

LV.—*On the Determination of Nitric Acid in Soils.*

By ROBERT WARINGTON.

As the nitrogen contained in cereal, and in many other crops, is at least in greatest part derived from the nitrates of the soil, the quantity of nitrates present in a soil becomes for many purposes a measure of the assimilable nitrogen which the soil contains. Investigations as to the increase or diminution of the nitrates of the soil under various circumstances of manuring, culture, or season, have been for some time past in progress at Rothamsted. As a part of this work, attention has naturally been directed to perfecting the methods employed for determining nitrates in soil. Some results of the experience thus acquired it is proposed to lay before the Society.

1. *Collection of the Soil Samples.*

A fair sample of soil is best taken by driving into the ground a short iron tube, of the depth which it is desired the sample shall represent. When the upper edge of the tube is level with the surface of the ground, the soil filling the tube is cut out, and constitutes the sample. If a sample of the second depth is desired, the earth surrounding the tube is cleared away, and the tube is once more driven down, till its upper edge is at the level which the lower edge previously occupied. By proceeding in this way the soil may be sampled to any required depth. The iron tube should be wide enough to prevent any abnormal consolidation of the soil within it, else the length of the tube will not exactly represent the depth of soil taken. The method here indicated has been employed by Messrs. Lawes and Gilbert during the last 25 years; the tubes made use of are rectangular, and 9 inches deep; the smallest is 6 inches square.

In sampling a soil for nitrates it is advisable to extend the collection to a considerable depth, as although nitrates are formed at the surface, they are readily washed down by rain, and distributed by diffusion; the whole range of soil available to the roots should therefore, if possible, be included. If only a comparatively small depth of soil can be sampled, it is very necessary that the sampling should be done after dry weather, when the nitrates are nearest the surface.

2. *Treatment of the Soil Samples.*

The first step to be taken is to bring the soil as quickly as possible to a dry condition. If this is not done, the quantity of nitric acid

found may greatly exceed that existing in the original soil, as nitrification will be continually in progress while the soil remains damp.

Experience has shown that it is not unimportant at what temperature the drying is effected. If a wet soil is dried in a water-oven at a temperature approaching 100° , the nitrates present will be more or less destroyed. This destruction is probably due to deoxidation by the organic matter present, and will be in proportion to the mass of the soil, its wetness, and its richness in organic matter. While, however, drying in a water-oven occasions loss of nitrates, drying by mere exposure to air is equally likely (in the case of surface soils at least) to occasion a gain in nitrates, the drying being so slow that a sensible amount of nitrification may occur.

The following test experiments have been made to ascertain the influence of various modes of drying:—An arable loam*, representing the first 9 inches from the surface, was passed through a sieve with meshes half an inch diameter, to separate stones; the sifted soil weighed about 280 lbs. The fine mould of this soil contained about 18 per cent. of water. The soil was well mixed, and divided into several portions. One-eighth was dried in the water-oven for 24 hours at about 90° ; one-eighth was dried in the stove room at 38° ; one-eighth was dried by exposure to air during 17 days, at a mean temperature of 10.2° ; one-half was placed in a bag, and kept in an outer shed during seven months (October to April). The whole of the samples were finally powdered and sifted, and all visible roots removed. The nitrogen existing as nitric acid was then determined in all the samples by the Crum-Frankland method. About four years afterwards the determinations were repeated, using the modification of Schloesing's method now adopted for soil analysis; the results are given in Table I.

TABLE I.—*Variations in the Quantity of Nitrates present in Soil resulting from Different Modes of Drying.*

Treatment of soil.	Analysed 1878.		Analysed 1882.	
	Water.	Nitrogen as nitrates in dry soil, Crum-Frankland method.	Water.	Nitrogen as nitrates in dry soil, Schloesing method.
	p. c.	per million.	p. c.	per million.
1. Dried in water-oven, 90°	0.99	1.08	1.57	4.17
2. Dried in stove, 38°	2.13	4.88	2.22	5.64
3. Dried in air, 10°	3.53	6.04	3.12	6.77
4. Kept in bulk 7 months, then dried in air	4.22	8.90	3.62	9.18

* The Rothamsted soil, to which all the experiments here quoted refer, may be described as a heavy loam with a clay subsoil.

The analyses made by the Crum-Frankland method show a wide range of variation in the quantity of nitric acid found, the amount being least when the soil was dried in the water-oven, and most when the soil had been left in bulk for several months and was finally sifted and powdered without the use of artificial heat. The later analyses of the same series of soils by the Schloesing method show much less variation in the contents of nitric acid, but the differences all lie in the same direction as before. The want of agreement in the two series is principally due to the much greater amount of nitric acid found by Schloesing's method in the case of the soil dried in the water-oven; we shall see presently that this higher result is probably more correct than that shown by the Crum-Frankland process.

We shall probably have no difficulty in concluding that the quantity of nitric acid found in the soils numbered 3 and 4 is in excess of that originally present, the process of drying in these cases having afforded more or less opportunity for nitrification; but the facts before us do not prove that the nitrates found after drying in the water-oven were too low. The following experiments supplement those just quoted, and show the influence of heat and moisture in diminishing the amount of nitrates in a soil.

In a dry powdered sample of arable soil, representing the first 9 inches from the surface, nitric acid was in the first place determined. Three quantities of this soil were then taken, each of 300 grams. One lot was treated with 60 c.c. of water free from ammonia, the water being carefully added so as not to destroy the open texture of the soil; the moistened soil was then made into a cubical mass, and placed in the middle of a basin. The second lot was similarly treated, placed loosely in a beaker, which it nearly filled, and covered with a clock-glass. The third lot was gradually introduced into a similar beaker containing 130 c.c. of water; the soil in falling through the water parted with most of its air; the water was sufficient to slightly cover the mass of soil. This beaker was also covered by a clock-glass. The three soils were then placed in a large water-oven for about 24 hours; the water was in actual ebullition during eight hours. The quantities of nitric acid found before and after this treatment were as follows; the analyses were all made by Schloesing's process:—

TABLE II.—*Influence of Heat and Moisture in reducing the Nitrates present in Soil.*

Treatment of soil.	Nitrogen as nitrates per million of soil.
1. Original soil	8·08
2. Ditto, moistened, and quickly dried in water-oven	7·73
3. Ditto, moistened, and slowly dried in water-oven.....	6·34
4. Ditto, thoroughly wetted, and heated in water-oven	1·83

It appears from these figures that with the particular soil in question little error was introduced by heating in the water-oven, if only drying was quickly effected; but where, as in Experiment 3, the escape of water was hindered, a very distinct reduction of nitrates took place. The fourth experiment proves that in the case of a mass of soil saturated with water, a comparatively short exposure to a high temperature is sufficient to destroy most of the nitric acid present. Other experiments made at Rothamsted (*Jour. Roy. Agri. Sec.*, 1881, 332) have shown that a soil kept saturated with water will lose nitrates even at ordinary temperatures, and similar facts have been noticed by Schloesing and others.

As drying wet soil at a high temperature thus tends to a loss of nitrates, while slow drying at low temperature admits, on the other hand, of their production, the following course has been adopted at Rothamsted:—The soil is broken up immediately it is received from the field, and spread in trays, in layers about 1 inch in thickness; the trays are then placed in a stove room, kept at about 55°; the drying is usually completed in 24 hours. As the temperature of the room is one at which nitrification by an organised ferment does not occur, it is probable that very little production of nitric acid takes place during the operation. After drying, stones and roots are removed, and the soil is finely powdered and placed in bottles. Soil samples thus prepared are not absolutely dry, but the small amount of water present is apparently insufficient to allow of organic change.

3. *Preparation of a Watery Extract.*

The mode of extracting the nitrates employed by Boussingault, and still recommended in works on agricultural analysis, is to take 500—1000 grams of the soil, add its own weight of water (twice its weight is recommended by Wolff), and shake thoroughly; after standing, a portion of the fluid is removed for analysis. This mode of proceeding

demands a considerable amount of soil, the extraction occupies a good deal of time, and the extract obtained is weak and turbid. Moreover some amount of uncertainty will generally attach to the calculated relation between the weight of soil taken and the nitric acid found; for if the soil is moist it will be difficult to decide how much of this moisture is diffusible water, and how much exists as hydrates; while if the soil has been dried at 100°, a part of the water added will doubtless combine with the soil, and cease to form part of the solution.

Grandeau (*Traité d'Analyse des Matières Agricoles*, 1877, 157) has proposed to extract the nitrates by simple percolation; but as, according to his directions, four hours are required to extract 50 grams of soil, while the resulting extract measures 150 c.c., the advantages offered seem very small.

The method now employed at Rothamsted is to extract the soil by percolation on a vacuum filter. A funnel $4\frac{3}{4}$ inches wide is made by cutting off the top of a Winchester quart bottle; at the bottom of this funnel a disc of copper gauze is laid, and on this two discs of filter-paper, each slightly wider than the one beneath. The filter is first moistened, and the dry powdered soil is then introduced; 200—500 grams are usually taken, according to the supposed richness of the soil in nitrates. If the soil is of loose texture, it is shaken firmly together, but with a clay soil consolidation is better avoided. The funnel is now connected by a caoutchouc stopper and glass tube, with a strong flask, water is poured on the soil, and the flask is put in connection with a water-pump. The water descends through the soil, and is collected in the flask. When 100 c.c. have passed through, it may be concluded that all nitrates have been extracted. The collection of this extract may take from 10 minutes, in the case of a surface soil of loose texture, to 45 minutes in the case of a subsoil. The extract is nearly clear. Second extracts have frequently been taken, but no chlorides or nitrates have been found in them.

The small volume of the extract in which all the chlorides and nitrates of a soil may be obtained, if the soil is taken dry, and percolation is conducted on a vacuum filter, is truly astonishing. In an experiment already published (*Jour. Roy. Agri. Soc.*, 1881, 329), 7 lbs. of dry powdered soil were placed on a filter, similar to that just described, the soil forming a column 8 inches in height; the filter was then put in connection with the pump, and water applied to the surface of the soil. In $2\frac{1}{4}$ hours the water had descended through the column of soil, and percolation commenced. It was found that the first 50 c.c. of extract contained more than three-quarters of the chlorides and nitrates present in the soil, while in the first 150 c.c. the whole of the chlorides, and 98.8 per cent. of the nitrates were found. It would

appear that as a column of water descends through a dry powdered soil, it dissolves the soluble salts at its lower edge, and pushes this solution before it till the area of discharge is reached. If the soil were wet instead of dry, a much larger extract would be required to obtain all the chlorides and nitrates, as it would then be necessary to displace all the water present in the soil.

4. *Analysis of the Soil Extract.*

The watery extract obtained by the method just described is placed in a small basin, and evaporated nearly to dryness on a water-bath. The extract is usually acid to litmus, and when highly concentrated may be strongly so. I have usually made the solution slightly alkaline with lime-water before evaporation, but some test experiments with and without lime-water have not shown that this treatment is of any importance. The extract from an arable soil yields, when concentrated, a very small quantity of pale-brown syrupy liquid; a pasture soil, being much richer in organic matter, yields a much more considerable extract.

The extract from a soil which has been dried at a high temperature is much richer in organic matter, and apparently also in some saline constituents, than the extract from the same soil dried at a low temperature. Thus the extract (100 c.c.) from 300 grams of the soil dried in the water-oven (Experiment 1, Table I), gave a dry residue of 0.239 gram, while similarly prepared extracts from the soils dried at 10° and at 38°, gave only 0.107 and 0.104 gram, of solid matter. The temperature at which a sample of soil is dried thus considerably affects other ingredients besides the nitrates.

Two methods have been employed at Rothamsted in recent years for determining the quantity of nitric acid in soil extracts. The earlier determinations were made by the well known Crum-Frankland method, in which the concentrated fluid is introduced into a tube of special construction, mixed with $1\frac{1}{2}$ times its volume of concentrated sulphuric acid, and shaken with mercury, the resulting nitric oxide gas being then measured. Test experiments made with this method have been already communicated to the Society (*Trans. Chem. Soc.*, 1879, 375).

In applying this method to the analysis of soil extracts, it was soon found that the amount of soluble organic matter present was far too great, at least in the case of extracts from surface soils, for its convenient or accurate use; much froth was produced in the shaking tube, and the results obtained were proved to be below the truth. The effect of organic matter in diminishing the amount of nitric oxide obtained has been already pointed out in the communication just referred to.

Further experiments with soil extracts showed, however, that the greater part of the organic matter could be removed by treatment with alcohol. The mode of operation was to concentrate the watery extract from the soil to a small bulk, then add several times its volume of strong spirit, and filter. The bulky precipitate was well washed with spirit, and the filtrate and washings evaporated to dryness. The residue left had the appearance of a thin varnish; this was dissolved in a few drops of water and introduced into the shaking tube.

A later improvement consisted in the introduction of a single drop of dilute hydrochloric acid into the shaking tube before commencing the agitation; by this means the attack on the mercury is much intensified, and the evil influence of organic matter diminished. When using this small quantity of hydrochloric acid, no instance has occurred of a subsequent development of gas in the laboratory vessel of the gas analysis apparatus due to an incomplete reaction in the shaking tube.

To ascertain whether the organic matter in a purified soil extract had any influence on the result, test experiments were made. Extracts were prepared in the usual way from a pasture soil proved to contain no nitrates; to each of these extracts 10 c.c. of a solution of nitre were added; the extracts were then concentrated, purified with alcohol, and analysed with the addition of hydrochloric acid. In some cases the

TABLE III.—*Determinations of Nitric Acid by the Crum-Frankland Method. Nitre Solutions alone, and mixed with Soil Extracts.*

	Nitrogen found. Total gas reckoned as nitric oxide.
10 c.c. Normal Nitre Solution.	
1. Nitre only	1·362
2. Ditto	1·369
3. Ditto	1·370
4. Nitre evaporated with 1st extract from soil	1·354
5. „ added to alcohol extract	1·447
6. „ evaporated with 1st extract from soil	1·593
7. „ added to alcohol extract	1·569
8. „ evaporated with 2nd extract from soil	1·263
9. Ditto ditto	1·279
10. Ditto ditto	1·297
11. Nitre added to alcohol extract	1·330
10 c.c. $\frac{1}{4}$ Nitre Solution.	
12. Nitre evaporated with 2nd extract from soil	0·166
13. „ added to alcohol extract	0·234
10 c.c. $\frac{1}{8}$ Nitre Solution.	
14. Nitre added to alcohol extract	0·037

nitre was not evaporated with the original extract, but added to the residue left on evaporating the alcohol extract, any possible reduction of nitrates during the evaporation, or loss during treatment with alcohol, was thus avoided. In several of the experiments a second extract from the soil was made use of. The results will be found in Table III.

The normal nitre solution employed contained in 10 c.c. 1.388 mgrms. of nitrogen.

In the above results the whole of the gas obtained on shaking with mercury has been reckoned as nitric oxide; this, however, is not absolutely the case. When using the Crum-Frankland method in the presence of organic matter, any gas produced before shaking with mercury cannot safely be removed from the tube, as this gas may consist in great part of nitric oxide (*Trans. Chem. Soc.*, 1879, 383); indeed, in some soil extracts, rich in organic matter, two-thirds of the whole gas has been evolved before shaking. That some gas other than nitric oxide was produced, was proved on several occasions. Thus a soil extract precisely similar to that employed in Experiments 4 and 5, but without nitre, when shaken with sulphuric acid yielded gas which would have been reckoned as 0.051 mgrm. of nitrogen. Of the large gas obtained in Experiment 6, 0.257 mgrm. was found to be unabsorbed by ferrous chloride. There is no doubt therefore that the quantities of nitrogen calculated from the volumes of the gas are rather higher than those actually obtained.

In the experiments in which 10 c.c. of normal nitre solution were added to the soil extract, the nitrogen introduced was on the whole fairly recovered on analysis. The results are not nearly so good when we turn to the smaller quantities of nitre. In Experiment 13 about two-thirds of the nitrogen added is recovered on analysis, and in Experiment 14 less than one quarter; in both these experiments the reaction was pushed as far as possible, the solutions being heated in the shaking tube and reshaken. In the earlier investigation of the Crum-Frankland method, already referred to, the same fact appeared; a small quantity of nitric acid suffering a greater absolute loss from the presence of sugar than a large quantity. When applying the method to actual soil analysis, the same truth is manifest, an increase in the quantity of soil taken producing an increase in the percentage of nitric acid found when the soil is poor in nitrates.

The Crum-Frankland method having proved only partially satisfactory, trials were made with the method recommended by Schloesing for the determination of nitrates in organic extracts, namely, heating with ferrous chloride and hydrochloric acid, and collection of the nitric oxide evolved. A general investigation of this method has been already published (*Trans. Chem. Soc.*, 1880, 468); a description of

improvements recently adopted will be found in the present volume, pp. 345—350. The method has been found to yield excellent results in the presence of organic matter. With this method a few test-experiments with soil extracts have been made, the same soil being used as in the preceding series. The extracts were used without purification with alcohol. The results will be found in Table IV.

TABLE IV.—*Determinations of Nitric Acid by Schloesing's Method. Nitre Solutions alone, and mixed with Soil Extracts.*

	Nitrogen found as nitric oxide.
	milligrams.
1. Nitre only.....	2·713
2. „ evaporated with 1st extract from soil	2·699
3. „ added to extract after evaporation.....	2·691
4. „ only.....	1·325
5. „ evaporated with 1st extract from soil	1·325
6. Ditto ditto	1·376

The quantity of nitre solution employed in Experiments 4 to 6, was rather less than that used in the experiments quoted in Table III.

The results obtained are seen to be quite satisfactory, the known quantity of nitrate added being fully recovered on analysis; the organic matter present in the soil extract is, apparently, with this method entirely without effect on the result.

As the organic matter of soil has no influence, when the analysis is made by Schloesing's method, while it lowers the result, even after treatment with alcohol, when the Crum-Frankland method is employed, it follows that the same soil analysed by these two methods will give somewhat higher results by the former than by the latter; this has uniformly proved to be the case when duplicate determinations have been made. This fact will serve to explain the discrepant results found in Table I.

We have apparently in Schloesing's method a really satisfactory means of determining nitrates in soil. The soil extract requires in this case no preliminary purification, but may be analysed as soon as concentrated. The method is equally capable of determining large or small quantities of nitric acid, while the amount of nitric oxide produced is ascertained with the greatest precision by gas analysis. Full details respecting the conduct of this method will be found in the papers above referred to.

The indigo method for determining nitric acid is quite unsuitable for soil analysis. In an earlier communication (*Trans. Chem. Soc.*, 1879,

588) some comparative determinations by the indigo and Crum-Frankland methods were given; I may here add a few comparative determinations by the indigo and Schloesing methods of the nitrates in an arable soil, showing that the indigo method fails even in the analysis of the extract from a clay subsoil. The figures represent the nitrogen existing as nitrates per million of soil.

	Schloesing's method.	Indigo method.
First 9 inches from surface.....	8·08	5·18
Second „ „	4·98	3·78
Third „ „	2·66	2·03

The nitric acid shown by indigo is in the first 9 inches 64·1 per cent., in the second 9 inches 75·9 per cent., and in the third 9 inches 76·3 per cent. of the truth, the result improving somewhat as the amount of organic matter diminishes.
