Stability, Linearity and Repeatability of Nitrogen Determination by Flash Combustion using Argon as Carrier Gas

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Overview

Purpose: To show nitrogen determination by Organic Elemental Analysis (OEA) using argon as carrier gas.

Methods: Organic pure standards were analyzed through an elemental analyzer with an automatic autosampler using argon as the carrier gas.

Results: Data collected of nitrogen from different pure organic standards are discussed to assess the performance of the OEA analyzer using argon as the carrier gas.

Introduction

An elemental analyzer with a thermal conductivity detector for nitrogen determination typically uses a helium carrier gas due to its optimum sensitivity. However due to worldwide shortages and the high increase in the cost of helium, it has been necessary to test an alternative gas, argon, which is readily available.

The Thermo Scientific™ FLASH 2000 analyzer (Figure 1), based on the dynamic flash combustion of the sample, copes effortlessly with the wide array of laboratory requirements such as accuracy, day to day reproducibility and stability. The instrument was tested with argon as the carrier gas in comparison with helium using the Thermo Scientific™ Eager Xperience OEA dedicated data handling software for the quantification of the nitrogen content.

This paper presents data on nitrogen determination of pure organic compounds in a large range of concentrations in order to demonstrate the performance of the instrument using argon gas in terms of stability, linearity, accuracy and repeatability.

FIGURE 1. FLASH 2000 Elemental Analyzer

Methods

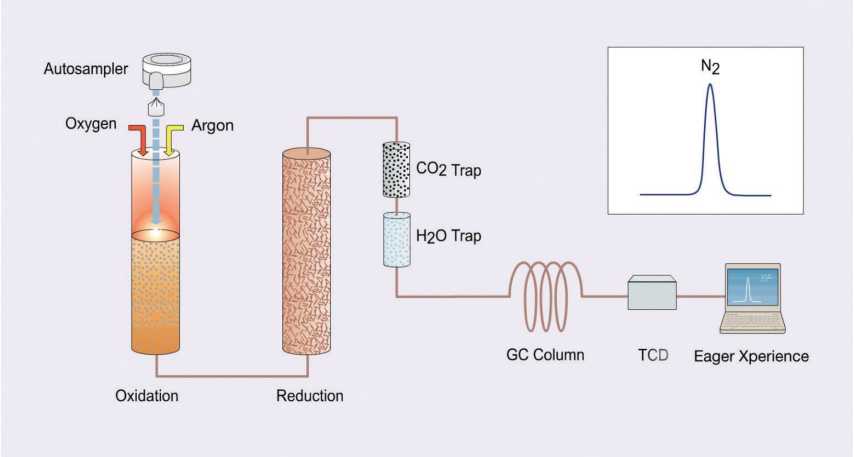
Samples are weighed in tin capsules and introduced into the combustion reactor via the Thermo Scientific™ MAS™ autosampler together with the proper amount of oxygen. After combustion, the produced gases are carried by an argon flow to a second reactor filled with copper, then swept through CO_2 and H_2O traps, a GC column, finally being detected by a thermal conductivity detector (TCD). The analytical configuration as well as the TCD detector are the same as those used with helium as the carrier gas see (Figure 2).

A complete report is automatically generated by the Eager Xperience data handling software and displayed at the end of the analysis. The Eager Xperience software provides a new *AGO* (Argon Gas Option) function through which modifies the argon carrier flow during the run to optimize the analysis.

Analytical conditions

Combustion Furnace Temperature:	950 °C
Reduction Furnace Temperature:	840 °C
Oven Temperature:	50 °C (GC column inside the oven)
Argon Carrier Flow:	60 ml/min
Argon Reference Flow:	60 ml/min
Oxygen Flow:	300 ml/min
Oxygen Injection End:	30 sec
Sample Delay:	10 sec
Run Time:	10 min

FIGURE 2. FLASH 2000 Nitrogen Configuration



Results

The stability of the system was evaluated analyzing Aspartic acid (10.52 %N) as standard to calibrate the instrument using K factor as calibration method, and as unknown to assess the accuracy and repeatability of the data obtained.

Two tests were performed to demonstrate the stability, accuracy and repeatability: one sequence in a working day, and a sequence of 10 days (day-by-day repeatability). Table 1 shows the sequence of analysis of approximately 60 mg of Aspartic acid (10.52 %N) in one working day, analyzed as standard (STD) and as unknown (UNK).

The average 10.50 N% and RSD % 0.55 indicates that the values obtained are comparable with the theoretical data (10.52 %N) and inside the technical specification of the system (range 10.42 – 10.62 %N) while the repeatability is more than acceptable.

Figure 3 shows a typical calibration with Aspartic acid using K factor as calibration method.

FIGURE 3. Calibration Curve / K Factor

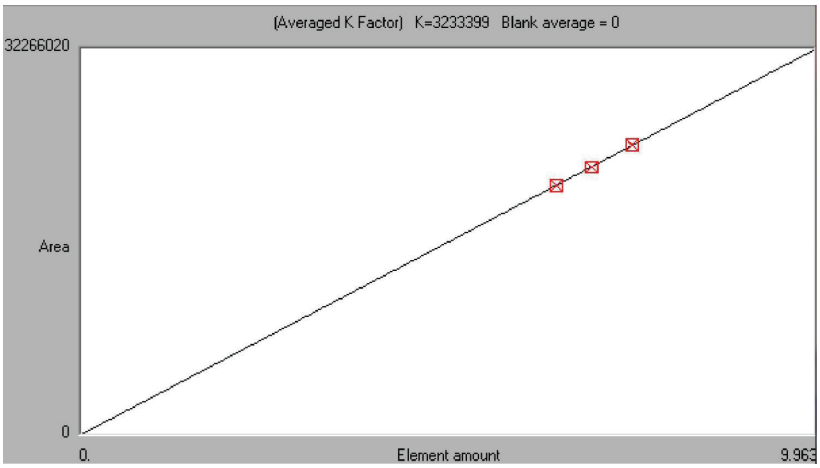


TABLE 1. Sequence of one working day of Aspartic acid analysis.

No.	Inj.Time	Type	Weight (mg)	N %
1	10:36	STD	60.465	10.52
2	10:50	STD	60.253	10.52
3	11:03	STD	60.387	10.52
4	11:16	UNK	60.320	10.58
5	11:30	UNK	60.310	10.56
6	11:57	UNK	60.283	10.62
7	12:11	UNK	60.216	10.59
8	12:38	UNK	60.262	10.63
9	12:51	UNK	60.236	10.53
10	13:04	UNK	60.349	10.54
11	13:18	UNK	60.369	10.54
12	13:31	UNK	60.292	10.51
13	13:45	UNK	60.361	10.48
14	13:58	UNK	60.382	10.51
15	14:11	UNK	60.356	10.48
16	14:25	UNK	60.257	10.47
17	14:38	UNK	60.367	10.59
18	14:52	UNK	60.326	10.44
19	15:05	UNK	60.213	10.46
20	15:19	UNK	60.397	10.42
21	15:32	UNK	60.377	10.48
22	15:45	UNK	60.340	10.49
23	15:59	UNK	60.299	10.43
24	16:12	UNK	60.357	10.46
25	16:26	UNK	60.410	10.49
26	16:39	UNK	60.280	10.47
27	16:52	UNK	60.392	10.50
28	17:06	UNK	60.010	10.42
29	17:19	UNK	60.368	10.45
30	17:33	UNK	60.230	10.45
31	17:46	UNK	60.347	10.42
32	17:59	UNK	60.367	10.46
33	18:13	UNK	60.373	10.50
34	18:26	UNK	60.294	10.47
35	18:40	UNK	60.247	10.51

Table 2 shows the accuracy and repeatability of the data obtained for Aspartic acid in a sequence of 10 days (day-by-day repeatability). The weight of standard was about 50 –60 mg and the system was calibrated using the K factor as calibration method. During this period the maintenance of the instrument was performed changing the reduction reactor and cleaning the ashes from the crucible. The data obtained are according to the technical specification demonstrating the stability of the system. No influence in the results was observed after the maintenance..

TABLE 2. Day by day repeatability

Sample name	Inj Date	Inj Time	Type	Weight (mg)	N %
Aspartic acid	10/05/2013	11:10	STD	56.703	10.52
Aspartic acid	10/05/2013	11:23	STD	54.489	10.52
Aspartic acid	10/05/2013	12:57	UNK	54.215	10.59
Aspartic acid	10/05/2013	15:32	UNK	56.294	10.47
New reduction reactor					
Aspartic acid	14/05/2013	12:24	UNK	55.892	10.59
Aspartic acid	14/05/2013	12:38	UNK	63.466	10.63
Aspartic acid	14/05/2013	12:51	UNK	59.012	10.61
Aspartic acid	14/05/2013	13:04	UNK	58.779	10.62
Aspartic acid	14/05/2013	14:05	UNK	56.278	10.57
Aspartic acid	14/05/2013	16:06	UNK	56.35	10.51
Aspartic acid	15/05/2013	08:35	UNK	60.069	10.5
Aspartic acid	15/05/2013	08:49	UNK	62.374	10.55
Ash removal					
Aspartic acid	16/05/2013	10:01	UNK	68.577	10.56
Aspartic acid	16/05/2013	10:15	UNK	57.017	10.5
Aspartic acid	17/05/2013	09:25	UNK	54.06	10.45
Aspartic acid	17/05/2013	09:38	UNK	61.287	10.58
Aspartic acid	20/05/2013	08:38	UNK	59.806	10.6
Aspartic acid	20/05/2013	08:52	UNK	52.063	10.59

To evaluate the linearity of the system, pure organic compounds with different nitrogen concentrations were chosen.

Instrument calibration was performed with Atropine (4.84 %N), Methionine (9.39 %N), Nicotinamide (22.94 %N) and Imidazole (41.15 %N) standards (STD) using Linear Fit as calibration method.

Pure organic standards in a large range of nitrogen concentrations (from 4.84 to 46.65 %N) were selected and analyzed as unknown (UNK). The weight of sample was 60 – 70 mg and all STD and the UNK were analyzed in duplicate.

Table 3 shows the sequence of analyses for the calibration of the instrument including the theoretical nitrogen values and the range accepted according to the technical specification.

TABLE 3. Sequence of standards for the Linear Fit calibration.

Sample Name	File Name	Inj. Time	Type	W (mg)	Theor. N %	Range (±)
Atropine	LinearFitN003	15:23	STD	60.209	4.84	0.07
Atropine	LinearFitN004	15:36	STD	70.465	4.84	0.07
Methionine	LinearFitN005	15:49	STD	60.237	9.39	0.10
Methionine	LinearFitN006	16:02	STD	70.116	9.39	0.10
Nicotinamide	LinearFitN007	16:16	STD	60.200	22.94	0.22
Nicotinamide	LinearFitN008	16:29	STD	70.831	22.94	0.22
Imidazole	LinearFitN009	16:42	STD	60.341	41.15	0.30
Imidazole	LinearFitN010	16:56	STD	70.442	41.15	0.30

Table 4 shows the relationship between the theoretical nitrogen percentages of the pure organic standards analyzed as unknown, the accepted range according to the technical specification of the system, and the average of the experimental N% obtained. All data are acceptable and no memory effect was observed when changing the sample.

TABLE 4. Correlation of Nitrogen values.

Sample name	Theoretical N %	Accepted Range (±)	Experimental N %
Atropine	4.84	0.07	4.78
Methionine	9.39	0.1	9.36
Nicotinamide	22.94	0.22	22.85
Imidazole	41.15	0.3	40.95
Acetanilide	10.36	0.1	10.4
Aspartic acid	10.52	0.1	10.61
BBOT*	6.51	0.1	6.42
CHDNPH*	20.14	0.2	20.33
Sulfanilamide	16.27	0.16	16.18
EDTA***	9.59	0.1	9.59
Urea	46.65	0.3	46.69

* BBOT: *2,5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene*
** CHDNPH: Cyclohexanone 2,4-dinitrophenylhydrazone
*** EDTA: EthyleneDiamineTetraAcetic acid

Figure 4 shows the calibration and the relative correlation factor.

FIGURE 4. Calibration curve / Linear Fit.

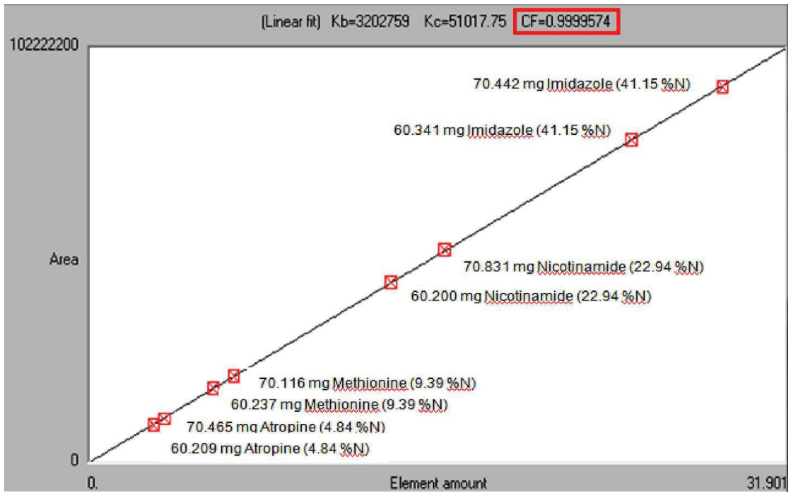
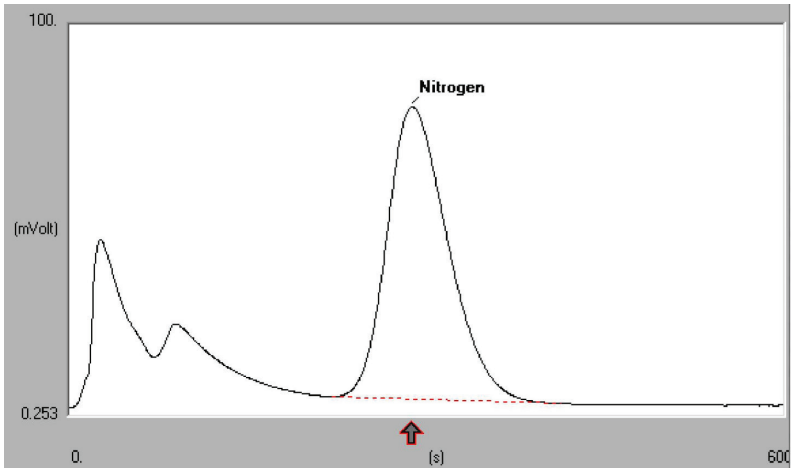


Figure 5 shows a typical nitrogen chromatogram.

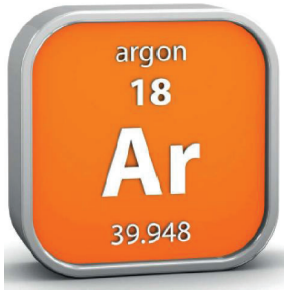
FIGURE 5. Typical Nitrogen chromatogram.



Conclusions

The results of the tests obtained with the FLASH 2000 Nitrogen Analyzer using argon as carrier gas demonstrate the day-by-day stability of the system independent of the maintenance performed, with good repeatability, accuracy and precision.

No memory effect was observed when changing the type of sample, indicating complete combustion and detection of the element.



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