Determination of Atmospheric Aluminium by Graphite Furnace Atomic Absorption Spectrophotometry Under Ar+CH$_4$ Flow

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DETERMINATION OF ATMOSPHERIC ALUMINIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY UNDER Ar+CH4 FLOW

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An improvement of sensitivity and reproducibility in the determination of Al by graphite furnace atomic absorption spectrophotometry is described in this paper. The main problem of Al analysis is here the high temperatures required for the atomization phase, during which refractory compounds are formed and the sensitivity decreases. Moreover, furnace lifetime is shortened and peak heights strongly decrease within a series of measurements. An additional flow of methane is tried, in order to create a reducing environment and to produce *in situ* a layer of atomic carbon and thus to improve furnace lifetime. This method appears to be slightly more sensitive than the use of additional hydrogen flow, but is far more interesting for furnace lifetime.

A set of Al concentrations is provided for aerosols as well as for rainwater. This data, established on the basis of a two year sampling at Cap Ferrat (French Riviera), allows to discuss the behaviour of Al in relation with heavy metals (Pb, Cd, Cu and Zn) and Saharan dust.

KEY WORDS: Aluminium, aerosols, rain water, heavy metals, GFAAS, NW Mediterranean

INTRODUCTION

The improved determination of atmospheric Al concentrations should be of great interest, because Al has been usually considered as a crustal tracer and its importance increases nowadays with the development of Saharan dust event studies. Among others, Al is a necessary reference in the atmospheric heavy metal studies which use a non-destructive method of analysis of several elements on the same sample.

In the case of Al analysis by graphite furnace atomic absorption spectrophotometry

(GFAAS), atomization temperatures are very high. The lifetime of tubes is determined by the atomization conditions under which the analysis is carried out, (temperature and delay) and the problems of reproducibility and sensitivity are particularly significant for this element. Slavin et al. [1] have shown that the Al absorbance profile is dependent on the age of the furnace.

In order to improve the determination of atmospheric Al concentrations, both in aerosols as well as in rainwater, the present paper reports a method for an *in situ* improvement of pyrolytic graphite lifetime, thus providing better sensitivity and reproducibility.

It is known that pyrolytic graphite offers many improvements in GFAAS, [2] i.e. better vapor confinement, due to lower permeability to gases, increased thermal resistance because of a higher sublimation point, higher resistance to oxidation and better thermal conductivity, and thus, increased sensitivity and reproducibility and, therefore, lower detection limit. Standard graphite is still used for certain elements, particularly because of the high price of pyrolytic graphite, and some studies attempted to develop techniques for coating conventional tubes *in situ* with pyrolytic graphite[3].

The use of CH_4 is proposed here for the analysis of Al within a study of atmospheric Pb, Cd, Cu and Zn.

EXPERIMENTAL

Sampling

The sampling station was very close to the Cap Ferrat signal-station (43° 41' 10" N, 7° 19' 30" E), on the southeastern coast of France. The characteristics of this location have been discussed elsewhere[4,5]. The sampling site is fairly sheltered from continental sources and is under local marine influence. The low impact of local anthropogenic sources has also been reported. A two year continuous sampling was carried out for rainwater, while, in the case of aerosols, 32 samples were collected during different and typical meteorological situations, according to their frequency, since it has been shown that the chemical composition of aerosols is strongly influenced by the origin of the incoming air mass arriving at the sampling site[6,7].

Wet deposition was collected with a rain collector previously described[4,8], which automatically opens when it rains. Rainwater was automatically filtered on cellulose acetate filters (Sartorius SM 11106, porosity 0.45 μm, diameter 47 mm) which were previously ultrasonically cleaned with diluted 1–2 N HCl (Merck Suprapur). The filters were not dried before use.

Dry deposition was sampled at the top of a six meter-high mast, without any particle size distinction. Each filtration equipment was a filter holder Sartorius SM 16510 connected to a pump (Reciprotor, 40 W) and to a volumetric counter (Gallus). The flow rate of the pumps was typically 1 m^3. h^{-1} and filtration was carried out over 4–8 hours. Filters were cellulose acetate membranes (Sartorius SM 11106) and they were not cleaned by acid treatment because, after drying, they get deformed and the filtration was no longer

Table 1 Experimental conditions of Al concentration measurements.

Phase	Wavelength	Dry T (°C)	Time (s)	Ash T (°C)	Time (s)	Atomize T (°C)	Ramp (°C.s⁻¹) rate	Hold (s)
Rainwater (tube)	309.3	80	30	700	10	2500	400	1.5
Aerosol (cup)	309.3	450	10	1500	6	2700	400	1

homogeneous besides the fact that the blank levels for the studied elements were negligible.

Rainwater was stored in polyethylene bottles and acidified with Suprapur HNO₃ at pH ranging from 1 to 2. Aerosol samples were stored in cleaned polystyrene Petri dishes until analysis.

Analysis

The atomic absorption spectrophotometer used was a Varian Techtron AA 1275 equipped with a CRA 90 atomizer. Ultra Carbon pyrolytic graphite cups were used for direct solid analysis of aerosols. For rainwater analyses, an auto-sampler Varian ASD 53 was used with Ultra Carbon pyrolytic graphite tubes (about 3 times more sensitive). Laboratory grade (> 99.99%) gases (argon, hydrogen and methane) were purchased from Liquéfaction de l'Air. Milli-Q® Millipore water was used (resistivity: 18 MΩ. cm).

For aerosols, small disks of the membrane filters (3 mm in diameter) were punched out and directly introduced into the carbon-rod atomizer. Several measurements with heavy metals have shown that this technique can be used (variability < 5%[4]) and that the distribution of particulate matter on the filter is homogeneous. This approach avoids the problems of acid treatment and solubilisation of aluminosilicates. Direct solid measurements should also remove possible interferences with heterogeneous dissolved solids, i.e. masking effects[9]. Moreover, it has been observed that cellulose acetate, as well as other organic additives, removes or decreases matrix effects[10,11]. In addition, the air volume sampled, being reduced on purpose to 4–8 m³, implies the metal concentrations analysed are very low and matrix effects could be neglected. In fact, the matrix should be essentially cellulose acetate. Therefore, it is possible to calibrate solid samples with aqueous standards, i.e. blank membrane sample + standard solution spike. Standards were acidified with Suprapur HNO₃ to pH = 1.2, in order to avoid any adsorption problem.

The experimental conditions of GFAAS measurements are given in Table 1. According to the low concentration levels encountered, the most sensitive radiation (309.3 nm) was used for both dissolved and particulate Al. The whole set of data, including concentration for each sample in rainwater and aerosol, is summarized at Tables 2 and 3. The meteorological conditions, as well as Pb, Cd, Cu and Zn concentrations, are given elsewhere[4,5].

For each sample (rainwater + aerosols), 10 measurements were carried out. The detection limits (3σ) were 30 pg Al for rainwater and 80 pg Al for aerosols. Blank levels were negligible, both in rainwater (0% of mean concentrations) and aerosol (0–2%).

Table 3 Al concentrations in rainwater, expressed in $\mu g.l^{-1}$.

event	$Al(\mu l^{-1})$	event	$Al(\mu l^{-1})$
9/2/86	70	11–12/2/87	0
14/2/86	30	16/2/87	10
18/2/86	5	18–19/2/87	45
1–2/3/86	890	20/2/87	15
10–11/3/86	125	11/3/87	340
6–7/4/86	275	25/3/87	25
16/4/86	35	3/4/87AM	20
23–25/4/86	190	3–5/4/87	865
4–5/5/86	415	9/4/87	30
21/5/86	205	3/5/87	305
31/5/86	345	4/5/87	260
12/6/86	320	17–19/5/87	25
14/6/86	320	4/6/87	70
19/6/86	150	12/6/87	120
26/8/86	155	15/6/87	405
8/9/86	1600	8/7/87	790
9/9/86AM	210	6–7/8/87	45
9/9/86PM	40	23–24/8/87	85
24/9/86	235	27/8/87	10
25/9/86	25	1/9/87	480
28/9/86	185	3/9/87	25
12/10/86	480	4–6/10/87	75
2/11/86	540	10–11/10/87	0
13/11/86	610	14–15/10/87	10
14/11/86	25	21/10/87	65
19–20/11/86	30	23/10/87	45
8–9/12/86	140	28–29/10/87	15
14/12/86	55	9/11/87	5
12–14/1/87	35	23–24/11/87	60
16/1/87	20	4–5/12/87	235
10–11/2/87	125		

Alternatively, CH_4 was used instead of H_2. CH_4 should provide two advantages: on the one hand, atomic hydrogen is thermally created in situ and reacts with ambient O_2 and thus should be an efficient sink for oxidizing agents. On the other hand, as a result of an atomic carbon production, the pyrolytic graphite furnaces are continuously overlayed with pyrolytic carbon. Therefore, lifetime of cups and tubes is strongly increased and the sensitivity does not decrease in time. Moreover, despite a slight increase of their thermal inertia, cups and tubes should be submitted to a surface passivation which improves the sensitivity and the reproducibility of measurements[15].

In fact, a mixture of H_2 and CH_4 (90 and 10% respectively) has been used for Al analysis by GFAAS already[3]. In this study, the concentration of CH_4 was adjusted in an empirical way, by setting the admission pressure to 0.5 bar at the auxiliary inlet of the power supply of the atomizer.

The comparison of calibration curves (Ar; Ar + H_2; Ar + CH_4) is given in Figure 1. The standards (1000, 2000 and 3000 ng Al for the whole membrane filter as well as samples were acidified to avoid Al adsorption.
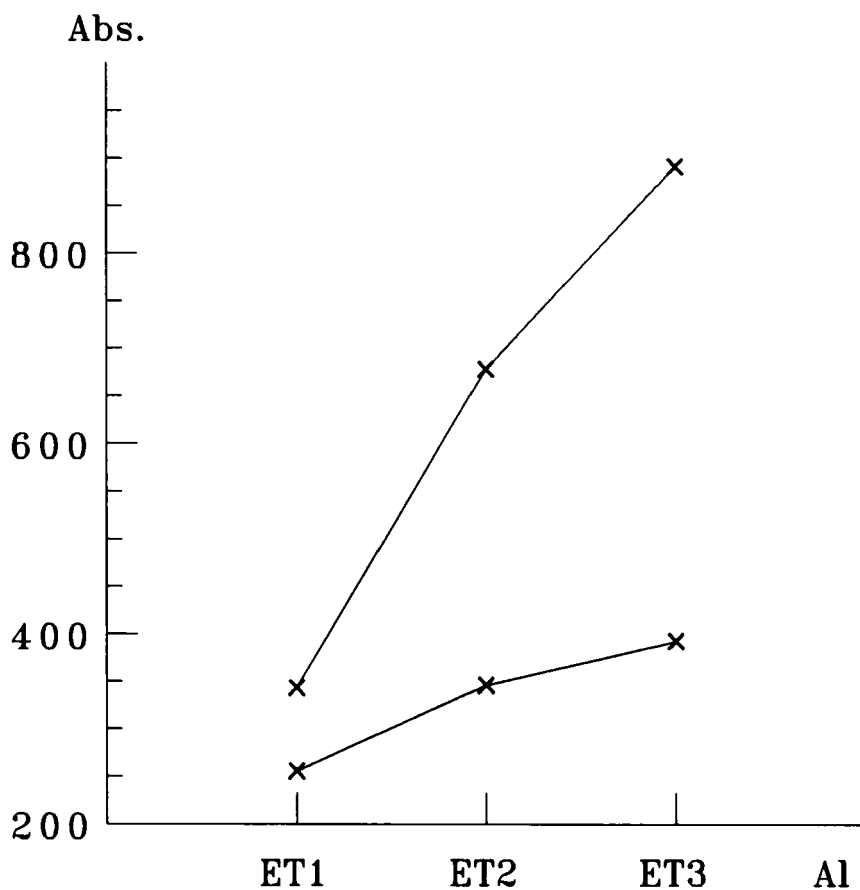
Figure 1   Calibration curves of Al analysis in the aerosols: Ar + CH₄ additional flow (1) and Ar only (2).

Geochemical discussion

This improvement of atmospheric Al analysis enables to obtain reliable data for an evaluation of mean concentrations in aerosol and rainwater samples collected during two years (1986 and 1987), in the Ligurian Sea. 32 values of airborne Al are recorded in Table 2 and 61 values of rainwater dissolved Al are given in Table 3. The mean concentrations for the region were 115 ng.m^{-3} for particulate Al in the aerosol and 75 μg.l^{-1} for dissolved aluminium in rainwater.

However, Al is generally associated with partially insoluble material and an assessment of atmospheric fluxes of Al cannot be carried out without special consideration of particulate Al fraction in rainwater [16]. Moreover, Al granulometric profiles show large distortions [17] and thus an estimation of dry deposition is very questionable for this element. For example, Dulac[18] proposed 0.8 cm.s^{-1} as a dry deposition velocity for Al in the northwestern Mediterranean, while Bergametti[19] gives the mean value of 3.6 cm.s^{-1}.

The high variability of Al concentrations, presented in Tables 2 and 3, has been discussed

(a)   (b)

Al

Pb

Cu
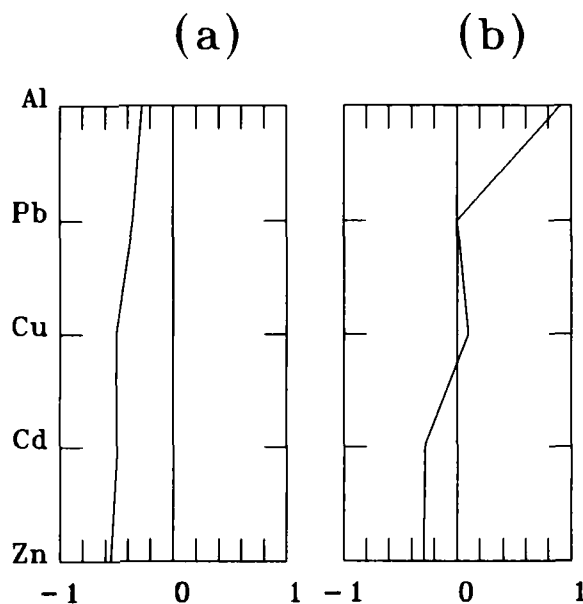
Cd

Zn

−1   0   1   −1   0   1

Figure 2 Correlation analysis based on the singular value decomposition of a matrix (equivalent to a principal component analysis): Representation of the two first left singular vectors (a) and (b).
A: The first vector shows the highly significant correlation between Al and Pb, Cd, Cu and Zn.
B: The singularity of Al against heavy metals appears with this second vector.

in detail elsewhere [20,21,] where its relation with rainfall variability has been highlighted.

An objective analysis based on the singular value decomposition of a matrix (equivalent to a principal component analysis) underlined the correlations between Al and four heavy metals (Pb, Cd, Cu and Zn) simultaneously analysed on the same site samples. (see Figure 2a). It is indeed well known that anthropogenic emissions have a continental origin in the Mediterranean Sea. Long-range transport of particulate matter from continental sources should be responsible for the Al and heavy metal concentrations over the northwestern Mediterranean Sea[7,19], as pointed out by 3-dimensional air mass trajectographies[4,20]. Besides, a covariability can be noticed between Al and NO_3^- in the dissolved phase, considering nitrates as pollutant tracers[22].

Nevertheless, the apparent singularity of Al, in relation with Cd, Cu and Zn, is illustrated in Figure 2b. Al, as a continental tracer, involves a strong natural component. For example, Saharan atmospheric inputs, coming from unpolluted locations, exhibit very high Al concentrations and generally low heavy metal concentrations[4,23]. For example, two rain events (1–2/3/86 and 3–5/4/87) exhibit very high Al concentrations (890 and 865 $\mu g.l^{-1}$ respectively) while their heavy metal levels are low (Pb: 4.1 and 1.7 $\mu g.l^{-1}$;Cd: 0.2 and 0.16 $\mu g.l^{-1}$; Cu: 3.7 and 0.6 $\mu g.l^{-1}$, respectively). These values are to be compared with estimated mean concentrations in rainwater, i.e. 4.8, 0.18, 2.15 and 6.3 $\mu g.l^{-1}$, repectively[4].

These results suggest that Al behaves both as a pollutant tracer, since the anthropogenic emissions originate from land-based sources, and as a natural crustal tracer, e.g. in the case

of Saharan dust events. This situation shows that Al can only be strictly considered as a continental tracer. It must be noticed that most of 3-dimensional trajectographies are representative of mixed situations, where different incoming air masses move at different barometric levels and originate from very different sources[4,5]. It is thus difficult to conclude, on the only basis of high Al concentrations, that a given atmospheric input has a Saharan origin.

CONCLUSION

Despite the increasing environmental interest pointed out earlier, the analysis of Al in the environment by GFAAS is still a problem mainly due to the high temperatures used during the atomization phase. Several solutions can be proposed now and this paper attempted to develop the use of CH_4 as an additional gas flux. A presentation of the advantages of CH_4 is given and a brief interpretation is suggested, i.e. creation of a reducing environment with atomic H and *in situ* resurfacing of the furnace with atomic C. This method appears to be adapted to atmospheric Al analysis within the study of heavy metals, which implies low air volume sampling in the case of aerosols.

In rainwater, only dissolved Al was measured and an estimation of total atmospheric Al deposition is not possible. However, a range of concentrations is given for dissolved phase in rainwater as well as for aerosol. According to the common use of Al as a continental tracer, the behaviour of this element in relation with heavy metals is discussed.

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