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A new non-destructive method for chemical analysis of particulate matter filters: The case of manganese air pollution in Vallecamonica (Italy)

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ABSTRACT

Total Reflection X-ray Fluorescence (TXRF) is a well-established technique for chemical analysis, but it is mainly employed for quality control in the electronics semiconductor industry. The capability to analyze liquid and uniformly thin solid samples makes this technique suitable for other applications, and especially in the very critical field of environmental analysis. Comparison with standard methods like inductively coupled plasma (ICP) and atomic absorption spectroscopy (AAS) shows that TXRF is a practical, accurate, and reliable technique in occupational settings. Due to the greater sensitivity necessary in trace heavy metal detection, TXRF is also suitable for environmental chemical analysis. In this paper we show that based on appropriate standards, TXRF can be considered for non-destructive routine quantitative analysis of environmental matrices such as air filters. This work has been developed in the frame of the EU-FP6 PHIME (Public Health Impact of long-term, low-level Mixed element Exposure in susceptible population strata) Integrated Project (www.phime.org). The aim of this work was to investigate Mn air pollution in the area of Vallecamonica (Italy).

1. Introduction

Particulate matter (PM) represents a hazardous air pollutant that is recognized to have negative health impacts such as increased mortality and morbidity from respiratory and cardiovascular diseases [1]. Although specific mechanisms are not known, a number of studies have demonstrated that exposures to various air pollutants are associated with reductions in lung function and growth, asthma, allergic rhinitis and respiratory infections in children [2].

PM can be composed of a variety of materials including inert carbonaceous cores with multiple layers of various adsorbed or mixtures of many materials including metals, organic vapors, acid salts and biological elements such as endotoxins, allergens, and pollen fragments [3].

Particle size and particle composition are the main properties responsible for the impacts on human health, with particle composition influencing its toxicity [4]. Burnett et al. [5] found that daily mortality in eight Canadian cities was more strongly associated with the constituents of fine PM than the fine mass alone.

Urban PM has been found to contain significant amounts of metals [6], which may mediate the health related effects of PM exposures, as demonstrated in a number of studies [7–9]. Bioavailable metals in airborne PM have been particularly associated with enhanced airway hyperresponsiveness, altered immune resistance and pulmonary inflammation [10].

Heavy metals such as Cd, Hg and Au have been shown to have immunotoxic effects and be potent inducers of autoimmunity [11,12], which may lead to the onset and/or exacerbation of autoimmune diseases such as Type 1 diabetes, multiple sclerosis, systemic lupus erythematosus, rheumatoid arthritis and Parkinson's disease [13,14].

The effects of PM exposures on certain vulnerable populations, such as the elderly, those with compromised cardiopulmonary health, and children, are of particular concern for public healthcare institutions.

PM is routinely collected on filters and subsequently analyzed gravimetrically and/or by chemical analysis. Several techniques are available for compositional analysis, including atomic absorption spectroscopy (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), ion chromatography [15] and voltammetry [16]. The analysis of PM filter samples requires involved digestion procedures, making routine analysis expensive and time-consuming.

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Moreover, this analytical preparation may alter the elemental composition of the sample, by increasing the content of some elements by contamination or decreasing the content of some elements by losses, for example due to chemical reaction or degradation.

Current European Directives concerning air pollutant sampling and analysis [17,18] have established reference methods for heavy metals, including graphite furnace atomic absorption spectroscopy (GFAAS) and ICP-MS methods [19]. Energy dispersive X-ray fluorescence (EDXRF) has been used for many years for the direct analysis of aerosol filter samples. Detection limits can be found in Refs. [20,21]. However, other methods may be used if they yield equivalent results to the reference methods. Due to continued research and development [22], Total Reflection X-ray Fluorescence (TXRF) analysis has become a well-accepted chemical technique for quality control in the semiconductor industry [23]. The reflection of X-rays close to the critical angle makes this technique extremely sensitive with improvements in limits of detection. The development of compact and more sensitive instruments offers new opportunities for further improvement of this technique. TXRF appears particularly promising for environmental analysis, especially when heavy metals must be detected at very low concentrations, in the range of ng/m^3 [24]. Several reviews are available, providing detailed information on the TXRF technique and its main applications [25–27] including its use in environmental analysis [28].

TXRF has been reported as an alternative technique to monitor air particulate composition. This technique requires only microgram amounts of sample, much less than that needed for ICP-MS analysis [29,30].

Recently, we have reported [31] that the direct analysis of PM filters without the delay and difficulty posed by digestion needs much shorter preparation time (from hours to minutes) and provides reliable results. The analysis of solid samples by TXRF can be performed directly on particles (suspension or slurry of finely powdered materials), on thin foil or on deposited material. In this manuscript we show that TXRF can be a good alternative to other standardized methods for PM filter analysis. In particular, we introduce a new method for samples analysis that was recently patented [32].

This method offers the possibility to analyze filter samples without digestion, making TXRF extremely competitive compared to other techniques such as AAS and ICP. This approach allows non-destructive analysis of filters to obtain quantitative information about heavy metals in airborne particles [31,33]. However, it requires suitable reference samples to convert the measured fluorescence intensities into concentrations.

The proposed method was applied to investigate the concentration of manganese (Mn) in air filters sampled in the Italian province of Brescia (see Fig. 1). Samples were collected both in the pre-Alps valley of Vallecamonica in the vicinity of Mn–Fe-alloy industries and in a reference area in the southeastern Garda Lake area of the province. This exposure assessment was part of the previously mentioned EU-FP6 Integrated PHIME Project.

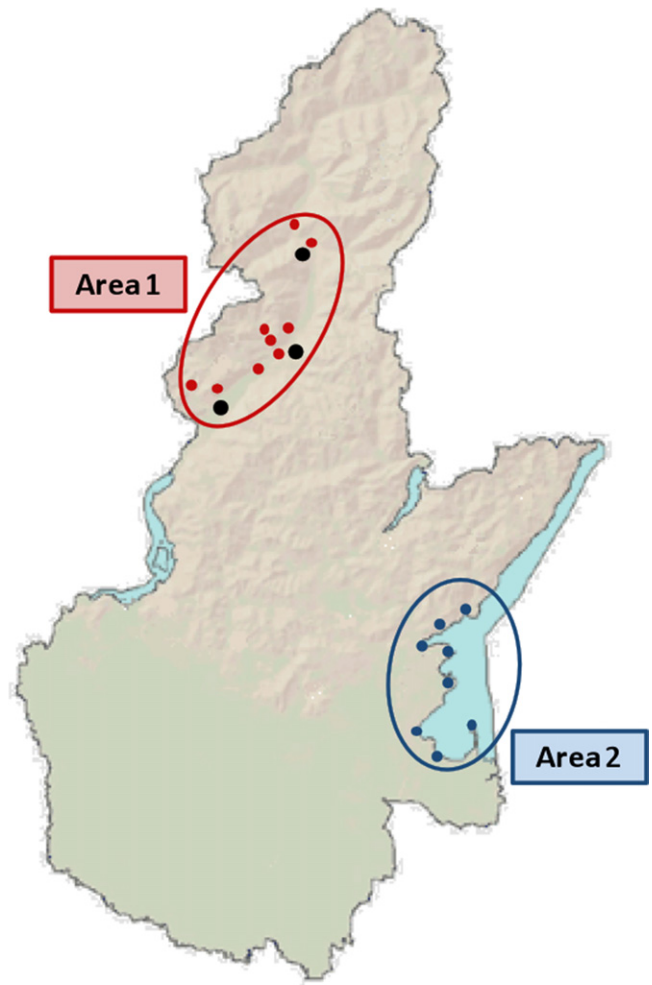

Fig. 1. Map of Brescia province. The red points indicate Breno (the most polluted municipal district for Mn presence) and surrounding valley sampling locations (area 1). Blue points represent locations where samples were collected in the Garda Lake reference area (area 2). Black points show the location of the Fe-alloy plants. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2. Materials and methods

2.1. Air filter sample collection

Atmospheric aerosols were collected on commercial filters (37 mm diameter, PTFE-Teflon) for PM_{10} in selected municipal districts of Brescia, one of the largest provinces in the Lombardia Region of Italy, with a total land surface area of 4784 km^2. The filters were collected with personal samplers on volunteer student adolescents. The samplers used were 10 μm particle diameter cut-point Personal Environmental Monitors (PEMs) of SKC, Inc., Eighty-Four, PA, each of which was attached to a student's backpack strap, located near the breathing zone. Each PEM was connected to a Leland Legacy pump of SKC, Inc., Eighty-Four, PA, which was carried in the backpack. The pumps were pre-calibrated to a 10 l/min flow rate with a soapless piston primary calibrator, the Defender, BIOS, Butler, NJ, with post-sampling flow rate confirmed as well. The pumps were run for 24 consecutive hours with the child's school backpack either carried by the child or placed near the child during school or in the room while they were sleeping. Samplers were kept in a special case that reduces the noise significantly. Each child was asked to complete a personal diary with complete records of their activities and locations during the sampling period. The study site was chosen because in a previous study [14] an increased prevalence of Parkinsonism was observed in the vicinities of Mn–Fe-alloy plants located in Vallecamonica, a narrow valley in the pre-Alps in the northern part of the Brescia province which once contained three active Mn–Fe-alloy foundries. Based on the results of an initial environmental survey, the potentially most polluted areas for Mn in the Brescia province have been selected [34] and a total of 188 filter samples were collected and analyzed. They included 31 samples collected in the village of Breno, located in the central area of Vallecamonica. Breno was the site of one of the largest and most active of these foundries that operated from 1902 until 2002. In addition, 94 samples were collected in other municipal districts