

arsenate is about 450° C. The fact that these two oxidations take place best at the same temperature lead one to think that possibly the lead oxide has played the role of a catalyst in this formation of lead arsenate; that is, that the litharge is first oxidized to red lead, which in turn oxidizes the arsenious oxide to the pentoxide, or the lead arsenite to lead arsenate. From this it would follow that the temperature at which a catalyst for oxidation would work best would be that temperature at which it is most easily oxidized to the higher oxide. Then in selecting a catalyst for any particular

oxidation, that catalyst should work best which is oxidized most easily at that temperature at which the desired oxidation is most easily effected.

SUMMARY

- 1—Lead arsenate is produced by roasting a mixture of litharge and white arsenic at the proper temperature.
- 2—The best temperature for roasting is about 450° C.
- 3—The first part of the oxidation is very rapid, while later it becomes very slow.
- 4—The possibility of catalytic action has been pointed out.

The Determination of Dicyanodiamide and of Urea in Fertilizers¹

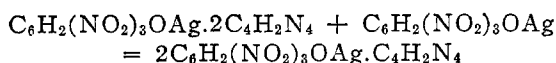
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DICYANODIAMIDE

In the course of work upon cyanamide about four and a half years ago, it became necessary to find a more rapid method for the determination of dicyanodiamide in cyanamide and mixed fertilizers. At that time the author and Mr. Berbm obtained the same dicyanodiamide-silver picrate complexes as have recently been described by Harger.² The results of this work are published at this time as confirmatory and supplementary to those of Harger.

For the purpose of rapidity, a volumetric determination is desirable. Such a determination of dicyanodiamide in the mono-compound is practically impossible on account of the large excess of silver salt necessary in its preparation. Attention was therefore directed to the double complex, silver picrate dicyanoguanidine, $C_6H_2(NO_2)_3OAg \cdot 2C_4H_2N_4$. Under certain conditions the di-compound is so insoluble, and its conversion into the mono-compound according to the reaction



is so slow that the amount of standard silver solution used can be made the basis of a volumetric method. The conditions necessary involve dilute solutions, low temperature, and a large excess of picric acid.

DESCRIPTION OF METHOD

REAGENTS. *Silver Nitrate*—Stock solution (0.223 N), containing 18.96 g. $AgNO_3$ in 500 cc. From this the standard solution is made by diluting 100 cc. to 500 cc. (0.0446 N).

Sodium Picrate—Solution made by neutralizing 7.5 g. picric acid with sodium carbonate and making up to 100 cc. This solution must be used at about 40° C., because the salt crystallizes out at lower temperatures.

Ammonium Thiocyanate—About 0.00446 N, standardized against the standard silver nitrate solution.

Ferric Sulfate—Five per cent solution acidified with nitric acid.

Glacial Acetic Acid.

Nitric Acid—Twenty per cent.

PROCEDURE—For material containing from 5 to 15 per cent of dicyanodiamide nitrogen, a 5-g. sample is

necessary. With a lower content a correspondingly larger sample must be taken.

The weighed sample is placed in a 500-cc. bottle, which is then filled with 450 cc. of water at 10° to 25° C. If the material is nitrolime or other lime-containing substance, there is next added approximately enough glacial acetic acid to dissolve the lime. (For 5 g. of ordinary nitrolime 5 cc. of the acid are sufficient.) By this treatment the nitrolime is hydrolyzed, and the nitrogen compounds are dissolved more completely and rapidly than if no acid is used. A slight excess of acetic acid does no harm, whereas the stronger mineral acids cause a change in the nitrogen compounds. Furthermore, the acetic acid solution can be used for a Kjeldahl determination of total water-soluble nitrogen. This is not the case if nitric acid is used, as has been suggested, to shorten the shaking time.

The bottle is now shaken on a machine for 3 hrs., then filled to the 500-cc. mark, and the contents filtered. To a 100-cc. sample of the filtrate in a 200-cc. graduated bottle are added 5 cc. of 20 per cent nitric acid and 20 cc. of sodium picrate solution. (These amounts are sufficient so that there is present a slight excess of nitric acid, while sufficient free picric acid is formed to saturate the solution when made up to the mark.)

The mixture is now cooled to about 5° C. by standing in ice water, and the standard silver nitrate solution is added drop by drop from a buret, with constant shaking, until a slight excess (about 2 cc.) over what is required for the dicyanodiamide assumed to be present has been added.

It may be added that the reaction of dicyanodiamide with greater excesses of silver nitrate and picric acid offers a means of demonstrating the course of a time reaction. The thick gel of the di-compound changes over, more or less rapidly, depending upon the excess of silver and the concentration, into the small characteristic crystals of the mono-derivative.

The double compound comes down as a gel, more or less thick, depending upon the amount of dicyanodiamide present. After shaking vigorously, the mixture is left at 5° C. for 15 min., shaken two or three times to make the precipitation of the dicyanodiamide as complete as possible, made up to the mark with cold water, and filtered.

To 100 cc. of the filtrate are added 5 cc. of nitric

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acid and 2 cc. ferric sulfate solution, and the excess silver is titrated with the thiocyanate solution.

CALCULATION OF RESULTS—For a 5-g. sample the silver solution is of such strength that 1 cc. = 1 per cent of nitrogen as dicyanodiamide. This is indicated by the following calculation:

5 g. sample.
AgNO₃ solution = x cc.
For formula C₂H₂(NO₂)₂OAg.2C₂H₅N₄, 8 N require 1 Ag, or 22,400 cc. of solution.

$$N = \frac{112 \times 100 x}{22,400 \times 0.5} = x \%$$

For satisfactory results certain corrections are necessary. These every analyst should work out for himself, since the personal factor plays an important part. In the hands of a competent analyst, however, the method gives a rapid method of determining the approximate amount of dicyanodiamide.

The following data show the corrections found necessary at 7° C. and applied by the author.

EXCESS OF SILVER NITRATE—Inasmuch as the di-compound goes over into the mono-compound with excess of silver, the excess of silver nitrate solution used may be expected to affect the results. That this is so is indicated by the data of Table I and Fig. 1. In this case pure dicyanodiamide is used, with 1 cc. 20 per cent nitric acid added.

DICYANODIAMIDE NITROGEN PRESENT	G.	Per cent	DICYANODIAMIDE NITROGEN FOUND			
			2 Cc. Excess AgNO ₃	4 Cc. Excess AgNO ₃	6 Cc. Excess AgNO ₃	Percentage of N
0.05	5	4.90	98	5.15	103	108
0.10	10	9.95	99.5	10.00	100	101.5
0.15	15	14.50	97	14.65	97.5	101.5

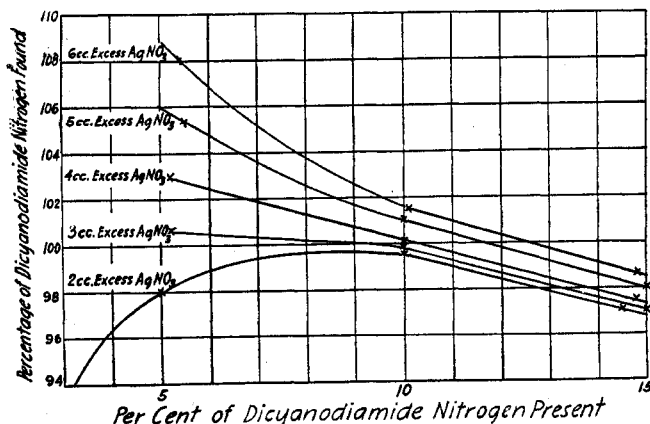


FIG. 1—INFLUENCE OF EXCESS SILVER SOLUTION ON TITRATION OF DICYANODIAMIDE

NITRIC ACID—Table II and Fig. 2 show the influence of increasing additions of nitric acid.

TABLE II—NITRIC ACID					
DICYANODIAMIDE NITROGEN PRESENT		DICYANODIAMIDE 1 cc. HNO ₃ Percentage of N Present		NITROGEN FOUND— 10 cc. HNO ₃ Percentage of N Present	
Gram	Per cent	Per cent	of N Present	Per cent	of N Present
0.05	5	4.90	98	4.5	90
0.10	10	9.95	99.5	9.5	95
0.15	15	14.50	97	14.3	95.5

NITRIC ACID AND ACETIC ACID—Table III and Fig. 3 show the effect of varying amounts of nitric acid and of calcium acetate, which will be present when acetic acid has been used in the preparation of the sample. The curves and the effect of the varying amounts upon the precipitation of the dicyanodiamide offer many points for discussion which must be omitted at present.

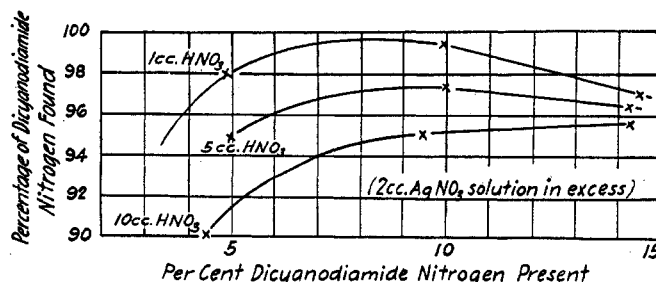


FIG. 2—INFLUENCE OF VARYING AMOUNTS OF NITRIC ACID

TABLE III—NITRIC ACID AND CALCIUM ACETATE											
DICYANO- DIAMIDE NITROGEN PRESENT		DICYANODIAMIDE NITROGEN FOUND									
		1 Cc. HNO ₃		1 Cc. HNO ₃ + 1G. CaAc		1 Cc. HNO ₃ + 5G. CaAc		5 Cc. HNO ₃ + 1G. CaAc		5 Cc. HNO ₃ + 5G. CaAc	
G.	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
0.05	5	4.90	98	4.5	90	4.0	80	5.10	102	4.20	84
0.10	10	9.95	99.5	9.8	98	8.9	99	9.98	99.8	9.50	95
0.15	15	14.50	97	14.8	98.7	14.20	94.7	14.65	97.5	14.40	96

TEMPERATURE—Table IV and Fig. 4 show the influence of the temperature.

TABLE IV—TEMPERATURE									
DICYANO- DIAMIDE NITROGEN PRESENT	DICYANODIAMIDE NITROGEN FOUND								
	5° C.		10° C.		20° C.		25° C.		
	Per- centage of N	Gram	Per- centage of N	Gram	Per- centage of N	Gram	Per- centage of N	Gram	
Gram	Per cent	Present	Present	Present	Present	Present	Present	Present	Present
0.10	10	0.0996	99.6	0.098	98	0.0964	96.4	0.0850	85.0

It is obvious from the above results that good approximate results, without corrections, are obtained with nitrolime when 5 cc. of 20 per cent nitric acid per 1 g. calcium acetate and about 2 cc. excess silver nitrate are employed.

The new method has been tested in the presence of urea and of dicyanodiamidine, neither of which affects the results. When chlorides or soluble sulfides are present, a blank test must be run by titrating the silver solution without the addition of picric acid.

The analyses in Table V show the reliability of the new dicyanodiamide method as applied to samples of cyanamide.

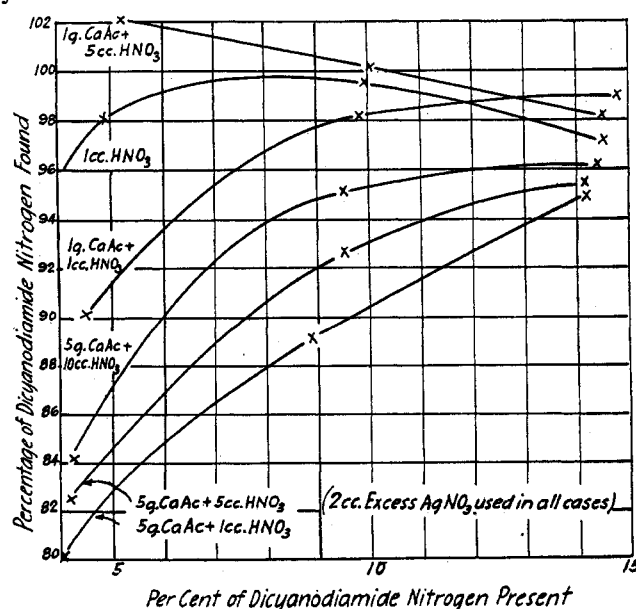


FIG. 3—INFLUENCE OF ADDITION OF DIFFERENT AMOUNTS OF NITRIC ACID AND CALCIUM ACETATE

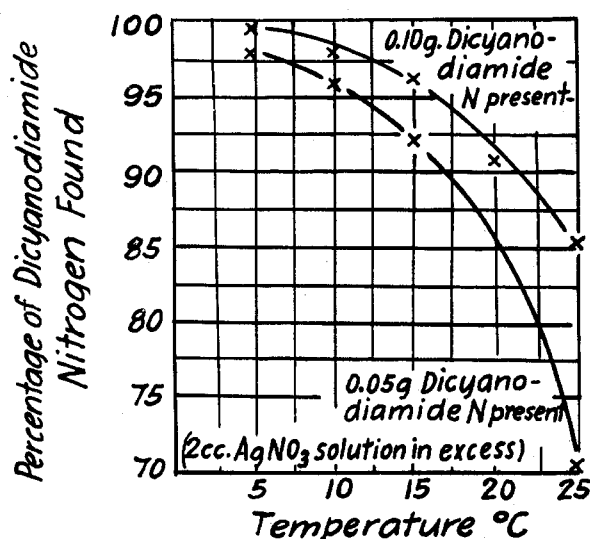


FIG. 4—EFFECT OF TEMPERATURE

TABLE V

SAMPLE	ANALYST	DICYANODIAMIDE NITROGEN PER CENT
1a	E. J.	2.86
1b	D.	2.74
2a	E. J.	2.99
2b	D.	2.82
3a	E. J.	2.70
3b	M. D.	2.50

Some samples of old cyanamide gave the analytical results recorded in Table VI.

TABLE VI—COMPARISON OF OLD AND NEW METHOD

Sam- ple	NEW METHOD				OLD METHOD				TOTAL
	Cyana- mide Ni- trogen	Di- cyanodi- amide Ni- trogen	Urea Ni- trogen	Water-sol- uble Ni- trogen	Cyana- mide Ni- trogen	Di- cyanodi- amide Ni- trogen	Urea Ni- trogen		
I....	1.11	10.67	1.14	12.92	1.11	10.62	1.21		12.94
II....	0.86	10.16	1.96	12.98	0.86	9.94	1.89		12.69
III....	0.86	10.31	1.27	12.44	0.86	10.22	1.29		12.37
IV....	0.77	10.49	1.59	12.85	0.77	10.51	1.62		12.90
V....	1.12	10.44	0.96	12.52	1.12	10.46	1.00		12.58
VI....	13.25	1.76	0.45	15.46	13.25	1.8	0.4		15.45
Av.	2.995	8.97	1.23	13.20	2.995	8.93	1.24		13.16

¹ A modified Caro method.

² Sum of cyanamide, dicyanodiamide, and urea nitrogen.

OTHER DICYANODIAMIDE-SILVER COMPLEXES

Further research showed at once that the formation of these complexes is not limited to picric acid. The reaction is typical for all aromatic water-soluble nitrophenol compounds. Further investigation will show whether other groups than the nitro will give the hydroxyl groups of phenol and naphthol the property of reacting with silver salts and dicyanodiamide. It is to be expected that all benzene and naphthalene derivatives containing phenolic hydroxyl groups, which give definite silver salts, will give mono- and di-compounds with dicyanodiamide. Compounds such as trinitrobenzoic acid do not give the reaction. Nitrohydroxybenzoic acids, however, should give it.

The following new compounds have been prepared:

Silver dinitrophenol monocyanoguanidine
 Silver dinitrophenol dicyanoguanidine
 Silver trinitrodiphenol monocyanoguanidine
 Silver trinitrodiphenol dicyanoguanidine
 Silver trinitroresol monocyanoguanidine
 Silver trinitroresol dicyanoguanidine

Of these, the trinitroresorcinol (styphnic acid) seems to give a more quantitative precipitation and better results than picric acid.

DETERMINATION OF UREA IN FERTILIZERS

A new standard method for the determination of urea in fertilizers and fertilizer mixtures depends on

the well-known fact that urea gives a characteristic, difficultly soluble salt with oxalic acid. By selecting the right conditions the solubility can be made so slight that a quantitative determination can be made.

METHOD—From 2 to 5 g. of the urea-containing sample are dried and shaken out with 100 cc. of amyl alcohol. From 25 to 50 cc. of the filtrate are mixed with the same volume of ether, and the urea is precipitated as oxalate with 25 cc. of a 10 per cent solution of anhydrous oxalic acid in amyl alcohol. After completing the precipitation by stirring and standing in cold water for half an hour, the mixture is filtered through a Gooch crucible, and washed by filling one time totally and one time half with mixture of half amyl alcohol and half ether, then in the same way with ether alone. The precipitate is dried in a vacuum desiccator and weighed. According to the formula $(\text{COOH})_2 \cdot 2\text{CO}(\text{NH}_2)_2$, it contains 26.67 per cent nitrogen and 57.01 per cent urea.

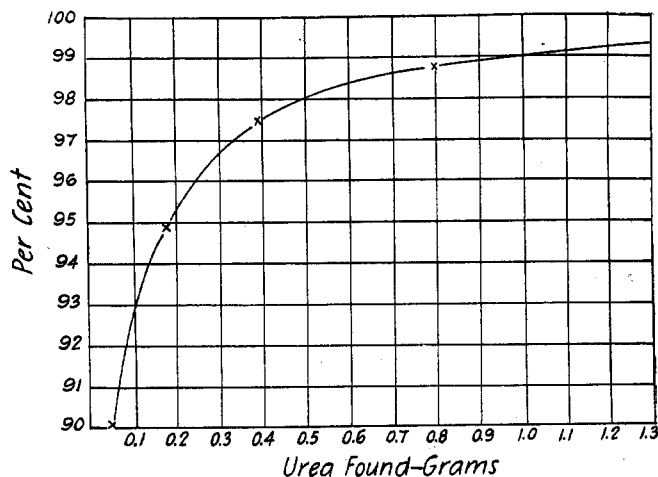


FIG. 5—CORRECTION CURVE FOR DETERMINATION OF UREA AS OXALATE

Fig. 5 shows the necessary corrections with regard to solubility.

In some cases when urea is present as a salt or in complexes such as $\text{Ca}(\text{NO}_3)_4 \cdot \text{CO}(\text{NH}_2)_2$, the urea does not go into solution without calcium with amyl alcohol, but must first be set free. It is of importance that sample and reagents be as nearly anhydrous as possible.

The National Fertilizer Association

The Twenty-eighth Annual Convention of the National Fertilizer Association, which will be held at White Sulphur Springs, W. Va., the week beginning June 20, 1921, will have a program of reconstruction and coöperation.

The program will include addresses and discussions on subjects of vital interest to the fertilizer manufacturer, in view of present business conditions. These subjects will include costs and cost accounting systems, chemical and manufacturing problems, sales methods, labor and transportation problems, etc.

During the same week the Southern Fertilizer Association will hold its summer meeting; the Soil Improvement Committee of the National Fertilizer Association will hold a subscribers' and committee meeting; and the Soil Improvement Committee of the Southern Fertilizer Association will hold a committee meeting.