

THE DETERMINATION OF MERCURY OXYCYANIDE

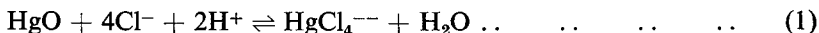
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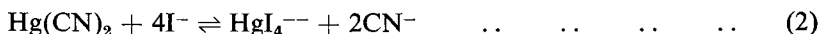
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The reaction between mercuric oxycyanide and hydrochloric acid, in the presence of certain salts, has been examined. The reaction between potassium thiocyanate and mercuric oxide in aqueous solution appears to go to completion. The reaction between mercuric cyanide and potassium iodide (or sodium thiosulphate) is complete in the presence of formaldehyde. These reactions form the basis of a method for the determination of mercuric oxycyanide which is considered more satisfactory and accurate than that in the British Pharmacopoeia, 1953.

THE method of determination of mercuric oxide in mercuric oxycyanide is due to Holdermann¹, who showed that, in the presence of chloride ions, direct titration of the oxide with decinormal hydrochloric acid (methyl orange indicator) was possible.

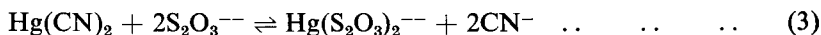


Tagliavini² extended the titration to include a determination of mercuric cyanide, by adding potassium iodide after completion of the titration of mercuric oxide.



Continued titration with decinormal hydrochloric acid enables this reaction to proceed more or less completely to the right, since the cyanide ions are removed as the slightly ionised hydrogen cyanide. Methyl orange indicator is again used. This is the method described in the British Pharmacopoeia, 1953.

Rupp³ described a modification in which sodium thiosulphate replaced the potassium iodide.



He recommended the use of methyl orange (pH 2.8–4.0) or methyl yellow (pH 2.8–4.0).

TABLE I

TITRATION OF CYANIDE IN MERCURIC OXYCYANIDE WITH 0.1N HYDROCHLORIC ACID, IN THE PRESENCE OF POTASSIUM IODIDE, USING METHYL ORANGE INDICATOR

Volume of acid added (ml.)	pH (glass electrode)	Indicator colour
40.3	4.57	Yellow
40.4	4.23	Orange-yellow
40.5	3.88	Orange
40.6	3.58	Orange
40.7	3.35	Orange-red
40.8	3.29	Red

Methyl red indicator (pH 4.2–6.3) was used by Vieböck⁴, who adapted the reaction between mercury oxycyanide and halides to determine chloride and bromide resulting in the acid digestion of halogen-containing organic compounds.

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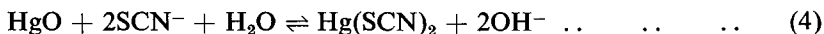
Using the procedure of the British Pharmacopoeia, 1953, we have experienced difficulty in detecting the end point, especially in the cyanide determination, as a result of slow change of pH with added acid. Consequently the methyl orange indicator slowly changes colour during the addition of about 0.5 ml. of 0.1N hydrochloric acid (Table I). This is presumably due to buffering caused by the presence of hydrogen cyanide and a change of indicator fails to provide a remedy. The present paper suggests a method to avoid the difficulty.

EXPERIMENTAL

Determination of Mercuric Oxide

The reaction between the oxide portion of mercuric oxycyanide and sodium chloride was investigated by titrating with 0.1N hydrochloric acid (i) 50 ml. of solution of mercuric oxycyanide and (ii) 50 ml. of a solution of mercuric oxycyanide with the addition of 1 g. of sodium chloride. The pH changes were recorded potentiometrically using a glass electrode. The results in Figure 1 show that the first sign of a colour change with methyl red should give a suitable indication of the end point.

The pH of the solution, after addition of sodium chloride, was not higher than pH 9.5, suggesting that the reaction of equation (1) does not go to completion (Fig. 1). The substitution of potassium thiocyanate⁵ for sodium chloride was considered, since mercuric thiocyanate ionises only to a slight extent (Equation 4). The titration with 0.1N hydrochloric acid of a solution of mercuric oxycyanide containing 1 g. of potassium thiocyanate is also recorded in Figure 1. The curve approximates closely to that obtained by titrating with 0.1N hydrochloric acid 50 ml. of a carbonate free N/70 (approx.) potassium hydroxide solution containing 1 g. of potassium thiocyanate, thus the reaction



proceeds almost completely to the right.

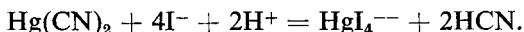
The end point is well marked by the change to the full yellow colour of phenol red. Any precipitation of mercuric thiocyanate can be disregarded. It is desirable to remove dissolved carbon dioxide from the solution before the addition of potassium thiocyanate.

Determination of Mercuric Cyanide

The reaction of the mercuric cyanide of mercuric oxycyanide with (i) potassium iodide and (ii) sodium thiosulphate was examined. To the neutral solution obtained above was added 2 g. of each of these in turn. The resultant solution was titrated with 0.1N hydrochloric acid, pH changes being recorded potentiometrically using a glass electrode. The results (Figure 2) show that in both cases the end point is not sharp, and that neither methyl orange nor methyl red can be used to indicate it properly.

Since the unwanted buffering must be caused mainly by the presence of the weak acid, hydrogen cyanide, it was considered that its removal would

not only reduce buffering, but also encourage the completion of the reaction,



Attempts were made, by titration in the presence of small amounts of water soluble carbonyl compounds to find a convenient reagent capable of removing hydrogen cyanide. Of these, acetone and formaldehyde showed the most promise (Fig. 2). Even with excess hydrochloric acid, no odour of hydrogen cyanide was perceptible in the presence of acetone

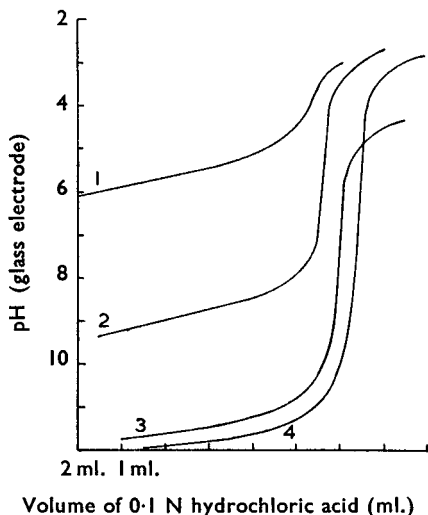


FIG. 1. Titration of oxide in mercuric oxycyanide. Curves originate at 0.5 ml. intervals.

1. 50 ml. mercuric oxycyanide solution.
2. 50 ml. mercuric oxycyanide solution containing 1 g. sodium chloride.
3. 50 ml. mercuric oxycyanide solution containing 1 g. potassium thiocyanate.
4. 50 ml. N/70 potassium hydroxide solution containing 1 g. potassium thiocyanate.

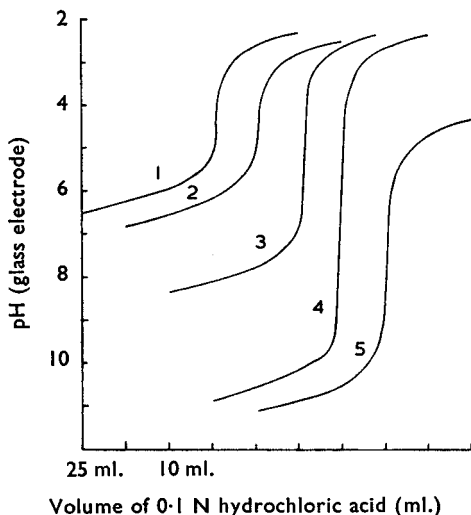


FIG. 2. Titration of cyanide in mercuric oxycyanide. Curves originate at 5 ml. intervals.

1. 50 ml. mercuric oxycyanide solution containing 2 g. potassium iodide.
2. 50 ml. mercuric oxycyanide solution containing 2 g. sodium thiosulphate.
3. 50 ml. mercuric oxycyanide solution containing 2 g. potassium iodide and 2 ml. acetone.
4. 50 ml. mercuric oxycyanide solution containing 2 g. potassium iodide and 2 ml. formaldehyde.
5. 50 ml. mercuric oxycyanide solution containing 2 g. sodium thiosulphate and 2 ml. formaldehyde solution.

or formaldehyde. Formaldehyde was further investigated for this purpose.

The neutralisation of the mercuric oxide was first effected by taking 50 ml. portions of a stock solution of mercuric oxycyanide, and adding 1 g. of potassium thiocyanate and 10 ml. of 0.1N hydrochloric acid. Two g. of potassium iodide and various volumes of 40 per cent solution of formaldehyde (neutralised to phenol red) were then introduced, and the solution titrated with 0.1N hydrochloric acid, pH changes being recorded.

The use of large volumes of formaldehyde solution re-introduced some buffering probably caused by the formate present in the neutral solution ;

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but too little formaldehyde resulted in a slow removal of hydrogen cyanide and consequently the pH of the solution on the addition of acid fell sharply and subsequently returned slowly to its equilibrium value. A suitable compromise was reached by using 2 ml. of formaldehyde solution free from formic acid (as distinct from one containing neutralised formic acid).

This was obtained by passing formaldehyde solution through a twelve inch column of "De-Acidite G" or "De-Acidite FF" in the basic form.

A solution prepared by boiling paraformaldehyde with water and filtering was almost as suitable, and the titration curves show little sign of formate buffering (Fig. 3). It is essential that the temperature of the solution should not exceed 20°. At higher temperatures the alkaline formaldehyde reduces mercuric ion to mercury with production of formic acid and consequent invalidation of the determination. With deionised formaldehyde there is no danger of elevating the temperature and this was therefore preferred.

By carrying out the titration using various weights of potassium iodide, the minimum satisfactory amount was found. No further improvement in the end point occurs on increasing the amount beyond 4 g.

The following process for the determination of mercuric oxycyanide is therefore recommended:

Mercuric oxide. Dissolve about 0.5 g., accurately weighed, in 50 ml. of water and boil gently for ten minutes. Cool to 20° without agitation, add 1 g. of potassium thiocyanate and titrate against decinormal hydrochloric acid, using phenol red indicator, until the full yellow colour of the indicator is obtained. Each ml. of 0.1N hydrochloric acid is equivalent to 0.01083 g. of HgO.

Mercuric cyanide. Continue the titration after the addition of 4 g. of potassium iodide and 2 ml. of *deionised solution of formaldehyde*. Each additional ml. of 0.1N hydrochloric acid is equivalent to 0.01263 g. of Hg(CN)₂.

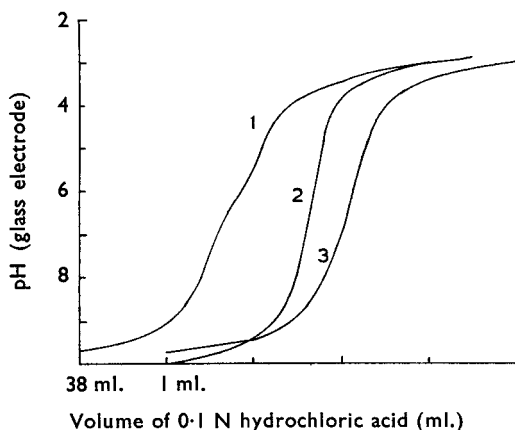


FIG. 3. Cyanide titration—effect of formate ion. Curves originate at 0.5 ml. intervals.

1. 50 ml. mercuric oxycyanide solution, 2 g. potassium iodide, and 2 ml. formaldehyde, neutralised with sodium hydroxide solution.
2. 50 ml. mercuric oxycyanide solution, 2 g. potassium iodide and 2 ml. formaldehyde treated with "De-acidite FF".
3. 50 ml. mercuric oxycyanide solution, 2 g. potassium iodide and the filtrate from 1 g. paraformaldehyde and 10 ml. boiling water.

Deionised solution of formaldehyde. Solution of Formaldehyde B.P. from which the formate ions have been removed by treatment with a basic ion exchange resin. 5 ml. of the solution is not coloured red by the addition of 5 drops of solution of phenol red and requires not more than 0.05 ml. of 0.1N hydrochloric acid to produce a red colour.

TABLE II

DETERMINATION OF A COMMERCIAL SAMPLE OF MERCURIC OXYCYANIDE B.P.

(a) *Proposed method*

Operator A		Operator B		Operator C		Operator D	
HgO per cent	Hg(CN) ₂ per cent	HgO per cent	Hg(CN) ₂ per cent	HgO per cent	Hg(CN) ₂ per cent	HgO per cent	Hg(CN) ₂ per cent
15.5	84.0	15.2	84.4	15.1	84.4	15.4	84.0
15.5	84.3	15.3	84.3	15.2	84.4	15.5	83.9
15.6	84.0	15.3	84.1	15.3	84.4	15.6	84.3
15.6	84.3	15.1	84.4	15.4	84.4	15.3	84.0
15.5	84.2	15.0	84.4	15.4	84.0	15.3	84.1
15.2	84.4	15.0	84.4	15.4	84.1	15.3	83.8

Mean of 24 results
= 15.35 per cent HgO
= 84.2 per cent Hg(CN)₂

Standard deviation
= 1.174 per cent of mean
= 0.2315 per cent of mean

(b) *Method of B.P. 1953*

Operator A		Operator B		Operator C		Operator D	
HgO per cent	Hg(CN) ₂ per cent	HgO per cent	Hg(CN) ₂ per cent	HgO per cent	Hg(CN) ₂ per cent	HgO per cent	Hg(CN) ₂ per cent
15.2	83.6	15.7	84.2	15.5	84.2	15.6	84.3
15.0	82.5	15.8	84.0	15.4	84.8	15.3	82.6
14.9	83.0	15.6	83.7	15.4	84.4	15.7	84.4
15.0	84.3	15.4	84.4	15.5	84.5	15.8	84.0
15.0	83.8	15.9	84.4	15.5	84.2	15.5	84.5
14.8	83.7	15.5	84.6	15.8	85.2	15.5	84.2

Mean of 24 results
= 15.4 per cent HgO
= 84.0 per cent Hg(CN)₂

Standard deviation
= 1.95 per cent of mean
= 0.763 per cent of mean

Comparison of Proposed Method with other Methods

(i) A sample of mercuric cyanide determined by the proposed method gave a result of 99.5 per cent Hg(CN)₂ and independently by means of standard ammonium thiocyanate gave 99.5 per cent Hg(CN)₂.

(ii) A solution was prepared by dissolving in water accurately weighed amounts of mercuric oxide and mercuric cyanide, which had previously been determined by independent methods. This solution was titrated for both components using the suggested procedure. Each 50 ml. of solution contained, HgO calcd. 0.0507 g., found 0.0500 g.; Hg(CN)₂ calcd. 0.3190 g., found 0.3200 g.

(iii) A commercial sample of Mercuric Oxycyanide B.P. was assayed using first, the proposed method, and second, the method of the British Pharmacopoeia, 1953. The results are given in Table II.

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