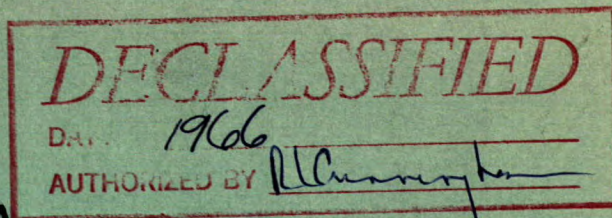


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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 66-53

**THE DETERMINATION OF URANIUM IN A SET
OF PROPOSED URANIUM ORE STANDARDS
FROM THE INTERNATIONAL ATOMIC
ENERGY AGENCY, REF. NO. 5/66-6**

by

J.B. ZIMMERMAN AND J.C. INGLES

EXTRACTION METALLURGY DIVISION

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J.B. Zimmerman* and J.C. Ingles**

SUMMARY

The uranium values obtained by this laboratory as part of a collaborative effort on the certification of international standards for low-grade uranium ores are reported. The confidence levels for the values obtained, and operating details of the analytical methods employed, are also described.

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INTRODUCTION

In a letter dated May 2nd, 1966 (Appendix), the Chemical Analysis Section was invited by Dr. L. Kosta, of the International Atomic Energy Agency, Vienna, to participate in a program for the establishing of a series of low-grade uranium ore standards. The ore samples, which were received May 20th, consisted of a torbernite ore from Spain, a torbernite ore from Australia, a uraninite ore from Australia and a carnotite ore from the United States. Analyses of the ores for all constituents except uranium were provided by Dr. Kosta, along with an estimate of the range of the uranium content.

The chemical analysis group at the Ottawa Metallurgical Laboratory of Eldorado Mining and Refining Ltd. also participated in this program and received a separate set of samples. As an added check, our two laboratories exchanged the sets of samples received, and each repeated the analyses on the samples received originally in the other laboratory. The samples sent directly to this laboratory by Dr. Kosta are so designated in this report, while those sent originally to the Eldorado laboratory are referred to as the Eldorado samples.

EXPERIMENTAL

The general procedure employed in analyzing these samples is outlined in our method U-1 (1), using the dissolution and pipetting procedures described below. The samples sent directly to this laboratory were analyzed according to the plan requested by Dr. Kosta; that is, a separate, single analysis* on a single dried, weighed portion of each of the four ore samples, and a Canadian standard ore sample, was carried out on each of five successive days. A record of the weight loss in the drying process, which was carried out at 110°C, was also made. The Canadian standard sample analyzed was the Canadian Uranium Producers' Beaverlodge Standard CUP 117, certificate value 0.174% U_3O_8 , (\pm .003% at the 95% confidence level). The dissolution and pipetting procedure employed in obtaining the officially-reported values is described below under the heading "Scheme 1".

* A single analysis consists of one fusion set, that is to say, 10 aliquots of one sample solution and 10 aliquots of a standard solution, dried and fused with mixed-fluoride pellets, simultaneously.

Two additional sets of check analyses were carried out to confirm the officially reported values. In the first set, duplicate analyses (that is, two sets of fusions as described in the footnote on page 1) were carried out on single, weighed portions of the same dried samples used in obtaining the officially reported values. The dissolution procedure employed in these analyses is that described under the heading "Scheme 2". It differs from Scheme 1 principally with respect to the use of hydrofluoric acid in place of the aqua regia employed in Scheme 1. The purpose of this set of analyses was to establish whether the samples contained uranium which could not be liberated using the routine 3-acid treatment of Scheme 1, but which might be brought into solution by a more drastic attack on the silicate minerals.

The second set of check analyses was carried out on the samples which had been sent originally to the Eldorado laboratory by Dr. Kosta. These samples were also analyzed using hydrofluoric acid, as described under Scheme 2 below.

Dissolution and Pipetting Procedures

Scheme 1

- (1) Weigh approximately 1 gram of sample into a 600-ml beaker.
- (2) Add 15 ml of aqua regia, cover, and digest 30 min.
- (3) Remove the cover and evaporate to about 5 ml.
- (4) Add 4 ml of concentrated sulphuric acid and fume to dryness.
- (5) Add 25 ml of concentrated nitric acid and 200 ml of water, then boil for 30 minutes.
- (6) Cool, dilute to 500 ml in a volumetric flask. Aliquot 5 ml into a 50-ml volumetric flask and make to the mark with 5 % v/v nitric acid.
- (7) Pipette, with a micropipette, 0.10 ml of the sample solution into each of 10 platinum dishes. Into another 10 platinum dishes, pipette 0.10 ml of the 1.00 mg U_3O_8 /litre standard solution.
- (8) Add a Ridsdale 17g sodium fluoride-2% lithium fluoride (.600g) tablet to each dish, and fuse samples and standards together on a Fletcher burner.

Scheme 2

- (1) Weigh approximately 1 gram of sample into a 250-ml Teflon beaker.
- (2) Moisten with 10 ml of water.
- (3) Add 5 ml of concentrated hydrofluoric acid and evaporate to dryness at low heat.
- (4) Add a further 3 to 4 ml of concentrated hydrofluoric acid and again take to dryness.
- (5) Add 10 ml of concentrated nitric acid and boil.
- (6) Transfer the contents of the Teflon beaker to a 600-ml Pyrex beaker.
- (7) Treat the Teflon beaker to remove adherent residue by adding 3 ml of concentrated nitric acid and 3 ml of concentrated sulphuric acid, and fuming.
- (8) Combine this acid wash with the main portion of the sample solution in the Pyrex beaker and fume the combined solution to dryness.
- (9) Add 25 ml of concentrated nitric acid and 10 ml of water, and boil.
- (10) Transfer to a 500-ml volumetric flask and dilute to volume with water.
- (11) Aliquot 5 ml into a 50-ml volumetric flask and dilute to volume with 5% nitric acid.
- (12) Pipette and fuse as described above for Scheme 1.

RESULTS

The results on the group of samples received directly at the Mines Branch, analyzed according to the plan requested by Dr. Kosta, are presented in Table 1.

The results of check analyses on these same samples, using the more drastic acid attack of Scheme 2, will be found in Table 2. Table 3 gives the values obtained on the Eldorado samples, on an "as-received" basis, using the same acid treatment used in obtaining the values given in Table 2.

TABLE 1

Analytical Results of U₃O₈ and "Loss at 110°C" Determinations on the Proposed International Standard Ore Samples Received Directly at the Mines Branch, Scheme 1. (Single Fusion Set * on Each Weighed Sample - One per Day)

Lab. No. EMM	Sample Designation	Loss at 110°C, %	Individual Values, % U ₃ O ₈ (dry basis)	Average % U ₃ O ₈ (dry basis)
228	Torbernite, Australia	.21	.474; .466; .469; .470; .485	.473
229	Torbernite, Spain	.39	.293; .310; .299; .296; .324	.304
230	Uraninite, Australia	.79	.361; .359; .368; .360; .380	.366
231	Carnotite, U.S.A.	.47	.415; .393; .426; .410; .420	.413
237	Beaverlodge Std. CUP 117	.24	.173; .166; .170; .168; .166	.169

* A fusion set consists of ten 0.10-ml aliquots each, of the sample solution and of the standard uranium solution.

TABLE 2

Analytical Results of U₃O₈ Determinations on the Proposed International Standard Ore Samples Received Directly at the Mines Branch, Scheme 2.
(Duplicate Fusion Sets* on Aliquots of the Solution from a Single Weighed Sample)

Lab. No. EMM	Sample Designation	Individual Values, % U ₃ O ₈ (dry basis)	Average, % U ₃ O ₈ (dry basis)
228	Torbernite, Australia	.479; .483	.481
229	Torbernite, Spain	.317; .300	.308
230	Uraninite, Australia	.373; .363	.366
231	Carnotite, U.S.A.	.429; .422	.426
237	Beaverlodge Std. CUP 117	.168; .170	.169

* A fusion set consists of ten 0.10-ml aliquots each, of the sample solution and of the standard uranium solution.

TABLE 3

Analytical Results for U₃O₈ on the Proposed International Standard Ore Samples Received Originally at Eldorado Laboratory, Scheme 2. (Duplicate Fusions Sets * on Aliquots of a Solution from a Single Weighed Sample)

Lab. No. EMM	Corresponds to EMM	Sample Designation	Individual Values % U ₃ O ₈ (as received basis)	Average % U ₃ O ₈ (as received basis)
470	228	Torbernite, Australia	.461; .482	.472
471	229	Torbernite, Spain	.312; .305	.309
469	230	Uraninite, Australia	.364; .351	.358
472	231	Carnotite, U.S.A.	.426; .419	.423

* A fusion set consists of ten 0.10-ml aliquots each of the sample solution and of the standard uranium solution.

DISCUSSION

A comparison of the results of Table 1 and Table 2 indicates that there is no significant amount of uranium in the proposed standard ore samples which can not be liberated by 3-acid treatment, and that the use of hydrofluoric acid for sample dissolution is therefore unnecessary. The results of Table 3, on the samples sent originally to the Eldorado laboratory, provide added corroboration to this view, and show that two different sample cuts of the ores provided substantially identical analytical values for uranium content.

The average value reported for the CUP 117 standard ore sample in the present work, 0.169 (Tables 1 and 2), agrees well with the certificate value of 0.174, and, coincidentally, is identical with the value obtained by our laboratory during the original certification of this standard sample in 1961.

CONCLUSIONS

The values for the uranium content of the proposed International Atomic Energy standard ore samples, expressed as % U_3O_8 , dry basis, together with the respective confidence intervals (95% level), are given in Table 4 and represent the official values for this laboratory.

TABLE 4

Official Mines Branch Values for Uranium Content of the Proposed International Atomic Energy Agency Standard Ore Samples. (Samples Received Directly at the Mines Branch)

Identification	% U_3O_8 , dry basis	95% Confidence Level, on average of 5 determinations
Torbernite, Australia	.473	\pm .012
Torbernite, Spain	.304	\pm .020
Uraninite, Australia	.366	\pm .014
Carnotite, U.S.A.	.413	\pm .022

REFERENCES

1. J.C. Ingles, "Manual of Analytical Methods for the Uranium Concentrating Plant", Mines Branch Monograph 866, Ottawa, the Queen's Printer, 1959.

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(a 3 page Appendix
follows)

APPENDIX



INTERNATIONAL ATOMIC ENERGY AGENCY
AGENCE INTERNATIONALE DE L'ENERGIE ATOMIQUE
МЕЖДУНАРОДНОЕ АГЕНТСТВО ПО АТОМНОЙ ЭНЕРГИИ
ORGANISMO INTERNACIONAL DE ENERGIA ATOMICA

VIENNA I, KAERNTRERING, AUSTRIA
TELEPHONE: 52 45 25, CABLE: INATOM

2 May 1966

Dear Mr. Ingles,

We were very pleased to hear that you are prepared to participate in our programme of standardization of low grade uranium ores. We will therefore send you four samples of uranium ore by air in the next few days. They are two torbernites, one originating from Spain and one from Australia, a uraninite from Australia and a carnotite from the United States. The samples are contained in polyethylene bottles which are in addition sealed in polyethylene bags. Please also note the attached which are some notes we have prepared for this exercise.

Thanking you very much for your cooperation
I remain

Yours sincerely,


L. Kosta

Mr. J.C. Ingles
Head, Control Analysis Section
Extractive Metallurgy Division
Mines Branch
Dept. of Mines & Technical Surveys
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Canada



INTERNATIONAL ATOMIC ENERGY AGENCY
AGENCE INTERNATIONALE DE L'ENERGIE ATOMIQUE
МЕЖДУНАРОДНОЕ АГЕНТСТВО ПО АТОМНОЙ ЭНЕРГИИ
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VIENNA 1, KAERNTNERRING, AUSTRIA
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"Analysed Samples" of Low Grade Uranium Ores

The primary objective of this work is to establish by international collaboration, the uranium content of samples of low grade uranium ores. The intended purpose of these samples is for checking chemical procedures for the determination of uranium in low grade ores in the laboratories of Member States.

The samples of the ore, i.e. two "torbernites", one originating from Australia and one from Spain, "uraninite" from Australia and "carnotite" from the U.S.A., have been milled and ground to pass 200 mesh. Homogeneity tests have been performed.

We ask you to determine the uranium content as a referee analysis. We hope for a minimum of 3 (but preferably 5) analyses per sample and we ask that the results be returned to us in full, preferably to one figure more than you consider significant as this will aid subsequent statistical calculations. (Results should be calculated on the basis of the ores dried at 110°C.) Please use the method which in your experience you consider to be the best for the samples. We would appreciate if you could include the details of the procedure which you use. The U_3O_8 content of the samples, the composition of which is given below, lies in the range 0.25 - 0.50 %.

You will receive a report containing all results when the work is completed. Any questions should be addressed to Dr. L. Kosta, IAEA, Kärntnerring 11, 1010 Vienna, Austria.

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Torbernite (Australia)

Quantitative analysis: Al_2O_3 6.4 %, Fe_2O_3 3.6 %, K_2O 1.1 %, MgO 0.39 %, SiO_2 85.0 %.

Semiquantitative analysis: B_2O_3 0.04 %, BaO 0.03 %, CaO 0.06 %, Cr_2O_3 0.01 %, CuO 0.04 %, Ga_2O_3 0.002 %, Li_2O 0.006 %, MnO 0.03 %, Na_2O < 0.1 %, NiO 0.002 %, PbO 0.02 %, SrO < 0.04 %, TiO_2 0.5 %, V_2O_5 0.03 %, P_2O_5 < 0.7 %.

Torbernite (Spain)

Quantitative analysis: Al_2O_3 4.5 %, CaO 0.078 %, CuO 0.24 %, Fe_2O_3 10.0 %, MgO 0.15 %, Na_2O 0.07 %, SiO_2 76.0 %.

Semiquantitative analysis: B_2O_3 0.02 %, BaO 0.03 %, BaO < 0.003 %, Cr_2O_3 < 0.001 %, Ga_2O_3 0.002 %, Li_2O 0.06 %, MnO 0.02 %, NiO < 0.001 %, PbO 0.003 %, SnO 0.003 %, TiO_2 0.04 %, V_2O_5 0.008 %.

Uraninite (Australia)

Quantitative analysis: Al_2O_3 16.5 %, CaO 0.52 %, CuO 0.02 %, Fe_2O_3 12.6 %, K_2O 1.4 %, MgO 10.6 %, MnO 0.35 %, Na_2O 0.18 %, P_2O_5 0.54 %, SiO_2 58.0 %, TiO_2 0.81 %, V_2O_5 0.08 %.

Semiquantitative analysis: B_2O_3 0.05 %, BaO 0.03 %, CaO 0.004 %, Cr_2O_3 0.006 %, Ga_2O_3 0.005 %, Li_2O 0.02 %, NiO 0.004 %, PbO 0.1 %.

Carnotite (U. S. A.)

Quantitative analysis: Al_2O_3 6.0 %, CaO 0.55 %, Fe_2O_3 0.5 %, MgO 1.2 %, Na_2O 1.05 %, TiO_2 0.33 %, V_2O_5 0.58 %.

Semiquantitative analysis: B_2O_3 < 0.003 %, BaO 0.04 %, Cr_2O_3 < 0.004 %, K_2O 2.5 %, SiO_2 > 80 %, SrO < 0.04 %, ZnO 0.04 %, CuO < 0.02 %, MnO < 0.09 %, P_2O_5 < 0.1 %.