THE HYDROCHLORIDE METHOD FOR THE DETERMINATION OF ALKALOIDS¹

By GEO. D. BEAL AND ST. ELMO BRADY

The present research was undertaken in the hope of securing a method for the precipitation of alkaloids which might be used as a combined gravimetric and volumetric analytical method, each end point serving as a check on the other. The method, in brief, consists in the extraction of the alkaloid with ether, precipitation from this solution as the hydrochloride by passing in dry, gaseous, hydrochloric acid, evaporating off the ether and weighing the salt, then dissolving the hydrochloride in water and titrating the hydrochloric acid with standard alkali, using phenolphthalein as indicator. The results obtained have been checked in each case by a standard method already in use, that of the U. S. P. VIII being used wherever available.

The first sample used consisted of conium seeds from the grounds of the College of Pharmacy building in Scio, Ohio. These were ground to No. 60 powder and extracted with a mixture of ether, alcohol and ammonia. The extract was shaken out with *N*/1 sulfuric acid to free the alkaloid from coloring and fat. The acid solution, which contains the alkaloids, was made alkaline with ammonia and the freed alkaloids extracted with ether.

The ether extract, colorless and free from fat, was saturated with gaseous hydrochloric acid, which had been dried by passing through concentrated sulfuric acid. On this treatment, the hydrochloride of the alkaloids separated, partly as a crystalline solid and partly as an oil. When the ether was evaporated on the water bath crystalline coniine hydrochloride was left behind, which was weighed and the percentage of coniine calculated for the drug. The salt was then dissolved in water and the solution titrated with standard alkali to the phenolphthalein end point, and the result calculated on the assumption that the salt formed was the monohydrochloride.

PER CENT CONIINE	Sample A ₁	Sample A ₂	Sample A ₃
By weight.....	1.74	1.72	1.725
By titration.....	1.67	1.67	1.70

To test the accuracy of the above results the seeds were then analyzed by the U. S. P. method, in which

the ether extract is evaporated with an excess of aqueous hydrochloric acid and the dry salt weighed, with the additional step added that this U. S. P. residue was dissolved and titrated as above described.

PER CENT CONIINE	Sample B ₁	Sample B ₂	Sample B ₃
By weight.....	1.73	1.72	1.74
By titration.....	1.70	1.705	1.69

Some redistilled coniine was dissolved in ether, precipitated, weighed and titrated as above described.

GRAMS CONIINE	Sample C ₁	Sample C ₂
Theoretical.....	0.125	0.030
By weight.....	0.12525	0.03006
By titration.....	...	0.02887

Sample C₂ was treated with silver nitrate in the presence of nitric acid and the silver chloride formed weighed and calculated for the monohydrochloride of coniine.

GRAMS AgCl	Theory, 0.0084	Found, 0.0085
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These last results serve to confirm the nature of the precipitate obtained.

Because of our success in this work we determined to extend the field, and have applied the method to the analysis of tobacco and colchicum root. The extraction followed was practically the same as in the case of the conium. In each case the oil was observed, as well as the crystalline salt, on the addition of the gaseous HCl.

PER CENT ALKALOID	COLCHICUM ROOT		TOBACCO	
by method	Sample D ₁	Sample D ₂	Sample E ₁	Sample E ₂
New { Gravimetric.....	2.22	2.30	2.65	2.61
Volumetric.....	2.19	2.28	2.66	2.49
Standard (U. S. P.).....	2.25	2.28 (Kisslings)	2.64	2.67

This work is being continued on other alkaloidal drugs, and in addition the nature of the insoluble oil is being investigated. From some recent work on the nature of some oils obtained with amines, it appears that it is simply a higher hydrochloride, as some of the latter have been obtained carrying as many as ten molecules of HCl. If the oil be washed with cold ether until it is free from free HCl, it still fumes in moist air, and if it be placed in a vacuum desiccator with some stick potassium hydroxide, it is converted to the monohydrochloride, and the alkali becomes encrusted with potassium chloride.

LABORATORY OF ORGANIC ANALYSIS
UNIVERSITY OF ILLINOIS, URBANA

LABORATORY AND PLANT

EXTRACTION AND RECOVERY OF RADIUM, URANIUM AND VANADIUM FROM CARNOTITE²

By CHARLES L. PARSONS, R. B. MOORE, S. C. LIND, O. C. SCHAEFER
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The work of the Bureau of Mines on radium began in the fall of 1912. A preliminary report published in the summer of 1913³ outlined the conditions of mining and the wastes involved in the carnotite ore

¹ Presented at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

² Authors' abstract from *Bull.* 104, U. S. Bureau of Mines. The bulletin contains complete detail descriptions of operations with full drawings both of floor plan and sections of the radium plant, as well as half-tones of plant and apparatus.

³ *Bull.* 70, Prel. Rept., "Uranium, Radium and Vanadium," by R. B. Moore and K. L. Kithil.

region of the West. As a result of this investigation, Dr. Howard A. Kelly, of Baltimore, and Dr. James Douglas, of New York City, were interested, and they incorporated the National Radium Institute. This institute leased certain carnotite claims in Long Park, Col., with the right to extract 1,000 tons of carnotite ore therefrom. The National Radium Institute arranged with the Bureau of Mines for a coöperative investigation of the methods of extracting radium from this ore and the saving of the wastes by the concentration of the low-grade ore formerly thrown on the dump.

Sufficient funds were furnished to be expended under the direction of the Director of the Bureau of

Mines, and the first plant was built in the spring of 1914, beginning production on an experimental basis in June, 1914. The result of the preliminary investigation was so successful that the institute authorized the construction of a second and larger plant which began operations in February, 1915; the two plants have been run continuously since that time.

The object of the investigation was to procure an adequate supply of radium for the treatment of cancer in the two hospitals connected with the Radium Institute and to develop methods of extraction whereby the miners might obtain a more adequate return for their ore, which, before this investigation began, had been sold largely to foreign manufacturers. Incidentally, methods have been developed for the preparation of sodium uranate, uranium oxide, and iron vanadate—by-products from the extraction of carnotite ore. Before the Bureau's operations began, several methods, the details of some of which have been kept secret, had been devised, for the extraction of radium from pitchblende and from carnotite.

FIG. 1.—RADIUM PLANT: NATIONAL RADIUM INSTITUTE

These involved (1) the use of an acid leach; (2) the use of an alkaline leach followed by acid; and (3) fusing the ore with some material that would make extraction of the valuable contents possible. The acid leaches had been extensively used abroad and had shown an extraction of not over 70 per cent and probably little over 50 per cent of the radium content, owing to the fact that the ores contain sulfates, and any radium sulfate present was not removed under these conditions. The alkaline leach followed by an acid leach would probably remove more radium but involves such grave difficulties of filtration that it seemingly has not been put into commercial use. Fusing the ore with sodium sulfate was long employed on pitchblende¹ and has been used in Australia by Radcliffe in treating carnotite that is obtained at Olary, South Australia. This carnotite, being mixed with ilmenite, is very different from the American carnotite. Fusion with sodium carbonate has also

been employed in this country on carnotite ores but has the great disadvantage that it carries a large part if not all of the silica into solution. This adds greatly to the cost of operation and tends to give radium-barium sulfates of a rather high degree of impurity which require special treatment. From the best accounts available, it appears that this method does not successfully extract more than 70 per cent of the radium present in the ore.

METHOD OF ORE TREATMENT

The method devised by the Bureau of Mines is based upon the fact that strong, hot nitric or sulfuric acid dissolves radium-barium sulfates in considerable quantities, as well as the other soluble constituents of the ore. Hence the radium-barium sulfate left behind when dilute acids are used for leaching is obtained in solution and recovered. The use of strong, hot nitric acid, although it presented many difficult problems of chemical engineering, was chosen because the radium-barium sulfate could be precipitated at once in a remarkably pure form and the nitric acid could be largely recovered in the form of sodium nitrate and used again. Accordingly a nitric acid plant was built in connection with the radium plant and has been regularly operating since February, 1915.

In the Bureau of Mines method, the ore, pulverized to 20 mesh, is fed into an earthenware boiling kettle containing 38 per cent nitric acid. The nitric acid (121 lbs. HNO_3 diluted to 38 per cent) is brought nearly to boiling by means of steam passed through a glass tube. When the boiling point has been nearly reached the ore is added a shovelful at a time and the whole stirred, heating being continued. After the ore has all been added, heating is continued for 15 minutes when the mass is run on to an earthenware filter and the nitric acid separated from the ore by suction. The ore is re-treated with hot nitric acid of one-third the original strength, and is then washed with hot water. This treatment brings into solution nearly all of the uranium, about 50 per cent of the vanadium, and practically all of the radium present in the carnotite. The residue is discarded. The filtered solution is stirred, and sodium hydroxide is run in slowly with the object of reaching as nearly as possible the neutral point without forming a precipitate. If too much sodium hydroxide is added, both iron and vanadium are precipitated, discoloring the radium-barium sulfate. On the other hand, if not enough sodium hydroxide is added, the acid remains too strong and the solvent action of the nitric acid on the radium-barium sulfate is not sufficiently decreased. By a little practice the right point is easily obtained. Barium chloride is then added in the proportion of 2 lbs. of BaCl_2 to 1 ton of ore and is thor-

¹ Haitinger, Luding and Ulrich, *Bericht, über die Bearbeitung der Pechblend-Rückstände*, K. K. Akad. Wissenschaft., **117** (1908), 619.

oughly stirred in, and 15 lbs. of sulfuric acid to 1 ton of ore are then added. As the ore contains some barium it is necessary to add only a comparatively small amount of this material to accumulate the radium. The whole mass is vigorously stirred for 1 hour; the solution is then elevated to conical tanks where it is allowed to settle, usually for 3 to 4 days. The supernatant liquid is siphoned off for the recovery of uranium and vanadium and the radium-barium sulfates are collected on an earthenware filter, washed, treated with dilute sodium hydroxide, and dried.

RADIUM REFINING

One of the most important features of the Bureau of Mines method is that the radium-barium sulfates first precipitated are of high grade, comparatively free from impurity, and are ready for immediate conversion into chlorides without further purification.

FIG. II—EXTRACTION POTS FOR CARNOTITE ORE

The amount of radium in these sulfates has averaged about 1 mg. of radium element per kilogram of material. It was early found in the work of the bureau that the older methods of converting radium-barium sulfate into soluble form were unnecessarily tedious for the material produced. Accordingly other methods of reduction were tried and it was finally determined that the best method to use is reduction with carbon in graphite crucibles. For this purpose the purest possible charcoal is used, about one-fifth the weight of the total sulfates being taken. The charcoal is mixed with the sulfates in a ball mill and is then transferred to a No. 100 graphite crucible and heated for 7 to 8 hours to a temperature around 800° C. Reduction takes place readily, the carbon monoxide burning out at the spout of the crucible. Three crucibles are heated in the same furnace. A reduc-

tion of over 90 per cent is usually obtained. The radium-barium sulfide is dissolved in pure hydrochloric acid and the residue of unconverted sulfate is re-treated in like manner. The solution should, of course, be performed out doors or under a hood with a good draft, especially as the hydrogen sulfide sometimes catches fire spontaneously; the danger is minimized if the residue is slowly added to the acid in an open vessel. In the re-treatment of the residues a third residue is also obtained. As there is a tendency to an accumulation of lead and other impurities in these residues, it is advisable to fuse the third residue with sodium carbonate rather than to attempt to reduce in the ordinary way with carbon. As the weight of the second residue is only 1 or 2 per cent of the original radium-barium sulfate treated, this special treatment is required only once or twice

FIG. III—STONEWARE FILTERS FOR FILTERING HOT NITRIC ACID SOLUTIONS

a year. The acid filtrate from the radium-barium sulfate is an almost saturated solution of radium-barium chloride and is ready for fractionation. Fractionation takes place much more rapidly in strong hydrochloric acid solution than it does if the solution is nearly neutral. However, the obtaining of containers that will withstand hot solutions of hydrochloric acid is difficult. Ware sufficiently resistant has been found in the silica-lined, acid-proof apparatus made by the Danto Rogeat Company, Lyons, France, and steam-jacketed kettles made of this ware have now been in use for over a year with almost no evidence of erosion.

For the first crystallization, steam-jacketed kettles of 250 liters capacity are preferable although in a series of five the capacity of the last two need not exceed 200 liters. The evaporators are placed under hoods in order to remove acid fumes, and the evapora-

tion is so conducted that the crystals move in one direction and the mother liquors in the other, the crystals from a given evaporation being dissolved in the mother liquors from the kettle second preceding. The crystallization factor of hydrochloric acid solutions averages between 1.5 and 1.6, *i. e.*, if 50 per cent of the barium chloride is removed there will be 50 per cent more radium in the crystals remaining, or if 50 per cent of the barium chloride is crystallized out there will be 50 per cent more radium in the crystals than in the liquor left behind. In a short time, therefore, the crystals in these larger kettles can be brought to a strength of 4 to 10 parts of radium per million; at this stage the crystals are taken from the plant to the laboratory for crystallization in smaller apparatus of the same general type.

The salts of most metals such as iron, aluminum, and vanadium that may occur with the radium-barium solutions as impurities pass into the mother liquors and give no difficulty in the richer radium fractionations. Lead is, however, an exception and

water, the solution is made neutral with ammonia, and the lead is precipitated with ammonium sulfide. The solution is then filtered, and powdered ammonium carbonate is added until all of the barium has been precipitated as carbonate. The precipitate, of course, also contains radium as carbonate. It is washed and dissolved in chemically pure hydrobromic acid, after which crystallization proceeds, an excess of hydrobromic acid also being desirable for the rapid separation of radium from barium. Usually 10 or 12 fractionations are required in the form of bromides to bring the radium up to a strength of from 1 to 4 per cent radium bromide, the factor of concentration for each step in the hydrobromic acid solution being about 2 to 2.2. This makes rapid crystallization possible. Every two or three days the strong crystals are placed aside until the end of the month when they are mixed together in one lot and crystallized in hydrobromic acid solution to high concentration. Three or four crystallizations only are necessary to bring the major part of the radium to a concentration of 60 to 80 per cent radium bromide. One of the surprises of the radium work has been the ease with which separation of radium from barium is brought about. The crystallization is rapid and no difficulty whatever has been experienced in obtaining a high-grade material.

The bromide can be easily converted again into the chloride by one or two evaporations with hydrochloric acid and in this form can be sealed in small glass tubes for transportation. The recovery of radium from carnotite shows so high an efficiency that over 90 per cent of the radium present in the ore may be recovered.

SEPARATION AND PURIFICATION OF URANIUM

The acid solution from which the radium-barium sulfate has been precipitated is run directly from the settling tanks into large vats containing an excess of boiling sodium carbonate solution. Under these conditions the uranium and vanadium go into solution as sodium uranyl carbonate and sodium vanadate. For a solution from an ore containing 2.5 to 3 per cent uranium oxide, 250 lbs. of sodium carbonate in excess of that necessary to neutralize the acid originally used is required. This means about 650 lbs. sodium carbonate per ton of ore. It is important that the sodium carbonate solution be hot and be vigorously stirred; that the acid solution be added slowly; and that the boiling be continued for some time. Only in this way will the solution of uranium and vanadium obtained be anywhere near complete. Of course at the same time iron, aluminum, and calcium present in the solution are precipitated, and these are filtered off in filter presses, washed, and thrown away. The filtrate from the iron, aluminum, and calcium precipitate carrying uranium and vanadium, is partly neutral

FIG. IV—VIEW IN NEW PLANT SHOWING FILTER PRESSES

requires special treatment although it might be expected that when the radium-barium sulfide is dissolved in hydrochloric acid, the copious evolution of hydrogen sulfide would remove the lead as lead sulfide. This does not occur owing to the high concentration of barium chloride and the lead can be completely removed only after neutralization with ammonia when the addition of ammonium sulfide causes it to be thrown down in an insoluble condition.

The crude radium-barium chloride containing 4 to 10 parts radium element per million is brought from the plant to the laboratory where it is dissolved in water in large porcelain dishes, and hydrochloric acid is added. After the solution has stood over night it is filtered to remove the small part of lead that has been separated as chloride, and to remove whatever carbon and barium sulfate may have escaped previous filtration. After three or four recrystallizations of the chloride, the chloride crystals are dissolved in

ized with nitric acid until a yellow precipitate just begins to form. At this point sodium hydroxide is added to the hot liquid until uranium is completely precipitated as sodium uranate. The sodium uranate at this point generally carries 7 to 9 per cent vanadic oxide, and must be precisely treated to remove the vanadium therefrom. This is best done by fusing

described practically all of the uranium is dissolved in the nitric acid, only a small part (averaging 2.3 per cent) remaining in the insoluble residue because of incomplete washings. The loss of uranium in the iron-calcium precipitate runs usually from 10 to 15 per cent of the material originally present in the ore. The recovery of uranium as sodium uranate has varied between 75 to 94 per cent of the uranium present in the ore, the average on the last 10 carload lots treated being 84.4 per cent.

VANADIUM—The conditions making for the highest recovery of radium, which is the real value of the ore, do not generally coincide with the conditions necessary for the highest recovery of vanadium. It has accordingly been necessary to sacrifice the vanadium in order to get large recoveries of the more valuable element. Strong nitric acid tends to cause separation of vanadium from the solution, even after it has been dissolved, and this separated vanadium is filtered with difficulty and tends to decrease the radium extraction.

More prolonged treatment with nitric acid would dissolve more vanadium but this is not desirable and it has been found best to use just as short a treatment with nitric acid as will insure the

FIG. V—OIL FURNACE FOR REDUCTION OF BARIUM SULFATE AND PURIFICATION OF SODIUM URANATE

the sodium uranate with salt in large, wrought-iron or steel crucibles. When the salt is dissolved in water it carries the vanadium in solution as sodium vanadate and leaves behind a practically pure sodium uranate.

RECOVERY OF VANADIUM

The filtrate from the sodium uranate together with any sodium vanadate dissolved out of the sodium uranate by fusion with salt is brought to the boiling point and neutralized with nitric acid, the boiling being continued long enough to eliminate carbon dioxide. At this point a solution of ferrous sulfate is run into the hot solution while under agitation by means of compressed air. As a rule about 75 lbs. of ferrous sulfate are required per ton of ore treated. The heating of the solution is stopped before the addition of the ferrous sulfate is complete, for if heating is continued longer a complete precipitation of the vanadium is not obtained. Iron vanadate obtained under these conditions usually contains 32 to 33 per cent V_2O_5 . If the solution is slightly alkaline the percentage of V_2O_5 diminishes, while on the other hand if the solution is slightly acid when precipitation begins, a much richer product can be obtained. This is accompanied, however, by a loss of vanadium, as some of it passes into the filtrate and causes difficulty in subsequent operations.

NITRATE RECOVERY

After precipitation and filtration of the iron vanadate, the solution remaining contains chiefly sodium nitrate with small amounts of sodium chloride and sodium sulfate. It is evaporated to dryness, the sodium nitrate being crystallized out in crystallizing pans and used again for the production of nitric acid.

RECOVERY AVERAGES

URANIUM—In the extraction process previously

FIG. VI—NITRIC ACID PLANT

complete extraction of the uranium. Fifteen minutes' heating in the extraction apparatus after complete addition of the ore is all that is necessary. Under these conditions, however, scarcely 50 per cent of the vanadium goes into the filtrate and 15 to 20

per cent is lost in the iron calcium precipitate. Accordingly the total average recovery of vanadium, including that from the sodium uranate, has been a little less than 30 per cent of that present in the ore. The recovery of vanadium has barely covered the expense incident thereto.

SODIUM NITRATE—By using nitric acid for neutralization throughout the process, a large proportion of the nitric acid used both for the solution of the original ore and for the neutralization of the alkaline solutions is recovered in the form of sodium nitrate. During the months of May, June, and July, for which full figures are available, the average recovery was 87.5 per cent (minimum 84.87 and maximum 90.4). This high recovery has of course greatly decreased the expense of the nitric acid used in the operations as a nitric acid plant was built to work up the recovered nitrate. During May, June, and July, 1915, the expenditure for nitric acid was only 2.411 cents per lb. of 100 per cent acid.

RADIUM—When an element exists in an ore in the proportion of 1 part to 200,000,000, its extraction and recovery present difficulties not ordinarily encountered in metallurgy. A recovery of 60 to 70 per cent, or even 50 per cent might, under such conditions, appear to be satisfactory. A much larger recovery than 70 per cent is undoubtedly exceptional. The unusually high recovery of 90 per cent and over of the radium present gives the nitric acid method its real value.

COST DATA

In figuring the total costs of the first 4,258 mgs. of radium element produced, the uranium and vanadium products may be either included or excluded. By subtracting the actual costs connected with the production of the uranium and vanadium compounds from the total cost, a close approximation of the cost of radium, provided the uranium and vanadium were not recovered, will be obtained, but such a figure will not be exact, as under the changed conditions various factors would enter in, the effects of which can only be estimated. On this basis the average cost of 1 gram of radium element, including the more expensive early treatment, is as follows:

COST OF RADIUM PRODUCTION TO AUG. 1, 1915

Operating costs to Aug. 1:	
Total expenditures.....	\$129,907.42
Construction and equipment.....	52,453.60
	<hr/>
Cost of ore treated.....	\$ 77,453.82
Amortization of plant and equipment at 20 per cent per annum.....	69,767.99
Cost of U. S. Bureau of Mines cooperation (plant dept.)..	9,065.90
Cost of refining 2611.44 mgs. radium element (est.)....	13,628.38
	<hr/>
	5,353.00
	<hr/>
	\$175,269.09
Less costs in connection with the production of the uranium and vanadium compounds.....	19,947.00
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TOTAL COST OF 4,258 MGS. RADIUM ELEMENT.....	\$155,322.09

As already stated, refining losses have almost certainly been less than 2 per cent and probably less than 1 per cent. In order, however, to be on the safe side, an allowance of 3 per cent is made for such losses; 4,258 mgs. less 3 per cent is 4,131 mgs., which represents the radium fully recovered as high-grade salts. The average cost of 1 gram of radium element has therefore been \$37,599. It should be remembered that this

cost included the proportionally much higher operating costs of the smaller experimental plant and that the first 2 grams of radium extracted cost considerably more per gram than the last 3 grams; also there have been extracted 31,650 lbs. of uranium oxide and 11,528 lbs. of vanadium oxide. This material has all been contracted for and in part delivered. The returns from its sale will considerably more than cover the cost of its production, and this profit, together with other credits, will ultimately lower by several thousand dollars the cost per gram of radium.

As the price of ore is variable, the question will naturally arise as to the influence of the price of ore on the figures given above. A simple calculation will show at once that the cost of extracting radium, exclusive of the cost of the ore, has been \$20,710 per gram. The ore included in the figure of \$69,767.99 cited for the cost of ore used in the investigation herein outlined was partly purchased before the war and partly mined by the National Radium Institute at Long Park, Col. As 723.97 tons were used, the average cost was \$96.36 per ton. If the ore had cost \$120 per ton, the cost of radium would have been \$41,742 per gram, and for every additional amount of \$20 per ton above these figures the cost of radium would increase approximately \$4,000 per gram.

U. S. BUREAU OF MINES, WASHINGTON

A METHOD FOR THE DETERMINATION OF THE STRENGTH AND BAKING QUALITIES OF WHEAT FLOUR

By C. H. BAILEY

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It is quite generally recognized that some form of practical test is necessary in determining the baking quality of wheat flour. Chemical analyses are of value, but the relation between composition and quality is not perfectly understood despite the great amount of research which is directed toward the solution of this problem. It is also probable that if infallible chemical tests were announced which would serve to indicate the relative baking value of flour, they would be too numerous, and require too much time and technical skill to make their use possible on the extended scale necessary in the flour trade. In other words, there are so many factors involved in the chemistry of baking strength, and the determination of all of these would, in most instances, be so difficult that actual baking tests would probably be resorted to in the majority of cases where rapid and voluminous work must be disposed of. For these reasons the development of methods for conducting careful and accurate measurements of flour quality in a practical way are justifiable and necessary.

In developing practical flour tests, a comprehension of the purposes for which the flour is to be used, and of the manner in which it is ordinarily treated in trade practices, are essential. At the present time flours of good baking "strength," color, absorption, flavor and odor are in greatest demand by the bread-making trade. The term "strength" has been used rather loosely at times, although the definition of Humphries