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COMPARATIVE SURVEY OF METHODS FOR THE DETERMINATION OF URANIUM IN ORES

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ABSTRACT

Results are given for an inter-laboratory comparison of methods for the determination of uranium in ores. Four different uranium ores were carefully prepared and samples distributed to eleven participating laboratories. The ores were analysed by several techniques, including spectrophotometric, fluorimetric, X-ray fluorescence, radiometric, and titrimetric procedures. Statistical analysis of the results showed that there was no significant difference between the uranium values found using spectrophotometric, fluorimetric, or X-ray fluorescence methods.

An Appendix contains some suggested modifications to the A.A.E.C. bromo-PADAP spectrophotometric method.

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DATA; FLUORESCENCE; QUANTITATIVE CHEMICAL ANALYSIS; SPECTROPHOTOMETRY; TITRATION; URANIUM; URANIUM ORES; X RADIATION

CONTENTS

1. INTRODUCTION

In May 1970 a Symposium was held at Lucas Heights, Sydney, on The Analytical Chemistry of Uranium and Thorium (Florence 1970). It became evident during the Symposium that there was some disagreement about the relative advantages of various methods for the determination of uranium in ores. It was also obvious that there was a need for a set of carefully-analysed Australian uranium ores which could be used as standards for the calibration of instruments and for checking new methods. Accordingly, an inter-laboratory analytical survey of methods for the determination of uranium in ores was organised. It was hoped that the results of the survey would indicate the precision and accuracy of the various techniques, and that the analysed ores would then serve as reference standards for uranium.

Four large samples of uranium ore were carefully ground and mixed, and portions sent to the eleven laboratories participating in the comparative survey (Appendix I). A letter accompanying the samples outlined the way in which we wished them to be analysed (Appendix II). The analytical results were examined statistically and conclusions drawn regarding the merits of the different methods of analysis.

2. MINERALOGICAL DESCRIPTION OF THE URANIUM ORES

Ore samples 1, 2 and 3 were taken from Rum Jungle Creek South. Mineralization is mainly confined to chlorite schists and black shales of Lower Proterozoic age. The main uranium mineral is pitchblende.

Sample 4 is from Mary Kathleen, which has a pyrometasomatic deposit of uranium. Mineralization consists of uraninite/rare earth silicates and sulphide minerals occurring in a garnetized zone of calc-silicate rocks of early Lower Proterozoic age. The deposit also contains thorium.

Sample 2 was in approximate radioactive equilibrium, whereas samples 1 and 3 were not, being low in uranium relative to decay products. Because of the presence of thorium it was difficult to establish the state of radioactive equilibrium of sample 4.

The approximate chemical composition of each ore is shown in Table I.

3. PREPARATION OF THE ORE SAMPLES

The crushed ores were ground on a Siebtechnik disc mill, then sieved through a vibrating 200 mesh sieve. The minus 200 mesh material was thoroughly mixed then stored in airtight jars.

Homogeneity tests were carried out on each ore sample by taking portions from different positions in the jars and analysing for uranium using the bromo-PADAP spectrophotometric method. Samples 1, 2 and 3 were found to be homogeneous, but slight variations in uranium content were found in sample 4. These variations are believed to be due to the unusual matrix of the Mary Kathleen ore, together with the relatively coarser nature of the sample, and the high uranium content of the minus 400 mesh fraction (Table 2). The non-homogeneity can be eliminated by grinding a small sample (Siebtechnik) so that it all passes 400 mesh.

Samples 1 to 3 contain a small amount of graphite which tends to clog filter paper. Participants were advised that before wet analysis these samples should be roasted for two hours at 800°C to burn off carbon.

4. RESULTS

Results of the survey are shown in Tables 3 to 6, and analysis of these results is in Tables 7 to 10. The figures quoted for 'number of results' (Tables 3 to 6) refer to different sample weighings, and in Tables 7 to 10, 'adjusted results' are those obtained after elimination of results more than two standard deviations from the mean.

The A.A.E.C. results for sample 4 were obtained on a portion of the minus 200 mesh ore which had been ground until it all passed 400 mesh. Spectrophotometric analysis of eight portions of the original minus 200 mesh sample 4, taken from different positions in the storage jar, gave results in the range 0.284 to 0.342% U_3O_8, with a mean and standard deviation of 0.320 ± 0.021% U_3O_8. This can be compared with the value of 0.316 ± 0.003% U_3O_8 found for 16 portions of the minus 400 mesh sample (Table 3).

5. METHODS OF ANALYSIS

The analytical methods used in the survey are summarised below.

5.1 Bromo-PADAP Spectrophotometric

The A.A.E.C. results (Table 3) were obtained using the method given in AAEC/TM552 (Florence 1970), with a sample weight of 0.25g and HNO_3-HF dissolution. Laboratories 1 to 5 used the same method, with the exceptions that Laboratory 1 used fluoborate fusion for dissolution, and Laboratory 4 took a 1 gram sample of each ore and after dissolution diluted to 100 ml before taking aliquots. Laboratory 4 also reported that sample 4 was ground to pass 400 mesh before analysis.

5.2 Fluorimetric

The fluorimetric method (Table 4) used by the A.A.E.C. and laboratories 6 and 7 was that described in AAEC/TM552. Laboratory 1 used a HNO_3-HF dissolution followed by sulphuric acid fuming, but omitted the solvent extraction of uranium. Laboratories 2 and 4 preferred an ethyl acetate extraction of uranium from an aluminium nitrate salting solution. Laboratory 5 fused the samples in pyrosulphate and dissolved the melts in 5% HNO_3. After extraction with methyl i-butyl ketone from aluminium nitrate salting solution, uranium was determined in a Na_2CO_3-K_2CO_3-NaF flux.

5.3 X-ray Fluorescence

The direct XRF method described in AAEC/TM552 was used to obtain the A.A.E.C. results (Table 5). With sample 4 very low results were found unless the sample was ground to pass 400 mesh. Laboratory 1 dissolved the samples in HF-HNO_3 and carried out XRF analysis of the solutions, using a standard addition of uranium for calibration. Laboratory 3 used a briquetted sample and a peak-to-background measurement (uranium L α)method with a silver anode X-ray tube. This laboratory also reported that further grinding of sample 4 was necessary to eliminate particle size effects. Laboratory 5 used a total mass absorption coefficient correction to compensate for matrix absorption at the peak angle for uranium. Laboratory 9 prepared a series of 'spiked' samples for each ore by mixing and grinding known weights of ore and pure U_3O_8, then measuring the fluorescent radiation for sample pellets of the original ore and the 'spiked' samples at peak and background positions.

5.4 Miscellaneous Methods

In Table 6 the emission spectrography and gamma spectrometry methods are those given in AAEC/TM552, while the β,γ radiometric method (Laboratory 5) is a modified and improved version of the procedure outlined in AAEC/TM552. The titrimetric method used by Laboratory 1 involves reduction of uranium in strong phosphoric acid solution with ferrous sulphate, followed by titration with dichromate (Eberle et al. 1970). The dibenzoylmethane procedure (Laboratory 6) includes an extraction of uranium from aluminium nitrate salting solution into tributyl phosphate, after which the uranium-dibenzoylmethane colour is developed directly in the organic phase.

6. DISCUSSION AND CONCLUSIONS

The results are compared in Tables 7 to 10. An examination of these Tables leads to the following conclusions:

(a) There is no significant bias between the mean results obtained by the bromo-PADAP spectrophotometric, the fluorimetric, and the X-ray fluorescence techniques (Tables 7 to 9). This is an important and gratifying result.

(b) The bromo-PADAP spectrophotometric method gave the most precise results, with X-ray fluorescence and fluorimetry showing similar and lower precision. The results did not indicate a clear-cut superiority for any of the various XRF techniques applied to these ores (Table 5).

(c) Emission spectrography and gamma spectrometry (Florence 1970) are intended only as sorting techniques, and the results show that they have some value for this purpose (Table 6). The β,γ radiometric method used by Laboratory 5 gave precise and fairly accurate results, and is obviously a useful technique if applied by an experienced operator.

The dibenzoylmethane spectrophotometric method failed on sample 4, but unfortunately it cannot be determined if this was a fault of the method or was operator error. The direct titrimetric method is reliable for ores with uranium contents above 0.1% U_3O_8.

Ore samples 1, 2 and 3 are suitable for use as uranium standard reference materials, and the following values have been assigned to these standards.

Standard No.	% U_3O_8 (dry basis)
1	0.0123 ± 0.0003
2	0.137 ± 0.002
3	0.748 ± 0.008

Although sample 4 was ground to pass 200 mesh, and in fact 64% passes 300 mesh (Table 2), it is not completely homogeneous. It is evident from Tables 3 to 6 that the individual 50-gram samples of No. 4 sent to the various laboratories were almost homogeneous within themselves, but that there were greater variations between the 50-gram lots. A value of 0.31 ± 0.03% U_3O_8 was assigned to sample 4, but this sample cannot be recommended for standardization purposes. The Mary Kathleen ore has an unusual matrix, which may be the main cause of the non-homogeneity. Nevertheless it would appear safer if uranium ore samples prepared for referee analysis or inter-laboratory comparisons were ground to 400 mesh, rather than 200 mesh which is usually considered adequate.

Appendix III contains our recommended procedure for the spectrophotometric determination of uranium in ores using bromo-PADAP reagent (Florence, Johnson and Farrar 1969; Florence and Farrar 1970; Johnson and Florence 1971). The changes to the procedure given in AAEC/TM552 (Florence 1970) are mainly in the acid dissolution procedure, and were made as a result of experience in applying the method to a wide range of uranium ores. None of the laboratories using the bromo-PADAP method have reported any difficulties in its application.

The method given in AAEC/TM552 for the determination of thorium in ores was found later to suffer from titanium interference. This problem has now been resolved, and a modified procedure has been published (Pakalns 1972).

7. REFERENCES

Eberle, L.R., Lerner, M.W., Goldbeck, C.G., and Rodden, C.J. (1970) - Titrimetric Determination of Uranium. USAEC rept. NBL-252.

Florence, T.M., Johnson, D.A. and Farrar, Y.J. (1969). Anal. Chem. 41, 1652.

Florence, T.M. and Farrar, Y.J. (1970). Anal. Chem. 42, 271.

Florence, T.M. (editor), (1970) - Proceedings of a Symposium on the Analytical Chemistry of Uranium and Thorium. AAEC/TM552.

Johnson, D.A. and Florence, T.M. (1971). Anal. Chim. Acta. 53, 73.

Pakalns, P. (1972). Anal. Chim. Acta. 58, 463

TABLE 1

A.A.E.C. URANIUM ORE ANALYSIS SURVEY

COMPOSITION OF STANDARD ORES

Weight per cent

Constituent \ Ore No.	1	2	3	4
SiO_2	61.0	57.1	61.0	37.5
Fe_2O_3	9.46	11.1	8.25	20.0
Al_2O_3	12.9	12.6	12.7	6.95
TiO_2	1.56	1.36	1.21	0.42
CaO	0.21	0.29	0.42	27.0
MgO	7.43	7.36	5.91	1.19
Na_2O	0.038	0.038	0.042	0.32
K_2O	1.3	1.3	2.3	7.3
ThO_2	<0.005	<0.005	<0.005	0.038
U_3O_8	0.01	0.14	0.75	0.30
Loss on ignition (1200°C)	8.99	8.71	10.4	1.68
Moisture (24 hrs. at 110°C)	2.43	2.06	2.93	0.16

Spectrographic analysis also detected traces of Pb, Cu, V (except No. 4), Cr, Mo, Mn, and Ni.

TABLE 2

SIEVE ANALYSIS OF SAMPLES 3 AND 4

Sample No.	Mesh Fraction	Per cent of Total Weight	U_3O_8 (%, Dry Basis)
3	-200	100	0.754
	-200, +300	9.7	0.593
	-300, +400	23.4	0.535
	-400	67	0.813
4	-200	100	0.316
	-200, +300	30.7	0.210
	-300, +400	63.6	0.306
	-400	5.7	1.01

TABLE 3

RESULTS OF URANIUM ORE ANALYSIS SURVEY

BROMO-PADAP SPECTROPHOTOMETRIC METHOD

Per cent U_3O_8 dry basis*

Laboratory \ Ore No.	1	2	3	4
A.A.E.C.	0.0123; 0.0001 8; 0.0122-0.0124	0.138; 0.001 8; 0.137-0.139	0.754; 0.005 12; 0.749-0.764	0.316; 0.003 16; 0.312-0.320
1	0.0133; 0.0001 4; 0.0132-0.0134	0.132; 0.001 4; 0.131-0.132	0.751; 0.004 4; 0.748-0.755	0.295; 0.002 4; 0.292-0.296
2	0.016; 0.002 2; 0.014-0.018	0.145; 0.003 2; 0.142-0.148	0.733; 0.007 2; 0.725-0.740	0.286; 0.004 2; 0.281-0.290
3	0.0115; 0.0005 2; 0.011-0.012	0.135; 0.005 2; 0.13-0.14	0.74; 0.00 2; 0.74	0.265; 0.005 2; 0.26-0.27
4	0.0115; 0.0002 3; 0.0113-0.0117	0.137; 0.003 3; 0.134-0.140	0.758; 0.003 2; 0.755-0.761	0.340; 0.000 3; 0.340

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* Results show mean; standard deviation; number of results; range

TABLE 4

RESULTS OF URANIUM ORE ANALYSIS SURVEY

FLUORIMETRIC METHOD

Per cent U_3O_8, dry basis[*]

Laboratory / Ore No.	1	2	3	4
A.A.E.C.	0.0128; 0.0003 4; 0.0124-0.0130	0.129; 0.007 4; 0.120-0.135	0.730; 0.03 4; 0.703-0.764	0.313; 0.003 4; 0.308-0.315
1	0.0135; 0.0001 4; 0.0134-0.0138	0.134; 0.004 4; 0.131-0.141	0.764; 0.009 4; 0.741-0.780	0.283; 0.006 4; 0.273-0.300
2	0.0147; 0.0006 2; 0.0141-0.0153	0.135; 0.005 2; 0.129-0.140	0.803; 0.006 2; 0.796-0.809	0.315; 0.002 2; 0.313-0.317
4	0.0115; 0.0002 3; 0.0114-0.0118	-	-	-
5	0.011; 0.001 2; 0.010-0.012	0.137; 0.001 2; 0.136-0.138	0.711; 0.008 2; 0.703-0.719	0.251; 0.000 2; 0.251
6	0.008 3	0.137 3	0.600 3	0.247 3
7	0.010 1	0.13 1	0.63 1	0.32 1

[*] Results show mean; standard deviation; number of results; range

TABLE 5

RESULTS OF URANIUM ORE ANALYSIS SURVEY

X-RAY FLUORESCENCE METHOD

Per cent U_3O_8, dry basis*

Laboratory / Ore No.	1	2	3	4
A.A.E.C.	0.0116; 0.0006 2; 0.0110-0.0122	0.135; 0.007 2; 0.128-0.142	0.744; 0.03 2; 0.71-0.77	0.354; 0.005 2; 0.349-0.359
1	too low	0.134; 0.003 4; 0.131-0.142	0.764; 0.011 4; 0.742-0.772	0.301; 0.008 4; 0.287-0.313
3	0.017; 0.000 2; 0.017	0.15; 0.00 2; 0.15	0.715; 0.005 2; 0.71-0.72	0.21; 0.00 2; 0.21
5	0.012; 0.001 2; 0.010-0.012	0.138; 0.001 2; 0.137-0.139	0.735; 0.002 2; 0.733-0.736	0.258; 0.002 2; 0.255-0.260
8	0.0139 1	0.149 1	0.69 1	0.29 1
9	0.0102; 0.0006 2; 0.00973-0.0108	0.134; 0.007 3; 0.128-0.142	0.874; 0.02 3; 0.838-0.899	0.270; 0.004 2; 0.265-0.274

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*Results show mean; standard deviation; number of results; range

TABLE 6

RESULTS OF URANIUM ORE ANALYSIS SURVEY

MISCELLANEOUS METHODS

Per cent U_3O_8, dry basis[*]

Laboratory / Ore No.	1	2	3	4
A.A.E.C. (emission spectrography)	<0.02	0.10	0.50	0.17
A.A.E.C. (gamma spectrometry)	0.057	0.106	0.540	0.323
1 (titrimetric)	too low	0.139; 0.001 2; 0.138-0.141	0.780; 0.007 2; 0.773-0.789	0.272; 0.007 5; 0.261-0.280
3 (HNO_3, ether sepn., then Br-PADAP spectrophotometric)	0.012; 0.000 2; 0.012	0.14; 0.00 2; 0.14	0.745; 0.005 2; 0.74-0.75	0.265; 0.005 2; 0.26-0.27
5 (β,γ-radiometric)	0.017; 0.000 2; 0.017	0.138; 0.000 2; 0.138	0.747; 0.017 2; 0.730-0.764	0.262; 0.002 2; 0.260-0.264
10 (dibenzoyl methane spectrophotometric)	0.011 1	0.138 1	0.740 1	0.140 1

[*] Results show mean; standard deviation; number of results; range

TABLE 7

A.A.E.C. URANIUM ORE ANALYSIS SURVEY

BROMO-PADAP SPECTROPHOTOMETRIC METHOD. CALCULATIONS

Mean per cent U_3O_8, dry basis, and standard deviation

Ore No. Laboratory	1	2	3	4
A.A.E.C.	0.0123±0.0001	0.138±0.001	0.754±0.005	0.316±0.003
All Laboratories	0.0129±0.0019	0.137±0.005	0.747±0.010	0.300±0.029
All Laboratories adjusted results*	0.0122±0.0009	0.137±0.005	0.747±0.010	0.300±0.029

*Results remote from mean rejected

TABLE 8

A.A.E.C. URANIUM ORE ANALYSIS SURVEY

FLUORIMETRIC METHOD. CALCULATIONS

Mean per cent U_3O_8, dry basis, and standard deviation

Ore No. Laboratory	1	2	3	4
A.A.E.C.	0.0128±0.0003	0.129±0.007	0.730±0.03	0.313±0.003
All Laboratories	0.0116±0.0023	0.134±0.003	0.706±0.08	0.288±0.033
All Laboratories adjusted results*	0.0123±0.0017	0.134±0.003	0.728±0.06	0.288±0.033

*Results remote from mean rejected

TABLE 9

A.A.E.C. URANIUM ORE ANALYSIS SURVEY

X-RAY FLUORESCENCE METHOD. CALCULATIONS

Mean per cent U_3O_8, dry basis, and standard deviation

Ore No. / Laboratory	1	2	3	4
A.A.E.C.	0.0116±0.0006	0.135±0.007	0.744±0.03	0.354±0.005
All Laboratories	0.0129±0.0026	0.140±0.008	0.754±0.06	0.281±0.048
All Laboratories adjusted results*	0.0119±0.0016	0.140±0.008	0.730±0.03	0.281±0.048

[*] Results remote from mean rejected

TABLE 10

A.A.E.C. URANIUM ORE ANALYSIS SURVEY

RELATIVE STANDARD DEVIATIONS

	Relative standard deviation, per cent[*]			
Method / Ore No.	1	2	3	4
Br-PADAP	0.8,14.7,7.4	0.7,3.7,3.7	0.7,1.3,1.3	1.0,9.7,9.7
Fluorimetric	2.3,19.8,13.7	5.4,2.2,2.2	4.1,11.3,8.2	1.0,11.4,11.4
X-ray	5.2,20.2,13.4	5.2,5.7,5.7	4.0,8.0,4.1	1.4,17.1,17.1
β,γ-radiometric[††]	-	-	2.3	0.8
Titrimetric[‡]	too low	0.9	0.9	2.6

[*] Results shown in order: A.A.E.C., all laboratories, all laboratories adjusted.

[††] Laboratory No. 5.

[‡] Laboratory No. 1.

APPENDIX I

LIST OF PARTICIPANTS

The number of the participating laboratories has no connection with the order in which the analytical results are listed.

1. Mr. T.M. Florence, Australian Atomic Energy Commission, Research
   Establishment, Lucas Heights, N.S.W. 2232.
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4. Mr. P. Farquhar, Geochemical and Mineralogical Laboratories Pty. Ltd.,
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5. Mr. R.W. Yerbury, Geophoto Resources Consultants, 30-33 Herschel Street,
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9. Mr. J.F. Westley, Territory Enterprises Pty. Ltd., G.P.O. Box 384D,
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10. Mr. D.J. O'Hearn, The Broken Hill Proprietary Co. Ltd., P.O. Box 196,
    Newcastle, N.S.W. 2300.
11. Mr. B.J. Heffernan, University of Queensland, St. Lucia, Brisbane,
    Queensland, 4067.

APPENDIX II

LETTER TO PARTICIPANTS

Dear Sir,

COMPARATIVE SURVEY OF URANIUM ANALYTICAL METHODS

I have forwarded, by separate post, four 50-g samples of uranium ore to be used in the 'round-robin' analytical survey which we discussed at the A.A.E.C. Symposium held in May 1970.

The samples are marked 1, 2, 3 and 4. The U_3O_8 contents are in the ranges:

Sample No.	% U_3O_8 (dry basis)
1	0.008 - 0.015
2	0.08 - 0.15
3	0.5 - 0.7
4	0.2 - 0.4

Results should be reported as % U_3O_8 on a dry basis, moisture being determined by heating in an air oven at 110°C for 24 hours.

To make the survey meaningful, I would be grateful if you would -

(a) analyze the ores by the methods described in the Symposium Proceedings (AAEC/TM552), using as many of the different techniques as you have at your disposal;

(b) report any variations you make to the recommended procedures;

(c) also analyze the samples by any method which you believe to be superior to those given in the report; and

(d) try as far as possible to relate the results to a normal routine analysis situation by taking no unusual precautions, and using the staff who would normally do analyses of this type.

The ores have been gound to pass 200 mesh, but I would suggest that the bottle be shaken before each sample is removed. At least two portions of each ore should be used for analysis.

Please report the results directly to me, showing the result of each individual analysis. Comments on any difficulties encountered and suggestions for improvements would be appreciated.

The analysis figures from the twelve laboratories participating in the survey will be subjected to statistical examination and a report issued as soon as possible after all analyses have been received. Correspondence will be completely confidential, and the report summarizing the survey will not identify a laboratory to any set of results.

Could I please have the reports in by the end of April.

Yours faithfully,

(T.M. FLORENCE)
Head, Inorganic Chemistry Section

APPENDIX III

RECOMMENDED PROCEDURE FOR THE DETERMINATION OF URANIUM IN ORES WITH BROMO-PADAP

(i) Weigh 0.5g of ore (400 mesh) into a platinum dish, add 5 ml of 15M HNO_3 and 5 ml of 40% HF, and evaporate to dryness on a water bath. Add a further 5 ml of 15M HNO_3 and 5 ml of 40% HF and again evaporate to dryness on the water bath. Add 4 ml of 4.5M (1:3) H_2SO_4 and 3 ml of 72% $HClO_4$ and fume on a hot plate for 5 minutes. Cool and dissolve the residue in 20 ml of 5M HNO_3. Filter the solution through a small paper into a 100 ml volumetric flask. Ash the filter paper in the platinum dish, add 0.3g of sodium carbonate and fuse for 5 minutes. Dissolve the melt in 20 ml of 5M HNO_3 and add to the 100 ml volumetric flask. Dilute to volume with water.

(ii) Pipette an aliquot (not more than 50 ml) of the sample solution (1-150 μgU) into a separating funnel. Add 5.0 ml of 2% sodium fluoride, 5.0 ml of 5% ascorbic acid, and sufficient 2M HNO_3 to make the total volume of solution in the funnel equal to 60 ml. Mix. Pipette in 5.00 ml of 0.1M TOPO and extract for one minute. Allow the phases to separate and run off the aqueous phase.

(a) The ore sample (0.1g) can also be attacked by fusion with sodium fluoroborate (1g). The melt is then dissolved in 40 ml of 5M HNO_3, and diluted to 100 ml with water.

(b) If the sample contains graphite, ash for 2 hours at 800°C before acid dissolution.

(c) The residue from the H_2SO_4-$HClO_4$ fuming usually does not contain uranium, and sodium carbonate fusion can be omitted (Florence and Farrar 1970). If sodium carbonate fusion is omitted, dissolve the residue in 40 ml of 5M HNO_3.

(d) If sodium fluoroborate fusion was used for sample dissolution, add 0.3g of NaF in place of 5 ml of 2% NaF.

APPENDIX III (Cont'd.)

(iii) Pipette 2.00 ml of the organic phase into a dry 25 ml volumetric flask. Add 1.0 ml of dilute complexing solution, 4.00 ml of 0.05% bromo-PADAP, and 1.0 ml of triethanolamine buffer pH 8.35 in that order, mixing thoroughly after each addition. Stopper the flask and allow to stand for 10 minutes. Add 16.0 ml of ethanol and dilute to volume with water.

(iv) Measure the colour at 574 nm in a stoppered cell against a reagent blank carried through the extraction procedure.

(e) The method is based on the use of a 2.00 ml aliquot of the organic phase. No other aliquot size should be used.

(f) Thorough mixing is essential for good precision.

(g) Standards and blanks should be extracted from 2M HNO_3. 4 cm or 5 cm path length cells can be used for low uranium concentrations.

(h) Beer's Law is obeyed up to an absorbance of 1.3.