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**METHODS OF ANALYSIS USED IN THE
TREATMENT OF COLORADO PLATEAU
CARNOTITE FOR AGE STUDIES**

By
Robert G. Milkey

August 1952

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uranium deposits.**



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UNITED STATES DEPARTMENT OF THE INTERIOR
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METHODS OF ANALYSIS USED IN THE TREATMENT OF THE COLORADO
PLATEAU CARNOTITE FOR AGE STUDIES*

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*This report concerns work done on behalf of the Division
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METHODS OF ANALYSIS USED IN THE TREATMENT OF COLORADO
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ABSTRACT

This paper presents the methods of chemical analysis that were used to aid in mineralogic studies of Colorado Plateau carnotite for purposes of determining age of materials.

Detailed methods were carried out to establish the validity of the procedures, together with the more important analytical techniques and precautions that are necessary to insure satisfactory analyses.

INTRODUCTION

In connection with mineralogic studies of Colorado Plateau carnotite ores, for purposes of determining age of materials, standard chemical procedures were used although some modifications were found necessary in the application of these methods to carnotite ores.

These changes will be of interest to those engaged in similar types of work.

For example, it was found that the dithizone used to extract the lead from carnotite was oxidized completely by some constituent of the ore, and this difficulty had to be overcome before the method could be made applicable to the analysis.

In addition to the modified procedure for quantitative determination of lead, also included is the procedure devised for the preparation of lead iodide from carnotite ores for purposes of lead-isotope analysis, as well as a volumetric and a fluorimetric method for determining the uranium content of carnotite.

This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

PREPARING LEAD IODIDE FOR ISOTOPE ANALYSIS

I. Solution of sample

A. For samples of relatively high lead content

1. Five or ten grams of carnotite ore were placed in a 50-ml beaker, and 20 ml aqua regia were added.
2. The sample was digested for 1 to 2 hours on the hot plate, and filtered through no. 42 filter paper. Complete solution of the sample was not accomplished, because interest centered mainly in the acid-soluble constituents.
3. The filtrate was diluted with sufficient glass-distilled water to make a 0.3 N acid solution.

B. For samples of low lead content

1. Three hundred or four hundred grams of ore, depending on the lead content, were weighed into a 600-ml beaker.
2. To it were added 40-ml aqua regia, and the sample was digested on the hot plate for several hours.
3. Then 400-ml of glass-distilled water were added, the sample stirred vigorously, and allowed to settle overnight.

4. The solution was filtered through a no. 42 paper, catching the filtrate in a 2-liter beaker.
5. The filtrate was diluted with glass-distilled H_2O to make a 0.3 N solution (volume of solution was about 1720 ml).

II. Separation of lead sulfide

1. The solution was gassed with H_2S for one hour. It was left standing overnight tightly covered, and gassed again for 10 minutes.
2. The solution was filtered through no. 41 filter paper, and washed with 0.3 N HCl saturated with H_2S .
3. The paper and precipitate were placed in a 50-ml beaker. To it were added 30-ml (1 + 1) HNO_3 , and 2 ml conc. H_2SO_4 .

III. Separation of lead sulfate

1. The solution was evaporated to a volume of 5-ml, transferred to a hot plate, and taken to fumes of H_2SO_4 .
2. Fuming HNO_3 was added, dropwise, to the covered beaker, allowing the nitrous oxide fumes to disappear between additions.
3. When sulfur and carbon were destroyed, the solution was allowed to cool, then diluted with H_2O to a volume of 25 ml, stirring well.
4. Again the solution was evaporated to fumes of sulfuric, and allowed to fume strongly, then cooled.
5. The solution was diluted to 20 ml with H_2O , stirring the solution vigorously. It was left to stand 4 hours.
6. The supernatant liquid was filtered off with a medium-porous filter stick, and the precipitate washed twice with (3 + 97)

H_2SO_4 . Wash liquid was drawn off with the filter stick.

7. Ten milliliters of 20 percent ammonium acetate solution (previously made lead free by means of dithizone extraction) were added and the solution warmed gently on the hot plate to dissolve the PbSO_4 . (The filter stick was washed thoroughly before removing from solution.)

IV. Second precipitation of lead sulfide

1. The solution was diluted to 25-ml with H_2O , and gassed for 20 minutes with H_2S (or until the PbS precipitate coagulated).
2. The beaker was covered securely, and left to stand for 1 or 2 hours.
3. The PbS was filtered onto a no. 40 filter paper, and washed with 0.3 N HCl saturated with H_2S .
4. 5-ml aliquots of hot (1 + 1) HNO_3 were poured through the filter until all the PbS was dissolved.

V. Precipitation of lead iodide

1. The solution was evaporated to dryness in a 30-ml beaker on the hot plate.
2. After 2-ml of 10 percent KI were added, the solution was allowed to digest on the steam bath until PbI_2 was precipitated completely. (Sample was stirred well during the digestion.)
3. The yellow PbI_2 was transferred to a small centrifuge tube using a minimum of cold wash water.
4. The precipitate was washed by adding a few milliliters of ice-cold water to the centrifuge tube, stirring the precipitate at the bottom of the tube by centrifuging for

several minutes, and drawing off the supernatant liquid by means of a medicine dropper. The washing was repeated.

Discussion of procedure.--Occasionally the nature of the samples made it advantageous to modify the above procedure. For instance, several samples consisted of uraninite, pitchblende, or even practically pure lead that is used as standard material in spectrographic analysis. For these samples, comparatively richer in lead, the first sulfide precipitation was omitted. Thus, H_2SO_4 was added to the solution of the sample directly, and $PbSO_4$ precipitated. The precipitate was washed, dissolved in 20 percent hot NH_4Ac solution, and gassed with H_2S for 15 minutes, to precipitate PbS . Succeeding steps were similar to the preceding procedure.

Also, when the amount of PbI_2 obtained was relatively large, the precipitate was washed in the beaker. Two 3-ml aliquots of ice-cold water were added to the precipitate, and after stirring, the supernatant wash liquid was drawn off by means of a fine porosity filter stick. Finally, the precipitate was dried in the beaker at 110 C, and transferred to a small tube.

Special pains were taken to insure that a minimum of common lead was introduced to the sample by way of the reagents used:

The C.P. grade of hydrochloric and nitric acids were distilled in an all-glass apparatus.

The NH_4Ac solution was extracted with dithizone until it was observed to be lead free.

By test the C. P. grade H_2SO_4 was ascertained to have an insignificant lead content.

Ordinary distilled water in the laboratory was found to contain an average of 7 micrograms of lead per liter. For some of the samples, the quantities of water introduced would carry significant quantities of common lead. Distilled water was accordingly redistilled in all-glass apparatus.

KI was found by spectrographic analysis to be free of lead.

It will be noted that no carrier was added to the solution to help precipitate lead sulfide even when the lead content was very low. The precipitation of the sulfides of copper and other heavy metals invariably was found heavy enough to serve that purpose without the addition of further material.

In precipitating PbI_2 , the concentration of the KI solution was kept at 10 percent or below. When the concentration of the KI solution is too high, a double salt, such as $K(PbI_3)$, is formed. However, upon the addition of water with constant stirring, the double salt dissolves, and PbI_2 is then precipitated.

QUANTITATIVE LEAD DETERMINATION

I. Solution of sample

- A. A 1-g sample was weighed into a 50-ml beaker. To it were added 10-ml (1 + 1) HNO_3 , and the solution was allowed to digest on the hot plate for 1 to 2 hours. Complete decomposition of the sample was not accomplished, because interest centered mainly in the acid-soluble constituents.
- B. Insoluble material was filtered off on a small no. 42 filter paper and washed with water.

- C. The filtrate was transferred to a 100-ml volumetric flask, made up to volume, and a 10-ml aliquot transferred to a 30-ml beaker.

II. Preliminary extraction of lead

- A. To the solution was added:
1. 0.5-ml hydroxylamine solution. The solution was warmed gently, then cooled.
 2. 2-ml sodium citrate solution.
 3. Three drops phenol red indicator.
- B. The solution was neutralized with NH_4OH , and an excess of 2 drops was added.
- C. To the solution was added 2.5-ml 10-percent KCN solution.
- D. The solution was transferred to a 60-ml separatory funnel, rinsing the beaker thoroughly.
- E. The lead was extracted with dithizone, beginning with a 10-ml portion of dithizone solution (48 mg/liter), shaking the funnel for 1 minute. Extractions were continued with 5-ml portions until the dithizone layer appeared unchanged in color.
- F. To the accumulated dithizone layer were added 25-ml (1 + 99) HNO_3 , and the separatory funnel was shaken for 1 minute. When the organic layer was drawn off and discarded, the Pb remained behind in the aqueous layer.

III. Final extraction of lead.

- A. Exactly 5-ml ammonia-KCN solution and 15-ml of standard dithizone solution (8 mg/liter) were added to the aqueous solution, and the separatory funnel shaken for 1 minute.

- B. The layers were allowed to separate, and the dithizone layer drawn off into a glass-stoppered test tube.
- C. After a few minutes a part of the dithizone layer was transferred from the test tube to a spectrophotometer tube which had been cleaned and dried.
- D. Density of the solution was read at a wavelength of 520 $m\mu$ and slit width of 0.03 mm.

Discussion of procedure.--The composition of the solutions used in the analysis was as follows: sodium citrate solution, 50 g in 100-ml H_2O ; potassium cyanide, 10 percent solution; hydroxylamine hydrochloride, 20 g in 100-ml H_2O ; ammonia cyanide, 20 g KCN and 150-ml concentrated ammonia diluted to 1 liter (an addition of 5-ml produces a pH of 9.1 to 9.5 for the final extraction).

Necessary precautions were taken to reduce to a minimum the introduction of lead by way of these reagents:

HNO_3 and HCl were distilled in all-glass apparatus
Water used was redistilled in glass apparatus
 NH_4OH was prepared from NH_3 gas and glass-distilled water
KCN used was determined to be acceptable from the standpoint of lead content
Sodium citrate was stripped of all lead by means of dithizone extraction
Hydroxylamine was purified by the addition of sodium diethyldithiocarbamate and extraction of the metal carbamates with chloroform

Preliminary experiments established the fact that dithizone accomplished good extraction of lead under existing conditions. To carnotite samples of predetermined lead content, known amounts of lead were added by means of a standard lead solution, and total lead content

then determined. The results obtained were:

Sample no.	Pb content (γ)	Pb added (γ)	Pb total (γ)	Pb determined (γ)
1	5.7	10	15.7	15.5
2	5.7	5	10.7	11.1
3	5.7	10	15.7	15.5
4	6.7	4	10.7	10.7

In most of the samples there appeared to be some constituent which attacked and decolorized to varying degrees the preliminary extraction. In order to eliminate this factor, it was hoped that a preliminary separation of Pb could be made by means of a sulfide precipitate. To 50-ml of solution containing various amounts of lead, 1 g of Cu^{++} was added to act as a carrier in the sulfide precipitate. Before gassing with H_2S , the pH of the solutions were adjusted (pH meter) to amounts shown in the following table. The sulfide precipitate was then dissolved in HNO_3 , and the lead determined with dithizone.

Pb in sample (γ)	Pb retrieved (γ)	Net Pb retrieved (γ)	Notes
0	0.3		pH = 3+
5	1.5	1.2 (24 percent)	pH = 3+
10	8.9	8.6 (86 percent)	pH = 6
14	12.0	11.7 (83 percent)	pH = 6
15	12.8	12.5 (83 percent)	pH = 3+

In view of these figures this step was abandoned.

Further investigations into the type and extent of oxidation of the dithizone were made as follows:

0.5 ml of hydroxylamine was added, and the solution extracted with 8 successive 10-ml portions of dithizone solution, of strength 16 mg/liter. Each portion of extraction solution was more or less effectively decolorized. When the amount was increased three-fold, to 1.5 ml of hydroxylamine, the results were much the same.

The strength of the dithizone solution was next increased in order to provide more dithizone to offset the oxidation in solution. When the concentration was 48 mg/liter, extraction with one 10-ml portion and five 5-ml portions showed appreciable decolorization in the first extractions, dropping to a very slight amount in the last extractions.

The amount of hydroxylamine was increased seven-fold to 3.5 ml and in conjunction with the greatly more concentrated dithizone solution, an extraction with one 10-ml portion and two 5-ml portions showed very little oxidation. Thereafter, the preliminary extraction of lead was made with a dithizone solution that had a concentration of 48 mg/liter. As evidenced by the unchanged color of the last portion, dithizone in excess of the amount necessary to effect complete lead extraction was present for each sample.

The standard curve for lead was constructed by extracting portions of a solution of $\text{Pb}(\text{NO}_3)_2$ by the standard procedure, and determining the density of the final extract solution by means of the spectrophotometer. The resulting curve showed a linear relationship between lead content (0-20 micrograms), and density of solution, at a wavelength of 520 m μ and a slit width of 0.03 mm.

DETERMINING URANIUM

Volumetric procedure for more than 1 percent uranium

I. Solution of the sample

1. A 1-g sample was weighed into a 100-ml beaker. To it were added 40-ml (1 + 1) HNO_3 and 5-ml H_2SO_4 , and the sample was digested on the hot plate for 1 to 2 hours.
2. The solution was filtered through no. 42 filter paper, into a 50-ml beaker and evaporated to fumes of sulfuric acid. It was then cooled, water was added, and the procedure repeated, allowing the solution to fume strongly.
3. To the solution were added 15-ml HCl , and the volume was adjusted to 170-ml.
4. The solution was cooled in an ice bath and then transferred to a 600-ml separatory funnel.

II. Precipitation with cupferron

1. To the funnel was added 100-ml chilled 6 percent cupferron solution (6 g cupferron + 100-ml H_2O), and the funnel was shaken for a few seconds.
2. 150-ml cold ethyl acetate was now added, and the separatory funnel shaken for 1 minute.
3. The water layer and ethyl acetate layer were drained into separate beakers.
4. The water layer was returned to the separatory funnel, and 100-ml chilled ethyl acetate were added. The funnel was shaken for 1 minute, and then the layers were allowed to separate.

5. The water layer was set aside, and both ethyl acetate portions combined in the separatory funnel. To the ethyl acetate was added 50 ml chilled 8 percent HCl, and the funnel was shaken for 15 seconds.
6. The layers were allowed to separate, and the aqueous layer was drawn off and saved. The ethyl acetate was then rejected.
7. The water layer used to clean the ethyl acetate was finally washed with 50 ml ethyl acetate in the separatory funnel. The ethyl acetate was rejected, and the water layer combined with the main portion reserved under step 7.

III. Oxidation of dissolved organic matter

1. The combination water layer was evaporated to half its volume, 20 ml conc. HNO_3 were added, and the evaporation was continued until the volume was approximately 25 ml. The solution was then transferred to a 50-ml beaker, and carried to fumes of H_2SO_4 .
2. From 1 to 3 ml fuming HNO_3 were added cautiously to the fuming solution, and the fuming continued until all organic matter had been removed. Finally heating was continued until dense fumes of H_2SO_4 were given off. The solution was diluted with 30 ml H_2O and digested to dissolve salts and then cooled.

IV. Precipitation of uranium hydroxide

1. Ammonium hydroxide was added slowly until a permanent precipitate formed. Then 2 ml in excess were added.
2. Some paper pulp was stirred into the solution, and it was filtered through no. 40 filter paper and washed with hot 2 percent NH_4NO_3 .

3. The precipitate and paper were ignited in a platinum crucible. A minimum of KHSO_4 was added to fuse the residue, and the melt was then leached out with 5 ml of 10 percent H_2SO_4 , and warmed on the steam bath.

V. Reduction of uranium and titration with KMnO_4

1. Final volume was brought to approximately 100 ml by the addition of 10 percent H_2SO_4 .
2. The solution was passed through the Jones reductor at the rate of 40 ml per minute, and the beaker and reductor were washed, first with 15 ml diluted (1 + 19) H_2SO_4 , and then with H_2O .
3. The solution was aerated for 5 minutes, and titrated with 0.03 N KMnO_4 to a pinkish-yellow endpoint.

NOTES:

1. The KMnO_4 was standardized by fusing a known amount of pure (99.96 percent) U_3O_8 with KHSO_4 in a platinum crucible, leaching out with 10 percent H_2SO_4 , passing it through the reductor, and titrating the reduced solution after aeration.

$$1 \text{ ml } 0.1\text{N } \text{KMnO}_4 = 0.01191 \text{ g U}$$

2. The results should be accurate to ± 0.5 percent of the total uranium.

Fluorimetric procedure for less than 1 percent uranium

A. Discussion:

1. The direct method depends on using very small samples to eliminate quenching of uranium fluorescence due to foreign elements.

2. The extraction method isolates the uranium by extraction of uranyl nitrate.

B. Direct method 1/

1. A sample weighing 0.2 g was placed in a 50-ml beaker. To it were added 20 ml of (1 + 1) HNO_3 , and the sample was digested on the hot plate for 1 to 2 hours.
2. The sample was filtered through no. 42 filter paper into a liter flask, and made to volume.
3. Depending on the approximate uranium content of the particular ore, some of the samples were further diluted in 100-, 200-, or 500-ml volumetric flasks.
4. In general the final size of sample used to prepare the fluoride phosphor was from 50 to 100 micrograms.
5. 3 g of flux, consisting of 9 percent NaF, 45 1/2 percent Na_2CO_3 , and 45 1/2 percent K_2CO_3 , by weight, were added, and the samples were heated for three minutes over a Meker burner, swirling to make a uniform fusion. After cooling the fused disc was removed intact from the crucible.
6. Fluorescence of the disc was determined in a fluorimeter that measures the fluorescence of the uranium in the flux, and a scale reading recorded.

C. Extraction method 2/

1. A 0.2-g sample was weighed into a 50-ml beaker.

1/ Grimaldi, F. S., and Levine, H., The rapid fluorimetric determination of uranium in low grade ores: AECD 2824, 1950.

2/ Fletcher, Mary H., A study of critical factors in the "direct" fluorimetric determination of uranium: U. S. Geol. Survey Trace Elements Investigations Rept. 130, 1950.

2. To it were added 20 ml (1 + 1) HNO_3 , and the sample was digested for 1 to 2 hours. The solution was then filtered through no. 42 filter paper into a 100-ml volumetric flask.
3. Depending on the uranium concentration of each particular sample, the solutions were further diluted, so that the final solutions were of such concentration that a 5-ml aliquot would contain between 1×10^{-7} and 5×10^{-7} g U and contain 15 percent by volume of HNO_3 .
4. The 5-ml aliquot was pipetted into a 30-ml glass-stoppered test tube, containing 9.5 grams uranium-free $\text{Al}(\text{NO}_3)_3$. The contents of the test tube were heated in a water bath until a clear solution was obtained.
5. To the cooled solution, 10 ml ethyl acetate were added, and the tightly stoppered test tube shaken for 1 minute.
6. After allowing the layers to separate, the ethyl acetate containing the extracted U was filtered through a no. 41 filter paper. A 5-ml aliquot was then pipetted into a 20-ml platinum crucible. The crucible was placed on a wet mat, and the ethyl acetate ignited and allowed to burn to dryness. Residual carbon was burned off over a flame.
7. To the crucible, 3 g of a flux consisting of 9 percent NaF, 45 1/2 percent K_2CO_3 and 45 1/2 percent Na_2CO_3 by weight, were added.
8. Samples were heated for 3 minutes over a Meker burner, swirling to make a uniform fusion. After cooling, the fused disc was removed intact from the crucible.
9. The disc was placed in a fluorimeter, and the degree of fluorescence on the instrument scale noted.

10. The amount of U was obtained by reference to a standard curve relating intensity of fluorescence of the discs with uranium content.

NOTE:

Accuracy of results from fluorimetric methods is approximately ± 5 percent.