

Summary

1. A curve showing the variation of density with concentration of uranyl nitrate has been constructed for 24°.
2. Uranyl nitrate icositetrahydrate has been shown to be capable of existing below -20°, forming spontaneously at about -35°.
3. Uranyl nitrate icositetrahydrate has been shown to exist by methods of thermal analysis; in one case by a cooling curve which might be compared to a method of synthesis, and in the other case by a heating curve, which might be regarded as a method of analysis.
4. The existence of the 5 distinct fluorescence spectra due to a single compound as published by Howes has been disproved and an explanation of the cause offered.
5. A new hydrate has been added to the uranyl nitrate series which will make possible an extension of the work on the effect of water of crystallization on the fluorescence and absorption spectra of these substances.

The experimental work was performed in the laboratories of the Department of Physics of Cornell University while the writer was a Carnegie Research Associate.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE KELLY-SPRINGFIELD TIRE COMPANY]

SYMMETRICAL DIPHENYL-GUANIDINE AS A STANDARD IN ACIDIMETRY AND ALKALIMETRY

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Various substances have been proposed as standards for use in preparing solutions of acids and alkalies of known concentration for use in volumetric analysis. The accuracy attainable with the various methods and substances now in use depends upon the manipulative skill of the operator and upon the time at his disposal; but taking into account economy of time and ease of operation for the routine chemist these methods leave much to be desired.

All methods of standardization can be divided into two classes, direct and indirect. The direct method involves the use of standard pure substance which can be accurately weighed and directly titrated. This is the ideal method, as to both time necessary and accuracy of results, provided a thoroughly suitable standard substance is at hand.

Dodge,¹ in an article on the Standardization of Alkalimetric Solutions, gives the following requirements for an ideal standard substance: (1) the standard should be easily obtained in a state of sufficient purity; (2)

¹ Dodge, *J. Ind. Eng. Chem.*, 7, 29 (1915).

it should be unalterable in the air, at ordinary or moderately high temperatures, *i. e.*, neither hygroscopic nor efflorescent; hence, hydrated compounds are, in general, undesirable; (3) it should be readily soluble in water or alcohol, thus allowing immediate titration in the cold; (4) it should have a high molecular or equivalent weight, thus lessening the effect of small errors in weighing; (5) on titration no interfering product, such as carbonic anhydride, should be present; (6) the standard should be free from color, before and after titration, to avoid interference with indicators.

Potassium hydrogen phthalate, first suggested by Dodge,¹ and later subjected to a rigid investigation by Hendrixson,² meets all the above requirements for a standard in preparing alkali solutions, but as far as the writer has been able to ascertain no standard substances so far suggested for use in the direct standardization of acid solutions answers these requirements perfectly.

Pure sodium carbonate, dried by fusion in an atmosphere of carbon dioxide,³ is the most accurate and available alkaline standard so far proposed but has the disadvantages of a low equivalent weight and of liberating carbonic anhydride on titration which must be removed by long boiling. Guanidine carbonate, proposed by Dodd,⁴ offers no advantages and is less readily obtained. Calcium carbonate, even Iceland spar, is very difficult to obtain pure and is insoluble in water.

Having had occasion to analyze samples of crude diphenyl-guanidine, the writer developed the method of dissolving the sample in alcohol, and titrating directly with standard hydrochloric acid, using bromophenol blue as indicator. The sharpness of the end-point and the ease with which the diphenyl-guanidine can be purified suggested at once the possibility of its use as a standard substance for preparing acid solutions.

Until recently diphenyl-guanidine has been a rare organic chemical of very little scientific value, but with the discovery of its value as an accelerator in the vulcanization of rubber it has become of considerable importance, and is now an article of commerce.

Sym.-diphenyl-guanidine, $(C_6H_5NH)_2CNH$, *m. p.* 147°, is a mono-acid base, readily soluble in dil. mineral acids, exceedingly soluble in alcohol, chloroform and in carbon tetrachloride, soluble in hot benzene and toluene, but almost insoluble in cold toluene. It is sparingly soluble in water, and the aqueous solution is strongly alkaline to phenolphthalein. It crystallizes from toluene in very fine needle-like crystals, pure white in color.

The crude substance contains approximately 97% diphenyl-guanidine, 0.25% ash, and 0.5-1.0% moisture, the balance being a gummy, resinous

² Hendrixson, *THIS JOURNAL*, **37**, 2352 (1915); **42**, 724 (1920).

³ Richards and Hoover, *ibid.*, **37**, 109 (1915).

⁴ Dodd, *J. Soc. Chem. Ind.*, **40**, 89T (1921).

material of unknown composition. This gummy material is readily soluble in cold toluene, so that three or four recrystallizations from toluene yield a sufficiently pure product.

Diphenyl-guanidine is unalterable in the air. It has the highest equivalent weight (211.19) of any substance so far proposed as a standard for acids. It is free from color before and after titration, and no interfering products are formed during the titration. Thus it will be seen that it meets all the requirements for an ideal standard.

No reference to its use as a standard reagent has been found in the literature. In order to prove its value, the following brief experimental study was made, and the results are submitted with the hope that some one will see fit to subject it to a more rigid examination.

Experimental

Purification of Materials.—One hundred g. of the crude diphenyl-guanidine⁵ was dissolved in 800 cc. of toluene (thoroughly dried over calcium chloride and redistilled) by heating nearly to the boiling point, the solution filtered through a hot water funnel, and the filtrate cooled with cold water while vigorously stirred. The crystals obtained were recrystallized thrice, using approximately 8 cc. of toluene for each gram of diphenyl-guanidine. The melting points of the products obtained in the third and fourth recrystallizations were identical. The crystals obtained in the fourth crystallization were washed twice on a Büchner funnel with cold toluene, sucked dry, and then dried in an electric oven, first at 90°, and finally for 2 hours at 120°. A yield of 82 g. of pure material was obtained.

The alcohol was purified by adding 10 cc. of conc. sulfuric acid to each liter of alcohol and distilling to remove any amines and most of the water and then distilling from a little potassium hydroxide to remove acidic substances. The alcoholic hydrochloric acid solution was made by adding 10 cc. of c. p. conc. hydrochloric acid to sufficient pure alcohol to make one liter. The sodium carbonate was purified in the usual way from pure sodium hydrogen carbonate, and the usual precautions were taken in its preservation and use. All water used was doubly distilled.

Alcoholic hydrochloric acid was used in this work, for, as has been shown by previous investigators,^{6,7} the end-points obtainable are somewhat sharper in alcoholic than in aqueous solution. However, aqueous solutions of hydrochloric acid have been standardized with equally good results by dissolving the diphenyl-guanidine in 50 cc. of alcohol, so that the final solution contains at least 50% of alcohol.

Standardization by Means of Silver Chloride.—The concentration of the hydrochloric acid solution was determined by precipitating the chloride ion as silver chloride, filtering and weighing in Gooch crucibles. A counterpoise crucible was used in weighing and the weights were calibrated. Both the solution and the wash water contained about 1% of nitric acid. The filtrates were measured and usually amounted to about

⁵ Purchased from The National Aniline and Chemical Company.

⁶ Folin and Flanders, *THIS JOURNAL*, **34**, 774 (1912).

⁷ Bishop, Kittredge and Hildebrand, *ibid.*, **44**, 135 (1922).

450 cc. To compensate for solubility, 1.4 mg. of silver chloride per liter of filtrate was added to the weight. The same volume of hydrochloric acid was employed as was used in titrating the samples of diphenyl-guanidine to eliminate any error in the buret. The temperature change of the solution during the course of the work was negligible.

Four 40cc. samples of the hydrochloric acid solution were analyzed by precipitation as silver chloride and were found to contain 4.437, 4.437, 4.433 and 4.433 mg. of hydrochloric acid per cc., or an average of 4.435 mg., with an average variation of 0.002 mg. per liter.

Standardization by Means of Diphenyl-guanidine.—The diphenyl-guanidine was weighed on a small watch glass, and glass and sample transferred to a 250cc. beaker. Twenty-five cc. of alcohol was added and 5 drops of a solution of 1 g. of bromophenol blue in 1 liter of alcohol. The color change of bromophenol blue, in alcohol solution, is from blue in alkali to pale yellow in acid solution. The solution being titrated was viewed against a yellow paper, making the color change blue to colorless. In aqueous solution the color passes from blue through green to yellow, and there is an indeterminate range equivalent to 1–2 drops of acid. This green color is seldom obtained in the alcohol solution, and if it is, less than $\frac{1}{2}$ drop of acid is required to discharge it completely. The end-point is so sharp that there is danger of overstepping it. It was discovered in the latter part of this work that this danger could be very easily eliminated by using as indicator a combination of bromophenol blue and methyl red, in the proportion of 5 drops of the former to 2–3 drops of the latter. The color of this solution in alkali is dark green. As the end-point is approached the red color of the methyl red appears before the added drop is stirred in. At the end-point the color suddenly changes to violet, and $\frac{1}{2}$ drop of acid changes the color to deep orange. This combination makes an ideal indicator for the above titration.

	Diphenyl-guanidine G.	HCl Cc.	HCl in 1 cc. of sol. G. $\times 10^3$
1	1.0008	38.95	4.437
2	1.0014	39.00	4.434
3	1.0002	38.90	4.440
4	1.0007	38.95	4.436
5	0.9999	38.92	4.436
6	1.0004	38.95	4.435
7	0.9998	38.90	4.438
8	1.0005	38.95	4.436
9	1.0003	38.95	4.435
10	1.0006	38.95	4.436
			Av. 4.436
A THrice RECRYSTALIZED SAMPLE			
1	1.0002	38.95	4.434
2	1.0001	38.96	4.433
			Av. 4.434

The last two analyses show that the product obtained by three recrystallizations is sufficiently pure for ordinary work.

Standardization by Means of Sodium Carbonate.—The sample of sodium carbonate was dissolved in 20 cc. of water and titrated in the cold, using 5 drops of bromophenol blue as indicator. In this titration the color change is from blue to green to yellow, and the end-point must be taken at the first change to green.

	Na ₂ CO ₃ G.	HCl Cc.	HCl in 1 cc. of sol. G. × 10 ³
1	0.3306	51.30	4.434
2	0.3451	53.50	4.438
			<u>4.438</u>
			Av. 4.436

In titrating sodium carbonate better results are obtained by using methyl red or bromocresol purple as indicator, in place of bromophenol blue. As both methyl red and bromocresol purple are sensitive to carbonic acid, it was necessary to expel this gas by heating the solution to boiling. The end-points are very sharp, being sensitive to 1/2 drop of the alcoholic hydrochloric acid.

The results given below were obtained by standardizing an alcoholic solution of hydrochloric acid against diphenyl-guanidine, and then against sodium carbonate, using the indicators mentioned above.

HYDROCHLORIC ACID SOLUTION 2, STANDARDIZED AGAINST DIPHENYL-GUANIDINE

	Diphenyl-guanidine G.	HCl Cc.	HCl in 1 cc. of sol. G. × 10 ³
1	1.0004	39.38	4.387
2	1.0003	39.36	4.388
3	1.0001	39.35	4.389
4	1.0002	39.35	4.389
			<u>4.388</u>
			Av. 4.388

HYDROCHLORIC ACID SOLUTION 2, STANDARDIZED AGAINST SODIUM CARBONATE

	Na ₂ CO ₃ G.	Indicator	HCl Cc.	HCl in 1 cc. of sol. G. × 10 ³
1	0.2061	Bromophenol blue	32.35	4.384
2	0.2519	Bromophenol blue	39.55	4.382
3	0.2900	Methyl red	45.45	4.390
4	0.2652	Methyl red	41.60	4.386
5	0.2203	Methyl red	34.55	4.387
6	0.2615	Bromocresol purple	41.02	4.386
7	0.2366	Bromocresol purple	37.15	4.382
8	0.2266	Bromocresol purple	35.52	4.384
				<u>4.385</u>
				Av. 4.385
				Av. using bromophenol blue 4.383
				Av. using methyl red 4.388
				Av. using bromocresol purple 4.384

It will be seen from the above table that bromophenol blue gives low results. Methyl red gives results which are closest to the value obtained by standardizing against diphenyl guanidine.

To review the work, we have the following values for the amount of hydrochloric acid in 1 cc. of the hydrochloric acid solution as determined by three different methods.

		G. $\times 10^3$
1	Silver chloride	4.435
2	Diphenyl guanidine	4.436
3	Sodium carbonate	4.436
	Av.	4.436

The following comparisons are on Solution 2 as determined by diphenyl-guanidine and by sodium carbonate using various indicators.

1	Diphenyl guanidine	4.388
2	Sodium carbonate using bromophenol blue	4.383
3	Sodium carbonate using methyl red	4.388
4	Sodium carbonate using bromocresol purple	4.384

Summary

1. Diphenyl-guanidine is easily obtained in a state of sufficient purity for use as a standard substance by three recrystallizations of the crude material from toluene.

2. It is stable in the air.

3. It is readily soluble in alcohol and can be titrated directly in the cold with either an alcoholic or an aqueous solution of hydrochloric acid, using bromophenol blue or methyl red as indicator.

4. The results obtained by its use are comparable to those obtained with sodium carbonate or silver chloride, and the substance is more convenient to use.

5. It is the only basic substance so far proposed that meets all the requirements of an ideal standard.

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