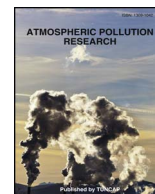


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## Multi-elemental analysis of particulate matter samples collected by a particle-into-liquid sampler

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## ABSTRACT

Time-resolved elemental analysis of particulate matter (PM) helps in the reliable identification of specific source tracers and study of mixing dynamics in the lower atmosphere. In this study, a new flow system (FS) for the introduction of samples into the inductively coupled plasma mass spectrometry (ICP-MS) instrument, which consists of on-line filtration and acidification of samples collected by a particle-into-liquid sampler (PILS), was optimised. Through this system, the limits of detection and quantification were significantly reduced, compared to those of ICP-MS analysis of samples collected by a PILS after off-line filtration. This makes it possible to conduct multi-elemental analysis of the samples collected by the PILS without any pre-treatment. The optimised FS-ICP-MS system was directly coupled with a PILS in order to study the profiles of some selected indoor and outdoor sources of PM (cigarette smoking, incense burning, brushwood burning, pellet burning, and road dust resuspension). The application of the FS-ICP-MS system for off-line elemental analysis of samples collected by a PILS during spot events in indoor and outdoor environments allowed us to verify the suitability of this system for the time-resolved (10 min) analysis of PM. The results indicate a significant increase in the indoor concentrations of some toxic elements (such as, Cd, and Pb) during the cleaning operation of domestic biomass burning systems (pellet stoves and thermo-fireplaces). Similarly, increases in the concentration of these elements were also observed in the outdoor environment during spot events of agricultural waste combustion, an illegal activity frequently practiced in many rural areas.

## 1. Introduction

Particulate matter (PM) is a mixture of solid particles and liquid droplets in the air (Knudsen and Rasmussen, 2012). It is largely recognised that human exposure to air pollution has severe consequences for human health such as diseases of the respiratory and cardiac systems (Pope and Dockery, 2006). Suspended particles vary in size, composition, and origin. The chemical composition, diameter, morphology, surface area, structure, electric charge, and solubility are important parameters for the characterisation of the behaviour of dust particles in the atmosphere. The most important parameters that influence the chemical and physical properties of PM are its source, mechanism of formation, emission process, and distance from the source. Several studies have shown that elementary analysis of particulate matter (PM) in the atmosphere helps understand the origin of the particles and characterize the emission sources. In this context, improving the selectivity of source tracers may be the key to developing emission reduction strategies for the protection of both human health and environment. The main problem in the identification of source

tracers is that they are not selective i.e. the same elements can be emitted from several different sources (Querol et al., 2001, 2006; 2007a; Lee et al., 2003; Gotschi et al., 2005; Viana et al., 2007; Jeong et al., 2008). In light of this, development of highly sensitive methods for the study and characterisation of emissions from particular processes is required. Such methods allow simultaneous analysis of a large number of tracers without using a large sample amount. A number of studies on the temporal variability of the concentration of atmospheric pollutants on a 24-h sampling basis have been reported in literature (Kidwell and Ondov, 2004; Bukowiecki et al., 2005). The problem with this approach is that the obtained concentrations are mediated over a period (24 h) during which the strength of sources and the dilution capacity of the atmosphere are subject to wide variations. Information on the time-resolved variation of tracers in ambient air significantly facilitates the identification of pollution sources because it allows the decoupling of each time trend. Generally, the rate at which the strength of sources and the dilution capacity of the atmosphere changes influence the elemental composition of PM. Variations in emission rates, meteorological parameters, and atmospheric processes (Kidwell and

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Onodov, 2001) are fast (minutes to hours) and cannot be captured by conventional 24-h filter measurements. During the last few years, optimisation of the new high time-resolved monitoring systems has been an exciting challenge in atmospheric pollution research. Different techniques for optimisation have been proposed in literature. These include aerosol mass spectrometer (AMS), semi-continuous elements in aerosol sampler (SEAS), streaker sampler followed by analysis with proton-induced X-ray emission (PIXE), particle-into-liquid sampler (PILS), and bio-sampler with ambient metals monitor (Weber et al., 2001; Pancras et al., 2005; Li et al., 2015; Sowlat et al., 2016; Barnaba et al., 2017; Furger et al., 2017).

The operating principle of a PILS is to grow the sampled atmospheric particles by mixing them with supersaturated steam in a specific chamber, so that they can be collected by inertial impaction at the top of the impactor plate. The particles are continuously washed from the impactor plate by a water solution. PILS is generally used in combination with ion chromatography (PILS-IC) for on-line monitoring of water-soluble inorganic ions. However, it has also been used as a sampler for the analysis of other analytes (Hecobian et al., 2010; Timonen et al., 2010). The main limitation of this system is that samples are highly diluted by the wash solution, thus leading to a considerable increase in the detection limits. This does not allow the application of this system in areas with low concentration of pollutants (Wang et al., 2013; Perrino et al., 2015).

Despite the importance of time-resolved elemental analysis for source apportionment studies, only a few PILS applications involve elemental analysis. To our knowledge, there are two experimental PILS applications concerning elemental analysis. One involves the study of certain heavy metals (Zn, Cd, Pb, and Cu) using anodic stripping voltammetry (ASV) (Bogenschütz et al., technical report) and the other involves measurement of water-soluble Fe (II) with a particle into liquid sampler (PILS) coupled to a liquid waveguide capillary cell (LWCC) and a UV/VIS spectrometer (Oakes et al., 2010).

In light of this, the aim of this study is to combine the sampling advantages of a PILS (high time-resolution and low costs) with the flexibility and sensitivity of inductively coupled plasma mass spectrometry (ICP-MS). This would help achieve simultaneous analysis of time-resolved pseudo-total (soluble in 1% HNO<sub>3</sub> solution) concentrations of a large number of elements. The current paper describes the optimisation of a new flow system (FS) for introducing the samples collected with a PILS into the ICP-MS instrument. This system allows the PILS and ICP-MS to be directly coupled for the on-line analysis or the PILS samples collected off-line to be analysed by ICP-MS with an increased sensitivity. The optimised system was used to obtain elementary profiles of some specific indoor and outdoor sources, such as cigarette smoking, wood and incense combustion, and road dust resuspension (on-line measurements), and for short indoor and outdoor monitoring campaigns (off-line measurements).

## 2. Material and methods

### 2.1. Particle-into-liquid sample

The PILS (ADI 2081, Metrohm AG, Herisau, Switzerland) consists of a vapour generator that is placed perpendicular to the entrance of the sampled air stream, a central cylinder that acts as an expansion chamber, and an impactor plate where particles are captured by inertial impaction and are subsequently washed with a wash solution before their collection. All the solutions entering and exiting the PILS were managed by a single eight-channel peristaltic pump (model 205S, Watson-Marlow Inc., Wilmington, MA, USA) running at a speed of 24 RPM. The operative flow rates were as specified in the PILS operating conditions manual. Water used for the collection of ambient PM and for system rinsing was purified by a water purification system (EMD Millipore, Billerica, MA, USA). It is important to note that the water solution introduced at the top of the impactor plate to transport the

particles down to its base was spiked with 50 µg/L of LiBr (Merck KGaA, Darmstadt, Germany), which was used as an internal standard. The output flow rate (union of sample and acid lines) is 0.6 mL/min. Samples exiting the PILS were either collected in vials using a fraction collector (Varian SPS 5 Auto sampler) or connected to the ICP-MS instrument for on-line analysis, as described below.

Operatively, the blank values were obtained by placing a filter pack, comprised of one Teflon filter, one Nylon filter, and one paper filter, impregnated with H<sub>3</sub>PO<sub>3</sub> solution at the inlet of the PILS. This filter pack was able to restrict the passage of particles and inorganic vapour (Perrino et al., 2015).

### 2.2. ICP-MS analysis

Samples collected by the PILS that are to be analysed by the conventional off-line procedure were mixed with 2% HNO<sub>3</sub> (obtained by diluting 65% HNO<sub>3</sub>, Suprapur, LGC, Promochem) and filtered with a syringe filter (Millipore membrane, pore size: 0.45 µm) before analysis. ICP-MS conditions used for this analysis were as described in a previous study (Protano et al., 2016). Matrix-matched calibration was obtained by using yttrium (Y) (20 µg/L) as an internal standard. The instrument was calibrated for each element within a range of concentrations likely to be encountered in the field samples.

The new FS for sample introduction used for on-line and off-line field measurements is described below (section 2.5). In this case, the ICP-MS operating conditions were modified (Table 1) in order to achieve a fast instrumental response. In particular, the rinse time and stabilization delay were set to zero, which is usually done when the ICP-MS instrument is used like a chromatographic detector. In contrast to when the ICP-MS instrument is used as a detector, the replicates read times were maintained at 10 s in order to avoid reduction in the signal/background ratio.

### 2.3. Application in obtaining source profiles

The sources tested were individually simulated in a laboratory inside a Plexiglas box (volume: 1 m<sup>3</sup>) and the emissions were directly sampled and analysed by the coupled PILS-FS-ICP-MS system. Inside the Plexiglas box, we controlled the emission conditions as much as

**Table 1**  
ICP-MS operating conditions used during FS-ICP-MS analysis.

Parameter	Value
<b>Flow Parameters (L/min)</b>	
Plasma Flow	18
Auxiliary Flow	1.8
Sheath Gas	0.18
Nebulizer Flow	1.0
<b>Torch Alignment (mm)</b>	
Sampling Depth	7.0
<b>Other</b>	
RF power (kW)	1.4
Pump Rate (rpm)	7.0
Stabilization delay (s)	0
Rinse time (s)	0
Replicate read time (s)	10
<b>Ion Optics (volts)</b>	
First extraction lens	−1.0
Second extraction lens	−180
Third extraction lens	−205
Corner Lens	240
Mirrors lens left	34
Mirrors lens right	28
Mirror lens bottom	29
Entrance lens	0.0
Fringe Bias	−4.0
Entrance plate	−4.0
Pole Bias	0.0

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