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SUBJECT: Comparison of Two Colorimetric Methods for Uranium

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ABSTRACT

In order to establish the feasibility of using two colorimetric methods for the determination of uranium interchangeably, according to the interferences encountered in a particular sample, results were obtained by each of the methods and compared. The two methods, the dibenzoyl methane method and the ethyl acetate-ammonium thiocyanate procedure, were compared on the basis of values secured on the same day, on different days, on an analysis of the variance, and on an analysis of the residual error for the methods on different days. On the basis of the findings of these tests, it is concluded that the two methods can be used interchangeably to determine the uranium content of the ethyl acetate extracts of samples. Since the interferences in the two methods are different, the uranium content of a variety of materials can be determined without additional separations being required, which, of course, will result in better and faster service.

DISCLAIMER

COMPARISON OF TWO COLORIMETRIC METHODS FOR URANIUM

R. L. McCutchen

Early last year, when the dibenzoyl methane (DBM) method, in which uranium is extracted by means of tri-n-octylphosphine oxide (TOPO) in cyclohexane, was being considered as a replacement method for the ethyl acetate (EtAc)-ammonium thiocyanate (CNS) procedure then in use for the determination of uranium in the colorimetric range, it was noted that the uranium content of the EtAc extract could be determined by both methods. Inasmuch as the results secured by the TOPO-DBM method had been less precise than expected, the possibility that an EtAc-DBM procedure would yield reliable results was investigated. Since the interferences in the CNS and DBM methods are different, it was believed that the uranium content of a variety of materials could be determined, without additional separations being required, if the two methods could be used interchangeably. If this proved to be feasible, the time required to analyze certain types of samples would be decreased and, as a consequence, better and faster service could be given.

Accordingly, the uranium content of 11 samples was determined in duplicate by each of these methods; the duplicate determinations were made on different days. In all, four values were obtained for each sample; one value per method per day or two results per sample were obtained by each method. The procedures for the two methods are given on the attached sheets.

When these results were compared, see Table I, it was noted that the values obtained by means of the CNS method on the first day were about 15 µg/ml higher than those secured by the DBM method; on the second day, the DBM results were higher by about 7 µg/ml.

Table I

Comparison of Uranium Values Secured by
Two Colorimetric Methods on the Same Day

Sample Designation	First Day (A)			Second Day (B)		
	CNS	DBM	Difference	CNS	DBM	Difference
	Uranium, µg/ml			Uranium, µg/ml		
R-4523	96	88	+ 8	78	90	- 12
24	116	104	+ 12	94	100	- 6
25	80	95	- 15	96	100	- 4
26	120	101	+ 19	98	103	- 5
27	119	114	+ 5	102	112	- 10
28	99	92	+ 7	100	90	+ 10
29	108	86	+ 22	82	90	- 8
30	91	77	+ 14	80	84	- 4
31	116	82	+ 34	81	87	- 6
32	149	129	+ 20	119	122	- 3
33	128	117	+ 11	119	128	- 9
		Average:	+ 15		Average:	- 7

"A" = First Series of Tests
"B" = Second Series of Tests

CNS = Ammonium Thiocyanate
DBM = Dibenzoyl Methane

Since one extract per sample was made on each of the two days, and the uranium content of these extracts was determined by both methods, a comparison of results by method was made to determine the significance of the difference between the two methods. This comparison is given in Table II.

Table II

Comparison of Uranium Values Obtained by the Same Method on Different Days

Sample Designation	Thiocyanate Method			Dibenzoyl Methane Method		
	A	B	Difference	A	B	Difference
	Uranium, µg/ml			Uranium, µg/ml		
R-4523	96	78	+ 18	88	90	- 2
24	116	94	+ 22	104	100	+ 4
25	80	96	- 16	95	100	- 5
26	120	98	+ 22	101	103	- 2
27	119	102	+ 17	114	112	+ 2
28	99	100	- 1	92	90	+ 2
29	108	82	+ 26	86	90	- 4
30	91	80	+ 11	77	84	- 7
31	116	81	+ 35	82	87	- 5
32	149	119	+ 30	129	122	+ 7
33	128	119	+ 9	117	128	- 11
		Average:	+ 16		Average:	- 2

A = First series of tests
B = Second series of tests

From the compilation given in Table II, it appears that the results secured by the CNS method on the first day are about 16 µg/ml higher than those obtained on the second day, whereas there is little difference between the uranium values determined by means of the DBM method on the two days.

In order to evaluate the significance of these observations, an analysis of variance was made; see Table III.

Table III

Analysis of Variance

Source	Degrees of Freedom D.F.	Total Sum of Squares T_{ss}	Mean Sum of Squares M_{ss}	Variance Ratio $F_{exp.}$	Variance Ratio $F_{theor.}$	Variance Ratio Sign.
Methods	1	146	146	1.8	4.2	-
Samples	10	8,902	890	11	2.1	+
Days	1	428	428	5.3	4.2	+
Residual	32	2,579	81			
Total	43	12,055	280			

$F_{theor.}$ = Value taken from table of F-values at $D.F_1$ = 1 or 10 and $D.F_2$ = 32; 95-per cent confidence level.

From this analysis, it was found that the reproducibility of the two methods is essentially the same. Since the experimental variance ratio, F_e, is less than the theoretical value, F_t, at a 95-per cent confidence level, the difference in these two methods is not significant. When the variability attributable to the days is considered, however, a significant difference is indicated; in this case, F_e is greater than F_t at a 95-per cent confidence level. As was expected, a test of significance was obtained for the samples; eleven different samples were analyzed in this test.

While it is unlikely that the DBM method contributed to this test of significance, a residual analysis was made to determine the experimental error attributed to the two methods. A summary of this residual analysis is given in Table IV.

Table IV

Analysis of Residual Error for the CNS and DBM Methods on Different Days

Method	Day	Degrees of Freedom D.F.	Residual Error: Total Sum of Squares T_{ss}	Residual Error: Mean Sum of Squares M_{ss}
CNS	A	8	1098	137
	B	8	608	76
DBM	A	8	528	66
	B	8	306	38
CNS	A	8	1098	137
DBM		8	528	66
CNS	B	8	608	76
DBM		8	306	38

In both cases, the residual, or experimental error, was less on the second day and apparently is independent of the method used. The reason for this has not been established.

When the results of these evaluations were summarized, it was noted that the uranium values obtained by means of the CNS procedure, on the first day, were about 15 µg/ml higher than those secured by the DBM method, while on the second day, the DBM results were higher by 7 µg/ml. The difference between the results obtained on different days by the DBM method was small, 2 µg/ml, as compared to 16 µg/ml for the CNS method but, when an analysis of variance was made, the two methods were found to be essentially the same. The difference between the tests that were made on two separate days, however, was found to be significant, but apparently independent of the method used.

It may be necessary to modify this last observation if the results of future tests do not confirm this hypothesis. On the basis of these tests, however, it is concluded that the CNS and DBM methods can be used interchangeably to determine the uranium content of the EtAc extracts of samples. Since the interferences in the two methods are different, the uranium content of a variety of materials can be determined without additional separations being required.

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Uranium: Ethyl Acetate Extraction

Reagents:

1. Aluminum Nitrate-Tartaric Acid Solution: Dissolve 2,270 grams of $Al(NO_3)_3 \cdot 9H_2O$ and 80 grams of tartaric acid in 2,270 ml of water. The final volume of this reagent should be 3560 ± 60 ml.

2. Ethyl Acetate: Reagent grade.

3. Nitric Acid: Concentrated.

Procedure:

1. Transfer a test portion, which should not exceed 2 ml, into an extraction flask.

2. Evaporate to dryness on a hot plate.

3. Add 2 ml of water and 2 drops of nitric acid to each flask.

4. Heat to effect solution and then allow the solution to cool.

5. Add 15 ml of the aluminum nitrate-tartaric acid reagent and 20 ml of ethyl acetate to each flask.

6. Place tops on extraction flasks, invert and place in mechanical shaker.

7. Shake flasks for two minutes.

8. Remove extraction flasks from shaker, invert, place in racks and allow the phases to separate.

   Note: The organic phase, containing the uranium, is on top.

9. Determine the uranium content of the ethyl acetate phase by means of the colorimetric, ammonium thiocyanate-stannous chloride - ethyl alcohol procedure or the dibenzoylmethane method.

Uranium: Ammonium Thiocyanate-Ethyl Alcohol Method

Reagents:

1. Ammonium Thiocyanate-Ethyl Alcohol-Stannous Chloride Reagent: Dissolve 65 grams of NH_4CNS in 23 ml of water; add 10 ml of ethyl alcohol (95%). Heat to 26°C and mix with a Thermo-stirrer. Filter through a No. 1 filter paper.

   Note: This quantity of reagent is sufficient for 9 samples.

2. Stannous Chloride Solution: Dissolve 10 grams of $SnCl_2 \cdot 2H_2O$ in 10 ml HCl. Dilute to 100 ml with water. Filter if necessary.

Procedure:

1. Transfer 10 ml of the ethyl acetate phase* into a 25-ml volumetric flask.

2. Dilute to volume with the ammonium thiocyanate-stannous chloride-ethyl alcohol reagent. Stopper flask and shake well.

3. Measure the absorbancy of the sample, immediately, at a wave-length of 375 mμ. A reagent blank which is processed the same as the samples is used as a reference solution. The absorbancy measurements are secured by means of a Beckman Model B Spectro-photometer; see Notes A and B.

NOTE A

Fill both cells with water and measure the absorbancy of the solution in one cell against that in the other cell. If the cells do not match perfectly, arrange the cells in the holder so that the "high" cell is in the number two position of the holder and the "low" cell is in the number one position. Use the slit width knob to set the absorbancy of the water in the cell, which is in the number one position, on "zero"; then measure and record the absorbancy of the water in the second cell (Reading A). Now fill the number two cell with a solution of the blank, cap the cell, and measure the absorbancy of this solution (Reading B). Record the true absorbancy of the solution of the blank as follows:

Reading B - Reading A = True absorbance of blank

* See procedure for ethyl acetate extraction.

Use the slit width knob to adjust the absorbancy of the blank to Reading A, above. Fill the cell, in position one, with the solution whose absorbancy is to be measured; then adjust the absorbancy of the blank, cell two, to reading A. Measure and record the absorbancy of the solution in cell one. Continue in this manner, until the absorbancy of all the solutions has been measured.

NOTE B

If the absorbancy of the sample is 0.5 or greater at a wavelength of 375 mμ, measure the absorbancy at a wavelength of 420 mμ.

References:

1. DeSesa, M. A., Nietzel, O. A., U. S. Atomic Energy Comm. ACCO-54 (July 19, 1954).

2. DeSesa, M. A., Nietzel, O. A., "Spectrophotometric Determination of Uranium with Thiocyanate in Butyl Cellosolve-Methyl Isobutyl Ketone-Water Medium", Anal. Chem. 29, 756, (1957).

3. Roemer, A. F., "Uranium, Spectrophotometric Ethyl Acetate - Ammonium Thiocyanate - Ethanol Method," The ORNL Master Analytical Manual, TID-7015, Method No. 1 219212.

Uranium: Dibenzoyl Methane Method

Reagents:

1. Dibenzoyl Methane-Ethyl Alcohol Reagent: Dissolve 0.1 gram dibenzoyl methane in 100 ml of ethyl alcohol; (0.1% w/v).

2. Pyridine-Ethyl Alcohol Reagent: Dilute 25 ml of pyridine to 100 ml with ethyl alcohol (25% v/v); mix well before using.

3. Ethyl Alcohol: 95 per cent.

Procedure:

1. Transfer a 3-ml portion of the ethyl acetate extract* into a 25-ml volumetric flask.

2. Add 5 ml of the pyridine-ethyl alcohol reagent and 5 ml of the dibenzoyl methane-ethyl alcohol reagent to each flask.

3. Dilute to volume with ethyl alcohol and mix well.

4. Measure absorbancy at a wavelength of 405 mμ. A reagent blank is used as the reference solution. Measurements are made by means of a Beckman B Spectrophotometer.

   Note: The colored complex of uranium and dibenzoyl methane is stable - absorbancy measurements can be made whenever it is convenient to do so.

* See procedure for ethyl acetate extraction.

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