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#### Review

# Recent developments in assessment of bio-accessible trace metal fractions in airborne particulate matter: A review



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#### HIGHLIGHTS

- ► Survey of leaching agents used for sample extraction.
- ► Multi-step fractionation schemes.
- ► Dynamic extraction procedures.
- ► Analytical approaches for element specific measurement.
- Detailed compilation of published results.

#### GRAPHICAL ABSTRACT

#### Leaching Agent **APM Procedure Analysis TSP** Water Single step **PM10** Salt solutions Multi step PM2.5 **Buffer solutions** Batch-wise Synth. body fluids PM1.0 Dynamic

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#### ABSTRACT

In the last years a great deal of research has been focused on the determination of harmful trace metals such as Cd, Co, Cr, Cu, Ni or Pb in airborne particulate matter (APM). However, the commonly applied determination of total element concentrations in APM provides only an upper-end estimate of potential metal toxicity. For improved risk assessment it is important to determine bio-accessible concentrations instead of total metal contents. The present review gives an overview of analytical procedures reported for measurement of bio-accessible trace metal fractions in APM. The different approaches developed for extraction of soluble trace metals in APM are summarized. Furthermore the analytical techniques applied for accurate determination of dissolved trace metals in the presence of complex sample matrix are presented. Finally a compilation of published results for bio-accessible trace metals in APM is included.

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**Azam Mukhtar** completed his PhD at the Vienna University of Technology (Austria) at the Institute of Chemical Technologies and Analytics. His research work is dedicated to the field of environmental analytical chemistry with special emphasis on the measurement of bio-accessible trace element fractions in airborne particulate matter. Application of slurry procedures for the analysis of total element contents in aerosol samples is another important topic.



Andreas Limbeck is Privatdozent at the Vienna University of Technology (Austria), currently he is head of the research division of Instrumental Analytical Chemistry at the Institute of Chemical Technologies and Analytics. His research interests are focused on the application of ICP-MS, ICP-OES and ET-AAS for analysis of trace elements in environmental samples including the development of improved sample pre-treatment procedures. A further research field is the use of Laser-Ablation and Electro-Thermal-Vaporization for the direct analysis of solid samples.

#### 1. Introduction

Airborne particulate matter (APM) is contributed through various natural as well as anthropogenic sources [1]. Primary particles are directly emitted as liquid or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruption, and wind-driven or traffic related suspension of road, soil, and mineral dust, sea salt and biological materials (plant fragments, micro-organisms, pollens, etc.). Secondary particles, on the other hand, are formed by gas to particle conversion in the atmosphere [2–5]. The suspended airborne particles undergo various physical and chemical interactions and transformations (atmospheric aging), that is, changes of particle size, structure, and composition (e.g. coagulation, restructuring, gas uptake, and chemical reactions). Therefore the concentration, composition, and size distribution of atmospheric aerosol particles are temporally and spatially highly variable. The components of APM can generally be classified as carbonaceous fractions including organic carbon, elemental carbon, carbonate carbon and inorganic components consisting of crustal elements, trace metals and ionic species. Each of these components typically contributes about 10-30% of the overall mass load. Depending on aerosol properties and meteorological conditions, the characteristic residence times (life times) of aerosol particles in the atmosphere range from hours to weeks [6,7]. The particles with diameter from some nm to tens of  $\mu$ m can remain buoyant in the atmosphere for days and thus can be transported over a long distance from the original source resulting in an enhanced level of ambient PM concentrations even at rural or background sites.

A particular APM component that is known to exert toxic effects on human being is metallic fraction [8]. Many elements, like Cd, Cr, Cu, Mn, Ni, Pb, V and Zn are widely distributed in PM and, hence, are suspected to be an important source of PM toxicity [9]. Therefore, trace element analysis of APM is highly demanded for assessing air quality and health risks [10]. Many epidemiological studies have demonstrated that exposure to such metals can cause adverse human health effects at concentrations commonly found in urban areas around the world [11,12]. Additionally, it has also been

demonstrated in several recent studies conducted in vitro simulating the respiratory environment, or in vivo by animal models, that metal components of APM are correlated with the observed pulmonary toxicity [13–17]. Therefore, a great deal of research has been focused on the metal composition of atmospheric suspended particulate matter. However, most of the studies dealing with determination of trace metals in APM focus on the determination of total metal concentration without distinguishing the various species that are present [18]. But for risk assessment of metal toxicity, it is important to determine bio-accessible concentrations instead of total metal contents. Therefore, it is necessary to study the impact of easily released metallic components in APM on human health. This includes health research involving both epidemiology and toxicology, which continue to implicate metals as a possible cause of the observed adverse effects on human health.

The bio-accessibility of a metal indicates the upper level estimate of risk assessment and is defined as the value representing the availability of metal for absorption when dissolved in synthetic body fluid or juices in vitro, whereas bioavailability is the amount that is actually taken across the cell membrane [19,20]. There is misconception about the use of terms "bio-accessibility" and "bioavailability" in literature where determination of merely bio-accessibility is considered as bio-availability. But in fact, bioaccessibility measurement of trace metals in various fluids provides only the data about metallic fractions which could be available to living organisms for absorption in their physiological systems. Therefore, in lieu of obtaining bioavailability data from samples of body fluids like urine, blood, or other tissues, the measurement of metal "bio-accessibility" can be used as an in vitro substitute for measuring potential metal bioavailability [20,21]. The potential health effects from the trace metal fractions present in APM depend upon the bonding and hence solubility of metallic components in addition to particle size, shape, total human exposure and the health status of the population [22], whereas the solubility of an aerosol-borne trace metal is dependent on its source of origin (chemical form), the size of aerosol particle that bears it and the pH of the sample [23,24]. In general, metallic components of APM with high solubility can be more readily bio-activated and thus may be potentially more harmful for humans [25].

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