SOLVENT EXTRACTION OF CALCIUM AND MAGNESIUM

by

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ABSTRACT

This research problem is an extension of a general research program dealing with the utilization of 8-quinolinol or derivatives of 8-quinolinol in the solvent extraction of metals. The purpose of this study was to develop a solvent extraction method for the determination of calcium and magnesium.

Magnesium was quantitatively extracted as the tetra-n-butylammonium-8-quinolinolate into methyl isobutyl ketone or 1, 2-dichloroethane. Calcium was extracted as the tetra-n-butylammonium-8-quinolinolate into the same solvents. However, the final estimation of the extracted species in 1, 2-dichloroethane could not be made spectrophotometrically because of a changing optical density, and further study with this solvent was not carried out.

It was possible to determine magnesium in the presence of calcium by controlling the pH. Magnesium was also determined in the presence of iron (II) by complexing the interfering ion with cyanide and removing the excess cyanide.

It was found that calcium could be determined in the presence of magnesium by extracting the latter at a pH of approximately 11.70 and then raising the pH to approximately 12.8 to extract calcium. Calcium could also be extracted in the presence of iron (II) by complexing the interfering ion with cyanide and removing the excess cyanide.

Although 5,7-dibromo-8-quinolinol and 5,7-dichloro-8-quinolinol did form chelates with calcium and magnesium, the extraction with these two reagents were not investigated further because the final estimation of the extracted species could not be made spectrophotometrically.

Acknowledgment

The author is indebted to Dr. Henry Freiser for his advice and encouragement throughout the experimental portion of this work and for assistance in the preparation of this thesis.

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I. INTRODUCTION

A. 8-Quinolinol in Solvent Extraction

8-Quinolinol (8-hydroxyquinoline, oxine) is one of the most widely used organic reagents in solvent extraction because of its ability to react with a great number of metals. Welcher[1] has claimed that forty three metals combine with this versatile reagent and Morrison and Freiser[2] have summarized the extraction of twenty metals with oxine into various organic solvents. However, only recently the feasibility of the extraction of the alkaline earth metals with this reagent have been investigated extensively.

Luke and Campbell[3] used a butyl Cellosolve-chloroform mixture and a concentration of 8-quinolinol that was somewhat higher than usual (3%) to satisfactorily extract magnesium. They found that maximum extraction occurred at a pH of approximately 10.0 to 10.2. Their

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[1]Welcher, F. J., "Organic Analytical Reagents," Vol I, D. Van Nostrand Co., Inc., Princeton, N. J. (1947).

[2]Morrison, H. and Freiser, H., "Solvent Extraction in Analytical Chemistry," John Wiley and Sons, Inc., New York, 1957.

[3]Luke, C. L. and Campbell, M. E., Anal. Chem., 26, 1778 (1954).

final estimation of the magnesium was made spectrophotometrically by measuring the optical density of the magnesium 8-quinolinolate at 400 mu.

Strontium has also been extracted with 8-quinolinol into chloroform with a high reagent concentration. The extracted species has been described as $Sr(Ox)_2 \cdot 2HOx$.[1]

Umland and Hoffman[2] were able to extract magnesium as the anionic tris-8-quinolinate complex by using the protonated n-butylamine to associate with the anionic chelate. The species which was extracted into chloroform was found to have the formula $(RNH_3^+)(MgOx_3^-)$. They found that maximum extraction occurred at a pH range of 10.5 to 13.6 at a minimum concentration of 0.007 M 8-quinolinol and a 2% solution of the amine for approximately 0.0001 M magnesium.

Following this trend of ion association, Jankowski[3] used a similar system to extract the anionic three to one magnesium 8-quinolinolate into chloroform with various quarternary ammonium salts. The extractions were performed using tetra-methylammonium bromide,

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[1]Dyrssen, D., Swensk. Kem. Tidskr., 67, 311 (1955), Chem. Abst., 49, 15390a (1955).

[2]Umland, F., and Hoffman, W., Anal. Chim. Acta., 17 234 (1957).

[3]Jankowski, S. J., Doctoral Dissertation, University of Pittsburgh, 1959.

tri-methylphenyl ammonium iodide, tetra-n-propylammonium iodide, and tetra-n-butylammonium iodide. Only the latter quarternary ammonium salt gave 100% extraction into the organic phase. The investigation of extraction as a function of tetra-n-butylammonium iodide concentration showed that a minimum of 0.0052 N was necessary for complete extraction for approximately 0.0001 M magnesium. It was also found that a minimum concentration of 0.007 M 8-quinolinol must be used to give complete extraction in the pH range of 11.0 to 11.5.

The remaining group II elements were found to extract at a pH greater than 11.5. However, at a pH of approximately twelve, a reaction was found to take place in the extraction system which gives a green solution in the organic phase. This reaction, a variation of the Reimer-Tiemann reaction of chloroform with phenols[1], severely interfered in the final colorimetric estimation. Therefore, calcium, strontium, and barium could not be determined by this method.

Among the other solvents used in the extraction of metal 8-quinolinolates, methyl isobutyl ketone has been widely utilized. The distribution coefficient of 8-quinolinol in a methyl isobutyl ketone-aqueous phase (log K_{dr} = 2.18) is of the same order of magnitude as that in a

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[1] Jankowski, S. J., Doctoral Dissertation, University of Pittsburgh, 1959.

chloroform-aqueous phase (log $K_{dr} = 2.66$)[1].

Dyrssen and Dahlberg[2] have reported the extraction of lanthanum, hafnium, samarium, and uranium with 8-quinolinol into chloroform or methyl isobutyl ketone. Except for the greater solubility of the metal 8-quinolinolates in the former solvent very little difference was noted in the extraction into the two solvents.

B. 5,7-Dihalo-8-Quinolinol in Solvent Extraction

Some advantages and disadvantages have been noted in the use of the dihalo derivatives of 8-quinolinol in comparison to extraction with 8-quinolinol. The rare earth elements have been found to extract at a lower pH with 5,7-dihalo-8-quinolinol.[3,4] The solubility of the 5,7-dihalo-8-quinolinols in the aqueous phase were less than the solubility of 8-quinolinol, but the distribution coefficient of the chelates was great enough to give quantitative extractions, since the acid ionization constants of the phenolic groups in the dihalo-oxines are sufficiently greater

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[1]Dyrssen, D., Swensk. Kem. Tidskr., 64, 213 (1952), Chem. Abst., 47, 384h (1953).

[2]Dyrssen, D., and Dahlberg, V., Acta. Chem. Scand., 7, 1186 (1953).

[3]Dyrssen, D., Dyrssen, M., and Johansson, E., Acta. Chem. Scand., 10, 341 (1956).

[4]Rulfs, C. L., Anil, D. K., Lakritz, J., and Elving, P. J., Anal. Chem., 27, 1802 (1955).

than that of oxine to overcome the lower chelate formation constants in these substituted oxines. Therefore, extraction occurs at somewhat lower pH values than is possible with oxine itself. However, the greater bathochromic shift in the spectrum upon chelation is greater for oxine itself which tends to make this reagent more generally useful where spectrophotometric means for final determination are utilized.

Although erbium and neodymium could not be quantitatively extracted with 8-quinolinol into chloroform, 5, 7-dichloro-8-quinolinol was found to give quantitative extraction of these metals into the same solvent.[1]

Moeller and Cohen[2] were able to determine gallium in the presence of aluminum by precipitating with 5, 7-dibromo-8-quinolinol, dissolving the chelate in chloroform, and making the final estimation spectrophotometrically at a wavelength of 410 mu.

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[1]Moeller, T., and Jackson, D. E., Anal. Chem., 22, 1393 (1950).

[2]Moeller, T., and Cohen, A. J., Anal. Chim. Acta., 4, 316 (1950).

II. STATEMENT OF PROBLEM

The present work is an extension of a general research program dealing with the utilization of 8-quinolinol or derivatives of 8-quinolinol in the solvent extraction of metals. The purpose of this study has been to investigate the feasibility of utilizing 8-quinolinol or 8-quinolinol derivatives in the extraction of magnesium and calcium.

This work may be divided into two general segments: (1) Use of the dihalo derivatives of 8-quinolinol to determine whether extraction could be accomplished at a lower pH in comparison to using 8-quinolinol. 5,7-Dibromo-8-quinolinol and 5,7-dichloro-8-quinolinol were selected for the extraction studies. (2) Use of some other solvent besides chloroform which would not interact with 8-quinolinol at very high pH values. 1,2-Dichloroethane and methyl isobutyl ketone were selected for investigation.

Studies of extraction variables and spectrophotometric investigations were planned to determine the practicability of the extraction in analytical applications.

III. EXPERIMENTAL

A. Instruments and Apparatus

Spectrophotometer, Ultraviolet and Visible Regions. The absorption spectra was measured with a Cary Model II recording spectrophotometer. The wavelength on this instrument can be varied from 200 mu to 800 mu. The cells used were the one centimeter cylindrical type made of silica. The optical densities at specific wavelengths were measured with a Beckman DU spectrophotometer with quartz optics equipped with a photomultiplier attachment. The cells for the Beckman were the one centimeter rectangular type made of corex and were matched at various wavelengths.

pH Meter. A Beckman Model G pH meter with external glass and saturated calomel electrodes was used for the determination of pH values. The instrument was standardized with Beckman solutions.

Rotary Shaker. A Burrell Model BB wrist action shaker with clamps to attach the separatory funnels was used.

Centrifuge. An International Centrifuge, type B, size 2 was utilized to give better separations of the aqueous and organic phases.

B. Reagents

Cation-free Water. Ordinary distilled water was found to be insufficiently pure. All the aqueous solutions were prepared with water which was passed through a cation exchange resin to remove cations.

8-Quinolinol. Reagent grade 8-quinolinol obtained from Matheson, Coleman, and Bell was recrystallized from absolute ethanol or benzene.

5, 7-Dibromo-8-Quinolinol. The 5, 7-Dibromo derivative of 8-quinolinol was prepared by brominating the 8-quinolinol in acetic acid, and adding sodium acetate to precipitate the product. The precipitate was filtered and washed with a suction filter and recrystallized with benzene. The melting point was 195-197° C (reported[1] m.p. 196° C). This reagent was also bought from Eastman Organic Chemicals.

5, 7-Dichloro-8-Quinolinol. This reagent was prepared by chlorinating 8-quinolinol in glacial acetic acid and precipitating the product by neutralizing with ammonium hydroxide. The precipitate was filtered and recrystallized from acetone.[2] The melting point was 179° C (reported[3] m.p. 180-1° C). 5, 7-Dichloro-8-quinolinol was also

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[1] Heilbron, I., and Bunbury, H. M., "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, 1953, p. 92.

[2] Moeller, T., and Jackson, D. E., Anal. Chem. 22, 1393 (1959).

[3] Reference 1, p. 150.

obtained from Eastman Organic Chemicals.

Tetra-n-Butylammonium Iodide. The tetra-n-butylammonium iodide obtained from Eastman Organic Chemicals was purified by dissolving it into one to three methanol in acetone, filtering with suction, recrystallizing with cation-free water, and drying.[1]

Methyl Isobutyl Ketone. This solvent, which was obtained from Copper State Chemical Corporation, was distilled before using it in the extractions. The boiling range was 111-113° C/699 mm (reported[2] b.p. 116.85° C/760 mm).

1, 2-Dichloroethane. The 1, 2-dichloroethane obtained from Fisher Scientific Company was distilled. The boiling range was 82-83° C/699 mm (reported[3] b.p. 83.7° C/760 mm).

Chloroform. Analytical reagent grade chloroform obtained from Fisher Scientific Company was used without further purification.

Magnesium Solution. A sample of magnesium perchlorate obtained from G. Frederick Smith Chemical Company was dissolved in water to give approximately a 0.01 M solution. The solution was standardized by titrating with a previously standardized ethylenediamine

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[1] Silverman, L., and Bradshaw, W. G., Anal. Chem., 31, 1672 (1959).

[2] Heilbron, I., and Bunbury, H. M., "Dictionary of Organic Compounds," Vol III, Oxford University Press, New York, 1953, p 442.

[3] Reference 2 Vol II, p 502.

tetra-acetic acid solution, using Eriochrome Black T as the indicator. The ethylenediamine tetra-acetic acid was standardized with calcium carbonate using the same indicator.[1] Suitable aliquots of the magnesium perchlorate solution were used for the extraction studies.

Calcium Solution. A sample of calcium perchlorate obtained from G. Frederick Smith Chemical Company was dissolved in water to give an approximately 0.01 *M* solution. This solution was standardized in the same manner as the magnesium solution and the appropriate aliquots were used.

Sodium Hydroxide. An approximately 0.01 *M* solution of sodium hydroxide was prepared by weighing out sodium hydroxide pellets obtained from Fisher Scientific Company, and dissolving it in water.

Ammonium Hydroxide. An approximately six normal solution of ammonium hydroxide was prepared by diluting the concentrated ammonium hydroxide bought from Du Pont.

Iron (II) Cyanide Solution. Iron (II) sulfate obtained from Matheson, Coleman, and Bell was converted to the cyanide following the method of Westwood and Mayer.[2] An iron (II) sulfate solution was prepared so as to contain 2 mg of the metal per ml of solution. Two ml

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[1] Willard, H. H., Furman, N. H., and Bricker, C. E., "Elements of Quantitative Analysis," D. Van Nostrand Company, Inc., New York, 1956, p 135.

[2] Westwood, W., and Mayer, A., Analyst, 73, 275 (1948).

of citric acid containing 0.5 g in 10 ml was added and the solution was made slightly alkaline with ammonium hydroxide. Then 20 ml of a potassium cyanide solution (4 g KCN and 0.15 g NaOH per 100 ml) was added and the solution was heated to boiling. The iron was reduced to the divalent state with 0.5 g sodium dithionite and the solution was cooled. Aliquot portions were taken for the extraction studies.

C. Extraction of Magnesium and Calcium 8-Quinolinolates and 5,7-Dihalo-8-Quinolinolates

1. General Extraction Procedure

The chelating agent was initially in the organic phase. This phase was shaken with a previously prepared aqueous phase containing the metal ion, tetra-n-butylammonium iodide, and base, for a period of time which preliminary investigation showed to be sufficient to attain equilibrium. The two phases were then allowed to separate. The contents in the separatory funnel were centrifuged to give better separation of the phases. The aqueous phase was drawn off and the pH was measured. The organic phase was drawn off into glass-stoppered bottles. The absorbance of this solution was measured against a blank prepared in an identical manner except for the absence of the metal ion. A plateau of maximum absorbance between 390-400 mu was observed for both calcium and magnesium complexes. Readings were made at 400 mu.

2. Extraction of Magnesium

a. <u>Extraction with 5, 7-Dibromo-8-Quinolinol into Chloroform.</u> The extraction was performed by pipetting into 125 ml separatory funnels, 20 ml of the aqueous phase containing 48 ug of magnesium, and 0.01 M tetra-n-butylammonium iodide and 20 ml of the organic phase containing 0.01 M 5, 7-dibromo-8-quinolinol. The pH was then adjusted to approximately 11.00-11.50 with the addition of 2 N sodium hydroxide dropwise. Upon shaking the organic phase turned dark blue or brown almost immediately and after several minutes of standing, all the samples turned brown. Because the adverse reaction was thought to be due to decomposition by light, aluminum foils were wrapped around the flasks before shaking and the extraction was repeated. The extraction system remained yellow after shaking. However, in making the final spectrophotometric estimation, it was found that the absorbance varied rapidly (the yellow magnesium 5, 7-dibromo-8-quinolinolate turning dark blue) so that it was not practicable to carry on further investigation with this reagent.

b. <u>Extraction of Magnesium with 5, 7-Dichloro-8-Quinolinol into Chloroform.</u> After addition of 20 ml of the organic phase containing 0.01 M 5, 7-dichloro-8-quinolinol and 20 ml of the aqueous phase containing 48 ug of magnesium and 0.01 M tetra-n-butylammonium iodide, the pH was adjusted to 11.00. The absorption spectra of the blank versus chloroform and the samples versus the blank was measured in the 200 mu to 800 mu region. The spectra of the blank and samples were identical, indicating either that no extraction of metal occurred or that the chelate absorbed at the same wavelength as the reagent.

c. Extraction of Magnesium with 8-Quinolinol into Methyl Isobutyl Ketone.

(1) Extraction as a Function of pH.

To a 125 ml separatory funnel was added 20 ml of a 0.01 M solution of 8-quinolinol in methyl isobutyl ketone. To this was added 20 ml of the aqueous phase containing 24 ug of magnesium and 0.01 M tetra-n-butylammonium iodide. The pH was adjusted with ammonium hydroxide or sodium hydroxide and the funnel was shaken for twenty minutes. The pH of the aqueous phase was measured after each extraction. The optical density of the organic phase was measured at the appropriate wavelength relative to a blank which contained the same components except the metal. The results are shown on table 1.

(2) Extraction as a Function of Concentration.

The extraction was performed in similar manner as in the investigation of extraction as a function of pH except that the solution was kept at the optimum pH and the concentration of the metal ion was varied. The results are shown on table 2.

(3) Extraction as a Function of Time of Shaking.

Into a 125 ml extraction flask was pipetted 20 ml of an aqueous solution containing 48 ug of magnesium and 0.01 M tetra-n-butylammonium iodide. To this was added the organic phase which contained 0.01 M 8-quinolinol in methyl isobutyl ketone. The pH was adjusted to approximately 11.70. The shaking time was varied for four samples from three to twenty minutes. The extraction system was centrifuged and the phases were separated. The optical density of the organic phase was measured at 400 mu.

(4) Extraction in the Presence of Interfering Ions.

The aqueous phase of two samples were prepared so as to contain 80 ug of calcium and 48 ug of magnesium per 20 ml of solution and 0.01 M tetra-n-butylammonium iodide. The aqueous phase of two other samples were prepared in the same manner except that calcium was not present. The four samples were pipetted into 125 ml extraction flasks. To this was added 20 ml of the organic phase containing 0.01 M 8-quinolinol. The pH was adjusted to approximately 11.75 and the flasks were shaken for ten minutes. After separation of the phases, the organic phase was drawn into 50 ml volumetric flasks and stoppered. The final colorimetric estimation was made on the Beckman Model DU Spectrophotometer at

400 mu. In the same method as outlined above the extraction of magnesium in the presence of 1 mg of iron as iron (II) cyanide per ml of solution was carried out. The results of the extractions in the presence of interfering ions are shown on tables 3 and 4.

d. Extraction with 8-Quinolinol into 1, 2-Dichloroethane.

(1) Extraction as a Function of pH.

To 20 ml of the aqueous phase containing 48 ug of magnesium and 0.01 M tetra-n-butylammonium iodide was added 20 ml of a 0.01 M solution of 8-quinolinol in 1, 2-dichloroethane. The pH was then adjusted with ammonium hydroxide or sodium hydroxide. The separatory funnel was shaken for 20 minutes and after complete separation of the two phases the pH of the aqueous phase was measured. The optical density of the organic phase was measured at the appropriate wavelength. The results are given on table 5.

(2) Extraction as a Function of Concentration.

The extraction was performed in the same manner as in section III-C-2-d-(1) except that the solution was kept at the optimum pH and the concentration of magnesium was varied. The results are shown on table 6.

(3) Extraction as a Function of Time of Shaking.

Into a 125 ml extraction flask was pipetted 20 ml of aqueous solution containing 48 ug of magnesium and 0.01 M tetra-n-butylammonium iodide. To this was added the organic phase containing 0.01 M 8-quinolinol in 1,2-dichloroethane. The pH was adjusted to approximately 11.40. The shaking time was varied for four samples from three to twenty minutes. The extraction system was centrifuged and the phases were separated. The optical density of the organic phase was measured at 400 mu.

3. Extraction of Calcium

a. Extraction with 8-Quinolinol into Methyl Isobutyl Ketone.

(1) Extraction as a Function of pH.

Into a 125 ml separatory funnel was pipetted 20 ml of a 0.01 M solution of 8-quinolinol in methyl isobutyl ketone. To this was added 20 ml of aqueous phase containing 80 ug of calcium and 0.01 M tetra-n-butylammonium iodide. The pH was adjusted with sodium hydroxide and the funnel was shaken for twenty minutes. The pH of the aqueous phase was measured after each extraction. The optical density of the organic phase was measured at the appropriate wavelength relative to a blank which contained the same components except the metal. The results are shown on table 7.

(2) Extraction as a Function of Concentration.

The extraction was performed in a similar manner as in the investigation of the pH dependence of extraction except that the solution was kept at the optimum pH and the calcium concentration was varied. The results are shown on table 8.

(3) Extraction as a Function of Time of Shaking.

Into a 125 ml separatory funnel was pipetted 20 ml of a 0.01 M solution of 8-quinolinol in methyl isobutyl ketone. To this was added 20 ml of the aqueous phase containing 40 ug of calcium. The pH was adjusted for maximum extraction. The shaking time was varied. Each time the pH of the aqueous phase was remeasured after shaking and the optical density of the organic phase was obtained.

(4) Extraction in the Presence of Interfering Ions.

Into a 125 ml extraction flask was pipetted 10 ml of a solution containing 24 ug of magnesium and 10 ml of a solution containing 40 ug of calcium. To this was added 20 ml of a 0.01 M solution of 8-quinolinol in methyl isobutyl ketone. The pH was adjusted to approximately 11.70 and magnesium was extracted. Another 20 ml of the organic phase was added to the remaining aqueous phase and the pH was raised approximately to 12.8. The extraction was carried out and the optical density of the organic phase was measured at 400 mu. Calcium was also extracted in the presence of iron (II) by pipetting into a 125 ml extraction flask, 10 ml of a solution of ferrous cyanide containing 2 mg per ml of iron (II) and 10 ml of a solution containing 40 ug calcium. To this was added 20 ml of a 0.01 M solution of 8-quinolinol in methyl isobutyl ketone. The pH was adjusted to approximately 12.80. The extraction was carried out and the optical density of the organic phase was measured at 400 mu. The results of the extractions in the presence of interfering ions are given on tables 9 and 10.

b. Extraction with 8-Quinolinol into 1, 2-Dichloroethane.

The extraction was carried out in the same procedure as the extraction into methyl isobutyl ketone except 1, 2-dichloroethane was used as the organic solvent. The yellow color of the calcium 8-quinolinolate faded rapidly and further spectrophotometric studies were not undertaken.

IV. DISCUSSION OF RESULTS

A. Reliability of Extraction Data

1. Experimental Errors

In general spectrophotometric methods were used for the final estimation of the components under investigation. Since the absorbance cannot be read more closely than ± 0.002 and since the absorbance in general averaged about 0.400, individual concentration values were in error by about $\pm 0.5\%$ from this source.

The volumes of the phases were measured in calibrated volumetric pipettes so the errors contributed were of the order of 0.1%.

The limit of error of the Beckman Model G pH meter is ± 0.02 pH units. Above a pH of 12.5 the pH was calculated from the sodium hydroxide added.

Another significant source of error is the variation of the temperature during extraction. In each case room temperature was taken as the extraction temperature. During the course of this research, the temperature varied between 18° C and 28° C.

2. Attainment of Equilibrium

The shaking time was varied from three minutes to twenty minutes. It was found that the concentration of the species under investigation was the same within this time interval of shaking when the extraction was performed in methyl isobutyl ketone. The minimum shaking time for maximum extraction in 1,2-dichloroethane was found to be ten minutes.

3. Effect of Atmospheric Oxygen on the Chelate

It was important to keep the organic phase stoppered in volumetric flasks because the chelate was found to decompose in the presence of oxygen.

B. Use of Tetra-n-Butylammonium Iodide in the Extraction of Magnesium and Calcium

1. Function of Tetra-n-Butylammonium Iodide

Jankowski[1] showed that the extracted species is composed of the ion-pair tetra-n-butylammonium cation and the metallic tris-8-quinolinolate anion. He also found that a minimum concentration of 0.0052 $\underline{M}$ of the quarternary ammonium salt was necessary for

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[1] Jankowski, S. J., Doctoral Dissertation, University of Pittsburgh, 1959.

quantitative extraction for a metal concentration of approximately 0.0001 M. In view of this previous work, all extractions were performed with a tetra-n-butylammonium iodide concentration of 0.01 M.

2. Extraction of Magnesium

a. Extraction with 5,7-Dibromo-8-Quinolinol into Chloroform.

Because Dyrssen et al.[1] have found that 5,7-dichloro-8-quinolinol could be used to extract the rare earth elements at a lower pH in comparison to using 8-quinolinol, it seemed possible to extract magnesium and calcium at a lower pH with 5,7-dibromo-8-quinolinol and thereby eliminate the reaction of the chelate with chloroform as reported with 8-quinolinol at high pH in the presence of tetra-n-butylammonium iodide.[2] They found that no reaction took place in the absence of the quarternary ammonium salt.

Since the hydroxyl group of 8-quinolinol is an ortho and para directing group, it was also believed that the reaction site was the five and seven positions and the bromines at these positions would possibly prevent the adverse reaction with the solvent.

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[1]Dyrssen, D., Dyrssen, M., and Johansson, E., Acta. Chem. Scand., 10, 341 (1956).

[2]Jankowski, S. J., Doctoral Dissertation, University of Pittsburgh (1959).

However, in the extraction of magnesium with this reagent, the organic phase turned brown even at a pH less than 11.5. Since the reaction was thought to be light-catalyzed, aluminum foil was wrapped around each flask and the extractions were performed. The organic phase remained yellow after shaking, but the optical density kept changing and the solution turned blue while making the final colorimetric estimation. Due to this unfortunate interference, 5,7-dibromo-8-quinolinol could not be used as an extraction reagent for the determination of magnesium or calcium in chloroform.

b. Extraction with 5,7-Dichloro-8-Quinolinol into Chloroform.

5,7-Dichloro-8-quinolinol was also used in the extraction of magnesium. No interaction with the solvent was noted at high pH. However, the absorption spectra showed that the reagent absorbed at the same wavelength as the chelate so that the final estimation could not be made colorimetrically.

c. Extraction with 8-Quinolinol into Methyl Isobutyl Ketone.

The extraction data showed that 100% extraction took place in the pH range of 11.58 to 11.92 (see table 1). The extraction followed Beer's law at a wavelength of 400 mu in the concentration range of 12-96 ug of magnesium per 20 ml of solvent, with a 4.5% relative standard deviation. The molar extinction coefficient was determined from the least square line and was found to be 5800 liter per mole centimeter. The results which are given on table 2 indicate that magnesium can be determined satisfactorily with 8-quinolinol in methyl isobutyl ketone. The separation of magnesium from calcium was possible by controlling the pH. The extraction was performed at a pH less than 11.80. The results for the same concentration of magnesium in the presence and absence of 80 ug of calcium coincided quite well as shown on table 3. Jankowski[1] was able to extract magnesium quantitatively in the presence of up to 500 ug of calcium. Magnesium could also be extracted in the presence of iron (II) by complexing the interfering ion with potassium cyanide and removing the excess cyanide. Unless the excess cyanide were removed, low results were obtained because of the possible formation of an extractable ion-pair ($R4N^{+}$, CN^{-}). As indicated by equation (22) in the appendix; such formation would result in lowering the extraction ratio.

d. <u>Extraction with 8-Quinolinol into 1, 2-Dichloroethane.</u>

The extraction curve showed that 100% extraction took place in the pH range of 10.68 to 11.84 (see table 5). The absorption spectra of the magnesium tetra-n-butylammonium-8-quinolinolate followed Beer's law at a wavelength of 400 mu in the concentration range of 4.8 ug to

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[1] Jankowski, S. J., Doctoral Dissertation, University of Pittsburgh, 1959.

72 ug of magnesium. The standard per cent error was 3.2% and the molar extinction coefficient as determined from the least square line was found to be 7250 liter per mole centimeter. The results, given on table 6, show that magnesium can be determined in this solvent with 8-quinolinol.

3. Extraction of Calcium

a. Extraction with 8-Quinolinol into Methyl Isobutyl Ketone.

The extraction data show that 100% of calcium was extracted in the pH range of 12.2 to 12.9 (see table 7). The investigation of extraction as a function of concentration showed that Beer's law is obeyed at a wavelength of 400 mu in the concentration range of 20 to 80 ug of calcium per 20 ml of solvent. In determining the calibration curve it was noted that the optical density of the blank versus methyl isobutyl ketone changed from day to day. However, the data taken on separate days gave a series of parallel lines. The calibration curves could be made to coincide if pure methyl isobutyl ketone was taken as the reference and a correction factor was added. The standard per cent error was 2.9% and the molar absorption coefficient as determined from the least square line was found to be 7760 liter per mole centimeter. The results are shown on table 8. The determination of calcium in the presence of magnesium was possible by first extracting the magnesium at the appropriate pH and then raising the pH to extract calcium. Calcium could also be extracted in the presence of iron (II) by complexing the interfering ion with potassium cyanide and removing the excess cyanide. Unless the excess cyanide were removed, low results were obtained as previously discussed for the extraction of magnesium in the presence of iron (II). The results of the extraction of calcium in the presence of interfering ions are shown on tables 9 and 10.

b. Extraction with 8-Quinolinol into 1, 2-Dichloroethane.

The yellow color of the organic phase after shaking and separating turned colorless quite rapidly so that the final colorimetric estimation could not be made.

TABLE 1

EXTRACTION OF MAGNESIUM TETRA-N-BUTYLAMMONIUM-8-QUINOLINOLATE INTO METHYL ISOBUTYL KETONE AS A FUNCTION OF pH

24 ug magnesium/20 ml solvent

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

λ = 400 mu

Slit Width = 0.01 mm

pH	Absorbance	% E $\pm$ 4.5 (Magnesium)
10.34	0.051	19
10.42	0.118	42
11.08	0.183	64
11.17	0.221	78
11.28	0.232	83
11.42	0.258	92
11.58	0.289	100
11.64	0.288	100
11.68	0.297	100
11.84	0.276	98
11.92	0.291	100

TABLE 2

EXTRACTION OF MAGNESIUM TETRA-N-BUTYLAMMONIUM-8-QUINOLINOLATE INTO METHYL ISOBUTYL KETONE AS A FUNCTION OF CONCENTRATION

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

λ = 400 mu

Slit Width = 0.01 mm

pH approximately 11.75

Magnesium Concentration ug/20 ml solvent	Absorbance	Deviation from Least Square Line in ug
12	0.212	-1.2
19.2	0.328	+0.4
24	0.357	-1.8
28.8	0.416	-1.5
36	0.535	+0.5
43.2	0.632	+1.0
48	0.696	+2.0
48	0.698	+2.0
72	0.954	-0.3
72	0.958	-0.3

TABLE 2—continued

Magnesium Concentration ug/20 ml solvent	Absorbance	Deviation from Least Square Line in ug
86.4	1.12	-1.8
96	1.29	+2.5

Standard Deviation = 2.2 ug

Relative Standard % Deviation = 4.5

Molar Absorptivity as Determined from the Slope of the Least Square Line = 5800 liter/mole cm

TABLE 3

EXTRACTION OF MAGNESIUM IN THE PRESENCE OF CALCIUM

48 ug magnesium/20 ml solvent

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

$\lambda =$ 400 mu

Slit Width = 0.01 mm

pH approximately 11.75

Amount of Calcium Added in ug	Absorbance	% E (Magnesium)
0	0.664	99
0	0.672	100
80	0.666	99
80	0.659	97

TABLE 4

EXTRACTION OF MAGNESIUM IN THE PRESENCE OF IRON (II) AFTER MASKING WITH CYANIDE

24 ug magnesium/20 ml solvent

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

λ = 400 mu

Slit Width = 0.01 mm

pH approximately 11.70

Amount of Iron Added in mg/ml	Absorbance	% E (Magnesium)
1.00	0.379	99
1.00	0.375	98

TABLE 5

EXTRACTION OF MAGNESIUM TETRA-N-BUTYLAMMONIUM 8-QUINOLINOLATE INTO 1, 2-DICHLOROETHANE AS A FUNCTION OF pH

48 ug magnesium/20 ml solvent

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

λ = 400 mu

Slit Width = 0.01 mm

pH	Absorbance	% E ± 3.2 (Magnesium)
10.27	0.587	90
10.50	0.601	92
10.68	0.642	98
11.40	0.678	100
11.53	0.682	100
11.77	0.650	99
11.84	0.665	100
11.95	0.597	92
12.09	0.570	88

TABLE 6

EXTRACTION OF MAGNESIUM TETRA-N-BUTYLAMMONIUM 8-QUINOLINOLATE INTO 1, 2-DICHLOROETHANE AS A FUNCTION OF CONCENTRATION

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

λ = 400 mu

Slit Width = 0.01 mm

pH approximately 11.75

Magnesium Concentration ug/20 ml solvent	Absorbance	Deviation from Least Square Line in ug
4.8	0.074	0
7.2	0.118	+0.5
12.0	0.183	+0.2
12.0	0.194	+0.6
24.0	0.341	-0.8
24.0	0.342	-0.8
28.8	0.404	-1.6
36.0	0.524	-0.6
36.0	0.529	-0.6

TABLE 6—continued

Magnesium Concentration ug/20 ml solvent	Absorbance	Deviation from Least Square Line in ug
48.0	0.687	-1.8
72.0	1.10	+1.2

Standard Deviation = 0.9 ug

Relative Standard % Deviation = 3.2

Molar Absorptivity as Determined from the Slope of the Least Square Line = 7250 liter/mole cm

TABLE 7

EXTRACTION OF CALCIUM TETRA-N-BUTYLAMMONIUM 8-QUINOLINOLATE INTO METHYL ISOBUTYL KETONE AS A FUNCTION OF pH

80 ug Calcium/20 ml solvent

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

λ = 400 mu

Slit Width = 0.01 mm

pH	Absorbance	% E $\pm$ 2.9 (Calcium)
11.4	0.080	12
11.8	0.425	68
12.1	0.492	80
12.2	0.625	100
12.6	0.620	100
12.9	0.612	99
12.9	0.627	100
13.0	0.442	71

TABLE 8

EXTRACTION OF CALCIUM TETRA-N-BUTYLAMMONIUM 8-QUINOLINOLATE INTO METHYL ISOBUTYL KETONE AS A FUNCTION OF CONCENTRATION

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

$\lambda = 400$ mu

Slit Width = 0.01 mm

pH approximately 12.8

Optical density of blank versus methyl isobutyl ketone = 0.446

Calcium Concentration ug/20 ml solvent	Absorbance	Deviation from Least Square Line in ug
20	0.078	-1.0
32	0.219	+1.6
40	0.294	+1.6
52	0.353	-3.6
60	0.457	-1.5
60	0.463	-1.0
72	0.580	-0.5
80	0.679	+1.5

TABLE 8—continued

Calcium Concentration ug/20 ml solvent	Absorbance	Deviation from Least Square Line in ug
80	0.673	+1.0

Standard Deviation = 1.69 ug

Relative Standard % Deviation = 3.1

Molar Absorptivity as Determined from the Slope of the Least Square Line = 7760 liter/mole cm

TABLE 9

EXTRACTION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

40 ug Calcium/20 ml solvent

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

λ = 400 mu

Slit Width = 0.1 mm

pH approximately 12.8

Optical density of blank versus methyl isobutyl ketone = 0.625

Amount of Magnesium added in ug	Absorbance	% E (Calcium)
24	0.085	97
24	0.096	99
24	0.084	96

TABLE 10

EXTRACTION OF CALCIUM IN THE PRESENCE OF IRON (II) AFTER MASKING WITH CYANIDE

40 ug Calcium/20 ml solvent

0.01 M 8-Quinolinol

0.01 M Tetra-n-Butylammonium Iodide

λ = 400 mu

Slit Width = 0.01 mm

pH approximately 12.8

Optical density of blank versus methyl isobutyl ketone = 0.542

Amount of Iron added in mg/ml	Absorbance	% E (Calcium)
1.00	0.182	98
1.00	0.174	97
1.00	0.176	97

V. FUTURE WORK

This research study has been only a slight extension of the utilization of 8-quinolinol or 8-quinolinol derivatives in solvent extraction. The extraction possibilities of the remaining alkaline earth metals which have not been covered in the scope of this research could be investigated to see whether the procedure carried out in the extraction of calcium and magnesium could be applied.

Many reagents have been discovered which could be used in the extraction of the transition and rare earth elements, but few chelating agents have been found to form stable chelates with the alkaline earth metals. Tropolone and its derivatives[1], and cupferron[2] have been found to form chelates with magnesium and the possibilities of using these reagents in the extraction of the alkaline earth metals could be investigated. Another reagent that has recently been described in the literature which has favorable properties to form chelates with the alkaline earth metals

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[1] Bjerrum, J., Schwarzenbach, G., and Sillen, L. G., "Stability Constants," Metcalfe and Cooper Ltd., London, 1957.

[2] Fritz, J. S., Richard, M. J., and Bystroff, A. S., Anal. Chem., 29, 577 (1957).

is 2-hydroxy-methyl-benzimidazole ($pK_1 = 4.90$, $pK_2 = 12.70$).[1]

The possibilities of extracting the stable anionic ethylene-diamine tetra-acetic acid complexes of the alkaline earth elements using a quarternary ammonium salt could also be investigated.

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[1]Lane, T. J., and Daly, J. M., J. Am. Chem. Soc., 81, 2953 (1959).

VI. CONCLUSION AND SUMMARY

This research investigation has shown that magnesium could be extracted quantitatively as its tetra-n-butylammonium-8-quinolinolate into 1, 2-dichloroethane or methyl isobutyl ketone. Calcium could also be extracted in the latter solvent but not in the former as its tetra-n-butylammonium-8-quinolinolate. The final spectrophotometric estimation could be made for the chelates and were found to follow Beer's law. No adverse reaction took place in the organic phase at high pH as reported with extraction in chloroform.[1]

It was found that magnesium and calcium could be determined in the presence of iron (II) by complexing with potassium cyanide and reducing the iron with sodium dithionite.[2] It should be possible to separate other metals which form stable cyanide complexes by this method.

Magnesium could be determined in the presence of calcium by controlling the pH of extraction.

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[1] Jankowski, S. J., Doctoral Dissertation, University of Pittsburgh, 1959.

[2] Westwood, W., and Mayer, A., Analyst, 73, 275 (1948).

APPENDIX

DERIVATION OF EXTRACTION EQUATIONS FOR THE EXTRACTION OF QUARTERNARY AMMONIUM DIVALENT METAL TRIS-8-QUINOLINOLATES IN BASIC SOLUTION

In the derivation the following terms and equilibrium expressions are employed:

1. Distribution of 8-quinolinol between the organic and aqueous phase

$$HOx_w \underset{}{\overset{K_{dr}}{\rightleftharpoons}} HOx_o$$

2. Ionization of 8-quinolinol

$$HOx \overset{K_i}{\rightleftharpoons} H^+ + Ox^-$$

3. Formation of the metal chelate

$$M^{+2} + 3\ Ox^- \overset{K_f}{\rightleftharpoons} MOx_3^{-1}$$

4. Distribution of quarternary ammonium salt

$$(R_4N^+,\ I^-)_w \overset{K_{dq}}{\rightleftharpoons} (R_4N^+,\ I^-)_o$$

5. Association of quarternary ammonium salt

$$R_4N^+ + I^- \overset{K_{fq}}{\rightleftharpoons} R_4N^+,\ I^-$$

6. Formation of the ion-association complex with the anionic chelate

$$MOx_3^- + R_4N^+ \overset{K_a}{\rightleftharpoons} R_4N^+,\ MOx_3^-$$

7. Distribution of the ion-association complex between the organic and aqueous phases

$$(R_4N^+,\ MOx_3^-)_w \overset{K_{dx}}{\rightleftharpoons} (R_4N^+,\ MOx_3^-)_o$$

8. Formation of the ion-association compound with the anionic reagent

$$Ox^- + R_4N^+ \overset{K_{fr}}{\rightleftharpoons} (R_4N^+,\ Ox^-)$$

9. Distribution of the ion-association compound between the organic and aqueous phases

$$(R_4N^+,\ Ox^-)_w \underset{}{\overset{K_{dqr}}{\rightleftharpoons}} (R_4N^+,\ Ox^-)_o$$

D = distribution coefficient of metal between the organic and aqueous phases.

M^{+2} = metal ion whose ionic valence is 2.

Ox^- = 8-quinolinol anion.

$R_4N^+{}_T$ = total quarternary ammonium ion.

Subscripts o and w refer to organic and aqueous respectively. Terms in brackets[ ] refer to molar concentrations. Equal volumes of organic and aqueous phases are assumed.

If M^{+2} is assumed to be the only metal containing species in the aqueous phase and $(R_4N^+,\ MOx_3^-)$ is the only metal containing species in the organic phase, the distribution coefficient is defined as:

(1) $D = \dfrac{\text{total metal in organic phase}}{\text{total metal in aqueous phase}} = \dfrac{[(R_4N^+,\ MOx_3^-)]}{[M^{+2}]}$

(2) Since $[M^{+2}] = \dfrac{[MOx_3^-]}{K_f\,[Ox^-]^3}$

and

(3) $[MOx_3^{-1}] = \dfrac{[(R_4N^+,\ MOx_3^-)]_w}{K_a\,[R_4N^+]}$

and

(4) $[(R_4N^+,\ MOx_3^-)]_w = \dfrac{[(R_4N^+,\ MOx_3^-)]_o}{K_{dx}}$

(5) $D = K_f K_a K_{dx} \left[Ox^-\right]^3 \left[R_4N^+\right]$

since

(6) $\left[Ox^-\right]^3 = \dfrac{K_i \left[HOx\right]_w}{\left[H^+\right]^3}$

and

(7) $\left[HOx\right]_w = \dfrac{\left[HOx\right]_o}{K_{dr}}$

(8) $D = \dfrac{K_f K_a K_{dx} K_i \left[HOx\right]_o \left[R_4N^+\right]}{K_{dr} \left[H^+\right]^3}$

Grouping all constants

(9) $D = \dfrac{K^* \left[HOx\right]_o \left[R_4N^+\right]}{\left[H^+\right]^3}$

(10) $\left[R_4N^+\right]_T = \left[R_4N^+\right] + \left[(R_4N^+, I^-)\right]_o + \left[(R_4N^+, Ox^-)\right]_o + \left[(R_4N^+, MOx_3^-)\right]_o + \left[(R_4N^+, I^-)\right]_w + \left[(R_4N^+, Ox^-)\right]_w + \left[(R_4N^+, MOx_3^-)\right]_w$

Assuming that the initial quarternary ammonium salt concentration is large compared to the initial metal concentration and thereby neglecting the last four terms of equation (10) because of insignificant contribution to the total concentration of quarternary ammonium salt, the preceding equation can be reduced to:

(11) $\left[R_4N^+\right]_T = \left[R_4N^+\right] + \left[(R_4N^+, I^-)\right]_o + \left[(R_4N^+, Ox^-)\right]_o$

(12) $K_{dq} = \dfrac{\left[(R_4N^+, I^-)\right]_o}{\left[(R_4N^+, I^-)\right]_w}$

$$(13)\quad K_{fq} = \frac{\left[(R_4N^+, I^-)\right]_w}{\left[R_4N^+\right]\left[I^-\right]}$$

$$(14)\quad \left[(R_4N^+, I^-)\right]_o = K_{dq}K_{fq}\left[R_4N^+\right]\left[I^-\right]$$

$$(15)\quad K_{dqr} = \frac{\left[(R_4N^+, Ox^-)\right]_o}{\left[(R_4N^+, Ox^-)\right]_w}$$

$$(16)\quad K_{fr} = \frac{\left[(R_4N^+, Ox^-)\right]_w}{\left[R_4N^+\right]\left[Ox^-\right]}$$

$$(17)\quad \left[(R_4N^+, Ox^-)\right]_o = K_{dqr}K_{fr}\left[R_4N^+\right]\left[Ox^-\right]$$

Substituting for $\left[(R_4N^+, I^-)\right]_o$ and $\left[(R_4N^+, Ox^-)\right]_o$ in equation (11), the values obtained in equations (14) and (17).

$$(18)\quad \left[R_4N^+\right]_T = \left[R_4N^+\right] + K_{dq}K_{fq}\left[R_4N^+\right]\left[I^-\right] + K_{dqr}K_{fr}\left[R_4N^+\right]\left[Ox^-\right]$$

$$(19)\quad \left[R_4N^+\right]_T = \left[R_4N^+\right]\left(1 + K_{dq}K_{fq}\left[I^-\right] + K_{dqr}K_{fr}\left[Ox^-\right]\right)$$

$$(20)\quad \left[R_4N^+\right] = \frac{\left[R_4N^+\right]_T}{\left(1 + K_{dq}K_{fq}\left[I^-\right] + K_{dqr}K_{fr}\left[Ox^-\right]\right)}$$

If other anions are present which associate with the quarternary ammonium ion, a general expression can be written.

$$(21)\quad \left[R_4N^+\right] = \frac{\left[R_4N^+\right]_T}{1 + \sum_{i=1}^{i=\infty} K_{di}K_{fi}\left[Xi\right]}$$

Substituting for $\left[R_4N^+\right]$ in equation (9)

$$(22)\quad D = \frac{K^* \left[HOx\right]_o \left[R_4N^+\right]_T}{\left[H^+\right]^3 \left(1 + \sum_{i=1}^{i=\infty} K_{di}K_{fi}\left[Xi\right]\right)}$$

Equation (22) shows that if anions are present which associate with the quarternary ammonium ion to any extent, extraction of the metal into the organic phase would be inhibited.

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