Deep Investigation on Inorganic Fraction of Atmospheric PM in Mediterranean Area by Neutron and Photon Activation Analysis

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Abstract

Anthropogenic activities introduce into the environment materials that give rise to increasing levels of many substances which may endanger the environmental quality and represent a hazard to human health. Major attention has been given to those elements who are more liable to alter the environment and endanger human health.

The airborne particulate matter pollutant, expecially the distribution and multielemental PM composition, is considered one of the most difficult task in environmental chemistry for its complex composition and implications that complicate notably the behavior comprehension.

This study was therefore extended as far back as possible in time (from 1965 until 2000) in order to analyze the trend of airborne concentration of pollutant elements in connection with the industrial and lifestyle growth during the entire period.

Introduction

The element distribution in air is determined fundamentally by the resuspension from soil and water of various substances of natural and/or artificial origin, by their circulation due to the meteorological events and by the chemical element behavior. Furthermore, human activities introduce into the environment materials that give rise to increasing levels of many species which can endanger the environmental quality and represent an hazard for the population. In this way, among atmospheric pollutants trace elements in airborne particulate have a preeminent position because the presence of the most toxic elements (e.g. Cd, Hg and Pb) and because their levels may affect the biological systems [1]. The main problem of this task resides in the analytical determination of such species: in fact, their levels in atmosphere are at ultra-trace levels and a very specific methodology is necessary with regard to the accuracy and precision and contamination problems [2]. The nuclear techniques such as Instrumental Neutron Activation Analysis (INAA) and Instrumental Photon Activation Analysis (IPAA) assure these requirements.

In this paper a retrospective analysis of elements in air particulate collected in the last 4 decades has been carried out in order to study the trend of their environmental levels; INAA and IPAA have been used to determine elements of primary concern. In particular, over metals such as As, Cd, Cr, Hg, Pb, Sb, Zn considered of greater health concern, other elements of relevant environmental interest or less considered previously were measured.

Materials & Methods

About 300 air samples have been collected in urban area (characterized by high presence of anthropogenic activities) and outskirt (rural site) of Rome. The sampling was 24-hr long for each filter. All the storage and handling sample treatment were carried out at the ENEA and ISPESL laboratories. For particulate matter sampling a dichotomous sampler (mod. SA 241, Graseby,-Andersen) operating at 16.7 L min^{-1} was used.

Among the different analytical methodologies available for element determination we used nuclear approach for its important analytical properties [1,2].

INAA - Samples, blank and standards (USGS nn. 1, 4, 6 and NIST Coal Fly Ash n. 1633a), put

in nuclear-grade polyethene cylinders (Kartell), were irradiated at a neutron flux of 2.6×10^{12} $n\times cm^{-2}\times s^{-1}$ for 32.55 h in rotatory rack "Lazy Susan" of the nuclear reactor Triga Mark II of the ENEA-Casaccia Laboratories. Two series of measurements allowed to determine 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.

IPAA - Samples, blank and standards (NIST SRM 1571) were irradiated in the photon beam of the INFN Frascati National Laboratory Linear Accelerator (LINAC) at an average beam current of 40 μA, maximum electron energy of 300 MeV and a W converter of 0.3 mm thickness. Two series of measurements were carried out: As, Pb, Tl and Zr were measured.

Results

An important task was devoted to the investigation of Quality Control (QC) and Quality Assurance (QA) of the methodology used in this study. For these goals we performed irradiations of primary and secondary reference standard materials (RSMs) for matching the entire analytical methodology and for minimizing and/or avoiding matrix effects, respectively.

About the element levels it should be underlined that elements of artificial origin show winter concentration levels higher than the summer ones, probably owing to an enhanced production in the winter period; in contrast elements of natural origin show summer concentration levels higher than the winter ones, possibly as a consequence of an increased resuspension of soil matter in summer.

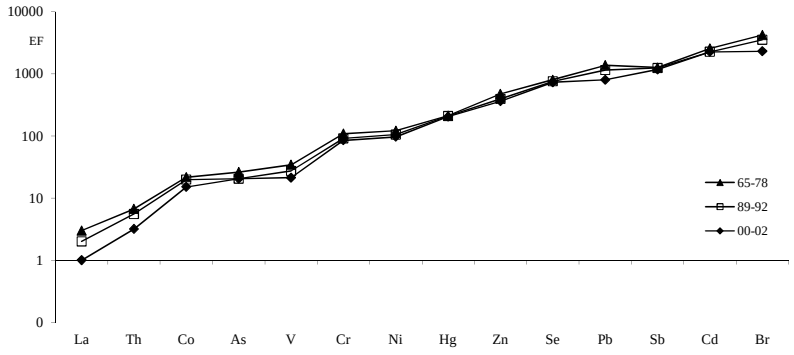

Fig. 1; The EF trend comparison during 4 decades of selected trace elements in PM10 fraction calculated using La as normalizing element.

In order to investigate a retrospective study of elements in PM10 and their evolution in relationship with the natural or anthropogenic origins, we investigated the Enrichment Factors (EFs). Elements with EF values much higher than 10 can be considered of non-crustal origin and may be attributed to long-transport phenomena from other natural and/or anthropogenic sources. Figure 1 shows the EF trend for selected elements in PM10 during four decades. As can be noted, almost all the elements may be attributed to long-range transport phenomena from other natural and/or anthropogenic sources: this behavior is common to all the period studied even if a very light decreasing trend can be evidenced from 1970 to 2002.

Conclusions

The experimentation has been addressed for getting the maximum analytical informative ability from the single sample determinations. The INAA and IPAA techniques have allowed to reach such elevated sensibility/accuracy levels to furnish discreet values for elements present at very low concentrations (trace and ultra-trace levels).

The element concentrations determined in this study do not show a significant level of attention from a toxicological point of view taking in account that the simple measurements of the total airborne concentration of a metal may not be representative of its potential to participate in processes deleterious to health.

References

1) P. Avino, G. Capannesi, A. Rosada, Heavy metal determination in atmospheric particulate matter by Instrumental Neutron Activation Analysis. *Microchem. J.* 88, (2008) 97-106.
2) P. Avino, G. Capannesi, A. Rosada, Characterization and distribution of mineral content in fine and coarse airborne particle fractions by neutron activation analysis. *Toxicol Environ. Chem.* 88, (2006) 633-647.