Potentiometric Determination of Cyanamide Using a Silver Sulfide Membrane-Type Ion-Selective Electrode

Tetsutaro YOSHINAGA, Masaaki KOGA and Kentaro KAWANO

*Department of Chemistry, Faculty of Engineering, Kyushu Institute of Technology,
Sensuicho, Tobata, Kitakyushu 804, Japan*

Potentiometric titration was successfully applied for the determination of cyanamide (Cy) using a silver sulfide membrane-type ion-selective electrode. In a Cy concentration range of 0.02 to 0.08 M in a 1 M NaOH solution, 98.9% of the cyanamide was recovered (RSD=0.08%, $n=10$). The detection limit of Cy by the present method is around 6×10^{-4} M with a positive error of *ca.* 1%, an RSD of 0.2%, and an n of 4. The coexistence of cyanoguanidine, urea, sulfide and chloride at a molar ratio of 0.3:1.5:0.3:1.0 to 1 part of Cy did not affect the determination of Cy.

Keywords Potentiometric titration, cyanamide, silver sulfide membrane, ion-selective electrode.

Calcium cyanamide is known to be a useful nitrogen fertilizer; cyanamide ($\text{H}_2\text{N}-\text{CN}$; Cy), a compound derived from calcium cyanamide, has been in widespread use as a chemical intermediate, such as cyanoguanidine, other guanidine derivatives and thiourea as well as being used in textile fire-proofing, defoliants and wood-pulp processing. Traditionally, Cy has been determined by precipitation with ammoniacal silver nitrate followed by the titration of silver in the precipitate by the Volhard method.¹⁻³ However, this method is time-consuming, applicable only to macro amounts of Cy and requires elaborate operations. On the other hand, several instrumental methods have been developed, such as spectrophotometry⁴, the reaction rate method³, potentiometry⁵⁻⁷, and HPLC⁸, for the determination of Cy. Buyske and Downing⁴ developed a spectrophotometric method for Cy based on the formation of a purple complex (λ_{max} : 530 nm) with sodium pentacyanoammineferrate(II) ($\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_2]$; SPF) in a carbonate buffer of pH 10.5. Their method had a lower limit of sensitivity (1 μg in 1.3 ml or 0.77 ppm) and exhibited a linear response from 1 to 52.5 μg (reproducibility, *ca.* 5%). Nieman *et al.*³ developed an initial-rate method for trace amounts of Cy. The initial rate was measured as the rate of absorbance increase due to the formation of an SPF-Cy complex. Their calibration curve was linear for 1×10^{-7} – 3×10^{-7} M with a detection limit of 13 ppb and a precision of 3.5%. A sensitive method for the determination of Cy in plasma was developed by Prunonosa *et al.*⁸ Their procedure involved extraction, derivatization and a posteriori analysis by HPLC with a fluorometric detector. The linearity ranged from 5 to 500 ng/ml and the lower detection limit of Cy in a plasma was 4 ng/ml with a precision of 3–8.9%. These results illustrate that instrumental methods generally do not give good reproducibility. Sato *et al.* studied the analytical meth-

ods for determining cyanide and Cy for use in the preparation of cyanide compounds from lime nitrogen. They proposed a potentiometric method to determine cyanide ions and Cy in a mixture of these compounds using a silver electrode; those species were determined by repetitive titrations under different conditions.⁵ Their method, however, is not appropriate for determining Cy under an alkaline condition. The influence of the ammoniacal alkaline condition was especially strong.⁶ In recent years, investigations of ion-selective electrodes (ISE) have been intensively carried out, and many sensitive and stable electrodes have been developed. ISE can now be used to determine even organic compounds indirectly. For example, Pungor *et al.*⁹ determined thiourea in 1 M and 0.1 M NaOH solutions using a silver sulfide electrode as an indicator electrode with a lower detection limit of 10^{-3} M. In the present work, considering the situations of the official analytical method of Cy¹, as mentioned above, the authors have established an accurate and precise potentiometric method for determining Cy in (1 M) NaOH solutions in the presence of several compounds using an ion-selective (silver sulfide membrane type) electrode with a detection limit of 6×10^{-4} M (or 6 μg) Cy.

Experimental

Reagents

Standard silver nitrate solution: an analytical-grade reagent of silver nitrate from Wako Pure Chemicals was dissolved in distilled water to obtain a 0.10 M standard stock solution.

Cyanamide (Cy): crude crystal cyanamide prepared from commercially obtained LN was purified by repeated extraction with dried diethylether and crystallization

by solvent evaporation. Analytical value: (1) official method¹=99.00%, (2) the calculated value from Kjeldahl nitrogen=99.04%. Based on these values, the purity of Cy is considered to be 99.0% in what follows.

Crystalline Cy is hygroscopic; an excess amount of a sample was weighed using a weighing bottle and dried on P₄O₁₀ until a constant weight was obtained in a desiccator. Then, a prescribed quantity of dried Cy was weighed immediately and dissolved into a 1 M NaOH solution to a given volume of a volumetric flask (Cy standard stock solution).

Dicyanodiamide (=cyanoguanidine, CG): An reagent-grade crystal obtained from Tokyo Kasei Co. Ltd. was recrystallized twice from water (m.p. 209°C (reference: 209°C¹⁰)). The purity from Kjeldahl nitrogen=100.0%.

Urea and sodium sulfide used were of reagent grade obtained from Wako Pure Chemicals. Sodium chloride used was a primary standard from Wako Pure Chemicals. For urea and sodium sulfide stock solutions, standardization was performed before use.

Apparatus

A potentiometer (Kyoto Electronic Industry; AT-06 type) was used to determine the cyanamide concentration. A silver-sulfide type ion-selective electrode (Toyo Scientific Industry) was used to detect silver ions. A sleeve-type electrode (Horiba Seisakusho No. 2630; Ag/AgCl), in which a 3.3 M KCl-AgCl(sat.) solution is used as an inner solution, was used as a reference electrode.

Potentiometric titration

The silver sulfide electrode was immersed in a Cy-dissolved solution (in 1 M NaOH), and connected to a reference electrode through a salt bridge (agar gel-KNO₃ aq.). A small amount of AgNO₃ std. solution was dropped intermittently through a micro-buret, and the potentials were measured at equilibrium.

Analytical reaction and principle

Cy reacts with silver ions, producing an insoluble yellow-silver cyanamide salt as follows (Eq. (1)):

Since the silver cyanamide that is formed can be dissolved in a weak acid, this reaction is reversible. It is thus necessary to neutralize the hydrogen ions produced to make the reaction proceed quantitatively.

The addition of a base to an amount of more than twice that of Cy (molar ratio) is required before titration. In an actual experiment, dark-brown precipitates (ppt.) appeared during the first titration; then, the color of the ppt. rapidly changed to yellowish. This means that silver ions initially reacted with hydroxide ions which existed in great excess to give silver hydroxide (AgOH), followed by silver oxide (Ag₂O). Immediately after, the equilibrium rapidly moved to the formation of silver cyanamide, which has a smaller solubility product.

The Nernst equation for silver ions is

$$E = E_0 + (RT/F)\ln[\text{Ag}^+]. \quad (2)$$

When silver ions (Ag⁺) were added to the sample solution under an alkaline condition, most of them were rapidly consumed and equilibrium was reached according to Eq. (1); also, a constant potential was attained due to a very small amount of residual Ag⁺ ions. The potential was nearly constant during titration, because of the constancy of the residual Ag⁺ concentration. After complete consumption of Cy, the Ag⁺ ions added to the solution remain unreacted, and the potential showed a rapid increase. This break point (end point) corresponds approximately to the equivalence point.

Results and Discussion

Titration under alkaline conditions

Ten milliliters of a Cy solution (6.0×10⁻² M in 1 M NaOH) was titrated with a 0.10 M AgNO₃ standard solution (std. Ag solution); the potentiometric titration curves are shown in Fig. 1. The broken curve exhibits a rapid rise in potential during the initial stage (P), followed by a plateau until the next (second) rapid rise occurs at around the equivalence point (v₁=12.0 ml) of Cy. To clarify the reason for the initial potential rise, microtitration was carefully carried out by limiting the titration to the initial region; the results are shown in Fig. 2. It can be seen that the rapid potential rise took place at a titration volume of 0.03 ml (v_p), where the formation of a black ppt. was observed. This black ppt. was considered to be sulfide, because a small amount of sulfide is usually contained in Cy. To confirm this, the

Fig. 1 Potentiometric titration curves of cyanamide in a 1 M NaOH solution. (1) cyanamide (0.6 mmol); (2) cyanamide (0.6 mmol)+sodium sulfide (0.25 mmol).

Fig. 2 Micro-titration curve of cyanamide and impurity (S^{2-}) in a 1 M NaOH solution. Amount of cyanamide: 0.6 mmol.

following experiment was carried out. A known amount of sodium sulfide was added to a Cy alkaline solution and titrated under the same condition as mentioned above, obtaining the solid curve in Fig. 1(2). As expected, the potential was nearly constant, showing no potential jump until the titration volume reached the volume corresponding to the quantity of sulfide added. A rapid potential jump appeared thereafter. Further titration gave the same length of plateau as that in Fig. 1(1), followed by a second potential jump. The distance between the two potential jump points in the abscissa remained the same upon titration with and without sodium sulfide. A correction value of 0.03 ml (corresponding roughly to 1 drop), due to sulfide, may be negligibly small, but requires a correction for an accurate determination. Since the potential jumps due to sulfide

and Cy are clearly separated from each other, the pre-addition of sulfide should give more accurate analytical results for the determination of Cy. Besides, this pre-addition method should yield the exact value of the sulfide quantity in the sample.

It must be noted here that the value of the initial potential (ca. -400 mV) at a sufficiently low concentration of sulfide (10^{-4} M) was quite different from the potential (ca. -800 mV) at a relatively high concentration of sulfide (10^{-2} – 10^{-1} M), which was intentionally added. This apparent discrepancy may be rationalized as follows. If the Nernst equation is to hold for sulfide ions, the use of the solubility product in water gives the equation $E(S^{2-}; \text{mV vs. Ag/AgCl}) = -900 - 29\log[S^{2-}]$. The present experiment, however, was carried out in a 1 M NaOH solution, and an appropriate Nernst equation under these conditions would be

$$E(S^{2-} \text{ in } 1 \text{ M NaOH; mV vs. Ag/AgCl}) \\ = -830 - 29\log[S^{2-}] \quad (10^{-4} \text{ M} < [S^{2-}] < 10^0 \text{ M}),$$

and at concentrations of 10^{-4} M or lower, the potential should show a rapid increase. A schematic figure illustrating this behavior is depicted in Fig. 3, where the broken curve shows an imaginary potential curve obeying the Nernst equation.

By varying the Cy concentration from 8.0×10^{-2} to 2.0×10^{-2} M, Cy was potentiometrically determined under the same conditions as stated above. A clear potential jump was obtained at each concentration; the results are summarized in Table 1. It can be seen that the percent recovery was nearly constant (98.9%), allowing for experimental error. The correlation between the analytical and calculated concentrations was nearly perfect ($r=1.0000$).

Fig. 3 Schematic titration curves for the interpretation of the shift of initial potentials as a function of the sulfide ion concentrations. $[S^{2-}]$: (1), 10×10^{-3} M; (2), 8×10^{-3} M; (3), 6×10^{-3} M; (4), 4×10^{-3} M; (5), 2×10^{-3} M; (6), 1×10^{-3} M; (7), 1×10^{-4} M.

Table 1 Determination of cyanamide in 1 M NaOH by potentiometric titration using a 0.1 M AgNO₃ solution as the titrant

Concentration of cyanamide ^a	Titrant (AgNO ₃) added/ml		Percent recovery
	Calcd.	Found	
8.0×10 ⁻² M	15.84	15.64	98.7%
6.0×10 ⁻² M	11.88	11.76	99.0%
4.0×10 ⁻² M	7.92	7.84	99.0%
2.0×10 ⁻² M	3.96	3.91	98.8%
			av. 98.9%

a. Sample volume: 10.0 ml.

As stated above, Sato *et al.* used a potentiometric method to determine Cy (especially in LN) with a silver electrode.^{4,5} Under their conditions, however, the existence of excess alkali led to a large positive error, while under our conditions, even in 1 M NaOH, high accuracy and precision were attained.

Detection limit of Cy

When the Cy concentration in a 1 M NaOH solution was decreased from 8.0×10⁻³ to 2.0×10⁻³ M and 10 ml of the Cy solution was titrated with a 10⁻² M AgNO₃ std. solution, the accuracy and precision were approximately the same as those for higher Cy concentrations, though the electrode response was slow. For example, it was 5 to 10 s for titration with a 0.1 M AgNO₃ std. solution, while it was around 1 min with a 10⁻² M AgNO₃ std. solution. By further lowering of the Cy concentration to 8.0×10⁻⁴ to 2.0×10⁻⁴ M, the response time became 3–4 min, and, as expected from the Nernst equation, the extent of the potential jump became small; hence, the end point became somewhat obscure. Thus, the relative positive error at a Cy concentration of 4×10⁻⁴ M amounted to *ca.* 5%. From the results given in Table 2, we conclude that the present potentiometric determination of Cy (in 1 M NaOH) accompanies a detection limit of 6×10⁻⁴ M (relative error=1%; reproducibility (RSD)=0.2%, *n*=4).

The time required for the titration method changes with the Cy concentration. It was around 20 min at Cy concentrations of 2.0×10⁻² to 8.0×10⁻² M, and around 100 min at 6.0×10⁻⁴ M (lower detection limit). From a practical point of view, the Cy concentration of 1×10⁻³ M, requiring *ca.* 30 min, may be a practical detection limit.

Influence of NaOH concentration

According to Eq. (1), the molar amount of the base quantity required to neutralize the acid produced by the Cy-Ag⁺ reaction is at least twice that of Cy. In the present work, the maximum concentration of Cy was 0.08 M, *i.e.*, the concentration of NaOH needed was at least 0.16 M. In view of this, we examined the effects of the NaOH concentration in the range of 0.2 to 2.0 M. The electromotive force (emf) was occasionally unstable at 0.2 M NaOH, but was stable in the 0.5 to 2.0 M range.

Table 2 Determination limit of the present method for cyanamide in 1 M NaOH

Concentration of cyanamide	100×(Δ <i>V</i> ^a /V _{theo})	Standard AgNO ₃ concentration
8.0×10 ⁻³ M	0.0%	10 ⁻² M
2.0×10 ⁻³ M	0.0%	10 ⁻² M
8.0×10 ⁻⁴ M	0.0%	10 ⁻³ M
6.0×10 ⁻⁴ M	0.9%	10 ⁻³ M
4.0×10 ⁻⁴ M	4.8%	10 ⁻³ M
2.0×10 ⁻⁴ M	8.2%	10 ⁻³ M

a. Difference of titrant volume added (V_{av}) at the end point and theoretical volume (V_{theo}) at the equivalent point Δ*V*=V_{av}-V_{theo}.

Finally, we chose 1 M as being the most convenient NaOH concentration. The use of a relatively high concentration of NaOH also serves to adjust the ionic strength and to give a stable emf.

Influence of coexisting substances

The determination of Cy described above was carried out in Cy solutions with no coexisting compounds. In practical analyses, such as, in an analysis of lime nitrogen, we must often determine Cy with several coexisting substances. Although Cy is relatively stable in a weakly acidic solution having a pH of around 5, in a weakly alkaline region (pH 8–10(12)), two Cy molecules dimerize to form CG; in strongly acidic (<pH 2) or strongly alkaline (>pH 12) regions, Cy is hydrolyzed to form urea as follows:¹¹

In addition to these compounds (CG and urea), which may be present in LN, sulfide and chloride, which are usually contained in LN in small amounts, were chosen as the coexisting compounds in the potentiometric determinations of Cy.

Influence of CG

CG is found in LN which has been stored for a long period. In the present measurement, the following CG-to-Cy (CG: Cy) molar ratios were selected: (1) 0.1:1.0, (2) 0.3:1.0 and (3) 0.7:1.0 ([Cy]=0.02 to 0.08 M in 1 M NaOH). For cases (1) and (2), the potentiometric titration curves with potential jumps at the end points were the same as those without CG, while in the case of (3) the potential jump at the end point was less sharp, although the titration value obtained at the end point coincided with the former ones. CG is known to form a white insoluble silver salt when acidified with nitric acid.

In the present measurement in a strongly alkaline solution, however, no silver salt ppt. formed and the Cy determination was not affected by CG.

Influence of urea

The urea-to-Cy (urea: Cy) molar ratios were selected in a range from 3.0:1.0 to 1.0:1.0 under the same titration conditions as those for CG. The results were exactly the same as those obtained without urea in the determination of Cy (RSD=0.12%, $n=4$).

Influence of sulfide

It was shown above that the existence of sulfide strongly affects the potentiometric titration profile. However, since the potential jump due to sulfide is very conspicuous and intense, it is easy to determine Cy by a differential titration method; *i.e.*, the correct quantity of Cy is obtained by measuring the difference between the two jumps due to sulfide and Cy at the respective equivalence points. It was concluded that the coexistence of sulfide does not affect the determination of Cy.

Influence of chloride

LN as a practical sample may contain a small amount of chloride as an impurity, and chloride ions in a Cy solution may react with silver ions to form silver chloride. Thus, chloride was added to the Cy solution and checked for interference with the determination of Cy. The chloride-to-Cy (Cl^- : Cy) molar ratios were chosen from 0.5:1.0 to 3.0:1.0, with the Cy concentration varying over a range of 0.02 to 0.08 M in 1 M NaOH. The results were as follows.

At a chloride concentration within the above-mentioned range, a yellow ppt. of silver cyanamide was always observed during titration with a 0.1 M AgNO_3 std. solution. After complete consumption of Cy, white precipitates were formed. In the potentiometric titration profile, although the potential jump at around the equivalence point of Cy and the subsequent plateau were found as usual, no subsequent potential jump corresponding to the chloride equivalent point was found, even when the titration was continued. The white color of the ppt. (silver chloride), however, changed to dark brown (silver oxide) upon continued titration beyond the equivalent point of chloride. The solubility products of silver sulfide, silver cyanamide, silver chloride and silver hydroxide are as follows: $K_{\text{sp}}(\text{Ag}_2\text{S})=6\times 10^{-50}$, $K_{\text{sp}}(\text{Ag}_2\text{N-CN})=7.2\times 10^{-11}$, $K_{\text{sp}}(\text{AgCl})=(0.8-2.0)\times 10^{-10}$, $K_{\text{sp}}(\text{AgOH})=2.6\times 10^{-8}-4\times 10^{-5}$. We cannot directly compare the solubilities of these salts in an alkaline solution using these data, because the latter were obtained in pure water. However, it is clear that silver cyanamide becomes more insoluble in an alkaline solution. On the other hand, silver chloride becomes more soluble, that is, $K_{\text{sp}}(\text{Ag}_2\text{N-CN})$ is far smaller than $K_{\text{sp}}(\text{AgCl})$ in an alkaline solution. It is concluded that the coexistence of chloride in the molar ratio range stated above has no effect on the determination of Cy.

Table 3 Effect of coexisting CG, urea, sulfide and chloride on the determination of cyanamide in 1 M NaOH

Coexisting compound	Molar ratio to cyanamide	Percent recovery of cyanamide	
		Singly added ^a	All coexisting
CG	0.3	98.9%	
Urea	1.5	98.8%	(98.8%)
Sulfide	0.3	98.9%	
Chloride	1.0	98.7%	

a. Average of four determinations for 0.02–0.08 M Cy in 1 M NaOH.

Table 4 Results of a lime nitrogen analysis

Component	Manufacturer names abbreviated		
	N	D	S
CaCN_2 (%)	57.20	58.61	58.54
CaS (%)	0.34	0.36	0.68

Influence of the mixture of CG, urea, sulfide and chloride

The possibility of some negative effect by a mutual interaction of these four compounds was investigated by selecting the molar ratio CG:urea:sulfide:chloride:(Cy) as 0.3:1.5:0.3:1.3:(1:0). The titration conditions were the same as those used for the coexistence of a single compound. As a result, the potentiometric titration curves for these solutions were just the same as those for a Cy solution with no coexisting compounds, as summarized in Table 3.

Influence of temperature

The temperature effect on the determination of Cy was studied in a range from 10 to 30°C; no effect was found on the determination of Cy.

Influence of light

During the titration, because silver ions are the titrants and the ISE is made of silver sulfide, the effect of light on the determination of Cy was examined. It was found that although weak light did not affect the results, strong light (*e.g.*, 10^4 lux) affected the electrode potential, and the potential was somewhat unstable (drifted). It is hence recommended to measure the potential under shaded conditions, though no influence is exerted by normal laboratory lighting.

Analysis of lime nitrogen

To assess the applicability of the present method, several commercial lime nitrogen (LN) products were analyzed; the results are given in Table 4. In this experiment, several portions of LN sampled out from a lot were mixed and ground to a particle size of less than *ca.* 37 μm (400 or higher mesh sieve). As can be seen in Table 4, the present method yielded satisfactory analytical values. The products of three manufactures gave

nearly the same contents for calcium cyanamide, and for calcium sulfide, except for that of one company. It was concluded from the results that the sulfide-to-cyanamide molar ratio in a product (ca. 7/1000 from N Co., Ltd.) was reduced to roughly one-seventh when it was purified (ca. 1/1000) (*c.f.* experimental section).

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