Elemental Analysis: N, NC, CHNS/O and TOC characterization of sewage sludge by the Flash*Smart* Elemental Analyzer

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Keywords

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Goal

Demonstrate the performance of the Thermo Scientific Flash*Smart* EA for the characterization of sludge samples.

Introduction

Sludge is a semi-solid slurry and can be produced as sewage sludge from wastewater treatment processes or as a settled suspension obtained from conventional drinking water treatment and numerous other industrial processes. Sewage sludge are rich in nutrients as nitrogen, organic matter and trace elements which are important of plants growth and better yield. Sewage sludge is also considered a substitute for commercial fertilizers, allowing a decrease in its use in agronomy. The organic carbon in sludge amended soil can increase as far as three fold compared to inorganic fertilizers amended soils. Application of sludge improves the properties of soils increasing the humus content of soils. Treated sewage sludge can enrich soils with macronutrients such as phosphorus, potassium, sulfur, calcium, magnesium and micronutrients. Sewage sludge is reliable source of nitrogen for plants, since it is a constituent of all proteins and nucleic acid and therefore protoplasm.

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For the agricultural use of sewage sludge as fertilizer, nitrogen represents the main element to be monitored, followed by total carbon, total organic carbon and sulfur.

Since traditional methods are no longer suitable for routine analysis, due to their time consuming preparation and the use of environmentally hazardous reagents, an accurate instrumental analytical technique is required. As the demand for improved sample throughput, reduction of operational costs and minimization of human errors is becoming every day more notable, a simple and automatic technique which allows fast analysis with an excellent reproducibility is the key for efficient element determination.

The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1), based on the dynamic combustion of the sample, provides automatic and simultaneous CHNS determination in a single analysis run and the oxygen determination by pyrolysis in a second run. The Flash*Smart* Elemental Analyzer is equipped with two totally independent furnaces allowing the installation of two analytical circuits, that can be used sequentially and are completely automatic through the Thermo Scientific™ MultiValve Control™ (MVC) Module. Each analytical circuit accepts its own autosampler. Besides, the Analyzer can determine simultaneous NC or only nitrogen by a double reactors system: first reactor for combustion and catalytic oxidation of the combustion gases, the second is used to reduce nitrous oxides as N_2. In this way the system copes effortlessly with the laboratory requirements such as modularity, accuracy, day to day reproducibility and high sample throughput.

Figure 1. Thermo Scientific Flash*Smart* Elemental Analyzer.

This application note reports data on N, NC, CHNS/O and TOC determination of sewage and sludge, and demonstrates the performance of the Thermo Scientific Flash*Smart* EA for quality control applications.

Methods

The Flash*Smart* Elemental Analyzer operates according to the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor via the Thermo Scientific™ MAS Plus Autosampler with oxygen.

For only nitrogen determination, after the combustion, the produced gases are carried by helium flow to a second reactor filled with copper, then they are swept through a CO_2 and H_2O traps, a GC column and finally detected by a Thermal Conductivity Detector (TCD) (Figure 2).
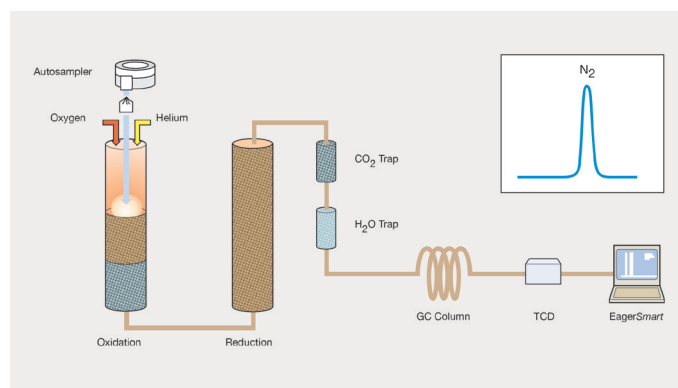

Figure 2. Nitrogen configuration.

For NC determination, after the combustion, the produced gases are carried by helium flow to a second reactor filled with copper, then they are swept through a H_2O trap, a GC column and finally detected by a Thermal Conductivity Detector (TCD) (Figure 3).
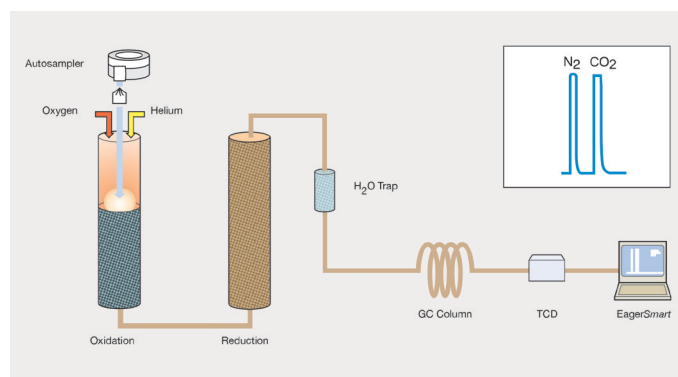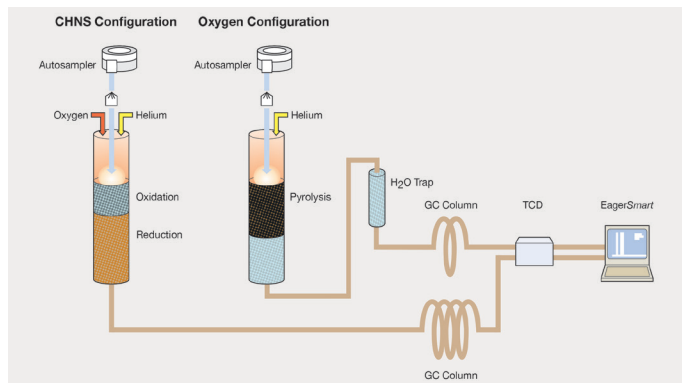

Figure 3. NC configuration.

For CHNS determination, after combustion the resulted gases are carried by a helium flow to a layer filled with copper, then swept through a GC column that provides the separation of the combustion gases, and finally, detected by a Thermal Conductivity Detector (TCD) (Figure 4).

Figure 4. CHNS/O Configuration.

For oxygen determination, the system operates in pyrolysis mode. Samples are weighed in silver containers and introduced into the pyrolysis chamber (right furnace) via the MAS Plus Autosampler. The reactor contains nickel coated carbon maintained at 1060 °C. The oxygen in the sample, combined with the carbon, forms carbon monoxide which is then gas chromatographically separated from other products and detected by the TCD detector (Figure 4).

A complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software and displayed at the end of the analysis.

Results

Several sludge samples from waste treatment plants were analyzed by Flash*Smart* EA using different configurations. In most of the cases, sludge samples were dried.

For nitrogen only determination, the system was calibrated with 10 – 15 mg of atropine standard using K factor as calibration method, the weight of dried sewage sludge was 20 – 30 mg for samples 1 to 3. For samples 4 and 5, 50 – 60 mg aspartic acid was used for calibration and sample 4 was weighed at 240 – 260 mg and sample 5 was weighed at 150 – 170 mg. Table 1 shows the data obtained analyzing the samples in triplicate.

Table 1. Nitrogen data of dried sewage sludge.

Sample	N%	RSD%
1	4.245 4.226 4.220	0.308
2	2.330 2.374 2.322	1.193
3	4.140 4.134 4.149	0.182
4	0.770 0.766 0.769	0.271
5	1.074 1.064 1.066	0.496

Also liquid sludge samples were analyzed in only nitrogen configuration. The calibration was performed with 5 – 10 mg atropine standard using K factor as calibration method. Samples were adsorbed on Chromosorb and the weight was 50 – 60 mg. Table 2 shows the nitrogen data obtained analyzing the samples in triplicate.

Table 2. Nitrogen data of liquid sludge.

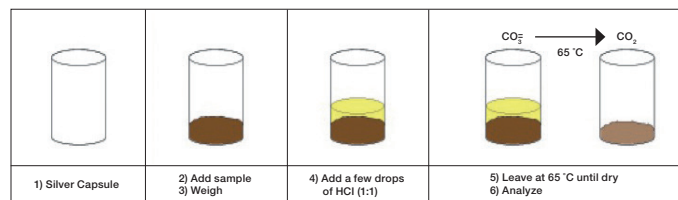| Sample	N%		
A	0.17	0.17	0.17
B	0.19	0.19	0.20
C	0.21	0.21	0.21

For NC determination, the system was calibrated with 4 – 5 mg of acetanilide standard using K factor as calibration method, the dried sludge samples 1 – 5 were weighed at 5 – 6 mg for samples, sample 6 was weighed at 100 – 110 mg. Table 3 shows the data obtained analyzing the samples in triplicate.

Table 3. Nitrogen data of dried sewage sludge.

Sample	N%	RSD%	C%	RSD%
1	11.468 11.425 11.449	0.190	58.104 58.179 58.122	0.068
2	3.492 3.504 3.486	0.270	31.067 30.937 31.091	0.267
3	4.053 4.103 4.097	0.662	31.147 31.338 31.139	0.362
4	4.615 4.626 4.603	0.246	36.761 36.869 36.816	0.147
5	2.385 2.312 2.395	1.906	25.162 25.127 25.313	0.391
6	0.0278 0.0275 0.0276	0.553	1.462 1.393 1.392	2.831

Other two dried sewage sludge samples were analyzed for NC and TOC determination. The system was calibrated with 4 – 5 mg of aspartic acid standard using K factor as calibration method. Sample 1 of dried sludge was weighed at 4 – 5 mg. Sample 2 was weighed at 40 – 50 mg. For TOC determination, sample 1 was weighed at 3 – 4 mg and sample 2 at about 15 – 20 mg.

The differentiation of Total Carbon (TC) and Total Organic Carbon (TOC) was performed by sample manipulation prior to analysis following the Official Italian Method on Soils Analytical Chemistry, Method 248 (Gazzetta Ufficiale). TOC was determined after removing carbonates by acidification of the sample with HCl 1:1 (Figure 5) using the kit showed in Figure 6. The analyses TC and TOC were performed consecutively using the same analytical conditions of the instrument. Table 4 shows the NC and TOC values obtained analyzing the samples in triplicate.

Figure 5. Method for TOC determination.

Figure 6. Kit for Total Organic Carbon (TOC) for solid samples.

Table 4. NC and TOC data of dried sewage sludge.

Sample	N%	RSD%	C%	RSD%	TOC%	RSD%
1	6.044 6.052 6.102	0.518	36.532 36.372 36.595	0.315	34.271 33.922 34.167	0.525
2	0.670 0.666 0.673	0.524	4.476 4.476 4.429	0.608	4.166 4.136 4.148	0.364

For CHNS/O determination, three dried sewage sludge samples were analyzed. For CHNS analysis, the instrument was calibrated with 2 – 3 mg BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene) using K factor as calibration method. Samples were weighed at 3 – 4 mg.

For oxygen determination, the system was calibrated with 1 – 2 mg of benzoic acid, Samples were weighed at 1 – 2 mg. Table 5 shows the NCS data obtained analyzing the samples in triplicate.

Table 5. CHNS/O data of dried sewage sludge.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%	O%	RSD%
1	3.8788 3.8220 3.8294	0.8034	26.6298 26.4631 26.6135	0.3459	4.5335 4.5342 4.5208	0.1665	1.0472 1.0459 1.0643	0.9757	22.9644 23.0424 22.9368	0.2383
2	0.7037 0.7005 0.7021	0.2279	59.4515 59.6610 59.3018	0.3034	4.8871 4.8825 4.8911	0.0881	0.2942 0.2927 0.2904	0.6545	25.7291 25.8408 25.4616	0.7589
3	1.2841 1.2834 1.2671	0.7526	32.5504 32.2068 32.6681	0.7381	2.5863 2.6431 2.6294	1.1315	0.8617 0.8575 0.8744	1.0178	8.8929 8.9031 8.9328	0.2327

Conclusions

Characterization of sewage sludge is important for agricultural purposes as the potential for nutrient supplementation and for increasing plant yields sewage by sludge need to be accurately determined.

The FlashSmart EA, based on the combustion method (Dumas), performs N, NC, CHNS determinations by combustion and oxygen determination by pyrolysis for the analysis of sludge samples. The method reports an excellent reproducibility, with no memory effect observed when changing the type of sample. This indicates the complete and accurate detection of the elements.

As a complete automated system, the FlashSmart Analyzer allows laboratories to analyze the five elements in a wide range from low to high content without matrix effect and without the use of sample digestion or toxic chemicals, needed when performing analysis following traditional methods.

In addition, the dual analytical configuration of the FlashSmart EA enables:

- Analysis of solids, liquids, viscous samples.

- One or two MAS Plus Autosamplers installed on the same system, controlled by the EagerSmart Data Handling Software.

- From only nitrogen or NC configuration:
  – Conversion to CHNS, NCS or CHN configuration
  – Conversion to only S configuration
  – Conversion to oxygen determination

- Full control of the workflow by the EagerSmart Data Handling Software.

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