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Heavy Metals Determinations in Atmospheric Particulate Matter by Instrumental Neutron Activation Analysis

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Abstract

Instrumental Neutron Activation Analysis (INAA) is employed for its important analytical properties. Fundamentally, INAA is a multielemental technique allowing the determination of about 30 elements with a good Limit of Detection. In this paper we applied this nuclear technique to the study of metal composition in *fine* and *coarse* fractions determining 25 elements.

The filters collected in Rome were irradiated at the nuclear reactor Triga Mark II (ENEA-Casaccia Laboratories). The measurements of the ?-ray allow the quali- and quantitative analysis. The elements levels in *fine* and *coarse* fractions with the relative correlations have been determined: basically, the concentrations are very low.

Furthermore, the enrichment factors of all elements will be reported in order to understand the natural or anthropogenic origins of the particulate matter.

Introduction

Among the various species present in the particulate matter, a greater attention has been devoted since many years to the study of elements at elevated toxicity and greater diffusion in environment (Cd, Cr, Ni, Pb, Zn, etc.) because of anthropogenic (autovehicular, domestic heating, industrial emission) and natural (air mass transport, volcanic eruption, desert, etc.) pollutant emissions. In particular, the metals differ from other toxic substances because they are neither created nor destroyed by humans. It should be considered that an important target in the atmospheric pollution evaluation is the acquisition of knowledges related to understand levels and behaviour of elements toxicologically and geochemically important (e.g.., Au and/or Sc, used for evaluation of the enrichment factors of anthropogenic elements).

In this paper the characterization of particulate fractions are reported in order to estimate the levels and distribution of 25 elements determined after sampling onto two different granulometric particulate fractions, *fine* and *coarse*, in a reserved area in downtown Rome. A particular attention is drawn to the *fine* fraction for its relevant toxicological interest.

Materials & Methods

For particulate matter sampling a dichotomous sampler (mod. SA 241, Graseby,-Andersen) operating at 16.7 L min-1 was used. This sampler has a PM10 size selective inlet and separates the aerosol into fine (aerodynamic diameter, Da, <2.5 μm) and coarse (2.5 μm<Da<10 μm) fractions.

Samples, blank and standards were irradiated at a neutron flux of 2.6×10^{12} n× $cm^{-2}\times s^{-1}$ for 32.55 h in rotary rack "Lazy Susan" of the nuclear reactor Triga Mark II of the ENEA-Casaccia Laboratories. After irradiation, ?-ray spectrometry measurements of different duration were carried out using a Ge(HP) Canberra detector (FWHM 1.68 keV at 1332 keV) for determining As, Au, Br, Cd, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, La, Mo, Nd, Ni, Rb, Sb, Sc, Se, Sm, Ta, Th, W, Yb, Zn [1].

Results

INAA is well known as reference analytical technique because all the experimental steps are totally traceability and there is absence of physical-chemical sample manipulation reducing the contamination probability or lack of elements, even if present at ultra-trace levels [1].

Generally, concentrations are very low: the whole situation is reassuring regarding the exposition to potential toxic elements. As is present at concentration levels < 1 ng/m^3 in the *coarse* fraction and below 3 ng/m3 in the *fine* fraction (correlation factor, R, fine/coarse 0.500). The Br concentrations are higher in *fine* (between 3 and 50 ng/m^3) than in *coarse* fraction: this can hypothesize an anthropogenic contribution confirmed by the good correlation with the Sb trend (R Br/Sb *fine* 0.951, R Br/Sb *coarse* 0.872). Cr has concentrations around 3.5 ng/m^3. Hg shows very similar levels (0.8-0.9 ng/m^3) in both *fine* and *coarse* fractions with discordant behaviour between them.

In order to investigate the natural or anthropogenic origins of the elements studied we calculated the enrichment factors (EF) with respect to the element abundance in the upper continental crust. The EFs have been calculated using La as normalizing element [2]. Analyzing Figure 1 elements with EF values higher than 1 can be considered of non-crustal origin and may be attributed to long-transport phenomena from other natural and/or anthropogenic sources. The figure shows the principal differences between the two granulometric sizes: in fact, in the *fine* fraction we have high EF values for 13 elements compared with the *coarse* fraction where 9 elements are of non-crustal origin. Further, it should be noted that the EF in *fine* fraction is more elevated that in *coarse* fraction: this could be due to the different granulometric size and the different ability to penetrate of the elements.

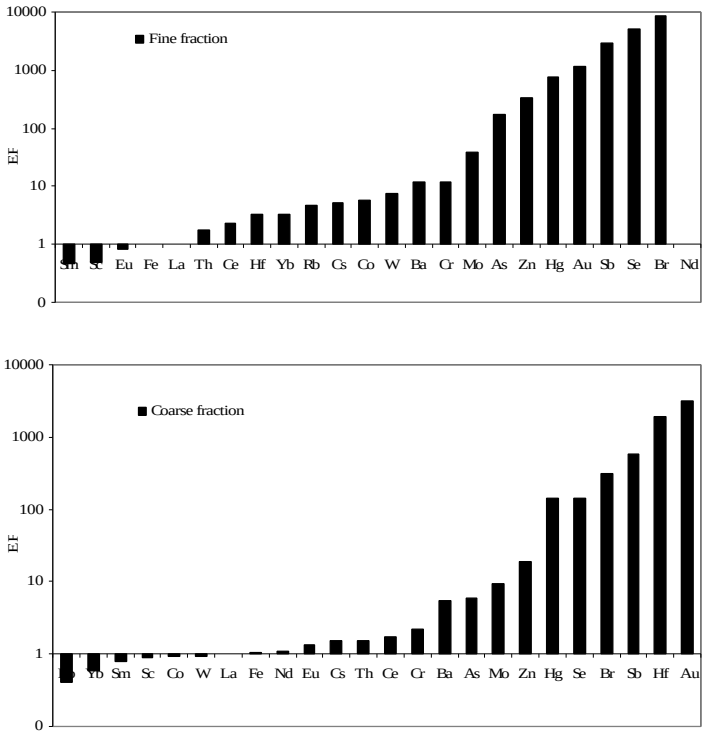

Fig. 1; Comparison of trace element EF in air particulate *fine* and *coarse* fractions calculated using lanthanum as normalizing elements.

Conclusions

The INAA technique has allowed to reach such elevated sensibility/accuracy levels to furnish discreet values for elements present at trace and ultra-trace levels. Particular attention has been devoted to reach elevated degrees of precision and accuracy for each element.

The results obtained and the relative implications for the human health can obviously be referred only to the airborne *fine* and *coarse* fractions. The element concentrations determined in this study do not show a significant level of attention from a toxicological point of view. Only few elements show a very good distribution between the two fractions whereas the greater part shows a distribution more elevated in the coarse fraction than in the fine fraction.

References

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