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The Uranato-Malate Complex

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THE URANATO-MALATE COMPLEX

LAUNCELOT W. ANDREWS

INTRODUCTION

The initial object of this research was the elaboration of an exact polariscopic method for the analytical determination of malic acid. The results, however, turned out to have a wider interest.

A number of years ago, Walden called attention to the fact that uranyl salts enhance in a remarkable degree the optical rotation of optically active organic compounds of certain classes, particularly of polybasic oxyacids of the aliphatic series. This enhancement does not extend to carbohydrates in a degree sufficient to interfere appreciably, according to observations of Grossmann and others. Yoder has laid the foundation of an analytical method based on the facts alluded to.

REAGENTS

Uranyl Acetate.

The uranyl acetate used in this investigation was labelled "Uranium Acetate. Free from sodium.C.P., Mallinckrodt Chemical Works." It had the characteristic odor of acetic acid, was practically free from alkali salts, dissolved slowly but almost perfectly in 10 parts of water, leaving a very minute precipitate, consisting of barium sulphate.

In the determination of uranium, in this and other organic compounds of the metal, the material was slowly ignited, finally heated to a bright redness with free access of air, cooled and weighed as $\text{U}_3\text{O}_8$. The residue was then dissolved in the smallest amount of nitric acid, the water and nitric acid cautiously evaporated and the mass ignited and weighed as before. The nitric acid treatment did not usually influence the weight of the oxide very much; in one case only, an increase of nearly one per cent was

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1 Ber. (1900) 30, 2889.
observed. The weight after the second ignition was always taken as final. By multiplying by the factor, 0.84824, it gives the corresponding weight of U.

In the ignition of these organic compounds, a strong tendency is manifested to spatter, during the last stage of evaporation or the first of ignition. In case of uranyl acetate, the addition of glacial acetic acid was found to effectually check this tendency. In operating on a solution, the latter was mixed with about half its volume of the acid before evaporation. In working with a dry salt, about 1 cc. was poured over the weighed sample in the crucible. In spite of the benefit from using acetic acid, other precautions can not be neglected. A large crucible is desirable. It is good practice to place in it a lid belonging to a smaller crucible half way down, leaving room for the liquid to boil gently beneath it, without foaming about the edges. For ignition, the crucible is set in a second one of the same size. This results in leaving an air gap between them. The outer or jacket crucible is now cautiously heated with a small flame. When the organic matter is destroyed, the jacket crucible is removed and the other is heated by direct flame, finally to the highest point the Bunsen will give, canting the lid during the last stage to admit air.

The uranyl acetate referred to above, when analyzed in this way, gave the following results:

\[
\% \text{ of } U \text{ found} = 56.19. \\
\% \text{ calculated from formula} = 56.17.
\]

An independent determination of the U content of this salt, (from another bottle of the same lot), may be found below, under the heading Solution of \(4U\).

From this uranyl acetate, a series of solutions were made up in the course of the work. Omitting details, it suffices to say that in every case the determination of the concentration of the solution, as derived from the weight of salt used, was controlled by analyses of the finished liquid. Proper account was taken of the temperatures of such solutions and corrections for volume made when needed. Incidentally, the densities and corresponding concentrations of two of these solutions were determined as accurately as possible. They are:

For Solution U, \( D \frac{25^\circ}{4^\circ} = 1.01772 \), Per cent \( U = 3.178 \).

For Solution 2U, \( D \frac{25^\circ}{4^\circ} = 1.09038 \), Per cent \( U = 14.853 \).
THE URA NATO-MALATE COMPLEX

Approximately,

\[
\frac{(D-1)}{D} \cdot 179.2 = \%
\]

a formula convenient for interpolation. The probable error in the density determination is a little less than 0.0001. The solubility of uranyl acetate at 22° was determined and found to be about 136.2 grams per liter of solution, which is 0.321 molar. The equilibrium between salt and solvent is very slowly established in this case.

**Malic Acid.**

The malic acid used was a preparation by Merck. An air dried sample showed on acidimetric titration 98.34% of malic acid, after 4 days drying in a vacuum dryer, 99.83%. On incineration, the acid left a visible but not weighable ash, probably consisting of CaSO₄, or CaO.

In making up the various stock solutions of malic acid used in the course of the investigation, acidimetric titration constituted the sole basis for determining the strength of the solution. A single example, given in detail, will suffice to show the method used, since all were made in a similar way. 7.5 grams of malic acid were made up to 500 cc. Two portions of 50 cc. each were removed by pipette for titrations, from which concordant determinations, the concentration was ascertained to be 14.760 grams malic acid per liter. Of the remaining solution, 118.55 cc. were accurately measured out, the calculated amount of \( N/2 \) carbonate-free NaOH added to neutralize, taking care that neutrality (to litmus) was not overstepped on the alkaline side, and the whole made up to 250 cc. In accordance with these data, the solution contains 7 grams per liter of malic acid, in the form of its neutral sodium salt.

**Preservation of Malate Solutions.**

It was, at first, feared that the solutions of malic acid and of the malates would be very prone to change and would require frequent renewal. However, it was found that chloroform is a perfectly satisfactory preservative for them. It has no measureable influence on their polarization and keeps the solution for a long time. For example, a solution (1MU) was made from sodium malate and uranyl acetate on Dec. 3rd. The mean of many determinations of its rotatory power was, \( V = 10.00 \). On Jan. 3rd following, an identical mixture was made up from the same malate solution that, at the earlier date had been dosed with
It showed on Jan. 5th a rotation of $V = 10.025$, mean of 5 observations. Of course this is, as to time, an extreme case. Many of the malate solutions (chloroformed) were kept and used for two weeks, but were always checked up to be sure no change had taken place. Other standardized malate solutions employed contained from 20 to 59 grams of malic acid per liter.

**Acetic Acid.**

The C.°P.° grade of Baker and Adamson was used. 10 cc. on evaporation gave no weighable or visible residue. By titration it contained 103.5 grams of acetic acid per 100 cc. It was labelled 99.5%.

**Citric Acid.**

This reagent, on ignition, left a visible but scarcely weighable residue. It required the correct amount of standard alkali for neutralization. A mixture of its solution with uranyl acetate, or with sodium molybdate was optically inactive (absence of tartaric acid).

**Polariscopic Observations**

The polariscope which was mainly used was a large Bates Saccharimeter (made by Franz Frick), arranged for variable brightness of field. A Schmidt and Haensch instrument was also occasionally used. Observations made with it are designated by the letters “S. & H.” The source of light was a so-called “stereopticon electric bulb,” used in connection with a 3 cm. cell filled with a 6% $K_2Cr_2O_7$ solution. A few observations were also made by sodium light, using a large Schmidt and Haensch polariscope with circular scale. The scale of the Bates instrument was controlled at several points by standard quartz plates made by S. and H.

I found it impossible, with the yellow uranyl solutions, to obtain satisfactory readings by white light illumination. With the dichromate cells, after a little practise, very good observations can be made, even though absolute equality of tint can not be secured in the two halves of the field.

The solutions were kept in the dark, in the polariscope room, which was kept at a nominally constant temperature of 20°, but which was subject to occasional variations of more than 1% above or below. Most of the readings were made in the 200 mm. tube, many in the 400 mm. They were made as a rule in groups of 5 or 10. In this paper, to save space, only the mean of each group...
THE URANATO-MALATE COMPLEX

will be reported, with the addition of a number descriptive of the accuracy of the observations. Thus, \( I' = 11.52 \pm 0.035 \) indicates that 5 readings were recorded, of which the mean is 11°.52 Ventske and that 0.035 is the average departure of a single reading from this mean. Since the average error of each observation is not more than 0°.04, the probable error of the mean of ten should, theoretically, be only about 0.01. In fact it is considerably greater than this, owing mainly to uncertainty as to the actual temperature of the solution, but also to a fluctuation of judgment in the matching of the halves of the field. When they differ slightly in color this fluctuation is disturbing. It may seem, then, that all the readings should have been made by monochromatic (Na) light. This was tried, but the concordance of the observations was not better, but worse. This seems to be owing to the severe strain put upon the eye by the inferior luminosity of the sodium flame and by its constant flickerings. The best evidence that this source of error is not really so bad as it seems to the observer himself is to be found in the data recorded in the tables and curve accompanying this paper.

It is very probable that greater precision could be obtained by a combination of color screens so selected as to allow only the yellow rays to pass, using the nitrogen filled tungsten lamp, or possibly a Cooper-Hewitt mercury lamp as light source. However, such a refinement would have little object unless a room of really constant temperature (i.e. to \( \frac{1}{5} ^\circ \)), or unless the observation tubes were so constructed that a thermometer could be placed therein and left there during the readings. These possible refinements are pointed out, because the author believes the method is intrinsically capable, if that were necessary, of more exact results than those recorded in this paper, though the latter appear to be satisfactory when compared with most other analytical processes.

Preparation of the Uranyl Solutions

A series of solutions were, in the course of the work, made up, details of which follow.

Solution U. 63.565 grams of uranyl acetate were made up to 2 liters and the solution was filtered. 25 cc. of this solution on evaporation and ignition, yielded 0.5252 g. of UO_3=21.008 g. per liter=0.074716 molar. 63.565 g. UO_2(C_2H_4O)_2=2H_2O per 2 liters=0.74857 molar. Hence, there is a satisfactory agreement between the two methods of determining the concentration of this solution. As a mean, the figure 0.0748 is adopted.
Solution 2U. Uranyl acetate, finely powdered, was shaken with water (at 23°.5) until apparently saturated. On standing over night, a very slight crystalline crust, looking like uranyl acetate, had separated on the walls of the flask. 10 cc. of the liquid, treated as above described, yielded 1.0550 g. of U₃O₈. The weight was not changed by ignition with nitric acid. This corresponds to a molar concentration of 0.3752, and the solution contains 159.3 g. uranyl acetate per liter. After standing for two weeks at about 23° in contact with the crystalline crust, the solution was once more analyzed, as before. It was found to be 0.34982 molar, having 148.52 gr. uranyl acetate per liter. This is regarded as representing the final solubility at the temperature named. It is extremely probable that slow changes take place in the constitution of the solution, subsequent to its preparation, which are reflected in the solubility data.

The densities of this and of the preceding solution were determined as follows:

Wt. in air of water in pyknometer 28.5389 g. Temp. of the water, 24°4; of the air, 25°6. Wt. of sol. of 2U in air in pyk., 31.2708 g.; temp. of air, 25°6; of sol., 24°8. Wt. of sol. U in air, 29.1223 g.; temp. of air, 25°6; of sol., 25°6

From these data are derived, for Sol. U \(D_{\text{sol/v}} = 1.01772\) with 3.178 g. per 100 cc.; for Sol. 2U. \(D_{\text{sol/v}} = 1.09038\) with 14.853 g. uranyl acetate per 100 cc. The fifth decimal figure is of course very dubious. For interpolation the formula is

\[ p = \frac{(D-1)}{D} \text{ 179.2.} \]

Solution 3U. The salt remaining undissolved from the preparation of 2U, together with a fresh portion of uranyl acetate, was shaken with hot water, till the latter was seemingly saturated, and was filtered hot. After standing over night a beautifully crystallized crust had separated. The solution was much paler than solution 2U in spite of its being more concentrated. The difference is believed to be due to the presence in the salt originally of a trace of ferric acetate, which demonstrates itself by the color and which dissolves with the first addition of water.

This solution, still greatly supersaturated, contained U corresponding to 207.8 g. per liter. After standing four days more at 20° to 25°, with frequent shakings, its strength was again determined, being now 0.3215 molar, which represents about the saturation point, since five days later it had become 0.3205 molar.

Solution 4U. Since the foregoing experiments pointed to the
desirability of avoiding the separation of a solid "basic" phase, so as to be able to make a rather concentrated and at the same time stable solution, it was decided to make up a solution containing a definite amount of free acetic acid. In view of the fact that small amounts of this acid do not have an appreciable effect on the rotation, this step seemed justifiable. Accordingly, 212.3 g. uranyl acetate and 10 cc. (10.35 g.) of HOC₂H₅O) of glacial acetic acid were dissolved in water with gentle heat and made up to 2 liters at 20°. 5 cc. at 23° by the method previously described gave 0.3500 gram. The solution is, therefore, 0.24896 molar at 23°.

**Preparation of the Sodium Malate Solutions**

In making up the various stock solutions used in the investigation, the acidimetric titrations constituted the sole basis for determining the malic acid concentration. A single example, in detail, will suffice to show the method used, as all the other solutions were made up in a similar way. 7.5 g. of malic acid were made up to 500 cc. Two portions of 50 cc. each were measured off by a standardized pipette. By these concordant titrations, the concentration was shown to be 14.760 g. malic acid per 1000 cc. Of the remaining solution, 118.55 cc. were accurately measured out, by pipette and burette, the calculated amount of N/2 carbonate-free NaOH added to neutralize, taking particular care that neutrality (to litmus) was not overstepped on the alkaline side, and the whole was made up to the volume, 250 cc. In accordance with these data, the solution contains 0.7% (i.e. U g. per liter) of malic acid in the form of its neutral sodium salt. This solution will be hereafter referred to as "Sol. M."

**Preservation of the Malate Solutions**

At first it was feared that the solutions of malic acid and the malates would be very subject to change and would require frequent renewal. It turned out, however, that chloroform is a perfectly satisfactory preservative for them. It has no measurable influence whatever on the polarization and keeps the solution to which it is added for a long time. Thus, a solution (1MU) was made on Dec. 3 by mixing 25 cc. each of Sol. U and of Sol. M. Many observations on this solution showed, as mean of all \( V = -10.00 \). An identical mixture was made up on Jan. 3 from the same malate solution, which at the earlier date had been dosed with chloroform. It exhibited on Jan. 5 a polarization of \( -10.025 \), mean of 5 obs. This is, as to time, an extreme case.
Many of the chloroformed malate mixtures were kept and used for two weeks, but were always checked up to be sure that no change had taken place.

Other malate solutions which will be referred to hereinafter by number, are the following:

*Sol. 2M.* 20 g. per liter at 20° of malic acid as neutral sodium salt.

*Sol. 3M.* 50.27 g. malic acid, as neutral sodium salt, per liter at 20°. This sol. is 0.275 molar.

*Sol. 4M.* 40.300 g. malic acid per liter at 20° as free malic acid. 0.3006 molar.

**POLARISCOPIC OBSERVATIONS**

A large Bates saccharimeter (made by Franz Frick), arranged for variable brightness of field, was employed for most of the polariscopic observations. Occasionally, a Schmidt and Haensch instrument was also used.

The source of light was a so-called "stereopticon electric bulb," used in connection with a 3 cm. cell, filled with 6 per cent K₂Cr₂O₇ solution, as light filter. A few observations were likewise made by sodium light with a large Schmidt and Haensch polariscope, having a circular scale. These are designated "S&H" in Table I.

It was found impossible, with the yellow uranyl solutions, to obtain satisfactory readings by white light. With the pyrocromate cells, after a little practice, it was possible to make very good observations, even though the two halves of the field could not be brought to absolute equality of tint.

The scale of the Bates instrument was controlled at several points by standard quartz plates, made by Schmidt and Haensch.

The solutions were kept in the dark polariscope room at a temperature of 20° ± 1°.

Most of the readings were made in the 200 mm. tube, many in the 400 mm. They were, as a rule, made in groups of 5 or 10. Here, to save space, only the mean of each group is recorded, with the addition of a number indicating the concordance of the observations. Thus:

"V = 11.52 ± 0.035 mean 5"

signifies that five readings were taken of which the mean is 11°.52 and that 0°.035 is the average departure of a single reading from this mean. Since the average error of a single observation, determined in this way, is not more than 0°.04, the error of the mean of ten should be, theoretically, 0°.013. In fact it is greater, owing in part to uncertainty as to the actual temperature and in part to
a psychological cause, to wit, a fluctuation of judgment as to when the two halves of the field match in shade while they differ slightly in color. For various reasons, the use of sodium light did not lead to more concordant readings, but, rather the reverse.

THE OPTICAL TIME FACTOR

A freshly mixed solution of sodium malate with one of uranyl acetate exhibits a rotatory power decidedly lower than that which it possesses after standing for some time. The rate of this enhancement depends upon the concentration of the solution and upon its acidity, very likely on other unknown conditions also. The change in polarization after the twelfth hour at 20° C is usually small, but not always. The data given in Table I exhibit the magnitude of the optical enhancement with time in a number of instances.

OPTICAL TEMPERATURE COEFFICIENT

Solution 14MU (see table) gave a rotation in the 400 mm. tube of 23°.053 as a mean of 13 readings at 18°, equivalent to 11°.526 in a 200 mm. tube. A 200 mm. jacketed tube was filled with this solution and the temperature raised to 40°. It was then permitted to cool (together with the hot water in the jacket), with the thermometer in the solution. When the temperature had fallen to 26°.5, the rate of cooling became so slow that it was possible to make a series of readings without appreciable variation. The mean of these readings was 11°.3215. Hence a difference of 8°.5 C corresponds to 0°.205 V. Interpolated rotation at 20° is 11°.48 and the temperature coefficient is: 0.205/8.5×11.48=0.0021, that is for small changes in the neighborhood of 20°, 1° C alters the reading by 0.21% of its value at 20°.

Solution 15MU gave, at 20° the rotation 10°.94±.052 in the 400 mm. tube=5.480 in the 200 mm. The jacketed 200 mm. tube referred to above, filled with the solution, was cooled in the ice box to about 4°. When the temperature had risen to 10°, the readings were begun; when they were completed it was 12°. 11° was assumed as the mean temperature. The mean rotation was 5°.59±.035, whence the difference due 9° C is 0°.120 V and the temperature coefficient is 0.0024. This is as close an agreement between the two determinations as can be expected from the rather rough method used. Assigning greater weight to the first determination, 0.22% is assumed as the correction per degree of departure from 20° C. $V$ = rotation at 20°. $V_t$ = rotation at $t°$. $V (1−0.0022[t−20])$. 

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Polariscopic Observations on Solutions of Various Concentrations of Uranyl and Malic Acid

In Table I are recorded the observed rotations at 20° C (or as noted) in Ventzke degrees for solutions of uranyl acetate and malic acid. The latter is in the form of neutral sodium salt except as otherwise noted. The unit for the concentration of the uranyl solutions is the molar solution having 238.5 grams of U per liter of solution, that for the malic acid is the molar solution containing 134.05 grams of C₄H₆O₅ per liter. All the rotations recorded are negative, the minus signs being omitted to avoid useless repetition. All observations made are recorded. None have been omitted because the results were unexpected or suspicious. The rotations of the mixtures appear in Column 3 accompanied, occasionally, by observations relating to the rate at which the solutions attain their ultimate rotatory power.

### TABLE I

**Optical Rotations in Ventzke Degrees of Uranoato-Malate Solutions**

<table>
<thead>
<tr>
<th></th>
<th>Mol. of Conc. of Uranyl</th>
<th>Rotations in V Deg. in 200mm. Tube</th>
<th>Mol. Conc. of Malic Acid</th>
<th>Grams Malic Acid per 100 cc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1MU</td>
<td>0.0375</td>
<td>Under 3 hrs. after mixing V=9.70±.04, 9.95, over 10 hrs. V=10.00±.045, mean of 25.</td>
<td>0.02610</td>
<td>0.3500</td>
</tr>
<tr>
<td>2MU</td>
<td>0.0375</td>
<td>Soon after mixing 4.74, mean of 5. Next day 4.86, mean of 5.</td>
<td>0.01309</td>
<td>0.1750</td>
</tr>
<tr>
<td>3MU</td>
<td>0.0375</td>
<td>Next day, V=8.00±.033, mean of 5 at 19°.</td>
<td>0.02088</td>
<td>0.2800</td>
</tr>
<tr>
<td>4MU</td>
<td>0.0375</td>
<td>V=1.68, mean of 5, soon after mixing. After 4 hrs., 1.85, 5 obs.</td>
<td>0.00522</td>
<td>0.0700</td>
</tr>
<tr>
<td>5MU</td>
<td>0.0375</td>
<td>Same day V=7.80, mean of 4</td>
<td>0.02088</td>
<td>0.2800</td>
</tr>
<tr>
<td>6MU</td>
<td>0.0375</td>
<td>After 1 hr. V=14.81, mean of 15. Next day, in 400mm. tube, V=29.714, mean of 5 at 21°5 and 14.84, 5 obs. at 19° in 200mm.</td>
<td>0.0745</td>
<td>1.0000</td>
</tr>
<tr>
<td>7MU</td>
<td>0.0375</td>
<td>First obs. =14.68, mean of 5 at 22°; later, 14.74, mean of 2. Next day, 14.72, mean of 5, 21°5, 14.84 at 19°, mean of 5.</td>
<td>0.0447</td>
<td>0.60000</td>
</tr>
<tr>
<td>8MU</td>
<td>0.0375</td>
<td>Soon after mixing, V=11.32±.037 at 19°5, mean of 10.</td>
<td>0.02984</td>
<td>0.4000</td>
</tr>
<tr>
<td>9MU</td>
<td>0.03606</td>
<td>Soon after acidifying, V=9.54 at 20°. After one day, V=9.98 cor. to 20°.</td>
<td>0.02865</td>
<td>0.3847</td>
</tr>
<tr>
<td>10MU</td>
<td>0.0375</td>
<td>After 6 minutes, V=11.36, mean of 5. Half hr. later, V in 400mm. 22.804±.12, mean of 5.</td>
<td>0.02984</td>
<td>0.4000</td>
</tr>
<tr>
<td>11MU</td>
<td>0.0375</td>
<td>Same day, in 400mm. V=10.92±.039 at 18°, mean of 10. 2 days later, V=11.01±.12, mean of 10, =10.96 at 20°.</td>
<td>0.01492</td>
<td>0.2000</td>
</tr>
</tbody>
</table>

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# THE URANATO-MALATE COMPLEX

<table>
<thead>
<tr>
<th>MU</th>
<th>Rotation</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.0375</td>
<td>0.0373</td>
</tr>
<tr>
<td>13</td>
<td>0.0375</td>
<td>0.0746</td>
</tr>
<tr>
<td>14</td>
<td>0.0375</td>
<td>0.0298</td>
</tr>
<tr>
<td>15</td>
<td>0.0375</td>
<td>0.0149</td>
</tr>
<tr>
<td>17</td>
<td>0.0375</td>
<td>0.0065</td>
</tr>
<tr>
<td>18</td>
<td>0.0375</td>
<td>0.0026</td>
</tr>
<tr>
<td>19</td>
<td>0.0375</td>
<td>0.0026</td>
</tr>
<tr>
<td>20</td>
<td>0.070</td>
<td>0.0601</td>
</tr>
<tr>
<td>21</td>
<td>0.0375</td>
<td>0.0300</td>
</tr>
<tr>
<td>22</td>
<td>0.0875</td>
<td>0.0751</td>
</tr>
<tr>
<td>23</td>
<td>0.0606</td>
<td>0.0706</td>
</tr>
<tr>
<td>24</td>
<td>0.0964</td>
<td>0.0750</td>
</tr>
<tr>
<td>25</td>
<td>0.1000</td>
<td>0.0119</td>
</tr>
<tr>
<td>26</td>
<td>0.1000</td>
<td>0.0298</td>
</tr>
<tr>
<td>27</td>
<td>0.1000</td>
<td>0.0375</td>
</tr>
<tr>
<td>28</td>
<td>0.1000</td>
<td>0.0375</td>
</tr>
<tr>
<td>29</td>
<td>0.1250</td>
<td>0.0750</td>
</tr>
<tr>
<td>30</td>
<td>0.070</td>
<td>0.3006</td>
</tr>
<tr>
<td>31</td>
<td>0.070</td>
<td>0.0180</td>
</tr>
<tr>
<td>32</td>
<td>0.125</td>
<td>0.0600</td>
</tr>
</tbody>
</table>

Rotation a maximum on second day, afterward, so long as observed, 5 days, no change beyond observation errors.

Some of these observations were made in 400 mm. tubes and calculated to 200 mm.

Acidified with acetic acid to 0.004N. This degree of acidity has no effect on the rotation, or almost none.

With this large excess of malate, the rotation is an exact measure of the uranium.

With this small excess of malate, the rotation is too low for an exact measure of the uranium.

This solution had not yet acquired its maximum rotation. It was used, immediately after readings, to make sol. 9MU q.v.

Made by adding 2 cc. of acetic acid to 50 cc. of 8MU. It is 0.663N as to acetic acid. The actual reading (9.54) is corrected to allow for dilution by the acetic acid in order to compare 8MU. The differences then show depression due to acidity.

compare with 14MU.

Reduced to 20° and 200 mm., the mean is 2.720±0.045.

1½ hour after mixing, V=22.84±0.05 at 18°, mean of 10 in 400mm. tube. A second preparation gave the following series of changes:

<table>
<thead>
<tr>
<th>Time</th>
<th>Rotation</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed at</td>
<td>10-34</td>
<td>11.28</td>
</tr>
<tr>
<td>First day</td>
<td>10-56</td>
<td>11.31</td>
</tr>
<tr>
<td>11-19</td>
<td>11.45</td>
<td>0.04 mean of 5</td>
</tr>
<tr>
<td>Second day</td>
<td>1-6</td>
<td>11.437</td>
</tr>
<tr>
<td>1-9</td>
<td>22.816</td>
<td>0.009 mean of 10</td>
</tr>
</tbody>
</table>

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Omitting observations on the first day and reducing the others to 20°, the general mean (of 57 readings) is: \( V = 11.458 \) with a mean error for each set of 0.02. The calculated probable error of the general mean is, therefore, ±0.008.

16 2 hrs. after mixing, \( V = 10.703 \pm 0.041 \) at 18°, mean of 9 in 400mm. tube. 44 hrs. after mixing, \( V = 10.833 \pm 0.103 \) at 18°, mean of 10. One day after, \( V = 10.986 \pm 0.111 \) at 18°, mean of 5. Two days after, \( V = 10.894 \pm 0.05 \) at 18°. Weighted mean, for 200mm. and 20° is \( V = 5.445 \).

17 Mean of 60 observations, from 15 min. to 4 days is: \( V = 4.67 \), mean of 20°, excl. all before 3 hrs. and after 3 days, 4.703 at 19°, 400mm. For 20° and 200mm., the mean is: \( V = 2.346 \).

19 After 7 minutes, \( V = 1.72 \) in 400mm., mean of 5. Next day, \( V = 1.886 \), mean of 15 at 18°. Mean of all obs. taken (25) is 1.825 at 20°.

19 After 1 day, \( V = 1.795 \pm 0.022 \), in 400mm. at 19°, mean of 5, equivalent to 0.896 for 20° and 200mm.

20 The malic acid in this is free, which fact, with the low excess of uranium, depresses the rotation below 23.5°, which it would have if it had been neutralized.

21 This also has its malic acid free and was very slow in reaching its maximum (more than 24 hrs.). Final reading subnormal, same reason.

22 First day, \( V = 29.254 \pm 0.038 \) at 21°, mean of 5. Second day, \( V = 29.306 \pm 0.005 \), mean of 5 at 20°. Mean for 20°: \( V = 29.364 \).

23 As the malate is in excess of the uranium, the observed rotation is limited and determined by the latter.

24 \( V = 29.326 \pm 0.07 \) at 19°, 28.896+0.069 at 24°, 29.030+0.030 at 21°, each being mean of 5 obs. Interpolated general mean for 20° is: \( V = 29.229 \).

25 The malic acid is free. The acidity due to it (0.04°) is too small in view of large excess of U, to appreciably affect the rotation.

26 This solution was made 2N acid by acetic acid. The large depression of the rotation (33%) is the result.

27 This solution is 0.02 molar as to citric acid (free), but no effect on rotation is apparent, in consequence of large excess of U.

28 This solution is 0.04 molar as to sodium citrate (0.84%), but an influence on the rotation is not detectable. Note excess of U!

29 This solution has same amount of Na citrate as 27MU, but a smaller excess of U, sufficient however, to drown the depressing influence of the citrate.

30 The malic acid is free and the solution contains free citric acid (0.008 molar). Total acidity, therefore, 0.064N. Compare with 20MU.

31 The malic acid is free and the solution contains free citric acid (0.016 molar). Total acidity, therefore, 0.084N. This and the previous solution, in spite of the acidity, show normal rotation, in contrast with 20MU, where the excess of U was much less.

32 This solution contains 0.84% of sodium citrate. The excess of U is less than in 28MU, but the depression of rotation due to citrate is almost entirely prevented by it.

**TABLE II**

**PERCENTAGES OF MALIC ACID IN SOLUTIONS CONTAINING AN EXCESS OF URANYL ACETATE, CORRESPONDING TO VARIOUS OPTICAL ROTARY POWERS, EXPRESSED IN VENZKE DEGREES**

<table>
<thead>
<tr>
<th>( V )</th>
<th>( p )</th>
<th>( V )</th>
<th>( p )</th>
<th>( V )</th>
<th>( p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03919</td>
<td>15</td>
<td>0.52110</td>
<td>30</td>
<td>1.02863</td>
</tr>
<tr>
<td>2</td>
<td>0.07487</td>
<td>16</td>
<td>0.55507</td>
<td>31</td>
<td>0.06236</td>
</tr>
</tbody>
</table>
### THE URANATO-MALATE COMPLEX

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>3</td>
<td>.10997</td>
<td>17</td>
<td>.58901</td>
<td>32</td>
<td>.09608</td>
</tr>
<tr>
<td>4</td>
<td>.14477</td>
<td>18</td>
<td>.62293</td>
<td>33</td>
<td>.12980</td>
</tr>
<tr>
<td>5</td>
<td>.17938</td>
<td>19</td>
<td>.65680</td>
<td>34</td>
<td>.16351</td>
</tr>
<tr>
<td>6</td>
<td>.21385</td>
<td>20</td>
<td>.69066</td>
<td>35</td>
<td>1.19722</td>
</tr>
<tr>
<td>7</td>
<td>.24822</td>
<td>21</td>
<td>.72451</td>
<td>36</td>
<td>.23091</td>
</tr>
<tr>
<td>8</td>
<td>.28251</td>
<td>22</td>
<td>.75834</td>
<td>37</td>
<td>.26460</td>
</tr>
<tr>
<td>9</td>
<td>.31673</td>
<td>23</td>
<td>.79217</td>
<td>38</td>
<td>.29828</td>
</tr>
<tr>
<td>10</td>
<td>.35088</td>
<td>24</td>
<td>.82599</td>
<td>39</td>
<td>.33196</td>
</tr>
<tr>
<td>11</td>
<td>.38500</td>
<td>25</td>
<td>.85980</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>.41909</td>
<td>26</td>
<td>.89360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>.45311</td>
<td>27</td>
<td>.92738</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>.48711</td>
<td>28</td>
<td>.96175</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>.52110</td>
<td>29</td>
<td>.99490</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>1.02863</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \nu = \text{Venzke degrees} \]
\[ p = \text{grams of malic acid per 100 cc.} \]

### TABLE III

**COMPARISON OF OBSERVATIONS WITH CALCULATION FROM EQ. 4**

\[ p = 0.033192 \nu + 0.006 \sqrt{\nu} \]

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>( p )</th>
<th>Calculated</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.896</td>
<td>0.0350</td>
<td>0.035420</td>
<td>0.00042 + 19MU</td>
</tr>
<tr>
<td>0.913</td>
<td>0.0350</td>
<td>0.036037</td>
<td>0.001037 + 18MU</td>
</tr>
<tr>
<td>1.85</td>
<td>0.0760</td>
<td>0.069566</td>
<td>0.000434 - 4MU</td>
</tr>
<tr>
<td>2.346</td>
<td>0.0875</td>
<td>0.087059</td>
<td>0.000441 - 17MU</td>
</tr>
<tr>
<td>2.72</td>
<td>0.1000</td>
<td>1.100177</td>
<td>0.00177 + 13MU</td>
</tr>
<tr>
<td>4.473</td>
<td>0.1605</td>
<td>0.161157</td>
<td>0.000657 + 25MU</td>
</tr>
<tr>
<td>4.86</td>
<td>0.175</td>
<td>0.174540</td>
<td>0.000460 - 2MU</td>
</tr>
<tr>
<td>5.445</td>
<td>0.2000</td>
<td>0.194730</td>
<td>0.005270 - 15MU</td>
</tr>
<tr>
<td>5.48</td>
<td>0.2000</td>
<td>0.195938</td>
<td>0.004062 - 11MU</td>
</tr>
<tr>
<td>7.92</td>
<td>0.28</td>
<td>0.279729</td>
<td>0.000271 - 5MU</td>
</tr>
<tr>
<td>7.98</td>
<td>0.28</td>
<td>0.281821</td>
<td>0.001821 + 3MU</td>
</tr>
<tr>
<td>10.00</td>
<td>0.35</td>
<td>0.350894</td>
<td>0.000894 + 1MU</td>
</tr>
<tr>
<td>11.46</td>
<td>0.40</td>
<td>0.400701</td>
<td>0.000701 + 14MU</td>
</tr>
<tr>
<td>11.51</td>
<td>0.403</td>
<td>0.402396</td>
<td>0.000604 - 30MU</td>
</tr>
<tr>
<td>14.46</td>
<td>0.50</td>
<td>0.502772</td>
<td>0.002772 + 12MU</td>
</tr>
<tr>
<td>14.51</td>
<td>0.503</td>
<td>0.504472</td>
<td>0.001472 + 28MU</td>
</tr>
<tr>
<td>14.55</td>
<td>0.503</td>
<td>0.505823</td>
<td>0.002823 + 27MU</td>
</tr>
<tr>
<td>23.392</td>
<td>0.50</td>
<td>0.505342</td>
<td>0.001042 + 32MU</td>
</tr>
<tr>
<td>29.22</td>
<td>1.0050</td>
<td>1.002304</td>
<td>0.002696 - 24MU</td>
</tr>
<tr>
<td>29.32</td>
<td>1.0058</td>
<td>1.005679</td>
<td>0.000121 - 29MU</td>
</tr>
<tr>
<td>29.364</td>
<td>1.0070</td>
<td>1.007163</td>
<td>0.000163 + 22MU</td>
</tr>
</tbody>
</table>

**Mean error 0.00135**

### DISCUSSION OF THE OBSERVATIONS

The relation between malic acid concentration and rotatory...
power as revealed by the data presented in Table I, will be discussed later. It is expressed by the equation:

\[ p = 0.033192V + 0.0060\sqrt{V} \]  

Eq. 4

from which Table II has been calculated, for practical use in deducing the percentage from observed saccharimeter readings. In this table:

\[ V = \text{rotation in Ventzke degrees at } 20^\circ C. \text{ in a 200mm. tube} \]

\[ p = \text{grams malic acid in 100 cc. at } 20^\circ \]

Table III has been assembled for the purpose of facilitating a comparison between the results of calculation by Equation 4 and the observations and to enable a judgment to be formed as to the accuracy of the determinations of malic acid in pure solutions and also in those which contain small amounts of citrate or which are acidified by acetic malic or citric acids in small amount.

From this comparison, all results are, of course, excluded, which, by undue acidity, by insufficient time, by deficient excess of uranium, or which by any known cause are disqualified. None, however, have been discarded merely because the result did not seem to be right.

Inspection of Table III shows that the mean error of the observations on 22 independent solutions is but little more than one one thousandth per cent (0.00135 per cent) for each solution, such being the mean error, not of each observation, but of each group of observations upon a given solution.

In as much as the most concentrated solution examined contained only about one per cent of malic acid, it is clear that the figures given in the table for stronger ones are extrapolated. Since the curve becomes almost a straight line for concentrations above one per cent, an extrapolation up to 2 per cent appears to be justifiable.

The form of Eq. 4, used in calculation i. e.,

\[ p = 0.033192V + 0.0060\sqrt{V} \]

was derived as follows:

Assuming that hydrolysis of the uranato-malate complex takes place in accordance with the reversible reaction: \( \text{HO}_2\cdot\text{C}_6\text{H}_5\text{O}_3\text{H} + 2 \text{H}_2\text{O} = \text{UO}_2(\text{O}_2\text{H})_2 + \text{C}_6\text{H}_5\text{O}_3\text{H}_2 \); and assuming that this dissociation conforms to the formula: \( K = \alpha C / (1 - \alpha) \), in which \( \alpha \) is the dissociated proportional part of the complex, and \( C \) is the molar concentration and \( K \) the dissociation constant. Noting that \( V \) is proportional to \( C(1 - \alpha) \) and denoting the proportionality constant by \( \Phi \), we have, after simple transformations:

\[ C = \Phi V + \sqrt{\Phi K V} \]  

(Eq. 3)
In order to evaluate the constants, $K$ and $\Phi$, $c$ is substituted by its equivalent, $13.405p$, and Eq. 3 is combined with Eq. 4. The computation gives, $K=0.0000809$, $\Phi=0.002476$.

It is based on the data for the 21 mixtures designated in Table III, the details of the observations being found in Table I. Greater weight was attached to those data that were a mean of more numerous observations, and readings obtained before the solution had reached equilibrium were discarded.

In using the table it should be noted that for low dilutions the ratio $p/V$ changes so rapidly that interpolation from the table cannot be very exact. In this case, i.e. for rotations below $2^\circ V$, it is accordingly better to use the formula, provided the observations are accurate enough and numerous enough to make this worth while.

In Figure 1, the curve of Eq. 4 is plotted and the observed points are marked by circles. The numerals refer to the mixtures listed in Table I.

**Influence of Uranium Concentration**

While most of the solutions listed in the table have an uranium concentration of 0.0375 molar, several contain more. The observations on solution 24MU show that an increase of U to 0.096 molar does not appreciably alter the rotation. This is confirmed by 25MU, which, although acid (free malic), is not sufficiently so to affect the rotation markedly. Solutions 27 to 30MU are to be interpreted in the same way, since, although citrate is present, the excess of uranium prevents any reduction in the rotation. 31MU can not be readily interpreted, as it presents the combined effects of free malic and free citric acids.

**Influence of Citrate**

The observations recorded above confirm those of Yoder (l.c. p. 335) to the effect that citrate depresses the rotation and that a sufficient excess of uranium counteracts this depression. The data adduced in Table I make it possible to define exactly what the conditions are, under which the influence of citrate becomes negligibly small. The controlling condition is (as might easily be predicted) the ratio of the sum of the molecules of malic and citric acids to the molecules of uranyl acetate; and it may be expressed in the following terms:

*When the molar concentration of the uranium exceeds (by about 25%) the sum of the molar concentrations of malate and citrate, the influence of the citrate becomes inappreciable.*
This assertion rests on the observations on solutions 27, 28, 29, and 32MU (see Table I) and is further confirmed by 30 and 31MU. The two latter contain free malic and citric acids; but the total acidity appears to be too small to influence the readings notably. Although the error involved in 31MU is larger than usual, it seems to have no significance beyond that of an accidental accumulation of small errors.

It is highly probable, citric acid is capable of giving rise to a uranato citrate. In this way, citric acid would compete with malic for the possession of the uranyl radical and, so, depress the rotation, unless an excess of U were present.

Calculation of the Molar Rotation of the Uranato-Malic Complex

If, in the dissociation formula,

\[
\frac{a^2c}{1-a} = K,
\]

the value of \(K\) (0.0000809) previously determined and that of \(c\) be selected as 0.1, the corresponding value of \(a\) is found to be 0.02804, that is, at decimolar concentration 2.804 per cent of the complex is dissociated and 97.196 per cent is intact. Now, by Table II, the rotation of a decimolar mixture is 39°.253V. Correcting this for the hydrolysis, we have 40°.385V (39.253 — .97196) as the rotation at 20° C of a decimolar solution if it were not hydrolyzed, therefore, the molar rotation of the non-dissociated uranato-malic complex is 4038.5 in Ventzke degrees.

Preparation of Ammonium Uranato-Malate

Malic acid (1.9 grams) was dissolved in a small quantity of water and the mixture warmed with 6 grams of uranyl acetate, which rapidly dissolved. No precipitate appeared, although a strong odor of acetic acid was evolved. To the solution ammonia water was added till a precipitate appeared, then a considerable excess of acetic acid, after which the liquid was boiled. On cooling an abundant precipitate formed, consisting of cadmium yellow needles. This was separated from the liquor by suction and washed with alcohol. After drying in a dessicator a uranium determination was made.

<table>
<thead>
<tr>
<th>Substance taken</th>
<th>0.3350 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₂O₅ found</td>
<td>0.2062 g</td>
</tr>
<tr>
<td>% U calculated</td>
<td>0.1749 g</td>
</tr>
<tr>
<td>% U found</td>
<td>52.21</td>
</tr>
</tbody>
</table>
THE URANATO-MALATE COMPLEX

% U theoretical 52.35 calculated from the formula, UO₄(C₄H₂O₅NH₄)₂H₂O (Mol. wt. 455.57)
% H₂O lost at 100° 6.11
% H₂O cal. for 1½ Mols. 6.37

A second preparation was made as follows: 13.6 grams of malic acid were dissolved in 50 cc. of hot water and to the boiling solution 42.4 grams of uranyl acetate were added. All dissolved and after standing a day, protected from light, nothing had crystallized out. The liquid was then heated to boiling, about 25 grams of ammonium acetate added, and a little water to replace that evaporated, and 7 cc. of glacial acetic acid. While cooling, an abundant precipitate of lemon yellow, acicular crystals slowly separated. The deposit continued to grow for a long time. About 24 grams were obtained from the first crystallization and a considerable amount of the same salt from a further concentration of the mother liquor. Analysis showed that this salt contained less water on crystallization than the first preparation.

Substance taken 0.3518 g., U₂O₈ found 0.2299 g., U fd. 0.1950, % U found 55.43, theoretical % U for UO₂(C₄H₃O₅NH₄)½H₂O, 55.65 (Mol. wt. 428.56). This salt lost no weight on drying at 100°. Its composition is the same as that of the first preparation, subsequent to drying at 100°.

The ammonium was determined in the usual manner: NH₄ found 4.136%, calculated from above formula, 4.179.

These analyses establish the character of the salt as being a mono-ammonium mono-uranatomalate.

Di-Barium Mono-Uranatomalate

The addition of barium hydroxide to a solution of ammonium uranatomalate, or to a solution of free uranatomalic acid produces a lemon yellow precipitate. It appears to be possible in this way to remove all U and all malic acid from the solution.

Some of this yellow salt was dried in a vacuum dessicator, then a portion weighed and carefully ignited. Substance taken, 0.2258 g.; ignited residue, 0.1794 g. If we assume the residue to be BaUO₄, the corresponding weight of U is, 0.0976 gr. and the % of U found in the substance taken is 43.2. The formula, UO₂(C₄H₂O₅Ba) calls for 44.4, while the formula UO₂(C₄H₂O₅Bo)½H₂O requires 43.6% of U and 25.5% of Ba, nearly as found.

Theoretical Considerations

If we represent the developed formula of a uranato-malic salt (indicating the basic element by M) after Itzig, as follows:

Andrews: The Uranato-Malate Complex

Published by UNI ScholarWorks, 1925
in its first state, formula 1:

\[
\begin{align*}
**H & \quad *H-O-UO_2 \\
O & \quad O \\
OC-CH_2-CH-COM & \quad CH_2-CH-COM
\end{align*}
\]
Formula 1

It seems probable that it will change to its anhydride, forming an inner salt, by a reaction between the carboxyl H marked ** and the hydroxyl of the uranyl group, marked *, with the production of a compound of the constitution shown in formula 2.

The justification for preferring this formulation to that of Itzig can be briefly given.

The extraordinarily high rotatory power that characterizes the compound is entirely in harmony with the ring of six links, which, by setting up a stress within the molecule would be very likely to enhance its optical activity generally, that is, to increase its refractive index and its rotatory power.\[34\]

Furthermore, the complex represented by the ring would, as salt of a weak base, be subject to partial hydrolysis in dilute solution, leading to formation of the compound shown in formula 1, which, presumably would only have a rotatory power comparable with that of ordinary salts of malic acid.

Hence, such a substance would have a lower specific rotatory power in dilute solutions. This is, of course, in accordance with the properties of sodium uranato-malate.

The proposed formula also explains the action of acids or alkalis in reducing the optical activity of the uranato-malate, since either agent must break the ring between carboxyl and uranyl.

With regard to this, the observations of Yoder\[37\] appear on the whole to indicate that smaller amounts of acetic acid, up to 0.26 N, enhance the rotation, while larger amounts reduce it. Yet, his results on this point are not consistent with one another, since elsewhere\[38\] his data show that a non-acidified solution gave a rotation of 29°.28, while after acidification with acetic acid to normality 0.167, the rotation became 29°.24 per 1% of malic acid. Here no enhancement comes from acidification. My own observations show no enhancement at any point, but a depression, steadily increasing with the acidification.

\[34\] The correlation between closed aromatic rings and extremely high rotatory power has been clearly pointed out by van't Hoff (Lagerung der Atome in Raume, 1894, p. 109) and by Walden (Zeit. ph. Chem. 20, 569).

\[37\] Henderson, Orr and Whitehead (Jour. Lond. Ch. Soc. 75, 542) present a partially analogous formula for molybdato-malic acid.

\[38\] L. c., Table 2, p. 335.
The explanation of the divergent results between the results of Yoder and those herein recorded are not far to seek. First, Yoder was not aware that the uranato-malate mixtures require a certain time to reach a maximum and stable rotation. So, it is probable that some of his solutions were polarized during the period of changing rotation. I have twice noticed that of two solutions, one acidified, the other not, the one which is acidified may show a slightly higher rotation if both are examined within 15 minutes, but, after standing 4 to 20 hours, the unacidified sample invariably has the higher rotation. The small errors introduced in this way and those due to the fact that the uranyl acetate solutions examined by Yoder were deficient in purity, as shown by his analysis and by his description of the color, are sufficient to explain the divergence in question. The low uranium content and its poor solubility, point to a contamination with sodium. Now, in this case the H ion content of the solutions must have been abnormally low and the rotation correspondingly depressed. Under these circumstances, addition of acetic acid in amount to bring the H ion concentration to the normal would naturally enhance the rotation.

**Analytical Applications**

It seems desirable, in conclusion, to put the results discussed in the foregoing pages in the form of specific instructions suitable for applying them to the determination of malic acid. Such instructions involve the consideration of interfering substances.

In the absence of citric acid\(^{39}\) and of other optically operative substances, a large excess of uranium is needless and for two reasons is objectionable. First, because a moderately dilute uranyl acetate solution is more permanent than one nearly saturated; second, because the reading errors are greater in the more highly colored, concentrated solutions, than in those of lower U content.

In presence of citrates (very small amounts excepted), the concentration of the uranium must be increased or that of the malic and citric acids be diminished, in order to have the needed excess of the former. Two procedures will therefore be suggested, the first to be followed in the absence of citrate, the second adapted for use in its presence.

**Method 1, for Use when Citrate is Absent.**

Prepare a solution\(^{29}\) of uranyl acetate containing 33.966 g. per

\(^{29}\) It is presumable that other hydroxyl aliphatic acids will be found to show a similar behavior to citric acid.

\(^{39}\) If desired, the solution may with sufficient accuracy be made of the correct strength by density, using the data furnished on p.
litter of the pure salt. This stock solution is 0.08 molar. The uranium content of this salt should be determined and, if it is a little below 56.17%, a correspondingly larger amount of the acetate is to be taken. If it is several per cent too low, a purer material should be obtained. A sample having more than traces of sodium ought not to be used.

Measure into a 50 cc. graduated flask 25 cc. of the stock uranyl solution and 25 cc. of the malic acid solution (if this contains 1% or less). If the malic acid is of more than 1%, a smaller volume is to be measured, such that the resulting mixture shall have not over 0.5%, and the total volume made up to 50cc. Shake well, add a drop of chloroform and keep in the dark.

Polarize after standing at 20° for at least 5 hours, better 10, in a 200 mm. tube if the amount of malic acid is relatively large, or in a 400 mm. tube if smaller. Table II will then give the percentage of malic acid from the rotation if the latter is greater than 2°, if less, the formula should be used.

Method 2, for Use in Presence of Citrate.

Prepare a 0.25 molar solution of uranyl acetate by making up 106.15 g. to one liter. Although this solution is by no means saturated, yet a good deal of time,—two or three days, is necessary to dissolve this amount of salt with constant stirring. It is, in fact, more convenient to use an excess, then to determine the strength of the solution and dilute to the proper concentration.

Measure 20 pr 25 cc. of this stock solution by pipette into a 50 cc. graduated flask, add a measured amount of the neutral malate solution and make up to the mark. The mixture should stand at least 10 hours before polarizing. The molar concentration ought to be at least one-fourth greater than the sum of the molar concentrations of the malic and citric acids. In case the amount of citric acid is not known, in a second determination the U concentration should be greatly increased, all else remaining the same. If the rotation is as before, the excess of U was already sufficient, if not, a third trial must be made with still more uranyl acetate. In general, it may be said, that, when the rotation of a given (malate) solution is the same when a very small excess of U (compared with malate) is used, as it is when the excess of U is greater; then, the absence of more than traces of citric acid is assured.

---

40 This solution is supposed to have been neutralized by carbonate-free NaOH. Care must be taken to avoid the least alkalinity. It may safely be faintly acid to litmus.

41 V. p.
Determination of Uranium by Reversal of the Process.

Since the uranato-malate complex involves its components (uranyl and malic acid) molecule for molecule, it appears a priori probable that the rotatory power of the complex can be used just as well for the determination of the uranium as for the malic acid. The condition is, of course, that there must be more than one molecule of malic acid present for each atom of uranium. If the reversibility is complete, one would expect to find the factors for malic acid and for uranium respectively, inversely proportional to their molecular weights. Now: Atomic weight of U / Mol. wt. malic acid = 238.5 / 134.05 = 1.779, whence, it should be possible to use Table II for the determination, simply by multiplying the per cent (malic acid) by 1.779 to get the per cent U corresponding to the same rotation. Observations recorded in Table I on solutions 6MU, 7MU, and 23MU supply the data for testing these deductions.

Solution 6MU is 0.0375 molar as to uranyl and 0.0745 molar as to malate. It has, accordingly, by computation (based on an exact analysis) 0.8944 g. of U per 100 cc. and it has the necessary excess of malate. Its rotation is (mean of all observations subsequent to reaching equilibrium), 14°.84'. By Table II, this corresponds to 0.5156% of malic acid, which multiplied by 1.779 gives 0.917 as the per cent of U found. Sol. 7MU is 0.0375 molar as to uranyl and 0.0447 molar as to malate. Its rotation was 14°.80, corresponding by a similar computation to 0.5143 % malic acid and to 0.915% of U. Sol. 23MU is 0.06066 molar as to uranyl and 0.0707 as to malate. It contains 1.4467 g. of U per 100 cc. Its rotation is 23°.79 at 20°, corresponding to 0.8189% of malic acid or to 1.4568% of U.

These results are all a little too high, but fairly concordant. Whether the suggested method for the determination of uranium has a field of usefulness remains for future investigation to determine. The author will not be able to pursue it further. This investigation was carried out in the Bureau of Chemistry, U. S. Dept. of Agriculture.

Summary

1. The enhancement of the optical activity of malic acid by uranyl salts has been studied.

2. The uranato-malate complex, to which this high polarizing power is due, has been isolated as an ammonium salt, UO$_2$:C$_4$H$_3$O$_5$NH$_4$, in two forms, with \( \frac{1}{2} \) and 2 molecules of H$_2$O respectively, and as a barium salt.
3. It is shown to be very probable that the formula:

\[
\begin{array}{c}
O \quad \text{UO}_2 \\
\text{CO} \quad \text{O} \\
\text{CH}_2 \quad \text{CH} \quad \text{COM}
\end{array}
\]

expresses the constitution of the uranatomic complex correctly.

4. The formation of this complex by the action between uranyl acetate and sodium malate takes place slowly. The optical activity of the mixture increases on standing. Three to ten hours are usually required to reach a maximum.

5. At high dilution, there is a diminution of the specific rotatory power of such mixtures. This phenomenon is explained by the hydrolytic dissociation of the active complex. A rigorous, quantitative concordance is shown to exist between the observations and the theoretical dissociation formula. The constants in question have been determined.

6. The molecular rotatory power of the non-hydrolysed uranyl-malate complex is computed to be \(-4038\) Ventzke deg. in a 2dm tube at \(20^\circ\) C.

7. The relation between grams of malic acid per 100 cc. and rotatory power (at \(20^\circ\), 2dm tube, in \(V^0\)) is exactly represented by the expression: \(p=0.033192V+0.006V\).

8. A table is presented showing for each Ventzke deg. the corresponding malic acid percentage.

9. The densities of uranyl acetate solutions have been determined and found to be approximately expressed by \(P=179.2\ (d-1)/d\) in which \(P\) is the number of g. salt per 100 cc. and \(d\) the density at \(25^\circ\) C.

10. The conditions for the successful application of the results to the analytical estimation of malic acid, in absence and in presence of citric acid have been determined.

11. A method for the determination of uranium polariscopically by the use of an excess of sodium malate has been outlined.