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DETERMINATION OF TRIVALENT URANIUM WITH METHYLENE BLUE

W. J. Ross
A. S. Meyer, Jr.
J. C. White

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DETERMINATION OF TRIVALENT URANIUM WITH METHYLENE BLUE

W. J. Ross, A. S. Meyer, Jr., J. C. White

ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director
C. D. Susano, Associate Director

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ABSTRACT

A direct titrimetric method for the determination of trivalent uranium in uranium trifluoride and mixtures of fused fluoride salts was developed. The method is based on the stoichiometric oxidation of trivalent uranium to the tetravalent oxidation state with an acidic solution of methylene blue. The sample containing trivalent uranium is dissolved at room temperature in an excess of standard methylene blue solution in a carbon dioxide atmosphere; the excess oxidant is determined by titration with standard chromous sulfate. The coefficient of variation of the method is 1.5 per cent for 5-mg quantities of trivalent uranium. The method was applied to various mixtures of fluoride salts containing both trivalent and tetravalent uranium.

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DETERMINATION OF TRIVALENT URANIUM WITH METHYLENE BLUE

INTRODUCTION

Studies of the chemical behavior of uranium in fused salt mixtures require an analytical method for the determination of trivalent uranium in the presence of tetravalent uranium.

The reactions of trivalent and tetravalent uranium compounds are essentially identical since the unstable, trivalent, oxidation state is converted to the tetravalent state during dissolution in aqueous media. This similarity makes it impossible to determine the two forms of uranium by any procedure that entails dissolution of the solid prior to separation of the oxidation states. Dissolution, separation, and determination of the two species must be performed simultaneously. Selective oxidation of trivalent to tetravalent uranium by an oxidizing solvent has been considered the most feasible method for attacking such a problem. The oxidation potentials[1]

$$U^{3+} = U^{4+} + e \ (1\ \underline{M}\ HClO_4) \qquad E^{o} = +0.631\ V \qquad (1)$$

$$U^{4+} + 2H_2O = UO_2^{++} + 4H^{+} + 2e^{-} \qquad E^{o} = -0.41\ V \qquad (2)$$

afford a one-volt difference that could be applied to such a method. These potentials, and all following, are referred to a normal hydrogen electrode.

The selection of an oxidizing agent that can convert trivalent to tetravalent uranium is complicated by the inherent instability of trivalent uranium in aqueous media. Previous studies in this laboratory have shown that oxidation of trivalent uranium by hydrogen ion occurs readily, even in the presence of stronger oxidants[2]. Several possible oxidizing agents with potentials of 0 to -0.3 v have been tested. Competitive oxidation by

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hydrogen ion occurred in every test that was performed in an acid solution. Manning, et. al. have shown that oxidation of trivalent to tetravalent uranium by hydrogen ion is stoichiometric under certain conditions[3]. This reaction has been made the basis of a method for determining trivalent uranium by measurement of the hydrogen formed through the reduction of hydrogen ion. The sensitivity of this hydrogen evolution method is limited by the accuracy with which gasometric measurements can be performed.

An oxidizing agent with a potential more negative than -0.3 v cannot be applicable to the selective oxidation of trivalent uranium if tetravalent uranium is also oxidized to UO_2^{++} by the same oxidant. It has been considered worth-while to investigate some of these stronger oxidizing agents as the basis for a method similar to the hydrogen evolution method. To be of any practical value, such a method should be more sensitive and less time consuming than the hydrogen evolution procedure.

Methylene blue has been considered a possible oxidizing agent that could be applied to a colorimetric or volumetric method for the determination of trivalent uranium. This water soluble dye, $C_{16}H_{18}N_3SCl$, exhibits a potential which is dependent upon the pH of the solution as shown in Table 1[4].

Table 1

Effect of pH Upon the Oxidation Potential of Methylene Blue

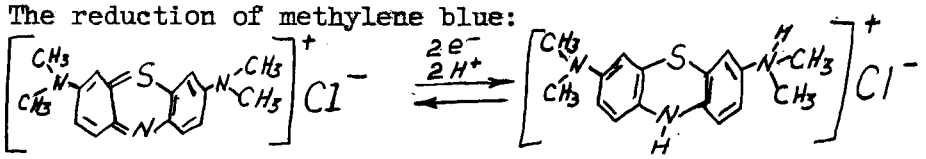
pH	Eh[a]	pH	Eh
0	+0.52	6	+0.04
1	+0.44	7	+0.01
2	+0.35	8	-0.03
3	+0.26	9	-0.05
4	+0.17	10	-0.08
5	+0.10	11	-0.11

[a] Eh is the potential of the system at half titration.

The variability of its potential has led to many applications of methylene blue as an indicator and oxidizing agent[4,5].

Neutral and acidic solutions of methylene blue are stable. Rabinowitch[6] states that neutral, aqueous solutions undergo very slow decomposition through contact with glass containers. This deterioration is eliminated if the pH is lowered to 3.5.

The reduction of methylene blue:



(3)

yields the colorless leuco-base, methylene white, which is oxidized very easily by air.

The possibility also existed that the decolorization of methylene blue would make this reagent applicable to a colorimetric method based upon the extent of reduction by trivalent uranium. The absorption spectrum of methylene blue, between 320 and 750 mμ, has one maximum at 655 mμ. The extinction coefficient of an 0.01 N solution, however, is too high to be measured and a more dilute solution would be impractical as an oxidizing agent. Furthermore, dilution with water causes partial oxidation of methylene white solution. An appreciable amount of methylene blue, in excess of that required to oxidize trivalent uranium would make it impossible to measure any changes in absorbancy which occur due to the formation of methylene white.

The potential difference of methylene blue and trivalent uranium, in strongly acidic solution, is sufficiently large to permit quantitative conversion of trivalent to tetravalent uranium:

$$\text{Methylene blue} + 2U^{3+} \longrightarrow \text{methylene white} + U^{4+} \qquad E = +1.16\ v \qquad (4)$$

Inasmuch as UF_3 and the fluoride mixtures are soluble only in strongly acidic solutions, the EMF of the methylene white-methylene blue couple has been assumed to be -0.53 v. The EMF of the U^{4+}-UO_2^{++} couple varies with pH. In strongly acidic solutions, the potential difference of methylene blue and tetravalent uranium is not sufficiently large to cause oxidation of tetravalent uranium to UO_2^{2+}:

$$\text{Methylene blue} + 2U^{4+} \longrightarrow \text{methylene white} + UO_2^{++} \quad E = +0.12 \text{ v.} \qquad (5)$$

The potential difference between methylene blue and hydrogen is large enough to give quantitative oxidation of hydrogen to hydrogen ion in an acid solution. The dissolution of trivalent uranium in HCl media is known to be accompanied by the liberation of a stoichiometric volume of hydrogen. The presence of methylene blue in HCl media could result in the oxidation of trivalent uranium ions which exist momentarily or in the oxidation of hydrogen formed through the reaction between HCl and trivalent uranium. In either event, a stoichiometric relationship between trivalent uranium and methylene blue is obtained. These assumptions have been tested experimentally in this investigation.

EXPERIMENTAL

The Reaction Between Methylene Blue and Hydrogen

The reduction of solutions of methylene blue by hydrogen was easily confirmed by bubbling hydrogen through an 0.02 M solution, pH 2.9. The methylene blue solution was decolorized rapidly but was slowly reoxidized when the hydrogen flow was discontinued and the solution exposed to air. Under an atmosphere of dry CO_2, the methylene white was stable for as long as an hour after the hydrogen flow was discontinued. The same results were

obtained in 3 M HCl solutions of methylene blue. Since hydrogen is oxidized in very slightly acidic solutions where methylene blue has a potential of -0.26 v, the rate of oxidation should be even faster in strong acids where the potential of methylene blue is -0.53 v. This difference in rate was not measured in these tests.

Reaction Between Methylene Blue and Chromous Sulfate

The instability of trivalent uranium ion in solution and the difficulties involved in attempting to retain hydrogen until it could be oxidized precludes the direct titration of a solution of trivalent uranium in HCl. An alternative is the dissolution of the solid, trivalent, uranium in an acid solution which contains a known and excessive amount of oxidant. The unreduced methylene blue is determined by titration with a standard reducing agent. The determination of trivalent uranium is then accomplished through calculation of the amount of methylene blue which was reduced during the dissolution of the sample.

A suitable reducing agent must be stable and its potential sufficiently negative to reduce methylene blue quantitatively. The potential of the Fe^{++}, Fe^{3+} couple (-0.77 v) is too high for consideration. Titanous and chromous ions are stronger reducing agents than ferrous ions and therefore should reduce methylene blue quantitatively. Both of these ions are easily oxidized by air and must be stored under inert atmospheres if they are to be used as standard solutions.

$$Ti^{3+} \longrightarrow TiO^{++} + e^- \qquad E^o = -0.10 \text{ v} \qquad (6)$$

$$Cr^{++} \longrightarrow Cr^{3+} + e^- \qquad E^o = +0.40 \text{ v} \qquad (7)$$

Solutions of $Ti_2(SO_4)_3$ and $CrSO_4$ were prepared by reducing $Ti(SO_4)_2$ and $Cr_2(SO_4)_3$ with one per cent zinc amalgam. The solutions were stored over the

amalgam and under an atmosphere of hydrogen. Both reagents decolorized methylene blue in 0 to 6 M HCl.

Due to the ease with which it can be prepared and to its greater reducing potential, $CrSO_4$ was selected in preference to $Ti_2(SO_4)_3$ as a reducing agent in these studies. Lingane's method[7] for preparing $CrSO_4$ and standardizing it against $CuSO_4$ was followed. A standard solution of 0.05 N $CrSO_4$ was prepared by diluting 0.1 N $Cr_2(SO_4)_3$ with 0.5 M H_2SO_4 prior to reduction with zinc amalgam. The solution was stored under hydrogen in a 10-ml Machlett buret which had a one-liter reservoir. Standardization was performed by titrating potentiometrically 0.0500 N $CuSO_4$ solutions. A Beckman pH meter, Model H-2, with gold and saturated calomel electrodes was utilized to follow the titrations. An atmosphere of CO_2 was maintained over the solutions by adding small pieces of dry ice to the cuprous solution. The results given in Table 2 are representative of such standardizations versus three $CuSO_4$ solutions.

Table 2

Standardization of Chromous Sulfate with Copper Sulfate
0.5000 Meq $CuSO_4$

	$CrSO_4$ ml	$CrSO_4$ Normality
1a	10.47	0.0478
1b	10.43	0.0479
2a	10.43	0.0479
2b	10.52	0.0475
3a	10.47	0.0478
3b	10.47	0.0478
Average		0.0478
Coefficient of Variation		0.3 per cent

The reaction between Cr^{2+} and Cu^{2+} ions to form Cr^{3+} and Cu^{+} is rapid and stoichiometric. A potential change of 0.3 v occurs at the end point (+0.1 v vs NHE). Continued titration by $CrSO_4$ causes further reduction of Cu^{+} to metallic Cu with a much smaller potential change at the end point (-0.2 v vs NHE). The excellent precision afforded by the initial reaction precluded further study of possible application of the second equivalence point.

Solutions of 0.1 N and 0.05 N $CrSO_4$ in 0.5 M H_2SO_4 have been found to be completely stable for two months when stored under hydrogen.

The stoichiometry of the reaction between methylene blue and $CrSO_4$ has been investigated by visual and potentiometric titrations of 0.02 N methylene blue solutions. Visual titrations of methylene blue were performed by (1) transferring the required volumes of reagents to a 125-ml Erlenmeyer flask, (2) adding to the solution a piece of dry ice sufficiently large to maintain a heavy blanket of CO_2 over the solution during titration, (3) shaking the flask for 1 to 2 minutes to insure displacement of air by CO_2, and (4) titrating the deep blue solution with standard $CrSO_4$ until the last trace of blue color disappeared. The data given in Table 3 are indicative of the precision of such titrations.

Table 3

Visual Titration of Methylene Blue Solution with Chromous Sulfate

0.1000 N $CrSO_4$
2.4 to 4.8 N HCl

$CrSO_4$ Required, ml	Methylene Blue, N
4.02	0.0201
4.05	0.0203
4.07	0.0204
4.07	0.0204
4.07	0.0204
4.07	0.0204
Average	0.0203
Coefficient of Variation	0.6 per cent

The precision is entirely satisfactory despite the difficulty encountered in observing the color change produced by 0.01 to 0.02-ml increments of 0.1 N $CrSO_4$. The color change was indistinct when 0.02 to 0.03-ml increments of 0.05 N $CrSO_4$ were required to achieve a definite color transition.

The rate of reaction and the magnitude of the potential change at the end point were determined through potentiometric titrations of 0.02 N methylene blue solutions with $CrSO_4$ under an atmosphere of CO_2. Figure 1 shows the curve obtained with data from a Beckman pH meter, Model H2, when gold and saturated calomel electrodes were used. The equilibrium of the system is quickly restored after the addition of 0.02 to 2.0 ml of titrant when the solution is stirred magnetically. The potentiometric end point corresponds closely to the disappearance of the blue color.

The rapidity with which equilibrium was attained after the addition of each increment of titrant and the magnitude of the potential change (0.5 v) at the equivalence point agree with that expected from the 0.9 v potential difference between Cr^{2+} and methylene blue. The small difference between visual and potentiometric equivalence points is believed to be real rather than due to experimental error.

The effect of changes in HCl concentration upon the redox titer of methylene blue solutions was determined. Various acid concentrations were achieved by adding HCl to aqueous methylene blue solutions or to solid methylene blue. The solutions were titrated immediately with $CrSO_4$ solution. The results are given in Table 4.

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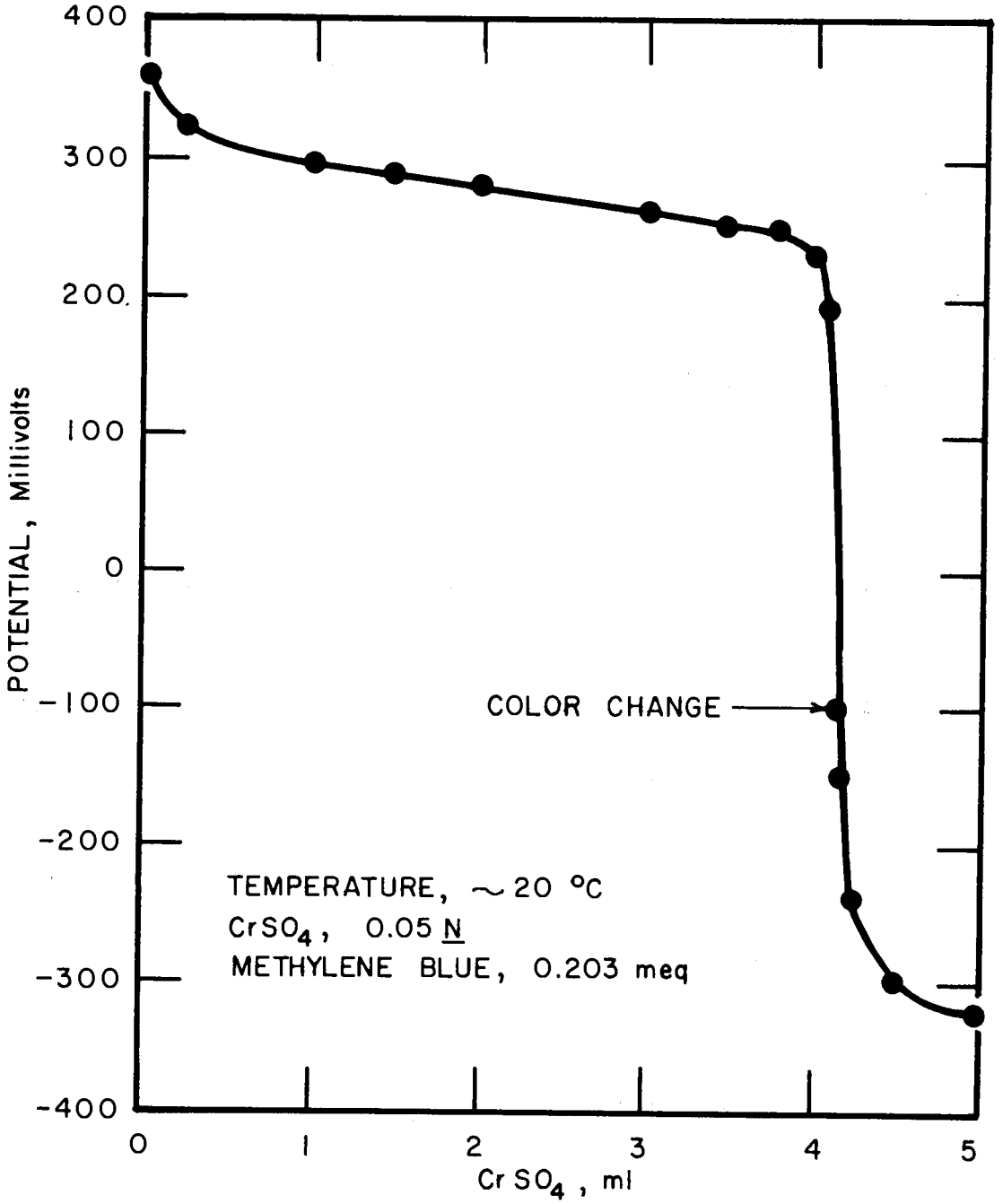

FIGURE 1. TITRATION OF METHYLENE BLUE WITH CHROMOUS SULFATE

Table 4

Effect of Hydrogen Ion Upon the Titration of Methylene Blue with $CrSO_4$

HCl, M	Methylene Blue Present	$CrSO_4$ Required meq	Difference
0	0.203	0.203	0.000
2.4	0.203	0.202	0.001
3.0	0.203	0.202	0.001
4.0	0.203	0.202	0.001
6.0	0.203	0.204	-0.001
11.4	0.346	0.352	-0.006
12.0	0.4	(a)	

(a) Methylene blue not decolorized.

Methylene blue apparently undergoes some chemical change in concentrated HCl, as such solutions are dark green rather than blue and are not decolorized by $CrSO_4$. The dye is stabilized appreciably by dissolution in water prior to acidification. The results show that methylene blue is unstable in nearly concentrated HCl. In less concentrated solutions, the material is apparently completely unaffected by HCl.

The stability of neutral, aqueous solutions of methylene blue was determined over a five-week period. The effect of time upon the titer of one such solution is shown in Table 5.

Table 5

Stability of Methylene Blue with Time

Time, days	Methylene Blue, N
0	0.0203
13	0.0200
14	0.0200
15	0.0200
16	0.0201
17	0.0199
18	0.0201
29	0.0204
31	0.0202
Average	0.0201
Coefficient of Variation	1.3 per cent

These results reveal that methylene blue in aqueous solution is stable for at least five weeks. The results shown in Table 4 also reveal that methylene blue is sensitive to concentrated HCl.

A further study of the stability of the dye in acid solutions was performed in order to determine if time has any effect other than that shown in Table 5 upon stability. Neutral, aqueous solutions of methylene blue were mixed with HCl to form 6 M and 11.4 M solutions. After standing for varying periods of time, the solutions were titrated with $CrSO_4$. The results are shown in Table 6.

Table 6

Stability of Acidic Methylene Blue Solutions

HCl, M	Time, Minutes	Methylene Blue, meq		
		Present	Found	Difference
		A	B	B-A
6	1	0.202	0.202	0
	15	0.202	0.197	-0.005
	30	0.202	0.197	-0.005
	60	0.202	0.198	-0.004
	120	0.202	0.197	-0.005
11.4	15	0.348	0.352	0.004
	30	0.348	0.337	-0.011
	60	0.348	(a)	-

(a) Solution not decolorized by $CrSO_4$.

The test results given in Table 6 reveal that the titer of 6 M HCl solutions of methylene blue is essentially constant over the two-hour period. The 2.5 per cent change noted during the first 15 minutes was the maximum which was found in these tests and is not considered to be real, especially as the titer does not change during the following 105 minutes. The deterioration of 11.4 M HCl solutions of methylene blue was accompanied by a change in color

from blue to dark green with the noticeable liberation of hydrogen sulfide. The decomposition was sufficiently complete after one hour to prevent the decolorization of methylene blue with $CrSO_4$. Such reactivity was similar to that exhibited by 12 M HCl solutions and it is believed that this indicates a different molecular structure than methylene blue.

The absorption spectra of methylene blue in H_2O, 6 M HCl, and 12 M HCl are shown in Figure 2. The spectra of H_2O and 6 M HCl solutions of methylene blue are almost identical, thus leading to the conclusion that the same molecular species exist in water and 6 M HCl. The spectra of a 12 M HCl solution of methylene blue is different in all major respects from that observed in 6 M HCl. This difference gives positive confirmation that methylene blue has undergone decomposition in the more concentrated HCl solution.

When 6 M HCl solutions of methylene blue are heated to boiling evidence of decomposition somewhat similar to that of concentrated solutions was observed. It has been found possible, however, to titrate neutral and 1 M HCl solutions of methylene blue with $CrSO_4$ at 90° C under an atmosphere of He without evidence of decomposition. The end points (Figure 3) are not sharp because methylene white and chromous ions are easily oxidized by traces of air at elevated temperatures.

Solutions of methylene blue in 9 M H_2SO_4 and in solutions which are 4.5 M with respect to H_2SO_4 and 3 M with respect to HCl are stable at room temperature but not at higher reflux temperatures.

Since boric acid and aluminum chloride are often used as complexing agents to facilitate the dissolution of fluoride salts in acid media through the removal of fluoride ions, it is of interest to note that neither of these reagents has any effect upon the titration of methylene blue with $CrSO_4$.

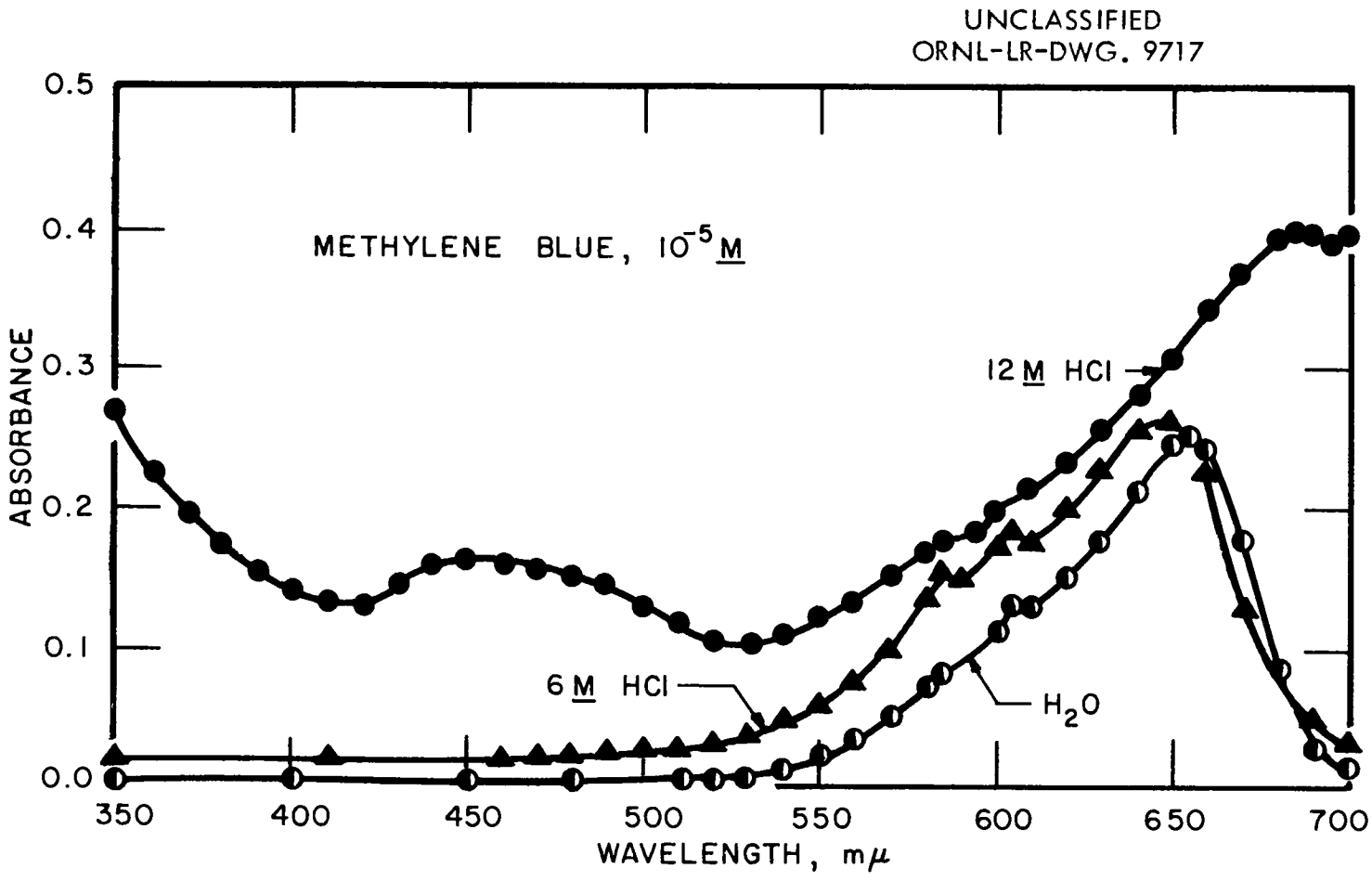

FIGURE 2. ABSORBANCE SPECTRA OF METHYLENE BLUE SOLUTIONS

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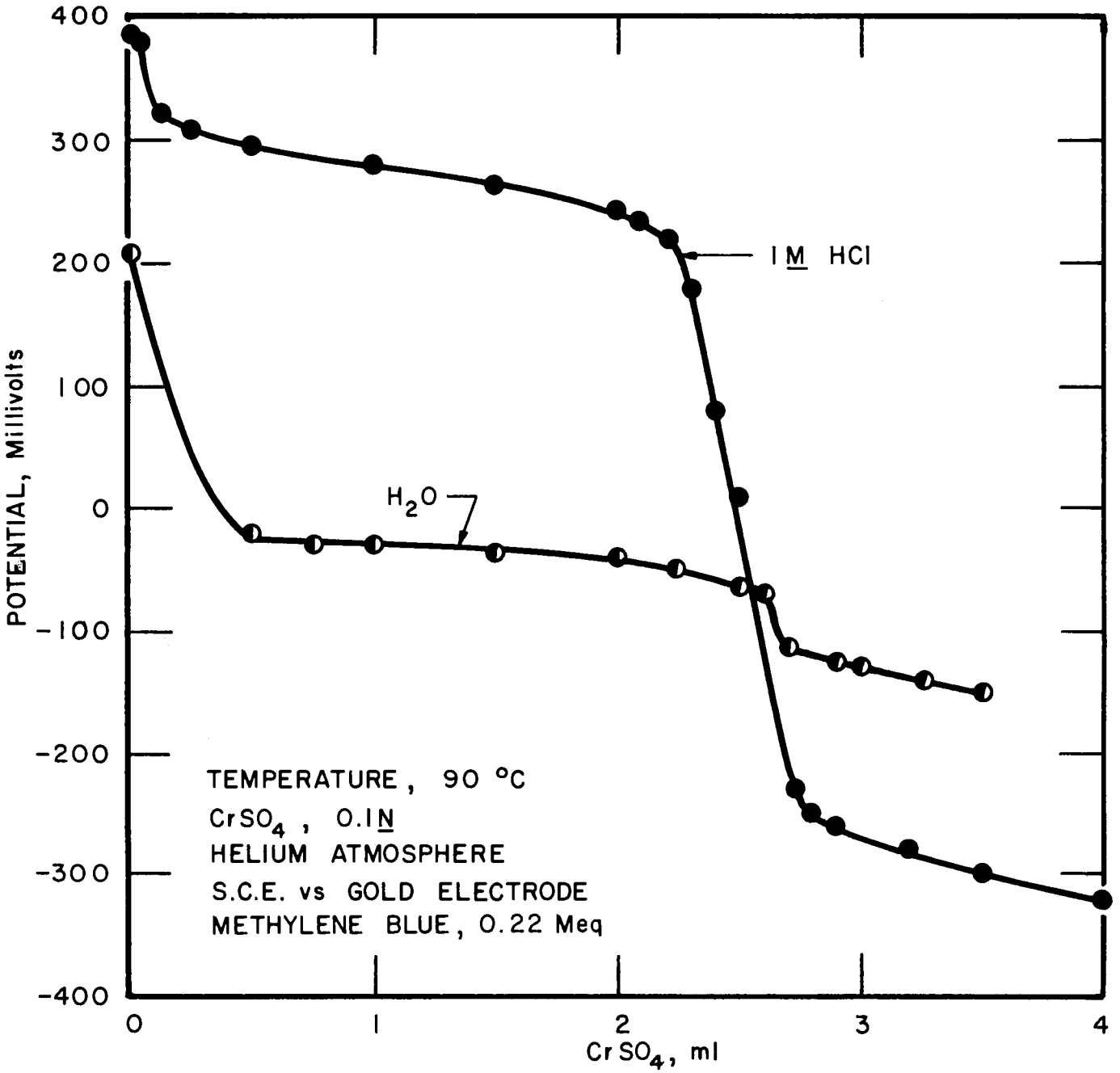

FIGURE 3. TITRATION OF METHYLENE BLUE WITH $CrSO_4$

THE METHOD

Apparatus

The apparatus used in the titration of methylene blue with $CrSO_4$ is shown in Figure 4.

Reagents

1. Chromous sulfate, $CrSO_4$, 0.1 N. Dissolve 29.4 g of pure, dried potassium dichromate in 500 ml of water in a 2-liter, erlenmeyer flask. Acidify the solution with 28 ml of H_2SO_4. Add 75 ml of 30 per cent hydrogen peroxide dropwise into the flask. Stir the solution well, then heat to incipient boiling until all oxygen has been evolved. Cool the solution to room temperature, then transfer to a 2-liter, volumetric flask. Add 50 ml of H_2SO_4, then dilute the solution to 2 liters with H_2O to form an 0.1 N $Cr_2(SO_4)_3$ solution in 0.5 M H_2SO_4. Transfer one liter of this solution to a 2-liter volumetric flask, then dilute to the mark with 0.5 M H_2SO_4 to form 0.05 N $Cr_2(SO_4)_3$ solution.

Amalgamate one kg of pure mossy zinc with 1 per cent mercuric chloride solution in dilute HCl, then wash thoroughly with water. Place a plug of glass wool in the bottom outlet tube of the reservoir of a 1-liter Machlett buret. Fill the reservoir half full with Zn-Hg amalgam.

Rinse the reservoir with about 100 ml of 0.05 N $Cr_2(SO_4)_3$, then nearly fill the reservoir with this solution. Stopper the buret securely, close the exhaust tube to air with a clamp, then connect the reservoir inlet tube to a Kipp hydrogen generator. Shake the contents of the buret reservoir occasionally until the solution has been converted to a clear blue color without any tinge of green. Standardize chromous sulfate against standard $CuSO_4$ solution.

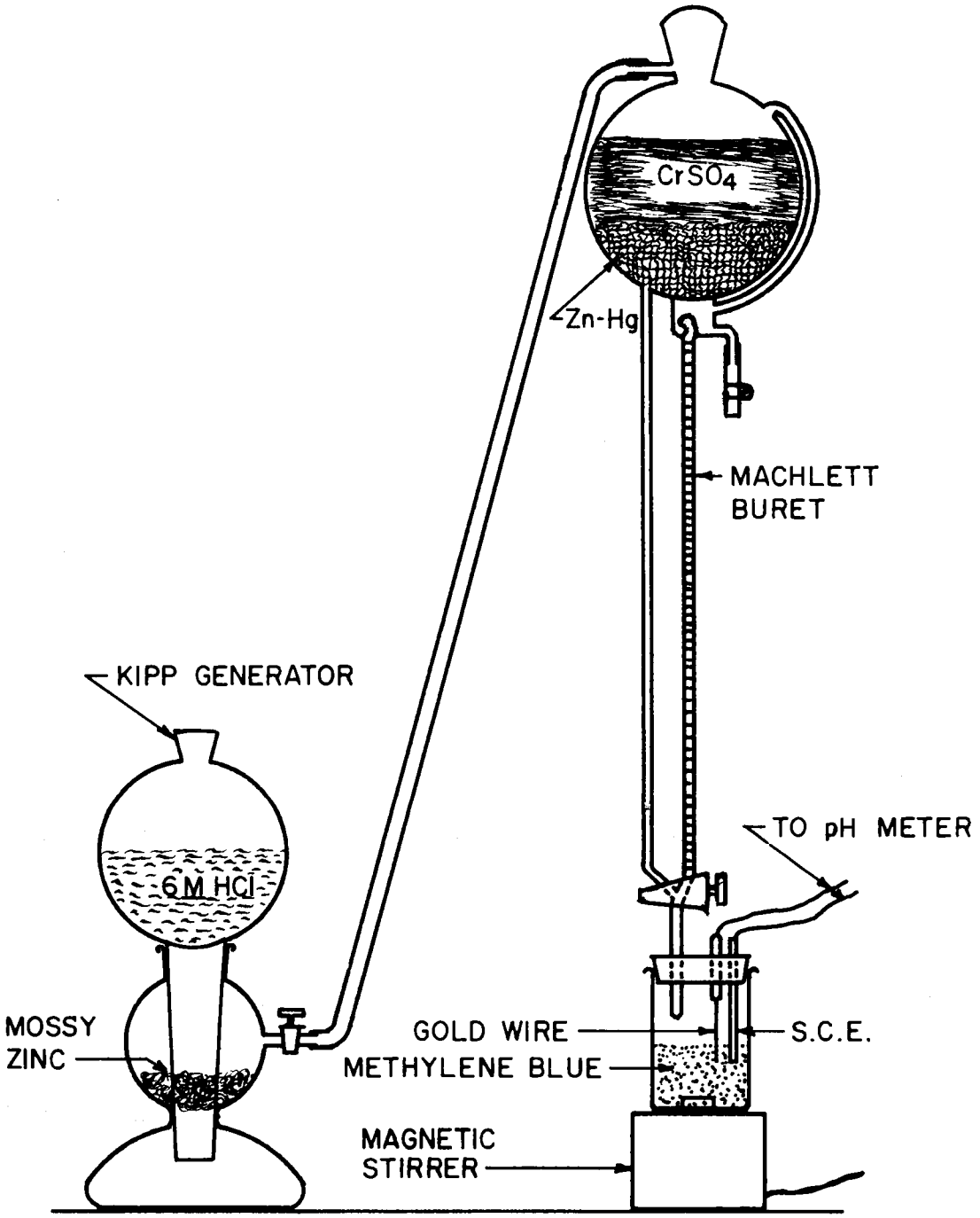

FIGURE 4. APPARATUS FOR TITRATING METHYLENE BLUE WITH CHROMOUS SULFATE

2. Standard cupric sulfate, $CuSO_4$, 0.05 N. Dissolve 0.794 g of electrolytic copper in 50 ml of 2 N HNO_3 and 10 ml of H_2SO_4. Evaporate the solution to fumes of SO_3, cool, dilute with 25 ml of H_2O, then evaporate again to fumes of SO_3. Cool the solution to room temperature, then transfer to a 250-ml volumetric flask. Dilute the solution to 250 ml with water to form an 0.05 N solution of $CuSO_4$.

By means of a pipet, transfer 10 ml of $CuSO_4$ solution to a 150-ml beaker then dilute with 50 ml of 5 M HCl. With gold as the indicating electrode and calomel as the reference electrode, titrate potentiometrically the $CuSO_4$ solution with $CrSO_4$ under an atmosphere of CO_2.

3. Methylene blue, $C_{16}H_{18}N_3SCl$ (obtained from Matheson Coleman and Bell Division of the Matheson Company, Inc., Norwood, Ohio). Prepare an 0.02 N solution of methylene blue by dissolving 1.9 g of methylene blue chloride in 500 ml of deaerated water. Deaerate the H_2O by boiling 600 ml of H_2O for 10 to 15 minutes, then cool under CO_2.

Standardize methylene blue solution against $CrSO_4$ by transferring 20 ml of solution to a 125-ml erlenmeyer flask by means of a pipet. Add 20 ml of 6 M HCl to the flask. Titrate the solution, under CO_2, with $CrSO_4$ until the last traces of blue color disappear.

Sampling

All sampling operations must be performed in a dry and inert atmosphere.

Transfer a sample of the finely ground solid UF_3 or eutectic mixture which contains 50 to 75 mg of trivalent uranium to a 4-ml bottle which is fitted with a screw cap. Weigh the bottle to obtain the gross weight.

Procedure

By means of a pipet, transfer 20 ml of 0.02 N methylene blue solution to a 125-ml erlenmeyer flask. Add 20 ml of HCl to the solution in the flask. Dissolve 5 g of $AlCl_3 \cdot 6H_2O$ in the HCl-methylene blue solution. Remove the air from the flask by dropping a few small pieces of dry ice into the solution. The flask should have a loose glass stopper over the opening. When evolution of CO_2 ceases, transfer the sample quickly into the flask by gently tapping the sample bottle against the neck of the flask so that the solid falls into the solution. Add a small piece of dry ice to the solution. When evolution of CO_2 ceases, stopper the flask tightly, then stir the sample mixture magnetically for two hours. Reweigh the sample bottle to obtain the tare weight of the bottle.

When the stirring period is complete, place several pieces of dry ice in the open flask. Titrate the sample solution, under CO_2, with standard $CrSO_4$ until the last trace of blue color disappears. Whenever green tetravalent uranium or chromic ions are present in high concentration the visual end point of the titration is indistinct. When such is the case, potentiometric methods must be utilized.

If undissolved solid is visible in the flask after completion of the titration, discard the sample and stir a new sample for a longer period of time.

Calculations

Let W_1 = weight of sample + bottle, mg
W_2 = weight of bottle, mg
A = milliequivalents of methylene blue added
B = milliequivalents of $CrSO_4$ required

Then: $$\frac{(A - B) \times 238 \times 100}{W_1 - W_2} = \text{trivalent uranium, per cent.}$$

RESULTS

Uranium Trifluoride

The determination of trivalent uranium in a representative batch of UF_3 is shown in Table 7. Chemical analysis showed the composition to be 80.7 per cent uranium and 19.2 per cent fluoride. The trivalent uranium content was determined by the hydrogen evolution method to be 80.2 per cent.

Table 7

Determination of Trivalent Uranium in UF_3 by the Methylene Blue Method

Sample Weight, g	$CrSO_4$, N	Trivalent Uranium, per cent
0.1122	0.1	78.3
0.1113		81.5
0.1093		80.3
0.0595		81.5
0.0989		79.0
0.0892		77.9
0.1091		78.3
0.0850		78.9
0.0710		79.2
0.0760	0.05	78.3
0.0649		77.8
0.0769		78.0
0.0133		80.5
0.0764		77.2
0.0412		78.6
0.0672		78.6
0.0719		78.2
	Average	78.9
	Coefficient of Variation	1.5 per cent

The average result is approximately two per cent lower than that obtained by the hydrogen evolution method. The lower result is believed to be a result of partial air oxidation of UF_3 since some time had elapsed prior to analysis by the methylene blue method.

The method was tested further on two additional samples of UF_3. These samples were representative of what was considered to be "petrographically pure" UF_3 and were analyzed within seven days after being made. The results of chemical analysis of Batch B showed the UF_3 to be composed of 79.6 per cent uranium, 19.9 per cent fluoride, and 80.2 per cent trivalent uranium (hydrogen evolution method). Batch C was composed of 80.5 per cent uranium, 19.5 per cent fluoride, and 80.4 per cent trivalent uranium.

Table 8

Determination of Trivalent Uranium in UF_3 by the Methylene Blue Oxidation Procedure

UF_3, Batch	Sample Weight, g	Trivalent Uranium, per cent
B	0.0575	78.9
	0.0665	78.0
	0.0895	79.2
	0.0532	81.0
	Average	79.5
	Coefficient of Variation	1.6 per cent
C	0.0640	80.3
	0.0598	80.8
	0.0414	79.9
	0.0460	79.7
	0.0493	79.2
	Average	80.0
	Coefficient of Variation	0.8 per cent

The results show that the two methods agree within one per cent and that the samples are indeed essentially pure UF_3. The coefficient of variation is of the order of one per cent for these particular samples.

LiF-NaF-KF-UF_4-UF_3

Further evaluation of the methylene blue method has been made from the results of analyses of samples of LiF-NaF-KF-UF_3-UF_4 mixtures. Previous observations in this laboratory have shown that trivalent uranium is considerably more reactive in such mixtures than when present in UF_3. A comparison of analyses, by the methylene blue and hydrogen evolution methods, on this type of mixture is given in Table 9.

Table 9

Determination of the Trivalent Uranium Content of $LiF-NaF-KF-UF_3-UF_4$

Sample	Sample Weight, g	Trivalent Uranium, per cent Methylene Blue	Average A	Hydrogen Evolution B[a]	A - B
1	1.2465 0.5434	3.80 3.64	3.72	3.67	+0.05
2	0.8165 0.2352	3.88 3.83	3.86	3.34	+0.52
3	1.0182 0.7797	3.93 3.76	3.85	3.64	+0.21
4	0.6594 0.7803	5.63 5.59	5.61	5.71	-0.10
5	0.3736 0.6564	4.34 4.36	4.35	4.49	-0.14
6	0.3279 0.2378 0.5500	3.93 3.91 3.98	3.94	3.87	+0.07
7	1.2588 1.1892	4.07 3.88	3.98	7.33	-3.35
8	1.1895 0.7099	4.28 4.16	4.22	7.33	-3.11
9	1.5314 0.5183 0.5108 0.5309 0.5220	6.63 7.25 6.21 6.40 6.07	6.51	7.54	-1.03
10	1.2288 0.7607 0.4597	6.33 6.35 6.37	6.35	8.73	-2.38
11	0.1246 0.1653 0.1005	52.2 54.3 53.3	53.3	64.8	-11.5
12	0.4699 0.5025 0.3592	14.6 14.6 14.6	14.6	16.9	-2.3

[a] Average of two or more determinations.

The precision of the methylene blue method is excellent when the sample contains less than 5 per cent trivalent uranium. The sensitivity of the method is illustrated by the precision (coefficients of variation of 0.1 to 3.0 per cent) attained with samples between 0.2 and 1.2 g in weight. In this respect, the methylene blue method is more adaptable than the hydrogen evolution method for determining low concentrations of trivalent uranium.

The agreement between results by the two methods is less satisfactory when the trivalent uranium content is greater than 5 per cent. Inasmuch as complete dissolution of every sample was achieved, the cause of these discrepancies is not known. The precision which was attained by the methylene blue method is indicative of the absence of gross experimental deviation.

$NaF-ZrF_4-UF_4-UF_3$

Mixtures which are composed of $NaF-ZrF_4-UF_4-UF_3$, in variable concentrations, represent a paradoxical system which is much more difficult to dissolve in HCl at room temperature than is UF_3 but in which the trivalent uranium exhibits a much greater reactivity than it does in UF_3. Such mixtures are dissolved easily by warm ammonium oxalate solution whereby the uranium is oxidized rapidly to UO_2^{++}. Uranium trifluoride, on the other hand, is insoluble in ammonium oxalate solutions. Inasmuch as methylene blue is unstable in concentrated (11 to 12 M) HCl and is rapidly decomposed by heat, efficient dissolution of this type of mixture was achieved only after prolonged stirring or by the addition of large amounts (5 g) of $AlCl_3$ to complex the fluoride ions. The results which are listed in Table 10 were obtained from samples which were completely dissolved in 6 M HCl-methylene blue solutions which contained 5 g of $AlCl_3$. The dissolution was effected within two hours.

Table 10

Trivalent Uranium in Eutectic Mixtures of $NaF-ZrF_4-UF_4-UF_3$

Sample	Sample Weight, g	Trivalent Uranium, per cent: Methylene Blue	Methylene Blue Average A	Hydrogen Evolution B	A - B
1	1.9140	3.10	3.23	3.73	+0.50
	1.1920	3.36			
2	1.3876	3.48	3.61	1.35	+2.26
	1.5650	3.54			
	1.4304	3.71			
	0.4695	3.71			
3	0.1664	48.3	44.2	62.3	18.1
	0.1183	42.9			
	0.1044	49.0			
	0.1263	43.0			
	0.1471	43.4			
	0.1646	43.8			
	0.1290	44.5			
	0.0953	47.2			
	0.0795	36.2			
	0.1886	42.5			
	0.1373	45.4			
	0.1200	44.4			

These results show poor correlation with the values obtained by the hydrogen evolution method. The precision of the results (coefficients of variation of 6.6, 3.3, and 10 for samples 1, 2, and 3) is also much poorer than those obtained with other types of mixtures of fluoride salts. The primary cause of these discrepancies is believed to be the highly unstable nature of trivalent uranium in such mixtures. Since complete dissolution of each sample is achieved, the low values could be due to oxidation of trivalent uranium by hydrogen ion with subsequent loss of hydrogen gas.

Other Fluoride Salt Mixtures

The applicability of the methylene blue method to the determination of trivalent uranium in two other types of fluoride salts, $LiF-UF_3-UF_4$ and

$NaF-ZrF_4-LiF-UF_3-UF_4$ was studied. These two types of salts are relatively soluble in 6 M HCl. The results of the analyses of three samples are shown in Table 11.

Table 11

Determination of Trivalent Uranium in $LiF-UF_3-UF_4$ and $NaF-ZrF_4-LiF-UF_3-UF_4$

Mixture	Sample	Trivalent Uranium, per cent: Methylene Blue	Methylene Blue Average A	Hydrogen Evolution B	A - B
$LiF-UF_3-UF_4$	1	7.83 8.44 8.11	8.1	7.9	+0.2
	2	18.0 18.0 18.1	18.0	18.9	-0.9
$NaF-ZrF_4-LiF-UF_3-UF_4$	1	3.97 4.06 3.75	3.93	3.96	-0.03

The precision of the above results and the close correlation between average values obtained by the two methods are indicative of the validity of the methylene blue method.

DISCUSSION

An analysis of the results given in Tables 7 through 11 must of necessity be only comparative because of the lack of an absolute standard for trivalent uranium. Inasmuch as the hydrogen-evolution method represents the only other known method for determining trivalent uranium, this method has been used as a basis of comparative accuracy for the methylene blue method. The hydrogen evolution method has an established coefficient of variation of 1 per cent in the analysis of UF_3. As long as one cc or more of hydrogen could be evolved by a sample, the results of the hydrogen-evolution method were assumed to be correct and were used as standards for the methylene blue method.

All samples were exposed only to dry, inert atmospheres. Degradation of the samples through slow oxidation of trivalent uranium to tetravalent uranium was apparently inevitable when the sample bottle was opened several times.

The fundamental theory underlying the methylene blue method, i.e., stoichiometric reduction of methylene blue by trivalent uranium, has been proven in the analyses of UF_3. The results obtained indicate that the two procedures are of equal accuracy. In the absence of a primary standard, the absolute purity of the UF_3 samples had to be based partially upon the detection of impurities by petrographic analysis and partially upon the total uranium content. This basis is not entirely valid due to the difficulties involved in detecting impurities included with the crystalline structure of UF_3 and the lack of knowledge concerning the reactivity of uranium metal. If, however, such a basis of standardization is considered sufficient both methods are approximately 99 per cent accurate.

The analyses of samples of UF_3 show that the results obtainable with the methylene blue method have a coefficient of variation of 1.5 per cent which is equivalent to that for the hydrogen evolution method, and is limited mainly by the precision, 0.03 ml, with which the end point can be detected during the titration of methylene blue with $CrSO_4$.

The agreement of results between the two methods for determining trivalent uranium varies considerably in the analyses of fluoride mixtures. Close correlation is obtained with $LiF-UF_3-UF_4$, $NaZrF_5-LiF-UF_3-UF_4$, and with $LiF-NaF-KF-UF_3-UF_4$ when the latter eutectic mixture contains trivalent uranium in low concentrations.

When the trivalent uranium concentration of $LiF-NaF-KF-UF_3-UF_4$ mixtures is above 5 per cent, the results of the two methods differ considerably although the precision of the methylene blue method is satisfactory. The two

methods similarly exhibit only fair agreement in the analyses of $NaF-ZrF_4-UF_3-UF_4$ mixtures.

The exact mechanism of the reactions involved in the dissolution and oxidation of trivalent uranium compounds in methylene blue-HCl solutions is unknown. It would appear that the mechanism includes the formation of hydrogen through oxidation of trivalent uranium by the hydrogen ion. The capacity of methylene blue to oxidize hydrogen before the gas escapes has been studied with uranium trichloride. The very low stability of UCl_3 in aqueous media and the rapidity with which hydrogen is evolved during the dissolution of UCl_3 make this compound an excellent example of a very reactive form of trivalent uranium.

The instability of UCl_3 in the presence of moisture made it difficult to secure pure samples of this material. Standard samples were established by determining the trivalent uranium content through a modified hydrogen evolution procedure. This modification consisted primarily in the maintenance of a continuous atmosphere of CO_2 over the sample during its transfer from weighing bottle to reaction flask, and during the period while the air was being purged from the apparatus. The analyses of an available batch of UCl_3 revealed that the trivalent uranium content was only 61.2 per cent, although the theoretical value of pure UCl_3 is 69.0 per cent. This material was believed to represent the purest UCl_3 available and consequently was used in subsequent tests to establish the validity of the methylene blue method.

A preliminary series of experiments was performed in order to determine the effect of hydrogen-ion concentration upon the determination of trivalent uranium in UCl_3 by the methylene blue method. When the concentration of HCl was varied from 0 to 8 M, the amount of methylene blue which was reduced

corresponded to 35 to 60 per cent of the actual concentration of trivalent uranium present in the samples. The poor precision obtained with identical concentrations of acid indicated that all of the trivalent uranium was not being oxidized by methylene blue alone. When the acid concentration was below 2.5 M, high and erratic results were obtained. These results were believed to be caused by the further oxidation of tetravalent uranium to UO_2^{++}. In acid solutions which were greater than 2.5 M with respect to HCl, the results were lower than the true value (61.2 per cent trivalent uranium). Such low results would occur if the trivalent uranium were partially oxidized by hydrogen ion and the hydrogen gas not subsequently oxidized by methylene blue. The results which were obtained with 3 M HCl solutions of methylene blue were erratic but within 10 per cent of the true value.

The methylene blue procedure was combined with the hydrogen-evolution procedure in an effort to determine both the extent to which methylene blue is reduced by UCl_3 in 3 M HCl and the extent to which hydrogen gas is evolved from a methylene blue solution. The apparatus shown in Figure 5 was employed for these tests. Air was removed from the apparatus as completely as possible with CO_2, and then acidic methylene blue was added to the UCl_3. The mixture was stirred vigorously in an effort to prevent hydrogen gas from escaping before being oxidized by methylene blue. After the sample was completely dissolved, the system was swept with CO_2, and the volume of insoluble gas was measured over 50 per cent KOH. This gas was assumed to be hydrogen. The amount of trivalent uranium present in the sample was based on that equivalent to the evolved hydrogen plus that equivalent to the methylene blue reduced during dissolution. The results obtained by this combined procedure are shown in Table 12.

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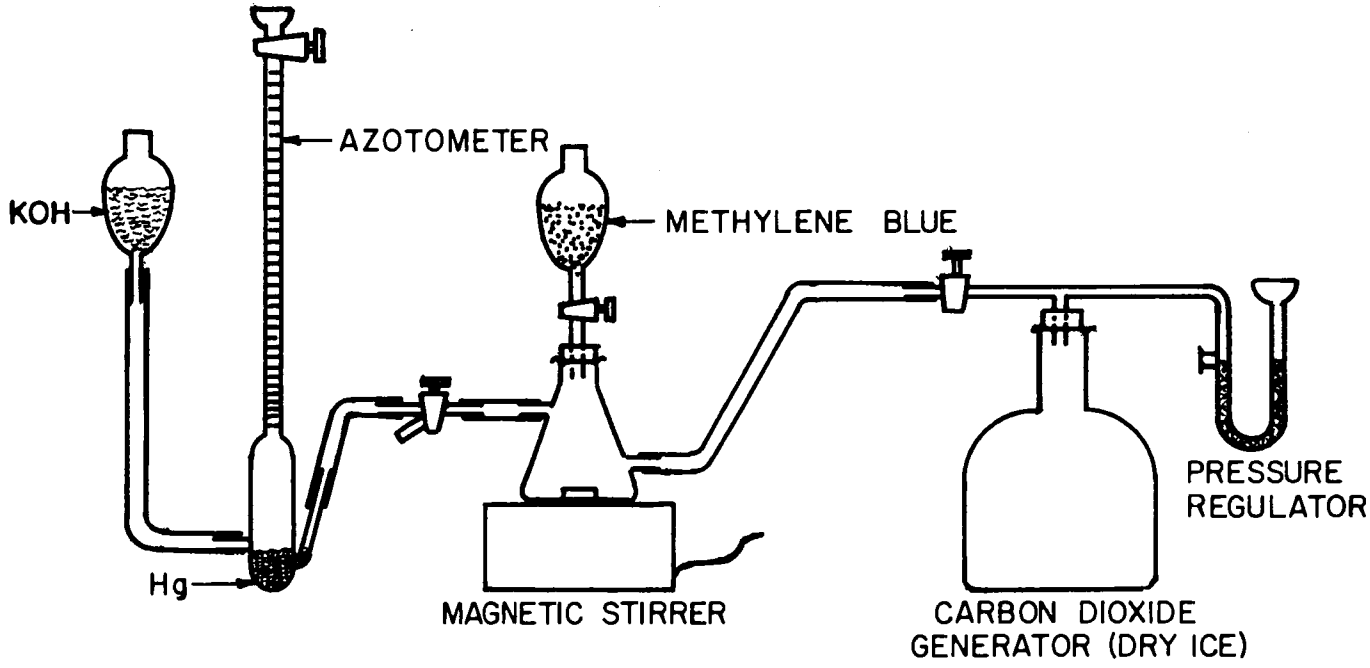

FIGURE 5. APPARATUS FOR THE DETERMINATION OF TRIVALENT URANIUM IN URANIUM TRICHLORIDE

Table 12

Determination of Trivalent Uranium in UCl_3 by a Combination Methylene Blue-Hydrogen Evolution Procedure

Methylene Blue, 0.764 meq
HCl, 3.0 M

Sample	$CrSO_4$ Required, meq	Hydrogen Evolved, cc	Trivalent Uranium, per cent: Methylene Blue	Hydrogen Evolved	Total
1	0.212	0.22	60.3	2.0	62.3
2	0.383	0.17	62.5	2.2	64.7
3	0.262	0.20	61.9	2.0	63.9
		Average	61.6	2.1	63.6

The average value for the trivalent uranium concentration as determined by the methylene blue titration is very close to the actual value (61.9 per cent) for this batch of UCl_3. This correlation indicates that methylene blue stoichiometrically oxidizes trivalent uranium and any hydrogen formed during the dissolution of UCl_3 in an acidic medium. This value is considered more accurate than the total percentage because the difficulties involved in maintaining a constant gas blank cast doubt upon the validity of the calculations involving the evolved gas. The total volume of gas which was evolved never exceeded the blank by more than 50 per cent.

The results of these tests involving UCl_3 do not fully elucidate the mechanism which is involved when a trivalent uranium compound is dissolved in HCl-methylene blue solutions. The results do verify the previously made assumption that trivalent uranium can be oxidized by hydrogen ion in an HCl-methylene blue medium. The transient existence of the red-colored U^{3+} ion in concentrated HCl has, however, been reported in the literature[8] and verified in this laboratory. The possibility exists that methylene blue is reduced by U^{3+}, or H^+, or both. The total reduction is stoichiometric with UF_3 and UCl_3,

so that one equivalent of methylene blue is reduced for each equivalent of trivalent uranium present. A stoichiometric relationship is maintained despite the instability of the trivalent uranium in the solid compound. Since UCl_3 can be quantitatively oxidized by methylene blue, the discrepancies which were found in the analyses of $LiF-NaF-KF-UF_3-UF_4$ and $NaF-ZrF_4-UF_3-UF_4$ eutectic mixtures cannot be attributed to changes in reactivity of the trivalent uranium as it exists in the mixtures. Inasmuch as each sample of any mixture represents a class in itself as far as homogeneity, purity, and particle size is concerned, the differences in the results obtained by the methylene blue and hydrogen evolution methods could be due to any or all of these factors.

SUMMARY

A method has been developed for the determination of trivalent uranium. The method is based upon the oxidation of trivalent uranium to the tetravalent state by a measured excess of standard methylene blue solution in 3 to 6 M HCl solutions. The unreduced, excess methylene blue is determined by titration with standard $CrSO_4$, from which the trivalent uranium content is calculated. Uranium in other oxidation states does not reduce methylene blue. The accuracy of the method compares favorably with that of the hydrogen-evolution method in the analysis of UF_3 and certain pure fluoride eutectic mixtures containing trivalent uranium. The coefficient of variation of the method is 1.5 per cent when as little as 5 mg of trivalent uranium is present. The methylene blue method requires only readily available reagents and equipment. No difficult techniques are involved.

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