that this salt had been prepared by a different method from a different preparation the two results seem to agree tolerably well with the average of the first five. In considering the variation in the series it must be borne in mind that samples 1 to 5 had not been recrystallized on account of the difficulties previously explained; as the columbate tends to hydrolyze in water solution, apparently little is to be gained even by a recrystallization. Although this circumstance may be pointed out as a weakness of the method, it should be borne in mind that practically all columbium derivatives suffer from similar or even more serious defects.

Summary.

(1) The relation existing between the 7:6 and 1:1 sodium columbates has been established; they have been shown to be mutually convertible, and both have been prepared by new methods. Characteristic differences between these salts have been pointed out.

(2) Sulfur monochloride has been used, for the first time, directly for the determination of an atomic ratio; its applicability has been demonstrated. The method and the apparatus devised may be of value in other work.

(3) The atomic weight of columbium, as obtained from the ratio $NaCbO_3$: NaCl, was found to be 93.13. Although this figure is considerably lower than the present international value, 93.50, it is hoped that the former will prove more reliable than those recorded heretofore.

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THE EXTRACTION AND SEPARATION OF THE RADIOACTIVE CONSTITUENTS OF CARNOTITE.

BY H. M. PLUM.

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Ever since the discovery of radium by Mme. Curie and the announcements of its wonderful properties, there has been a very great demand for this element. On account of its scientific interest, such extensive investigations have been carried out that the supply of radium at all times has fallen short of the demand. The more recent claim that it has therapeutic value in the treatment of such diseases as cancer has so greatly increased the demand, that the study of the radium-producing ores, along with the best methods of extracting the radioactive material, has become extremely important. In view of these facts it can readily be seen that the demand for radium will be on the increase, and that any research which would point out efficient and practical methods for the recovery of this element will be of both scientific and practical value.

This paper presents the results of a critical investigation, carried out under the direction of Dr. Herbert N. McCoy, of various methods of treating carnotite with the object in view of extracting not only uranium, vanadium, and radium, but also its other long-lived radioactive constituents, ionium, radium D, radium F, and actinium. It has been established by McCoy,[1] Boltwood[2] and Strutt,[3] that there is a constant ratio between uranium and radium in ores. Consequently, the ores richest in uranium contain most radium. Among the most important of these ores are pitchblende, autenite, chalcolite and carnotite. Of these, until recently, pitchblende has been looked upon as the best source of uranium, the mineral usually containing from 40–90% of uranoso-uranic oxide, U_3O_8. The great demand for the radioactive elements, however, has nearly exhausted the known deposits of this ore.

The main source of supply for uranium at the present time is carnotite. It is a hydrated vanadate of uranium and potassium,[4] and usually occurs as a canary-yellow powder disseminated in sandstone. It does not occur, as a rule, in a pure state, but as a mixture of minerals containing—in addition to uranium, vanadium and potassium—varying amounts of silica associated with such elements as barium, calcium, and iron. The principal carnotite deposits are those of Colorado and Utah, where uranium ore is found in far larger quantity than in any other region in the world.

Many of the commercial methods proposed for treating uranium ores, or ores containing both uranium and vanadium, have had as their object the extraction of these elements only, without reference to the recovery of the radium. In such cases the radium has been lost because operators have often not known the methods best suited for obtaining it. A considerable amount of American carnotite has been shipped to Europe. These ores have been purchased mainly for their radium content, and the profit has come largely in connection with the extraction of the radium. Richard B. Moore and Karl L. Kithil,[5] in a preliminary report on uranium, radium and vanadium, and Siegfried Fischer,[6] in an article on the carnotite industry, have discussed quite fully the principal methods now in use for treating carnotite.

There are two principal methods of attack: acid processes and basic processes. Three of the former may be mentioned: Fleck's method, which consists in leaching the ore with dilute sulfuric acid; Radcliff's,[7] in which the ore is fused with sodium acid sulfate; and that of Moore and Kithil who effect a partial solution by treatment with boiling nitric or hydro-

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[1] McCoy, *Ber.*, **37**, 2641 (1904).

[2] Boltwood, *Nature*, **70**, 80 (1904); *Phil. Mag.*, **9**, 599 (1905).

[3] Strutt, *Nature*, **69**, 473 (1904); *Proc. Roy. Soc.*, (*A*) **76**, 81, 312 (1905).

[4] Hillebrand and Ransome, *Am. J. Sci.*, **10**, 120 (1900).

[5] *Bulletin* **70**, U. S. Bureau of Mines, Denver (1913).

[6] *Trans. Amer. Electrochem. Soc.*, **24**.

[7] U. S. patent No. 1,049,145 (1913).

chloric acid. Among the basic methods, Bleeker's[1] process consists of roasting the ore with sodium chloride and sodium hydroxide; Fischer's,[2] of evaporating with caustic soda solution and roasting; while Haynes and Engle[3] boil with carbonate of soda.

In most of the recent commercial methods which have had to do with carnotite, the investigators have generally been satisfied to find the best means of extracting vanadium, uranium and radium, without regard to the other radioactive elements. In the present work, in addition to the above, the aim has been to follow the other long-lived radioactive elements and to find means of recovering them also.

The ore used in these experiments represented the concentrates from a Colorado carnotite.[4] It was in a very finely divided form, dark in color, and had been thoroughly mixed in the process of concentration. This concentrate contained approximately 6% of vanadium, 4% of uranium, and 4% of iron. There were only small amounts of barium and lead in the ore, the barium radium sulfate from one kilogram of carnotite weighing about 7 g. The rare earths were lacking and very little, if any, thorium could be detected.

The analysis of the concentrate was made in several ways; the simplest and most satisfactory method consisted in boiling 5 g. of material with a large excess of concentrated nitric acid for about an hour, by which time complete decomposition had taken place. In case vanadium was to be determined, the nitric acid was completely expelled by evaporation to fumes with an excess of sulfuric acid. Water was added and the whole boiled for some time with a large excess of sodium carbonate solution and filtered. The insoluble residue, consisting of the carbonates and hydroxides of iron, etc., was dissolved in hydrochloric acid and again treated with sodium carbonate solution and filtered, and this filtrate added to the main filtrate. This solution now contained all the uranium and vanadium but was free from iron. It was acidified, boiled to expel carbon dioxide, and made alkaline with sodium hydroxide (free from carbonate). The uranium was precipitated as yellow sodium uranate while the vanadium remained in solution as easily soluble sodium vanadate. In case all the vanadium was not present in the pentavalent form, the addition of a little bromine water to the alkaline solution completed the oxidation and rendered the vanadium readily soluble in the sodium hydroxide, thus giving an easy and complete separation of the former from the uranium. The precipitate of sodium uranate was dissolved in sulfuric acid, reduced

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[1] U. S. patent No. 1,015,469 (1912).

[2] U. S. patent No. 986,180 (1911).

[3] U. S. patent No. 808,839 (1905).

[4] This material was furnished by Mr. J. M. Flannery, president of the Standard Chemical Company of Pittsburgh, to whom I wish here to express my thanks for his generosity.

with zinc and titrated with standard permanganate.[1] The mean of concordant analyses was 4.27% uranium. Vanadium was determined in the filtrate from the sodium uranate by acidifying with sulfuric acid, boiling to expel bromine, reducing with sulfur dioxide and then titrating with standard permanganate after freeing the solution from the excess of sulfur dioxide. The average of the results gave 5.5% vanadium.

The total activity of this ore was calculated from the percentage of uranium it contained. According to the method used by McCoy,[2] 1 g. of an ore containing 4.27% of uranium made into a very thin film, should show a total α-ray activity 1.94 times our standard, which was a thick film of U_3O_8 of 35.41 sq. cm. area. The distribution of this activity, as calculated from the ranges of the radioactive elements on the assumption[3] that the intensity of activity is proportional to $R^{2/3}$ (R = range), gave the following results for 100 g. of our ore, for which the total activity should be 194 times that of the U_3O_8 standard:

Element.	Range.	Calculated activity (Ra = 1).		Distribution of activity from 100 g. ore.
Uranium 1	2.50	0.831		36.3
Uranium 2	2.90	0.917		
Ionium	3.00	0.938		19.5
Radium	3.30	1.000	5.085	105.5
Radium Em	4.16	1.170		
Radium A	4.75	1.275		
Radium C	6.94	1.640		
Radium F	3.77	1.090		22.6
Actinium and its active products				11.0
Total				194.9

The activity of actinium was calculated from Boltwood's determination of the activity due to actinium in uranium minerals.[4] The above figures were used as the basis for finding the percentage of recovery of the different radioactive elements in the experiments carried out in this work. In the case of uranium, however, the percentage of recovery of that element was found directly by analysis, while with radium the determination of the amount of emanation present gave the most satisfactory results. To get the activity of radium, the emanation liberated by fusing samples of the material to be tested with anhydrous potassium acid sulfate was collected and then measured in an emanation electroscope after the manner described in a later paragraph. The activity of polonium was determined by depositing it on copper,[5] and then comparing the activity with that of

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[1] McCoy and Bunzel, THIS JOURNAL, **31**, 367 (1909).

[2] *Phil. Mag.*, **2**, 176 (1906).

[3] McCoy and Viol, *Ibid.*, **25**, 357 (1913); McCoy, *Phys. Rev.*, **1**, 401 (1913).

[4] *Am. J. Sci.*, **25**, 269 (1908).

[5] Marckwald, *Physik. Z.*, **4**, 51 (1903); *Ber.*, 2662 (1903).

the standard uranium film. In the case of ionium, where the final residue containing it was very small, the material was dissolved and thin films, satisfactory for α-ray measurement, obtained from the deposit left by evaporating portions of this solution. The activity of the radio-lead and actinium was determined by thin films made in a manner similar for those used for measuring the activity of the original ore, the final measurements being made after the films were a year old.

Since no single method has yet been found that is applicable for treating all carnotites, it was thought desirable in this work to make a study of some of the principal methods already proposed, and to determine, therefore, to what extent these methods must be modified in order to be most effective in the treatment of our ore. Accordingly, the following experiments were made:

(*a*) **Extraction of Vanadium with Caustic Soda.**—This method is based on the fact that a vanadium ore forms a soluble metavanadate by treating it with a caustic soda solution. Fischer, in a paper on the extraction of vanadiferous sandstone concentrates,[1] states that in his opinion only methods which employ a caustic alkali promise commercial success. In working on crude ore, Fischer found it impossible, by wet methods, even by boiling, to obtain satisfactory results unless he used commercially prohibitive quantities of alkali in which case nearly complete extraction of vanadium was obtained. Excessive consumption of caustic alkali was apparently due to its action on the silica in the ore. With carnotite, however, he was able to get from 87–98% extractions of vanadium with much smaller consumption of alkali, by treating them in the following manner: The concentrates were added to water containing alkali, in the proportion of five parts of concentrates to one part of alkali, and the whole mixed to a pasty consistency and then evaporated to dryness, finishing at a temperature ranging between 200° and 300°. This method, when applied to a *crude* ore, on the contrary, yielded only about a 65% extraction of the vanadium.

The following are the results of my experiments: 100 g. of carnotite were mixed with 50 g. of caustic soda dissolved in 200 cc. of water and boiled for three hours in a flask with a reflux condenser. A sample of the solution then showed about 45% of the vanadium had been extracted. When the mass was boiled for six hours longer, the amount of vanadium extracted had not increased. Thus it was evident that this method could not be used if the vanadium were to be removed completely by a single treatment. Fusion with caustic soda was tried, but not very thoroughly investigated, for it was evident that with such a procedure much difficulty in filtering and washing would be experienced, because

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[1] *Met. Chem. Eng.*, 10, 469 (1912).

some of the silica in the ore was converted into sodium silicate which, on acidifying, interfered with subsequent processes.

(*b*) **Treatment of Carnotite with Carbonate of Soda.**—A method of extracting uranium and vanadium from carnotite with sodium carbonate solutions has been patented by Haynes and Engler.[1] This method, as described by Moore and Kithil,[2] involves the boiling of the carnotite ore, which has been crushed to twelve mesh with an alkaline carbonate solution until the uranium and vanadium have dissolved. The time of boiling and the strength of solution depend upon the proportion of the two elements present. In the clear filtrate resulting, the uranium is then separated from the vanadium by precipitating the former with sodium hydroxide. This process in actual operation with carnotite is said to give an extraction of 80% of uranium and 60–65% of vanadium.

After some preliminary experiments which seemed to promise good results, the above method, with modifications, was carefully investigated. 100 g. of carnotite were boiled with reflux condenser for three hours with 100 g. of anhydrous carbonate of soda dissolved in 250 cc. of water. After filtering, a sample of the filtrate was neutralized with acid, reduced with zinc and sulfuric acid, and the resulting solution titrated with potassium permanganate. The solution was filtered and the residue treated twice successively in a similar manner with soda solutions, except that the heating in each of these last two cases was continued for only $1^1/_2$ hours. Analyses of the solutions showed the relative extracts to be approximately as 9 : 2 : 1/3. A test on the third filtrate showed very little uranium present. When these three solutions were combined and concentrated by boiling, a yellow precipitate appeared, which was found on subsequent analysis to be sodium uranyl carbonate. By removing this precipitate and further concentrating the filtrate it was possible, on cooling to low temperatures, to crystallize out a large part of the unused sodium carbonate in a form easy to wash free from impurities. When the insoluble residue from the three consecutive treatments with soda solutions was boiled with hydrochloric acid, the filtrate was green in color and contained large quantities of vanadium. This experiment showed that two treatments with a boiling sodium carbonate solution removed most of the uranium from the ore, giving a solution from which both the uranium and most of the soda could be recovered by simple processes. This method, however, had failed to bring the vanadium completely into solution, a result which is in accord with that found by Haynes and Engler, as cited above.

(*c*) **Treatment of Carnotite with Carbonate of Soda in the Presence of an Oxidizing Agent.**—Since the treatment of carnotite with soda alone,

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[1] U. S. patent 808,839 (1905).

[2] *Bulletin* 70, Bureau of Mines (1913).

as described in (*b*), had failed to bring all the vanadium into solution, it was thought that by converting this element into its most highly oxidized form, its extraction might be more complete. In impure carnotites in which the vanadium often occurs both in the trivalent and pentavalent forms, it has been observed that the vanadium dissolves much more readily in alkaline solvents in the latter condition. With these facts in mind, therefore, the following experiment was made:

100 g. of carnotite were boiled with reflux condenser for 41 hours with a concentrated sodium carbonate solution. The heating was continued for so long a time in order to secure maximum extraction by the soda alone. Samples of the solution were examined from day to day, as in (*b*), but no increase in extraction was noticeable after the boiling had continued 26 hours. During the last six hours of the boiling, a current of chlorine gas was passed into the solution but, on comparing samples of the solution both before and after the introduction of the chlorine gas, no change in the vanadium content was found. In this experiment nearly all of the uranium was found in the soda solution while a considerable part of the vanadium was left in the insoluble residue. These facts show that that part of the vanadium not readily soluble in a soda solution is present in some inert form, probably a silicate such as roscoelite.

(*d*) **Treatment of Carnotite with Hydrochloric Acid.**—Among the various methods of treating carnotite is one proposed by Moore and Kithil,[1] which consists in treating the ore directly with concentrated nitric or hydrochloric acid. Pure carnotite dissolves in cold, even dilute acids. In the case of vanadiferous silicates such as roscoelite, Moore and Kithil state that they were able to decompose such ores by boiling them for an hour with the concentrated acids. With the ore used in this work, hydrochloric acid did not seem to bring the vanadium completely into solution, for in an experiment in which 5 g. of the ore were boiled with concentrated acid for intervals of twenty to thirty minutes, ten or twelve successive treatments were required to extract all vanadium. In dealing with kilogram lots, where the ore had been previously treated with sodium carbonate solution, the residue, after three consecutive treatments with concentrated hydrochloric acid diluted with three times its volume of water and boiling for two or three hours, still held vanadium. Although Moore and Kithil are correct in stating that pure carnotite is readily soluble in hydrochloric acid, the facts just stated show that so-called carnotite of the kind here studied, the one which constitutes the bulk of the material available in America for technical processes, is a complex mixture, not all of which is readily attacked even by boiling hydrochloric acid.

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[1] *Bulletin* 70, Bureau of Mines (1913).

(*e*) **Treatment of Carnotite with Dry Hydrogen Chloride.**—It was shown by Smith and Hibbs[1] that sodium pyrovanadate is acted on by dry hydrogen chloride between room temperature and 440° with the formation of common salt and the complete elimination of the vanadium in volatile form. The application of a gentle heat caused a reddish brown vapor to appear which condensed in the combustion tube as an oily liquid easily taken up by water. They explained the reaction, in this case, in the following way:

$$\text{I.}\quad Na_4V_2O_7 + 4HCl = 4NaCl + V_2O_5.2H_2O$$

$$\text{II.}\quad V_2O_5.2H_2O + 6HCl = 2VO_2.3H_2O.4HCl + Cl_2$$

except that they were not certain that the volatile compound had the composition $2VO_2.3H_2O.4HCl$. Ephraim,[2] however, in working on the same problem, showed that the volatile compound of Smith and Hibbs is vanadyl trichloride, $VOCl_3$, and has given the following equations in support of his concentration:

$$\text{I.}\quad Na_4V_2O_7 + 4HCl = 4NaCl + V_2O_5.2H_2O$$

$$\text{II.}\quad V_2O_5 + 6HCl = 2VOCl_3 + 3H_2O$$

In analyzing carnotite, Hillebrand[3] has used this method for the separation of vanadium. It was necessary, however, for him to oxidize with nitric acid any vanadium reduced during the process and to repeat, therefore, the treatment with dry hydrochloric acid gas before complete separation could be effected.

To see if this same method would remove the vanadium from our ore, the following experiments were made: 20 g. of carnotite were heated for one or two hours in a retort through which dry hydrogen chloride was passed. Reddish brown fumes of vanadyl trichloride appeared at once and condensed in the neck of the retort, or collected in the water in the receiver. During the process, the retort was frequently shaken so as to insure contact of the gas with all parts of the ore. Seemingly, the method promised success; but analysis of the distillate showed that only about 20% of the vanadium had been removed. On continuing the process for some time longer with increased heating, more of the vanadium passed over, but the distillate, at these higher temperatures, contained considerable ferric chloride. When the involatile residue was washed with water, and the filtrate treated with sodium hydroxide, a heavy precipitate of sodium uranate formed, indicating that during the operation the uranium had been brought into a condition soluble in water. On account of the appearance of the iron in the distillate and the low percentage of vanadium extracted, the process was modified as follows:

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[1] THIS JOURNAL, **16**, 578 (1894).

[2] *Z. anorg. Chem.*, **35**, 66 (1903).

[3] Hillebrand, *Am. J. Sci.*, **10**, 120 (1900).

An electric furnace was substituted for the retort in order to be able to control the temperature. 10 g. of the dried ore were placed in a quartz tube into which dry hydrogen chloride gas was passed as the temperature was gradually increased. This tube was frequently rolled to insure uniform heating and mixing, and the process continued for the greater part of a day. In the light of Hillebrand's[1] observations, *i. e.*, that hydrochloric acid reduces a good deal of the vanadium and leaves it in a condition incapable of forming the volatile body, some dry chlorine gas was conducted through the tube during the latter part of the period, in the hope that the vanadium would be kept completely oxidized, and consequently, a complete extraction be obtained. On examining the distillate, however, it was found that ferric chloride had again been carried over, and that not more than about 40% of the vanadium had been removed from the ore, even when the process had been continued throughout the day. On account of the slowness of the reaction and the incompleteness of the extraction, the method was abandoned as an impractical one for treating carnotite on a large scale. It is probable that all the vanadium in the form of true carnotite is volatile, under the conditions of the experiment, incomplete extraction being due, as in other methods, to the presence of vanadium silicates.

(*f*) **Treatment of Carnotite with Nitric Acid.**—In working on the new American ore, to which they gave the name carnotite, Friedel and Cumenge,[2] after having extracted the vanadium by using dilute nitric acid, were able to separate the vanadium in the filtrate from other ingredients by evaporating the solution to dryness. Under these conditions, they claim, the vanadium, in excess of nitric acid, becomes insoluble upon evaporation and can be separated quantitatively from uranium whose nitrate is soluble in water. Hillebrand,[3] however, in using this method of Friedel and Cumenge on some complex ores, found that he could not always get perfect separation, because it was impossible for him, first, to prevent a little of the vanadium going into solution with the uranium, and, second, to prevent small amounts of the uranium being retained with the vanadium.

In working on our carnotite, it was not possible with dilute nitric acid to get the vanadium completely into solution, as had Friedel and Cumenge. Besides, when the filtrate obtained in this way was concentrated, the insoluble vanadium precipitate which formed carried with it radioactive matter. These results indicate that nitric acid is not a suitable reagent for the primary treatment of carnotite. Naturally there are other reasons why the use of nitric acid would be avoided, if possible, in a technical process.

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[1] *Am. J. Sci.*, **10**, 120 (1900).

[2] *Chem. News*, **80**, 16 (1899); *Compt. rend.*, **128**, 532 (1899).

[3] *Am. J. Sci.*, **10**, 120 (1900).

(*g*) **Treatment of Carnotite with Sulfuric Acid.**—A method of treating carnotite, originated by Herman Fleck, which uses dilute sulfuric acid directly on the crushed ore, is said to have been employed practically for extracting uranium and vanadium from carnotite. This method which brings the two elements mentioned into solution leaves the radium in the residue.

With our ore, that part of the vanadium held in the residue left from a carbonate treatment, such as described in (*c*), could be removed if treated with sulfuric acid. In an experiment on 100 g. of material, this extraction was practically complete, when the residue mixed with 35 cc. of concentrated acid and 115 cc. of water was heated to boiling for $2^1/_2$ hours. The extraction of vanadium was very complete when the ore, mixed with sulfuric acid and water, was heated until the excess of acid slowly fumed away. This method, nevertheless, even though it did remove uranium and vanadium completely, was not used because of the difficulties it involved in recovering radium with any high degree of efficiency.

(*h*) **Treatment of Carnotite with an Acid in the Presence of a Reducing Agent.**—In all the acid extractions, except perhaps in some stages in the nitric acid treatment, the filtrate appeared green or blue, depending upon the degree to which the vanadium had been reduced. Acid solutions of vanadium pentoxide are reduced to vanadium dioxide in the presence of sulfurous acid, and by the evaporation with hydrochloric acid. Magnesium with hydrochloric acid reduces the pentoxide to vanadium trioxide, while zinc and hydrochloric acid carry the reduction to vanadium monoxide. Since vanadium, therefore, takes a reduced form in acid solutions, it was thought that the introduction of a reducing agent at the time the acid was acting on the original ore might, perhaps, increase the degree of extraction. Accordingly, 5 g. of ore were placed in each of two flasks containing three cc. of concentrated sulfuric acid diluted with 15 cc. of water. In the one flask were added some pieces of zinc, and the two solutions heated to boiling for some time, under the same conditions; but when the filtrate was examined no increased extraction had occurred from the use of the reducing agent. Similar experiments, using dilute sulfuric acid with and without the addition of sulfur dioxide, showed no difference in the degree of extraction.

As a result of the foregoing experiments, it was evident that this carnotite held part of the vanadium in a condition very difficult to remove by a single operation. In studying some of the Colorado carnotites, Hillebrand[1] had found the vanadium to exist in the ores in two distinct forms: (*a*) the one, the pentavalent vanadium, quite easily soluble, and (*b*) the other, a trivalent form, a vanadiferous silicate, extremely difficult to

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[1] *Am. J. Sci.*, **10**, 120 (1900).

bring into solution. While pure carnotite dissolves at once in cold dilute nitric acid, the vanadiferous silicate yields only to more powerful attacks. The ore used in this work resembled the latter closely in its characteristics, and after the series of preliminary experiments, it was decided that it would be more advantageous not to try to remove the vanadium by a single process, but to treat the ore by methods calculated to recover the radioactive materials, leaving the vanadium to be dealt with wherever it occurred in the various solutions. On the basis of the foregoing work and that described in succeeding pages, the following method was adopted as the most satisfactory: The ore was treated first with a boiling solution of sodium carbonate, then with hydrochloric and nitric acids, respectively, and finally with sulfuric acid. The details of the complete process, with descriptions and discussions of how the different radioactive ingredients were obtained, are given below.

Details of the Method Used in Treating Kilogram Lots of Carnotite.

Since the foregoing experiments seemed to indicate that the treatment of the ore with sodium carbonate solution gave most satisfactory results, this method, therefore, was carefully investigated. Various experiments were made on 100 g. lots to ascertain, first, what concentration of sodium carbonate solution was most effective and, second, what conditions of temperature gave best results. The mass of ore was then increased to a kilogram; and after five or six of these had been worked over, a final kilogram was treated in the following manner:

One kilogram of carnotite and 400 g. of chemically pure anhydrous sodium carbonate were mixed with about two liters of water and heated to boiling for several hours. This mixture was frequently stirred to secure uniform heating, water being added as the mass thickened. While still hot, it was filtered under suction through a filter cloth, and the filter cake washed with hot water. The washing was a slow process, but attempts in preceding experiments on boiling up the residue with water had proved that it made the mass more colloidal and, consequently, more difficult to filter. Decantation processes were also abandoned because of the slowness with which the mud-like material settled. The brown filtrate thus obtained contained most of the uranium, less than half of the vanadium, and the unchanged portion of the sodium carbonate. After attempts to separate the uranium from the carbonate solution by means of a variety of reactions, a very simple and effective method was finally discovered. It was found that when the carbonate solution was evaporated so that the solution became nearly saturated with sodium carbonate, the uranium settled out as a beautiful, yellow product easily filtered from the hot solution. This substance which on analysis proved to be uranyl sodium carbonate, $UO_2CO_3.2Na_2CO_3$, was quite heavy, and settled quickly. To obtain the maximum recovery of this compound, the evaporation was continued up to the point at which the sodium carbonate just began to crystallize out, and the hot solution was filtered at once. Strong suction left the uranyl sodium carbonate almost free from impurities, so that very little, if any, water was required in washing to give a relatively pure product. The amount of dry precipitate obtained in this way from each kilogram of carnotite concentrate varied from 85 to 90 g. In this final kilogram lot, the weight of the uranyl sodium carbonate was 88.1 g.; this was 88% of the total amount of uranium in the ore. An examination of the filtrate from the uranyl sodium carbonate precipitate showed it still contained 2% of the uranium. When the residue from the first carbonate extraction was treated again with 300 g. of sodium carbonate under conditions similar to the above, the amount of uranium carried in this filtrate was too small to be recovered as uranyl sodium carbonate. On examining the filtrate, however, the uranium found was only 2.8% of the total amount in the ore. It thus appears that a second treatment with sodium carbonate solution is an unnecessary step in the operation.

The identity of the yellow compound referred to in the preceding paragraph was established by analysis. Some of the material was heated at 125° to constant weight. The loss, which amounted to about 1%, was due undoubtedly to moisture held mechanically. The residue of silica, etc., left on dissolving some of the compound in dilute sulfuric acid, amounted to about 0.3%. The determination of the uranium was made by reducing a weighed amount of the yellow body with zinc and sulfuric acid, and then titrating with potassium permanganate. Sodium was determined by removing the uranium with ammonium hydroxide, and then converting the sodium compound into the sulfate. This analysis, as indicated by the figures below, proved the compound to be uranyl sodium carbonate.

RESULTS OF ANALYSIS.

	Per cent.
Loss on heating at 125°	0.98
Insoluble residue	0.31

COMPOSITION OF THE PORTION FREE FROM VOLATILE AND INSOLUBLE MATTER.

	Found.	Calculated for $UO_2CO_3.2Na_2CO_3$.
Uranium	43.65	43.97
Sodium	17.07	16.96

The uranyl sodium carbonate obtained by the same method on other kilogram lots, had been carefully examined to see if any of the other radioactive substances had been carried along with the uranium. Portions of the compound were dissolved and attempts made to find polonium, radium, ionium and actinium by methods described in later paragraphs of this paper, but in none of these experiments was there found any active substance other than uranium. The solution filtered from the uranium carbonate contained a large excess of unchanged soda together with the sodium vanadate. This solution was evaporated until it became saturated with the soda, and then cooled to 0°. Sodium carbonate is more than six times as soluble at 100° as at 0°, so that large masses of crystals were obtained when the boiling saturated solution was cooled. With a little ice water these crystals could be washed nearly free from the vanadium which remained in solution. By further evaporation, other crops of crystals could be obtained, and in this way most of the uncombined soda recovered. The sodium carbonate thus obtained could be used repeatedly in treating the original ore and thereby a great saving of that compound be realized. As vanadium can be obtained from its solutions by well-known methods, the sodium vanadate solution left after the removal of the uranium and the excess of sodium carbonate, was studied only in so far as to find that none of the radioactive elements were present in it.

After the original ore had been treated with a solution of carbonate of soda, the next step was to boil the residue with hydrochloric acid. In preceding experiments it had been found that, if dilute acid were used only in such quantities as to break up the easily decomposed carbonates and not in sufficient amounts to bring into solution any of the iron or vanadium, the yield of radium was not more than 60–65% of the total amount in the ore. By boiling with more concentrated acid, the percentage of radium recovered could be greatly increased. Further, three consecutive treatments with boiling hydrochloric acid, made by mixing one volume of concentrated acid with about three volumes of water, still left radium in the residue, most of which could be removed by boiling the residue with nitric acid diluted with three or four times its volume of water. Consequently, a single treatment with hydrochloric acid, followed by one with nitric acid, was found to be the most satisfactory method to follow. In accordance with these results, the residue left from the carbonate treatment of the last kilogram of ore was boiled with 400 cc. of concentrated hydrochloric acid diluted with two or three times its volume of water. The heating was continued for about eight hours, water being added as it disappeared by evaporation. The hot mixture was then filtered and the filtrate evaporated to a smaller bulk. This solution was then carefully examined for radioactive elements. Fifty cc. of a 1% bismuth nitrate solution were added and completely precipitated with hydrogen sulfide, the excess of which was removed from the filtrate by boiling it, after the sulfides had been collected on a filter. These sulfides were then dissolved in concentrated nitric acid, sulfuric acid was added to the solution, and the lead was separated from bismuth by the customary analytical methods. The lead sulfate removed in this way contained the radio-lead. The bismuth in the filtrate was precipitated with ammonium hydroxide, and after filtering and washing it was dissolved in hydrochloric acid. It was in this solution that most of the polonium appeared. To the filtrate from the sulfides, 3 or 4 cc. of concentrated sulfuric acid were added which caused the precipitation of radium and barium as sulfates. Small amounts of barium chloride were now added, and a second and third precipitation was made for the purpose of carrying down the radium and actinium more completely, especially the latter. The filtrate from barium sulfate was then neutralized with ammonia up to the point of precipitation of the hydroxides, 5–10 g. of cerium chloride or nitrate were added, and the cerium was precipitated with oxalic acid. This was a troublesome process, as it necessitated the use of large amounts of oxalic acid before precipitation of cerium oxalate could be brought about. The activity of the cerium oxalate, precipitated in this way, was much too little to account for all the ionium and it was the lack of radioactivity at this point which led to the belief that the ionium had not yet been removed from the residue. When some thorium nitrate was added to this filtrate, instead of cerium, and a precipitation of thorium oxalate was made with oxalic acid, no better recovery of ionium was obtained.

The residue from the hydrochloric acid extraction was next treated with 200 cc. of concentrated nitric acid diluted with about a liter of water. This was kept at boiling temperature for a day, at the end of which time the mass was filtered. The resulting filtrate was examined for radioactive elements by methods similar to those used in studying the hydrochloric acid filtrate, but none of these elements could be found except radium. On the addition of a few cc. of sulfuric acid to the filtrate, a precipitate formed which showed the presence of considerable activity. In short, nitric acid always brought into solution soluble matter containing radium, which hydrochloric acid was incapable of dissolving out of the ore.

The final step in the process was that which involved the use of sulfuric acid. The residue left from the foregoing extractions was mixed with twice its weight of sulfuric acid which had been diluted with water in the proportions of about five of acid to four of water. This was slowly heated and the temperature so regulated that most of the acid fumed away. If the heating was not excessive, on digesting the resulting mass with hot water, the residue was pure white, for all vanadium and iron remaining in the ore were completely removed by this process. It was in this filtrate that most of the ionium was found. To remove it, about 10 g. of cerium nitrate were added, and the excess of sulfuric acid was neutralized with ammonium up to the formation of a small amount of the hydroxides. A large quantity of oxalic acid was then added, which dissolved the slight hydroxide precipitate, and after some time precipitated the cerium as oxalate. This process was difficult to carry out, for it seemed impossible to precipitate the cerium oxalate until the solution was almost saturated with oxalic acid. Keeping the solution well stirred and rubbing the sides of the containing vessel with a glass rod aided considerably in the precipitation. In order to recover the ionium more completely, a second portion of cerium nitrate was added to the solution and a second precipitation of cerium oxalate was obtained. The methods used in concentrating the ionium and in measuring its activity are given later in the special paragraph on ionium.

Radium.

The complete method of treating the ore, as described in preceding paragraphs, gave a good recovery of radium, the greater part of which appeared in the solution obtained from the hydrochloric acid extraction. To get the best results it was necessary, however, to follow the hydrochloric acid treatment with a nitric acid extraction because the latter always dissolved material insoluble in hydrochloric acid, which still contained about 8–10% of the radium. In working up the last kilogram of ore, the barium radium sulfate precipitate obtained from the hydrochloric acid filtrate weighed 7.36 g. and that from the nitric acid solution 0.45 g. By the addition of successive small equivalent amounts of barium chloride and sulfuric acid, 9.30 g. of barium sulfate were precipitated in the filtrates from the first precipitates of this substance.

The percentage of recovery of radium was determined by comparing the activity of the original ore with that of the radium barium sulfate, the emanation method being used for the purpose. To do this, one-half gram of the original ore, after being mixed with 5 or 6 g. of anhydrous potassium acid sulfate, was carefully fused in a hard glass test-tube and then made air tight. After several days this mass was again fused, the emanation transferred completely to an emanation electroscope (without the use of water), and the time of discharge observed. By knowing the exact interval the tube was sealed, the time of discharge for the maximum amount of emanation could be calculated from the known rate of decay and growth of radium emanation. In a similar way, the activity of the radium barium sulfate was obtained, except that in this determination only 0.0150 g. of material was used in each fusion. On comparing these results, it was found that 89.9% of the total radium had been recovered in the barium radium sulfate precipitated from the hydrochloric and nitric acid solutions. The barium sulfate obtained by adding small amounts of barium chloride to the filtrates, as described above, was only slightly active and held but 2.7% of the radium. The residue left after all extraction processes, contained only 4.2% of the total radium contained in the ore. This leaves 3.3% of the radium unaccounted for.

Polonium and Radio-lead.

The filtrates from the first three treatments of the ore, *i. e.*, with carbonate of soda, with hydrochloric acid and with nitric acid, were examined for polonium and radio-lead, which were found only in the chloride solution. When the filtrate from the carbonate extraction was examined for polonium by adding to it a little bismuth nitrate and then precipitating with hydrogen sulfide, no polonium was found in the bismuth sulfide. The sulfides, obtained by treating the hydrochloric acid filtrate in a similar manner, were comparatively active. These sulfides were dissolved in boiling concentrated nitric acid, sulfuric acid was added to the solution, and the lead was separated from the bismuth by the usual analytical methods. It was not necessary in any of these experiments to add any lead salt to carry down the radio-lead, since the original ore contained small quantities of that element. The lead sulfate which was only slightly active at first, greatly increased in radioactivity in the course of ten months. The bismuth and polonium, after being separated from the lead, were further purified by precipitating them with ammonium hydroxide. This precipitate was then filtered out and, after being dissolved in a few drops of hydrochloric acid, the solution was examined quantitatively for polonium by depositing it on copper. In the last kilogram lot the bismuth chloride obtained, as described above, was diluted with water up to 250 cc., enough hydrochloric acid being added to keep the bismuth in solution. Five cc. samples of this solution were further diluted with about the same volume of water and introduced into a beaker containing a clean piece of copper foil, the under side of which had been covered with wax. Under these conditions, the polonium deposited on the copper, the process being hastened by stirring with a current of air, so that in 30 or 40 minutes a large part of the polonium had collected on the copper foil. In an experiment which had run 30 minutes, the first foil was removed and a second and a third were introduced into the same solution, for about the same length of time. The activity of the polonium deposited on these three foils varied as 11 : 2 : 1/6, showing that more than 80% of the polonium, in the 5 cc. sample, had deposited on the first copper foil in 30 minutes. When the total polonium activity was calculated, it was found that about 50% of the amount in the original ore had been recovered in the filtrate from the hydrochloric acid extraction. When the nitric acid solution was treated in the same way as the hydrochloric acid filtrate, the bismuth sulfide obtained did not contain any polonium.

Ionium.

In this research, great effort was made to discover what course the ionium took and how it could be recovered to best advantage. The filtrate from each of the first three extractions, *i. e.*, with soda, with hydrochloric acid, and with nitric acid—was therefore carefully examined. As this ore contained only small quantities of the rare earths, a little thorium or cerium salt had to be introduced into the filtrate in order to get a precipitate on the addition of oxalic acid. The oxalates thus obtained should have carried down whatever ionium there was in the filtrate. When the solution from the sodium carbonate extraction was examined in this way, no ionium was found. Likewise the filtrates from the hydrochloric and nitric acid extractions showed but very little more activity than could be accounted for by the thorium added. From these results it was evident that the ionium had either escaped detection or had not yet been removed from the insoluble siliceous residue. An examination of the latter, by means of the emanation method, showed that approximately 95% of the radium had already been removed from the original ore. But the α-ray activity of the residue, as measured by thin films, was considerably greater than could be accredited to the 5% of radium left therein. In order to remove this radioactive substance, the residue was finally treated with sulfuric acid, as already described, because it was believed that if any radioactive matter were dissolved by this acid, it would not be radium, but might be ionium. Further, it was thought that the rare earths might be present in some form like the fluorides and that drastic treatment such as boiling with concentrated sulfuric acid would be required to remove them. This method proved successful, for, when this mass was digested with boiling water, the filtrate not only contained all the vanadium left in the residue, but also the greater part of the ionium. When a small amount of thorium nitrate was added to the filtrate, thus obtained, and the thorium precipitated as oxalate, it always possessed much greater activity than had been observed in the filtrates from any of the other extractions. The ore did not contain enough, if any, thorium to carry down the ionium without the addition of thorium. But as thorium and ionium cannot be separated by any known reaction and as we wished finally to obtain ionium mixed with a minimum of thorium, cerium was added to the sulfate solution instead. It was found difficult, however, to precipitate cerium oxalate in acid solution in the presence of vanadium and iron, but it could be accomplished by almost neutralizing the sulfuric acid with ammonium hydroxide and then adding oxalic acid until it had nearly saturated the solution. To get the ionium in a more concentrated condition, the resulting cerium oxalate was thoroughly shaken with a solution made by dissolving 40 g. of dry sodium carbonate and 20 g. of sodium bicarbonate in 400 cc. of water, 10 cc. of which were used for each gram of cerium oxalate. Under these conditions a large portion of the ionium was dissolved while the cerium remained behind as an insoluble carbonate. When the cerium carbonate thus obtained was dissolved in nitric acid, the solution neutralized with ammonia, and then hydrogen peroxide added, upon heating to 70° the balance of the thorium and ionium were precipitated. The residue carrying the ionium was very small; it probably consisted essentially of thorium, which may have been contained originally as an impurity in the cerium used. A test made on some of this material by means of the emanation method showed not the slightest trace of radium and films made from these ionium residues remained constant in activity for ten months. When the ionium was separated from the last kilogram of ore in the manner just described and its activity measured by the method given in a preceding paragraph, the results showed the recovery for this element to be about 61% of the total amount calculated for the original ore.

Actinium.

Just as in the case of the other radioactive elements, the filtrates obtained from treating the ore in succession with carbonate of soda, with hydrochloric acid, and with nitric acid, were examined for actinium. As actinium is said to occur with ionium in the rare earth precipitates, all the precipitates of cerium and thorium oxalates made in studying ionium were likewise examined for actinium, but there was no evidence to show that the actinium accompanied the ionium in the course the latter took before being recovered from this ore. Actinium, however, was found to be carried down with the barium sulfate containing the radium. That it might be the more completely recovered, small amounts of barium chloride were added and several precipitations of the barium sulfate made in the filtrates from the hydrochloric and nitric acid extractions. These combined sulfates were then fused with a mixture of sodium and potassium carbonate in molecular proportions, the barium carbonate was thoroughly washed, and then converted into chloride. On adding ammonium hydroxide to this solution, a precipitate formed which, although but slightly active at first, grew in activity until the increase amounted to fifteen- or twenty-fold, the rate of increase being about that expected for actinium initially free from radioactinium and actinium X. The actinium, moreover, was not all removed from the barium in this way for, by adding 1 or 2 g. of an aluminium salt to the radium barium solution and then precipitating the aluminium with ammonium hydroxide, a precipitate was obtained which also increased many-fold in activity. To prevent any radium from being held by the aluminium hydroxide, the latter was dissolved and reprecipitated three times and the activity of the actinium under these conditions was then measured. In the experiments on the last kilogram of ore, 2 g. of aluminium nitrate were added to the barium solution and precipitated in the manner described above. The aluminium hydroxide thus obtained increased in activity about thirty-five-fold in twenty-five days. A second precipitation using the same amount of aluminum nitrate gave a precipitate which, while not so active at first as the former one, increased more than seventy-five-fold in the same interval of time. From these results it is clear that the actinium contained in the barium radium solution cannot be separated completely by a single precipitation of aluminium hydroxide in this solution. The percentage of actinium found by the above treatment, was 52% of the total amount as calculated in a preceding paragraph.

Summary.

In this paper a careful study has been made of a Colorado carnotite and a satisfactory method worked out for the extraction of the radioactive ingredients. Several of the commercial methods now in use for removing vanadium and uranium from a carnotite ore have been examined and modified so as to be effective in treating our ore which was found not to be a pure carnotite, but a mixture of this mineral with a vanadiferous silicate, containing the vanadium in a condition difficult to remove. The method finally adopted gives good results. The uranium is removed **by** boiling the carnotite concentrates with a sodium carbonate solution, precipitated as uranyl sodium carbonate by merely concentrating the filtrate, and the soda is again recovered. The radium, actinium and radio-lead are contained in the filtrate obtained by boiling the residue insoluble in soda solution with hydrochloric acid. That part of the radium still held in the residue is then removed with boiling nitric acid. The ionium is finally recovered from the residue by boiling with sulfuric acid and is then concentrated with cerium rather than with thorium, from which it cannot be separated by any known reaction. A summary of the processes used and the results obtained from the last kilogram of carnotite concentrates is here given.

One kilogram of carnotite concentrates was boiled for several hours with 2 liters of a solution containing 400 g. of anhydrous sodium carbonate. The filtrate yielded 88.1 g. of uranyl sodium carbonate, $UO_2CO_3.2Na_2CO_3$, which represented 88% of the total uranium in the sample. The filtrate still held 2% of the uranium in solution. A second treatment of the ore with 300 g. of sodium carbonate, under the same conditions as above, dissolved out only 2.8% of the uranium. The residue was treated with 400 cc. hydrochloric acid diluted with about a liter of water, and boiled eight hours. The barium radium sulfate separated from the filtrate weighed 7.36 g. The residue was next heated a day with 200 cc. of nitric acid diluted with about a liter of water. The barium radium sulfate precipitated in this filtrate weighed 0.453 g. The percentage of radium in these combined sulfates was 89.8% of the total amount in the ore. Reprecipitations of barium sulfate in the two acid filtrates carried down 2.7% more of the radium. The lead sulfate, separated from bismuth and containing the radio-lead, weighed 0.49 g. The polonium precipitated with bismuth and then deposited on copper was 50.1% of the total amount in the ore as calculated from the ranges of the radioactive elements. The residue was finally treated with twice its weight of sulfuric acid after being diluted with about an equal weight of water, and then heated until most of the sulfuric acid had escaped in fumes. The activity of the ionium found in this solution was 61% of the total amount in the original carnotite, as calculated in a preceding paragraph. The residue left after all ex-

traction processes weighed 507 g., 50.7% of the original ore used. Its activity as measured by the emanation method showed that only 4.2% of the radium still remained in the residue.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

BINARY AND TERNARY SYSTEMS OF THE NITRATES OF THE ALKALI AND ALKALINE EARTH METALS.

BY WILLIAM D. HARKINS AND GEORGE L. CLARK.

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In view of the fact that very few complete ternary systems of mixtures of dry salts have been worked out,[1] the following investigations of new systems were made: (1) a study of the complete system comprising barium, sodium, and potassium nitrates; (2) a study of the eutectic and all neighboring points of the system, strontium, sodium, and potassium nitrates; and (3) a study of the system barium, lithium and potassium nitrates as far as the point beyond which marked decomposition prohibited further determinations. The work of Menzies and Dutt on the system calcium, sodium, and potassium nitrates has been utilized for comparison with these systems by means of the respective triangular diagrams.[2]

Method of Procedure.

The freezing points of the various salt mixtures were determined by the usual method. Weighed amounts of the dried salts in the calculated proportion were carefully ground together and then melted with the thermometer bulb immersed. As soon as the melts were perfectly clear, the temperature was lowered at the rate of two degrees per minute, and at the same time the temperature was kept constant through the mixture by constant stirring. Upon the appearance of the first minute crystal, the temperature was carefully noted. Such a method permitted several repetitions so as to obtain a good check on the primary results.

Preparation of the Salts.

The salts used were Kahlbaum's "Zur Analyze" preparations, with the exception of the lithium nitrate which was made by J. T. Baker. Preliminary examinations of the purity of the salts made it clear that nothing was to be gained by recrystallization, except that it was found necessary to recrystallize the lithium nitrate from nitric acid solution because the original salt gave a basic reaction with rosolic acid.

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[1] The following are the ternary systems which have been completely investigated: The system $Ca(NO_3)_2$, KNO_3 and $NaNO_3$ by Menzies and Dutt, THIS JOURNAL, 31, 1366 (1909). The system $LiNO_3$, KNO_3 and $NaNO_3$ by Carveth, *J. Phys. Chem.*, 2, 206 (1898). The system Al_2O_3, SiO_2 and CaO in the Geophysical Laboratory, Washington, D. C., by Rankin and Wright, *Am. J. Sci.*, 39, 1–79 (1915).

[2] Roozeboom, *Z. physik. Chem.*, 15, 143 (1894); Bancroft, *J. Phys. Chem.*, 24, 441.