[CONTRIBUTION FROM THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Radiochemical Methods for the Isolation of Element 87 (Francium)[1]

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Radiochemical methods are presented for the isolation of element 87, francium. Since the longest lived isotope of francium has a half-life of 21 minutes, these are necessarily short. The methods used by Mme. Perey for the isolation of AcK are reviewed. Procedures based on her work and on the work of others concerned with the isolation of radioactive cesium fission products are presented for the isolation of francium isotopes from thorium targets bombarded with high energy protons. An entirely new method for the rapid isolation of a carrier-free francium fraction based on the coprecipitation of this element with free silicotungstic acid is introduced and applications to francium and cesium radiochemical problems are discussed.

Introduction

During the course of a program of study of those isotopes of francium (element 87) produced by bombardment of thorium with protons of energy up to 346 Mev., a need arose for a radiochemical isolation method for francium. This element, in common with the other alkali metals, may be expected to form few insoluble compounds and to show no complex ion formation or solvent extraction behavior useful as a means of purification. The chemical isolation methods developed by Mme. Perey[2] during her extensive researches on AcK are based upon the coprecipitation of francium with one of the few insoluble alkali salts or on the removal of the interfering contaminants with by-product precipitations after which the francium is sought in the final filtrate.

For example, a procedure recommended by Mme. Perey[2] for the specific problem of the isolation of AcK from Ac^{227} is the following: Actinium in equilibrium with its decay products is placed in solution as the chloride and after addition of a slight excess of sodium carbonate, the solution is brought to a boil. The actinium and some unseparated lanthanum are precipitated carrying down AcX (Ra^{223}), RdAc (Th^{227}), AcB and AcC (Pb^{211}–Bi^{211}). The AcK (Fr^{223}) and AcC″ (Tl^{207}) are left in the filtrate together with traces of the other nuclides. This filtrate is acidified with hydrochloric acid and brought to a boil to destroy excess carbonate. Then small amounts of lanthanum and barium chlorides are added. These are precipitated as the chromates by the addition of potassium chromate and ammonia. The AcC″ and the trace contaminants coprecipitate leaving radioactively pure AcK in the filtrate.

Mme. Perey studied the coprecipitation of francium on insoluble salts of cesium (the element closest to francium in the homologous series of the alkali metals) and found 50 to 100% coprecipitation on such salts as cesium perchlorate, cesium picrate, cesium chloroplatinate, cesium chlorobismuthate, cesium chloroantimoniate, cesium chlorostannate, the double cobaltinitrite of sodium and cesium, and others. She also suggested the use of such salts as cesium fluosilicate, cesium silicotungstate (silicowolframate), cesium silicomolybdate, etc.

Some of these cesium compounds have been employed by fission product chemists interested in the isolation of fission-produced cesium isotopes. Since francium has been found to resemble cesium closely in its coprecipitation behavior, these procedures with appropriate changes may be employed for the isolation of francium.

For example, in the isolation of fission product cesium activities from neutron-irradiated uranium, Glendenin and Nelson[3] precipitated added cesium carrier as the perchlorate from cold perchloric acid. The insolubility of the compound was enhanced by the addition of alcohol. To eliminate certain other radioactive contaminants such as zirconium, niobium, molybdenum, tin, antimony and tellurium, ferric hydroxide was thrown down as a by-product precipitate. Rubidium, if present, was removed by a preliminary precipitation of cesium silicotungstate from 6 N HCl which left the rubidium unprecipitated.

A carrier-free method of isolation[4] is described by these same authors in which cesium activities are coprecipitated on ammonium perchlorate from cold perchloric acid with absolute ethanol. A by-product ferric hydroxide precipitate removes contaminating activities. In the final solution the NH_4^+ ion and ClO_4^- ions are destroyed with aqua regia leaving pure cesium. A disadvantage of this procedure is that any sodium or rubidium initially present is not removed.

Evans[5] has published a cesium fission product isolation method based on the precipitation of the double salt $Cs_3Bi_2I_9$ from cold acetic acid solution. A preliminary precipitation of a mixed hydroxide and carbonate precipitate is used to remove many interfering activities.

The method of Glendenin and Nelson[3] was selected as the most suitable for the adaptation to the problem discussed at the onset of this paper; namely, the isolation of francium from thorium targets. It was necessary to shorten the procedure considerably because of the short half-lives of the francium isotopes. Fr^{223} (AcK) with its 21 minute half-life is the longest lived of the known francium isotopes. Francium has the distinction of being the most unstable to radioactive disintegration of the presently known 98 elements. Nevertheless, the specificity of the procedure had to be high in order to eliminate a great number of radioactive fission and spallation products. The procedure developed

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[1] This work was performed under the auspices of the United States Atomic Energy Commission.

[2] M. Perey, Thèses, "L'Élément 87: Actinium K," Université de Paris, 1946.

[3] L. E. Glendenin and C. M. Nelson, National Nuclear Energy Series, Plutonium Project Record, Vol. 9B, "Radiochemical Studies: The Fission Products," Paper 283 (McGraw-Hill Book Co., Inc., New York, N. Y., 1951).

[4] *Ibid.*, Paper 285.

[5] H. B. Evans, *ibid.*, Paper 284.

for initial studies[6] of the 19.3 minute isotope Fr^{212} and of the 15 minute isotope[7] Fr^{222} is given in detail in Section A immediately following.

Experimental

A. The Cesium Silicotungstate–Cesium Perchlorate Method for the Isolation of Francium from Bombarded Thorium Targets.—Small bombarded strips of thorium metal (approximate dimensions 0.5 × 1.5 × 0.005 inches) are dropped into a 15-ml. centrifuge cone containing 5 ml. of hot concentrated hydrochloric acid to which has been added a few drops of 0.2 M ammonium fluosilicate to serve as a dissolution catalyst. The thorium dissolves within a few seconds. The solution is diluted to 20 ml. with 15 ml. of ice-cold 6 M hydrochloric acid containing four drops of cesium chloride carrier solution (10 mg. cesium per ml.). The centrifuge cone is placed in an ice-bath and stirred for 1 to 2 minutes while 1 ml. of $^1/_8$ M silicotungstatic acid is added. The cesium silicotungstate is centrifuged down and the supernate discarded to active waste. The precipitate is washed twice with 5 ml. of cold 6 N hydrochloric acid, and these washings are discarded. The precipitate is then dissolved in 6 N sodium hydroxide. Five ml. of 70% perchloric acid is carefully added (safety glasses or face mask), and the solution is evaporated by swirling the tube over a burner until copious white fumes of perchloric acid are evolved. After cooling, the solution is diluted to 10 ml. and centrifuged to remove a precipitate of silica and tungstic acid. The supernatant solution is again evaporated to dense white fumes of perchloric acid by careful swirling over a burner. It is then cooled and 15 ml. of absolute ethyl alcohol is added. The solution is stirred for 1 minute and centrifuged to bring down the cesium perchlorate precipitate. The supernatant solution is disposed of at once since it contains ethyl perchlorate, which is extremely explosive when heated. The cesium perchlorate is washed twice with 5 ml. of ice cold absolute ethyl alcohol. The final washed precipitate is dissolved in a small amount of distilled water.

For the study of the α-particle characteristics of francium isotopes where thin samples are highly desirable, very thin samples may be prepared on platinum disks from the final francium solution by the following volatilization procedure. An aliquot of the solution is evaporated on a platinum plate. A second platinum catcher plate is inverted above the first using an asbestos washer to maintain a separation of a few millimeters. By touching the bottom plate for a fraction of a second with a gas–oxygen flame, the cesium and francium are deposited on the catcher plate in an extremely thin film.

Transfer of more than 90% of the francium is effected if the amount of cesium in the sample is quite small. This volatilization technique is useful not only for preparation of thinly spread plates, but also for preparation of a francium fraction completely free of an emanation daughter at a precisely measured time. The volatilization behavior of francium was noted previously by Hagemann, *et al.*[8]

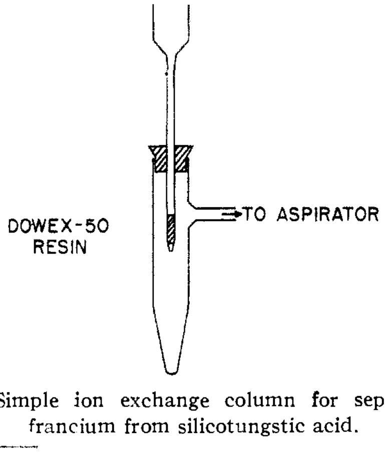

Fig. 1.—Simple ion exchange column for separation of francium from silicotungstic acid.

B. Carrier-Free Method for Isolation of Francium from Thorium Cyclotron Targets.—The above procedure requires about 1 hour and produces francium of high purity except for the cesium added as carrier and the cesium fission products resulting from the bombardment. It is frequently desirable to eliminate the carrier completely and to reduce the time required if at all possible. This has been done in the following procedure which is based on the fact that silicotungstic acid is insoluble in concentrated hydrochloric acid and that trace amounts of francium will coprecipitate with the free acid. The francium is then separated from the silicotungstic acid by a simple ion exchange or ether extraction method.

Small bombarded strips of thorium metal foil (approximate dimensions 0.5 × 1.5 × 0.005 inches) are dropped into a 50-ml. centrifuge cone and quickly put into solution with 5 ml. of hot concentrated hydrochloric acid containing a few drops of 0.2 M solution of ammonium fluosilicate. (The fluosilicate catalyzes the dissolution of the thorium.) This solution is diluted with 15 ml. of ice-cold concentrated hydrochloric acid which has been presaturated with hydrogen chloride gas. A small amount of insoluble material is centrifuged down and removed. With the clear solution stirring vigorously three drops of a 0.4 M solution of silicotungstic acid is added. A white crystalline precipitate of free silicotungstic acid forms and is centrifuged down. This precipitate is washed twice with 15 ml. of concentrated hydrochloric acid which has been saturated with hydrogen chloride gas and after centrifugation and decantation of the bulk of the hydrochloric acid the remaining drops of excess hydrochloric acid are carefully removed by pipet. The precipitate is dissolved in 1.0 ml. of redistilled water. A column of Dowex-50 cation exchange resin with the approximate dimensions 1 cm. × 4 mm. is prepared previous to the bombardment from 250–500 mesh resin in the ammonium form as shown in Fig. 1. This column is carefully rinsed with redistilled water. The 1.0 ml. of solution containing the francium and the silicotungstic acid is pipetted on top of the column and drawn through the column by suction at the rate of about 0.5 ml. per minute. The column is rinsed with 1–2 ml. of redistilled water at the same rate. The non-ionic silicotungstic acid passes through the column without sticking. A white precipitate with solution properties distinct from the normal form of silicotungstic acid may form in the solution which passes through the column. The francium adsorbs strongly on the column. This adsorption is a strong function of acid concentration and the success of this step depends on freeing the silicotungstic acid precipitate sufficiently from hydrochloric acid that the acid concentration in the 1.0 ml. of solution is < 0.5 M. The column is inserted in a second 15-ml. side-arm tube and the francium is rapidly desorbed by pulling 500 μl. of clean concentrated hydrochloric acid through the column in a period of 2–3 minutes. The resulting 500 μl. solution is a pure carrier-free solution of francium uncontaminated with any radioactivity except that of cesium fission products which are not separated. Rubidium fission product activities are separated.

A small amount of solid matter will appear in this final solution unless the glass vessels used are very clean, the resin is carefully rinsed to remove the excess ammonium ion used in regeneration, the distilled water is of high purity and the hydrochloric acid is freshly prepared from redistilled water and hydrogen chloride gas. This entire procedure is quite rapid, can be completed in 30 minutes or less and has given excellent results in repeated use. On the few occasions when slight radioactive contaminants were encountered, the difficulty was traced to the small amount of insoluble matter formed in the dissolution step which sometimes is hard to remove completely by centrifugation. When 10–15 minutes more time may be spent on purification, a precipitation of Th(OH)$_4$ using calcium hydroxide as the precipitant may be introduced between the silicotungstic acid precipitation and the ion exchange step. The Th(OH)$_4$ helps to ensure separation of this solid matter and many possible contaminants (notably traces of protactinium) coprecipitate with it.

After the initial precipitation and hydrochloric acid wash-

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[6] E. K. Hyde, A. Ghiorso and G. T. Seaborg, *Phys. Rev.*, **77**, 765 (1951).

[7] E. K. Hyde and A. Ghiorso, University of California Radiation Laboratory Declassified Report UCRL-593 (May 31, 1950).

[8] F. Hagemann, L. I. Katzin, M. H. Studier, G. T. Seaborg and A. Ghiorso, *Phys. Rev.*, **79**, 435 (1950).

ing of the silicotungstic acid, the solid is dissolved in 1 ml. of water. One mg. of thorium ion is added and precipitated as the hydroxide by the addition of approximately 100–200 mg. of solid calcium hydroxide. After centrifugation, the clear supernatant solution is transferred to a clean 15-ml. centrifuge cone and saturated with gaseous hydrogen chloride to reprecipitate the silicotungstic acid. After centrifugation, the supernatant hydrochloric acid is completely removed, the acid is dissolved in 1.5 ml. of pure water and adsorbed on the Dowex-50 column as described above.

Check experiments showed that recovery of cesium (as stand-in for francium) was $> 96\%$ through this procedure. A small amount of calcium ($\sim$0.1 mg.) appears in the final francium fraction when this procedure is followed. If this is undesirable, the manganese dioxide by-product precipitate discussed in section 6 below may be substituted.

Instead of the ion exchange method it is possible to use the solvent extraction method described in the next paragraph to effect separation of francium from the bulk of the silicotungstic acid.

The precipitate is dissolved in 500 μl. of distilled water and stirred with 1 or 2 ml. of ethyl ether. In the three phase system produced, the bottom layer consists of a liquid compound of silicotungstic acid and ether, the uppermost phase is ethyl ether and the intermediate phase is a water solution of francium. This method is not as satisfactory as the ion exchange method since a small part of the silicotungstic acid remains in the aqueous phase, but is useful when the most rapid separation is necessary (see section E below) and a small amount of inert solid matter may be tolerated.

C. **Notes on the Carrier-Free Silicotungstic Acid Method.**—The details of the carrier-free silicotungstic acid procedure were worked out using 37 year Cs^{137} tracer as a stand-in for francium and some findings concerning the chemical yield and the effects of other ions on the yield may be mentioned.

(1) Free silicotungstic acid precipitated from a concentrated hydrochloric acid solution of Cs^{137} tracer carries more than 98% of the cesium activity.

(2) If the silicotungstic acid carrying cesium tracer from a concentrated hydrochloric acid solution is dissolved in pure water and reprecipitated by adding concentrated hydrochloric acid, the cesium is again coprecipitated quantitatively. These reprecipitations may be carried out repeatedly.

(3) Sodium ion interferes with the coprecipitation of cesium. When Cs^{137} tracer in 0.5 ml. of 6 N sodium hydroxide was added to 10 ml. of concentrated hydrochloric acid and hydrogen chloride gas passed in, a precipitate of sodium chloride formed. When silicotungstic acid was precipitated from the clear hydrochloric acid solution after removal of the solid sodium chloride, only 15–30% yield of the initial Cs^{137} was obtained. None of the missing Cs^{137} was found with the sodium chloride. This result is important since it means that sodium ion must be absent from the solution and that a by-product precipitate such as Fe(OH)$_3$ cannot be used in the isolation procedure if sodium hydroxide is used to precipitate the iron. This was verified in an experiment in which silicotungstic acid was precipitated from concentrated hydrochloric acid to carry Cs^{137} tracer. The precipitate was dissolved in pure water. One mg. of ferric ion as ferric chloride was added and precipitated with sodium hydroxide. The supernate was added to 15 ml. of concentrated hydrochloric acid and the solution was saturated with hydrogen chloride. After removal of a sodium chloride precipitate, 0.4 M silicotungstic acid was added to precipitate the free heteropoly acid. Only 10% of the Cs^{137} was found on this precipitate.

(4) Ammonium ion may not be used in the by-product scavenge precipitation of thorium hydroxide because of the precipitation of ammonium chloride and ammonium silicotungstate when the supernate is later saturated with hydrochloric acid. This introduces ammonium chloride into the final francium fraction and also drastically reduces the coprecipitation of francium. (In check experiments using Cs^{137} as a stand-in for francium losses of $> 90\%$ were observed.) In other applications such as those given below any ammonium salts originally present should be destroyed in a preliminary step such as by evaporation with aqua regia.

(5) The separation factor of rubidium from cesium was shown to be greater than 300 by a determination of the amounts of 19 day Rb^{86} and 13 day Cs^{136} present in the final cesium–francium fraction from a thorium target. This determination was made more sensitive by adsorbing this final fraction on a column of Dowex-50 cation resin and eluting with 1 M hydrochloric acid to separate rubidium and cesium. The cross section for formation of Rb^{86} in the bombardment was equal to or several-fold greater than that for formation of Cs^{136}; yet no Rb^{86} was observed above background. A cesium peak of $> 10^7$ disintegrations per minute (starting two days after bombardment) was Cs^{136} of $> 99\%$ purity by decay measurements. The rubidium–cesium separation factor of 300 is conservative.

(6) Manganese dioxide may be precipitated instead of Th(OH)$_4$ as a by-product scavenger precipitate between the initial precipitation of silicotungstic acid and the final ion exchange separation. This is done as follows: The silicotungstic acid precipitate is dissolved in 1.5 ml. of water. One drop of a 56% solution of Mn^{++} and one drop of 1 M potassium permanganate are added to precipitate manganese dioxide. After 2 minutes, this is centrifuged off and discarded. The supernatant solution is pipetted into a 15-ml. centrifuge cone containing 8 ml. of cold hydrochloric acid. Gaseous hydrochloric acid is passed into the solution to bring down the silicotungstic acid. After centrifugation, the acid is dissolved in four drops of pure water and again precipitated by adding 5 ml. of cold hydrochloric acid saturated with gaseous hydrogen chloride. This precipitate is separated by centrifugation, carefully freed of excess hydrochloric acid and dissolved in 1.0 ml. of redistilled water in preparation for the ion exchange step described above. Recovery of cesium or francium is essentially quantitative.

(7) The presence of thorium does not interfere with the quantitative coprecipitation of cesium.

(8) In the ion exchange step the column procedure described is to be preferred to a batch procedure in which the resin is stirred with the water solution of Cs^{137} to effect adsorption and with a concentrated hydrochloric acid solution to effect desorption. In repeated trials of batch procedures, yields were erratic and low (20–70%).

On the other hand, nearly quantitative adsorption and desorption of Cs^{137} tracer was found using the column shown in Fig. 1. For example, Cs^{137} tracer in 1.0 ml. of 0.5 M hydrochloric acid was adsorbed on the column and rinsed with 2.0 ml. of pure water in a period of only 3 minutes. It was desorbed with 1.0 ml. of concentrated hydrochloric acid in a period of only 3 minutes. More than 97% of the original activity was found in the first 500 μl. of final hydrochloric acid solution.

(9) It was thought desirable to ascertain the coprecipitation behavior of radium with silicotungstic acid since some of the barium salts of the heteropoly acids are isomorphous with the free acids. In check experiments using Ra^{226} tracer less than 0.2% coprecipitation was observed. This was borne out by the use of the method in thorium bombardments. No radium activities were ever found in the final francium fraction although as much as 0.01% would easily have been observed.

Applications

A. **Preparation of AcK.**—The carrier-free silicotungstic acid method is a very simple and effective method for the isolation of AcK (Fr^{223}) from Ac^{227}. In this case the sample of Ac^{227} is simply placed in saturated hydrochloric acid solution and a few drops of 0.4 M silicotungstic acid is added to bring down the AcK. The precipitate is washed and subjected to the ion exchange step described above. The AcK samples may be prepared in a carrier-free condition ready for counting within one half-life (21 minutes) of the time of separation from actinium. The actinium is left in the hydrochloric acid solution so that a fresh sample of AcK may be removed later simply by adding more silicotungstic acid.

This application has been checked starting with an actinium sample of 2.6×10^7 dis./min. Ac^{227}. The decay of the AcK samples so isolated was followed with a Geiger counter to establish the 21 minute half-life. Then these samples were counted in an alpha counter to measure the exact amount of the α-emitting daughters of AcK. The α-particle energies were measured in a 48 electronic channel differential pulse analyzer[9] connected to an ionization

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[9] A. Ghiorso, A. H. Jaffey, H. P. Robinson, and B. B. Weissbourd, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper 16.8 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

chamber to prove that the α-activities present were AcX and its daughters and no others. The absence of RdAc α-particles was specifically verified. From these data, with proper allowance for the 1.2% α-branching[10,11] of Ac^{227} and for decay since time of separation, etc., it was possible to calculate the chemical yield of AcK. This yield was quantitative within the experimental error of 5%.

B. Preparation of Fr^{221}.—The 4.8 minute isotope of Fr^{221} may be isolated from its 10 day parent Ac^{225} which in turn is isolated from the decay products of U^{233} or is prepared by the cyclotron bombardment of thorium. The shortness of the half-life requires that the isolation procedure be as brief as possible. If one first carefully purifies the actinium parent, the number of possible contaminating radioactivities is quite limited and a single precipitation of silicotungstic acid and a single hydrochloric acid wash give a nearly quantitative separation of the Fr^{221} from its parent. If one can tolerate a small amount of inert solid matter in the final francium solution, the ethyl ether method of separating the bulk of the free silicotungstic acid may be used and the total elapsed time for the isolation of Fr^{221} can be cut to 10 minutes.

C. Isolation of Radioisotopes of Cesium.—The main defect of the silicotungstic acid method is that no separation of francium from fission product cesium is obtained. It might be hoped that some heteropoly acid could be found which would carry francium without also carrying cesium.

This quantitative coisolation of cesium, however, suggests that the method may have wide applicability in radiochemical and nuclear chemical studies involving the isotopes of cesium. With the exception of those applications in which the chemical yield must be determined by weighing a cesium compound, this new procedure would appear to be superior to any cesium radiochemical isolation procedure previously published. In particular in the study of cesium radioisotopes in a β-ray spectrometer or mass spectrograph where a weightless sample is desirable or absolutely essential, it should be particularly applicable. It might also prove useful as part of a procedure for the isolation of the valuable isotope, Cs^{137}, from aged fission product wastes.

Discussion

A word might be said concerning the coprecipitation behavior which forms the basis of the carrier-free method since at first sight it seems rather strange that a cation should coprecipitate so well with a free acid. It is felt that a reasonable explanation lies in the unusual isomorphism displayed by the salts of the heteropoly acids and the corresponding free acids. Borotungstic acid is isomorphous with ammonium borotungstate,[12] silicotungstic acid with lithium silicotungstate[13] and phosphotungstic acid with sodium phosphotungstate.[14] Even more surprising is the fact that the alkaline earth salts of some heteropoly acids are also isomorphous with the free acids.[15] With this isomorphism and the known low solubility of cesium silicotungstate, it is not surprising that trace amounts of francium and cesium coprecipitate so well with free silicotungstic acid. Presumably other ions such as Rb^{+}, Ba^{++} and Ra^{++} do not coprecipitate because of the higher solubility of the corresponding salts.

Other heteropoly acids may be substituted for silicotungstic acid but none of those so far studied in a preliminary way are to be preferred. Phosphotungstic acid, for example, will carry cesium from a concentrated hydrochloric acid solution.

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(10) M. Perey, *J. chim. phys.*, **43**, 155, 269 (1946).

(11) S. Peterson and A. Ghiorso, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper 19.10 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

(12) H. Copaux, *Bull. soc. chim. France*, **3**, 101 (1908) (IV).

(13) H. Copaux, *Bull. soc. franc. mineral.*, **29**, 77 (1906).

(14) M. Sobolew, *Z. anorg. Chem.*, **12**, 16 (1896).

(15) W. Hückel, "Structural Chemistry of Inorganic Compounds," Elsevier Publishing Co., Inc., Amsterdam, 1950, p. 185.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Metal–Amino Acid Complexes. II. Polarographic and Potentiometric Studies on Complex Formation between Copper(II) and Amino Acid Ion[1,2]

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Polarographic studies on the copper(II) complexes of glutamate, phenylalaninate, threoninate, serinate, arginine and lysine are made and the stability of the complexes decreases in the order given. The ratio of amino acid to copper in each of the complexes is 2 to 1, and this ratio is in agreement with potentiometric data. Further potentiometric results are presented on interaction between copper(II) and serine, arginine hydrochloride, argininate, lysinate, biglutamate and methioninate. Interpretation of the results on the basis of the molecular structures of the amino acids is given.

As part of a general program on complex formation between metallic and amino acid ions, this paper presents the results on the glutamate, phenylalaninate, threoninate, serinate, arginine, lysine and methioninate complexes of copper(II), using the methods of polarography and potentiometry. Complex formation between copper(II) and the unsubstituted neutral amino acids, glycine and alanine, as well as an acidic amino acid, aspartic acid, have been investigated[2-4]; however, quantitative results on the nature and stability of the copper(II) complexes of the amino acids presented in this paper have not yet been reported in the literature. The ultimate purpose of this study is to facilitate the elucidation of the more complicated systems in which the heavy metal ions interact with proteins and enzymes, inasmuch as these substances are largely composed of amino acids.

Results

Reagent quality chemicals were used without further purification. The preparation and analyses of solutions, together with the apparatus

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(1) This paper represents a part of the dissertation to be submitted by Brother Edward Doody to the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented in part before the 12th International Congress of Pure and Applied Chemistry, New York, September, 1951.

(2) Paper I in this series: N. C. Li and E. Doody, THIS JOURNAL, **72**, 1891 (1950).

(2a) Department of Chemistry, Duquesne University, Pittsburgh, 19, Pa.

(3) R. M. Keefer, THIS JOURNAL, **68**, 2329 (1946).

(4) H. A. Laitinen, E. I. Onstott, J. C. Bailar, Jr., and S. Swann, Jr., *ibid.*, **71**, 1550 (1949).