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DETERMINATION OF CALCIUM CYANAMIDE IN CRUDE CALCIUM CYANAMIDE

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**US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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DOVER, NEW JERSEY**

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A rapid method of analysis for the assay of crude calcium cyanamide is proposed for the monitoring of calcium cyanamide in the nitroguanidine continuous process line. The proposed method consists of (1) micromilling the crude material, (2) extracting the milled material with a sodium acetate/acetic acid buffer, and (3) determining the cyanamide by the Pinck precipitation/titration procedure.		

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INTRODUCTION

The U.S. Army recently completed construction of a plant at the Sunflower Army Ammunition Plant (SFAAP) site, in Kansas, for the manufacture of nitroguanidine by a continuous process based on the British aqueous fusion batch process. The plant, operated by Hercules Inc., is entering its "prove out" phase to determine operational parameters critical to the continuous process. To implement this phase, methods of analysis are required for monitoring several points along the continuous process line. One of these methods is required for the assay of crude calcium cyanamide prior to its being fed to the guanidine nitrate reactor. Under a Manufacturing Methods and Technology (MM&T) program this method has been developed and is described herein. The remaining methods will be described in another report.

Crude calcium cyanamide is used in agriculture as a source of fixed nitrogen and by the cyanamide industry as a chemical raw material. Because of this, many methods of analysis for the assay of the crude material have been reported over the years. These methods can be grouped into those capable of determining total nitrogen and those for determining the cyanamide nitrogen. Since the material balance for the nitroguanidine continuous process requires the exact amount of cyanamide in the crude material, interest was, therefore, centered on the latter group.

One of the earliest methods, proposed by Pinck (ref 1), calls for a water extraction of crude calcium cyanamide, precipitation of the extracted cyanamide as silver cyanamide, and volumetric determination of silver as a measure of cyanamide. Nearly all of the later methods are based on the Pinck method, but differences are found in the extraction of calcium cyanamide from the crude material. The American Cyanamide Corp. (ref 2) method prescribes the use of a sodium acetate/acetic acid buffer solution as the extractant. Takei and Kato (ref 3) recommend dilute acetic acid for the extraction of calcium cyanamide. Except for Takei and Kato, who reported extraction data for dilute acetic acid, these published methods do not give enough data with respect to the accuracy, elapsed time for one determination, and completeness of extraction. As a consequence, an evaluation of the methods was made and a reliable and rapid assay method was developed. This report describes the results of this evaluation.

EXPERIMENTAL

Crude calcium cyanamide, from the Suddestche Kalk Stickstoff Werke (SKW), Trosberg, Germany, was used for the evaluation and

experimental work. The SKW material is typical of the crude calcium cyanamide to be manufactured at the SFAAP nitroguanidine plant.

Preparation and Purity Determination of Silver Cyanamide

The purity of silver cyanamide prepared from a sodium acetate/acetic acid buffer solution extract of the SKW material, and from an aqueous solution of sublimed cyanamide was obtained by the following procedures:

Procedure A

Six 2 g portions of SKW material were extracted by the procedure described in the "Proposed Method" section and carried through the precipitation of the silver salt. Three of the precipitates were filtered through tared crucibles, washed, dried in an oven at 110°C and weighed. The weighed precipitates were then dissolved in 1N nitric acid and the crucible washed with water, dried at 110°C and weighed. The loss in weight of the crucible was taken as the weight of silver cyanamide. The percent silver cyanamide of each precipitate was calculated from the determination of silver in the 1N nitric acid solution. The remaining three precipitates were filtered, washed, and dried at 100°C. The total nitrogen content of each precipitate was then determined by the Kjeldahl method. The percent purity based on the total nitrogen was calculated for each precipitate.

Procedure B

Five grams of micromilled SKW material was slowly introduced into a stirred 300 mL volume of water, the pH of which had previously been adjusted to 7 with carbon dioxide. The slurry was stirred for 30 minutes, with carbon dioxide being bubbled through the mixture to maintain the pH at 7. The mixture was filtered and the filtrate rotary evaporated to a solid residue. The solid was dissolved in ethyl ether and transferred to a sublimater cup. Under a stream of dry air the ether solution was evaporated to a small volume. The cup was attached to a sublimater cold finger and the assembly slowly and carefully evacuated to remove the remaining ether. The sublimater was lowered into a water bath maintained at 55°C, making sure the solid was below the water level. The assembly was evacuated to 1 mm pressure, at which pressure the cyanamide easily sublimed and condensed on the cold finger surface. After sublimation, the pure cyanamide was quickly dissolved in 100 mL of water. Ten percent ammoniacal silver nitrate was immediately added dropwise to the aqueous cyanamide solution until the cyanamide had completely precipitated as the silver salt. Completeness of precipitation was

determined by allowing the precipitate to settle and then adding a drop of silver nitrate solution to the clear solution above the precipitate. Absence of a precipitate in the supernatant liquid indicated the complete precipitation of cyanamide as silver cyanamide. The silver cyanamide was filtered, washed with water, and dried at 100°C. Portions of the dried silver cyanamide were used in the determination of silver by the volumetric procedure and total nitrogen by the Kjeldahl method. The percentage purity of the silver cyanamide was calculated from the silver and nitrogen values.

Determination of Stability of Cyanamide

Two gram portions of SKW material were extracted with sodium acetate/acetic acid buffer solution. The extracts were filtered and filtrates made up to 500 mL volume with distilled water. Aliquots were taken from each extract solution at various time intervals and the calcium cyanamide determined by the precipitation/volumetric procedure.

Completeness of Extraction

Two gram portions of sample, one "as received" and the other milled, were extracted for varying lengths of time. The percent calcium cyanamide in each extract was determined by the precipitation/volumetric procedure. Extraction of calcium cyanamide was considered complete when the calcium cyanamide extracted became constant for a set of extraction times.

Proposed Method

Apparatus

Micromill, Chemical Rubber Co. (Stock No. 547011) or equivalent, for pulverization of crude calcium cyanamide.

Reagents

Buffer solution - Dissolve 20 g sodium acetate trihydrate, reagent grade, in 20 mL water. Add 20 mL of glacial acetic acid to the acetate solution and dilute to 1 L with distilled water.

Silver nitrate solution - Add sufficient concentrated ammonium hydroxide to 100 g silver nitrate, reagent grade, previously dissolved in 500 mL of distilled water, to just dissolve the brown precipitate formed on addition of ammonium hydroxide. Dilute the solution to 1 L with water.

Ferric alum indicator - Dissolve 140 g of ferric ammonium sulfate, reagent grade, in 400 mL of hot, distilled water. Cool, filter, and dilute the filtrate to 500 mL with 6N nitric acid.

Potassium thiocyanate, 0.1N - Dissolve about 10 g of reagent grade potassium thiocyanate in 1 L of distilled water and standardize with reagent grade silver nitrate.

Procedure

Preparation of sample: Place 25 g of crude calcium cyanamide in the micro-mill and grind the sample for 4.5 minutes. If the mill becomes extremely hot during the milling operation, cool the mill in accordance with the manufacturer's instructions.

Extraction of the ground sample: Place 2 g of the milled sample, accurately weighed, in a 600 mL beaker containing a 3 in. stirring bar. Add 300 mL of buffer solution to the sample and, using the magnetic stirrer, vigorously stir the mixture for 15 minutes. Transfer the mixture quantitatively to a 500 mL volumetric flask and dilute to volume with water. Filter about 70 mL of the extract through a No. 41 Whatman filter paper and pipet 50.0 mL of the filtrate into a 250 mL beaker containing a 1 in. stirring bar.

Analysis of the extract: To the 50 mL extract, contained in the 250 mL beaker, add 50 mL of water. Neutralize the diluted extract with 6N ammonium hydroxide. Place the beaker, containing the neutralized extract, on a magnetic stirrer and, with vigorous stirring, add 15 mL of silver nitrate solution dropwise. After the addition of silver nitrate, stir the mixture for 7 minutes to coagulate any colloidal silver cyanamide. Assemble the suction flask assembly with a 30 mL filtering crucible. Decant a portion of the mixture into the 30 mL crucible and aspirate. Continue decanting, allowing the bulk of the precipitate to remain in the beaker. Wash the precipitate with about 10 mL of water, decant, and aspirate. Repeat 2 or 3 times and quantitatively transfer the remaining precipitate to the crucible with a minimum amount of water. Washing is complete when addition of a few drops of 10% sodium chloride solution to 1 to 2 mL of the filtrate shows no precipitate of silver chloride. Discard the filtrate and washings.

Dissolve the silver cyanamide in the crucible with 10 mL of 1N nitric acid using a glass rod to mix and break any lumps. Aspirate and repeat dissolution of any remaining silver cyanamide with 10 mL increments, until a total of 50 mL of 1N nitric acid is used. The absence of any yellow precipitate indicates complete dissolution of silver cyanamide. Disregard the small quantity of brownish solid

remaining in the crucible, which may be dissolved later with concentrated nitric acid to clean the crucible.

Add 1 mL of concentrated nitric acid and 1 mL of ferric alum indicator solution to the combined silver cyanamide solution and washings in the suction flask. Transfer to a 250 mL beaker using a minimum amount of water from the wash bottle to complete the transfer. Add 50 mL of the water and titrate, with vigorous stirring, with 0.1N potassium thiocyanate to a pink color end point which remains permanent for at least 10 seconds after washing down the sides of the beaker.

Calculation: Calculate the percent calcium cyanamide in the crude calcium cyanamide as follows:

$$\% \text{ Calcium cyanamide} = \frac{4.005 \times N \times A}{W}$$

N = normality of standard potassium thiocyanate.

A = mL of standard potassium thiocyanate.

W = weight of sample in aliquot.

RESULTS AND DISCUSSION

Data showing the precision and elapsed time per determination by the Pinck, American Cyanamide, and Takei and Kato methods are presented in table 1. The latter two methods have acceptable precision but have long run times for one determination. Poor agreement was found among the methods with respect to percent calcium cyanamide determined for the SKW crude material. This indicated that either (1) the extraction solvents did not completely extract calcium cyanamide; (2) the precipitation/titration procedure (common to all methods) did not quantitatively precipitate the cyanamide, or (3) the cyanamide underwent chemical changes.

The complete precipitation of cyanamide as silver cyanamide is an accepted fact as indicated by the numerous publications on the quantitative determination of cyanamide in solution. For this reason there was no need to study the parameters affecting the precipitation of silver cyanamide except for the effect of impurities present in the SKW type calcium cyanamide (table 2). To determine this effect, if any, purity determinations were made on silver cyanamide precipitated from a sodium acetate/acetic acid buffer solution extract and from an aqueous solution of sublimed cyanamide. The latter was carried out as a comparison "standard," since it was free

of SKW material impurities. The purity data are shown in table 3. It appears that the impurities in the SKW crude calcium cyanamide do have a very slight effect, as indicated by the relative error of 0.7% for the SKW material as compared to the 0.4% for the sublimed cyanamide.

The chemical instability of cyanamide is well known (ref 2). Between pH 8 and 12 cyanamide dimerizes to dicyandiamide, and at or below pH 2, and above pH 12, cyanamide hydrolyzes to urea. The rate of formation of each compound is shown by figure 1.

Water extraction of the crude SKW material produced extracts having a pH of approximately 10; the high pH was due to the formation of calcium hydroxide from the hydrolysis of calcium cyanamide. At this high pH the dimerization of cyanamide is favored, making water a poor extractant. The stability of cyanamide in 1N nitric acid and sodium acetate/acetic acid buffer extracts are shown in table 4. The data shows cyanamide in the buffer extract to be very stable over a 19 hour period. In comparison, cyanamide in 1N nitric acid started to decompose after 20 minutes of storage at room temperature.

The buffer solution used for the extraction of the "as received" SKW material required 45 or more minutes for the complete extraction of calcium cyanamide, a time-consuming step. Table 5 shows a typical particle size distribution of the SKW crude material. Over 25 % of the particles are $\geq$ 250 micron in size, indicating the probable cause for the long extraction time. By pulverizing the SKW material prior to extraction by a 4.5 minute micromilling, the extraction time was reduced by 25 minutes as shown by the data in table 6.

The proposed method for the assay of crude SKW calcium cyanamide is based on the results of the evaluation of the three methods, and on the experimental work described herein. The percent calcium cyanamide in the crude SKW material, as determined by the proposed method, is given in table 7. The elapsed time for one determination, in comparison to the three older methods, was reduced by at least 30 minutes. The precision compared favorably with that of the American Cyanamide and Takei and Kato methods.

A comparison of a 65.7 % calcium cyanamide content of the SKW material, as determined by the proposed method, to a 67.8 % content, as determined by the Kjeldahl (total nitrogen) method indicated that the SKW sample contained nitrogen compounds other than calcium cyanamide. The data, therefore, clearly shows the capability of the proposed method to determine the true calcium cyanamide content of the crude material.

CONCLUSIONS

The proposed method has been found to be reliable for the determination of calcium cyanamide in crude SKW material. The elapsed time for one determination is 1 hour and is the most rapid of the methods available. Total nitrogen values for SKW type material do not indicate the true cyanamide content of the material.

RECOMMENDATIONS

The proposed method is recommended for the assay of crude calcium cyanamide manufactured at the Sunflower nitroguanidine plant.

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4. "Facility Project Status Report - Part III, Commentary," Sunflower Army Ammunition Plant, Hercules Inc., Monthly Report, DeSoto, KS, June 30, 1977.

Table 1. Calcium cyanamide in crude SKW material

<u>Method</u>	<u>No. of det'ns</u>	<u>CaCN₂ (%)</u>	<u>Std dev</u>	<u>Elapsed time per determination</u>
Pinck (water)	3	61.24	0.34	4 hours
American Cyanamide (buffer soln.*)	8	62.90	0.25	1 hour 50 min
Takei & Kato (0.5N acetic acid)	3	63.36	0.19	1 hour 30 min

*Buffer solution - mixture of sodium acetate and acetic acid.

Table 2. Typical impurities in crude SKW calcium cyanamide*

	<u>%</u>
hydrochloric acid insolubles	0.11
silicon dioxide	1.20
calcium fluoride	1.15
ferric oxide and aluminum oxide	1.30
carbon (free)	12.99
calcium oxide	11.80
calcium carbonate	0.70
calcium sulfide	0.90
calcium sulfate	0.09
calcium carbide	0.04
calcium phosphate	0.03
magnesium oxide	0.15
water	1.85

*From ref 4.

Table 3. Purity of silver cyanamide

	Purity, %		Relative error*
	<u>Based on Ag content</u>	<u>Based on total nitrogen content</u>	
silver cyanamide prepared from sublimed cyanamide	99.60	100.40	+0.4%
silver cyanamide obtained from extract of SKW crude calcium cyanamide	99.34	99.30	-0.7%

*Based on the silver determination and 100.0% recovery value.

Table 4. Completeness of extraction of crude SKW calcium cyanamide

<u>Time after extraction</u>	<u>1N nitric acid (% CaCN₂)</u>	<u>Sodium acetate/acetic acid (% CaCN₂)</u>
20 min	63.71	63.64
50 min	63.42	63.64
1 hr 20 min	62.95	-
1 hr 50 min	62.84	-
3 hours	62.09	-
19 hours	-	63.53
24 hours	56.24	-

Table 5. Particle size distribution for the SKW crude calcium cyanamide

<u>Particle size, μm</u>	<u>%</u>
greater than 841	7.8
250 - 840	17.3
125 - 250	7.3
94 - 125	27.2
44 - 94	37.0
less than 44	3.05

Table 6. The effect of micromilling of crude SKW calcium cyanamide on extraction time

<u>Extraction time (buffer solution used) (min)</u>	<u>% Calcium cyanamide</u>	
	<u>as received</u>	<u>micromilled</u>
15	63.64	65.53
45	65.32	65.45
60	65.33	65.35

Table 7. Assay of SKW crude calcium cyanamide using the modified method

<u>Determination no.</u>	<u>% CaCN₂</u>
1	65.70
2	65.41
3	65.50
4	65.94
5	65.77
6	65.49
7	65.48
8	<u>66.07</u>
Average	65.67
Standard deviation, s	0.27
Elapsed time for one determination: 1 hour.	

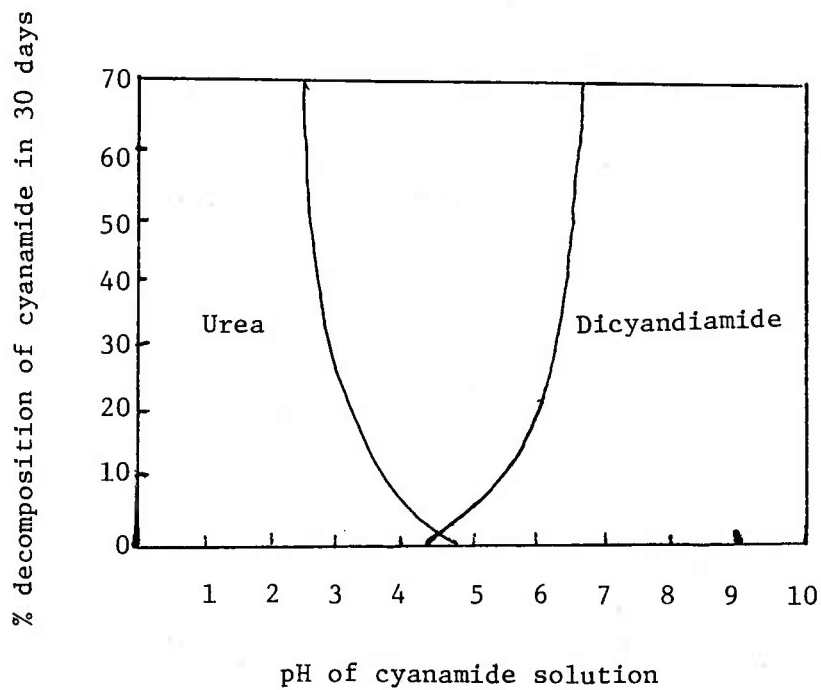


Figure 1. Formation of dicyandiamide and urea from 25% aqueous cyanamide solution at 40°C*

*From reference 2.

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