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# KJELDAHL DIGESTION AS SILVER SALT OF CYANO COMPOUNDS

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Cyano nitrogen in inorganic compound was satisfactorily determined by precipitating cyanide or cyano complex ion with silver sulfate solution prior to Kjeldahl digestion.

It has been reported[1] that securing of high concentration of sulfuric acid at the beginning of digestion process made possible the determination of inorganic cyano nitrogen by Kjeldahl method, with the elucidation that the concentration of 84% sulfuric acid which corresponds to the addition of 2ml of conc. sulfuric acid to 0.5ml of aqueous sample solution resulted in the satisfactory CN determination on either cyanide salts or cyano complexes except potassium hexacyanoferrate(III), for which only 95% nitrogen-recovery could be attained at the concentration stated above and 98% recovery even when the compound in a solid state was digested with conc. sulfric acid.

The present work provides a determination method of cyano nitrogen in a case when the sample is dilute solution so as to obliges us to take more than 0.5ml of it or the sample contains a hardly decomposable compound such as $K_3Fe(CN)_6$.

To an aliquot of sample solution containing about 1mg of cyano nitrogen taken in a digestion-flask, 10ml of 0.5% $Ag_2SO_4$ solution was added to precipitate the cyano nitrogen. After the centrifugation, the supernatant was carefully removed by suction through a small glass tube with a small pad

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* Partly presented at International Congress on Analytical Chemistry in Kyoto (1972).

of glass wool at the bottom of it to prevent any small particles of the precipitate from passing through the tube. Allowing the glass tube left in the digestion-flask, the digestion was performed with 2ml of conc. sulfuric acid at first at about 100°C for one hour and then at 200°C for two hours. The digestion-flask and glass tube as illustrated in the Figure 1 were used. (Usual test tubes and the glass tubes for centrifuge were found not to be used in the place of Kjeldahl-flask in this digestion because the bulb-shaped curvature of bottom was necessary for turning back the released hydrogen cyanide gas to the surface of the conc. sulfuric acid repeatedly.)

This method gave the accurate results even at 10ppm of cyano nitrogen concentration and for all examined cyano compounds (shown in Table 1) regardless of the sorts of central metals, their oxidation state and co-ordination numbers. The only exception was $Hg(CN)_2$ which did not precipitate with $Ag^+$ ion.

Furthermore, besides the contemplated water-removal effect, this method proved to have special significance for the aqueous solution of the indecomposable compounds such as potassium hexacyanoferrate(III) which was very difficult to be satisfactorily analysed even in the digestion of the solid sample with conc. sulfuric acid. It suggests the catalytic role of $Ag_2SO_4$ on the decomposition in addition to its role as a precipitating reagent.

Coexistence of either ammonium ion or nitrate ion gave no interference on the determination of cyano nitrogen by this method, because these ions do not precipitate with $Ag^+$ ion, and halogen ions which precipitate with $Ag^+$ ion, too.

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## Reference

1) Y. Matsumoto, T. Kawashima and M. Shirai, Chemistry Letters, 1973, 347.

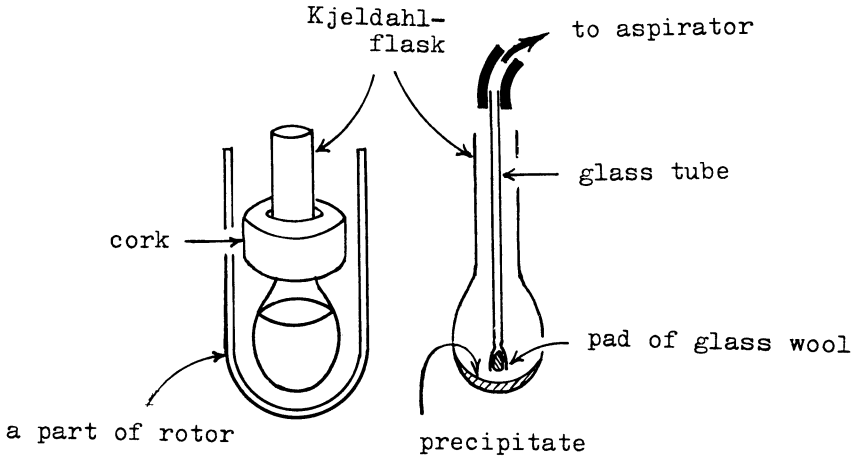


Figure 1 Device for water-removal

Table 1 Determination of cyano nitrogen

| Compound | Obsd. nitrogen per cent of the compd. (dissolved in aqueous solution) ——by this method | Cald. nitrogen per cent of the compd. | (for comparing) Obsd. nitrogen per cent of the compd. in solid state ——by Dumas method |
|---|---|---|---|
| KCN | 21.50 % (100) | 21.57 % | |
| $K_4Fe(CN)_6 \cdot 3H_2O$ | 19.86 (100) | 19.90 | 19.92 % (100) |
| $K_3Fe(CN)_6$ | 25.79 (101) | 25.53 | 25.37 ( 99) |
| $K_3Cr(CN)_6$ | 25.81 (100) | 25.83 | 25.90 (100) |
| $K_3Co(CN)_6$ | 25.25 (100) | 25.29 | 25.51 (101) |
| $K_2Ni(CN)_4$ | 22.79 ( 98) | 23.25 | 22.82 ( 98) |
| $K_2Zn(CN)_4$ | 22.31 ( 99) | 22.63 | 22.94 (101) |
| $Na_2Cu(CN)_3 \cdot 3H_2O$ | 17.41 (100) | 17.39 | 17.72 (102) |
| $K_3Cu(CN)_4$ | 19.56 ( 99) | 19.67 | 19.61 (100) |

( ): per cent recovery of nitrogen

Each value for this method is a mean value of the closely similar results of three or more experimental runs, while each value for Dumas method is the result of a single experiment.

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