DETERMINATION OF METAL CYANIDE AND THIOCYANATE COMPLEXES BY KJELDAHL-GUNNING AND CARIUS SEALED TUBE DIGESTION METHODS

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A variety of methods have been reported for the determination of the cyanide ion employing all of the general techniques of analytical chemistry as volumetric[1], spectrophotometric[2], and amperometric[3], to mention only a few. None of these methods are applicable to the determination of cyanides in the inert transition metal complexes. Many investigators have described the determination of metal cyanide complexes. Generally, each method is limited in its application to a specific compound and the iron cyanide complexes have been studied almost exclusively. Some other methods have been attempted for the determination of the cyanide complexes. Chief among these is the evolution method of RUBNER AND BACHKA as applied by BIEG[4]. Although this method is applicable to the inert transition metal complexes it requires much time and the handling of large amounts of distillate.

The chief limitation of the methods developed to date is that they may not be readily applied to the determination of the inert transition metal cyanide and thiocyanate complexes. Carbon analyses of these complexes are generally difficult. The same is true of the Dumas nitrogen determination.

This paper describes methods which are applicable to the determination of metal cyanide complexes using the classical Kjeldahl digestion or Carius combustion followed by a Kjeldahl type of distillation.

The use of the Kjeldahl apparatus has been reported by HORAN AND EPPIG[5] for the determination of ammonia in cobalt penta- and hexa-ammines. The Kjeldahl-Gunning method as described in A.S.T.M. has been used by JUNG AND COPELLO[6] for the analysis of blue pigments. The destruction of ferrocyanide in an autoclave at 130° employing ammonium polysulfide as the reducing agent has been reported by ADELSBERGER[7]. Also, the hydrolysis of cyanides in hydrochloric acid at 140° has been reported by GETTER AND GOLDBAUM[8], followed by a colorimetric determination of ammonia.

The modified Kjeldahl-Gunning method or the combined use of the Carius sealed tube digestion and Kjeldahl distillation enable the analysis of the metal cyanide, thiocyanate and mixed cyanodiphenanthroline complexes with greater ease and accuracy than provided by the existing methods. These procedures are especially applicable to micro analytical techniques and may be applied to for the analysis of metal cyanide, thiocyanate complexes.

EXPERIMENTAL

Reagents and apparatus

Reagent grade concentrated sulfuric acid, $d = 1.84$ was used for the digestion. Decomposition was catalysed by the reagent grade anhydrous mercuric sulfate and mercuric oxide mixture. The receiving flask contained 4% boric acid. Titration was carried out using approximately 0.015 *N* hydrochloric acid, the normality of which was checked against anhydrous sodium carbonate and ammonium sulfate using methyl red and methylene blue mixed indicator. 50% sodium hydroxide containing 5% thiosulfate was used to neutralize sulfuric acid in a distillation flask. Reagent grade sodium salt of ethylenediaminetetraacetic acid (EDTA) was added to break ammonia complexes of some of the transition metals.

Reagent grade potassium ferro- and ferricyanides, and mercuric thiocyanate were obtained from the Baker and Adamson Co.; potassium cobalticyanide was procured from the G. F. Smith Chemical Co. Sodium aquo-, amminopentacyanoferrates(II) and Reinecke's salt were prepared by the procedure described in the BRAUER's "Handbuch der Präparativen Anorganischen Chemie". Potassium salts of cyanide complexes of chromium(III), manganese(III), nickel(II) and molybdenum(IV) were obtained from G. ATKINSON, and dicyano-bis(1,10-phenanthroline)-iron(II) from A. SCHILT (both from our laboratories). All compounds were analysed for water of crystallization and metal contents.

Kjeldahl distillations were carried out using one piece micro Kjeldahl distillation apparatus.

PROCEDURE

Kjeldahl-Gunning method

The digestion of the transition metal cyanides was carried out essentially by the Kjeldahl-Gunning method. A sample weighing approximately 10 to 25 mg was placed directly from the charging tube into the micro Kjeldahl digestion flask. About 50 mg of mercuric sulfate and mercuric oxide mixture was then added to the digestion flask followed by the addition of 2.0 ml of concentrated sulfuric acid saturated with mercuric oxide. The contents were mixed slowly, and the flasks were placed on a low flame for about 10 min, then digestion was continued for an additional 80 min on full heat. Prolonged digestion caused poor reproducibility and low results. Throughout the digestion period flasks were rotated frequently to ensure complete mixing and to get all the spattered solid sulfates from the walls of the digestion flasks. At the end of the digestion the flasks were cooled. The contents were diluted with approximately 3–4 ml of water. The diluted digest was then transferred to the micro Kjeldahl distillation flask. About 150 mg of sodium salt of ethylenediaminetetraacetic acid (EDTA) was added. (The addition of EDTA was necessary with all the transition metal cations forming inert ammonia complexes). Six ml of 50% sodium hydroxide containing 5% thiosulfate was then added and the distillation was started. Samples were distilled for 7 min. The distillate was collected in 4% boric acid. The ammonia absorbed was titrated with a standard hydrochloric acid using methyl red and methylene blue mixed indicator.

Carius sealed tube method

An alternative Carius sealed tube digestion method was found to be superior (than the Kjeldahl-Gunning procedure). A micro sample was placed into the Carius combustion tube from the charging tube. Mercuric oxide and mercuric sulfate mixture and sulfuric acid were added as in the above procedure. The sealed tubes were placed in the Carius heating furnace. The samples were heated for 2 h at 315°. The tubes were cooled and they were opened taking regular precautions by releasing pressure first. The opened tubes were heated on the micro burner and they were boiled for about

TABLE I

ANALYSIS OF NITROGEN IN METAL CYANIDE AND THIOSULFATE COMPLEXES

Substance analyzed	*Method of digestion*	*Method of distillation*	*% calculated*[a]	*Ammonia found*	*Recovery of nitrogen %*	*Average deviation*[b] *p.p.t.*
Potassium ferrocyanide	Kjeld.-Gunn.	No EDTA	19.89	20.01	100.6	6
Potassium ferrocyanide	Carius	No EDTA	19.89	19.97	100.4	2
Potassium ferricyanide	Kjeld.-Gunn.	No EDTA	25.51	25.11	98.43	7
Potassium ferricyanide	Carius	No EDTA	25.51	25.34	99.33	5
Sodium ammonopentacyanoferrate(II)	Kjeld.-Gunn.	No EDTA	24.56	24.36	99.18	5
Sodium ammonopentacyanoferrate(II)	Carius	No EDTA	24.56	24.50	99.75	4
Sodium aquopentacyanoferrate(II)[c]	Kjeld.-Gunn.	No EDTA	21.41	21.63	101.0	9
Sodium aquopentacyanoferrate(II)[c]	Carius	No EDTA	21.41	21.52	100.5	5
Dicyano-bis(1,10-phenanthroline)-iron(II)	Kjeld.-Gunn.	No EDTA	5.98	11.30[d]	188.9	30
Dicyano-bis(1,10-phenanthroline)-iron(II)	Carius	No EDTA	5.98	6.03	100.8	5
Tetrapyridinodithiocyanato-iron(II)	Kjeld.-Gunn.	No EDTA	5.74	9.57[e]	166.7	100
Tetrapyridinodithiocyanato-iron(II)	Carius	No EDTA	5.74	8.32[e]	144.9	100
Potassium hexacyanochromate(III)	Kjeld.-Gunn.	EDTA added	24.46	24.58	100.5	11
Potassium hexacyanochromate(III)	Carius	EDTA added	24.46	24.42	99.83	4
Potassium hexacyanocobaltate(III)	Kjeld.-Gunn.	EDTA added	25.28	24.85	98.30	9
Potassium hexacyanocobaltate(III)	Carius	EDTA added	25.28	25.13	99.40	2
Potassium hexacyanomanganate(III)	Kjeld.-Gunn.	No EDTA	24.90	24.79	99.56	9
Potassium hexacyanomanganate(III)	Carius	No EDTA	24.90	24.97	100.3	4
Potassium octacyanomolybdate(IV)	Kjeld.-Gunn.	No EDTA	22.56	22.55	99.95	5
Potassium octacyanomolybdate(IV)	Carius	No EDTA	22.56	22.51	99.78	4
Potassium tetracyanonickelate(II)	Kjeld.-Gunn.	EDTA added	20.92	20.95	100.1	5
Potassium tetracyanonickelate(II)	Carius	EDTA added	20.92	20.95	100.1	5
Ammonium diammonotetrathiocyanatochromate(III)	Kjeld.-Gunn.	EDTA added	27.65	27.64	99.96	
Ammonium diammonotetrathiocyanatochromate(III)	Carius	EDTA added	27.65	27.63	99.93	3
Dithiocyanatomercury(II)	Kjeld.-Gunn.	No EDTA	8.84	8.77	99.20	5
Dithiocyanatomercury(II)	Carius	No EDTA	8.84	8.82	99.77	3

[a] Calculated values are based on the results of the analyses rather than expected formula weights.
[b] Average deviation in p.p.t. is based at least on five determinations.
[c] Sodium aquopentacyanoferrate(II) contains sodium ferrocyanide and sodium nitroprusside as impurities.
[d] Some of the phenanthroline is decomposed during the digestion. Results depend on the digestion conditions.
[e] Some pyridine is distilled and the results vary with the time of distillation.

4 min until sulfur dioxide fumes were expelled. The digest was then diluted with water and the contents were transferred to the distillation flask.

RESULTS AND DISCUSSION

In concentrated sulfuric acid and in presence of mercuric ion as a catalyst conversion of metal cyanide complexes to ammonium sulfate proceeds rather rapidly. However, quantitative recovery of nitrogen as ammonia is greatly dependent upon the digestion conditions. Thus, Kjeldahl-Gunning and Carius sealed tube digestion methods have been investigated to a greater extent. The results of the analyses of metal cyanide, thiocyanate and ammonia complexes are summarized in Table I.

The phenanthroline–cyanide complexes yield high and irreproducible results when using the Kjeldahl-Gunning digestion method. Apparently, phenanthroline is decomposed somewhat under these conditions. In the Carius sealed tube digestion phenanthroline is not attacked and the cyanide is hydrolyzed to ammonia exclusively. The mixed complexes of pyridine–thiocyanate or cyanide cannot be analyzed by these methods. Pyridine is distilled with ammonia, and the results depend upon the time of distillation. The somewhat low results for the potassium ferricyanide are attributed to the absorption of water on the powdered sample.

Recovery of nitrogen as ammonia after the digestion by Kjeldahl-Gunning method is in the order of 99%. The results obtained are mostly low and there is a considerable scattering of the values. This is probably due to the loss of nitrogen during the digestion as has been observed by SELF[9] and CARPIAUX[10] when the final digest is a solid. Indeed, metal cyanide complexes during digestion yield insoluble sulfates. Reproducibility becomes poorer if the digestion has been extended over 3 h. In general, 90 min time of digestion is sufficient to decompose metal cyanide and thiocyanate complexes.

In the Carius sealed tube digestion method recoveries are better than 99% and the scattering of the results is less than in the Kjeldahl-Gunning method. The digestion temperature should be high enough to decompose cyanide and thiocyanate complexes and not too high to shatter the tubes. At 250° only about 90% of the cyanide is converted to ammonia; thiocyanates are not effected at this temperature. At 315° all of the metal cyanide and thiocyanate complexes studied are converted to ammonia quantitatively.

The conversion of cyanide to ammonia in the Kjeldahl-Gunning method is also greatly effected by the amount of water present in the original digest. The results are low by a few per cent and not reproducible if the sulfuric acid concentration falls below 15 *M*. At lower concentrations of sulfuric acid the recovery of ammonia becomes poorer. This is probably due to the loss of hydrocyanic acid. The evolution of cyanide as hydrocyanic acid has been used for the determination of cyanide by the Liebig method.

SUMMARY

Small amounts of metal cyanide and thiocyanate complexes can be determined using either the Kjeldahl-Gunning or Carius sealed tube digestion method. The results obtained by the Kjeldahl-Gunning method are somewhat low and the values are scattered. The Carius sealed tube digestion enables analysis not only of metal cyanide and thiocyanate but also of mixed phenanthroline–cyanide complexes. The results are reproducible and more accurate than in the Kjeldahl-Gunning method.

RÉSUMÉ

Les auteurs ont examiné le dosage des complexes métalliques cyanés et thiocyanés, soit par la méthode de Kjeldahl-Gunning, soit par la méthode en tube scellé de Carius. C'est cette dernière qui a donné les résultats les meilleurs. Elle permet en outre l'analyse de complexes mixtes phénanthroline-cyanure.

ZUSAMMENFASSUNG

Die Bestimmung von komplexen Metallcyaniden und thiocyanaten kann entweder nach der Kjeldahl-Gunning oder Carius Methode erfolgen. Die Kjeldahl-Gunning Methode ergibt etwas zu tiefe und streuende Werte. Die Carius Methode gibt bessere Werte und kann ausserdem auch für Phenanthrolin-Cyanid Komplexgemische angewandt werden.

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FURTHER APPLICATIONS OF ELECTRO-STATIC DISCHARGE CURRENT (ES. D.)

VII. A MOISTURE GAUGE FOR CHROMATOGRAPHS

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The importance of moisture in determining the conductance of chromatograph zones which contain soluble compounds is well known. By placing the chromatograph in a "humidiser" prior to zone location the writer showed[1] that the conductivity of an otherwise almost undetectable zone or spot could be located and underlined automatically.

The correct length of exposure to moisture in the "humidiser" varies in accordance with the humidity of the atmosphere. Automatic underlining is possible over a comparatively wide range of humidity, from a degree where there is only just sufficient moisture to permit reliable operation to the point where the chromatograph becomes oversaturated.

The simple device described in the present paper is a gauge whereby the gradual conditioning of the chromatograph can be monitored until it reaches the most favourable condition.