# NOTES ON THE GRANDEAU METHOD FOR THE DETERMINATION OF HUMUS IN SOILS.

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THE Grandeau method for the determination of humus in soils, without some modifications, is open to serious objections: (1) It is difficult to obtain a complete extraction of the humus materials with ammonia, as ordinarily carried on, especially when the soil is very fine and of a clayey nature. (2) The filtration is frequently so slow that a week is sometimes required before the filtrate becomes clear. (3) During all of this time the laboratory is so filled with fumes of ammonia as to seriously interfere with other lines of work.

To say the least, the present method is slow, cumbersome, and gives unsatisfactory results with many kinds of soils. The author has had in use during the past year, a few simple modifications, that have given good results.

After treatment with the dilute acid, the soil is transferred to either a glass-stoppered bottle, or a glass-stoppered Erlenmeyer flask of 100 cc. capacity, using fifty or sixty cc. of the dilute ammonia solution for that purpose. The contents of the bottle or flask are then well shaken at frequent intervals, and then allowed to settle. After settling, the dark colored solution is decanted into a filter, a fresh fifty cc. portion of the dilute ammonia solution is then added to the flask, and the same treatment repeated. It usually requires three or four such treatments before the filtrate becomes clear; the contents of the flask are then brought on to the filter, and require but little farther washing in the usual way before this part of the operation is completed. While the second, third, and fourth treatment with the ammonia is being carried on, the first portion of the filtrate can be evaporated on the water bath, and thus save time when that part of the operation is reached. The most progress can be made by making as large a number of determinations at one time as a person can conveniently take care of, so as not to unnecessarily hurry the operations, nor loose too much time in

making the humus determinations of the soil. A separate room for such work is a great convenience.

The results obtained by this method of treatment are much higher than those obtained when working in the usual way. This is to be expected, inasmuch as more complete extraction of the humus materials are obtained by using the glass-stoppered flasks. Duplicate results with the ordinary Grandeau method are far from being concordant, while with the glass-stoppered flasks reasonably concordant results are secured.

The Grandeau method for the determination of humus, when properly carried out, is capable of giving results that are of practical agricultural value. The examination of a few typical cases out of over a hundred samples of soil examined in the laboratory of the Minnesota Experiment Station, during the past two years, will show that the results obtained by the modified Grandeau method are well worth all of the time and labor that has been spent. Before examining the results, two points are to be noted:

*First.* There are many other organic compounds of equal agricultural value that are not included in the ammonia extract. Take for example any of the soils that show from ten to fifteen per cent. of volatile matter. The combined water, carbon dioxide, and humus, as well as volatile mineral matters account for sixty to seventy-five per cent., only, of the volatile material, leaving twenty-five per cent. of the volatile organic materials not accounted for. These organic materials, may, in time, become soluble in the ammonia solution, and finally be classed as humus materials. The Grandeau method gives us no idea of the extent to which these organic substances may be present in the soil.

*Second.* Along with the humus soluble materials are variable amounts of phosphoric acid. A careful study of the total phosphates, humus and phosphates soluble with the humus fails to indicate any chemical combination between the humus and the ammonia soluble phosphates. At this point another serious difficulty presents itself: Some soils which are rich in both phosphoric acid and lime, will give up some of their phosphoric acid to the dilute hydrochloric acid solution

that is first used to remove the lime. This appears to be quite prominent with some of the native soils that are particularly rich in total phosphates, humus, and lime. The analyses of many of these soils showed that the phosphates soluble in the dilute ammonia, and supposed to be in combination with the humus as available phosphoric acid, was less, in many soils, even when the humus was found to be high, than in other soils that were known to be far less fertile. A repetition of the work showed that the dilute hydrochloric acid used in removing the high percentages of lime, also removed a large portion of the phosphates that would have been soluble in the ammonia. Is not this phosphoric acid equally as valuable, agriculturally, as that soluble in the dilute ammonia? Qualitative tests can easily be made of the hydrochloric acid washings, to determine the presence or absence of phosphates.

In the native soils there is quite a close relation between the humus, as determined by the modified method, and the total nitrogen. The table given, shows the amounts of humus and nitrogen, as well as the ratio between the two, in a number of native soils, and soils that have been cultivated for various periods without the use of fertilizers. The volatile matter given includes both the total organic matter and the combined water, the carbon dioxide, hydroscopic moisture, etc., having been separately determined and subtracted from the total volatile matter.

RATIO OF NITROGEN TO HUMUS.

| Description of soil. | No. of soil. | Total volatile per cent. | Humus per cent. | Total nitrogen per cent. | Ratio. |
|---|---|---|---|---|---|
| Virgin soil | 203 | 15.55 | 5.34 | 0.38 | 13.97 |
| 10 years cultivation | 298 | 5.58 | 3.02 | 0.25 | 12.10 |
| Virgin soil | 202 | 8.10 | 5.16 | 0.41 | 12.60 |
| 10 years cultivation | 236 | 5.48 | 2.87 | 0.21 | 13.60 |
| Virgin soil | 272 | 14.29 | 5.16 | 0.39 | 13.23 |
| 8 years cultivation | 309 | 9.67 | 3.16 | 0.25 | 12.60 |
| 6 " " | 224 | 10.90 | 5.12 | 0.38 | 13.20 |
| Native prairie | 224 | 12.05 | 4.04 | 0.37 | 10.91 |
| 10 years cultivation | 312 | 8.15 | 2.60 | 0.22 | 11.80 |
| 6 " " | 249 | 11.50 | 4.92 | 0.41 | 12.00 |
| 10 " " | 208 | 7.13 | 2.68 | 0.24 | 11.18 |
| 8 " " | 210 | 4.04 | 3.02 | 0.24 | 12.60 |

| Description of soil. | No. of soil. | Total volatile per cent. | Humus per cent. | Total nitrogen per cent. | Ratio. |
|---|---|---|---|---|---|
| 10 years cultivation..... | 257 | 8.68 | 2.48 | 0.19 | 13.10 |
| 15 " " ..... | 234 | 6.47 | 2.48 | 0.20 | 12.40 |
| 3 " " ..... | 220 | 12.40 | 4.17 | 0.37 | 11.28 |
| 3 " " ..... | 218 | 6.56 | 3.73 | 0.30 | 12.43 |
| 20 " " ..... | 261 | 8.73 | 2.84 | 0.26 | 11.31 |
| 30 " " ..... | 279 | 8.31 | 1.80 | 0.16 | 11.25 |
| 40 " " ..... | 242 | 7.04 | 2.41 | 0.21 | 11.50 |
| 6 " " ..... | 222 | 10.33 | 3.42 | 0.28 | 13.00 |
| 18 " " ..... | 269 | 9.44 | 3.91 | 0.34 | 11.50 |
| 25 " " ..... | 290 | 3.54 | 2.27 | 0.17 | 13.35 |
| 6 " " ..... | 273 | 8.13 | 4.18 | 0.37 | 11.33 |
| 18 " " ..... | 249 | 7.94 | 2.04 | 0.17 | 12.00 |

There is, on the average, about twelve parts of humus in the soil, as determined by the method given, to every one part of nitrogen. In the long cultivated soils which have received no fertilizers, the nitrogen and the humus have decreased in about the same ratio. The losses and relationships are not in strict accordance to a mathematical ratio, but it is sufficient to show that there is a relationship between the humus and the nitrogen in a virgin soil, and in soils which have been cultivated without the use of fertilizers.

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## NOTES.

*The Opening of the Kent Chemical Laboratory of the University of Chicago.*—In response to invitations sent out by the authorities of the University of Chicago to the chemists throughout the country to be present at the formal opening exercises of the Kent Chemical Laboratory, January 1 and 2, 1894, about fifty chemists assembled in the auditorium of the laboratory, at two o'clock P. M., January 1. It was proposed that the first meeting should be a conference of teachers of chemistry. President Harper delivered a brief address of welcome and closed by saying that Prof. Remsen had consented to act as chairman of the conference—Prof. Remsen then took the chair and after a few introductory remarks introduced Prof. Paul C. Freer, of the