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DETERMINATION OF CYANO NITROGEN IN INORGANIC CYANO COMPOUNDS BY KJELDAHL METHOD*1

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By retention of a high level of sulfuric acid concentration at the beginning of digestion process and use of a subsidiary decomposition-reagent, determination of inorganic cyano-nitrogen by Kjeldahl method was made possible.

A simple and accurate method was established for determining cyano nitrogen in inorganic simple or complex cyano compounds in the state of an aqueous solution as well as a solid. The proposed method is based on the ordinary Kjeldahl digestion and requires no cumbersome procedure such as either application of a sealed tube[1,2] in the digestion process or adjunction of some trapping system[3] to a usual digestion equipment to avoid loss of cyano nitrogen as hydrogen cyanide on acidifying the aqueous solution.

Firstly, the effect of the concentration of sulfuric acid on the nitrogen recovery was surveyed for aqueous solutions of potassium cyanide and potassium hexacyanoferrate(II).

As shown in Table 1 the initial concentration of sulfuric acid in the digestion process was found to be of primary importance for these samples; the increasing initial concentration of sulfuric acid improved the recovery of cyano nitrogen. When the initial concentration of sulfuric acid was increased to 75% (the ratio of 2ml conc. sulfuric acid to 1ml aqueous sample solution), the nitrogen recovery for potassium hexacyanoferrate(II) reached 100%. Digestion with 84%

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*1 Partly presented at the 18th Symposium on Co-ordination Chemistry (1968).

sulfuric acid (2ml conc. sulfuric acid added to 0.5ml aqueous sample) gave 100% recovery of nitrogen for both potassium hexacyanoferrate(II) and potassium cyanide.

The retention of this 84% level in sulfuric acid concentration assured satisfactory determination for either cyanide or cyano complexes (Table 2) except potassium hexacyanoferrate(III) for which a reduced nitrogen recovery (95%) was attained at the same favorite initial concentration level of sulfuric acid.

Vanetten and Wiele[2] suggested the hydrolytic decomposition of a large number of organic nitriles and two solid inorganic cyano complexes, showing the 102.1% and 98% recovery of cyano nitrogen for the solid samples of potassium hexacyanoferrate(II) and hexacyanoferrate(III), respectively, on digestion with conc. sulfuric acid.

Secondly, subsidiary decomposition reagents were searched for. Each reagent in solid state was added to a sample solution by a full micro-spatula amount before the conc. sulfuric acid was introduced.

Anhydrous aluminium chloride (Table 1), lead chloride, lead sulfate and tin(II) chloride proved to be effective in the determination of cyano nitrogen in potassium cyanide. For the decomposition of complex cyanides including potassium hexacyanoferrate(III), aluminium chloride was most effective. Zinc chloride, hydrogen peroxide*2, potassium sulfate + hydrogen peroxide*2, iron(II) sulfate + hydrogen peroxide*2, and vanadium(V) oxide showed no effect. Use of the usual catalysts as copper(II) sulfate + potassium sulfate and potassium sulfate alone should be avoided, since they always gave lower recovery of cyano nitrogen for the simple inorganic cyanides (Table 1).

In all cases presented here, the amount of cyano-nitrogen in a sample solution was administered to be about 1mg, and the temperature in the digestion process was maintained at about 100°C for the first one hour and 200°C for further two hours.

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*2 0.5ml of 30% aq.soln. was used.

Conc. sulfuric acid means commercially available 95% sulfuric acid.

References

1) A. Friedrich, E. Kühaas, and R. Schnürch: Z. Physiol. Chem., 216, 68 (1933).

2) C. H. Vanetten and M. B. Wiele: Anal. Chem., 23, 1338 (1951).

3) L. C. Smith, J. Kleinberg and E. Griswold: J. Amer. Chem. Soc., 75, 449 (1953).

Table 1 Effect of sulfuric acid concentration on the nitrogen recovery

volume of aqueous sample solution to 2ml of conc. sulfuric acid (ml)	concentration of H_2SO_4 (%)	nitrogen recovery (%)					
		KCN			$K_4[Fe(CN)_6]$		
		decomposition reagent			decomposition reagent		
		H_2SO_4 alone	H_2SO_4 + $AlCl_3$	H_2SO_4 + $CuSO_4$ + K_2SO_4	H_2SO_4 alone	H_2SO_4 + $AlCl_3$	H_2SO_4 + $CuSO_4$ + K_2SO_4
2.0	62	70	94	81	93	98	88
1.6	66	83	97	83	96	100	98
1.4	69		98	81	99	100	99
1.2	72	95	99	88	100	100	100
1.0	75	97	99	97	100	100	100
0.9	76	98	100	91			
0.7	80	99	100	85			
0.5	84	100	100	88			

Table 2 Determination of nitrogen in inorganic cyano compounds

sample	nitrogen content		
	calculated	by Kjeldahl method*	by Dumas method** (burnt in the presence of V_2O_5 + WO_3)
KCN	21.57%	21.50% (100)	
$K_4Fe(CN)_6 \cdot 3H_2O$	19.90	19.86 (100)	19.92% (100)
$K_3Fe(CN)_6$	25.53	24.17 (95)	25.37 (99)
$K_3Cr(CN)_6$	25.83	25.58 (99)	25.90 (100)
$K_3Co(CN)_6$	25.29	25.00 (99)	25.51 (101)
$K_2Ni(CN)_4$	23.25	22.85 (98)	22.82 (98)
$K_2Zn(CN)_4$	22.63	22.70 (100)	22.94 (101)
$Na_2Cu(CN)_3 \cdot 3H_2O$	17.39	17.25 (99)	17.72 (102)
$K_3Cu(CN)_4$	19.67	19.45 (99)	19.61 (100)

( ) percent recovery of nitrogen

* 0.5ml of aqueous solutions of the cyano compounds were digested with 2ml of conc. sulfuric acid.

** Solid samples were used.

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