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Elemental analysis: CHNS/O characterization of particulate matter in water and air (filters)

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Keywords

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Goal

Demonstrate the performance of the Thermo Scientific FlashSmart EA for the CHNS/O characterization of particulate matter.

Introduction

Determining nitrogen, carbon, hydrogen, sulfur and oxygen in particulate matter in water and air provides useful information for biology, ecology, marine science, chemistry and environmental studies, which investigate them, their chemical forms, their biological and physic-chemical transformations and their monitoring of the pollution.

The demand and the importance of determining CHNS/O have grown dramatically in the last years and many of the classical methods are no longer suitable for routine analysis, as they are time consuming and employ environmentally hazardous reagents. Laboratories need automated system, providing robust performance and reproducible data.

The Thermo Scientific™ FlashSmart™ Elemental Analyzer (Figure 1), based on the dynamic combustion of the sample, provides automated and simultaneous NC determination in a single analysis, run 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. Besides, the Analyzer can determine also simultaneous CHNS or only sulfur by combustion and oxygen determination by pyrolysis.

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

The Flash*Smart* Elemental Analyzer (Figure 1) 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 (Figure 2). Each analytical circuit accepts its own autosampler. In this way the system copes effortlessly with the laboratory requirements such as modularity, accuracy, day to day reproducibility and high sample throughput.

This note presents data on the performance of the Flash*Smart* Elemental Analyzer for the CHNS/O determination of particulate matter in air and water filters.

Methods

Particulate matter in water was analyzed after being filtrated on quartz or glass filters. The filters are then dried and analyzed. For sulfur determination, filters were cut in pieces and put into tin containers with about 10 mg of vanadium pentoxide for the complete sulfur conversion. Figure 2 shows the workflow indicating the different steps of sampling, weighing and analysis of 25 mm filters (particulate matter in water) for NC determination.

The filters of particulate matter in air (45 mm diameter) were cut in pieces for CHNS/O analysis and they were put into the tin containers with about 10 mg of vanadium pentoxide for CHNS determination.

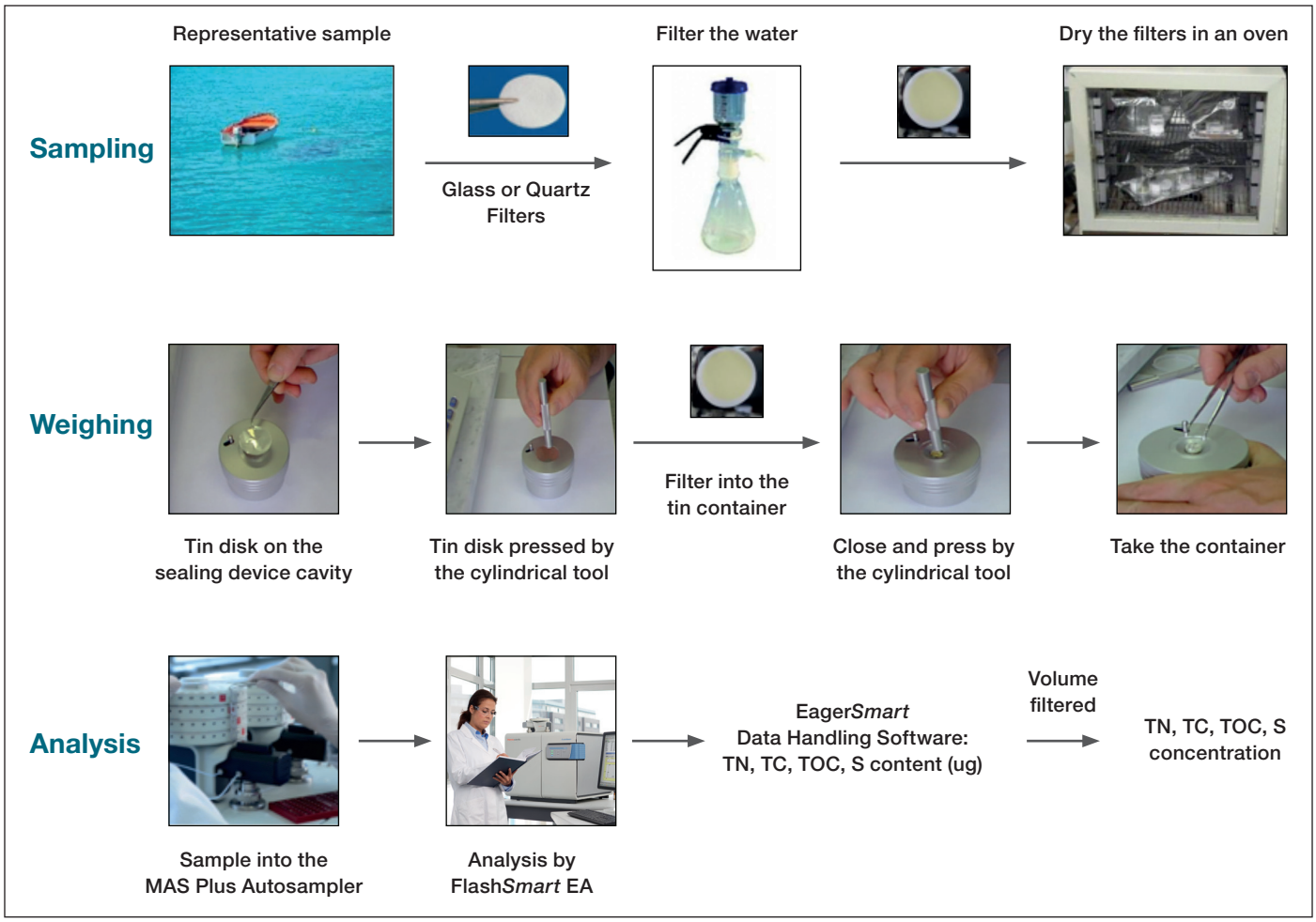

Figure 2. Particulate matter in water (Filters) workflow for NC determination.

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

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. Finally they are detected by a Thermal Conductivity Detector (TCD) (Figure 3).

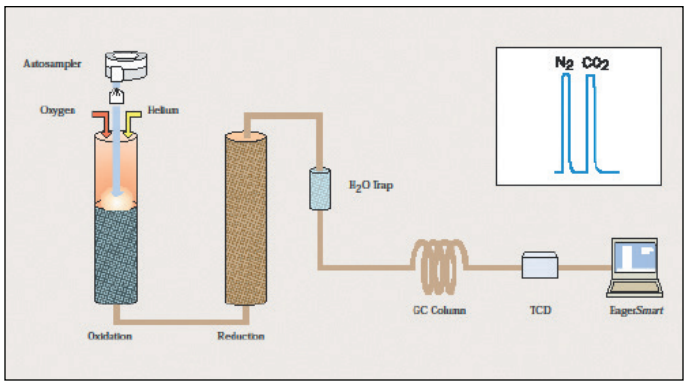

Figure 3. NC configuration.

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

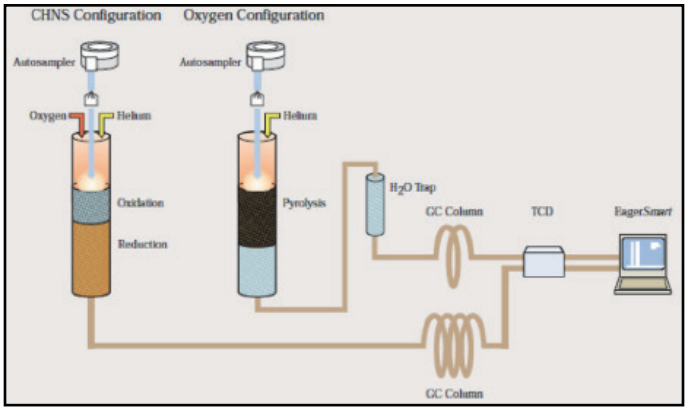

Figure 4. CHNS/O Configuration.

For sulfur analysis, after combustion the resulted gases are carried by a helium flow to a catalyst, a layer filled with copper and a water trap. Then, they are swept through a GC column that provides the separation of the combustion gases. Finally, they are detected by a Thermal Conductivity Detector (TCD).

For oxygen determination, the system operates in pyrolysis mode. Samples are put in silver containers and introduced into the pyrolysis chamber 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 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

Different filters containing particulate matter in water and air were analyzed to demonstrate the performance of the Flash*Smart* EA using different configurations.

For NC determination, samples collected in different periods were analyzed. Each representative sample was filtered in three filters (24 mm), dried and analyzed. Weighing of the sample is not required, as it is the total content of the elements which is being determined following the following steps:

1. **Determination of the area (mVolt/s) of 1 ug nitrogen and the area (mVolt/s) of 1 ug carbon through the analysis of atropine standard:**
   a) Analysis of the blank (only tin container) in triplicate (in general the nitrogen blank is not noteworthy).
   b) Analysis of atropine in duplicate (Table 1).
   c) Values of N area/ug N and C area/ug C for sample calculation (Table 1).
2. **Analysis of the filters:**
   a) Analysis of the blank (tin container plus filter) in triplicate (Table 2).
   b) Analysis of samples (Table 3).
   c) Calculation of ug N and ug C (Table 3).

Table 1. Area determination by microgram.

Weight (mg)	N amount (ug)	C amount (ug)	N area (mVolt/s)	C area (mVolt/s)	C area corrected by blank (mVolt/s)	N Area/ug	C Area/ug
1.384	66.98	976.55	110903	4897750	4889399	1656	5007
1.305	63.16	920.81	104818	4632224	4623873	1660	5021

Table 2. Blank area determination.

No. of runs	N area (mVolt/s)	C area (mVolt/s)	Average C area (mVolt/s)
1	-	17016	14938
2	-	13349	
3	-	14449	

Table 3. NC data of particulate matter in water.

Sample	No. filters	N area (mVolt/s)	C area (mVolt/s)	C area corrected (mVolt/s)	N Area / ug	C Area / ug
A	1 2 3	541 585 618	41475 37275 41079	26537 22337 26141	0.33 0.35 0.37	5.29 4.45 5.21
B	1 2 3	3857 3878 3820	78837 78166 77138	63899 63228 62200	2.33 2.34 2.30	12.74 12.61 12.40
C	1 2 3	10367 10990 10274	41666 46245 43952	26728 31307 29014	6.25 6.63 6.20	5.33 6.24 5.78

For sulfur determination, steps 1 and 2 were performed using BBOT (2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene) as standard to calculate the area of 1 ug sulfur. Table 4 shows the micrograms of sulfur present in 18 filters including the depth (m) in which the sample and the volume (ml) filtered were collected.

Table 4. Sulfur data of particulate matter in water.

Filter number	Depth (m)	Volume (ml)	S (ug)
1	10	350	43.49
2	15	300	28.80
3	20	350	39.64
4	0	200	42.66
5	5	300	34.29
6	10	300	68.65
7	15	200	33.88
8	20	200	33.94
9	15	50	29.94
10	15	50	22.62
11	15	100	43.14
12	15	100	56.60
13	15	200	58.21
14	15	200	47.47
15	15	300	58.68
16	15	300	39.02
17	15	400	54.99
18	15	400	40.31

Two filters of particulate matter in air were analyzed using CHNS/O configuration. The blank and samples filters (45 mm diameter) were cut in four parts. A quarter was used for CHNS analysis, while a quarter was used for oxygen determination. Each quarter was cut in six parts.

For CHNS determination, the following steps were performed:

1. **Determination of the area (mVolt/s) of 1 ug through the analysis of BBOT standard:**
   a) Analysis of the blank (tin container plus 10 mg vanadium pentoxide) in triplicate, determination of the average of the areas obtained (Table 5).
   b) Analysis of four BBOT standard, correction of the areas obtained by the blank, calculation of the ug of each element, calculation of the area/ug for each element and finally determination of the average of the area/ug (Table 6 and 7).

2. **Analysis of the filters:**
   a) Analysis of the blank (tin container, each sixth part of the blank filter and 10 mg vanadium pentoxide, V_2O_5); determination of the total areas obtained for one quarter of filter (Table 8).
   b) Analysis of samples: every sixth part of the fourth filter was weighed in a tin container with about 10 mg of vanadium pentoxide, V_2O_5; determination of the total areas obtained for one quarter of filter; correction of the areas by the total blank areas (Table 9).
   c) Calculation of the ug obtained of each element of the fourth filter (Table 9).

Table 5. Blank Area determination (tin container and 10 mg V_2O_5).

Run	N area (mVolt/s)	C area (mVolt/s)	H area (mVolt/s)	S area (mVolt/s)
1	292	11126	10681	0
2	246	9290	10618	0
3	400	14668	12732	0
Average	**312**	**11694**	**11343**	**0**

Table 6. BBOT areas corrected by the blank.

Run	Weight (mg)	Area (mVolt/s)				Area corrected by blank (mVolt/s)			
		N	C	H	S	N	C	H	S
1	2.047	265249	7854000	1969709	330294	264937	7842306	1958366	330294
2	2.028	262673	7792763	1959297	330133	262361	7781069	1947954	330133
3	2.013	260261	7727094	1942365	328990	259949	7715400	1931022	328990
4	2.063	265783	7911067	1990407	337394	265471	7899373	1979064	337394

Table 7. Amount (ug) and area/ug for each run, and the average area/ug for each element.

Run	Weight (mg)	Amount (ug)				Area/ug			
		N	C	H	S	N	C	H	S
1	2.047	133.26	1484.69	124.66	152.30	1988	5282	15709	2169
2	2.028	132.02	1470.91	123.51	150.88	1987	5290	15772	2188
3	2.013	131.05	1460.03	122.59	149.77	1984	5284	15752	2197
4	2.063	134.30	1496.29	125.64	153.49	1977	5279	15752	2198
Average						**1984**	**5282**	**15746**	**2188**

Table 8. Blank area determination (tin container, each sixth part of the blank filter and 10 mg V_2O_5).

Run No.	N area (mVolt/s)	C area (mVolt/s)	H area (mVolt/s)	S area (mVolt/s)
1	576	20435	21584	0
2	688	20313	21426	0
3	714	23609	22993	0
4	701	21411	21542	0
5	584	21158	20306	0
6	947	29500	27247	0
Total Area	**4210**	**136426**	**135098**	**0**

Table 9. CHNS amount (ug) in one quarter of filter.

Sample	A				B			
Element	**N**	**C**	**H**	**S**	**N**	**C**	**H**	**S**
Area (mVolt/s)	9807 7108 9051 4367 6541 5537	69390 57024 60126 34768 46656 45894	53094 39986 51709 27680 35027 33087	5008 3665 4662 2366 3661 2869	2302 3168 2012 2103 2371 1919	43826 47154 32166 33362 35189 30929	54279 55935 42618 47891 52594 43926	1621 1798 1223 1791 1403 1382
Total Area (mVolt/s)	42411	313858	240583	22231	13875	222626	297243	9218
Area corrected by blank (mVolt/s)	38201	177432	105485	39454	9665	86200	162145	9218
Total Amount (ug) in a quarter of filter	**19.25**	**33.59**	**6.7**	**10.16**	**4.87**	**16.32**	**10.3**	**4.21**

For oxygen determination, the following steps were performed:

1. **Determination of the area (mVolt/s) of 1 ug through the analysis of BBOT standard:**
   a) Analysis of the blank (empty silver container) in triplicate; determination of the average of the areas obtained (Table 10).
   b) Analysis of four BBOT standard; correction of the areas obtained by the blank; calculation of the ug of the element; calculation of the area/ug; determination of the average of the area/ug (Table 11).

2. **Analysis of the filters:**
   a) Analysis of the blank (silver container, each sixth part of the blank filter); determination of the total areas obtained for one quarter of filter (Table 12).
   b) Analysis of samples: every sixth part of the fourth filter was weighed in silver container; determination of the total areas obtained; correction of the areas by the total blank areas (Table 13).
   c) Calculation of the ug oxygen obtained of the fourth filter. (Table 13).

Table 10. Blank area determination (silver container).

Run No.	Area (mVolt/s)	Average Area (mVolt/s)
1	4201	**4247**
2	4173	
3	4368	

Table 11. BBOT area corrected by the blank, amount (ug), area/ug for each run, and the average area/ug.

Run	Weight (mg)	Area Oxygen (mVolt/s)	Area corrected by blank (mVolt/s)	Oxygen Amount (ug)	Oxygen Area / ug	Oxygen Average Area/ug
1	1.058	334156	329909	78.61	4197	4176
2	1.032	320983	316736	76.68	4131	
3	1.011	318984	314737	75.12	4190	
4	1.025	322941	318694	76.16	4185	

Table 12. Blank area determination (silver container and each sixth part of the blank filter).

Run No.	Area Oxygen
1	26164
2	27400
3	27106
4	26577
5	28794
6	27072
Total Area	163113

Table 13. Oxygen amount (ug) in one quarter of filter.

Sample	A	B
Element	Oxygen	Oxygen
Area (mVolt/s)	58540 57630 83729 78739 76927 72932	56627 39115 46198 46412 45989 35073
Total Area (mVolt/s)	349768	269414
Area corrected by blank (mVolt/s)	186655	106301
Total Amount (ug) in 1 quarter of filter	44.70	25.46

Conclusions

For the CHNS/O characterization of particulate matter in water and air filters, the Flash*Smart* EA, based on the combustion method (Dumas), showed automated and robust performance, required by routine laboratories.

Nitrogen, hydrogen, sulfur and oxygen were determined in the same system, with no need of changing hardware configuration.

For carbon determination, total carbon and total organic carbon (TOC) after an acid pre-treatment of the sample can be differentiated.

Being an all-in-one elemental analyzer, the Flash*Smart* Elemental Analyzer enables to perform CHNS/O determinations in a wide range of concentrations without matrix effect. The use of sample digestion or toxic chemicals, as needed by traditional methods is not required.

The Thermo Scientific Eager*Smart* Data Handling Software delivers comprehensive reports of the results, and allows customizations of the reports.

Find out more at **thermofisher.com/OEA**

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