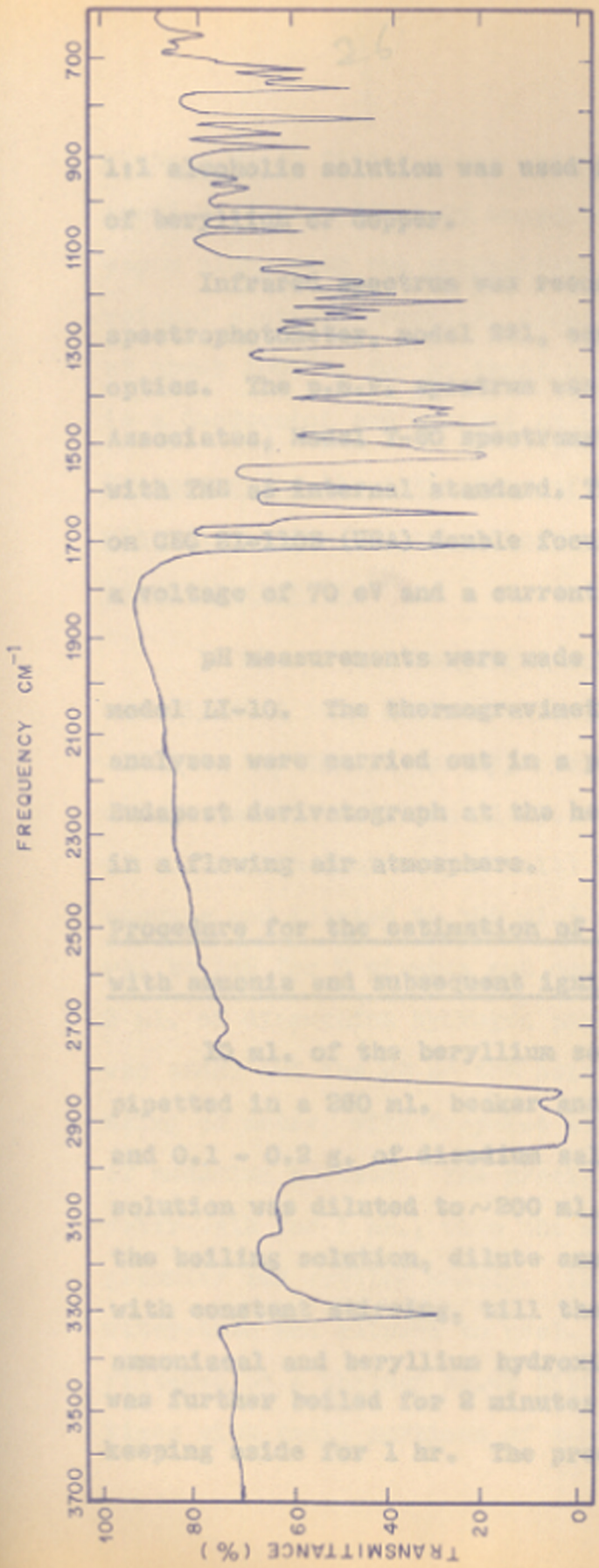


FIG. 1. INFRARED SPECTRUM IN NUJOL MULL OF 4-CHLORO-2,5-DIMETHOXYACETANILIDE

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1:1 alcoholic solution was used for the precipitation of beryllium or copper.

Infrared spectrum was recorded on a Perkin-Elmer spectrophotometer, model 221, equipped with sodium chloride optics. The p.m.r. spectrum was recorded on a Varian Associates, Model T-60 spectrometer, operating at 60 Mc/s with TMS as internal standard. The mass spectrum was recorded on CEC 21-110B (USA) double focussing mass spectrometer at a voltage of 70 eV and a current of 20 milliamperes.

pH measurements were made with ELICO pH meter, model LI-10. The thermogravimetric and differential thermal analyses were carried out in a platinum crucible in a MOM Budapest derivatograph at the heating rate of $10^{\circ}\text{C}/\text{min}$. in a flowing air atmosphere.

Procedure for the estimation of beryllium by precipitation with ammonia and subsequent ignition to beryllium oxide¹⁴⁹

10 ml. of the beryllium solution containing 8 mg. was pipetted in a 250 ml. beaker and 0.5 g. of ammonium chloride and 0.1 - 0.2 g. of disodium salt of EDTA were added, the solution was diluted to ~200 ml. and heated to boiling. To the boiling solution, dilute ammonia (1:2) was added dropwise, with constant stirring, till the solution is distinctly ammoniacal and beryllium hydroxide formed. The precipitate was further boiled for 2 minutes and allowed to settle by keeping aside for 1 hr. The precipitate was filtered on a

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Whatman No.41 filter paper and washed several times with small portions of hot 2% ammonium nitrate solution. The paper along with the precipitate was transferred to a weighed platinum crucible, dried in an oven and ignited at about 1000°C . for at least 1 hr. The crucible was cooled in a desiccator and weighed as BeO .

Procedure for the estimation of beryllium by precipitation with diammonium hydrogen phosphate and subsequent ignition to pyrophosphate.⁴⁶

10 ml. of the beryllium solution containing ~ 8 mg. was pipetted in a 250 ml. beaker, diluted with water to ~100 ml. and the pH was adjusted to 2, using pH meter, with dilute ammonia solution (1:4). EDTA solution [15 ml., 10 g. of solid EDTA (not sodium salt) was dissolved in concentrated ammonia and diluted to 100 ml.] was added and the solution was boiled for 2 minutes and cooled. To the cold solution 5 ml. of diammonium hydrogen phosphate solution (20% w/v) was added and the pH of the solution was adjusted to 5.2, using pH meter, with dropwise addition of a saturated solution of ammonium acetate. The precipitate formed was digested on water-bath for 1 hr., when the white bulky precipitate became granular and settled easily. The beaker was removed from water-bath and allowed to cool. The granular precipitate was filtered on a Whatman No.42 filter paper and washed several times with small portions of an acetate buffer solution of the

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pH adjusted to 5.2 (prepared by dissolving 2 g. of ammonium acetate and 3 ml. of glacial acetic acid and diluted to 1 litre and the pH adjusted to 5.2 with dilute ammonia). The paper along with the precipitate was transferred to a weighed platinum crucible, dried at 110°C . in an oven and then ignited to 1000°C , cooled in a desiccator and weighed as $\text{Be}_2\text{P}_2\text{O}_7$.

Procedure for the estimation of copper by sodium thiosulphate method.

¹⁵⁰
 10 ml. of the copper ^{sulphate} solution (containing ~10 mg. of Cu) was pipetted into a 250 ml. conical flask and the mineral acid was neutralized by the addition of solid sodium carbonate till a faint permanent precipitate was obtained. The cupric hydroxide formed was dissolved by adding a few drops of glacial acetic acid. To the clear solution, 1 g. of potassium iodide was added and the liberated iodine was titrated against standard sodium thiosulphate solution using starch indicator. The addition of the indicator solution was done at the end when the brown colour of the iodine solution turned pale yellow. The titration was continued until one drop of thiosulphate solution just discharged the blue colour.

(1 ml. N sodium thiosulphate = 0.06354 g. Cu.)

Procedure for the estimation of beryllium using
4-chloro-2,5-dimethoxyacetoacetanilide.

10 ml. of the standard beryllium solution containing approximately 10 mg. was pipetted into a 250 ml. beaker, diluted to about 100ml. with water and heated on a water-bath. To the hot solution, 80 ml. of hot ligand solution or the required quantity (a slight excess was used) was added with stirring. The pH of the resulting clear solution was adjusted by the careful drop-wise addition of dilute ammonia (1:4), with stirring, until neutral to methyl red indicator (pH papers may also be used). The addition of ammonia was stopped when the red colour of the indicator just disappeared (pH ~ 6.0 - 6.2). The final volume at this stage should be about 200 ml. The bulky white crystalline precipitate formed, settled down, on digestion for 1 hr., on the water-bath leaving a clear supernatant liquid. The precipitated complex was collected on a weighed sintered glass crucible (porosity No.3 or 4), while hot, washed with boiling water first (~ 200 ml.) and then with 1:1 cold aqueous alcohol (30-40 ml.). The ~~crucible~~^{precipitate} was dried at 115°-20°C for 2 hrs. cooled in a desiccator and weighed as $\text{Be}(\text{C}_{12}\text{H}_{13}\text{O}_4\text{NCl})_2$. The results are presented in Table I.

Procedure for the estimation of beryllium in presence of
 Al^{+++} and Fe^{+++} .

The procedure adopted was the same as above except that,

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when the foreign ions were present (~ 50 mg.) 0.5 - 1.0 g. of disodium salt of EDTA, was added to mask Al^{+++} or Fe^{+++} and the beryllium complex was precipitated with ammonia (1:4), with stirring. The solution was neutral to methyl red or slightly above ($pH \sim 6.5$). The results are presented in Table II.

Procedure for the estimation of copper using 4-chloro-2,5-dimethoxyacetoacetanilide.

An aliquot of the standard copper solution was pipetted into a 250 ml. beaker, diluted to about 100 ml. and heated on a water-bath. To the hot solution was added 80 ml. of the hot 1:1 alcoholic solution of 4-chloro-2,5-dimethoxyacetoacetanilide, with stirring. To the resulting clear solution dilute ammonia (1:4) was added drop-wise, with stirring, until the precipitation was complete (methyl red indicator was used). The final volume was adjusted to about 200 ml. The precipitated green complex, on digestion for 1 hr., on the water-bath, settled down. The complex was collected, while hot, on a weighed sintered glass crucible (porosity No.3 or 4), washed with boiling water (200 ml.) first and then with cold ^{aqueous} alcohol (30-40 ml.), dried at $115^{\circ}-20^{\circ}C$. for 2 hrs., and weighed as $Cu(C_{12}H_{13}O_4NCl)_2$. Results of the estimations are given in Table III.

Table I

Gravimetric estimation of Beryllium using 4-chloro-2,5-dimethoxyacetoacetanilide as a reagent.

Be taken (mg.)	Be found (mg.)	Error
3.80	3.75	-0.05
8.60	8.62	+0.02
	8.60	-
9.50	9.53	+0.03
	9.50	-

Table II

Separation of Beryllium from foreign ions

Be taken (mg.)	Foreign ion added (mg.)	Be found (mg.)	Error
7.80	-	7.85	+0.05
7.80	10(Al ⁺⁺⁺)	7.85	+0.05
7.80	25(Al ⁺⁺⁺)	7.80	0.00
7.80	50(Al ⁺⁺⁺)	7.78	-0.02
7.80	10(Fe ⁺⁺⁺)	7.80	0.00
7.80	25(Fe ⁺⁺⁺)	7.80	0.00
7.80	50(Fe ⁺⁺⁺)	7.89	+0.09

Table III

Gravimetric estimation of copper using 4-chloro-2,5-dimethoxyacetoacetanilide as a reagent.

Cu taken (mg.)	Cu found (mg.)	Error
4.63	4.62	-0.01
9.24	9.24	-
18.98	19.0	+0.02
23.72	23.9	+0.18
	23.7	-0.02

Table IV

Separation of copper from foreign ions

Cu taken (mg.)	Foreign ion added (mg.)	Cu found (mg.)	Error
9.10	-	9.05	-0.05
9.10	10(Zn ⁺⁺)	9.07	-0.03
9.10	25(Zn ⁺⁺)	8.98	-0.12
9.10	50(Zn ⁺⁺)	9.20	+0.10
9.10	5(Al ⁺⁺⁺)	9.08	-0.02
9.10	10(Al ⁺⁺⁺)	9.09	-0.01
9.10	20(Al ⁺⁺⁺)	9.08	-0.02
9.10	5(Cd ⁺⁺)	9.20	+0.10
9.10	10(Cd ⁺⁺)	8.98	-0.12
9.10	20(Cd ⁺⁺)	8.98	-0.12

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Procedure for the estimation of copper in presence of
Al⁺⁺⁺, Cd⁺⁺ and Zn⁺⁺.

The procedure adopted was the same as above except that in the presence of foreign ions (50 mg.), 0.5 to 1.0 g. of solid ammonium fluoride was added and copper was precipitated with dilute ammonia. (the solution was neutral to methyl red indicator or slightly above pH 6.85). Results of the estimations are given in Table IV.

Composition of the precipitate

The precipitated beryllium complex obtained, in the above manner was collected, washed and dried at 115°-20°C and was analysed for nitrogen and beryllium. Found: Be, 1.60; N, 5.11. Calcd. for Be(C₁₂H₁₃O₄NC1)₂: Be, 1.64; N, 5.09%.

Similarly the precipitated pale green copper complex was analysed for nitrogen and copper. Found: Cu, 10.4; N, 4.7; Calcd. for Cu(C₁₂H₁₃O₄NC1)₂: Cu, 10.52; N, 4.63%.

The i.r. spectra of the bis(4-chloro-2,5-dimethoxyacetoacetanilidato)beryllium(II) and bis(4-chloro-2,5-dimethoxyacetoacetanilidato)copper(II) are presented (Fig.II).

The influence of pH as well as that of the concentration of the reagent on precipitation were studied employing 10 ml. of standard beryllium(II) or copper(II) solutions. Varying quantities of dilute ammonia or ligand solution were used for precipitation. These studies revealed that the pH range of

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quantitative precipitation for beryllium was 5.8 - 6.5; for copper the pH range was 6.0 - 7.3, and that a slight excess of the reagent (~5%) should be present. Addition of undue excess of the reagent solution might present difficulties during washing and should be avoided.

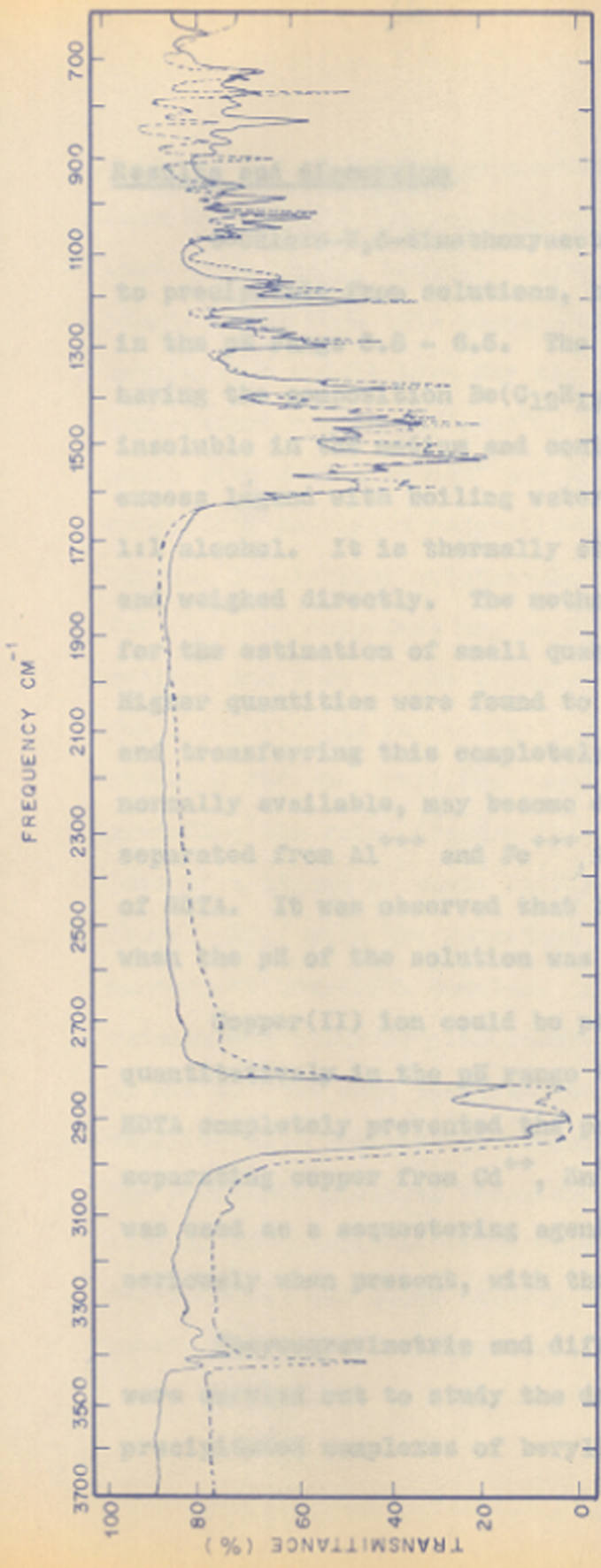


FIG. II. INFRARED SPECTRA IN NUJOL MULL OF
 a) — BIS(4-CHLORO - 2,5 - DIMETHOXYACETOACETANILIDATO) -
 BERYLLIUM (II)
 b) BIS (4-CHLORO - 2,5-DIMETHOXYACETOACETANILIDATO) -
 COPPER (II)

Results and discussion

4-Chloro-2,5-dimethoxyacetoacetanilide has been found to precipitate from solutions, beryllium(II) ion quantitatively in the pH range 5.8 - 6.5. The precipitated bulky complex having the composition $\text{Be}(\text{C}_{12}\text{H}_{13}\text{O}_4\text{NCl})_2$ was found to be insoluble in the medium and could be washed free from any excess ligand with boiling water and small quantities of 1:1 alcohol. It is thermally stable, could be dried at $115^\circ\text{-}20^\circ\text{C}$ and weighed directly. The method is particularly suitable for the estimation of small quantities of beryllium (3 to 10 mg.). Higher quantities were found to result in unwieldy precipitate and transferring this completely to the sintered glass crucible, normally available, may become difficult. Beryllium was separated from Al^{+++} and Fe^{+++} , in presence of disodium salt of EDTA. It was observed that better results were obtained when the pH of the solution was raised to 6.5.

Copper(II) ion could be precipitated from solution, quantitatively in the pH range 6.0 - 7.3. The presence of EDTA completely prevented the precipitation of copper. For separating copper from Cd^{++} , Zn^{++} and Al^{+++} , ammonium fluoride was used as a sequestering agent. Fe^{+++} , however, interfered seriously when present, with the estimation of copper.

Thermogravimetric and differential thermal analyses were carried out to study the decomposition processes of the precipitated complexes of beryllium(II) and copper(II) with

4-chloro-2,5-dimethoxyacetoacetanilide. According to the data from TG and DTA analyses (Figs. III and IV) the complexes were quite stable thermally upto 220°-240°C. Decomposition started only from this temperature region onwards and accelerated weight loss for the complexes occurred in the temperature region 400°-600°C. Broad and pronounced exothermic peaks with maxima at 540° and 520°C for beryllium(II) and copper(II) complexes respectively were observed in the DTA curves. The initial endothermic peaks observed at about 270°C for both the compounds may be due to the combined effects of melting and loss of the organic part of the compounds. The small but visible inflection (unresolved endothermic peak) observed for the beryllium complex at 400°C in the DTA curve preceding the rapid decomposition process could be due to the loss of a ligand molecule initially (theoretical 49.37%; found: 49%), with the formation of an apparently unstable monovalent beryllium complex. A small but noticeable endothermic peak was also observed for the copper complex at 360°C. The mass spectral studies on several beryllium chelates with β -diketones revealed that upon electron impact, the beryllium chelates break-down in a well-defined manner leading to changes in metal valency¹³. The existence of beryllium(I) ion under certain conditions (as a product of anodic oxidation) also was previously reported¹².

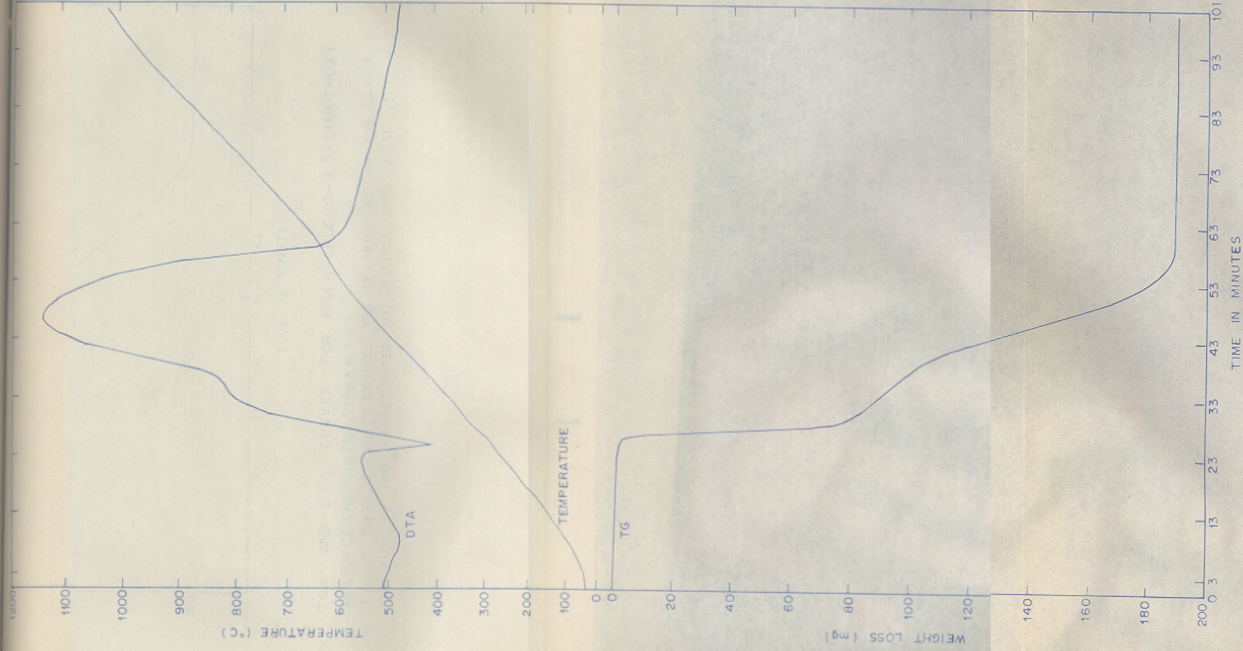


FIG. III. TGA AND DTA CURVES FOR BIS(4-CHLORO-2,5-DIMETHOXY-ACETOACETANILIDATO)BERYLLIUM(II)
(AMOUNT TAKEN, 200 mg, T DENOTES THE TEMPERATURE OF SAMPLE AS A FUNCTION OF TIME REPRESENTED BY ABSCISSA. DTA SENSITIVITY, 1/10.)

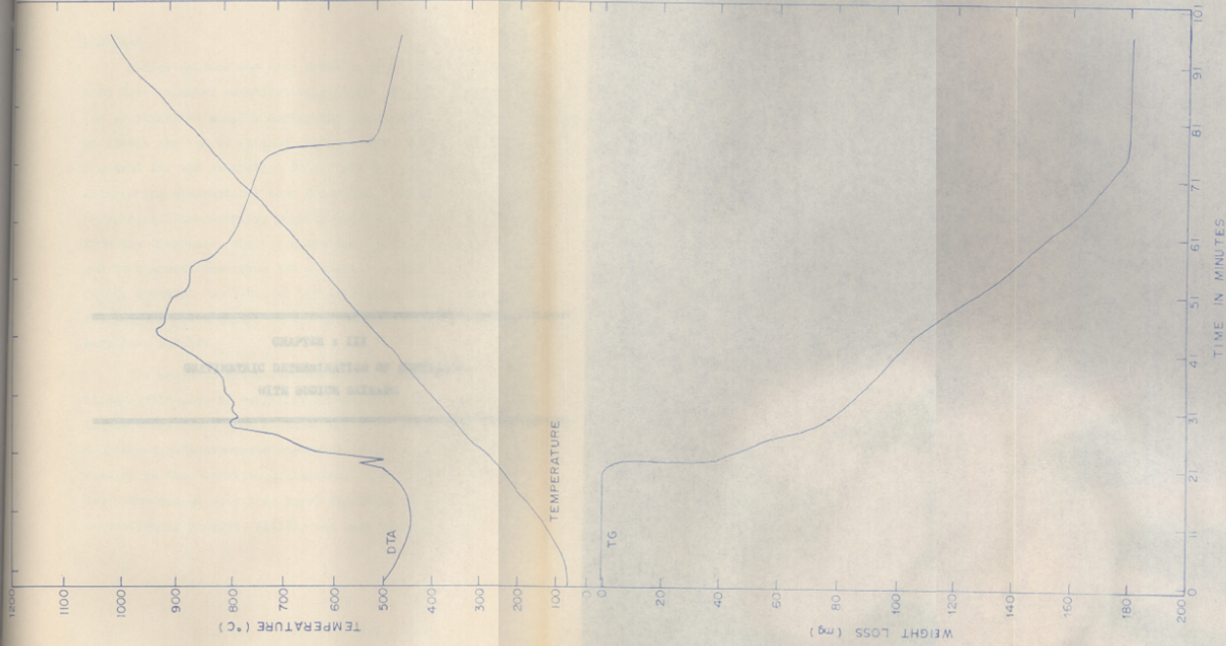


FIG. IV. TGA AND DTA CURVES FOR BIS(4-CHLORO-2,5-DIMETHOXY-ACETOACETANILIDATO)COPPER(II) (AMOUNT TAKEN, 200 mg, T DENOTES THE TEMPERATURE OF THE SAMPLE AS A FUNCTION OF TIME REPRESENTED BY ABSCISSA, DTA SENSITIVITY $\times 10$.)

CHAPTER : III

GRAVIMETRIC DETERMINATION OF BERYLLIUM
WITH SODIUM OXINATE

Abstract

Sodium oxinate has been found to precipitate Be(II) ions from solution quantitatively in the pH range 7.5 - 8.2. The precipitated complex having the composition, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$, is stable and can be weighed directly after drying at $105^\circ\text{--}110^\circ\text{C}$. A method for the estimation Be(II) and its separation from interfering elements has been described. Bis(8-quinolinolato)-beryllium(II)monohydrate, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{H}_2\text{O}$ has been isolated from the dihydrate, the weighable form of the beryllium complex, and is characterized from its elemental analyses, I.R. and P.M.R. spectral and T.G. and D.T.A. studies. The data show the presence of hydroxyl bridge bonds in the monohydrated beryllium complex.

The methods, using various organic reagents, for the direct estimation of beryllium in ores (beryl) and in alloys (Be-Cu alloy) have been examined and it is found that 4-chloro-2,5-dimethoxyacetoacetanilide gives satisfactory results in the beryllium estimation. A method for the determination of Be(II) in beryl involving no prior separation of Fe(III), Al(III) has been described.

Introduction

There is a general lack of specific organic precipitants for the direct gravimetric determination and separation of beryllium(II) from solutions. Many organic reagents form precipitates of definite composition with beryllium and these can be used as weighing forms. Although a few chelating agents, such as, β -diketones,^{63-65,67,68,93} Schiff-bases,⁷⁹ 8-quinolinol and its derivatives^{71,72,152} have been proposed as precipitants for the gravimetric determination of beryllium, these on closer scrutiny, have been found to be neither specific nor precise. However, selectivity has been attained in some instances, by masking the interfering elements by complexone III. Furthermore, the application of these reagents to the analysis of beryl which contains fair amounts of aluminium and to the analysis of alloys is complicated and involves a prior separation of interfering elements before the estimation of beryllium. Recently 4-chloro-2,5-dimethoxyacetoacetanilide has been used as a precipitant for beryllium(II) and it is found that the reagent can be directly used for the quantitative precipitation of beryllium from solution containing Fe(III) and Al(III) ions, in presence of disodium salt of EDTA.¹⁴ It is now observed that the method can be successfully applied to the direct beryllium determination in beryl.

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In addition, sodium oxinate, a water soluble compound has been also examined as a possible reagent for the determination of beryllium in solution. The reagent has been found to precipitate beryllium from solutions quantitatively in the pH range 7.5 - 8.2. Sodium oxinate forms a basic hydroxy quinolate of the composition, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$, which can serve as the weighing form in the determination. The experimental results obtained with various other reagents reported in literature for (a) the gravimetric estimation of beryllium(II) in pure Be(II) solutions (b) in ores (beryl) and (c) in alloys (Be-Cu alloy) have been presented for comparison along with those obtained with (1) 4-chloro-2,5-dimethoxyacetoacetanilide and (2) sodium oxinate in this Chapter. The relative merits (or otherwise) of these reagents are also discussed.

Experimental

Beryllium stock solution was prepared from beryllium nitrate trihydrate, $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or from beryllium hydroxide (Fluka AG; Chemische Fabrik, Buchs, S.G.) or from beryllium sulphate tetrahydrate, $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ (ANALAR). These were dissolved in appropriate acids and were diluted with water. The beryllium content was determined according to the standard procedures gravimetrically either as BeO^{149} or as $\text{Be}_2\text{P}_2\text{O}_7^{46}$. All the other reagents used were of A.R. grade.

The reagent, sodium oxinate, was prepared according to the reported methods.^{153,154} Yield, 90%; m.p. $> 300^\circ\text{C}$ (decom.) Anal. Found: C, 53.19; H, 4.71; N, 6.41%. Required for $\text{C}_9\text{H}_6\text{NONa} \cdot 2\text{H}_2\text{O}$: C, 53.20; H, 4.93; N, 6.90%. I.R. (Nujol), 3300 (m, broad, OH Str.), 1102 (vs, >C-O-M site^{155}), 718 (m, ONa),¹⁵⁶ cm^{-1} . (Fig.V).

Reagent solution:

1 g. of sodium oxinate dihydrate, ($\text{C}_9\text{H}_6\text{NONa} \cdot 2\text{H}_2\text{O}$) was dissolved in 100 ml. of water. The clear aqueous solution (filtered if necessary) was used for the precipitation of beryllium.

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, model 221, equipped with sodium chloride optics. The p.m.r. spectra were recorded on a Varian Associates,

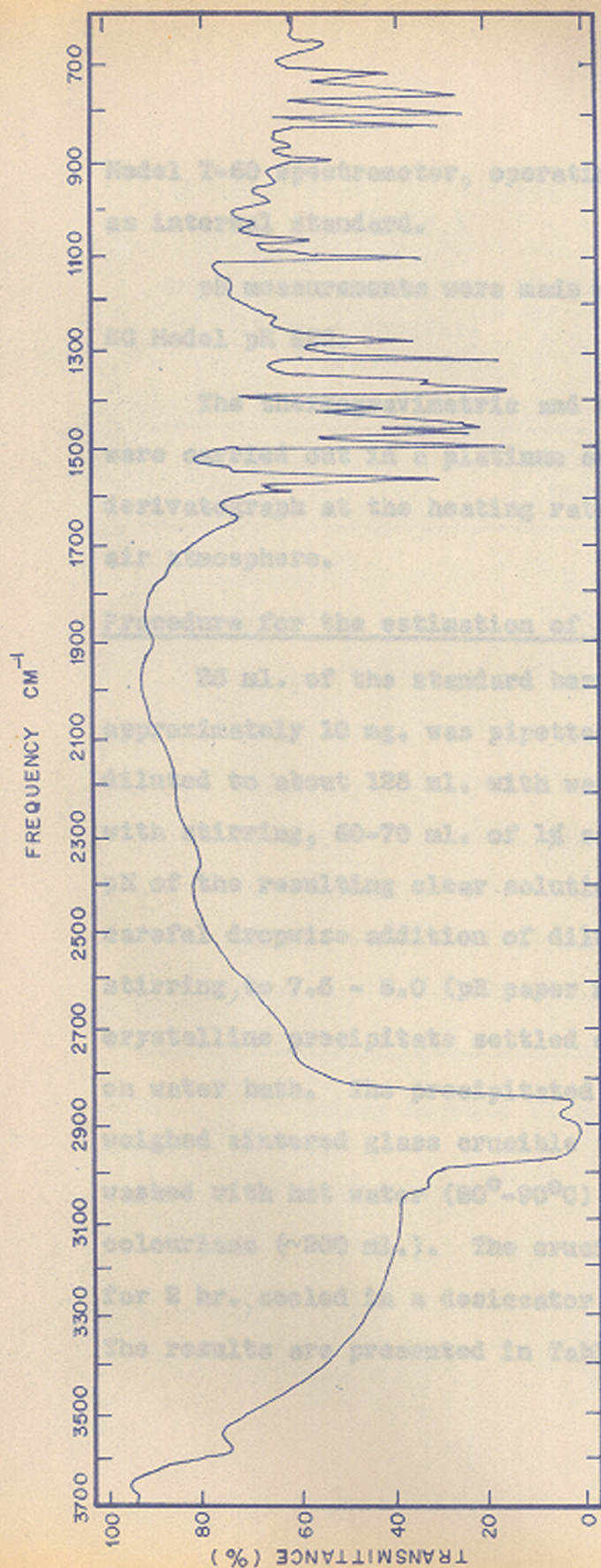


FIG. V. INFRARED SPECTRUM IN NUJOL MULL OF SODIUM OXINATE DIHYDRATE, $C_9H_6NO Na \cdot 2H_2O$

Model T-60 spectrometer, operating at 60 Mc/s, with TMS as internal standard.

pH measurements were made on Digital pH meter, EC Model pH 822.

The thermogravimetric and differential thermal analyses were carried out in a platinum crucible in a MOM Budapest derivatograph at the heating rate of $10^{\circ}/\text{min}$. in a flowing air atmosphere.

Procedure for the estimation of beryllium

25 ml. of the standard beryllium solution containing approximately 10 mg. was pipetted into a 250 ml. beaker and diluted to about 125 ml. with water. To this solution was added, with stirring, 60-70 ml. of 1% sodium oxinate solution. The pH of the resulting clear solution was adjusted, by the careful dropwise addition of dilute ammonia (1:4) with stirring, to 7.5 - 8.0 (pH paper may be used). The bulky yellow crystalline precipitate settled down, on digestion for 1 hr., on water bath. The precipitated complex was collected on a weighed sintered glass crucible (porosity No.4), while hot, washed with hot water (80° - 90°C) till the filtrate was colourless (~ 200 ml.). The crucible was dried at 105° - 110°C . for 2 hr., cooled in a desiccator and weighed as $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$. The results are presented in Table I.

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Table I

Gravimetric estimation of beryllium using sodium oxinate as a reagent.

<u>Be taken</u> (mg.)	<u>Be found</u> (mg.)	<u>Error</u>
3.83	3.83	0.00
5.75	5.75	0.00
7.66	7.67	+0.01
9.58	9.58	0.00
9.58	9.57	-0.01
9.58	9.57	-0.01
9.99*	9.96	-0.03
9.99*	9.96	-0.03
10.52	10.54	+0.02

* Sodium acetate (1 g.) was added.

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Procedure for the estimation of beryllium using sodium oxinate in presence of Al^{+++} , Fe^{+++} , Cu^{++} and Zn^{++} ions.

Masking of the foreign ions with disodium salt of EDTA was found not satisfactory. Reported methods were employed to remove or precipitate the interfering elements and from the filtrate, beryllium was estimated using sodium oxinate according to the above procedure.

Aluminium from beryllium solution was separated by precipitation as oxinate at pH 4-5 in an acetate buffer or by tannin in presence of ammonium nitrate, ammonium acetate and acetic acid.^{17,23,157,158} Iron from beryllium solution was removed as oxinate or as tannin complex. Copper from beryllium solution was removed by electrolysis^{159,160} or by precipitation of copper as oxinate at pH 4-5 in acetate buffer. Zinc was separated from beryllium solution as quinaldinate¹⁶¹ or as oxinate. The results are tabulated in Table II.

Table II

Estimation of beryllium in presence of Al^{+++} , Fe^{+++} , Cu^{++} and Zn^{++} ions.

<u>Be taken</u> (mg.)	<u>Foreign ion added</u> (mg.)	<u>Be found</u> (mg.)	<u>Error</u>
9.76	5(Al^{+++})	9.75	-0.01
9.76	10(Al^{+++})	9.75	-0.01
10.09	10(Al^{+++})	10.05	-0.04
10.09	25(Al^{+++})	10.02	-0.07
10.09	50(Al^{+++})	10.02	-0.07
9.76	5(Fe^{+++})	9.75	-0.01
10.09	10(Fe^{+++})	9.99	-0.10
10.09	25(Fe^{+++})	9.99	-0.10
9.59	10(Cu^{++})	9.60	+0.01
9.59	25(Cu^{++})	9.64	+0.04
9.59	50(Cu^{++})	9.58	-0.01
9.76	5(Zn^{++})	9.76	0.00
9.76	10(Zn^{++})	9.73	-0.03
9.76	25(Zn^{++})	9.72	-0.04

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The influence of the pH (Table III) as well as that of the concentration of the reagent on the precipitation were studied. To 25 ml. of beryllium solution (~ 10 mg.) in a 250 ml. beaker, 70 ml. of the reagent solution was added and to this mixture dilute ammonia (1:4) in small portions was added with mechanical stirring. The pH of the solution was measured at each successive addition. The precipitated complex was collected separately and the beryllium content was determined at successive pH values. These studies reveal that the pH range of the quantitative precipitation of beryllium is 7.5 - 8.0 and that 1.5 times excess over the stoichiometric quantity of the reagent is required for the complete precipitation of beryllium.

Table III

The effect of pH on the precipitation of beryllium

<u>pH</u>	<u>Be taken</u> (mg.)	<u>Be found</u> (mg.)	<u>Error</u>
4.00	9.67	No precipitation	-
4.50	9.67	-do-	-
5.10	9.67	-do-	-
5.64	9.67	-do-	-
6.10	9.67	-do-	-
6.50	9.67	Turbidity	-
7.28	9.67	8.78	-0.89
7.68	9.67	9.71	+0.04
7.95	9.67	9.64	-0.03
8.54	9.67	9.52	-0.15
8.80	9.67	9.43	-0.24
9.54	9.67	9.22	-0.45
10.00 and above	9.67	8.80	-0.87

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Composition of the precipitate

The precipitated beryllium complex obtained in the above manner (collected, washed and dried) was analysed. M.p., 295°-300°C (decom.). Anal. Found: C, 59.94; H, 4.82; N, 7.50 and Be, 4.95%. Calculated for $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$: C, 60.34; H, 4.49; N, 7.82 and Be, 5.03%.

Preparation of bis(8-quinolinolato)beryllium(II)monohydrate, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{H}_2\text{O}$.

The beryllium complex (dihydrate) was dehydrated by heating at 80°C. under vacuum (~3 mm) for 16 hrs. (Yield is quantitative), m.p., 306°-8°C. (decom.). Anal. Found: C, 63.42; H, 4.63; N, 8.03 and Be, 5.21%. Calcd. for $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{H}_2\text{O}$: C, 63.63; H, 4.12; N, 8.24 and Be, 5.30%.

The characteristic absorption bands (cm^{-1}) in the i.r. spectra of bis(8-quinolinolato)beryllium(II)dihydrate and bis(8-quinolinolato)beryllium(II)monohydrate, in nujol, are given below (Fig.VI): 3315 (m, OH Str.), 1112 (s, >C-O-M site), 928 (s, Be-O).

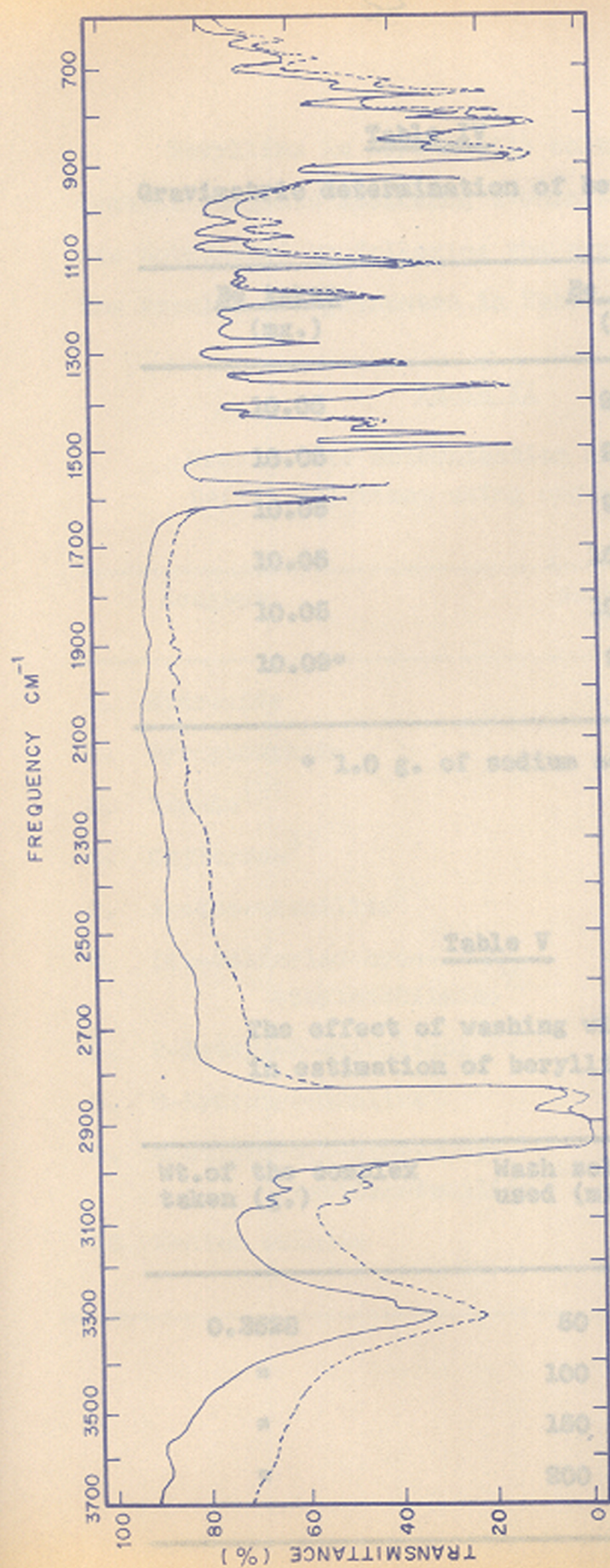


FIG. VI. INFRARED SPECTRA IN NUJOL MULL OF

a) ----- BIS(8-QUINOLINATO)BERYLLIUM(II) DIHYDRATE,
 $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$

b) ——— BIS(8-QUINOLINATO)BERYLLIUM(II) MONOHYDRATE,
 $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{H}_2\text{O}$

Table IV

Gravimetric determination of beryllium using 8-quinolinol

<u>Be taken</u> (mg.)	<u>Be found</u> (mg.)	<u>Error</u>
10.05	9.90	-0.15
10.05	9.66	-0.29
10.05	9.76	-0.29
10.05	10.07	+0.02
10.05	10.34	+0.29
10.09*	9.65	-0.44

* 1.0 g. of sodium acetate was added.

Table V

The effect of washing with dilute ammonia (1:100) in estimation of beryllium using 8-quinolinol.

<u>Wt. of the complex taken (g.)</u>	<u>Wash solution used (ml.)</u>	<u>Wt. of the complex after washing and drying (g.)</u>	<u>Loss</u>
0.3528	50	0.3402	0.0126
"	100	0.3305	0.0223
"	150	0.3278	0.0250
"	200	0.3221	0.0307

Beryllium in pure Be(II) solutions using various other organic reagents including 4-chloro-2,5-dimethoxyacetoacetanilide was determined by following the procedures described in literature. The results are presented in Table VI.

Table VI

Gravimetric determination of beryllium from pure Be(II) solutions using organic reagents.

Reagent	Be taken (mg.)	Be found (mg.)	Error
1. Hydroxide	9.76	9.76	0.00
2. Pyrophosphate	-	9.77	+0.01
3. Tannin ¹⁵⁸	-	9.76	0.00
4. Cupferron ⁶⁸	-	9.93	+0.17
5. Acetoacetanilide ⁶⁵	-	9.27	-0.39
6. Bis-Salicylaldehyde- ethylenediamine ⁷⁹	-	9.76	0.00
7. 2-Methyl-8-quinolinol ^{72,73}	-	9.72	-0.04
8. 8-Hydroxyquinoline ⁷¹	-	9.48	-0.28
9. 4-Chloro-2,5-dimethoxy- acetoacetanilide ¹⁴	-	9.76	0.00
10. Sodium oxinate	-	9.77	+0.01

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Determination of beryllium content in beryl

0.5 g. of finely powdered beryl was fused with 15 g. of sodium carbonate in a platinum crucible and kept in a molten condition for about 15 mts. The melt was cooled and taken up with dilute hydrochloric acid (1:1). The solution was evaporated to dryness and treated with 2 ml. of perchloric acid and 5 ml. of concentrated sulphuric acid and evaporated again to dryness. The residue was dissolved in hot water and silica was filtered off. The residue from silica estimation (after $\text{HF-H}_2\text{SO}_4$ treatment) was fused with potassium bisulphate. The bisulphate melt was dissolved in water and added to the main filtrate and made upto 500 ml. The beryllium content of the solution was determined by standard methods as well as with 4-chloro-2,5-dimethoxyacetoacetanilide and various other organic reagents according to the procedures described. The result are presented in Table VII.

Procedure for the determination of beryllium in beryl using 4-chloro-2,5-dimethoxyacetoacetanilide

50 ml. of the beryl solution was pipetted into a 250 ml. beaker and was diluted to 125 ml. with water. Sodium salt of EDTA (solid ~ 2 g.) was added to this and the solution was heated on a water-bath. To the hot solution,

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80-90 ml. of hot ligand solution (1%) was added, with stirring. The pH of the resulting clear solution was adjusted, by the careful dropwise addition of dilute ammonia (1:4), with stirring, until neutral to methyl red indicator (pH paper may also be used). The addition of ammonia is stopped when the red colour of the indicator just disappeared (pH ~ 6.0 - 6.2). The final volume at this stage should be about 200 ml. The bulky white crystalline precipitate formed settled down, on digestion, for 1 hr. on water-bath, leaving a clear supernatant liquid. The precipitated complex was collected on a weighed sintered glass crucible (porosity No.4), while hot, washed with boiling water first (~ 200 ml.) and finally with 1:1 cold aqueous alcohol (~ 25 ml.). The crucible was dried at 115°-120°C. for 2 hr., cooled in a desiccator and weighed as $\text{Be}(\text{C}_{12}\text{H}_{13}\text{O}_4\text{NCl})_2$.

Determination of beryllium in beryl using sodium oxinate

After removing Al^{+++} , Fe^{+++} , from the solution, the beryllium content was estimated by the earlier described procedure.

Procedures adopted for the estimation of beryllium content in beryl solution using organic reagents have been already described. The results are presented in Table VII.

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Table VII

Gravimetric determination of beryllium from beryl
using 4-chloro-2,5-dimethoxyacetoacetanilide, sodium
oxinate and other organic reagents.

Reagent or method used	Be%	Error
1. Hydroxide	4.91	-
2. Tannin ¹⁵⁸	8.11	+3.20
3. Cupferron ⁶⁸	6.03	+1.12
4. Acetoacetanilide ⁶⁵	6.77	+1.86
5. Bis-salicylaldehyde-ethylenediamine ⁷⁹	5.62	+0.71
6. 2-Methyl-8-quinolinol ^{72,73}	7.29	+2.38
7. 4-Chloro-2,5-dimethoxy- acetoacetanilide ¹⁴	4.91	-
	4.91	-
	4.92	+0.01
8. Sodium oxinate*	4.91	-
	4.91	-
	4.94	+0.03

* After removal of the interference

Gravimetric determination of beryllium in Be-Cu alloy using 4-chloro-2,5-dimethoxyacetoacetanilide and other organic reagents.

*

1.99 g. of the Be-Cu alloy was dissolved in 50 ml. of dilute nitric acid (1:1) by slow heating. The solution was boiled for 5-10 minutes, cooled and diluted to 500 ml. Beryllium content was determined first, by standard methods. It is found that copper(II) is quantitatively precipitated by 4-chloro-2,5-dimethoxyacetoacetanilide in the pH range 6.0 - 7.3. Hence, copper from the solution was separated electrolytically and then beryllium was estimated from the solution (Table VIII).

* Gift sample from BARC, Bombay

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Table VIII

Gravimetric determination of beryllium in Be-Cu alloy using 4-chloro-2,5-dimethoxyacetoacetanilide and other organic reagents.

Reagent or method used	Be taken (mg.)	Be found (mg.)	Error
1. Hydroxide	3.98	3.99	+0.01
2. Pyrophosphate	"	3.94	-0.04
3. Tannin ¹⁵⁸	"	3.96	-0.02
4. Cupferron ⁶⁸	"	3.47	-0.51
5. Acetoacetanilide ⁶⁵	"	3.47	-0.51
6. Bis-salicylaldehyde-ethylenediamine ⁷⁹	"	4.78	+0.80
7. 2-Methyl-8-quinolinol ^{72,73}	"	3.91	-0.07
8. 8-Hydroxyquinoline ⁷¹	"	3.74	-0.24
9. 4-Chloro-2,5-dimethoxy-acetoacetanilide ¹⁴	"	3.92	-0.06
10. Sodium oxinate	"	3.94 4.04	-0.04 +0.06

Results and discussion

Although 8-quinolinol has been proposed by earlier workers^{71,152} as a gravimetric reagent for the determination of beryllium, there is a considerable controversy concerning the nature of the precipitate formed in solution. Rao et al.¹⁵² reported quantitative precipitation of beryllium from aqueous solutions with 8-quinolinol in the pH range 7.16 - 8.12 and the composition of the beryllium oxinate has been shown to be $\text{Be}(\text{C}_9\text{H}_6\text{NO})_2$. Motojima⁷¹ proposed, however, the formula $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$ for the yellow crystalline insoluble precipitate formed in solution. The precipitated complex after washing and drying, may be directly weighed as such according to both the procedures but Rao et al.¹⁵² apparently preferred to ignite it to BeO in the beryllium determination. Magee and Gordon¹⁶² reported that beryllium with ionic radius 0.31 \AA might be expected not to form a complex with 8-quinolinol. The analytical procedures for the determination of beryllium with 8-quinolinol as well as the nature of the complex formed in solution are, therefore, examined and it is observed that consistently low beryllium values are obtained by the reported methods (Table IV). Further acetic acid interferes seriously with the estimation necessitating the use of undue excess of the reagent during estimation. During washing of the beryllium complex with dilute ammonia (1:100) to remove excess of the reagent, losses of the complex itself, due to dissolution are observed (Table V).

It is considered therefore interesting to examine the sodium salt of 8-quinolinol, sodium oxinate - a water soluble compound - as a possible reagent for beryllium(II). The reagent precipitates beryllium from solutions quantitatively in the pH range 7.5 - 8.2. The precipitated yellow crystalline basic hydroxy quinolate of the composition $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$ is found to be insoluble in the medium and could be washed free from excess ligand easily with boiling water. It is thermally stable and could be dried at 105°C - 110°C and weighed directly. It is found that sodium oxinate, unlike 8-quinolinol, gives consistently satisfactory results in the determination of beryllium. However, when beryllium is associated with Al(III), Fe(III), Zn(II), Cu(II), etc., a prior separation of these interfering elements is found necessary. Masking of the foreign ions with disodium salt of EDTA is found to be unsatisfactory. Ions such as, acetate, sulphate, chloride do not interfere in the estimation. The experimental data are presented in Tables I-III.

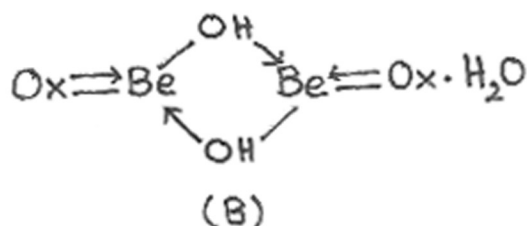
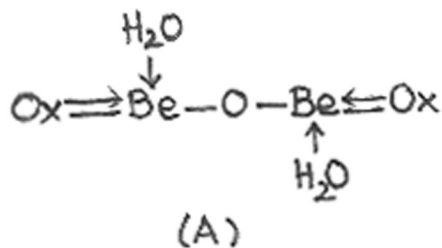
Thermogravimetric and differential heating curves for the complexes bis(8-quinolinolato)beryllium(II)dihydrate, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$ and bis(8-quinolinolato)beryllium(II)-monohydrate, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{H}_2\text{O}$ are shown in figures VII and VIII. Elemental analyses, I.R. spectra and T.G. and D.T.A. analyses clearly show that the precipitated beryllium complex has the composition $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$. The dihydrate formula

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has been confirmed in a recent study of beryllium oxinate prepared by mixing homogeneous solutions¹⁶³. The authors reported however that with the loss of one molecule of water during pyrolysis of the compound, an unstable intermediate is formed which immediately decomposed to form the oxide of beryllium. It is observed in our study, however, that with the volatilization of one water molecule from the dihydrate, a thermally stable intermediate product, monohydrated beryllium complex is formed which decomposes on further heating. The thermal stability of this intermediate product is amply demonstrated by the isolation of bis(8-quinolinolato)beryllium(II)-monohydrate, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{H}_2\text{O}$ by heating the dihydrate at 80°C under vacuum (~ 3.0 mm.) and is characterised from its elemental analyses, I.R. spectral and T.G. and D.T.A. data. The OH str. absorption in the i.R. spectrum of the compound is observed at 3315 cm^{-1} , and the other OH bending modes however could not be assigned unequivocally due to the absorption bands of the ligand in these regions. The compound shows loss corresponding to one mole of water at 240°C and volatilization of water is accompanied by decomposition of the complex suggesting that water is coordinatively attached, probably forming hydroxyl bridge bonds. Beryllium compounds and chelates containing such hydroxyl bridge bonds have been reported¹⁶⁴⁻¹⁶⁷. The presence of hydroxyl bridge bonds in bis(8-quinolinolato)beryllium(II)monohydrate is confirmed by P.M.R. studies. The P.M.R. spectrum of the compound in

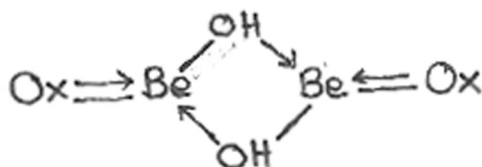
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trifluoroacetic acid (TAA) (Fig.IX) shows a broad absorption centred at -3.47τ arising from hydroxyl protons [aromatic protons are observed at 1.0τ (2H and 4H) and at 2.17τ (3,5,6 and 7H)] and furthermore, there is no change in the spectrum after 48 hrs. (no exchange of the hydroxyl protons with protons of the acid group), indicating probably the presence of bridged hydroxyl protons. The hydroxyl protons absorption disappears, with the addition of small amounts of D_2O to the sample, indicating that the monohydrate reverts to the dihydrate complex presumably containing no hydroxyl bridged structure as in (A) rather than to the form (B). The structure (B) was suggested by earlier workers for the dihydrate on the basis of pyrolysis data and to explain the stability of the molecule at $180^\circ C$ formula (A) is also favoured¹¹



$HOx = 8\text{-quinolinol}$.

These studies indicate that bis(8-quinolinolato)beryllium(II)-monohydrate may have the following structure.



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T.G. and D.T.A. data show bis(8-quinolinolato)beryllium(II)-dihydrate is thermally stable upto 150-160°C and decomposition starts only from this temperature region. Accelerated weight loss occurs in the temperature region 250°-500°C. Broad and pronounced endothermic peaks with maxima at 280°, 400° and 455° are observed in the DTA curve. An extreme deviation from the base line on the DTG curve corresponding to these changes are also visible. Complete volatilization is observed at 840° (theory 86.04%; found 86.0%). The weight loss in the vicinity 200-220°C suggests volatilization of one molecule of water. Further loss of the water of hydration, as shown by the peak at 280°C (loss observed 17%; required for 2 moles of water 10.01%) results in the decomposition of the complex itself. The pronounced endothermic peaks at 400° and 455°C are due to combined effects of melting and loss of a major portion of the organic part of the compound. The decomposition pattern for bis(8-quinolinolato)beryllium(II)monohydrate is similar to the dihydrate and shows that the compound is stable thermally upto 240°. Complete volatilization takes place at 780°C (Theory 85.29%; observed 86.0%).

The experimental data concerning the estimation of beryllium in beryl presented in Table (VII) clearly shows that amongst the reagents examined only 4-chloro-2,5-dimethoxyacetoacetanilide gives consistently satisfactory results. Prior removal of Al(III) and Fe(III) from the solution is not

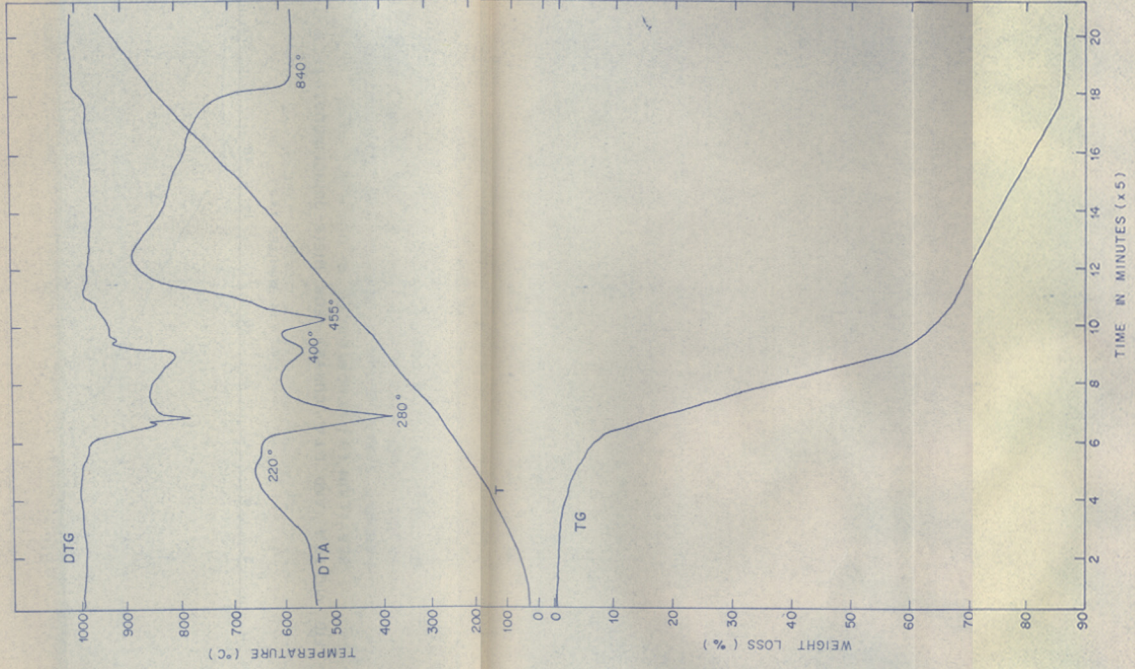


FIG. VII. T.G.A. AND D.T.A. CURVES FOR BIS(8-QUINOLINOLATO)-BERYLLIUM (II) DIHYDRATE, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$. (AMOUNT TAKEN 200 mg, T DENOTES THE TEMPERATURE OF THE SAMPLE AS A FUNCTION OF TIME REPRESENTED BY ABSCISSA. D.T.A. SENSITIVITY, 1/10)

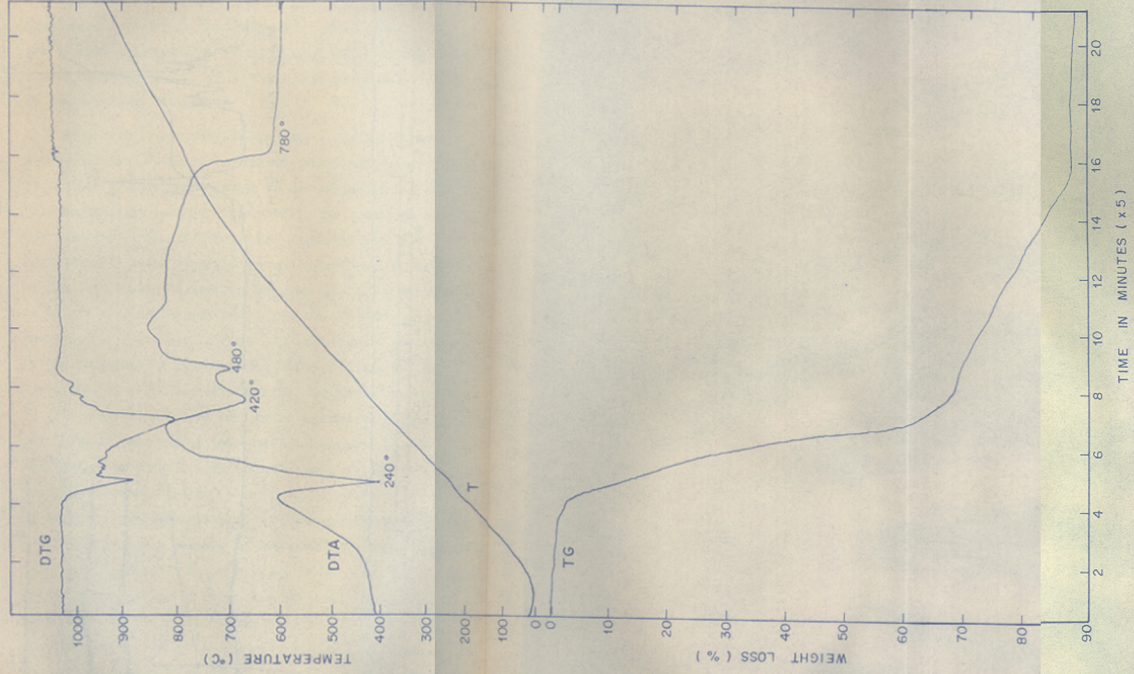


FIG. VIII. T.G.A. AND D.T.A. CURVES FOR BIS(8-QUINOLINOLATO)-
 BERYLLIUM (II) MONOHYDRATE, $\text{Be}_2\text{O}(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{H}_2\text{O}$.
 (AMOUNT TAKEN 200 mg., T DENOTES THE TEMPERATURE
 OF THE SAMPLE AS A FUNCTION OF TIME REPRESENTED
 BY ABSCISSA. D.T.A. SENSITIVITY, 1/10)

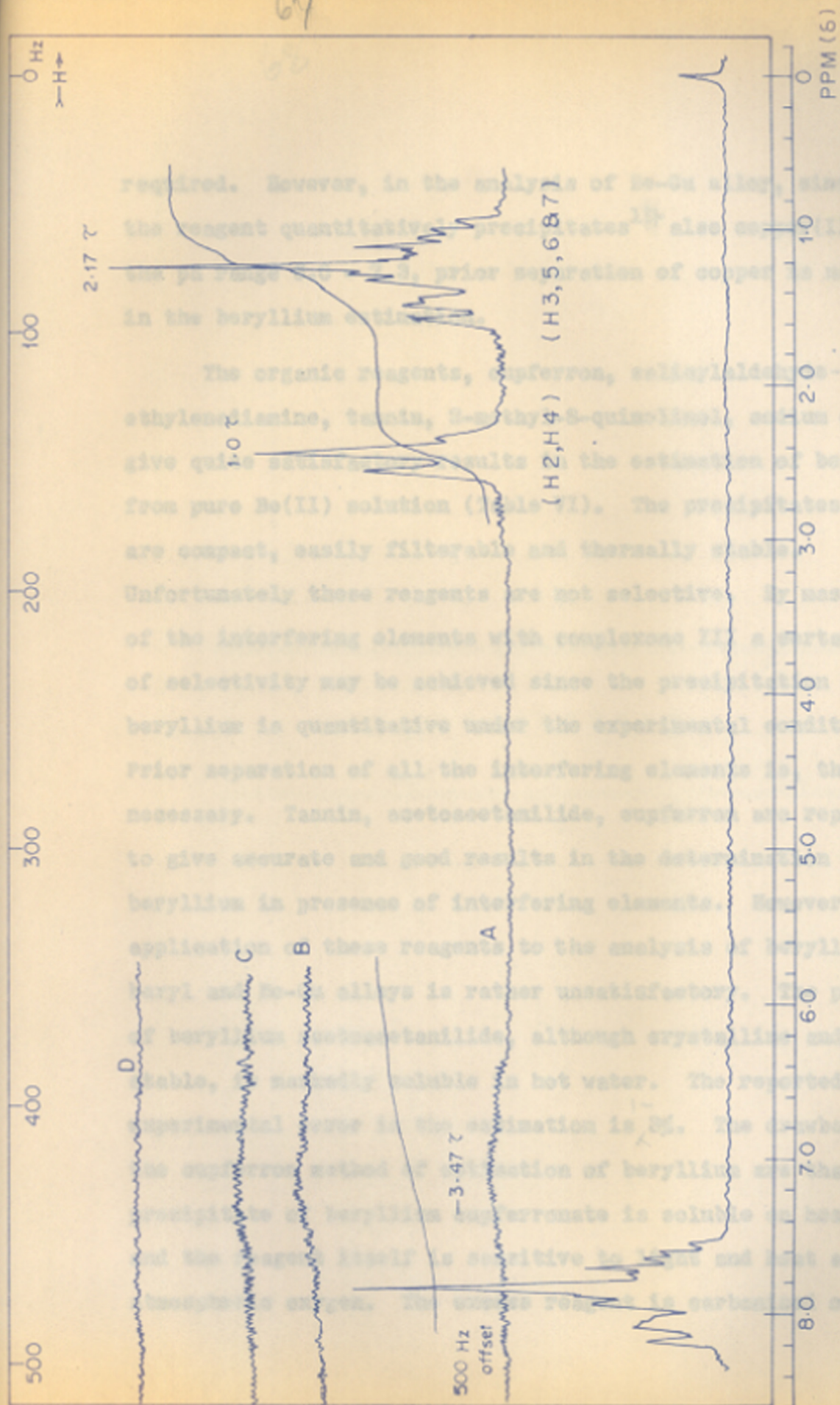


FIG. IX. PMR SPECTRA OF (A) BIS(8-QUINOLINOLATO)BERYLLIUM (II)-
MONOHYDRATE IN TAA (B) AFTER 24 HOURS. (C) AFTER

required. However, in the analysis of Be-Cu alloy, since the reagent quantitatively precipitates¹⁴ also copper(II) in the pH range 6.0 - 7.3, prior separation of copper is necessary in the beryllium estimation.

The organic reagents, cupferron, salicylaldehyde-ethylenediamine, tannin, 2-methyl-8-quinolinol, sodium oxinate give quite satisfactory results in the estimation of beryllium from pure Be(II) solution (Table VI). The precipitates formed are compact, easily filterable and thermally stable. Unfortunately these reagents are not selective. By masking of the interfering elements with complexone III a certain degree of selectivity may be achieved since the precipitation of beryllium is quantitative under the experimental conditions. Prior separation of all the interfering elements is, therefore, necessary. Tannin, acetoacetanilide, cupferron are reported to give accurate and good results in the determination of beryllium in presence of interfering elements. However, the application of these reagents to the analysis of beryllium in beryl and Be-Cu alloys is rather unsatisfactory. The precipitate of beryllium acetoacetanilide, although crystalline and thermally stable, is markedly soluble in hot water. The reported⁶⁶ experimental error in the estimation is 3%. The drawbacks in the cupferron method of estimation of beryllium are that the precipitate of beryllium cupferronate is soluble on heating and the reagent itself is sensitive to light and heat and also atmospheric oxygen. The excess reagent is carbonized on heating.

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