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Elemental analysis of tree leaves by total reflection X-ray fluorescence: New approaches for air quality monitoring

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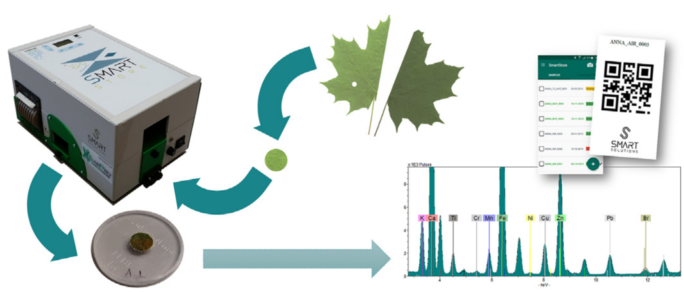
HIGHLIGHTS

- Elemental analysis of tree leaves is performed for air quality monitoring.
- TXRF analysis is performed on leaves from 6 tree species and 11 urban parks.
- Metals from anthropogenic sources contribute to differentiation of washed and unwashed samples.
- The novel SMART STORE method for sample preparation allows direct TXRF analysis.
- Advantages of the two sample preparation procedures are presented and discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

This work shows that total reflection X-ray fluorescence (TXRF) is a fast, easy and successful tool to determine the presence of potentially toxic elements in atmospheric aerosols precipitations on tree leaves. Leaves are collected in eleven parks of different geographical areas of the Brescia city, Northern Italy, for environmental monitoring purposes. Two sample preparation procedures are considered: microwave acid digestion and the novel SMART STORE method for direct analysis. The latter consists in sandwiching a portion of the leaf between two organic foils, metals free, to save it from contamination and material loss. Mass composition of macro, micro and trace elements is calculated for digested samples, while relative elemental amount are obtained from direct analysis. Washed and unwashed leaves have a different composition in terms of trace elements. Differentiation occurs according to Fe, Pb and Cu contributions, considered as most representative of air depositions, and probably related to anthropogenic sources. Direct analysis is more representative of the composition of air precipitations. Advantages and drawbacks of the presented methods of sample preparation and TXRF analysis are discussed. Results demonstrate that TXRF allows to perform accurate and precise quantitative analysis of digested samples. In addition, direct analysis of leaves may be used as a fast and simple method for screening in the nanograms range.

1. Introduction

Atmospheric pollution is one of the biggest problems of urban

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environments, due to the rapid population growth and the expansion of industrial activities. Among the atmospheric pollutants, heavy metals, such as Pb, Cd, Cr, Mn, Ni, Cu, Zn, and As, represent an important issue due to their toxic effects, and accumulation throughout the food chain, leading to serious ecological and health problems. In the past, Pb contamination was mainly due to its use as anti-detonating agent in fuels. Nowadays, Pb may come also from paintings, exhausted batteries, and industrial wastes. Oils, pneumatics and old car remains are the main sources of Cd, Ni, Cu and Zn pollution, while Mn has a predominant natural origin (Malizia et al., 2012). Many source apportionment studies report the distribution of these metals within atmospheric particles deposited on filtering membranes (Allen et al., 2001; Horvath et al., 1996; Amato et al., 2009; Samara and Voutsa, 2005).

Biological indicators are widely used to evaluate the deposition, accumulation and distribution of heavy metals in the environment (Borgese et al., 2009; Oliva and Espinosa, 2007; Oliva and Rautio, 2004; Patel et al., 2015; Bilo et al., 2015). Application of passive sample has some benefits such as low-cost information regarding the environmental quality, temporal resolution of environmental changes, and easy sampling procedures (Sawidis et al., 2011). Mosses, lichens (Borgese et al., 2009; Lippo et al., 1995), woody (Saarela et al., 2005), vascular plants, tree barks (Santamaría and Martín, 1997) and tree leaves (Sabry Mansour, 2014) are commonly used bio-indicators for pollution assessments studies. Indeed, these long-living organisms may accumulate heavy metals from different environmental sources (soil, water, air) and retain them for a long time.

Leaves are efficient systems to track air particulate matter (PM) and serve as sinks for aerosols and gases (Chen et al., 2015; Sawidis et al., 2011). Due to the tree structure, tree leaves have a higher ability to capture air precipitations than the shorter vegetation. The amount of particles collected on a leaf obviously depends on the air PM concentration, but it is also related to the leaf surface, morphology and anatomy, tree size, and climate conditions such as wind direction, season, and temperature. Sedimentation, Brownian diffusion, impaction and interception resulting from turbulent flow are the four known deposition processes of air PM on leaves. For example, when ultrafine PM (0.1 μm) is absorbed into the leaf tissues, Brownian diffusion is the main deposition mechanism (Lin and Khlystov, 2012; Hinds, 1999). Detailed studies of deposition mechanisms in real urban conditions are still lacking, requiring very high amount of air deposition information related to atmospheric conditions. The method presented herewith will provide an additional simple, cheap and easy to use tool to extract data on that purpose.

The amount of air PM deposited on leaves is usually about 70–235 μg/cm2, with an average deposition of 148.45 μg/cm2 (Song et al., 2015). For this reason, techniques with high sensitive are required. Atomic Absorption Spectroscopy (Barbeş et al., 2014; Ojekunle et al., 2015; Sabry Mansour, 2014), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Patel et al., 2015; Popescu et al., 2009), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Petrova et al., 2014; Mingorance and Oliva, 2006) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Tomašević and Aničić, 2010) are commonly employed for elemental analysis of leaves after total mineralization.

TXRF is a well established technique for elemental analysis of liquid samples deposited on the surface of polished reflectors where the dried residue is measured, being the first application reported more than 20 years ago (Wobrauschek, and Aiginger, 1975). Performances of TXRF are comparable with respect to the aforementioned techniques (Klockenkämper, and Bohlen, 2015). The first analytical application of TXRF is a variant of conventional XRF where the geometrical configuration enhances the sensitivity. The incident angle of the X-ray beam is lower than the critical angle for reflection of X-rays at the carrier surface. The detector is placed 90° with respect to incident beam and less than 0.5 mm above the sample surface. TXRF is a reliable and sensitive technique for elemental analysis of environmental samples (Bilo et al., 2014; Borgese et al., 2015, 2009; Marguí et al., 2010; Martinez et al., 2008; Montero Alvarez et al., 2007). It offers several advantages compared to other spectrometric techniques such as the simultaneous detection of elements, low amount of sample (few μL or ng), and the low time required for analysis. In total reflection conditions, matrix effects are negligible and quantification can be easily performed by internal standardization. Besides, new low power benchtop TXRF systems are cost-effective since they do not require gas or cooling media for operation (Klockenkämper and Bohlen, 2015).

In case of solid samples, the most common sample pretreatment methods for TXRF analysis are: mineralization, powder suspension or direct deposition on the reflector surface (De La Calle et al., 2013a,b). The direct TXRF measurement of the leaf allows to collect a signal representative of the upper leaf composition, where contribution from air deposition is more relevant. In this context the use of a surface sensitive technique allowing simple and fast multi-elemental analysis would be desirable. We have already demonstrated the successful use of TXRF for elemental analysis of lichens in comparison with AAS (Borgese et al., 2009). A rapid protocol for plant leaf analysis with TXRF was also presented (Höhner et al., 2016). Digestion requires the uses of strong and toxic acids and has disadvantage that sample is completely destroyed and elements may be lost (Bilo et al., 2016). However, TXRF offers the possibility for direct analysis of solid samples. As far as we know, there is no paper in the literature dealing with the direct analysis of leaves samples for air pollution monitoring.

In this work we present a new sample preparation approach for direct TXRF analysis of leaf samples, according to the one already proposed for air filtering membranes (Borgese et al., 2011; Borgese et al., 2012). Furthermore conventional TXRF analysis of digested leaf samples is performed. The aim is to demonstrate that TXRF is a useful and sensitive analytical tool for monitoring toxic elements of atmospheric origin on tree leaves within city urban region. We show that complete leaf decomposition enables accurate and precise quantitative analysis. On the other side, the SMART STORE approach, i.e. non destructive direct analysis, is environmental friendly, and it allows a fast and easy screening of the leaf samples with sufficient sensitivity. Advantages and limitations of these methods are reviewed and critically discussed.

2. Materials and methods

2.1. Leaves collection

Tree leaves of six different genera: *Maple*, *Elm*, *Ivy*, *Plan*, *Plum*, *Linden*, are collected in 11 urban parks in different areas of the Brescia city, Italy (45° 32′ 8 N, 10° 12′ 52 E). Fig. 1 shows a map of the sampling sites. In order to obtain representative samples, fully mature leaves are collected from not nearby trees, at the height ranging from 1,5 to 3 m above the ground level, depending on tree structure. The collected samples are transferred to the laboratory in clean plastic envelopes. Leaves are cut in two halves. One half is kept unwashed, while the other is rinsed with ultrapure de-ionized water (Millipore Corp., Bedford, Massachusetts). Both halves of the same leaf are punched to obtain 8 mm diameter discs, to be prepared for direct analysis, while the residuals proceed to mineralization.