teid with dilute potash water, as the treatment for removal of the other proteids rendered it insoluble, if it were not so already.

VI. The barley flour contained 1.83 per cent. of nitrogen, and if it be assumed that this all belonged to proteid-matter with seventeen per cent. of nitrogen, the flour would contain 10.75 per cent. of proteids. The barley accordingly contained about four and a half per cent. of insoluble proteid, four per cent. of hordein soluble in dilute alcohol, three-tenths per cent. albumin, and 1.95 per cent. of globulin and proteose.

THE DETERMINATION OF NITROGEN IN FERTILIZERS CONTAINING NITRATES.[1]

BY H. C. SHERMAN.

Received April 13, 1895.

AS soon as the accuracy of the Kjeldahl method for the determination of nitrogen was generally recognized, attention was turned toward the discovery of some simple modification by which it could be made applicable in the presence of nitrates.

Asboth (*Chem. Centrbl., 1886*) recommended the simple addition of benzoic acid to the decomposing mixture. It was soon found that this method was not sufficient.

The following year, two methods were brought before the Association of Official Agricultural Chemists, one by Mr. Scovell, the other by Mr. Farrington. The principal difference consisted in the use of salicylic acid with the sulphuric acid to fix the nitrogen oxides by the former, while phenol was used for the same purpose by the latter. Both used zinc dust as the reducing agent. The Scovell method was adopted and remains practically unchanged.

In 1890, the Association sanctioned the use of zinc sulphide as a reducing agent. In case of its use the acid mixture was to contain one gram of salicylic acid instead of two. The use of zinc dust with two grams salicylic acid was retained.

In 1892, sodium thiosulphate, which had been used for reducing nitrates in the Ruffle method, was adopted as a third reducing agent, and it was directed that five grams of the crystalized salt should be added "direct."

[1] Read before the Washington Section.

In 1893, the use of zinc sulphide was dropped, (because this reagent was likely to contain nitrogen) and a modification of the Gunning method was adopted. In the latter, five grams of thiosulphate and one gram of salicylic acid were used with the same amount of potassium sulphate as in the plain method (ten grams). It was claimed that that all the reagents could be added with the substance, but further trials disproved this, and in 1894 the requirement of first mixing the substance with the acid mixture was made practically the same as in the modified Kjeldahl.

It has been the experience of the writer, and the amount of work which has been done by the Association, indicates that it is the same with others, that the determination of nitrogen in fertilizers containing nitrates is attended with greater difficulty than in those free from nitrogen in this form. In the hope of discovering whether this is due to any considerable extent to the official methods, and, if so, the reasons therefor, the following experiments were undertaken.

A set of four samples was first prepared, composed of the following materials:

No. 1, sodium nitrate, ammonium sulphate, potassium chloride, acid phosphate.

No. 2, sodium nitrate, bone phosphate, dried blood, ammonite, marl filler.

No. 3, sodium nitrate, tobacco stems, cottonseed-meal, castor pomace.

No. 4, sodium nitrate, dried fish, natural guano.

In each case all the materials, except the nitrate, were first mixed, ground to pass through a five-tenths mm. sieve, and air-dried. Nos. 1, 2, and 3 were then mixed again, and the percentage of nitrogen carefully determined by both the Kjeldahl and Gunning methods. The guano used in preparing No. 4 contained a small amount of nitric nitrogen, and could not be determined in this manner.

An air-dried sample of sodium nitrate was then ground to pass through the same sieve, and its nitrogen content determined by the silica fusion method. This sample was then carefully mixed with those above described in such proportions as to give to each the desired percentage of nitrogen. Nos. 1, 2, and 3 were cal-

culated to contain ten per cent., eight and one-half per cent., and eight and one-half per cent. respectively. No. 4 was expected to show about eight per cent. These percentages are as high as are likely to be found in ordinary mixed fertilizers.

The materials employed represent all the general classes of ingredients commonly used in this section, and since no one of them composed less than fifteen per cent. of the mixture in which it occurred, any effect which it might tend to produce would be almost sure to be noticeable in the result.

The results on these mixtures by the official methods are given in Table I.

TABLE I. PER CENT NITROGEN FOUND IN KNOWN MIXTURES.

No.	Calculated.	Modified Kjeldahl Zinc dust.	Modified Gunning.
1.....	10.00	9.93	9.80
2.....	8.50	8.51	8.50
3.....	8.50	8.48	8.50
4.....	...	8.12	8.08

Except in the case of No. 1, the figures given are the averages of two (and only two) determinations. The greatest difference between duplicates was 0.08 per cent.; the average difference 0.03 per cent.

Four determinations were made by each method on No. 1. These are given below.

The official methods as given on page 347 (Bul. 43, U. S. Dept. of Agr., Division of Chemistry) were followed closely with the following additional precautions.

1. In working the modified Kjeldahl method, the zinc dust was added through a funnel tube, very slowly, and with constant shaking. About two minutes is required to add the zinc dust in this way. After the first boiling, the flasks were allowed to cool somewhat before the mercuric oxide was added.

2. In the modified Gunning method, the boiling was continued about thirty minutes after the contents of the flask had become "nearly colorless."

To test these points determinations were made on Nos. 2, 3, and 4 without the precautions noted, but in every other way as above. The average results, together with those given above, are shown in Table II.

TABLE II. SHOWING EFFECT OF PRECAUTIONS NOTED ABOVE.

		Modified Kjeldahl:		Modified Gunning:	
			Zinc added in three to five portions and HgO at boiling heat.		Boiling stopped when nearly colorless.
No.	Calculated.	As above.		As above.	
2	8.50	8.51	8.47	8.50	8.55
3	8.50	8.48	8.46	8.50	8.36
4	8.10[1]	8.12	8.05	8.08	7.95
Av.	8.37	8.37	8.33	8.36	8.22

It is noticeable that the duplicates agreed about as closely as when the precautions were taken, but the results were in every case too low. The average discrepancy was, in the Kjeldahl, 0.04 per cent.; in the Gunning, 0.14 per cent. It would seem, therefore, that both of these precautions are advisable, and the second absolutely necessary, at least when working with high percentages.

Table III shows the results obtained on No. 1 by the modified Kjeldahl and Gunning methods, and by Winton's modification of the latter.

TABLE III. RESULTS ON SAMPLE NO. 1.

Calculated.	Modified Kjeldahl.	Modified Gunning.	Winton's Modification.
10.00	9.93	9.86	10.03
....	9.98	9.72	9.97
....	9.97	9.83	9.99
....	9.84	9.80	10.02
Average	9.93	9.80	10.00

The results by Winton's method are highly satisfactory; those by the Kjeldahl hardly so when compared with the other samples, while the Gunning gives results which are entirely too low to be called good.

Winton's modification of the Gunning-Kjeldahl method is essentially as follows: The substance is treated with the usual acid mixture and allowed to stand two hours, with frequent shaking. Two grams of zinc dust are then added and the first heating performed as in the Kjeldahl. Potassium sulphate is then added and the operation finished as in the Gunning method. It

[1] Average by both methods, see above.

is, therefore, a combination of the two with the improvement of the longer digestion in the acid mixture.

To return to the results on sample No. 1, since all the mixtures contain more or less phosphoric acid, the only substances peculiar to this sample are ammonium sulphate and potassium chloride. Since ammonium sulphate is formed in the process and is the final form of all nitrogen present, its presence in the sample could hardly account for the discrepancy, which, therefore, appears to be due to the chloride.

In looking over the record of the Association of Official Agricultural Chemists, we find that the modified Kjeldahl method has been tested by the Association in the year of its adoption and, with one exception, every year since on from one to five samples. Only four of these have contained chlorides, and only one in any considerable quantity. The modified Gunning has been tested by the Association on only one sample containing chlorides. These samples with the approximate percentages of chlorine, total nitrogen, and nitric nitrogen, and the variation in results reported, expressed in percentage of total nitrogen present, are shown in Table IV. All results which are so far from the average as to indicate accident are omitted, according to the custom followed by the reporters of the Association in averaging their results.

TABLE IV. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.
SAMPLES CONTAINING CHLORIDES.

Sample	Method	Chlorine, per cent.	Total Nitrogen, per cent.	Nitric Nitrogen, per cent.	Variation, per cent.
No. 4, 1888	Modified Kjeldahl	5	3.16	1.64	33.4
No. 1, 1889	" "	1.5	15.91	15.91	3.0
No. 3, 1889	" "	2.5	3.55	1.48	14.1
No. 2, 1893	" "	1.5	5.77	3.47	8.8
No. 2, 1893	Modified Gunning	1.5	5.77	3.47	7.5

To further test this question, determinations were made, in duplicate, on samples Nos. 2, 3, and 4, with one-half gram of potassium chloride added. Table V shows the average results with and without chlorides, the methods being carried out in exactly the same way as before.

TABLE V. PER CENT NITROGEN FOUND WITH AND WITHOUT CHLORIDES.

		Modified Kjeldahl.		Modified Gunning.	
No.	Calculated.	Without KCl.	With KCl.	Without KCl.	With KCl.
2	8.50	8.51	8.37	8.50	8.35
3	8.50	8.48	8.40	8.50	8.25
4	8.10	8.12	8.04	8.08	7.92
Average	8.37	8.37	8.27	8.36	8.17

A portion of the sodium nitrate used in preparing these mixtures was now taken. It had shown by the silica fusion method 16.41 per cent. nitrogen. The modified Kjeldahl showed 16.39 per cent and 16.38 per cent.

Portions of one-half gram were taken for each determination, and mixed with the same amount of potassium chloride. The digestion was carried out in the usual way.

The results were :

Modified Kjeldahl.	Modified Gunning.
16.32	15.82
16.09	15.68
15.96	15.83
15.97	15.46
16.23	16.02[1]
15.95	15.99[1]
16.07	15.86[1]
16.13	

The Winton modification was then tried and care taken to warm gently for some time after adding zinc dust before raising the heat, which was done gradually.

Results were :

	16.27
	16.30
	16.30
	16.34
Average	16.30

Indicating that the greatest care in the reduction process will not entirely prevent loss.

To ascertain more definitely at what stage in the operation the loss occurs, mixtures of one gram each sodium nitrate and potassium chloride were treated as in an analysis, and the gases escaping from the flask were made to pass through a bulb-tube

[1] Two grams salicylic acid used.

containing potassium hydroxide. The nitrates and nitrites thus recovered were converted into ammonia and estimated by means of Nessler's reagent, using for comparison a solution of ammonium chloride containing 0.0001 gram nitrogen in each cc. The operation was divided into four stages: (a) addition of sulphuric salicylic acid mixture; (b) addition of reducing agent; (c) gentle heating till frothing ceased; (d) brisk boiling for a few minutes. After evolution of gas had ceased in the first and second stages, and after removal of the flame in the fourth, a glass tube was inserted through the stopper reaching nearly to the surface of the liquid, the bulb-tube attached to an aspirator, and the gases contained in the flask thus drawn through the alkali. The following table (VI) shows the results obtained, expressed in terms of per cent. nitrogen on the basis of one gram substance:

TABLE VI

		Nitrogen Recovered.					
Reducing Agent used.	Temperature.	a.	b.	c.	d.	Total.	b, c, and d.
Zinc dust	20°	0.023	0.006	0.026	0.008	0.063	0.040
" "	24°	0.027	0.005	0.034	0.013	0.079	0.052
$Na_2S_2O_3$ in presence of K_2SO_4	22°	0.090	0.027	0.061	0.017	0.195	0.105
$Na_2S_2O_3$ in absence of K_2SO_4	20°	0.090	0.027	0.035	0.013	0.165	0.075
Zinc dust[1]	27°	0.039	0.001	0.006	0.011	0.057	0.018

Where zinc dust was used the acid mixture contained two grams of salicylic acid; where thiosulphate was used, one.

The results indicate: 1. That the greatest losses occur on the addition of the acid mixture and on the first application of heat. The former is thought to be due to the liberation of hydrochloric acid in direct contact with the nitrate before the mass has become thoroughly wetted by the sulphuric salicylic acid mixture.

2. The total loss exclusive of the first stage is greater with thiosulphate than with zinc dust, and appears to be greater when potassium sulphate is added with the thiosulphate than when the latter is added alone. By exercising care in the addition of the reducing agent and the application of heat, the loss in the last three stages is reduced to a very small amount.

[1] Some precautions taken as in working Winton's modification on mixture of nitrate and chloride, see above.

3. At a given temperature, the loss on addition of acid is greater where the mixture containing less salicylic acid is used.

4. Using the same quantity of salicylic acid, the loss on addition of the acid mixture appears to increase with the temperature.

5. The total amount of nitrogen recovered being less than the average discrepancy showed by analysis under similar conditions, it appears probable that there may be some loss later on in the process.

These facts explain why the Kjeldahl gave better results on a mixture of nitrate and chloride than did the Gunning; while the Winton gave better than either.

In this connection the heat generated on the addition of the reducing agent is of interest. The average of seven determinations each on zinc dust and thiosulphate, both added in the usual way, showed, for the former, an increase of temperature of 21°; for the latter, of 40°.

In the opinion of the writer, the prolonged digestion of the Winton method is useful, in the presence of chlorides, not only in securing complete solution of the nitrate, but also in allowing the contents of the flask to cool (for the heat generated by the action of the acid mixture on the chlorides is considerable) and to absorb a slight amount of moisture from the air, thus rendering the action less violent when zinc dust is added.

Mixtures of one-half gram each sodium nitrate and potassium chloride, treated with acid mixture cooled down to 8°, and digested as in the Winton method before addition of zinc dust, showed by the modified Kjeldahl method 16.34 per cent. and 16.32 per cent., or 99.6 per cent. of the amount found in the absence of chlorides.

Determinations by the modified Gunning on the same mixtures, in which the acid mixture was cooled to from 8° to 12°, the thiosulphate added slowly and with constant shaking and cooling of the flask, and the boiling continued some time after the liquid had become colorless, showed 16.02 per cent., 15.88 per cent., 16.16 per cent., and 15.99 per cent.; average, 16.01 per cent., or only 97.8 per cent. of the amount found when chlorides were not present.

Determinations on the same sample of pure nitrate alone by the modified Gunning method, carried out in slightly different ways, gave the following results:

As usually carried out with mixed fertilizers, 16.16 per cent. and 16.13 per cent.

Thiosulphate added first and heated before adding potassium sulphate, 16.16 per cent. and 16.24 per cent.

Thiosulphate added slowly with shaking and cooling, but digestion stopped as soon as liquid became colorless, 16.10 per cent.

Thiosulphate added as above, digestion continued one hour after colorless, 16.31 per cent. and 16.32 per cent.

As above, permanganate used, 16.37 per cent.

Modified Kjeldahl, using thiosulphate (five grams added direct), showed 16.37 per cent. and 16.36 per cent.

It may be well to state now that all the results given in this paper are corrected for reagents. At first a blank was run with every five determinations. After three or four such blanks had been made for each method and found to agree closely, their average was taken and applied to every result obtained by that method. Whenever it was necessary to change any of the reagents, another blank was run.

The results here given would *seem* to warrant the following conclusions.

1. For ordinary fertilizers containing little or no chlorides, the official methods are perfectly reliable if the directions are followed closely and the digestion in the modified Gunning is continued for at least a short time after the liquid has become practically colorless. The discrepancies which sometimes occur under these circumstances are believed to be due to faulty preparation of the sample.

2. In working with samples containing considerable amounts of chlorides, it is advisable to use the modified Kjeldahl (zinc dust) method and to cool the acid mixture before adding it to the substance. It appears advisable also to digest for some time at ordinary temperature before adding zinc dust. No way has been found by which equally accurate results can be obtained by the modified Gunning method in the presence of large amounts of chlorides, together with high percentages of nitric nitrogen.

3. When determining high percentages of nitric nitrogen by the modified Gunning method, it is necessary either to continue the boiling for some time after the contents of the flask have become colorless, or to use permanganate to complete the action.

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ON CONDENSATION; AND ESPECIALLY ON THE CONDENSATION OF NITRIC ACID.[1]

BY EDWARD HART.

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THE ideal condenser, economically considered, is the one simplest in construction, most accessible for repairs or other purposes, and which, with a given efficiency, requires the least cooling liquid. The old-fashioned worm is certainly far removed from this ideal. The Liebig's condenser is a nearer approach. If the space between the inside and outside tube in Liebig's apparatus is made narrow enough it is possible to effect complete condensation in a relatively short tube, and to raise the cooling liquid to boiling temperature. At first sight it would seem that this gives a maximum efficiency; but it does not. If the water used as cooling liquid has, at the start, a temperature of 0°, and, as it issues from the condenser, a temperature of 100°, the heat absorbed by a given weight of water is approximately 100 units. If, however, the cooling liquid can also be made to evaporate, the heat absorbed is much larger in amount, and is equal to 100 units plus the amount required to evaporate it (526 units). This makes in all 626 units, or an efficiency six times as great. In the Liebig's condenser, also, the liquid condensed is cold or nearly so. In many cases this is not necessary and then an additional loss is sustained.

In the apparatus which I shall describe a very brief consideration will show that the maximum of efficiency may be attained. For, first, the cooling water is evaporated; second, the condensed liquid is boiling hot.

This condenser I have used in several modified forms adapted

[1] A paper with this title was read at the World's Congress of Chemists, Chicago, August 26, 1893. The present paper has been revised to accord with more recent experience and practice.