

# THE LIQUID AMMONIA-SODIUM METHOD FOR HALOGENS IN ORGANIC COMPOUNDS, THE FORMATION OF CYANIDE, AND METHOD OF REMOVING FROM THE SOLUTION.<sup>1</sup>

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The literature on the determination of halogens in organic compounds by utilizing metallic sodium or potassium dissolved in liquid ammonia is meager, only two articles<sup>2</sup> being available. Since this method has been known only a comparatively short time and is not widely used, an investigation of its accuracy was undertaken with a view of adopting it in this laboratory.

**The Liquid Ammonia-Sodium Method.**—The manipulation consists essentially in placing a small quantity of the sample in a Dewar flask and adding liquid ammonia. The material for analysis need not be soluble in the liquid ammonia; if it is insoluble it must be finely divided. Metallic sodium is then added in small pieces until an excess is evidenced by a permanent blue color throughout the solution. By this treatment the halogen of the organic compound is entirely converted into inorganic halide. After evaporation of the excess of ammonia a little alcohol is used to take up any sodium remaining uncombined. The residue is taken up with water and acidified with nitric acid. The halogen is determined usually by precipitation with standard silver nitrate in excess, followed by titration with sodium thiocyanate.

## Experimental.

**Substances for First Analyses.**—Carbon tetrachloride and carbon hexachloride (hexachloro-ethane) were taken as being typical organic compounds although high in halogen. The sample of hexachloride had been recrystallized from alcohol and the tetrachloride was redistilled from c. p. material.

**Indications of the Formation of Cyanide.**—Analysis of two samples of the tetrachloride sealed in glass bulbs gave an odor upon being acidified, similar to that of hydrocyanic acid, and the following percentages of chlorine were found: 98.40 and 96.80 (theoretical is 92.20).

**Proof of Cyanide Formation.**—Unweighed samples of both compounds were accordingly treated with sodium in liquid ammonia and qualitative tests for cyanide applied, with these results.

TABLE I.—TESTS FOR CYANIDE.

Method of testing for cyanide.	CCl <sub>4</sub> .	C <sub>2</sub> Cl <sub>6</sub> .	Blanks.
Ferric ferrocyanide test.....	positive	positive	negative
Ferric thiocyanate test.....	positive	positive	negative

<sup>1</sup> Published by permission of the Director of Chemical Warfare Service.

<sup>2</sup> E. Chablay, *Ann. chim.*, 9, I, 469-519 (1914); C. A., 8, 3422 (1914); Dains, Vaughan and Janney, *This Journal*, 40, 936 (1918).

The foregoing results prove the formation of cyanide in these cases. The blanks gave negative tests for halides showing the purity of all reagents in this respect. The formation of cyanide is not mentioned in the references. If formed it must be eliminated or determined in order to arrive at the true halogen content.

**Degree of Decomposition of Silver Cyanide and Elimination of Cyanide by Boiling the Nitric Acid Solution.**—Some cyanide will be eliminated during the heating of the solution and silver precipitate, as a result of the decomposition of the silver cyanide in the hot dil. nitric acid. Tests using known solutions were carried out to ascertain the completeness of this decomposition and of the elimination of cyanide by boiling in nitric acid solution. Solutions of sodium chloride, sodium bromide, sodium iodide, and sodium cyanide were made up to 0.032 *N* concentration. The chloride was recrystallized from c. p. material by means of hydrogen chloride; the bromide was c. p. material recrystallized once from hot water but was unsatisfactory, possibly due to impurities not removable by this operation; the iodide was c. p. material obtained from a reputable firm. Aliquots of each sodium halide solution equal to 40 cc. of 0.02 *N* were taken and an aliquot of sodium cyanide equal to 38.5 cc. of 0.02 *N* added to each. A definite excess (100 cc. except in two cases) of 0.02 *N* silver nitrate was next added, followed by neutralization with 6 *N* nitric acid, the addition of the specified amounts of 6 *N* nitric acid in excess, and dilution to 250 cc. In the control tests 50 cc. of the silver nitrate was added to the aliquot of the sodium halide before the nitric acid was added. The solutions were then boiled carefully for 3 hours, a much longer heating than in the regular volumetric procedure. The containers were 500 cc. Erlenmeyer flasks covered with watch glasses supported on glass rods. After cooling and filtering, the solutions were titrated with 0.02 *N* sodium thiocyanate, using ferric alum as the indicator. The graduated apparatus had been previously calibrated, and temperature corrections were applied to the solutions; this is true of all quantitative analyses reported in this paper.

TABLE II.  
Cc. of 0.02 *N* Cyanide Undecomposed by Boiling in Dil. Nitric Acid.

Concentration of acid.	Added 25 cc. 0.032 <i>N</i> .		
	NaCl.	NaBr.	NaI.
10 cc. free 6 <i>N</i> HNO <sub>3</sub> , 250 cc. vol. . . . .	0.07 <sup>1</sup> 0.06	0.15	0.24
50 cc. free 6 <i>N</i> HNO <sub>3</sub> , 250 cc. vol. . . . .	—0.01 <sup>1 2</sup> —0.18 <sup>2</sup>	—0.02 <sup>2</sup>	0.01 <sup>2</sup>

The decomposition of silver cyanide and the elimination of cyanide by

<sup>1</sup> 50 cc. silver nitrate used.

<sup>2</sup> Solubility of silver halide or volatilization of halogen may possibly affect these.

oxidation or volatilization by boiling in dil. nitric acid were approximately complete. This is shown by the results, summarized above.

It is evident, however, that the separation of cyanide and halide is not sharply accurate even with prolonged boiling.

An attempt was made to eliminate the cyanide by boiling the nitric acid solution before the addition of the silver nitrate, and by continuing the boiling until the volume was reduced from 150 cc. to 75 cc. In these experiments actual analyses by the liquid ammonia-sodium method were carried out, the cyanide being that formed in the reaction. Samples of hexachloro-ethane and an aromatic compound containing chlorine and nitrogen were used. The results for the hexachloro-ethane are close to the theoretical, and those for the aromatic compound check results by the sodium peroxide fusion.<sup>1</sup> It is possible that minute quantities of cyanide are retained<sup>2,3</sup> in these analyses, but if so it is in such small amounts that it does not appear in the results. The figures for chlorine were checked by titrating the cyanide<sup>4</sup> in an aliquot with 0.02 *N* silver nitrate (deducting an end-point blank of 0.02 cc.), and subtracting its equivalent from the silver halide plus silver cyanide precipitated in another aliquot of the same sample. As will be seen from the data, the cyanide formed is not a constant for each substance, and is apparently dependent upon factors not ordinarily regulated; in fact, later analyses indicate that in some cases no appreciable amount of cyanide is formed (for example, the analyses referred to by Note 5 under Table VIII, page 1058).

TABLE III.

Analysis of Carbon Hexachloride by the Liquid Ammonia-Sodium Method, Eliminating HCN from the Nitric Acid Solution.

% cyanide found.	% chlorine.	
	Calc.	Found.
4.78	...	89.70
4.35	...	89.87
4.91	89.86	90.0
5.11	...	89.66
3.07	...	89.22
0.87	...	90.19
		Av., 89.77

That the presence of nitrogen in the compound analyzed is without effect is shown by the following results:

<sup>1</sup> Lemp and Broderon, *THIS JOURNAL*, 39, 2069 (1917); Parr, *J. Ind. Eng. Chem.*, 11, 230 (1919).

<sup>2</sup> Richards and Singer, *Am. Chem. J.*, 27, 208 (1902); *Am. J. Sci.*, 163, 13, 315 (1902).

<sup>3</sup> Bruckmiller, *THIS JOURNAL*, 38, 1954 (1916); *Am. J. Sci.*, 192, 42, 498 (1916).

<sup>4</sup> Treadwell-Hall, *Analytical Chemistry*, 1915, II, 711.

TABLE IV.

Analysis of Aromatic Compound Containing Chlorine and Nitrogen.

% cyanide found.	% chlorine.		Remarks.
	Calc.	Found.	
2.92	...	{ 40.63 40.71	Tests on 2 blanks gave no cyanide and no halide. Color rendered end-point somewhat difficult to observe. Average of several analyses by sodium peroxide fusion was 40.20% Cl.
6.03	40.76	{ 40.67 40.64	
3.89	...	{ 40.22 40.3	

Av., 40.53

**Loss of Halogen in Boiling the Nitric Acid Solution.**—Rosanoff and Hill<sup>1</sup> state that in their experiments, boiling 200 cc. of 0.02 *N* potassium chloride after adding 4 cc. of conc. nitric acid, no halogen was found in the distillate of 15 cc., but that when the acid was increased to 6 cc., traces distilled over; with 200 cc. of 0.01 *N* potassium bromide, 3 cc. of the acid caused no loss of bromine, but 3.5 cc. did. Bruckmiller<sup>2</sup> found no loss of chlorine in boiling solutions containing 0.015 g. sodium chloride after adding from 1 to 5 cc. nitric acid in volumes varying from 100 cc. to 25 cc. Lemp and Broderson<sup>2</sup> found no loss of chlorine in boiling the sodium peroxide fusion extract acidified with nitric acid, but demonstrated the probability of inaccurate results in the case of fusions of compounds containing bromine or iodine.

It was desired to check the accuracy of the analyses of organic compounds for chlorine previously given, and to determine whether bromine would be lost in distillation with nitric acid, where an ordinary excess of nitric acid, say 10 cc. of the 6 *N* acid, was used. The following tests were carried out: The solutions of 0.032 *N* sodium chloride, sodium bromide, and sodium cyanide previously described, and 3% halide-free sodium hydroxide were used. Aliquots of the halides equal to 40 cc. of 0.02 *N* were taken and analyzed directly for control, adding first the silver nitrate, then the acid. An aliquot of each halide equal to 40 cc. of 0.02 *N* was then taken, an aliquot of sodium cyanide equal to 38.5 cc. of 0.02 *N* added, then sodium hydroxide equal to 0.8 g. sodium. Each was neutralized with 6 *N* nitric acid and an excess of 10 cc. of the 6 *N* acid added. Each solution was then distilled into 50 cc. of the 3% sodium hydroxide.

The results showed no loss of chlorine, although the boiling was continued until the original volume was reduced from 200 cc. to 100 cc. No chlorine was found in the distillate. However, a small amount of bromine did distil over, due either to oxidation of bromide or volatilization of hydrobromic acid, and here the last portions of cyanide seemed

<sup>1</sup> THIS JOURNAL, 29, 1470 (1907); *C. A.*, 2, 41 (1908).<sup>2</sup> *Loc. cit.*

difficult to distil. It is evident from a consideration of these results and those given in the references<sup>1</sup> that all concentrations of reagents must be carefully controlled, if complete and accurate separation of the cyanide and the bromide are to be obtained.

**Other Separations of Cyanide and Halide.**—Since distillation with nitric acid would require very careful regulation of concentrations in order to eliminate practically all cyanide with no loss of chlorine or bromine, and since nitric acid easily oxidizes hydriodic acid, liberating free iodine,<sup>2</sup> a study was made of various other possible methods of separating cyanide quantitatively from the halogens. The following methods were considered:

(a) The precipitation of silver cyanide and silver halide together, then making the concentration of nitric acid 10% to 25%, in which silver cyanide is soluble, followed by filtration and titration of the silver cyanide as a *soluble* silver salt.<sup>3</sup> (b) Precipitation of silver cyanide and silver halide, followed by separation by the use of mercuric oxide in acetic acid. (c) Aspiration of the nitric or acetic acid solution. (d) Carbonation of the alkaline solution. (e) Titration of the cyanide in one aliquot, using silver nitrate, followed by precipitation of both cyanide and halide with silver nitrate in another aliquot. This method was tried in several instances, but on account of the multiplication of errors does not give closely agreeing results. This is shown by the following analyses of hexachloro-ethane and an aromatic compound:

TABLE V.

Determination of Chlorine by Deducting Cyanide from Sum of Cyanide and Chloride.

Hexachloro-ethane.		Aromatic compound containing chlorine and nitrogen.	
Found.	Calc.	Found.	Calc.
89.85	...	43.54	...
88.92	...	0.41	...
91.11	...	40.63	...
91.83	89.86	40.7	40.76
90.65	...	41.84	...
89.89	...	39.6	...
Av., 90.37		Av., 41.13	

(f) Precipitation of silver cyanide and silver halide, followed by reduction with zinc and sulfuric acid overnight, filtration, and determination of the halogen. (g) Boiling off the cyanide as hydrogen cyanide after acidifying with sulfuric acid<sup>4</sup> (this for chlorides only). (h) Distillation of

<sup>1</sup> Rosanoff and Hill, *Loc. cit.*; Bruckmiller, *Ibid.*

<sup>2</sup> Lemp and Broderson, *Ibid.*

<sup>3</sup> Gregor, *Z. Anal. Chem.*, 33, 33 (1894).

<sup>4</sup> Richards and Singer, *Loc. cit.*

the cyanide as hydrogen cyanide from the acetic acid solution of the halide.<sup>1</sup>

**Method Selected, and Experimental Tests.**—The last separation gave promise of being the simplest. Using the previously mentioned solutions of sodium halides, sodium cyanide, and sodium hydroxide, this separation was tested qualitatively and quantitatively.

(1) The purpose of the qualitative tests was to establish the time necessary for the complete elimination of cyanide, with regard to various concentrations of halogen, cyanide, and acetic acid. An aliquot each of sodium chloride and sodium bromide equal to 40 cc. of 0.02 *N* was taken in a 500 cc. Erlenmeyer, an aliquot of cyanide equal to 0.02 g. CN added, then 50 cc. of halide-free sodium hydroxide, which was equal to 0.8 g. of sodium. Each solution was diluted to about 200 cc., neutralized to phenolphthalein with 6 *N* acetic acid, and an excess of about one cc. added. (Preliminary tests had shown that varying the excess of acetic acid from 0.1 to 2.0 cc. had little, if any, effect upon the time of elimination of hydrocyanic acid.) A few clean glass beads were introduced, the Erlenmeyer flask was covered with a watch glass supported on a piece of glass rod, and boiled for  $\frac{1}{2}$  hour. Each solution was then made slightly alkaline with ammonia, two drops of ammonium sulfide were added, and the solution was evaporated to about 20 cc. The addition of ferric chloride solution proved in each case that cyanide had been completely eliminated.

Tests with higher concentrations of halogen and cyanide were next made in the same manner as just described. The aliquots of halogen were equal to 160 cc. of 0.02 *N*, the cyanide aliquots were equal to 0.08 g. CN, and the sodium hydroxide aliquot was the same as previously. After half an hour's boiling cyanide was still present, so this series was repeated, employing a boiling time of one hour. Tests in this case showed cyanide to be completely eliminated. Aliquots of sodium iodide were not used in these tests, since the addition of ferric chloride would liberate iodine and mask a positive test.

(2) Careful analyses were made to test this method of separation quantitatively. These known solutions were used, and the conditions of the liquid ammonia-sodium method were duplicated as exactly as possible. Two series were run as described under (1). The first contained halogen equal to 40 cc. of 0.02 *N*, cyanide equal to 0.02 g. CN, and sodium hydroxide equal to 0.8 g. sodium, and was boiled for  $\frac{1}{2}$  hour. The second contained each halogen equal to 160 cc. of 0.02 *N*, cyanide equal to 0.08 g. CN, and sodium hydroxide equal to 0.8 g. sodium, and was boiled one hour. In the case of every solution, after the boiling the halogen was determined by the standard method of precipitation with 0.02 *N* silver nitrate. The solution was then filtered and the excess silver nitrate was titrated with 0.02 *N* sodium thiocyanate. Filtering off silver bromide

<sup>1</sup> H. E. Williams, "*Chemistry of Cyanogen Compounds*," 1915, 335.

and silver iodide is usually considered unnecessary,<sup>1</sup> but it was done here in order that the end-point might be more accurately observed.

Control determinations were made on an aliquot of each halide after adding an aliquot of sodium hydroxide, for the series of low concentration and the series of high concentration. Half of these were acidified with the acetic acid and boiled, while the remainder were analyzed directly for halogen content. All of these controls agreed within experimental error, showing no mechanical loss by the process of boiling. Duplicate analyses were made in every test described. It was assumed that the acetic radical is without effect in the halogen determination, since silver acetate is much more soluble than silver halide. The results verify this assumption.

TABLE VI.

Summary of Analyses of Known Solutions of Sodium Halide, Containing Cyanide.			
Halogen content, and variation	NaCl.	NaBr.	NaI.
G. total halogen per cc.....	0.0011479	0.0025699	0.0039987
G. total halogen per cc. found by experiments....	0.0011480	0.0025720	0.0039991
G. halogen per cc. maximum variation in controls.	0.0000022	0.0000125	0.0000075
G. halogen per cc. maximum variation in experiments.....	0.0000012	0.0000130	0.0000084
% maximum difference in experiments.....	0.10	0.51	0.21

A consideration of these results shows that in each case the order of accuracy in the experiments was approximately the same as in the controls.

**Conclusions from these Test Analyses.**—It is proved, then, that the modified liquid ammonia-sodium method is accurate at least within the following ranges:

TABLE VII.

Ranges Tested and Found Accurate for the Modified Method.		
Composition of solution.	Lower limit.	Upper limit.
Volume for boiling.....	175 cc.	400 cc.
Halide.....	0.002 <i>N</i>	0.020 <i>N</i>
Cyanide.....	0.05 g. per liter	0.46 g. per liter
Sodium other than sodium halide.....	0.0 g.	0.8 g. sodium
6 <i>N</i> acetic acid.....	0.1 cc.	2.0 cc.

### Analysis of Organic Compounds by the Modified Liquid Ammonia-Sodium Method.

Samples of carbon tetrachloride, hexachloro-ethane, and various organic substances sent into the laboratory for analysis were next analyzed by the modified liquid ammonia-sodium method.

**Procedure in Detail.**—Samples of liquids of high boiling points were weighed in very thin-walled glass bulbs having short, large, capillary necks. These were introduced into the ammonia and carefully broken with special

<sup>1</sup> Rosanoff and Hill, *THIS JOURNAL*, 29, 273 (1907); *C. A.*, 1, 1367 (1907); *Chem. Zentr.*, 1907, I, 1586.

tongs or by gentle pressure with a heavy glass rod spread at the bottom and having a concave under-surface. If this latter method is used, great care must be taken in order not to fracture the Dewar flask. Unsilvered flasks permit ready observation and allow fairly rapid evaporation. Samples of solids were introduced directly into the flask.

The sample of 0.05 to 0.25 g. in about 30 cc. of liquid ammonia was treated with an excess of sodium, added slowly in small pieces with frequent stirring, until the blue color persisted 15 minutes. The ammonia was allowed to evaporate. To let stand overnight is convenient, but the time of evaporation may be shortened by blowing dried air from a glass

TABLE VIII.  
Summary of Analyses of Organic Compounds by Modified Method.

Compound.	% halogen.			
	Original method.	Na <sub>2</sub> O <sub>2</sub> fusion.	Modified method.	Calc.
CCl <sub>4</sub> <sup>1</sup> .....	101.55	...	93.33 93.42	92.20
			Av., 93.37	
C <sub>2</sub> Cl <sub>6</sub> .....	89.90 <sup>5</sup>	...	90.37 89.74 90.23	89.86
			Av., 90.11	
Barium salt of organic sulfonic acid.....	15.23 <sup>6</sup>	15.17 15.05 15.05	15.02 15.2 ...	16.70
		Av., 15.09	Av., 15.13	
Aromatic arsenic-chlorine compound, <sup>2</sup> yellow.....	13.98 <sup>5</sup>	12.80 13.59 13.56 12.82 13.15	12.49 13.85 ... ... ...	12.80
		Av., 13.18	Av., 13.17	
Aromatic arsenic-chlorine compound, white.....	14.55	... 13.28 13.32	13.25 13.33 <sup>3</sup> 13.19 <sup>3,4</sup>	13.40
		Av., 13.30	Av., 13.26	

<sup>1</sup> Sample not redistilled.

<sup>2</sup> Compound probably impure, not homogeneous.

<sup>3</sup> Not filtered before precipitating silver halide.

<sup>4</sup> Silver halide not filtered off before titrating.

<sup>5</sup> Little or no cyanide apparently formed.



tube whose outlet is within a few centimeters of the surface. After adding a little alcohol to take care of the excess sodium, water was added, the solution was transferred to a 250 cc. beaker, diluted to about 150 cc., and filtered into a 500 cc. Erlenmeyer flask.<sup>1</sup> This filtration may be dispensed with in many cases. The solution was diluted to 200–250 cc., neutralized to phenolphthalein with 6 *N* acetic acid, and a slight excess (about one cc.) added. A few, clean, glass beads were then added, the flask was covered with a watch glass supported on a piece of glass rod, and boiled carefully at a rather moderate rate for one hour. If more than about 75 cc. of water was vaporized, it was replaced to maintain a fairly constant volume. The solution was cooled somewhat, and the halogen determined by precipitation with silver nitrate, filtration (in most cases), and subsequent titration with sodium thiocyanate.

**Method of Titrating to a Definite End-point.**—235 cc. of water, 10 cc. of 6 *N* nitric acid, and 5 cc. of 10% ferric alum were taken, and 0.12 cc. of 0.02 *N* sodium thiocyanate added. All determinations were titrated to this same color intensity, using a so-called "Daylight" electric bulb in absence of ordinary sunlight. The sodium thiocyanate was standardized on pure polished silver foil and the silver nitrate by weighing silver chloride, then by checking on the sodium thiocyanate.

Analyses of the last two compounds were completed by the volumetric method, in spite of interfering colors which were intensified by the addition of ferric indicator.

**Comparison of this Method, the Carius Method, and the Sodium Peroxide Fusion Method.**—This method is much more rapid than the Carius method. As compared with the sodium peroxide fusion, this method possesses the advantage that no blank is necessary, since all reagents can be obtained halide-free without trouble. In the determination of bromine and iodine by this method no oxyacid salts can be formed. The sodium peroxide fusion has been the most widely applicable rapid method for halogens (and sulfur) used in this laboratory. With the liquid ammonia-sodium method side reactions may occur and give rise to interfering compounds and colors, as in the case of aromatic compounds, which make it advisable to decolorize or determine gravimetrically.

#### Summary.

1. Cyanide is formed in many cases by the treatment of organic compounds with sodium in liquid ammonia. No mention of this is found in the literature.

2. The procedure outlined in the references cannot be followed without involving possibility of error. On acidifying, only a part of the hydrocyanic acid which may have been formed is expelled. At best, the de-

<sup>1</sup> A thin ring of stopcock grease around the top of the Dewar flask aids in transferring the contents quantitatively to the beaker.

composition of silver cyanide and elimination of cyanide by boiling in dil. nitric acid are only approximately quantitative.

3. The per cent. of cyanide formed is not a constant for each substance, under the conditions of analysis.

4. Treatment with sodium in liquid ammonia completely removes any halogen present in organic compounds. This method is accurate for halogen determination in organic compounds when the resulting halide is separated quantitatively from any cyanide present by acidifying the solution with acetic acid, and then boiling.

5. With chlorine, boiling the nitric acid solution has proved to be a sufficiently accurate elimination of cyanide. An approximate check may be obtained by subtracting cyanide determined in one aliquot from cyanide and halide determined in another aliquot.

The writer wishes to acknowledge his indebtedness to Dr. Albert Finck, under whose supervision this work was performed.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]  
**A METHOD OF GROWING LARGE PERFECT CRYSTALS FROM SOLUTION.**

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In the course of an investigation of some of the electrical properties of crystals, it became necessary to procure large pieces of wholly clear Rochelle salt crystals. It was found impractical to obtain these from commercial sources; a search through tons of crystals yielded only one or two pounds of suitable material. It therefore became necessary to work out some method of producing this material in the laboratory.

During the last few years, considerable work has been done along the line of producing perfect crystals from solution. In 1908, F. Krüger and W. Finke obtained a German patent (German patent 228,246) on an apparatus for the production of homogeneous crystals suitable for physical purposes by crystallizing in motion with a circulating solution. A heating element under delicate control is arranged in a super-saturation vessel and a means for cooling, also under control, between the super-saturation vessel and a crystallizing vessel. In 1915, J. J. Valetton<sup>1</sup> described an improved apparatus based on the above patent.

The growing of crystals by this type of method has apparently been carried to a high state of perfection by J. C. Hostetter,<sup>2</sup> who made various improvements in the details and the construction of the apparatus.

In 1916, the Elektrochemische Werke took out an Austrian patent

<sup>1</sup> *Ber. Sachs. Ges. Wiss.*, 67, 1-59 (1915).

<sup>2</sup> *J. Wash. Acad. Sci.*, 9, 85-94 (1919).