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## THE GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF BRUCINE AND STRYCHNINE AS DICHROMATE.\*

BY I. M. KOLTHOFF AND J. J. LINGANE.

Brucine and strychnine salts give crystalline precipitates with alkali dichromates and chromates. No use for quantitative purposes has been made of these precipitation reactions. In the following, the properties of the alkaloid dichromates are described and a procedure is developed by which brucine and strychnine can be determined quantitatively as dichromates. These are much less soluble than the corresponding chromates, the latter not being suitable for quantitative purposes.

*Materials Used.*—*Brucine* hydrochloride and *strychnine* sulphate solutions of known concentration<sup>1</sup> were used.

*Brucine Dichromate.*—This salt was prepared by precipitation of brucine hydrochloride with a slight excess of potassium dichromate solution. The precipitate was washed thoroughly with water; it consisted of very fine crystals. (Portion I.) Part was recrystallized from hot water in order to obtain larger crystals. (Portion II.) Both portions were dried in the air.

*Strychnine Dichromate.*—Two portions were prepared in a way similar to that described above.

*Potassium Dichromate.*—A C.P. product was thrice recrystallized from water and dried at 200°. Standard solutions were prepared by dissolving weighed samples in a known volume of water.

*Ferrous Ammonium Sulphate.*—C.P. Solutions were prepared in 0.5 to 1*N* sulphuric acid and standardized against dichromate.

### SENSITIVITY OF PRECIPITATION OF BRUCINE AND STRYCHNINE AS DICHROMATE.

One cc. of 1*N* potassium dichromate was added to 10 cc. of the alkaloid solution. A 0.004 molar brucine hydrochloride solution gave a crystalline precipitate after 1 minute of standing, 0.002 molar after 5 minutes, 0.001 molar after 15 minutes and 0.0005 molar solution a slight precipitate after 2 hours.

The sensitivity of the strychnine precipitation was the same but the precipitate was formed more quickly. Thus a 0.0005 molar strychnine solution gave a slight precipitate after 10 minutes of standing. According to the above about 2 mg. of brucine or strychnine can be detected in 10 cc. of solution by the dichromate test.

### COMPOSITION OF THE PRECIPITATES.

*Water Content.*—The samples were kept over deliquescent sodium bromide until constant weight was attained. They were then placed in vacuum desiccators

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<sup>1</sup> See THIS JOURNAL, April 1934, page 302.

over concentrated sulphuric acid or phosphorous pentoxide and kept therein until the weight was constant again. Upon continued drying in a vacuum oven at 70° no further loss in weight was noticed. The hydration and dehydration process appeared to be completely reversible, indicating that no decomposition had taken place on drying. It should be mentioned that brucine dichromate which had attained constant weight over deliquescent sodium bromide lost 0.5 to 0.6% water when placed over deliquescent calcium chloride. The strychnine compound lost under the same conditions 0.4 to 0.5% in weight. Fairly large crystals of strychnine dichromate after attaining constant weight over deliquescent calcium chloride lost 0.86% in weight on drying in a vacuum at 70°. The same crystals after having reached constant weight over deliquescent sodium bromide lost 1.35% in weight. The same preparation was ground to a fine powder; the corresponding losses in weight were 0.82% and 1.23%, respectively.

*Chromium Content.*—Samples which had attained constant weight over sodium bromide were ignited and weighed as Cr<sub>2</sub>O<sub>3</sub>. In order to test the purity, the latter was transformed by a sodium peroxide fusion and oxidation with potassium bromate in acid medium to dichromate and later titrated with a standardized iron solution. In other portions of the original samples, the dichromate content was determined in a volumetric way as will be described below.

*Alkaloid Content.*—Suspensions of the products were made alkaline with sodium hydroxide and the alkaloids shaken out with chloroform. The alkaloid content of the chloroform was determined by evaporation to dryness, weighing and titrating in the usual way.

The results given in Table I show that the brucine dichromate has the composition (C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·5H<sub>2</sub>O; M = 1096.6, and the strychnine dichromate (C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·1H<sub>2</sub>O, M = 904.4. It is possible, however, that the latter product contains only half a molecule of water of crystallization.

TABLE I.—COMPOSITION OF BRUCINE AND STRYCHNINE DICHROMATE.  
(After reaching constant weight over deliquescent sodium bromide.)

	(Brucine) <sub>2</sub> H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·5H <sub>2</sub> O.		(Strychnine) <sub>2</sub> H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O.	
	Found %.	Calculated %.	Found %.	Calculated %.
Water	7.8	8.2	1.3	2.0
H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	19.93	19.88	24.04	24.11
Alkaloid	71.8	71.87	73.7	73.91

#### SOLUBILITY OF BRUCINE AND STRYCHNINE DICHROMATE.

Samples were shaken with various solvents for 24 to 50 hours at room temperature. The amount dissolved was determined by making the filtrate ammoniacal and shaking out with chloroform. After evaporation of the latter the residue was titrated acidimetrically using methyl red as indicator. In the solubility determination in alcohol a known volume of the filtrate was evaporated to dryness and the residue weighed.

From the data given in Table II it is evident that the precipitation of brucine and strychnine is quantitative in a medium containing an excess of potassium dichromate amounting to a concentration of 0.05 molar.

TABLE II.—SOLUBILITY OF BRUCINE AND STRYCHNINE DICHROMATE. ( $22 \pm 2^\circ$ .)

Solvent.	Brucine Dichromate.		Strychnine Dichromate.	
	Moles p. l.	(Bruc) <sub>2</sub> H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> Mg. per 100 cc.	Moles p. l.	(Strychn) <sub>2</sub> H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> Mg. per 100 cc.
Water	0.000605	61.0	0.00050	45.0
0.0017 molar K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.00020	21.0	0.00020	18.0
0.05 molar K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.000065	6.5	0.000075	6.8
95% alcohol	0.00076	76.0	0.00069	62.0

## GRAVIMETRIC DETERMINATION OF BRUCINE AS DICHROMATE.

To 15 to 25 cc. of the brucine salt solution containing 100- to 200-mg. alkaloid, enough 0.25 molar potassium dichromate is added to make the concentration of the latter about 0.05 molar after the precipitation. The precipitate is allowed to stand for at least one hour, filtered on a sintered glass crucible (1G-3) and washed with a saturated solution of brucine dichromate in water. This is followed by three washings with 2-3-cc. portions of alcohol and a few washings with ether. Air is drawn through the crucible for a few minutes and the weighing made after standing in the air for at least 15 to 20 minutes. The brucine dichromate (Brucine)<sub>2</sub>H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.5H<sub>2</sub>O contains 71.87% brucine.

## VOLUMETRIC DETERMINATION OF BRUCINE AS DICHROMATE.

If brucine dichromate is dissolved in dilute sulphuric acid (1 to 2*N*), an appreciable oxidation takes place as indicated by the development of a red color of an oxidation product of brucine and the low values obtained in the titration with ferrous sulphate. However, if the thoroughly wetted precipitate is dissolved in an excess of an acid ferrous iron solution the loss by oxidation is very small (of the order of 0.5%). The dichromate content of samples which showed constant weight over deliquescent sodium bromide was determined by dissolving a known weight in a standard ferrous ammonium sulphate solution which was 1*N* with respect to sulphuric acid and back titrating with standard dichromate in the presence of phosphoric acid and diphenylamine sulphonate as indicator. The results of six determinations were 0.5 to 1% lower than those calculated. Blank titrations of ferrous iron in the presence of brucine showed that the dichromate-iron reaction induces a slight oxidation of brucine by dichromate. Thus it was found that in the titration of 250 cc. 0.01*N* ferrous sulphate in 1.5*N* sulphuric acid in the presence of 160-mg. brucine and 10 cc. 25% phosphoric acid the error amounted to only 0.5 to 0.6%.

## PROCEDURE FOR THE VOLUMETRIC DETERMINATION OF BRUCINE.

The washed precipitate as obtained in the gravimetric procedure is dissolved in an excess of a ferrous iron solution by adding 25 to 50 cc. 0.1*N* ferrous ammonium sulphate in 1*N* sulphuric acid to the precipitate in the crucible and receiving the filtrate in an Erlenmeyer flask. The crucible is washed thoroughly with 1 to 2*N* sulphuric acid and the excess iron in the combined filtrates titrated with 0.1*N* dichromate after addition of 10 cc. 25% phosphoric acid and 10 drops of 0.2% diphenylamine sulphonate as indicator. One cc. 0.1*N* ferrous sulphate corresponds to 13.14 mg. of brucine.

The results of gravimetric and volumetric brucine determinations carried out under different conditions are given in Table III. It is seen that both pro-

cedures give corresponding results. If the initial volume at the beginning of the precipitation is about 25 cc., the results are about 0.3% low; at a volume of 50 cc., 1.2%; and a volume of 100 cc., 2.2%.

TABLE III.—GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF BRUCINE.

(0.1585 Gm. brucine taken in all experiments.)

Total Volume, Cc.	Concentration $K_2Cr_2O_7$ in Excess Molar.	Time of Standing before Filtration, Hours.	Weight Ppt., Gm.	0.1N $Fe^{++}$ Used, Cc.	Brucine Grav., Gm.	Found Vol., Gm.	Error.	
							Grav. %.	Vol. %.
25	0.06	0.7	0.2206	12.10	0.1585	0.1590	0.0	+0.3
25	0.06	0.7	0.2203	12.08	0.1583	0.1587	-0.1	+0.1
25	0.06	0.7	0.2195	...	0.1578	....	-0.4	...
25	0.06	0.7	0.2198	...	0.1580	....	-0.3	...
25	0.06	16.0	0.2191	12.02	0.1575	0.1579	-0.6	-0.4
25	0.06	16.0	0.2196	12.07	0.1578	0.1586	-0.4	+0.1
50	0.08	0.5	0.2166	11.85	0.1557	0.1557	-1.8	-1.8
50	0.08	0.5	0.2166	11.77	0.1557	0.1547	-1.8	-2.4
50	0.08	16.0	0.2190	12.10	0.1574	0.1590	-0.7	+0.3
50	0.08	16.0	0.2192	11.96	0.1576	0.1572	-0.6	-0.8
100	0.08	16.0	0.2151	11.78	0.1546	0.1548	-2.5	-2.3
100	0.08	16.0	0.2189	11.94	0.1573	0.1567	-1.1	-0.8
100	0.08	16.0	0.2130	11.65	0.1531	0.1531	-3.4	-3.4
25 <sup>a</sup>	0.07	0.7	0.2203	12.08	0.1583	0.1588	-0.1	+0.2
25 <sup>b</sup>	0.07	0.7	0.2190	12.03	0.1574	0.1580	-0.7	-0.3
25 <sup>c</sup>	0.07	0.7	0.2186	...	0.1571	....	-0.9	...

<sup>a</sup> Solution was 0.01N in hydrochloric acid.

<sup>b</sup> Solution was 0.02N in hydrochloric acid.

<sup>c</sup> Solution was 0.04N in hydrochloric acid.

If the air-dried precipitates were kept over deliquescent sodium bromide until constant weight was reached, the results of the gravimetric determinations were about 0.5% higher than those reported. It is not recommended to dry the precipitates in an oven at 100° to 110° since part decomposes on removing the water of crystallization at this temperature.

The last three examples in the table show that the precipitations can be made from very dilute hydrochloric acid. At higher acidities (*e. g.*, 0.1N HCl) than those given, part of the brucine is lost by oxidation.

#### GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF STRYCHNINE.

The determinations are carried out in exactly the same way as described for brucine, except that after washing with a saturated solution of the precipitate in water, the washing is continued with a saturated solution of the salt in 95% alcohol instead of with pure 95% alcohol. If the latter is used, the precipitate shows a tendency to become colloidal and part of it runs through the filter. This difficulty is obviated by washing with a saturated solution of strychnine dichromate in alcohol.

It may be mentioned that the presence of strychnine is without influence upon the titration of ferrous iron with dichromate. Some of the results of the strychnine determinations are given in Table IV. The air-dried precipitate  $(Strychnine)_2 \cdot H_2Cr_2O_7 \cdot 1 H_2O$  contains 73.91% strychnine. One cc. 0.1N ferrous sulphate corresponds to 11.14 mg. of strychnine.

TABLE IV.—GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF STRYCHNINE.  
(0.1066 Gm. strychnine taken.)

Total Volume, Cc.	Concentration $K_2Cr_2O_8$ in Excess Molar.	Time of Standing before Filtration, Hours.	Weight Ppt., Gm.	0.1N Fe <sup>++</sup> Used, Cc.	Strychnine Grav., Gm.	Found. Vol., Gm.	Error. Grav. %.	Error. Vol. %.
25	0.08	0.7	0.1439	9.52	0.1064	0.1061	-0.2	-0.5
25	0.08	0.7	0.1439	9.52	0.1064	0.1061	-0.2	-0.5
50	0.08	1.5	0.1428	9.38	0.1055	0.1045	-1.0	-2.0
50	0.08	64.0	0.1428	9.35	0.1055	0.1042	-1.0	-2.3
50 <sup>a</sup>	0.08	0.7	0.3607	..	0.2666	....	0.0	...
100	0.04	20.0	0.1411	9.30	0.1043	0.1036	-2.2	-2.8

<sup>a</sup> 0.2665 Gm. strychnine taken.

In the first three experiments the concentration of the strychnine was 0.012 molar; in the next two, 0.006 molar; and in the last one, 0.003. It is evident that the determination gives results accurate to within 1% if the concentration of the strychnine salt is greater than 0.01 molar.

#### SUMMARY.

1. Brucine salts yield a precipitate with potassium dichromate, which after drying over deliquescent sodium bromide has the composition  $(C_{23}H_{26}N_2O_4)_2 \cdot H_2Cr_2O_7 \cdot 5 H_2O$ . Strychnine dichromate prepared under the same conditions has the composition  $(C_{21}H_{22}N_2O_2)_2 \cdot H_2Cr_2O_7 \cdot 1 H_2O$ .

2. Gravimetric and volumetric procedures are described for the quantitative determination of brucine and strychnine as dichromates.

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#### THE MICRO-PROJECTOR.\*

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Projection of the microscopic slides is fundamentally the same as projection of transparent slides with the magic lantern, or of films with the moving-picture machine. The machines all have the same essential parts and differ only in their construction, being altered according to the condition under which they are to be used and the purpose for which they are intended. In micro-projection, on account of the small aperture of the lens and the very short focal distance, all these parts must be as nearly perfect as possible and must be assembled with the greatest care. The modern projection microscope is of comparatively recent origin.

In early times the lack of proper lenses and adequate light supply hindered the development of all projection apparatus and especially the micro-projector. It is not known who first discovered the phenomenon of projection. Aristotle and Euclid mention the use of the principle in their writings, and Arabian works from the eleventh century give a description of the "camera obscura," the forerunner

\* Scientific Section, A. PH. A., Madison meeting, 1933.