Analysis of air particulate matter in TeflonTM and quartz filters by short-irradiation, epithermal-neutron activation with Compton suppression

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Summary. This work aimed at developing methodologies to characterize the elemental composition of air particulate matter (APM) collected in Portugal, at an urban area (Lisboa, mainland Portugal) and at a remote location (Terceira island, Azores, Portugal). The Azores' collections were based on quartz filters; TeflonTM filters were used at the urban area. The main components of TeflonTM and quartz filters are fluorine and silica, respectively, the latter featuring higher levels of elements in the blanks. Al and Ti are reduced to null values when the blanks are subtracted. Epithermal short irradiation associated to Compton suppression in the measurement allowed the determination of a set of elements potentially representative of important emission sources: sea-spray (Cl, Br, Na, Mg), fuel burning (V), incineration (Cl), soil resuspension (Mg, Mn, Na, U, V), and traffic (Br, Mn). The analysis was fast due to the use of an automatic system. In some cases, the same element had different origins in the urban and remote oceanic areas.

1. Introduction

At the Portuguese Research Reactor (RPI-ITN; Technological and Nuclear Institute), elemental assessment of air particulate matter from the Portuguese mainland and archipelagoes have been routinely carried out through instrumental neutron activation analyses (INAA), using thermal neutrons. Since the area is strongly influenced by marine elements (Cl, Br, Na) from the Atlantic Ocean, detection limits for some trace elements – that can appear in nanogram levels – remain excessively high, with poor counting statistics or detection limits due to high Compton backgrounds resulting from the INAA-produced isotopes ³⁸Cl and ²⁴Na. In several studies, the use of epithermal NAA (ENAA) and Compton suppression methods have been shown to be ideally suited for the analysis of low-level determinands, and also in particulate-matter samples [1, 2]. Usually, the constituents of aerosols are Na, Cl, Al and Mn, whose nuclides

have high cross sections to thermal neutrons. Epithermal-neutron irradiation essentially results in a lower background and better sensitivities.

Polycarbonate NucleporeTM filters were the subject of a former study through ENAA and INAA (using both short and long irradiations), combined or not with Compton suppression [3, 4]. The aim of this study is to apply short-irradiation ENAA combined with Compton suppression to TeflonTM and quartz filters from an urban area (Lisboa, Portugal) and a remote oceanic location (Terceira island, Azores, Portugal), respectively, as a fast tool to analyze filters loaded with air particulate matter, and to compare their performance on the present media with the one obtained on the polycarbonate filters.

2. Experimental

Between July 2002 and June 2004, air particulate matter with an equivalent aerodynamic diameter under 2.5 µm (PM_{2.5}) were weekly (7-d samples) collected in the south-west coast of Terceira island, Azores, Portugal, using a high-volume sampler [5]. The sampling site was located 50 m above mean sea level, adjacent to agricultural areas, grazing grounds and vineyards. The collection media were pre-fired quartz filters. Each quartz sheet was folded, and a circular cut with a 2-cm diameter was made in order to get two sandwiched discs with the particles inside. The same procedure was applied to blank sheets to get the analytical blanks. The loading area of particles in each sample was 17.34 cm².

In January and March 2007, air particulate matter with an equivalent aerodynamic diameter under 2.5 µm as well (PM_{2.5}) was collected for 24-h periods in central Lisboa, Portugal, at the main campus of the *Instituto Superior Técnico* (Technical University of Lisbon), relatively close to the downtown area, using a sequential Partisol[®] sampler. The collection media were 47-mm diameter TeflonTM filters. Each filter was cut in half. The same procedure was applied to blank filters to get the analytical blanks. The loading area of particles in each sample was 6.28 cm². Mass concentrations in quartz filters were 5 to 86 µg m⁻³; mass

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concentrations in Teflon™ filters were 5 to 96 $\mu\text{g m}^{-3}$. The concentrations' order of magnitude was thus similar.

All samples were irradiated in the fast pneumatic system of the Portuguese Research Reactor inside a cadmium fold (thermal/epithermal ratio $\cong 2$). Each irradiation set includes one outer polyethylene can (1.4-cm diameter; 3-cm height) where, at the bottom, the ultrapure polyethylene sample container is placed (1.2-cm diameter; 0.5-cm height), with two others filling up the gap between the sample container and the outer can. The quartz filters (samples and blanks, the latter with the sample containers empty) were irradiated for 180 s and measured for 120 s, after decaying for 400–600 s; the Teflon™ filters (samples and blanks) were irradiated for 400 s and measured for 400 s, after around 500–600 s of decay time.

Gold monitors were irradiated every suite of 10 samples to verify the neutron flux variation, as well as two NIST Standard Reference Materials® (NIST-SRMs; about 20 mg each replicate): NIST-SRM 1648 “Urban Particulate Matter” (irradiation: 180 s; decay: 150 s; counting: 120 s) and NIST-SRM 1633a “Trace Elements in Coal Fly Ash” (irradiation: 180 s; decay: 300 s; counting: 120 s), irradiated immediately after the gold monitors and before the samples. Measurements were done under Compton suppression (five Ortec® crystals around and one Ortec® crystal on top, with detector and electronics from Canberra®).

Elemental masses in the analyzed part of the filters were calculated through the relative method, that is, peak areas in sample spectra were compared with corresponding peak areas in both NIST-SRMs' spectra, which feature certified values for the analyzed chemical elements. Filter blank was subtracted. Usually, filters are determined for their elemental concentrations (mass over volume of air sampled); in this work, elemental masses are reported instead.

Table 1 lists the nuclides used for the determination of the elements herein – Al, Ba, Br, Cl, Cu, I, Mg, Mn, Na, Ti, U, V – together with their half-lives and the energies of the corresponding (measured) gamma rays. In principle, this set of elements may enable an identification of marine, anthropogenic and crustal emission sources. The effect of the Compton suppression in the spectra of irradiated filters – measured with and without such suppression – has been discussed elsewhere [3, 6, 7].

Table 1. Short-lived NAA using epithermal neutrons and Compton suppression.

Element	Nuclide	Energy (keV)	Half-life
Al	$^{27}\text{Al}(n, \gamma)^{28}\text{Al}$	1778.7	2.24 min
Ba	$^{138}\text{Ba}(n, \gamma)^{139}\text{Ba}$	165.8	83.1 min
Br	$^{79}\text{Br}(n, \gamma)^{80}\text{Br}$	616.3	17.68 min
Cl	$^{37}\text{Cl}(n, \gamma)^{38}\text{Cl}$	1642.4	37.2 min
Cu	$^{65}\text{Cu}(n, \gamma)^{66}\text{Cu}$	1039.2	5.10 min
I	$^{127}\text{I}(n, \gamma)^{128}\text{I}$	442.9	25 min
Mg	$^{26}\text{Mg}(n, \gamma)^{27}\text{Mg}$	1014.4	9.46 min
Mn	$^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$	1810.7	2.58 h
Na	$^{23}\text{Na}(n, \gamma)^{24}\text{Na}$	1368.6	15.02 h
Ti	$^{50}\text{Ti}(n, \gamma)^{51}\text{Ti}$	320.1	5.75 min
U	$^{238}\text{U}(n, \gamma)^{239}\text{U}$	74.7	23.45 min
V	$^{51}\text{V}(n, \gamma)^{52}\text{V}$	1434.2	3.75 min

3. Results and discussion

Table 2 presents the average results obtained by ENAA with Compton suppression in the two NIST-SRMs for 11 chemical elements; the certified or informative values are also shown. Data for Ba, Br, Cl, I, Mn and Ti in NIST-SRM 1648 are informative, as well as Ba and Ti values in NIST-SRM 1633a. The ratios between the average results and the NIST-SRMs' values were calculated and they are also reported, with uncertainties that include the uncertainties from both sample and reference material. Spectral and nuclear-reaction interferences were quantified and so considered in the assessment of results.

Accounting for uncertainties, the agreement between experimental and reference data may be viewed as good. Still, the actual uncertainties were relatively large for a few elements (Ba, Cl, I, Mn), which may be due to the use of reference-sample masses lower than 100 mg (suggested as an optimal minimum by the manufacturers), to avoid high activities that would demand extended decay times. Also, the neutron-flux variation may have influenced the variability of the results, which likely accounted for 10 to 12% [8], as well as the fact that the reference concentrations for those elements are not truly certified, that is, they are informative only.

Table 2. Results (in mg kg^{-1}) obtained in this work for the NIST Standard Reference Materials™ 1648 “Urban Particulate Matter” and 1633a “Trace Elements in Coal Fly Ash”, using ENAA with Compton suppression.

Elem.	This work ^a	NIST-SRM 1648	
		NIST value ^b	Ratio ^c
Al	$36\,600 \pm 3100$	$34\,200 \pm 1100$	1.17 ± 0.18
Ba	920 ± 280	737*	1.25 ± 0.37
Br	528 ± 15	500*	1.06 ± 0.07
Cl	4560 ± 280	4500*	1.01 ± 0.12
I	16.7 ± 1.6	20*	0.84 ± 0.16
Mg	n.d.	8000*	n.d.
Mn	647 ± 28	860*	0.75 ± 0.07
Na	3320 ± 710	4250 ± 20	0.78 ± 0.17
Ti	4570 ± 210	4000*	1.16 ± 0.10
U	5.41 ± 0.36	5.5 ± 0.1	0.98 ± 0.13
V	141 ± 8	140 ± 3	1.01 ± 0.12

Elem.	This work ^a	NIST-SRM 1633a	
		NIST value ^b	Ratio ^c
Al	$135\,800 \pm 3650$	$143\,000 \pm 1000$	0.95 ± 0.05
Ba	1500 ± 460	1500*	1.00 ± 0.31
Br		n.a.	
Cl		n.a.	
I		n.a.	
Mg	3870 ± 205	4550 ± 100	0.85 ± 0.09
Mn	166 ± 6	179 ± 8	0.93 ± 0.07
Na	1660 ± 600	1700 ± 100	0.98 ± 0.36
Ti	9400 ± 1200	8000*	1.18 ± 0.30
U	9.05 ± 0.47	10.2 ± 0.1	0.89 ± 0.09
V	315 ± 10	297 ± 6	1.06 ± 0.07

a: Uncertainty is the standard deviation on the mean;

b: Uncertainty is at the 95% confidence level;

c: Uncertainty is at the 95% confidence level, and includes uncertainty in both sample and standard;

* Informative value; n.a.: not available; n.d. not determined.

Fig. 1. Elemental-concentration ratios between the experimental results for analytes (replicate samples) in the NIST Standard Reference Materials™ and their certified or informative values. In all plots, X-axes stand for an arbitrary (nominal) sequence of analyses (no units), and Y-axes for the corresponding ratio data (no units).

Fig. 1 illustrates the distribution of ratios that contributed to the average data shown in Table 2. For most elements, the ratios are around the unity. Results for I, Mg and Mn are lower than the standard ones, which are informative nonetheless. The uncertainty in each Al ratio is very small, and the values varied between 0.8 and 1.3. The Mn result for NIST-SRM 1648 is low, and Fig. 1 shows that only one of the measurements is in agreement with the standard value. Since the latter is informative only, one can not be sure of the accuracy of our result. The Mn result for NIST-SRM 1633a (certified value for Mn) was accurately determined though. Sodium is also low for NIST-SRM 1648, whereas the agreement looks good in NIST-SRM 1633a. Analyses of NIST-

SRM 1648 by ICP-AES for Al, Mg, Mn, Na and Ti, and by ICP-MS for U have shown good agreement, with ratios varying between 0.93 and 1.04 [9]. Analysis of NIST-SRM 1633a by PGAA (prompt gamma activation analysis) for Al, Mn, Na and Ti has pointed out an overall agreement better than 20% with the corresponding certified/informative values [10].

Table 3 lists the elemental masses per unit area in blank (unexposed) Teflon™ and quartz filters. The amounts in the quartz material are higher than in the polymeric one, except for Br, Cl (both below their detection limit in the quartz) and Ti. Given the values of Al in both media, very few meaningful concentrations remained after

Table 3. Elemental masses per unit area (in $\mu\text{g cm}^{-2}$) in blank (unexposed) TeflonTM and quartz filters. n.d.: below detection limit.

Element	Teflon TM	Quartz
Al	1.7	116
Ba	n.d.	0.6
Br	0.02	n.d.
Cl	2.4	n.d.
Cu	n.d.	n.d.
I	n.d.	n.d.
Mg	0.3	1.0
Mn	n.d.	n.d.
Na	1.2	61
Ti	4.3	1.8
U	n.d.	0.05
V	n.d.	n.d.

the blank subtraction. The same applied to Ti in TeflonTM filters.

Fig. 2 shows the actual field data (mass loadings; blank discounted) for the elements Al, Br, Cl, I, Mg, Na, Ti, U and V in the quartz filters. Several features are apparent. The Al emissions are stronger during springtime, which may be related to an enhanced resuspension of soils due to farming activities, while Br, I and V signals are a constant presence the whole year round. As expected, Cl and Na levels are higher in the winter – especially in the winter of 2004, owing to particularly harsh weather conditions – and follow a similar pattern. The same trend may be seen to underlie the occurrences of Br (a secondary sea-salt tracer) in that particular period.

As mentioned above, and just from visualization, an apparent correlation is already observed for Cl and Na. To search for other correlations and to confirm the former, a parametric test (Pearson's r) was applied, and the results

Table 4. Pearson's product-moment correlation coefficients for the parametric degree of association between elemental masses in loaded filters. The upper part of the table (in *italic type*) refers to TeflonTM filters, and the lower part (in regular type) to quartz filters. Coefficients over 0.50 are set in **bold type**; n.d.: below detection limit.

	Br	Cl	I	Mg	Mn	Na	U	V
Br	1	0.17	0.05	0.69	0.15	0.70	0.26	-0.23
Cl	0.68	1	0.08	0.05	-0.08	0.82	-0.30	0.58
I	0.68	0.56	1	-0.38	-0.12	-0.01	-0.51	0.32
Mg	0.02	-0.03	0.39	1	-0.08	0.24	0.016	0.13
Mn	0.10	-0.12	-0.22	-0.27	1	0.77	0.86	0.80
Na	0.60	0.99	0.66	0.45	0.11	1	0.90	0.90
U	0.01	0.10	0.56	0.41	0.85	0.35	1	0.90
V	0.04	-0.01	0.09	0.22	0.79	0.06	0.15	1

are given in Table 4. The table also shows Pearson coefficients for the masses of elements found in the TeflonTM filters. Other than an excellent association between Cl and Na data, Br and I also correlate well with the two primary sea-salt tracers, putting in evidence an expected strong marine influence. Other significant correlations could be found between I and U, between U and V, and between Mn and both U and V. The volcanic origin of the island soil may be the cause for such relationships, due to its high contents in metals [11].

Good correlations were found in central Lisboa as well (TeflonTM filters). Bromine is one of the elemental markers for mobile sources [12], even if it may also originate from marine influxes and thus act as a secondary sea-salt tracer (see above). In Lisboa, Br is weakly correlated with Cl, and well correlated with Na and Mg, which may come from urban-dust resuspension due to the high vehicular traffic density around the sampling site.

Fig. 2. Masses (in μg) of the elements Al, Br, Cl, I, Mg, Na, Ti, U and V in the analyzed fraction of the quartz filters from Terceira island, Azores, along the sampling period.

Chlorine – mainly of marine origin from its good association with Na – is also correlated with V that might be fuel-combustion and/or waste-incineration derived [13, 14]. As a matter of fact, an oil-fired boiler for the purpose of heating an indoor swimming pool was often working in the vicinity of the Partisol® sampler. General-refuse incineration of household wastes that usually contain a significant share of plastic debris may as well have contributed to the Cl signal in such an inner-city location, hence explaining the Cl-V association in the Teflon™ filters.

Anthropogenic sources could also be recognized through the excellent correlations between Mn, U and V, even if that was hardly unexpected for an urban environment. With the present methodology, either Teflon™ or quartz or polycarbonate matrices are suitable for the analysis of ambient PM_{2.5}.

4. Conclusions

In this work, a fast methodology combining epithermal neutron activation analysis (ENAA) with Compton suppression, and featuring short irradiation, short decay and short measurement times, was attempted in order to access information on emission sources of elemental constituents of air particulate matter (APM). The methodology was applied to two types of filter materials – Teflon™ and quartz – loaded with airborne particulates (PM_{2.5}) from two completely different environments: an urban area (Lisboa; mainland Portugal) and an oceanic island (Terceira; Azores archipelago). The collected masses of PM_{2.5} were similar in both cases, as well as the analyzed filter areas. Due to their higher blank contents, the quartz filters were irradiated for shorter times, otherwise they would become too active for being measured after a reasonably short decay time. The following elements could be determined: Al, Br, Ba, Cl, Cu, I, Mg, Mn, Na, Ti, U and V. However, Al contents in unexposed filters (blanks of both types) and in loaded ones were in the same order of magnitude, and that was also the case of Ti in Teflon™ substrates. Accuracy of the determinations was asserted by analyzing two NIST Standard Reference Materials® (NIST-SRM 1648 and NIST-SRM 1633a), and it was considered good accounting for the uncertainties. Other than fast and reliable, the present methodology can really determine a suite of elemental tracers of relevant emission sources – marine, crustal, anthropogenic (combustion, incineration, traffic) – and, last but not least, seems to work well whatever collection substrate is dealt with – Teflon™, quartz or polycarbonate filters.

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