

**INTERNATIONAL UNION OF
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**COMMISSION ON RADIOANALYTICAL CHEMISTRY
AND NUCLEAR MATERIALS**

**PREPARATION OF REFERENCE
SAMPLES FOR URANIUM IN
LOW GRADE ORES**

**LONDON
BUTTERWORTHS**

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ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON RADIOANALYTICAL CHEMISTRY AND
NUCLEAR MATERIALS*

PREPARATION OF REFERENCE SAMPLES FOR
URANIUM IN LOW GRADE ORES

The analytical chemistry of uranium, especially methods for its determination in ores, has been the subject of intense research for some twenty years following the discovery of controlled uranium fission. Since the first Geneva Conference, however, interest has declined considerably which could be taken as an indication that the problems involved have been essentially solved. However, answering an enquiry by the International Atomic Energy Agency a large number of its Member States expressed their interest in reference samples for uranium in typical primary and secondary ores in the concentration range of tenths of one per cent.

As the result of action taken by the IAEA laboratory in Seibersdorf, four ore samples (two torbenites one originating from Australia and one from Spain, one carnotite from the USA and one uraninite of Australian origin) were made available by the courtesy of the respective Governments. The ores (50 kg of each) were milled and ground to pass a 200 mesh sieve, and homogeneity tests and general analysis were carried out. This work was performed by the laboratories of the Junta de Energia Nuclear, Madrid, Spain, who also participated in the assessment of the final values for uranium concentration.

In order to establish the uranium content of these samples appropriate aliquots were submitted to ten laboratories (including the IAEA laboratory Seibersdorf), most of whom were known to have a long analytical experience in the control of processing and production of uranium compounds from low grade ores. Participating laboratories were asked to use methods which, according to their experience, would be most appropriate for the types of ores and concentrations of uranium.

The primary objective of this work was to establish by international collaboration the best value for the uranium content of the samples so that the material could be used for checking chemical procedures for the determination of uranium in low grade ores. As a byproduct of this operation, information was obtained about methods currently used and an attempt has been made to compare the methods employed, although it is realized that this will not be so sound statistically as an exercise which had comparison of methods as its primary goal. On the basis of the reports submitted by the participating laboratories, the methods have been summarized and attempts have been made to compare them on the following points: dissolution of

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sample, separation methods involved, techniques and methods of determination. The results are also presented and the value for uranium proposed.

DECOMPOSITION OF SAMPLES

This is the first critical stage in the analysis as it could introduce a negative systematic error if the procedures used did not ensure complete dissolution of uranium.

In the first attempt to establish uranium concentrations, the two torbernites were distributed for analysis. Samples were treated by procedures chosen by the individual laboratories which, except in one case, were not based on total dissolution of the sample.

The treatments included:

- (a) Prolonged heating (four hours) of samples in nitric acid alone.
- (b) Heating with hydrofluoric acid followed by nitric acid and subsequent evaporation, fuming with sulphuric acid and finally taking up in nitric acid.
- (c) Heating with hydrochloric plus nitric acids (1:3) followed by fuming with sulphuric acid and taking up in nitric acid.
- (d) Heating the sample in a mixture of nitric, perchloric and hydrofluoric acids, fuming to small volume and taking up in either perchloric acid (for titrimetric finish) or in nitric acid (for spectrophotometric finish).
- (e) Sodium carbonate fusion, dissolution of the melt in nitric acid, insolubilization and subsequent volatilization of silica. The dissolved residue after the volatilization of silica is added to the first filtrate.
- (f) Repeated additions and evaporations with hydrochloric and hydrofluoric acids, or, alternatively, with nitric and hydrofluoric acids, followed by evaporation and taking up in nitric acid.

Upon the examination of the first set of results the discrepancy between averages was thought to be too high for the purpose of the work and losses of uranium with the insoluble residue were considered as a likely source of error.

Attention of the participating laboratories was drawn to the above possibility. The dissolution procedures were modified accordingly. Most laboratories repeated analyses modifying independently the dissolution procedures either by applying more drastic acid treatment, by predigestion of the sample with hydrofluoric acid in addition to treatment used before, by determining the amount of uranium in residues after the attack or by dissolving the sample completely.

Results of this investigation showed that all uranium is liberated after mixed acid attack with hydrofluoric, nitric and either sulphuric or perchloric acids. Nitric acid alone or in combination with hydrochloric acid can leave up to one per cent of uranium in residues. Similar increase in the average value became evident in results from two other laboratories after the decomposition procedure had been altered to include fuming with sulphuric acid.

DETERMINATION OF URANIUM

General composition of the intercomparison samples is shown in *Table 1*.

Table 1. General composition of the intercomparison samples

Sample	Major components, per cent										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	CuO	K ₂ O	Na ₂ O	TiO ₂	V ₂ O ₅	P ₂ O ₅
Torbernite, Australia	85.0	6.4	3.6	0.39	—	0.04	1.1	0.1	0.5	0.03	0.7
Torbernite, Spain	76.0	4.5	10.0	0.15	0.08	0.24	—	0.07	0.04	0.008	—
Uraninite, Australia	58.0	16.5	12.8	10.6	0.52	—	1.4	0.18	0.81	0.08	0.54
Carnotite, USA	80	6.0	0.5	1.2	0.55	0.02	2.5	1.05	0.33	0.58	0.1
	Minor components, per cent										
	B ₂ O ₃	Cr ₂ O ₃	Li ₂ O	MnO	NiO	PbO	BaO	SrO	Ga ₂ O ₃	CoO	ZnO
Torbernite, Australia	0.04	0.01	0.006	0.03	0.002	0.02	0.03	0.04	0.002	—	—
Torbernite, Spain	0.02	0.001	0.06	0.02	0.001	0.008	0.03	—	0.002	—	—
Uraninite, Australia	0.05	0.006	0.02	0.35	0.004	0.1	0.03	—	0.005	0.004	—
Carnotite, USA	0.003	0.004	—	0.09	—	—	0.04	0.04	—	—	0.04

Torbernite sample from Spain was also found to contain BeO and SnO at the concentration level of 0.003 per cent for both oxides. The results for most minor components and part of the major components, notably SiO₂ in carnotite USA, are semiquantitative.

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Spectrophotometric techniques were chosen by seven laboratories. With only a few exceptions the methods used were quite different and were based on colour reactions of uranium with the following reagents: thiocyanate, dibenzoylmethane, arsenazo and thioglycollic acid. Two laboratories used a fluorimetric technique and one titration.

All spectrophotometric methods involved the isolation of uranium by extraction. In the titrimetric technique, interfering iron (together with vanadium and/or copper) was removed as cupferrate. Only in the fluorimetric technique was the determination carried out without separation and the effects of components which interfered by quenching the fluorescence of uranium were eliminated by dilution.

In details there were considerable differences in thiocyanate as well as in dibenzoylmethane methods with regard to procedures applied by different laboratories.

In the case of thiocyanate method laboratories A and E followed the modification as described by C. J. Rodden¹. Uranium is first extracted into methylisobutylketone (MIBK) and the reagent in solution added to the organic phase. The procedure used by I differed only in that a mixture of alcohol and water (approximately 4:1)² was substituted for butyl cellosolve (BuCS) as solvent for thiocyanate. Laboratory H, although applying thiocyanate, used a procedure which can be regarded as a different method³. The uranylthiocyanate complex is formed in aqueous solution and then extracted into a mixed tributyl phosphate (TBP)-carbon tetrachloride solvent.

Table 2 gives the essential details of the above modifications. From a few comparative analyses carried out in one of the participating laboratories it was shown that using a mixture consisting of alcohol and water instead of butyl cellulose as solvent does not influence the results provided that a sufficient quantity of solvent is used to dissolve completely the solids (thiocyanate and ascorbic acid).

Table 2. Characteristic details of the thiocyanate method

Laboratory	Sample aliquot	pH	Salting agent	Solvent	Reagent	Absorbancy measured at
A, E	3 ml	0-3	Al(NO ₃) ₃ 15 ml	MIBK 20 ml	30% NH ₄ CNS in BuCS	375 nm
I	5 ml	same	same	same	23% NH ₄ CNS + 1.5% ascorbic acid in 77% alc.	370 nm
H	50 ml	3.6-3.7	none	TBP-CCl ₄ 1:2		350 nm

Procedures based on the application of dibenzoylmethane as the spectrophotometric reagent for uranium appear more delicate and seem consequently to require more skill from the operators. In view of the higher sensitivity of the reagent either dilution factors have to be increased or smaller aliquots taken. At the concentration range involved the method therefore becomes more vulnerable to systematic errors. According to observations

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in laboratory A results are affected by minor changes in pH, by the dilution factor, by varying amounts of complexing agents and by some components in the samples if the analysis is carried out by the procedure used in laboratories A and I⁴. They found that for samples containing higher concentrations of R₂O₃ (uraninite) the amount of complexing agents has to be increased proportionally. But if R₂O₃ exceeds 15 per cent, the interference becomes so serious that some other method has to be used for uranium determination.

Differences in detailed procedures as used by individual laboratories are even greater in the case of dibenzoylmethane as is shown in *Table 3*.

Table 3. Data characterizing alternatives in dibenzoylmethane method

Laboratory	Sample aliquot	Salting agent	Solvent	Reagent
A, I*	2 ml	Al(NO ₃) ₃ Sol. a	MIBK-TBP 10:1	0.3% in acetone-pyridine-alcohol 1:10:100
D	5 ml	Al(NO ₃) ₃	Ethylacetate ⁵	
E	1 ml	Al(NO ₃) ₃ Sol. b	MIBK	0.023% in pyridine ⁶ containing 5% alcohol
J	5 ml	Al(NO ₃) ₃ Sol. c	Isooctane-TBP 10:1	0.018% in acetone-pyridine-water ⁷ 17:1:3

* Sample aliquots complexed with complexone III, sodium sulphate, acetic and tartaric acids and pH adjusted to 2.8 prior to addition of salting out agent.

Sol. a: Solution prepared by dissolving 1 kg of aluminium nitrate nonahydrate in water and making up to one litre.

Sol. b: Dissolve 1050 g Al(NO₃)₃·9H₂O in 850 ml H₂O, add 67.5 ml of concentrated aqueous ammonia (25% w/t) during vigorous stirring followed by 10 ml of ten per cent tetrapropylammonium hydroxide and dilute to one litre with water.

Organic phase is scrubbed with a solution consisting of 940 g Al(NO₃)₃·9H₂O, 33 g tartaric acid, 31 g oxalic acid, 64 g ethylenediamine tetraacetic acid and 150 ml concentrated ammonia in one litre of solution.

Sol. c: Prepared by dissolving 900 g of Al(NO₃)₃·9H₂O in water to make up one litre of solution; pH is adjusted with ammonium hydroxide or nitric acid to give a pH of 3.0 if diluted 1:20 with distilled water.

Arsenazo

In the final set of measurements, only one laboratory (I) made use of arsenazo (trisodium salt of 3-[2-arsono-phenylazo]-4,5-dihydroxy-2,7-naphthalene disulphonic acid) as the spectrophotometric reagent⁸. Uranium was first extracted into mixed MIBK-TBP solvent from a solution containing EDTA, tartaric acid, hydrofluoric acid and hydroxylamine hydrochloride as reagents to eliminate the effects of interfering components; ammonium nitrate was used as salting out agent.

The usable concentration range of uranium in the ore solution is between 20 and 200 µg/ml and therefore this method also requires high dilution factors. Aliquots should not exceed 2 ml. The final volume of aqueous phase after the addition of reagents which should contain nitric acid in concentration between 0.2 and 0.75 M is 8 ml, that of the organic solvent 3 ml. The aliquots of the organic phase taken for the development of colour are 1 ml.

Traces of ferric iron carried over into the organic phase with uranium are reduced by hydroxylamine (0.5 ml one per cent solution) in alcoholic medium containing five per cent of pyridine, and complexed with *o*-phenanthroline.

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The colour is developed by adding 1 ml of 2×10^{-3} M aqueous solution of arsenazo reagent and the volume made up to 10 ml with alcohol. The measurement transmission is carried out at 600 nm in 1 ml cuvettes.

In the first tentative round, one more laboratory (D) determined uranium in the two torbernites by the same procedure. The agreement within the two sets of results was moderate but the averages were much below the accepted values; this was probably due to lack of familiarity with the method.

Thioglycollic acid

The method based on the application of thioglycollic acid (F) involves extraction of uranium with ethylacetate from 10 ml aliquots in which 8 g of solid aluminium nitrate had been dissolved⁹.

The combined organic phases from two extractions, with equal volumes of solvent were washed with a saturated solution of ammonium nitrate in 1 N nitric acid. Uranium was then stripped into 2 M perchloric acid (2×5 ml) and the solution evaporated to fumes. The colour is developed in aqueous solution containing tartaric acid (100 mg) and made ammoniacal after addition of ammonium thioglycollate reagent. Absorbancy of the solution is measured at 380 nm but a second measurement is usually necessary at 600 nm in order to correct for the interference due to iron. The agreement between individual measurements is good but in three out of four samples the average result was low compared with those by other methods.

Titration

Compared to techniques discussed so far, the classical titrimetric approach is the most direct. The amount of uranium is determined on the basis of the reaction with well established oxidizing agents the concentration of which can be determined very accurately. The method used in the present comparison¹⁰ (laboratory J) is based on the reaction of tetravalent uranium with ceric sulphate. Lead is used as reducing agent. All aspects of this titration are very well covered in the literature and it is known as one of the most precise and accurate alternatives for determining uranium. Possible interferences are eliminated in two stages: sparingly soluble sulphides are removed first by homogeneous precipitation with thioacetamide then cupferrates are precipitated and extracted into chloroform. Chromium, if present, is volatilized as chromyl chloride from boiling perchloric acid solution by adding solid sodium chloride. The solution is finally passed through the reductor, phosphoric acid added and uranium(IV) titrated with ceric sulphate using *o*-phenanthroline as indicator. The results are corrected for titration blank. The data in the respective tables indicate that the average values obtained by this method are very close to the estimated true value.

Fluorimetry

Fluorimetry is normally used for very low concentrations of uranium and cannot be regarded as very suitable for establishing standards at the concentration range dealt with in the present comparison because of lower precision. Nevertheless it appears that if care is taken to avoid systematic errors—by careful calibration of all instruments and apparatus, painstaking control of conditions, and cross checking with standards—it is possible to

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obtain quite accurate results. Limitations in precision are minimized by increasing the number of parallel determinations¹¹. In results by laboratory B, measurements obtained by evaporating and fusing five 0.1 µl aliquots of the sample solution and five aliquots of a standard solution are to be understood as a single determination. Similarly, in the case of laboratory C, averages of fluorescence measurements of ten sample aliquots compared with those of ten aliquots of the standard solution are taken as one single result. Therefore, although the procedure involves only diluting, pipetting, fusion and measurement of fluorescence, the method is first of all delicate and also requires high skill and considerable time.

Results

Table 4 summarizes the results grouped according to the methods including the number of determinations, the standard deviations and relative standard deviations for the individual results as well as the limits of the mean result at the 95 per cent confidence level. Values are also proposed (Table 5) which could be taken as the 'true' value for uranium in the four analysed samples. These were obtained for each sample, by evaluating the average for each method (after elimination of outliers) and then averaging the averages for the chemical methods used.

Table 4. Collected results for analysis of U₃O₈ content (%)
Torbernite (Australia) S1

Method	Lab.	n	Mean	s	s _r (%)	t _{0,05} sn ^{-½}	Notes
Thiocyanate	A1	10	0.469	0.0028	0.60	0.0020	1
	A2	4	0.469				1,2
	D1	6	0.479	0.012	2.64	0.013	3,4
	E	7	0.474	0.007	1.54	0.007	1
	H	9	0.475	0.0041	0.86	0.0032	5
	I	56	0.481	0.0056	1.16	0.0015	3,6
Dibenzoyl-methane	A1	10	0.460	0.002	0.43	0.0016	7
	A2	4	0.468				2,8
	A3	4	0.468	0.0006	0.13	0.0009	8
	D1	6	0.433	0.008	1.95	0.009	9
	D1a	10	0.451	0.024	5.28	0.017	7
	D2	6	0.496	0.004	0.83	0.004	9
	E	10	0.475	0.0087	1.83	0.0062	10
	G	5	0.467	0.004	0.92	0.005	11
	I	56	0.481	0.0069	1.43	0.0018	6,7
Titrimetric	J1	5	0.468	0.011	2.24	0.013	12
	J1	5	0.469	0.0009	0.2	0.0011	13
Arsenazo	J2	4	0.469	0.0014	0.30	0.0023	13
	D	7	0.433	0.057	12.86	0.052	14
Thioglycollic acid	I	56	0.483	0.0065	1.34	0.0017	6,14
	F	7	0.463	0.003	0.70	0.003	15
Fluorimetric	B	8	0.470	0.011	2.32	0.009	16
	C1	5	0.473	0.007	1.57	0.009	16,17
	C2	2	0.481				16,17

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Torbernite (Spain) S2

Method	Lab.	n	Mean	s	$s_r(\%)$	$t_{0.05} sn^{-\frac{1}{2}}$	Notes
Thiocyanate	A1	10	0.313	0.0045	1.44	0.0032	1
	A2	4	0.313				1,2
	D	9	0.307	0.027	8,67	0.020	3
	E	6	0.317	0.004	1.29	0.004	1
	H	9	0.310	0.0042	1.38	0.0032	5
	I	56	0.318	0.0065	2.04	0.0016	3,6
Dibenzoyl-methane	A1	10	0.298	0.0023	0.77	0.017	7
	A2	4	0.310				2,8
	A3	4	0.310	0.0006	0.19	0.0009	8
	D1	6	0.291	0.003	1.03	0.003	9
	D1a	6	0.322	0.017	5.41	0.018	7
	D2	6	0.315	0.003	1.02	0.003	9
	E	7	0.319	0.007	2.19	0.006	10
	I	56	0.316	0.0054	1.73	0.0014	6,7
Titrimetric	J	5	0.316	0.006	1.90	0.008	12
	J	5	0.313	0.0017	0.54	0.0021	13
Arsenazo	D	7	0.294	0.013	4.44	0.014	14
	I	56	0.313	0.0053	1.69	0.0014	6,14
Thioglycollic acid	F	4	0.299	0.002	0.74	0.004	15
Fluorimetric	B	8	0.324	0.005	1.66	0.005	16
	C1	5	0.304	0.0127	4.17	0.016	16
	C2	2	0.308				16,17

Carnotite (USA) S3

Method	Lab.	n	Mean	s	$s_r(\%)$	$t_{0.05} sn^{-\frac{1}{2}}$	Notes
Thiocyanate	A	10	0.410	0.0016	0.39	0.0011	1
	H	9	0.425	0.005	1.20	0.004	18
	I	56	0.426			0.001	3,6
Dibenzoyl-methane	A	10	0.416	0.0031	0.76	0.0022	8,19
	D	7	0.424	0.003	0.70	0.003	9
	E	11	0.417	0.005	1.22	0.003	10
	I	56	0.419			0.004	6,7
Titrimetric	J	5	0.417	0.0011	0.26	0.0014	13
Arsenazo	I	56	0.415			0.001	14
Thioglycollic acid	F	8	0.406	0.003	0.76	0.003	15
Fluorimetric	B	8	0.432	0.006	1.41	0.005	16
	C1	5	0.413	0.013	3.05	0.016	16,17
	C2	2	0.426				16,17

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Uraninite (Australia) S4

Method	Lab.	n	Mean	s	s _r (%)	t _{0.05} sn ^{-½}	Notes
Thiocyanate	A	10	0.368	0.0016	0.43	0.0011	1
	H	9	0.381	0.012	3.15	0.009	18
	I	56	0.381			0.003	3,6
Dibenzoyl-methane	A	10	0.379	0.0062	1.64	0.0045	8,20
	D	8	0.381	0.011	2.90	0.009	9
	E	11	0.369	0.007	1.95	0.005	10
Titrimetric	I	56	0.374			0.003	6,7
	J	5	0.377	0.0017	0.45	0.0021	13
Arsenazo	I	56	0.372			0.001	6,14
Thioglycollic acid	F	10	0.378	0.0056	1.48	0.0040	15
	B	8	0.377	0.007	1.85	0.006	16
Fluorimetric	C1	5	0.366	0.009	2.40	0.011	16,17
	C2	2	0.366				17

- Method as given in C. J. Rodden (see ref. 1).
- No detailed results given. Average was given with the limits ± 0.0007 , and these are believed to be the standard deviation of the mean.
- See ref. 2.
- Seven results were submitted but one was so far out of the range of the other six that it was omitted.
- Result corrected for the small amount of uranium in the insoluble residue after acid treatment of the ore.
Method involves extraction of ammonium thiocyanate complex into tributyl phosphate (see ref. 3).
- The values for confidence limits were obtained by analysis of variance from a much larger number of analyses than for the values from other laboratories.
- See ref. 4.
- Method used was a slight modification of 7, in which close control of pH was maintained.
- Method is based on the extraction of uranium with ethyl acetate and development of colour by addition of DBM to an aliquot of the solvent phase (see ref. 5).
- See ref. 6.
- No details of method known.
- Method is an adaptation of the procedure reported by C. Francois, *Analyt. Chem.* 30, 50 (1958) (see ref. 7).
- Method adapted from that of C. W. Sill and H. E. Peterson, *Analyt. Chem.* 24, 1175 (1952) (see ref. 10).
- Method as described in the report *Qa(1705)/N-17* of the Junta de Energia Nuclear, Spain (see ref. 8).
- Method is based on ethyl acetate extraction of uranium followed by stripping into the aqueous phase and adding thioglycollic acid and ammonia (see ref. 9).
- A single determination of a fusion set of either 5 (B) or 10 aliquots (C) of one sample solution and ten aliquots of the standard solution, dried and fused with mixed fluoride pellets, simultaneously (see ref. 11).
- Results obtained by a modification of the dissolution procedure for the ore sample. In C1, aqua regia followed by fuming with sulphuric acid to dryness was used to dissolve the uranium whereas in C2 the sample was evaporated twice with hydrochloric acid and then boiled with nitric acid.
- Method as in note 5, but with complete dissolution of the sample.
- Two sets of ten results were obtained by method of note 8, in one of which the amount of complexing agent to keep hydrated oxides in solution was double that of the recommended amount. Results agree to within one per cent. Results quoted are those obtained with the recommended amount.
- Two sets of ten results by essentially the same method but differing in dilution factor before extraction of uranium were prepared. The average of one set was 12 per cent higher than the second which agreed with the determination of other laboratories. It was, therefore, not considered for inclusion in the table.

Table 5. Average values for the four samples (% U₃O₈) based on material dried for one hour at 110°C

Sample	S1	S2	S3	S4
Thiocyanate	0.473	0.314	0.420	0.377
Dibenzoylmethane	0.470	0.314	0.419	0.376
Arsenazo		0.313	0.415	0.372
Titrimetric	0.469	0.313	0.417	0.377
Average	0.471	0.313	0.418	0.375

CONCLUSIONS

The following conclusions could be drawn on the basis of the evidence from the comparison:

(1) The assessment of 'true' value using existing procedures for determining uranium in typical ores in concentrations of the order of a few tenths of one per cent still presents certain difficulties.

(2) Accurate analysis does not require total dissolution of the sample or fusion and volatilization of silica. All uranium can be liberated by heating the sample in mixtures of nitric and hydrofluoric acids followed by fuming with either perchloric or sulphuric acid.

(3) The high precision obtained in some laboratories indicates that methods are precise and that varying degrees in precision observed between laboratories have to be attributed to individual factors rather than to technique or reagent as such.

(4) The titrimetric procedure, in the hands of the analysts of laboratory J, and for the types of ores and concentrations of uranium involved, gives very precise results which are apparently accurate since they all fall in the range of the most probable values from all methods. It is unfortunate that only one laboratory used the method.

(5) Thiocyanate and dibenzoyl-methane are suitable reagents but procedures based on the former differ considerably in detail so that one is actually dealing with two different methods which should not be compared directly.

The disagreement between the averages from the first set of results for the two torbernites was so high that the analyses had to be repeated in the case of thiocyanate as well as the dibenzoyl-methane methods. Even the final values by these methods still leave, with respect to accuracy, something to be desired.

In general small aliquots of sample solutions and small volumes of solvent, which are used, make the dibenzoyl-methane method very vulnerable to systematic error, although both methods appear to give results of equal accuracy and precision.

(6) This applies also and to a larger extent to the fluorimetric method. If we take the involved dilution factor into consideration, results obtained by this method could be regarded as excellent. In the present application, however, the precision is not satisfactory. The advantage of apparent simplicity is lost through the necessity to increase considerably the number of measurements.

(7) The use of arsenazo does not seem to offer any advantages or disadvantages over other reagents at these concentrations. However, its higher molar extinction coefficient may be advantageous at much lower concentrations.

(8) From a study carried out in laboratory F it was shown that the negative bias of the thioglycollic acid method was due to small losses during the extraction of uranium and to scrubbing of the solvent phase, preceding the development of colour.

Figure 1 represents the plot of averages, with separate designations according to the methods used.

The fact that there is such a diversity in the existing procedures for uranium, even when the determination is based on the same reagent, suggests that the

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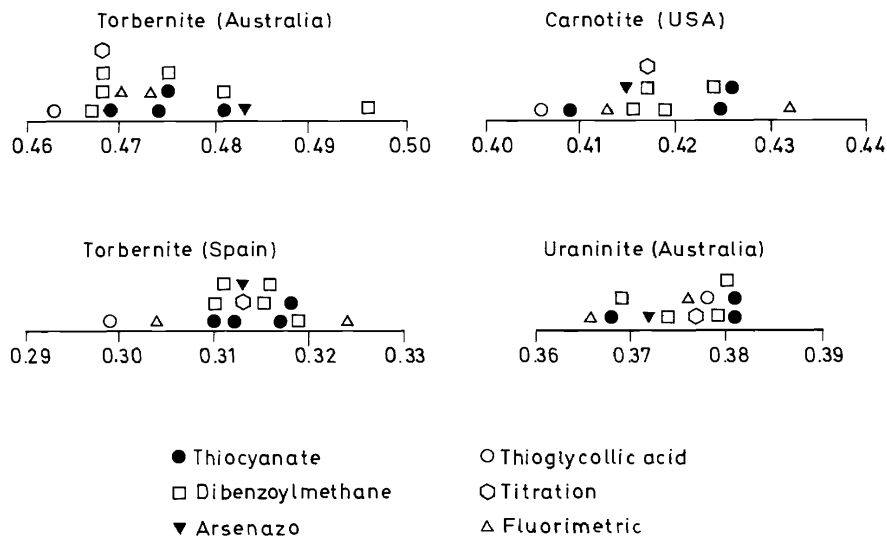


Figure 1. Distribution of laboratory mean values by method

exchange of experience, such as the present comparison, and additional studies might contribute to considerable simplifications and further improvement of their accuracy.

After this report was written, a new reagent, 2-(2-pyridylazo)-5-diethylaminophenol, has been suggested for uranium¹² which appears to be very sensitive and for which high reliability is claimed. Analyses of the four samples of uranium low grade ores¹³ gave the following results: S 1 0.472 per cent, S 2 0.316 per cent, S 3 0.424 per cent and S 4 0.370 per cent, in good agreement with the results in *Table 5*.

PARTICIPATING LABORATORIES

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