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Note

Improvement of a carbon–nitrogen elemental analyser for marine samples collected on glass-fibre filters

CHRISTIAN BECHEMIN[a], DANIEL DELMAS* and MARIE-JOSÉ GARET[b]
CREMA L'Houmeau (CNRS/IFREMER), Case 5, 17137 Nieul-sur-Mer (France)
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In the marine environment, organic carbon and nitrogen are involved in biological, chemical and geochemical processes. The measurement of particulate organic carbon (POC) and nitrogen (PON) by high-temperature combustion, with subsequent separation and detection, is the most efficient and widely used method[1–3]. In sea water, as particulate organic matter is very dilluted (a few milligrams per litre), it is concentrated by filtration on pre-combusted glass-fibre filters. Thus, in contrast with the normal situation, our samples are a mixture of a small amount of organic matter with a large amount of glass-fibre, which melts during the high temperature combustion. Owing to this fact and depending on the equipment used, some specific analytical problems occur. However, the glass-fibre melting can be overcome by using lower temperatures, but erratic results are obtained[4,5]. This depends on the nature of organic material and also on the combustion time, which is not generally adjustable for most elemental analysers. Therefore, we have tried to resolve the practical problem of high-temperature combustion in our apparatus.

EXPERIMENTAL

Several systems using the high-temperature oxidation process are available. In our laboratory we use a Carlo Erba Model 1500 elemental analyser.

Briefly, the sample, enclosed in a tin container, is introduced into the quartz oxidation column, which is maintained at 1020°C. The tin primes a "flash combustion" at about 1700°C; combustion products, carried by helium, pass through layers of catalysts. Then carbon dioxide and nitrogen are separated on a gas chromatographic column and detected by thermal conductivity. With our samples, the quartz oxidation reactor is damaged very rapidly and as a consequence the analysis costs are high.

Two facts can explain the damage to the quartz oxidation column: first, during the "flash combustion", the temperature is increased in the combustion zone from 1020 to 1700°C (near the melting point of quartz), so the quartz tube is submitted to high thermal stress every 6 min. Second, ashes, tin oxides and mainly melting glass

[a] Present address: LEC, Mus de Loup, 17390 La Tremblade, France.
[b] Present address: ECOCEAN, 17000 La Rochelle Pallice, France.

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filters (used to process our samples) mix with the top layer of catalyst. Therefore, when we remove the ash from the furnace after every 100 analyses, this residue has formed a very hard plug. The connection of this hard plug with the weakened zone of the quartz tube leads to breakage of the oxidation reactor after two or three cleanings.

Initially, Carlo Erba provided a nickel sheet to protect the quartz combustion tube against thermal stress, but unfortunately they no longer supply it, and anyway this nickel sheet does not prevent the plug formation in the top layer of catalyst.

In order to reduce this drawback, we have examined the use of a crucible in the oxidation reactor. The specific requirements were to protect the quartz column against thermal stress and to isolate the top layer of catalyst from ashes and melting products. However, such a modification to the system must not trap any carbon or nitrogen or hinder the flow of gases and carrier. This crucible also needs to be introduced and removed easily without any manipulation of the oxidation reactor.

Alundum is a refractory product made with 90% aluminium oxide (melting point 2015°C) Alundum crucibles are porous (5–20 μm) and show good chemical inertia. Moreover, pure aluminium oxide can be used as a catalyst instead of chromium oxide (Carlo Erba, technical information). We therefore tested this material in order to protect the oxidation reactor. The external diameter of the commercially available crucible is close to the internal diameter of the oxidation reactor, so it is necessary to file it in order to have 1 mm free space between the walls.

RESULTS

The use of alundum crucibles in the analysis of acetanilide standards had no effects on the carbon and nitrogen response factors or retention times (Table I).

As acetanilide is not representative of the more complex marine particulate organic matter, we tested the combustion efficiency of a large polymeric compound, chitin, a high-molecular-weight material widely distributed in marine samples. With the analytical conditions used here, with flash combustion and catalytic oxidation, the results showed that (i) the alundum crucibles and (ii) the melting glass filters do not

TABLE I

INFLUENCE OF ALUNDUM CRUCIBLE ON THE RESPONSE FACTORS (K, $\mu g\ \mu V^{-1}\ s^{-1}$) AND RETENTION TIMES ($t_{R,s}$) FOR ACETANILIDE STANDARDS

R.S.D. = relative standard deviation (%).

System	*Parameter*	*Carbon*		*Nitrogen*	
		K	t_R	K	t_R
No crucible	Mean[a]	$7.79 \cdot 10^{-4}$	179.0	$2.23 \cdot 10^{-3}$	105.2
	S.D.	$0.35 \cdot 10^{-4}$	1.8	$0.18 \cdot 10^{-3}$	0.4
	R.S.D. (%)	4.4	1.0	8.0	0.9
With crucible	Mean[a]	$7.76 \cdot 10^{-4}$	179.3	$2.33 \cdot 10^{-3}$	105.3
	S.D.	$0.25 \cdot 10^{-4}$	0.8	$0.12 \cdot 10^{-3}$	0.5
	R.S.D. (%)	3.3	0.4	5.1	0.5

[a] $n = 6$.

TABLE II

CARBON AND NITROGEN CONTENTS (%, w/w) AND CARBON/NITROGEN RATIO OF CHITIN (ASH = 5%) ANALYSED WITH AN ALUNDUM CRUCIBLE AND WITH OR WITHOUT A GLASS-FIBRE FILTER

System	*Parameter*	*Carbon*	*Nitrogen*	*Carbon/nitrogen*
	Theoretical value	44.92	6.54	6.86
Without glass-fibre	Mean[a]	44.26	6.50	6.83
	S.D.	0.40	0.31	0.28
	R.S.D. (%)	0.91	4.76	4.13
With glass-fibre[b]	Mean[a]	44.39	6.46	6.87
	S.D.	0.57	0.27	0.25
	R.S.D. (%)	1.29	4.14	3.62

[a] $n = 10$.
[b] The weight of glass-fibre represents at least ten times the mass of chitin analysed.

affect the combustion yield (Table II). Depending on the sample size, it is necessary to replace the crucible every 50–70 sample combustions. This is carried out in less than 1 min without any manipulation of the oxidation reactor. For samples free from glass-fibre filter (*e.g.*, sediments, organic standards) there is no problem in emptying the crucible and using it several times. With this slight modification we have performed 450 sample analyses during six working days without any significant change in the response factors (Table III). Now we currently analyse more than 1000 samples with the same quartz column and catalysts; as alumdum crucibles are very inexpensive, the analysis costs are substantially decreased.

The use of an alundum crucible is not restricted to the Carlo Erba elemental analyser. If necessary, this crucible can be employed with other analysers and also with some mass spectrometers. Further, alundum refractory cement offers the possibility of making less expensive and more thermally resistant sample boats than the quartz type used with some elemental analysers such as the Perkin-Elmer models.

TABLE III

DAY-TO-DAY VALUES FOR CARBON (K_C, 10^{-4} μg μV^{-1} s^{-1}) AND NITROGEN (K_N, 10^{-3} μg μV^{-1} s^{-1}) RESPONSE FACTORS WITH ACETANILIDE STANDARD USING ALUNDUM CRUCIBLES AND THE SAME OXIDATION REACTOR

Response factor	*Parameter*	*Days*					
		17/3 (n = 6)	*18/3 (n = 8)*	*22/3 (n = 12)*	*24/3 (n = 3)*	*28/3 (n = 6)*	*29/3 (n = 6)*
K_C	Mean	6.95	6.75	6.88	6.89	6.94	6.60
	R.S.D. (%)	1.8	1.3	2.9	2.2	3.3	2.2
K_N	Mean	1.85	2.23	2.28	2.22	2.1	1.84
	R.S.D. (%)	5.5	6.4	7.6	7.0	2.9	6.2

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