volved in perfecting this method of carbon combustions, and its success is largely due to his careful work, for which I sincerely thank him. I also wish to thank Mr. F. Cooper Pullman for his assistance in working up the electric spark as an oxidant.

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SOIL HUMUS. SOME SOURCES OF ERROR IN ANALYTICAL METHODS.

BY A. L. EMERY.

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DURING the past four years we have devoted considerable time in our laboratory to the analysis of California and Hawaiian soils for the purpose of determining the kind of fertilizer best adapted for each separate piece or tract of land. The analytical methods of Dr. E. W. Hilgard have been generally followed in our work and good results have been secured with the exception of the determination of humus and nitrogen in the humus. In order for a method to be practical for industrial work it must be rapid as well as accurate. Time is a very important factor. Many samples of soils require several days' leaching to free them of calcium salts and several days more for the extraction of the humus.

About two years ago while working with one of these slowly leaching soils it was observed that the caustic potash solution of humus was strongly ammoniacal. A slightly ammoniacal solution is, of course, unavoidable, for caustic alkalies will liberate the ammonia present in the form of ammonium salts and also readily decompose some of the weaker compounds of amid nitrogen. But where the time of leaching extended over several days more ammonia was apparently liberated, than was originally present in the form of these easily decomposed salts. Other work prevented further investigation at that time, and the subject was not taken up again until this winter when the rush of soil samples to the laboratory almost compelled experimenting with humus with a view of finding a more rapid method. During these experiments some interesting results developed.

Several samples of soil, washed free of calcium salts with dilute hydrochloric acid, were leached with a 4 per cent. solution of caustic potash. In the course of a few hours, varying with the richness of the sample in nitrogen, a piece of red litmus suspended in the mouth of the flask containing the leached solution would turn blue in ten or fifteen minutes. The same solutions, after standing twenty-four hours, would liberate enough ammonia to turn the litmus blue in about five minutes, and after standing several days the change of color was very quick. In several cases the ammonia could even be detected with the nose. From 5 to 10 grams of soil were used for leaching.

The above being true, it follows that the determination of nitrogen in the caustic potash extract is always too low by the amount of nitrogen lost in the form of ammonia. This loss apparently depends on the nature of the soil sample, the time occupied in leaching, and the care taken to prevent the ammonia escaping from the leaching apparatus. Therefore, since the nitrogen in the caustic potash extract is too low, it follows that the nitrogen in the humus would also be too low. This loss of ammonia doubtless partly explains the great liability of duplicate results of the determination of nitrogen in humus to disagree, and more particularly accounts for the variation in results by different analysts.

By Dr. Hilgard's method[1] humus is determined by evaporating the solution, leached from calcium-free soil with dilute ammonia, drying to constant weight, igniting, and weighing. The difference in weight is regarded as humus.

During the process of evaporation the ammoniacal humus solution undergoes digestion at the temperature of the water- or steam-bath. Either during this digestion or during the leaching process (probably during both), ammonia is absorbed from the leaching solution and enters into stable combination with the humus extract. The free ammonia is easily expelled by evaporation, but the humus residue left in the platinum dish after being dried at 100°, or even 110° C., retains part of the ammonia at least that it has taken into combination from the leaching solution. This added ammonia is easily expelled with lime or magnesia, but not all the nitrogen of the residue is thus driven off even with dilute caustic potash. The following analyses will illustrate this point:

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[1] Wiley's "Agricultural Analysis," Vol. I, p. 324, § 311.

Total nitrogen in soil by direct determination. Gunning method.[1] Per cent.	Humus. Per cent.	Nitrogen in humus extracted with caustic potash. Per cent.	Nitrogen in humus extracted with NH_3, evaporated and dried at 100° C. Per cent.
0.159	1.860	0.67	0.97
0.097	0.775	4.39	9.39

It was at first thought that the difference in the per cent. of nitrogen in the caustic potash extract and the ammonia extract represented the loss of nitrogen in the form of ammonia during the extraction with caustic potash, but it was found that a similar difference existed when the utmost care was exercised to prevent the escape of ammonia from the caustic potash solution, both during and after leaching.

These results led to the analysis of the soil residues which had been leached with caustic potash and those which had been leached with ammonia. *Approximately 50 per cent. of the total nitrogen originally present remained in the soil after leaching with caustic potash.*

Total nitrogen in soil. Per cent.	Nitrogen left in soil after leaching with caustic potash. Per cent.
0.159	0.097
0.132	0.066
0.097	0.038

The average of the second column of figures is very close to 50 per cent. of the first, or the total nitrogen in the soils. Present data is insufficient to determine whether this ratio is true for soils taken from all parts of the state. The above samples and others showing similar agreement are mostly from the Santa Clara valley.

After leaching with ammonia and drying the soil residue at 100°C. or distilling the residue until the distillate was neutral to litmus paper, from a little over ½ to 1½ the amount of total nitrogen originally present in the soil was found in the residue. Results seemed to vary somewhat with the time occupied in expelling the free ammonia from the soil residue by heat, the

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[1] Ten grams of soil may be readilv digested by this method.

distillation method giving slightly higher results than by drying at 100° C. This might have been expected since the conditions of the two processes are not exactly the same. One sample of Hawaiian soil containing 0.812 per cent. total nitrogen took up 0.430 per cent. of nitrogen from a 2 per cent. ammonia solution by digestion at the room temperature over night and retained it at 100° C. This gave a total nitrogen of 1.242 per cent.

These results seem to strongly indicate that the organic or mineral constituents of the soil left on the filter have the power to absorb ammonia from the leaching solution during the process of leaching to a far greater extent than has heretofore been supposed. It seemed highly probable that the soluble organic compounds in the extract, called humus extract, would also have this power of taking ammonia from the leaching solution. This point was demonstrated in the following manner: Five grams of soil, washed free of calcium salts, were distilled with lime and the nitrogen in the distillate determined. Then five grams of the same soil were extracted with ammonia after removing the calcium and magnesium salts according to Dr. Hilgard's method. The free ammonia was expelled from the extract by evaporating to dryness and the resulting residue distilled with lime and the nitrogen determined in the distillate. This was repeated with a number of samples and while the results seemed to vary considerably yet more nitrogen was invariably obtained from the ammonia extract distilled with lime, than from the soil distilled with lime. In the first case, that is where the soil was distilled with lime, it will be noted that the organic compounds which are insoluble in dilute caustic alkalies as well as the soluble ones were subjected to the action of lime in hot solution. Since lime will decompose some of these insoluble nitrogenous compounds it follows that more nitrogen should have been obtained in the first case than in the second had not the soluble organic compounds, leached from the soil, taken up nitrogen in the form of ammonia from the ammoniacal leaching solution. Hence, we conclude that Dr. Hilgard's method gives too high results for humus by the amount of ammonia taken up from the leaching solution and held in combination by the extracted organic matter.

Now, since nitrogen in the humus is determined by dividing the nitrogen in the caustic potash extract, which is too low, by the humus, which is too high, the error would be multiplied and the result would be invariably too low. That this error is quite large and not to be neglected is clearly shown by the figures given above.

By a slight modification of the method the ammonia can be prevented from escaping during leaching with caustic potash. The following method seems to overcome all difficulties : The soil to be leached with caustic potash is placed in a funnel which is closed at the top with a stopper through which the leaching solution is admitted by a separatory funnel. The glass support of a Gooch crucible serves very well for the funnel holding the soil. The solution from the soil is run directly into dilute sulphuric acid, the bottle containing the same being sealed with a U-tube containing sulphuric acid. Gentle suction can be applied to this apparatus which greatly hastens the process without the least danger of losing ammonia.

It is more difficult to correct the second source of error; *i. e.*, the absorption of ammonia by the organic matter extracted from the soil. No very satisfactory results have been obtained although considerable time has been devoted to the matter.

Before leaching the soil for the extraction of the humus, it is washed with dilute hydrochloric acid until the filtrate shows no reaction for calcium. It is well known that the organic acids of soils form single and double salts with the alkali earths and with the oxides of some metals. Calcium is a stronger base than ammonia ; therefore, an acid that would liberate calcium ought also to liberate ammonia from these double insoluble salts. We had supposed that this hydrochloric acid solution contained practically only the nitrates and nitrites present in the soil which would be worth considering only in exceptional cases.

Total nitrogen in soil.	Total nitrogen leached out with hydrochloric acid.	Nitrogen leached out with hydrochloric acid which is liberated with lime.
Per cent.	Per cent.	Per cent.
0.159	0.037	0.011
0.812	0.049	0.036

The above results show that it is not safe to assume the insolubility of organic matter and organic salts even in very dilute hydrochloric acid. We believe this also may be a source of no insignificant error in soil analysis.

It would be interesting to know whether the organic matter of soils of humid regions show the same tendency to absorb ammonia in such relatively large amounts as the soils that we have examined. This absorption of ammonia seems to take place at ordinary temperature as well as in hot solutions. The rate or maximum amount of absorption has not yet been determined. Hitherto we have regarded free ammonia as being occluded in the soil but it now seems highly probable that one of the functions of the organic matter of the soil is to absorb the free ammonia which comes to it in solution and that which is liberated in the soil itself. Possibly in nature occlusion precedes and directly aids absorption and combination.

Regarding the nature of humus little seems to be really known. If humus is regarded as the organic matter and mineral salts of organic acids extracted from soils by means of dilute alkalies we have to deal undoubtedly with a highly complicated mixture of chemical substances in various stages of decomposition and combination. Many organic nitrogenous substances are soluble in dilute alkalies without having undergone a process of decomposition. This is true of the organic matter of plants as well as that of animals. Sun-dried grass, weeds, or wood, according to the generally accepted idea of the term, would not be regarded as humus. Yet, 27.30 per cent. of a sample of clover meal dissolved in 25 cc. of a 5 per cent. solution of ammonia at room temperature by standing over night. The undissolved portion contained 2.94 per cent. nitrogen. Providing this residue took up no free ammonia from the solution, which is doubtful, 35.76 per cent. of the total nitrogen of the clover meal was readily soluble and probably more would have been dissolved had the leaching process been used.

This is more or less true of other organic substances which find their way into soils and form a part of them. While clover meal may be an excellent fertilizer much of it would, nevertheless, have to be regarded as humus by the present methods of analysis. In fact in many respects clover meal extract acts as humus is supposed to act. Part of it forms insoluble salts with calcium and is precipitated with alcohol.

If a soil be boiled with an excess of calcium or barium salts and the soil afterwards extracted with ammonia the filtrate will usually have a color closely matching that of dilute ferric chloride. If the same soil is then leached with hydrochloric acid and again leached with ammonia, the resulting solution will have a much darker color which is often almost black. Yet barium or calcium salts precipitate the organic matter in the caustic potash soil extract, leaving an almost colorless supernatant liquid. The precipitation is not quantitative.

Further experiments are already under way in the laboratory and we hope to have further data of interest in regard to humus and soil analyses in connection with field experiments with fertilizers.

CHEMICAL LABORATORY OF N. OHLANDT & CO.,
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LECTURE EXPERIMENTS. REVERSIBLE CHEMICAL REACTIONS.

BY W. LASH MILLER AND F. B. KENRICK.

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LECTURES on physical chemistry are, at present, less in need of experimental illustration than those on any other branch of the science, being delivered, for the most part, to small classes of advanced students, who have ample opportunity for experimenting in the laboratory. Some of the conceptions and discoveries which form the subject-matter of that department have, however, proved of such importance, that it is very desirable to incorporate them into the elementary course. This has hitherto been rendered difficult by the lack of suitable lecture experiments.

Among the most important of these discoveries, is that of the *incompleteness* and *reversibility* of a very large number of chemical reactions. The application of thermodynamical methods in the treatment of such cases is an achievement of the present day, and necessarily forms one of the chief subjects of study of advanced classes. The "average student," however, whose practical acquaintance with chemistry is limited to a course in