the other when the concentration of the acid is below 50%. Spectra of the complex, $CuSO_4.NO$, have also been obtained and the spectra of these complex salts have been compared with those of the so-called ferrous and cupric nitrosisulfonates and have been found to be identical.

3. A preliminary study of the absorption spectrum of "nitrosisulfonic acid" has shown it to be very similar to that of the ferrous sulfate-nitric oxide complex existing in concd. sulfuric acid solution. This finding supports the view that possibly nitrosisulfonic acid should be looked upon as an unstable solution of a complex compound of sulfuric acid and nitric oxide.

4. Examination of the spectra of solutions of nitric acid in concd. sulfuric acid, before and after heating the solutions, has shown that nitric acid is not readily decomposed in such solutions into nitrosylsulfuric acid, at least if the solution is not very concentrated with respect to nitric acid.

5. The character of the absorption spectrum of nitrosylsulfuric acid favors the view that this substance is present in solution largely as nitrosulfonic acid.

Further work along these lines is in progress. In addition, the investigation is being extended to other acids of sulfur, particularly the polythionates, polysulfides and to acids of sulfur and nitrogen.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GEORGE WASHINGTON UNIVERSITY MEDICAL SCHOOL]

# THE ESTIMATION OF SIMPLE, SOLUBLE CYANOGEN COMPOUNDS, MAKING USE OF THE PRINCIPLE OF AERATION

BY JOSEPH H. ROE

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The older methods for the estimation of cyanides have their limitations in the presence of interfering substances. When impurities are encountered the usual procedure has been to dissolve the sample, acidify with a mineral acid, distil, and determine the hydrogen cyanide in the distillate. Distillation of hydrocyanic acid from an acidified cyanide solution is objectionable as a quantitative procedure because (1) it involves some loss, because of hydrolysis according to the reaction $HCN + 2H_2O \longrightarrow HCOONH_4$; (2) great care must be exerted to prevent escape of hydrogen cyanide during the boiling, as this substance is highly toxic, making distillation undesirable from the point of view of safety to the operator; (3) a cyanide cannot be separated from complex cyanogen compounds such as ferrocyanides by distillation since boiling with an acid decomposes the latter, giving a false yield of hydrogen cyanide: $2K_4Fe(CN)_6 + 3H_2SO_4 \longrightarrow 6HCN + 3K_2SO_4 + K_2Fe_2(CN)_6$. Furthermore, distillation methods are not successful if it is desirable to determine slightly dissociable mercuric cyanide in the presence of interfering substance. Because of these limitations, a new method, making use of the principle of aeration, was developed.

**Principle.**—Hydrocyanic acid can be removed quantitatively from a solution at ordinary temperatures by passing a current of air through the solution for an appropriate time. If free hydrogen cyanide is present, it is thus aerated by means of an ordinary suction pump from one flask into another flask containing a solution of sodium or potassium hydroxide of correct concentration. The sodium or potassium cyanide solution thus obtained in the second flask is then titrated with standard silver nitrate solution using potassium iodide as an indicator (the Denigès modification of Liebig's method). When a cyanide is to be determined, it is dissolved in water, the solution is acidified properly and then aeration into a second flask is carried out, and the cyanide solution finally titrated as described above. This procedure overcomes all the objections to separation of a cyanide from impurities by distillation as pointed out above. The method thus possesses the advantages of being an easy procedure, yielding highly accurate results, and affording entire safety to the operator.

The titration is based upon the principle that when silver nitrate is added to an alkaline cyanide solution, a soluble double salt is formed. $AgNO_3 + 2KCN \longrightarrow KAg(CN)_2 + KNO_3$. After a few drops of a solution of potassium iodide have been added to the mixture, grayish-white insoluble silver iodide separates when all the cyanide has been converted into the double salt of silver. Potassium iodide thus produces a very sensitive end-reaction, since silver iodide is the most insoluble of all the silver salts. In this process, $1AgNO_3 = 2KCN$, and 1 cc. of a 0.1 $N$ standard solution of silver nitrate would have the following values: 0.005404 g. of hydrogen cyanide; 0.013022 g. of potassium cyanide; 0.009822 g. of sodium cyanide.

**Procedure:** *For simple, soluble, dissociable cyanides, such as potassium cyanide.*—Dissolve a convenient sample, such as 0.050 g. of potassium cyanide, in 100 cc. of water. Prepare apparatus suitable for aeration, as shown in Fig. 1. The double bubble breaker apparatus developed by Folin for determinations of ammonia has been found very serviceable for this work. In Cylinder A place the dissolved cyanide solution with a few added drops of amyl or caprylic alcohol to prevent foaming, and in Cylinder B 100–150 cc. of 5% sodium hydroxide solution. Close the apparatus and start the pump to produce a slow bubbling of air through the flasks. By means of a pipet, introduce into the apparatus at opening of tube marked "E" 25 cc. of saturated (1 g. per cc.) solution of tartaric acid. Adjust the pump until about 3 liters of air per minute passes through the apparatus. This speed is approximated when the films produced by the air bubbles leaving the surface of the fluid in the taller cylinder rise about 25 mm. above the surface of the liquid. Continue the aeration for 2 to 3 hours. Stop the pump, disconnect the flasks, add 10 drops of 10% potassium iodide solution to flask B and titrate with 0.01 *N* silver nitrate solution until a faint turbidity appears (as viewed against a dark background). As 1 cc. of 0.01 *N* silver nitrate solution equals 0.0013 g. of potassium cyanide, the reading of the buret is about 38 cc. and the calculation then is 38 × 0.0013 or 0.0494 g. of potassium cyanide.

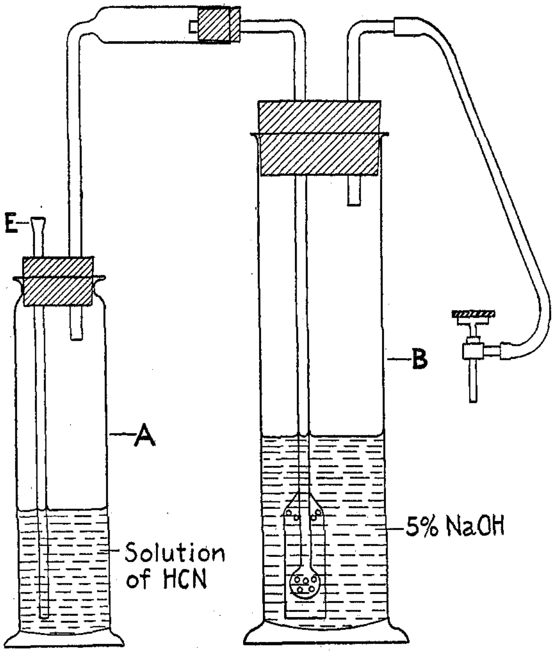

Fig. 1.—Aeration apparatus for determination of hydrogen cyanide

### Description and Discussion of the Method

The following factors are of importance.

1. **Time of Aeration.**—Quantitative recoveries were obtained from 2 hours' aeration with a Folin Ammonia Apparatus and a water vacuum pump adjusted to pass about 3 liters of air per minute through the apparatus. It is, therefore, essential to pass 360 to 500 liters of air through the apparatus when analyzing 50mg. samples of cyanide.

2. **Concentration of the Acid Added.**—This must be in excess of the amount necessary to convert all the cyanide present into hydrogen cyanide. Thus in the reaction, $2KCN + H_2SO_4 \longrightarrow 2HCN + K_2SO_4$, it will be seen that very little more than the theoretical amount required for a complete double decomposition is necessary, since hydrogen cyanide is such a weak acid and is constantly being removed from the field, thereby shifting

the equilibrium constant for the reverse reaction towards zero. However, it was found practical to have considerable acid present, since this reduces the time required for aeration; enough acid should be added to make the acid concentration of the solution about 20%; concentrations above this did not interfere with but did not facilitate the process.

3. **Kind of Acid.**—Probably any fairly strong acid could be used. Sulfuric, hydrochloric, and tartaric have been employed interchangeably, and accurate results secured. In practice, tartaric acid was used since it can be added in a highly concentrated form without the production of heat such as occurs when concd. sulfuric or hydrochloric acid is added to the water solution. However, it was found that the heat resulting from the addition of concd. sulfuric acid did not vitiate results, although it caused spattering and vaporization of the liquid not desirable from a mechanical point of view.

4. **The Concentration of the Alkali.**—The concentration of the alkali in the flask into which the hydrogen cyanide is passed is important. If aeration is carried on very slowly but little more than the calculated amount necessary for the neutralization will suffice, but for rapid aeration the solution should contain 100 times the calculated amount. So high a concentration is necessary to prevent the escape of some free hydrogen cyanide through the solution to the pump.

5. **The Amount of Indicator.**—It was found that 1 drop of a 10% solution of potassium iodide per 15 cc. of solution gives accurate results, as checked by other methods.

6. **The Air Drawn through the Solution.**—The atmospheric elements do not interfere with the determination, and the air drawn through the solution, therefore, need not be washed; carbon dioxide serves to facilitate (slightly only) the removal of hydrogen cyanide from the first cylinder. Hydrogen sulfide is the only common impurity of the laboratory that would interfere. When this gas is present in the laboratory, the air should first be passed through a solution of lead nitrate or sodium hydroxide before it is admitted to the cyanide solution.

7. **Sensitivity of the Method.**—It was found very easy to aerate 5 mg. of hydrogen cyanide from 100 cc. of solution and titrate the latter in a 150cc. volume of 5% alkali in the second cylinder. This shows a recovery of 0.00005 g. of hydrogen cyanide per cc. of solution.

This procedure is a highly accurate method for determining simple, soluble cyanides which readily dissociate in solution to produce free hydrogen cyanide when an acid is added. It can be used to determine cyanides in the presence of any impurity, except sulfides, which pass over in the aeration process as hydrogen sulfide and thus interfere with subsequent titration. When sulfides are present, it is necessary to add an excess of lead nitrate to the cyanide solution in Flask A before adding the acid and aerating. This treatment precipitates the sulfides as lead sulfide and the usual procedure can then be followed.

## The Estimation of Mercuric Cyanide

Mercuric cyanide dissociates so little in solution that it does not give a precipitate with silver nitrate. In a pure solution it can be titrated with standard iodine solution (the Fordos and Gelis process). But no method has been developed to determine this substance in the presence of foreign matter, since it defies distillation for quantitative recoveries. A method was, therefore, devised for converting mercuric cyanide into hydrogen cyanide which is then removed by aeration and determined as previously described.

**Procedure.**—Place 150 cc. of a 5% solution of sodium hydroxide in Cylinder B, and in Cylinder A place a 50mg. sample of mercuric cyanide dissolved in 100 cc. of water and add a few crystals of solid sodium chloride. Close the apparatus tightly and start the pump to aerate slowly. With a pipet introduce into Flask A, through Tube E, 25 cc. of tartaric acid, then 10 cc. of a 5% solution of stannous chloride. A gray to black precipitate of mercurous chloride and metallic mercury appears immediately in the flask, and hydrogen cyanide is evolved and passes over quantitatively into the sodium hydroxide solution in the second flask. Continue aeration at the same speed as described previously for the determination of potassium cyanide for 2 hours, then disconnect and titrate the contents of the second flask with 0.01 *N* silver nitrate, using 10 drops of 10% potassium iodide as an indicator. The reading of the buret multiplied by 0.002526 will give the number of g. of mercuric cyanide in the sample.

**Description of the Method.**—The principle involved here is that mercuric cyanide in solution is reduced to mercurous chloride and metallic mercury in the presence of hydrochloric acid and stannous chloride. The cyanide is liberated as hydrogen cyanide and passes over quantitatively into the second flask when aeration is applied; $2Hg(CN)_2 + 4HCl + SnCl_2 \longrightarrow 4HCN + 2HgCl + SnCl_4$; and $Hg(CN)_2 + 2HCl + SnCl_2 \longrightarrow 2HCN + Hg + SnCl_4$.

A mixture of stannous chloride with hydrochloric acid or with sulfuric acid and sodium chloride, or with tartaric acid and sodium chloride, will give satisfactory results. The author has consistently used tartaric acid as the acidifying agent for reasons previously given. The same principles, as discussed under the potassium cyanide determination, apply to all the other details of procedure for estimating mercuric cyanide.

The methods described above are universal in their application. They can be used to determine simple soluble cyanogen compounds in the presence of practically any other substances. To test their range of application, known amounts of potassium cyanide and of mercuric cyanide were added to mixtures of blood and organic matter, and quantitative recoveries were obtained by following the procedures as outlined above.

## Summary

An aeration procedure for estimating cyanides has been devised in which freed hydrogen cyanide is washed with air into dil. alkali solution, and the mixture then titrated with standard silver nitrate solution, using a little potassium iodide as indicator. The new method has the following marked advantages as compared with the older distillation methods: (1) it avoids loss from hydrolysis of hydrogen cyanide; (2) it can be used to determine cyanides in the presence of ferrocyanides, etc.; (3) it is entirely free from danger to the operator; (4) it offers an excellent method for determining mercuric cyanide provided the latter is previously reduced to mercurous chloride, metallic mercury and hydrogen cyanide with stannous chloride, in the presence of hydrochloric acid; (5) it involves easy technique, gives highly accurate results, and possesses a very wide range of application.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE ANALYTICAL LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# THE REACTION BETWEEN BROMINE AND AMMONIUM SALTS AND ITS EFFECT ON THE PRECIPITATION OF MANGANESE DIOXIDE

BY STEPHEN G. SIMPSON

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One of the standard methods for separating titanium, iron, aluminum and phosphoric acid from bivalent elements such as manganese, magnesium and calcium, is the basic acetate procedure. In the filtrate from this separation, manganese is often precipitated from hot solution by the addition of bromine water: $Mn^{++} + Br_2 + 3H_2O = MnO_2.H_2O + 2Br^- + 4H^+$.[1] In neutral solution the oxidation and precipitation of the manganese does not take place to an appreciable extent unless the acid formed by the reaction is neutralized, for hot, dil. hydrobromic acid dissolves manganese dioxide. After the basic acetate precipitation, however, the filtrate always contains enough acetate to prevent the formation of an appreciable quantity of free hydrobromic acid, owing to the formation of slightly ionized acetic acid. Sometimes it is the practice to neutralize the solution with dil. ammonia, but owing to the fact that bromine reacts with ammonia ($8NH_4OH + 3Br_2 \longrightarrow 6NH_4^+ + 6Br^- + 8H_2O + N_2$), a great deal of bromine is used up and it is a rather troublesome operation to precipitate

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[1] Compare Wright and Menke, *J. Chem. Soc.*, **37**, 22 (1880).