APPLICATION NOTE

Elemental Analysis

Organic Elemental Analysis of Soils – Understanding the Carbon-Nitrogen Ratio

Introduction

Understanding the health of the soil in which crops grow is fundamental in ensuring healthy yields. Two elements that are essential to this are Carbon and Nitrogen, especially in their proportion to each other. This relationship is called the Carbon-Nitrogen or CN ratio. This ratio is relatively simple to understand. If soil is made up of 30% Carbon and 2% Nitrogen then the CN ratio is 15 to 1. Carbon is important because of it's energy content in the form of species such as carbohydrates, whereas Nitrogen is essential for growth. Average CN ratios vary from country to country depending on the predominant soil type, but a value between 8 and 17 is typical.[1] Fertilizers, which are added to soils to regulate the CN ratio, should also be considered. When organic matter is added to soil the breakdown of the content by bacteria and fungi causes changes in the CN ratio. It is important that any fertilizer added has sufficient nitrogen levels or the addition will have a negative effect. The addition of composted manure, which typically has a CN ratio of about 20:1, is desirable however the addition of sawdust, which has a high CN ratio of 400:1, could be disastrous.[2] The microorganisms that break down the organic matter will very quickly run out of Nitrogen and therefore will start to consume the Nitrogen in the soil. This reduces the amount available to the plants and therefore depresses crop yield. In addition to these, both Carbon and Nitrogen can be further broken down into organic and inorganic subsections. Carbon in particular is often quoted as TOC, total organic Carbon, and TIC, total inorganic Carbon. TOC takes into account all the Carbon from such sources as decaying vegetation or bacterial growth. TIC includes all Carbon remaining so Carbon in the form of carbonates and bicarbonates, for example.

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These percentages can be ascertained by two techniques: Kjeldahl and Dumas. Kjeldhal methods involve time consuming and often complicated wet chemistry techniques, whereas Dumas is a simple combustion procedure. Dumas organic elemental analyzers involve combusting the soil matter in the presence of Oxygen into simple molecules or gases such as CO_2, H_2O and N and then separating these gases using chromatography techniques. The PerkinElmer® EA2400 CHNS/O and EA2410 Protein Analyzers are classic examples of these instruments utilizing combustion reagents and TCD, thermal conductivity detection, to give high accuracy and precision results.[3] In the case of the EA2400, the Carbon/Nitrogen percentages are outputted to database software whereby the CN ratio can be calculated automatically. If the TOC value is desired, then acidification of the sample can be carried out to remove the inorganic Carbon species before combustion.

Furthermore as:

TC = TIC + TOC (1)

knowing the total Carbon and the organic Carbon (i.e. Carbon percentage of acidification) allows calculation of total inorganic Carbon.

Experimental

All samples were dried at 80 °C prior to analysis. Each sample was placed in a tared large tin capsule (PerkinElmer, N2411362) and precisely weighed using a PerkinElmer AD6 Autobalance. Samples ranged in weight from 10 to 80 mgs. Due to the high mineral content of the soils, the standard vial receptacle (N2411335) was replaced with the quartz tube insert (N2411401) to prevent devitrification of the quartz combustion tube. All samples except the final batch were run on an EA2400 CHNS/O Elemental Analyzer with other samples being run on the EA2410 N Nitrogen Analyzer.

To ensure complete combustion of the organic matter was achieved, the following optimized combustion conditions were adhered to and are shown in Table 1:

Table 1. **Optimized combustion times for soil analysis.**

Optimize Combustion	Time (Sec.)
Oxygen Full	3
Combustion Time	20
Oxygen Boost 1	2
Oxygen Boost 2	1

Analysis time for the EA2400 measurements were around 5 mins, those for the EA2410 were approximately 4 mins. For these experiments the following samples were chosen: silt loam soil, fallow field soil, CANMET reference soils and USDA reference soils.

Results and discussion

1. Silt loam soil

Weight percentages quoted in Table 2 are for the average of three runs, with the first row showing the results of the as received samples and the second row showing the results after acidification using either hydrochloric or phosphoric acid.

Table 2. **Elemental percentages of silt loam soil as an average of 3 runs before and after acidification.**

		Average	Weight	%
Sample	**Weight (mgs)**	**C**	**H**	**N**
As Received	20-80	2.33	0.97	0.19
As Acidified	30-40	2.24	0.99	0.19

These results give us two important facets of information. Firstly, we can ascertain that the CN ratio is 12 to 1 (12.26) which, as stated previously, is the range which is common for soils. Secondly, we can see that the total inorganic Carbon content is low. The data gives a TIC of only 0.09%, whereas the TOC is 2.24%. The high organic content is encouraging for growing crops.

2. Fallow agricultural field soil

Two measurements were undertaken from a field that had been left fallow for one year prior to measurement. The results are presented in Table 3:

Table 3. **Elemental percentages for fallow field soil for 2 runs.**

		Average	Weight	%
Run	**Weight (mgs)**	**C**	**H**	**N**
1	30.41	1.25	0.54	0.11
2	50.75	1.21	0.56	0.10

The results show that there is very little organic content in the samples. This is as expected as the lack of plant life in the prior year would lead to a lack of humus and therefore organic content. Once again the CN ratio is 12 to 1 (11.71).

3. Canadian Centre for Mineral and Energy Transfer (CANMET) reference soils

Variation in soil type is also an important feature to study. For instance, soils from Savannah, Georgia have typically high organic contents (C = 3.70-17.5%) whereas in Florida, where soils are typically sandier, the organic content is much lower (C = 0.18-0.58%). To investigate, these three soil types were run and compared to reference values to confirm accuracy. The results are shown in Table 4 with the EA2400 data being an average of 5 runs.

Table 4. **Elemental percentages for 3 soil types averaged over 5 runs and compared to reference values.**

		EA2400	Weight	%	CAN.	Ref.	Values
Sample	**Weight (mgs)**	**C**	**H**	**N**	**C**	**H**	**N**
1	10-50	0.31	0.52	0.04	0.25	0.52	0.04
2	4-25	4.78	0.72	0.20	4.80	0.73	0.22
3	4-25	6.63	0.14	0.03	6.60	0.15	0.02

Sample 1 – Champlain sea clay; Sample 2 – ferro-humic podzol; Sample 3 – gray brown luvisol.

The samples were interesting due to their varying CN ratios. In the case of podzols, this variation is due to leaching of nutrients by rain water resulting in soil that is poor for agriculture. The results show that the sea clay has a CN ratio of 8:1 (7.75), the podzol has a ratio of 24:1 (23.9) and the luvisol has the highest ratio of 221:1. These values were checked against reference values supplied by CANMET, indicating that experimental results were in agreement. It should be noted that due to the low organic content of the sea clay a larger sample was used.

4. U.S. Department of Agriculture (USDA) reference soils

Samples from the USDA were also tested, this time using the EA2410 Nitrogen Analyzer. The measurement was purely for Nitrogen, but as the CN ratio was know to be 10:1 the Carbon values could also be calculated. The results are shown as an average of 3 runs in Table 5.

Table 5. **Elemental percentages for USDA samples averaged over 3 runs and compared to reference values.**

		EA2410	USDA Ref.
Sample	**Weight (mgs)**	**%N**	**%N**
1	10-50	0.24	0.23
2	10-50	0.41	0.39
3	10-50	0.15	0.13

The results indicate excellent synergy with the reference values. Using the CN ratio of 10:1 it can be calculated that Carbon values are approximately 2.4%, 4.1% and 1.5%.

Conclusion

The EA2400 CHNS/O Analyzer is shown to be a powerful tool for the analysis of soil samples of varying organic contents. It is shown that along with CN ratios, TOC and TIC measurements can also be performed to a high level of accuracy. It has also been shown that the EA2410 Nitrogen analyzer can also perform Nitrogen measurements on soil to high levels of accuracy.

References

1. Alistair F. Pitty, Geography and soil properties, Taylor & Francis, 1979.
2. Crow Miller, Understanding the Carbon-Nitrogen Ratio, 2000, **30**, Issue. 4, Pg. 20.
3. Robert F Culmo et al., Methods of Organic Nitrogen Analysis: Kjeldahl and the EA2410 N Analyzer (Dumas Method), PerkinElmer publication EAN-8.

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