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New approaches for characterization of inorganic bulk constituents and bio-accessible trace metal fractions in airborne particulate matter

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Dedicated to my beloved father, may his soul rest in eternal peace

Abstract

The presented thesis aims at the development of novel analytical procedures for the investigation of inorganic aerosol fractions and characterization of bio-accessible trace metals present in airborne particulate matter (APM). For risk assessment, source identification and ambient level reduction, routine monitoring of APM composition is highly needed. The major challenges for inorganic aerosol analysis are the presence of complex sample matrices which hamper the analysis of target analytes with very low concentration. Hence, improved sample pretreatment procedures are required to overcome such problems. Therefore, in the last decade, a lot of work has been dedicated to the development of accurate extraction and digestion methods for the conversion of solid or liquid samples into forms compatible with the utilized measurement techniques. The developed analytical methods allow the removal of complex sample matrix, analyte enrichment and isolation of the target elements prior to analysis.

Conventional microwave digestion procedures are usually used for sample preparation and mineralization, but these methods are limited by factors such as time consuming laborious sample handling steps, risk of analyte losses due to increased sample handling and sample contamination caused from increased reagent consumption. Furthermore, sensitivity of procedure is hampered due to unnecessary sample dilution. Thus, in the first part of thesis, a slurry procedure with ETAAS detection is proposed. In contrast to existing microwave digestion procedures, the developed approach excludes complex and troublesome sample pretreatment steps and use of hazardous hydrofluoric acid required for dissolution of silicates. The risk of sample contamination is reduced due to decreased reagent consumption and manipulation steps. Furthermore, the procedure is found to be advantageous over traditional microwave digestion procedures in terms of sensitivity and time consumption. The developed sample pretreatment procedure in combination with an optimized ETAAS method allowed highly sensitive element specific analysis of Si in PM10 samples collected for only 60 min, thus enabling monitoring of fast changes in ambient Si concentrations. After further optimization, the proposed slurry procedure in combination with inductively-coupled plasma atomic emission spectrometry (ICP-OES) was applied in the second part of current thesis for simultaneous multielement analysis of selected crustal and trace elements present in APM.

For risk assessment, knowledge about bio-accessible trace metals is required instead of total metal contents since these fractions are known to exert toxic effects on human beings. For determination of soluble trace metal fractions in environmental samples, generally batch-wise

extraction procedures are used which involve time consuming laborious sample handling steps. Additionally, information about kinetics of the leaching process is not accessible since extraction is usually performed using equilibrium conditions whereas in environmental systems the metals are released under dynamic conditions. In the third part of the thesis, a flow injection procedure coupled to flame atomic absorption spectrometry (FAAS) is proposed for online determination of water-soluble Zn in APM. The presented flow injection technique allows extraction of bio-accessible Zn in APM under dynamic conditions with element specific detection of the elution profile. In contrast to batch-wise systems, the developed online extraction procedure offers enhanced sensitivity and sample throughput, reduced risk of sample contamination and absence of metal re-adsorption processes. The procedure was applied for analysis of water-soluble Zn in aerosol samples from different urban sites in Austria.

For estimation of bio-accessible metal fractions the use of an in-vitro physiologically based extraction test (PBET) is recommended. With this approach risk assessment could be improved but analysis is hampered, since the organic matrix used for sample extraction causes spectral and non-spectral interferences during ICP-OES or ICP-MS measurement. The samples are usually diluted to reduce such interferences but in case of APM samples dilution may lead to insufficient sensitivity if a limited sample amount is available. Therefore, highly sensitive analytical procedures are required to quantify bio-accessible trace metal fractions in APM. In the final part of the thesis, electrothermal vaporization inductively-coupled plasma (ETV-ICP-OES) procedure is proposed. The method is based on the preliminary extraction of trace metals with synthetic gastric juice using a physiological based extraction procedure and the subsequent measurement of gastric extracts with ETV-ICP-OES. Careful optimization of the temperature program allowed removal of organic matrix compounds and interference free measurement of target analytes and allowed external calibration with aqueous standards to be used for quantification of the derived signals. Compared to conventional ICP-OES measurement of derived sample extracts a distinctly improved sensitivity could be achieved, which allows the measurement of toxic trace metals such as Co, Ni and Pb up to a level of some hundreds of pg m^{-3} in PM10 samples.

Kurzfassung

Die vorliegende Doktorarbeit hat die Entwicklung neuer analytischer Verfahren zur Untersuchung von anorganischen Aerosolfraktionen und zur Charakterisierung von Bio-verfügbaren Spurenmetallen in Feinstaub (airborne particulate matter- APM) zum Ziel. Die routinemäßige Überprüfung der Zusammensetzung von APM ist hinsichtlich Risiko-Abschätzung, Identifizierung von möglichen Quellen und Reduktion der Immissionswerte notwendig. Die komplexe Zusammensetzung der Proben- Matrix und die niedrige Konzentration der Analyten stellen mit die größten Herausforderungen bei der Analyse von anorganischen Aerosolen dar. Darüber hinaus zeichnen sich die gängigen Methoden zur Probenvorbereitung durch umständliche und zeitaufwändige Schritte sowie die Gefahr von Probenkontamination oder Analytverlusten aus. Deswegen wurde viel Anstrengung in die Entwicklung von verlässlichen Extraktions- und/oder Aufschlussmethoden investiert, die eine Umwandlung von festen oder flüssigen Proben in für die Messgeräte geeignete Formen ermöglichen. Die vorgestellten analytischen Methoden gewährleisten eine Abtrennung der Matrix und eine Anreicherung beziehungsweise eine Isolierung der analytisch relevanten Elemente vor der eigentlichen Analyse.

Herkömmliche Mikrowellenaufschlüsse werden häufig für die Probenvorbereitung und die erforderliche Mineralisierung der Proben eingesetzt. Mehrere Faktoren sind bei diesem Vorgehen jedoch hinderlich, beispielsweise Zeitaufwand, manuelle Probenmanipulation, Gefahr von Analytverlusten und Gefahr von Probenkontamination aufgrund der großen Mengen an zugesetzten Reagenzien. Desweiteren wird die Sensitivität der Analyse durch Verdünnen auf unnötige Weise herabgesetzt. Im ersten Teil dieser Doktorarbeit wird demzufolge eine Methode zur Probenvorbereitung mit teilweise gelösten Proben vorgestellt (die so genannte slurry-procedure). Im Gegensatz zu bestehenden Mikrowellenaufschlüssen erlaubt diese Methode, mit wenigen Schritten und ohne der Verwendung gefährlicher Chemikalien wie zum Beispiel Flusssäure, eine Probe zu analysieren. Die Gefahr von Verunreinigungen ist aufgrund des verringerten Einsatzes von Chemikalien und der direkteren Vorgehensweise deutlich geringer. Diese Methode, kombiniert mit optimierten ETAAS Messungen, erlaubt die äußerst nachweisstarke und elementspezifische Bestimmung von Si in PM10 Proben, wodurch die Untersuchung von Proben, welche nur über einen Zeitraum von 60 Minuten gesammelt wurden, möglich wurde. Somit wurde die Erfassung von kurzzeitigen Schwankungen in der Si-Konzentration möglich. Die hier vorgestellte slurry- procedure wurde außerdem in Kombination

mit ICP-OES Analysen verwendet, die eine simultane Multielementanalyse von ausgewählten Hauptbestandteilen sowie Spurenelementen erlaubte.

Für die Risikobewertung ist es notwendig, über die Bioverfügbarkeit von Spurenelementen Bescheid zu wissen. Anstatt den gesamten Metallgehalt zu bestimmen, hat sich die chargenweise Extraktion mit unterschiedlichen Lösungsmitteln etabliert. Diese Vorgehensweise ist wiederum sehr arbeitsintensiv und zeitraubend. Auch ist auf diese Weise keine Information über das dynamische Auswaschverhalten der Analyten zu bestimmen, wie es unter realen Bedingungen auftritt. Im dritten Teil der Arbeit wird eine Fließinjektionsmethode gekoppelt mit Flammen AAS für die online- Analyse von wasserlöslichem Zn in APM vorgestellt. Diese Methode ermöglicht die Extraktion des bio-verfügbaren Zn in APM unter dynamischen (nicht-Gleichgewichts-) Bedingungen. Die online Kopplung an die FAAS erlaubt elementspezifische Detektion der Elutionsprofile. Im Gegensatz zur chargenweisen Extraktion bietet diese Methode eine höhere Nachweisstärke bei reduzierter Kontaminationsgefahr und gleichzeitiger Vermeidung von erneuter Adsorption an der Matrix. Auf diese Weise wurde wasserlösliches Zn in Aerosolproben aus verschiedenen städtischen Gebieten in Österreich untersucht.

Für die Bestimmung des bioverfügaren Anteils an Metallen werden physiologisch basierte *in-vitro* Extraktionen empfohlen. Durch diesen Ansatz wird die Risikoabschätzung verbessert, jedoch werden Analysen erschwert, da die organische Matrix der Extraktionsmittel spektrale wie auch nicht-spektrale Interferenzen bei ICP-OES wie auch ICP-MS Messungen bewirkt. In solchen Fällen werden die Proben zur Reduktion der Interferenzen üblicherweise verdünnt, im Falle von APM Proben führt eine weitere Verdünnung jedoch zu ungenügender Empfindlichkeit, falls nur eine begrenzte Probenmenge zur Verfügung steht. Daher sind hochempfindliche Messmethoden notwendig, um bioverfügbare Spurenmetallfraktionen in APM bestimmen zu können. Im letzten Teil dieser Arbeit wird eine ETV-ICP-OES Methode vorgestellt, welche die Bestimmung von bioverfügbaren Spurenmetallanteilen in APM erlaubt. Die Methode basiert auf der vorherigen Extraktion der Spurenmetalle mit künstlichem Magensaft und der anschließenden Messung dieses Extraktes mit ETV-ICP-OES. Gründliches Optimieren des Temperaturprogrammes ermöglichte die vollständige Entfernung von organischen Matrixbestandteilen und somit das interferenzfreie Messen der Zielanalyten. Externe Kalibration mit wässrigen Standards konnte für die Quantifizierung der dergestalt erhaltenen Signale herangezogen werden. Im Vergleich zu konventionellen ICP-OES Messungen der Probenextrakte konnte eine deutliche Steigerung der Sensitivität erzielt werden, womit die

Messung von toxischen Spurenmetallen wie Co, Ni und Pb bis zu einer Konzentration von einigen hundert pgm^{-3} in PM10 Proben ermöglicht wurde.

Contents

1 Preface

The presented PhD-thesis was conducted at the Vienna University of Technology, Austria in the time between March, 2008 and September, 2011. The conducted work resulted in publication of four articles in reputable journals and three un-published papers. Additionally five oral and six poster presentations were made at international scientific conferences.

The main objectives of current thesis were;

1. To enable better characterization of mineral components and trace metals in airborne particulate matter in terms of improved sample pretreatment procedures. The goal was to propose sample preparation procedures involving less laborious sample handling steps, minimal reagent consumption thus reducing the risk of analyte losses and sample contamination. Furthermore, it was intended to improve the sensitivity of measurement for crustal and trace elements in APM which allows monitoring of fast changes in their concentrations over limited intervals of time.

2. Development of novel approaches for determination of bio-accessible trace metal fractions in APM since such fractions exert toxic effects on human beings. For this purpose, it was planned to propose automated dynamic extraction strategies implemented in continuous-flow FI-systems as convenient alternatives to batch wise counterparts to better ascertain the bio-accessibility of trace metals in airborne particulate matter.

3. To develop improved analytical procedures for estimation of bio-accessible trace metal fractions being obtained via leaching with synthetic body fluid where introduced organic sample matrix causes interferences in measurement with existing analytical procedures. The aim was to improve the analysis of bio-accessible metal fractions in the presence of complex sample matrix with enhanced sensitivity.

In the introduction part of this thesis, a short overview about the aerosols, their composition, impact on global climate and human health is described. Furthermore, a short discussion about the presence of bio-accessible trace metal fraction in APM is presented. After the introduction, a detail of proposed analytical procedures is discussed followed by a brief discussion of published manuscripts. The experimental work, the applied analytical methods and the obtained results are described in the selected publication section.

2 Introduction

Aerosol is defined as a disperse system of liquid or solid small particles suspended in a gas, usually air. The term aerosol applies to a very wide range of particulate clouds encountered terrestrially, including naturally occurring airborne dusts, mists, clouds, sandstorms and snowstorms, as well as the man-made smokes, fumes, dusts and mists that are found in our working and living atmospheric environments with particle diameters in the range of 10^{-9}-10^{-4} m [1-2]. The effect of aerosols on the atmosphere, climate, and public health are among the central topics in current environmental research. Aerosol particles scatter and absorb solar and terrestrial radiations, they are involved in the formation of clouds and precipitation as cloud condensation and ice nuclei, and they affect the abundance and distribution of atmospheric trace gases by heterogeneous chemical reactions and other multiple processes [1, 3-5]. Furthermore, airborne particles play an important role in the spreading of biological organisms, reproductive materials, and pathogens (pollen, bacteria, spores, viruses etc.), and they can cause or enhance respiratory, cardiovascular, infectious, and allergic diseases [1-2, 6-7].

Airborne particulate matter (APM) is contributed through various natural as well as anthropogenic sources [8]. Primary particles are directly emitted as liquids or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, 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 [3-9]. 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, chemical reactions). Therefore the concentration, composition, and size distribution of atmospheric aerosol particles are temporally and spatially highly variable. There are two major pathways for removal of aerosol particles from atmosphere. The major sink of atmospheric aerosols is by wet deposition in which aerosols are scavenged by precipitation. The other method of aerosol sink is dry deposition which involves convective transport, diffusion or adhesion to the Earth's surface. Dry deposition is less important on a global scale, but is highly relevant with respect to local air quality, health effects (inhalation and deposition in human respiratory system). Depending on aerosol properties and meteorological conditions, the characteristic residence times (life times) of aerosol particles in the atmospheric range from hours to weeks [10-11].

3 Composition of particulate matter

Ambient particulate matter (PM) is a complex mixture of various gaseous and solid compounds. The composition of aerosol particles varies largely depending upon meteorological conditions and emission sources related to their origin. The components of PM can 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. However, at different locations, times, meteorological conditions, and particle size fractions, the relative abundance of various PM constituents can vary by an order of magnitude or more [1, 3].

3.1 Carbonaceous compounds

The carbonaceous fraction of PM mainly consists of three components: black or elemental carbon (BC and EC), organic carbon (OC) and carbonate carbon (CC). Elemental and organic carbon are emitted during combustion processes such as wood combustion for heating purposes or wild fires, combustion of fuel and gas, industrial combustion processes and burning of wastes [12].

The composition of organic fraction is complex and they are made up of hundreds of individual organic species. Organic compounds that have been identified in ambient aerosol include n-alkanes, mono- and dicarboxylic acids, polycyclic aromatic hydrocarbons, steroids, steranes, saccharides [1] and humic like substances [13]. In addition to combustion related primary emitted organic pollutants there are also biogenically derived organics in atmospheric aerosol originating from plants, plant debris and soils. These primary biological aerosol particles (PBAP) contain pollen, fungal spores [14], bacteria, algae, yeasts, molds, mycoplasma, viruses, phages, protozoa, plant abrasion products like cellulose [15]. The secondary organic aerosols (SOA) are formed by the reaction of primary emitted organic species in the atmosphere which involve a gas to particle conversion. The organic species can be oxidized by a number of oxidants in atmosphere like hydroxyl radical, ozone, and nitrate radical, and secondary products thus formed are accumulate in the atmosphere [1].

3.2 Inorganic compounds

3.2.1 Carbonate carbon

Carbonate carbon (CC) is an important constituent of PM and is usually found in connection with soluble calcium and magnesium. CC is mainly contributed from mineral dust [16].

3.2.2 Ions

Particulate ammonium (NH_4^+), nitrate (NO_3^-) and sulphate (SO_4^{-2}) are among the major ions found in APM. These ions are mainly formed by secondary processes from the primarily emitted gaseous ammonia (NH_3), sulphur dioxide (SO_2) and nitrogen oxides (NO_x) and are thus referred to as secondary inorganic aerosol (SIA) [1]. SIA reduces visibility, contributes to dry acid deposition and can represent a respiratory health hazard [17].

Being a gaseous base, ammonia plays an important role in the neutralization of acids. It is primarily produced by livestock wastes and fertilizers, whereas smaller amounts are assumed to be generated by industrial activities and natural processes in soil [17]. By reaction of sulphuric and nitric acid, it is transferred to ammonium sulphate and nitrate [3, 1], thus producing SO_4^{-2} and NO_3^- in atmosphere. Sulphur dioxide (SO_2) is mainly produced by combustion processes of fossil fuels containing sulphur [1]. SO_4^{-2} can also be released into atmosphere by oxidation of SO_2 to H_2SO_4 [3].

Nitrogen oxides ($NO_x = NO+NO_2$) are formed by combustion processes like the burning of fossil fuels, biofuels and biomass in addition to natural sources like lighting and microbial processes. NO can be oxidized to NO_2 by ozone as well as by peroxy radicals (HO_2 and RO_2), but can also be produced by decomposition or oxidation of peroxyacylnitrates (PANs). NO_2 present in atmosphere can be lost through oxidation by OH at daytime to form HNO_3 or by O_3 to form NO_3 at night. Afterwards, NO_3 reacts with dimethyl sulphide (DMS) or hydrocarbons (HC) or with NO_2 to form N_2O_5 followed by hydrolysis to form HNO_3 [3].

3.2.3 Crustal elements

The crustal elements Al, Ca, Fe, Mg and Si are the most important inorganic contributors to ambient PM10 level. For example, Handler et al., [18] reported for a site in Vienna (Austria) that the mineral components Al, Ca, Fe, Mg and Si accounted together for 20.5±4.4 % of the PM10 mass. On the other hand, trace elements like Ba, Cu, Mn, Sr, and Pb are only minor constituents (together less than 1 %) of PM10 mass. However, since the mineral components Al, Ca, Fe, Mg and Si are assumed to be present rather in the form of oxides than in elemental form, usually the measured elemental concentrations are converted into the respective mass concentrations of the most common oxides for PM10 mass balances [19]. Considering this approach (considering the oxides SiO_2, CaO, MgO and Fe_2O_3), Limbeck et al., [20] have found that mineral fractions of these oxides contributed 31.7±16% (Kendlerstrasse), 27.8±14% (Rinnboeckstrasse) and 22.3±17% (Schafberg) to PM10 mass for three different sites in Vienna. Appropriate measures for reduction of ambient PM10 levels should therefore consider these

crustal elements. For this purpose more detailed knowledge about occurrence (spatial and seasonal patterns) and sources of mineral components in APM is required.

3.2.4 Trace metals

More than 40 trace elements are routinely found in atmospheric particulate matter samples. These elements arise from dozens of different natural as well as anthropogenic sources including volcanic eruption, forest fires, sea spray, combustion of coal, oil, wood burning, steel furnaces, boilers, smelters, dust, waste incineration, industrial processes and brake wear [8, 21]. Specifically, the combustion of fossil fuels constitutes the principal anthropogenic source for Be, Co, Hg, Mo, Ni, Sb, Se, Sn and V. It also contributes to anthropogenic release of As, Cr, Cu, Mn and Zn. The larger percentage of As, Cd, Cu, Ni and Zn is emitted from industrial metallurgical processes. Exhaust emissions from gasoline may contain variable quantities of Pb, Cu, Zn, Ni and Cd. Zn emission is also associated with tire rubber abrasion [21]. Depending on their sources, these elements can be found in either the fine or the coarse mode.

Trace metals are very important for living organisms because they perform a vital role in the metabolism of living organisms. Some trace metals are known as essential metals e.g., Zn is a vital component of many metalloenzymes such as carbonic anhydrase, which regulates CO_2 exchange [22]. But at the same time excessive amounts of essential metals can cause toxicity. Additionally, trace metals are involved in a number of atmospheric reactions including the decomposition and generation of H_2O_2 in cloud water and fog [23], the conversion of S (IV) to S (VI) [24], and the cycling of $\cdot$OH, $\cdot HO_2$ through the redox cycling of iron and copper [25]. Trace metals have therefore an impact on the acid-generating and oxidizing capacity of the troposphere.

4 Impact of particulate matter on global climate and human health

4.1 Impact on global climate

Climate change is defined as any change in climate over time, either due to natural variability or as a result of human activity. Like greenhouse gases, aerosols influence the climate (this influence is called climate forcing or radiative forcing). Radiative forcing are changes in the energy flux of the solar radiation (maximum intensity in the spectral range of visible light) and terrestrial radiation (maximum intensity in the infrared spectral region) in the atmosphere, induced by anthropogenic or natural changes in the atmospheric composition [9]. Atmospheric aerosols influence the transfer of energy in the atmosphere in two ways: directly through the reflection and absorption of solar energy; and indirectly through modifying the optical properties

and lifetimes of clouds. Aerosols effects on climate are generally classified as direct or indirect with respect to radiative forcing of the climate system. Direct effects of aerosols result from the scattering and absorption of radiation by aerosol particles, whereas indirect effects result from their cloud condensation nuclei (CCN) and ice nucleus (IN) activity (influence on clouds and precipitation), or from their chemical and biological activity (influence on aerosol and trace gas emission and transformation).

Estimation of aerosol's impact on climate is more complex and hence more uncertain than that due to the well-mixed greenhouse gases for several reasons. First, the climate forcing due to aerosol particles is strongly dependent on the particle size and chemical composition. Second, the indirect climatic effects of aerosols depend on complex processes involving aerosol particles and the seeding and growth of cloud droplets. Third, most aerosols have short lifetimes (days to weeks) and therefore their geographical distribution is highly variable and strongly related to their sources. Therefore, a better understanding of composition and source of aerosols is highly needed in order to predict contribution of aerosols to climate change.

4.2   Impact on human health

Many epidemiological studies have demonstrated association between exposure to particulate matter (PM) and adverse human health effects (including enhanced mortality, cardiovascular, respiratory and allergic diseases) at concentrations commonly found in urban areas around the world [26-29]. Particle size and composition are the dominant factors which determine the influence of APM toxicity on human health. Particles larger than 1.0 µm aerodynamic diameter (AED) occur in the coarse mode and are rapidly removed (in timescale of hours to a few days) near the source by gravitational sedimentation). On the other hand, smaller particles with AED less than 1 µm have a considerably longer residence time in the atmosphere and are much more efficiently transported. The degree of respiratory penetration of particles is directly related to the aerodynamic particle size. Coarse inhalable particles with AED in the range of 2.5 to 10 µm (PM2.5-10) deposit in the upper respiratory tract while fine particles (PM1) can reach alveolar region. However, the potential health effects of APM depend upon a number of factors other than particle size, e.g., the physiochemical characteristics of particles, their content of toxic substances, solubility in biological fluids, total human exposure, and the health status of population [30-31].

Urban populations are exposed to metals in suspended particles, and these are often well above natural background levels owing to anthropogenic processes. Elevated metal concentrations can pose serious risk to human health. Metals contained in suspended particulate

matter are considered to be a health hazard since they can be absorbed into human lung tissues during breathing. Transition metals are known to cause severe physiological disorders in human beings e.g., cancer. Prieditis and Adamson [32] have found that Cu and Zn are most likely to cause lung injury. Redox-active metals contained in APM, (particularly Fe) play a pivotal role in the generation of reactive oxygen species (ROS), and thus induced adverse health effects [33-36]. The omnipresent presence of trace metals in APM generates a potential risk for public health and environment. For this reason, a great deal of research has focused on the metal composition of atmospheric suspended particulate matter. Thus considering in view the above discussion, it can be concluded that a comprehensive investigation of trace metal monitoring is required in order to understand their role in human health and environment.

4.2.1   Bio-accessibility of trace metals

Most studies dealing with determination of metals and metalloids in APM focus on the determination of total metal concentrations without distinguishing the various species that are present [37-41]. The determination of total metal contents can only give some indication of the general pollution level in an area. However, toxicity of metal depends upon its species present in APM and their bio-accessibility. For risk assessment of metal toxicity, it is important to determine bio-accessible concentrations instead of total metal contents [42]. The bio-accessibility of a metal indicates the upper level estimate of risk assessment and is defined as value representing the availability of metal for absorption when dissolved in-vitro surrogates of body fluid or juices, whereas bioavailability is the amount that is actually taken across the cell membranes [43-44]. In recent years, water is chosen as the simplest and most universal extraction solvent for estimation of the bio-accessible fraction of trace metals in APM, for example extraction of APM samples is routinely used by United States Environmental Protection Agency (USEPA) workers for toxicity testing [45]. Determination of water-soluble fraction could be used as an upper level estimate for the bio-accessible fraction as it can easily be dissolved in body fluid and imparts toxicity to human beings and other living organisms [46]. However, water-soluble trace metal fraction may not represent bio-accessible fraction since water does not mimic the conditions of human body fluid. Particles in the 2.5- to 10-μm size fraction are in most cases deposited in the tracheal and the bronchial region, from where they are transported within hours by the so-called mucocilliary clearance adoral and are mainly swallowed. This fraction reaches the gastrointestinal tract (GIT), where it comes into contact with gastric juice. So it is necessary to use synthetic gastric juice as surrogate of body fluids or juices since several trace and heavy metals can be dissolved by gastric juice [43], thereby

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forming the bio-accessible metal fraction. The gastric juice has complex composition containing pepsin with comparatively higher acidity which can considerably increase the solubility of metals in digestive tract, thereby increasing the bio-accessible fraction. For this reason ongoing research has been focused on the determination of bio-accessible metal fraction in environmental compartments like soil and APM where synthetic gastric juice has been used for extraction of bio-accessible metal fraction [43-44, 47]. Now-a-days an in-vitro physiologically based extraction test (PBET) is recommended for estimating the bio-accessible metal fractions [43, 48-50]. In this case the APM is extracted with the help of synthetic gastric juice using ultrasonic agitation and subsequent measurement of extracts using different techniques like ICP-OES, ICP-MS etc.

5 Required scientific investigations

In light of above discussion it becomes clear that future work and research aims should be focused on the identification and characterization of aerosols in order to better understand their effects on climate and human health. A comprehensive knowledge about their sources and sinks (emission, transformation, deposition) might allow the optimization of air-pollution control and medical treatment of aerosol effects on human health. For this purpose, adequate chemical analysis performed under appropriate conditions are required. However, accurate measurement of environmental, biological and medical samples requires highly sophisticated and sensitive techniques since the complexity of sample matrices and very low analyte concentrations have to be identified in the presence of interfering matrix components. There is also need of improved sample preparation procedures in order to remove complex sample matrix, analyte enrichment and isolation of the target elements. In most cases, the existing analytical techniques are accompanied by a number of laborious sample preparation steps and use of hazardous chemicals like HF. Thus improved analytical procedures are required for fast and accurate determination of target elements and to avoid use of hazardous chemicals. Additionally, it has to be considered that some tasks possess analytical challenges which could not be addressed with the sample preparation and analysis techniques reported so far. The reported procedures suffer especially from limitations in selectivity and in some cases sensitivity which hamper the accurate determination of analytes for a specific task. Thus for many open questions new analytical strategies have to be developed in order to improve characterization of APM and to extend our present knowledge about the processes in the atmosphere.

5.1   Proposed analytical techniques

The accurate analysis of PM10 samples is associated with some limitations e.g., the restricted amount of collected samples and presence of highly complex matrix. In most of the routinely used methods for analysis of PM10 sample, the sensitivity is not sufficient enough to measure the trace elements. Similarly, the sample matrix can interfere considerably, thus resulting in overall reduction of method performance. For this purpose, some new techniques/strategies are required in order to overcome such limitations.

Microwave digestion procedure is the most commonly used method for digestion of PM10 samples, but preparation of PM10 samples via this procedure is accompanied by some disadvantages. For example, a number of sample handling and preparation steps can lead to contamination and analyte losses. Furthermore, unnecessary sample dilution is required in order to dilute the acid contents. The use of reagents can impart additional contamination to the samples. So an improved method is required in order to overcome above stated limitations. In this thesis, a slurry procedure has been proposed for the preparation of PM10 samples which involves less manual operation, use of smaller amount of reagents and there is no need for unnecessary sample dilution. In contrast to solution, slurry contains undissolved particles which are suspended in the solvent. The proposed slurry procedure also offers highly precised and accurate measurements of PM10 samples. The slurry procedure in combination with electrothermal atomic absorption spectrometry (ETAAS) was applied for the element specific analysis of Si in PM10 samples. There was no need of HF for the dissolution of siliceous particles, rather prepared slurry solutions were used for measurement of suspended siliceous particles, and complex sample matrix was removed by optimizing the ET-AAS furnace program. The proposed slurry procedure was also extended to the multi-element determination in APM using ICP-OES. The slurry preparation steps and ICP-OES parameters were optimized in order to quantify the selected crustal and trace metals accurately. The slurry ICP-OES procedure was found to be highly sensitive even for trace metals like Ba, Cu and Sr which are present in a very low amount in APM.

A flow injection (FI) technique was also proposed for on-line determination of water-soluble Zn in APM. In flow injection analysis (FIA), a carrier solution is passed through the sample which reacts with sample and a continuously flowing stream of solution containing some analyte is reached to the detector. The proposed method allowed the direct measurement of an aliquot from PM10 filter sample. In this case, an aliquot of filter sample having diameter of 9 mm was placed in an indigenously developed sample cartridge, followed by leaching with the

flowing stream of bi-distilled water and subsequent detection of Zn by flame atomic absorption spectrometry (FAAS). In contrast, the routinely used batch-wise procedures for extraction of water-soluble metal fraction involve considerable manual operations which can cause contamination and analyte losses. In addition, there are chances of analyte adsorption on the remaining filter particles which can affect the accuracy of measurement. Furthermore, the on-line enrichment of analyte was performed which allowed highly sensitive measurement of the target analyte (Zn).

For the determination of bio-accessible trace metal in APM, an electrothermal vaporization inductively coupled plasma atomic emission spectrometry (ETV-ICP-OES) procedure was used. An ETV system has high sample transport efficiency (~ 70-80 %) which is useful to improve the detection limits of the analytes. The complex sample matrix can also be removed by optimizing the temperature program of ETV furnace which helps to overcome spectral and non-spectral interferences. It is especially suitable for the analysis of trace metal in APM where the sample amounts are limited; especially bio-accessible trace metal fractions are present in a very low concentration in PM10 samples. Therefore, a highly sensitive method for accurate determination of these fractions is required. The PM samples are extracted with synthetic gastric juice which can impart additional complex organic matrix to the extracted samples. An ETV-ICP-OES procedure was developed for this purpose which offers the advantage of complex sample matrix removal thereby enabling highly sensitive measurement of bio-accessible trace metal fractions. Bio-accessible trace metals up to a level of some hundred Pico grams per cubic meter (pg m^{-3}) were possible to determine by the use of developed procedure.

6   Selected publications

The first publication (P 1, "A new approach for the determination of silicon in airborne particulate matter using electrothermal atomic emission spectrometry") is dedicated to determination of Silicon in airborne particulate matter. The urban populations are exposed to enhanced level of ambient PM in most of the European cities [51]. Crustal elements are identified as one of the major constituents of APM [52]. The most important single contributor of these elements is Si which accounts for 1-10 % of the PM10 mass [19-21, 53-54]. So accurate quantification of Si in APM is required in order to identify its sources and to formulate the strategies for its ambient reduction.

For measurement of this mineral component preferably non-destructive multi-elemental techniques, such as X-ray fluorescence (XRF), particle induced X-ray emission (PIXE) or

instrumental neutron activation analysis (INAA) have been used [55-57], but these methods experience distinct limitations. For example, the sensitivity of XRF to many elements is limited, and quantitative measurement of filter samples can be difficult without appropriate calibration in case of both XRF and PIXE. Similarly, INAA encounters with matrix problems, in particular the strong nuclear interference from other species present in APM. Additionally, destructive techniques like inductively coupled plasma-atomic emission spectrometry (ICP-OES] and inductively coupled plasma-mass spectrometry (ICP-MS) offers enhanced selectivity, reproducibility and in some cases also sensitivity in contrast to above mentioned non-destructive techniques. For ICP-OES and ICP-MS, the preparation of APM samples is prerequisite, (since samples in solution form are introduced into plasma) which can cause contamination and analyte losses due to use of reagents and sample handling steps. Additionally, use of hazardous chemicals like HF is necessary for sample preparation in most of the environmental tasks. Thus for environmental monitoring program, an improved approach is required which can minimize the above stated limitations.

A new procedure for element specific analysis of Si in APM based on a preliminary treatment of the aerosol samples with nitric acid and perchloric acid leading to mineralization of the organic sampling substrate, dissolution of soluble material and homogenous suspension of the remaining non-soluble sample fraction was developed. The proposed procedure excludes complex and troublesome wet-chemical sample pre-treatment steps (e.g. sample treatment with HF), furthermore desired time for sample preparation could be reduced and undesirable analyte losses could be prevented. Additionally, use of expensive equipment like microwave digestion system could be avoided. The prepared slurry solutions were measured using electrothermal atomic absorption spectrometry (ETAAS) using a Zr-coated graphite tubes and Co as a matrix modifier. The ETAAS procedure was optimized for accurate determination of Si in aerosol samples and it was found that developed procedure offers sensitivity even for PM10 samples with restricted sample amounts (ranging between less than 100 µg and some mg). The developed method was applied for the analysis of Si in PM10 samples collected at an urban site in Vienna (Austria). The highly sensitive method allowed sample collection intervals of only 60 min, which enables monitoring of fast changes in the Si concentration pattern.

In the second publication (P 2, "On-line determination of water-soluble zinc in airborne particulate matter using a dynamic extraction procedure coupled to flame atomic absorption spectrometry"), a flow injection procedure with flame atomic absorption spectrometry (FAAS) detection for the on-line determination of water-soluble Zn in APM is presented. Most of the

studies dealing with the determination of trace elements in APM focus on the total metal contents without distinguishing the various species which are present [58-60]. But for risk assessment of metal toxicity, it is important to determine the bio-accessible fraction instead of total metal contents. Water is usually used as the simplest and most universal solvent for determination of bio-accessible trace metal fraction in APM. For this purpose, APM samples are extracted with water for dissolving the toxic metal fraction [60]. The determination of water-soluble fraction could be used as an upper level estimate for the bio-accessible fraction as it can easily be dissolved in body fluid.

A batch-wise procedure is usually applied for extraction of various metals in APM [58-60], which involves the extraction of samples with different leaching agents with reaction times in the range of 30-90 min. The batch-wise extraction procedures are time consuming, troublesome, laborious and there are also chances of contamination as well as analyte losses. Additionally, there are problems of adsorption of dissolved species on remaining particulate matter due to long exposure times [61]. In order to overcome above stated problems, improved analytical procedures are required for determination of bio-accessible metal fractions. Keeping in view these requirements, a novel approach for on-line determination of water-soluble Zn in APM using a flow injection procedure coupled with flame atomic emission spectrometry was developed. The proposed on-line extraction procedure was found to be fast, excludes troublesome sample handling steps and reduces the possibility of sample contamination as well as analyte losses. Furthermore, compared to conventional batch-wise extraction, the proposed procedure offered an improved sensitivity, since enrichment of analyte was achieved by the enhanced sample throughput. Additionally, improvements in the procedure reproducibility were achieved which resulted in drastically decreased limits of detection and limit of quantification for water-soluble Zn in PM10 when compared to corresponding data of batch-wise procedure.

The third publication (P 3, "A new approach for determination of crustal and trace elements in airborne particulate matter") deals with the fast and accurate determination of various crustal (Al, Ca, Fe, Mg, Si) and trace elements (Ba, Cu, Mn, Na, K, Sr, Ti, Zn) in airborne particulate matter. For determining the elemental composition of atmospheric samples, the use of well-established non-destructive multi-elemental techniques, such as X-ray fluorescence (XRF), particle induced x-ray emission (PIXE) or instrumental neutron activation analysis (INAA) is reported [55-57], but the application of these cost intensive techniques requires skilled operators and laboratories with special safety arrangements. So the application of these techniques for routine analysis of aerosol samples is difficult. In contrast to above mentioned techniques, ICP-OES and ICP-MS

can also be used for determining the elemental composition of APM, but these techniques require increased efforts for sample preparation. The wet digestion procedures used for sample preparation are laborious, time consuming and require the use of expensive equipment like microwave digestion system and hazardous chemicals like HF and perchloric acid ($HClO_4$). This could lead to sample contamination due to use of increased amounts of reagents as well as analyte losses due to sampling handling steps. So an improved procedure is required which can minimize the sample preparation steps and use of hazardous chemicals.

For this purpose, an alternative approach was proposed which allows the introduction of sample slurries (containing soluble as well as insoluble species) into plasma which considerably reduces sample preparation time and efforts by combining matrix destruction, analyte atomization and excitation in a single step. In combination with ICP-OES the developed approach allows the simultaneous multielements determination of selected crustal and trace elements in PM10 samples. The proposed procedure was found to be advantageous over traditional microwave digestion procedure in terms of sensitivity and time consumption. The sensitivity was increased by avoiding the unnecessary sample dilution which is required in case of microwave digestion procedure for workable acid contents in resulting solutions.

In the fourth publication, (P 4, "Development of an ETV-ICP-OES procedure for assessment of bio-accessible trace metal fractions in airborne particulate matter") determination of bio-accessible trace metal fractions of Ba, Co, Cu, Mn, Ni and Pb in APM using electrothermal vaporization inductively coupled plasma atomic emission spectrometry (ETV-ICP-OES) is presented. For evaluation of metal toxicity, it is recommended to determine the bio-accessible metal fraction instead of total metal contents. A synthetic gastric juice solution has been used in most of the recent studies for estimation of bio-accessible trace metal fraction in contrast to water since water does not mimic the conditions of human body fluid [47-49]. The particles in the diameter range of 2.5 to 10 μm are usually swallowed during lung clearance process and reach the digestive tract where they come in contact with the gastric juice. The gastric juice being more acidic and having complex nature can dissolve comparatively larger amounts of trace metals as compared to water [43]. Therefore, for determination of bio-accessible metal fraction a physiologically based extraction test (PBET) is recommended. When the gastric extracts are introduced into ICP-OES or ICP-MS, complex matrix contained in synthetic gastric juice hampers the analysis by introducing spectral and non-spectral interferences. A common way to overcome these interferences is sample dilution, but it can lead to decreased sensitivity since the trace elements are present in very low concentrations in APM. Thus an improved analytical

procedure is required for highly sensitive measurement of bio-accessible trace metals which offers the advantage of sample matrix removal as well as exclusion of sample dilution step.

Therefore, an alternative method was developed in which an in-vitro physiologically based extraction test (PBET) has been performed with APM followed by subsequent measurement of resulting extracts using ET-ICP-OES. The developed procedure allows to separate organic matrix prior to element specific detection enabling highly sensitive measurement of trace elements in APM up to level of some hundred pg m^{-3} in contrast to conventional ICP-OES procedure. Furthermore, there is no need to digest or dilute sample extracts containing pepsin, thereby saving time and reducing the risk of sample contamination. Additionally, effective removal of organic sample matrix allowed the use of aqueous calibration solutions for quantification of derived analytical signals.

P1

6.1 A new approach for the determination of silicon in airborne particulate matter using electrothermal atomic absorption spectrometry

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A new approach for the determination of silicon in airborne particulate matter using electrothermal atomic absorption spectrometry

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ABSTRACT

In this work a new procedure for element specific analysis of silicon in airborne particulate matter is presented. The method is based on a preliminary treatment of the aerosol samples with nitric acid and perchloric acid leading to a mineralization of the organic sampling substrate, dissolution of soluble material and a homogeneous suspension of the remaining non-soluble sample fraction. ETAAS measurement of the derived slurries was performed using a Zr-treated graphite tube which prevents the formation of stable silicon carbide during sample measurement. Losses of volatile silicon species during sample pyrolysis were overcome by using Co(II) as matrix modifier and a pyrolysis temperature of only 300 °C. Furthermore this low pyrolysis temperature prevents charring of organic material which enables accurate ETAAS analysis. The method including the developed pretreatment procedure was evaluated using the Standard reference material® 2709 (San Joaquin Soil) from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA). Suitability for measurement of Si in airborne particulate matter with an aerodynamic diameter $\leq$10 µm (PM10) was demonstrated by the analysis of selected aerosol samples and comparison of derived results with the findings obtained for the same samples after microwave digestion and subsequent ETAAS measurement. Finally the developed procedure was applied for the analysis of silicon in PM10 collected at an urban site in Vienna (Austria). Matrix matched calibration has been used for quantification of derived absorption signals. With the use of 20 µL sample injection volume for ETAAS analysis an instrumental detection limit of 52.2 µg L^{-1} was obtained, which translates to method detection limits of approximately 0.52 µg m^{-3} when considering the volumes of air collected per investigated aerosol sample. The reproducibility of analysis given as the relative standard deviation was 4.4% (n = 12). Derived concentrations for Si in PM10 varied between 0.8 and 7.2 µg m^{-3} which is in good accordance with the literature findings.

1. Introduction

Measurements of the elemental composition of airborne particulate matter samples from different European Cities have revealed that crustal elements were major constituents of urban aerosol samples [1]. Silicon was found to be the most important single contributor which accounts for 1–10% of the PM mass [2–5]. For measurement of this mineral component preferably non-destructive multi-elemental techniques, such as X-ray fluorescence (XRF), particle induced X-ray emission (PIXE) or instrumental neutron activation analysis (INAA) have been used [6–8]. However although frequently applied all of these methods suffer from distinct limitations. XRF for example is hampered with problems in the analysis of low analyte concentrations. Furthermore XRF as well as PIXE requires a sophisticated calibration since signal response

is known to be influenced from the matrix composition. Similarly neutron activation analysis encounters with matrix problems, in particular the strong nuclear interference from other species present in airborne particulate matter. So the application of these techniques for routine analysis of Si in aerosol samples is difficult.

However, it is generally accepted that the use of inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) yields in comparison to the above-mentioned techniques an enhanced selectivity, reproducibility and in some cases also sensitivity. In case of Si analysis these improvements are associated with distinctly increased efforts in sample pretreatment which could affect the results badly due to an enhanced risk of analyte losses as well as contamination [9–11]. Thus for environmental monitoring programs, an improved approach is required which combines the speed of solid sampling analysis with the accuracy of solution based measurement techniques.

For this purpose slurry techniques for sample introduction have been reported in conjunction with element specific detection sys-

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tems such as ETAAS. Slurry approaches require less effort in sample preparation since total dissolution of the sample could be avoided [12]. Compared to solid sampling techniques slurry procedures allow measurement of several replicates from just only one slurry which improves the reproducibility of the analysis and it allows easy dilution of samples with high analyte content [13]. Additionally, the aqueous solution calibration and the standard addition calibration method could be applied for quantitative purposes in slurry sampling analysis, being much more troublesome for direct solid sampling techniques. However, although slurry ETAAS has been frequently applied in various research fields [14–18] until now there is no slurry approach for the measurement of Si in airborne particulate matter reported. A fact which could be related to the two major problems associated with the ETAAS measurement of Si—in particular the formation of stable silicon carbide and losses of volatile SiO during sample pyrolysis.

This work presents a new procedure for the accurate determination of silicon in airborne particulate matter by ETAAS. Pretreatment of collected PM10 samples included decomposition of the organic filter substrate with nitric acid and homogenous suspension of nonsoluble sample constituents. The prepared slurries were analyzed by ETAAS using a Zr-treated graphite tube and Co(II) as matrix modifier. This highly sensitive method was applied for the determination of the short term variation of Si concentrations in PM10.

2. Experimental

2.1. Standards and reagents

Hydrogen peroxide (H_2O_2, 30%, m/m), perchloric acid ($HClO_4$, 70%, m/m) and hydrofluoric acid (HF, 48%, m/m) were of suprapure grade quality (Merck, Darmstadt, Germany). Nitric acid (HNO_3, 65%, m/m), zirconium (IV) oxide chloride ($ZrOCl_2 \cdot 8H_2O$) and boric acid were used with analytical reagent grade (Merck, Darmstadt, Germany). High purity water was obtained by the re-distillation of de-ionized water derived from a reverse osmosis/ion exchange combination (Euro 20 plus-SG water system, Germany) using in house quartz apparatus. Certified standard stock solutions of Si ($1000\,mg\,L^{-1}$) and Co(II) ($1000\,mg\,L^{-1}$) were purchased from Merck (Germany), and diluted with 1% (v/v) HNO_3 in high purity water to get various working solutions. Standard solutions as well as prepared sample solutions were kept refrigerated at $4\,°C$ in cleaned polypropylene bottles till the further use. Standard reference material® 2709 (San Joaquin Soil) from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to verify the accuracy of the developed method for Si determination.

2.2. Instrumentation and analysis

A Perkin-Elmer 5100 ZL atomic absorption spectrometer provided with an autosampler AS-70 (PerkinElmer, USA) was used for analysis. It utilizes the inverse longitudinal Zeeman effect with an alternating magnetic field and has a ramp heating rate of $2000\,°C\,s^{-1}$ at the atomization stage. A Perkin-Elmer Intensitron hollow-cathode lamp for silicon was employed as specific light source. Analysis of Si was performed at wavelengths of 251.6, 221.6 and 288.2 nm depending on the silicon contents of investigated samples, a lamp current of 30 mA and a slit width of 0.2 nm using Zr-treated graphite tubes. Coating of the graphite tubes was performed prior to use by dipping the tubes in 20 mL of a 2% HNO_3 solution containing $13.5\,g\,L^{-1}$ of $ZrOCl_2 \cdot 8H_2O$, in a Teflon beaker under reduced pressure. After a reaction time of 60 min, the tubes were taken out of the beaker, shaken to remove adherent drops of solution and dried in an oven at $70\,°C$ for 3 h. Throughout all measurements, a sample volume of $20\,\mu L$ was injected in the

graphite tube for analysis and argon (99.998% purity) was used as purge gas. The temperature program applied in the present study is given in Table 1. Si absorption signals were measured as the integrated peak area using Zeeman background correction.

2.3. Sample collection

Sampling of size segregated airborne particulate matter samples was performed in September 2007 at the Getreidemarkt in downtown Vienna (16°24′E, 48°12′N), near to a heavy traffic road with occasional stop and go traffic. Airborne particulate matter samples with an aerodynamic diameter $\leq 10\,\mu m$ (PM10) were collected with an automated sampling device containing a PM10 pre-separation head (Leckel, Germany) with an intake volume of $2.3\,m^3\,h^{-1}$ (being equivalent to $40\,L\,min^{-1}$). Filter holders were equipped with GN-4 Metricel® mixed cellulose ester filters (diameter: 47 mm, pore size: $0.8\,\mu m$, PALL Life-sciences, Michigan, USA) as sampling substrates. The filter samples were automatically changed after a collection period of 60 min, the air volumes collected within these sampling intervals varied between 2.08 and $2.12\,Nm^3$ (standard temperature pressure, 273 K and 1013 hPa). To exclude any contamination from the sampling procedure itself field blanks were collected by purging sample air for 30 s through the filter. Collected PM10 samples were divided into two parts and stored in Petri dishes with seal of parafilm at room temperature. Cutting of filter samples and all other manual operations for filter samples (e.g. insertion of filters in filter holders) were conducted in a particle free environment inside a laminar flow hood (Weiss VFT 1525) using ceramic or metal free tools.

2.4. Sample pretreatment

Application of liquid samples or stable slurry solutions is a prerequisite for conventional ET-AAS analysis. Since a quantitative dissolution of siliceous species is rather complex and related with tedious laboratory work we decided to convert the collected aerosol samples into stable slurries. For this purpose a complete mineralization of the organic sampling substrate (thereby soluble aerosol constituents become dissolved) and homogeneous suspension of the remaining non-soluble fraction (including the oxides of crustal components such as Si or Al) is required. Slurry samples were prepared by treatment of half filter samples with a mixture of conc. HNO_3 and H_2O_2 as well as with a mixture of conc. HNO_3 and conc. $HClO_4$ in Bernas type Teflon-lined bombs. In case of treatment with nitric acid and hydrogen peroxide samples were heated in a refractory oven at $110\,°C$ for 1.5 h, after cooling $100\,\mu L$ of a $1000\,mg\,L^{-1}$ Co(II) solution was added as matrix modifier to each sample, finally the derived solutions were diluted to a final volume of 10 mL with 5% (v/v) HNO_3. However, while using mixture of nitric acid and perchloric acid, samples were heated only for 1 h at $110\,°C$, subsequently temperature was raised within 30 min to $150\,°C$ and kept constant for another 60 min. Purpose of this procedure was an enhanced decomposition of carbonaceous material. After cooling and addition of $100\,\mu L$ of a $1000\,mg\,L^{-1}$ Co(II) solution, the derived solutions including dissolved species as well as undissolved particles were completely transferred into 10 mL polypropylene tubes and diluted to final volumes of 10 mL with 5% (v/v) HNO_3 in high purity water.

Slurry solutions of SRM 2709 were prepared by treatment of approximately 20 mg of dried soil with 2 mL conc. HNO_3 and $500\,\mu L$ conc. $HClO_4$. Derived solutions including remaining particles were transferred into polypropylene bottles and diluted to 20 mL with 5% (v/v) nitric acid in bi-distilled water along with $400\,\mu L$ of Co(II) solution as matrix modifier.

Table 1
Temperature program used for ETAAS determination of silicon.

Step	Temperature (°C)	Heating rate (°C s^{-1})	Hold time (s)	Argon flow (mL min^{-1})
Drying	110	10	20	250
	150	20	20	250
Pyrolysis	800 (300[a])	20	30	250
Atomization	2400 (2450[a])	0	5	0
Clean out	2500	1	3	250

[a] Optimized parameters used for investigation of PM10 samples and SRM (NIST 2709).

3. Results and discussion

3.1. Optimization of sample pretreatment procedure

The slurry method demands the complete mineralization of the filter material used for collection of aerosol samples, furthermore dissolution and homogenous suspension of residual particles in the solution is required [19]. In a first series of experiments, a mixture of 2 mL conc. HNO_3 and 500 μL H_2O_2 (30%) was tried for decomposition of blank filters as well as PM10 test samples from Vienna. A problem with this approach was the failure to completely oxidize the elemental carbon present in airborne PM10 samples as black residues appeared in prepared slurry solutions, which showed sedimentation during sample storage, circumstances which might influence the performance of the procedure negatively. Additionally, it has to be considered that the presence of elemental carbon may cause the formation of stable silicon carbide during the heating cycle of the applied furnace program, thereby causing an underestimation of the true Si content since SiC does not evaporate during the measurement step. For these reasons an improved procedure was developed, using a combination of 2 mL conc. HNO_3 and 200 μL of the strong oxidant $HClO_4$ for sample treatment. The addition of perchloric acid was observed to be advantageous since the temperature of the reaction mixture could be increased to 150 °C, improving decomposition and mineralization of organic material. Application of this procedure to PM10 samples from Vienna revealed yellowish solutions; the remaining colorless residue indicated a complete decomposition of elemental carbon. Compared to the sample treatment with nitric acid and hydrogen peroxide, an enhanced sensitivity and improved reproducibility were observed for the ETAAS determination of Si.

3.2. Optimization of ETAAS procedure for slurry measurements

The well known problem of silicon carbide formation during ETAAS measurement can be avoided by pretreatment of graphite tube with W, Zr, Ta, or La which form thermodynamically stable carbides [20]. This coating of the tube surface prevents the reaction of silicon with carbon during ETAAS measurement, improving sensitivity and precision of analysis. Similarly, the use of transition metal ions like Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Pd and alkali metal fluorides is recommended since these modifiers prevent the volatilization of silicon as SiO by forming interstitial silicides M_xSi_y [21–24]. In a first step, the behavior of untreated and Zr-treated tubes and the suitability of different modifiers were investigated using aqueous standard solutions. Obtained results were in accordance with literature findings [20,24], confirming that Zr-coated tubes and the use of Co(II) as modifier yield best results. In a next step pyrolysis and atomization temperatures for ETAAS measurement were optimized. The optimum pyrolytic temperature for aqueous silicon solutions was found to be 800 °C. Application of this procedure for analysis of filter blank samples which were spiked with defined amounts of Si revealed a linear behavior between signal response and the investigated concentration levels, but the slope of the derived calibration curve was considerably different from those of aqueous silicon standard solutions. Furthermore, a decreased reproducibility of the ETAAS measurement and completely different absorption signals were observed for spiked filter samples. In contrast to the results of aqueous standard solutions, the background signal of the spiked filter blank samples was enhanced as compared to the analyte signal (Fig. 1a). An outcome which hints to the presence of dissolved organic material in the prepared synthetic sample solutions, indicating an insufficient mineralization of the filter material during sample pretreatment. Additionally the analyte signal for spiked filter samples showed a negative absorbance during ETAAS measurement, pointing to an overcorrection of molecular interferences and thus affecting the reproducibility of the analysis. Considering these findings the reduced sensitivity of spiked filter measurements could be explained with the reaction of silicon and remaining dissolved organic material leading to the formation of volatile organo-silicon species which were lost at a pyrolytic temperature of 800 °C. Simultaneously charring of less volatile organic species occurs. The formed macromolecular compounds were stable at the used pyrolysis temperature of 800 °C, but at the atomization temperature of 2400 °C decomposition of these charring products takes place which interferes ETAAS measurement. Thus for accurate measurement of silicon, it was important to avoid analyte losses prior to sample atomization and to overcome charring of organic material. Since sample pretreatment with increased reaction time and temperature yielded no improvement in analysis, indicating that even under enhanced reaction conditions no quantitative mineralization of filter substrate and sample was possible, it was necessary to optimize the temperature program of the ETAAS procedure to overcome the influence of remaining dissolved organic matter. For this purpose a spiked filter blank sample was prepared and analyzed using varying temperature programs for ETAAS measurement. The effect of the pyrolysis temperature on the absorption signal was investigated in the range from 150 to 800 °C, the atomization temperature has been varied between 2300 and 2500 °C. Final optimization of sample pyrolysis and atomization was based on the results achieved for intensity and reproducibility of analyte signal. Best results were obtained at a pyrolysis temperature of 300 °C, showing maximum analyte signals with background signals near to baseline. Similarly, an enhanced reproducibility was observed at this pyrolytic temperature. The behavior of analyte and background signals obtained at a pyrolysis temperature of 300 °C is depicted in Fig. 1b. Comparison with Fig. 1a, which has been observed for the same sample at a pyrolysis temperature of 800 °C, illustrates the improvements achieved for the atomic absorption signal as well as for the background signal. The apparent difference in the adsorption behavior of the background results from the prevention of any charring reactions at the reduced pyrolysis temperature which circumvents the formation of interfering macromolecular compounds. The optimum atomization temperature was found to be 2450 °C for slurry samples which was little higher than atomization temperature of 2400 °C for aqueous silicon solutions.
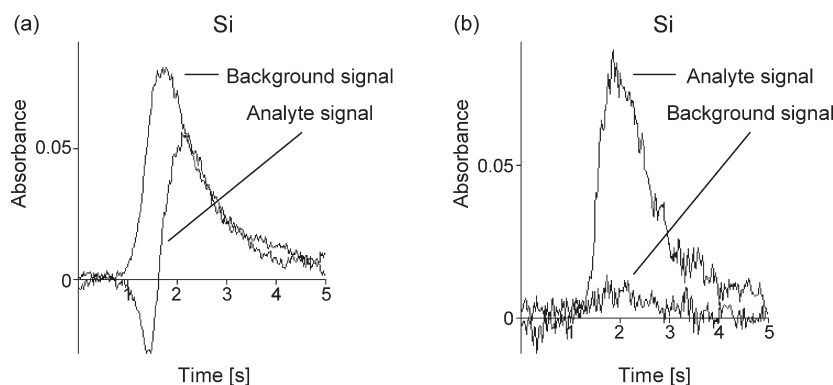
Fig. 1. Atomic absorption and background signals obtained for spiked filter blank samples at a pyrolytic temperature of 800 °C (a) and a pyrolytic temperature of 300 °C (b).

However, the matrix present in slurry solutions prepared from real PM10 samples was found to affect silicon determination by lowering the signal intensity and precision of the procedure when compared to the results of aqueous standard solutions. To overcome the influence of the additional matrix from the PM10 samples the concentration of cobalt as modifier has been increased to a level of 20 ppm Co(II) in the final slurry solution. The enhanced concentration of cobalt was found to reduce the influence of interfering sample constituents leading to improved signal intensity and reproducibility, but nevertheless the response of spiked samples containing aerosol matrix was still different when compared to that of aqueous standard solutions. Thus the method of standard addition has to be used for quantification.

3.3. Figures of merit

Analytical characterization of the procedure was performed by multiple analysis of synthetic silicon standard solutions prepared from filter blanks which were spiked with varying amounts of aqueous Si standard solutions and processed using the optimized pretreatment procedure. Analysis was conducted using the presented ETAAS procedure. At the most sensitive wavelength of 251.6 nm, the derived calibration curve was found to be linear up to a Si concentration of 600 μg L^{-1}. The relative standard deviation obtained from 6 determinations of spiked filter blanks resulting in final slurry concentration of 100 μg L^{-1} was 1.6%. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as 3 times the standard deviation (3σ) and 10 times the standard deviation (10σ) of the blank signals of unspiked filter samples and were found to be 15 μg L^{-1} (LOD) and 52.2 μg L^{-1} (LOQ), respectively. The accuracy of the proposed method was assessed by analyzing the silicon content of the SRM 2709. Derived absorption signals were quantified using the standard additions method, the determined silicon content of 29.1 ± 1.4% ($n = 5$) was in good accordance with the certified contents of 29.66 ± 0.23%.

Suitability of the proposed procedure for the analysis of Si in airborne particulate matter was investigated by analysis of a set of eight PM10 samples and comparison of derived results with the findings obtained for the same samples after microwave digestion and subsequent ETAAS measurement. These PM10 samples were collected at an urban site in Vienna and an industrial site in Salzburg using the procedure presented in Section 2, with the only difference that sampling periods were increased to 24 h to yield higher amounts of collected PM10 mass. One part of the divided filters has been analyzed using the proposed procedure, the second part of each sample has been microwave digested using a mixture of 5 mL HNO$_3$ and 50 μL HF. Microwave digestion was carried out with a Multiwave 3000 digestion unit (Anton Paar, Austria) at a maximum temperature of 180 °C and a maximum pressure of 20 bar.

After digestion the derived solutions were diluted to a final volume of 250 mL resulting in HF concentrations of 0.02% (v/v). This dilution was necessary since the hydrofluoric acid required for decomposition of siliceous materials was found to interfere ETAAS analysis, in particular losses of volatile SiF$_4$ occurred during sample pyrolysis, disabling accurate determination of silicon even in the presence of boric acid (0.1%, m/m), which has been added as complexing agent to improve reproducibility and sensitivity of ETAAS analysis. The relatively short time needed for this kind of sample preparation is advantageous (about 90 min), but the dilution to an appropriate level of hydrofluoric acid disables measurement of analyte traces. Accuracy of this digestion approach has been proved by analysis of SRM 2709, for this purpose a sample intake of 50 mg of dried SRM 2709 was digested with 5 mL HNO$_3$ and 1 mL HF and analyzed as described above. The results derived for SRM 2709 (30.6 ± 1.4%, $n = 5$) were in good agreement with the certified value of 29.66 ± 0.23%. Furthermore a good agreement between results of microwave digested samples and the proposed approach was found (Table 2), confirming that the developed procedure is also applicable for measurement of PM10 samples.

3.4. Determination of Si in airborne particulate matter

One filter half of each collected PM10 sample was processed using the developed sample pretreatment procedure. Quantification of derived absorption signals was performed using a matrix matched calibration; required standard solutions were prepared by spiking aliquots of a pooled sample solution with defined amounts of a silicon stock solution. The pooled sample solution was created by combining aliquots of 1 mL from each individual PM10 slurry solution. An excellent linearity ($r^2 = 0.997$) between signal response and spiked analyte concentration was found over the whole investigated concentration range (varying between the concentration of the unspiked pooled sample and a maximum spike level of plus 400 μg L^{-1} Si). The LOD (3σ) and LOQ (10σ) derived from multiple measurement of field blank samples were found to be 31 and 70 μg L^{-1}, respectively. These values were different from those

Table 2
Comparison of Si contents of microwave digested and slurry pretreated aerosol filter samples from an urban site in Vienna (1–4) and an industrial site in Salzburg (5–8).

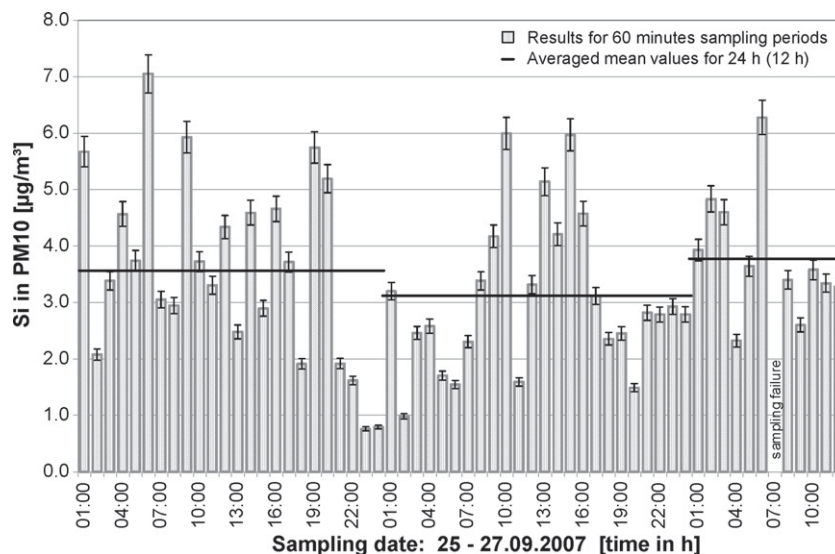| Sample no.	MW-digestion Si (μg m^{-3})	New procedure Si (μg m^{-3})
1	1.04 ± 0.05	1.07 ± 0.05
2	0.20 ± 0.01	0.18 ± 0.01
3	0.12 ± 0.01	0.15 ± 0.01
4	0.32 ± 0.01	0.35 ± 0.02
5	1.62 ± 0.07	1.65 ± 0.08
6	0.35 ± 0.02	0.33 ± 0.02
7	1.00 ± 0.05	1.06 ± 0.05
8	0.75 ± 0.04	0.74 ± 0.04

Fig. 2. Variation of the Si concentration in PM10 with time.

calculated for aqueous silicon solutions with blank filter papers as described above. The observed difference might be due to the additional influence of organic and inorganic matrix constituents present in PM10 samples. Furthermore it has to be considered that field blanks showed increased Si levels when compared to laboratory blanks, a result which reflects the influence of sample handling and storage. Considering the collected air volumes of approximately 1 m^3 for the investigated filter halves method detection limits in the order of 300 ng m^{-3} were achieved for the collected aerosol samples. A distinct reduction of the method detection limit is possible by increasing the air volumes of collected aerosol samples, e.g. the sample volume of conventional daily samples (approximately 50 Nm^3 collected within 24 h) translates to a LOD of only 6 ng m^{-3} Si in PM10. Results observed for slurry solutions of individual PM10 samples varied between 76 to 738 µg L^{-1}, which corresponds to silicon concentrations in the range of 0.8–7.1 µg m^{-3} in PM10.

For verification of the achieved Si results again the second half of each filter sample was digested using microwave procedure and analyzed as described in the previous chapter. External calibration with aqueous standard solutions containing 0.02% HF and 0.1% boric acid has been used for signal quantification. But in contrast to the PM10 samples with 24 h collection time, almost all PM10 samples with reduced sampling intervals of 60 min showed results in the order of the blank filter samples even at the most sensitive wavelength of 251.6 nm—thus quantification of Si levels in PM10 was not possible. This outcome results from the main disadvantages of the microwave digestion procedure—sample dilution to HF content of 0.02% prior to ETAAS measurement (in order to make accurate analysis possible) and the decreased sensitivity at this HF-level. In contrast to this the proposed pretreatment procedure requires no unessential sample dilution, leading to a distinctly decreased detection limit for ETAAS measurement of silicon.

The results derived with the developed procedure are in good agreement with literature findings. For example the Si concentrations in the urban area of Milan were found to be around 2.5 µg m^{-3} [4]; values ranging from 0.03 to 16.3 µg m^{-3} were reported for different sites in Vienna [5], whereas enhanced mean Si concentrations of 11.3 ± 7.7 and 20.6 ± 13.4 µg m^{-3} were found for two sites at the US/Mexico border [25]. However, as can be deduced from the relatively large concentration range (0.8–7.1 µg m^{-3}), the concentration of Si in PM10 varied distinctly during the entire

sampling period (Fig. 2). This information about the short term variation of ambient Si concentrations in PM10 is not accessible with conventional procedures, since they require sample intakes of various mg instead of some hundred µg, as a consequence PM10 samples with sampling intervals of 24 h were collected to overcome this limitation. Application of such procedures yield therefore only averaged Si concentrations for the investigated time periods, for illustration the calculated mean values of the individual sampling days were depicted in Fig. 2. Interpreting the results for 24 h mean values only minor differences in the Si concentration levels were observed, indicating more or less a constant Si concentration in PM10 throughout the whole investigated period. A conclusion which is obviously wrong since the Si concentration in PM10 showed distinct temporal variations, which could be explained with changes in the meteorological conditions as well as changes in the source emission and transformation rates of Si.

4. Conclusion

An ETAAS procedure for the accurate determination of trace levels of silicon in solid environmental samples such as soil or airborne particulate matter has been developed. Compared to common digestion procedures the proposed procedure excludes complex and troublesome wet-chemical sample pretreatment steps (e.g. sample treatment with hydrofluoric acid), furthermore time consumption could be distinctly reduced and undesirable analyte losses could be prevented. The absence of expensive instrumentation or equipment for sample preparation (such as microwave digestion systems) has additional impact on the economy and ease of use of this method. ETAAS analysis was performed with Zr-coated graphite tubes in the presence of Co(II) as modifier, to overcome the influence of organic material remaining after sample pretreatment an optimized temperature program has been used. Analysis of processed aerosol samples revealed that Zr-coated tubes allowed up to 200 measurements without any decrease in sensitivity or reproducibility, an important outcome since tube stability is a prerequisite for analysis of large sample series.

However, ETAAS measurement of Si in PM10 samples with Zr-coated graphite tubes in the presence of Co(II) as modifier was found to be interfered by the organic matrix remaining after decomposition of the cellulose ester filters used for aerosol

collection—disabling accurate analysis of Si. Since quantitative mineralization of the filter substrate was not possible with simple open vessel pretreatment procedures an improved ETAAS temperature program with a pyrolytic temperature of only 300 °C has been used to overcome the influence of remaining organic material. The suitability of the proposed method for the determination of Si in particulate environmental samples has been demonstrated by the analysis of the SRM 2709 and ETAAS reference measurements of selected PM10 samples after microwave digestion. The obtained sensitivity offers even for PM10 samples with restricted sample amounts (ranging between less than 100 μg and some mg) an accurate measurement of Si.

The method has been applied for the analysis of Si in PM10 samples collected at an inner city site in Vienna (Austria). The highly sensitive method allowed sample collection intervals of only 60 min, which enables monitoring of fast changes in the Si concentration pattern. Derived results indicated distinct variations in the Si concentration of urban PM10 samples during the day, information which is essential for a targeted reduction of ambient PM10 levels, but only accessible with analytical procedures providing sufficient sensitivity for the analysis of such low total sample amounts (approximately 0.1 mg aerosol per sample).

Acknowledgements

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6.2 A new approach for determination of crustal and trace elements in airborne particulate matter

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A new approach for determination of crustal and trace elements in airborne particulate matter

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Abstract

An ICP-OES procedure was developed for fast and accurate determination of various crustal (Al, Ca, Fe, Mg, Si) and trace elements (Ba, Cu, Mn, Na, K, Sr, Ti, Zn) in airborne particulate matter. The method is based on a preliminary treatment of the aerosol samples with a mixture of nitric acid and hydrogen peroxide at elevated temperature leading to a mineralization of the organic sampling substrate, dissolution of soluble material and homogeneous suspension of the remaining non-soluble fraction. After dilution the derived slurry solutions were measured using ICP-OES. The reproducibility of analysis given as the relative standard deviation (% RSD) varied between 3.2 and 6.8 % for bulk constituents such as Al, Ca, Fe, Mg and Si whereas values ranging from 3.5 to 9.1 % were obtained for trace metals present with distinctly lower abundance in PM10 (e.g. Ba, Cu, Mn, Sr, Zn). The limits of detection (LOD) calculated as three times the standard deviation (3σ) of the signal derived from filter blank samples ranged from approximately 1 ng m^{-3} (Sr) to 71 ng m^{-3}(Ca). The developed procedure was evaluated by comparing the obtained results with the findings derived for the same set of aerosol samples analyzed using a microwave procedure for sample dissolution with subsequent ICP-OES analysis. Finally the developed procedure was applied for the analysis of crustal and trace elements in PM10 samples collected at an urban site (Getreidemarkt, Vienna) and a rural site (Hartberg, Styria), in Austria. The concentrations of the investigated crustal elements varied between some hundred ng m^{-3} and few μg m^{-3} with highest concentrations for Fe and Si, distinctly reduced concentrations ranging from some ng m^{-3} (Sr) to more than hundred ng m^{-3} (K) were found for trace elements. Observed PM10 concentrations were found to be in accordance to literature findings from urban sites in central Europe.

Keywords: ICP-OES; airborne particulate matter; crustal elements; trace metals;

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1. Introduction

Airborne particulate matter (APM) is contributed to atmosphere through various natural as well as anthropogenic sources [1]. The particles with diameter from some nm to tens of μm 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. Among the various anthropogenic sources of APM, traffic emissions are the major source of APM in urban areas around the world [2]. The increasing number of motor vehicles contributes to the increase in particulate pollution [3]. In Europe, exhaust from motor vehicles is considered to contribute more than 50% for emission of PM10 (particles with an aerodynamic diameter less than 10 microns) [4]. The resuspension of dust, industrial and civil population emissions also contribute to atmospheric particulate matter [5]. The most important inorganic contributors to ambient PM10 levels are the crustal elements Al, Ca, Fe, Mg and Si. For example, Handler et al. [6] reported for a site in Vienna (Austria) that the mineral components Al, Ca, Fe, Mg and Si accounted together for 20.5 ±4.4% of the PM10 mass. On the other hand, trace elements like Ba, Cu, Mn, Sr and Zn are only minor constituents (together less than 1%) of PM 10 mass. Nevertheless, the determination of metals and metalloids in atmospheric aerosol is important since their occurrence in aerosol results in human exposure, especially in industrial and urban sites. Exposure to APM has been found to be linked with different respiratory as well as cardiovascular diseases in human beings because the presence and concentration of various elements above the permissible level can exert fundamental influence on the vital functions of living organisms [7].

For determining the elemental composition of atmospheric samples, the use of well-established non-destructive multi-elemental techniques, such as X-ray fluorescence (XRF), particle induced x-ray emission (PIXE) or instrumental neutron activation analysis (INAA) is reported [8-9], but the application of these cost intensive techniques requires skilled operators and laboratories with special safety arrangements. So the application of these techniques for routine analysis of aerosol samples is difficult. However, the use of inductively coupled plasma atomic emission spectroscopy (ICP-OES) in comparison to above mentioned techniques, offers advantages of selectivity, reproducibility and in some cases also sensitivity, but these improvements are always associated with distinctly increased efforts in sample pre-treatment [10]. The wet digestion procedures usually applied for sample dissolution are time consuming and require the use of expensive equipment like microwave digestion systems and hazardous chemicals like hydrofluoric acid and perchloric acid. However, an attractive alternative to

overcome the problems associated with sample digestion is the introduction of sample slurries into the plasma which considerably reduces sample preparation time and efforts by combining matrix destruction, analyte atomization and excitation in a single step [10-11].

The application of the slurry approach as a sample introduction technique in ICP-OES has been successfully reported by several workers for the determination of a variety of elements in coal [12], cement [13-14], clay [15], ceramic materials [16], fly ash [17], geological materials [18] and sewage sludge [19]. However, no study is reported in literature where a slurry procedure is applied for simultaneous analysis of various elements in airborne particulate matter using ICP-OES, until now only slurry sampling procedures using atomic absorption spectroscopy have been reported [20-21]. The present study describes the development of an ICP-OES procedure for fast and accurate multielement measurement of crustal elements and selected trace metals in PM10 aerosol samples. The procedure is based on a preliminary mineralization of sampling substrate with oxidizing agents thereby a partial dissolution of particles occurs resulting in solutions containing some dissolved as well as suspended fine particles. Derived solutions including suspended particles were measured using ICP-OES. The procedure has been applied for analysis of PM10 samples collected from one urban site and one rural site in Austria.

2. Experimental

2.1 *Instrumentation*

An iCAP 6500 series ICP-OES spectrometer (Thermo Scientific, USA) has been used for simultaneous multi-element analysis. Sample introduction was performed using two types of sample introduction kits i.e., a Thermo Scientific high solid kit consisting of an aerosalt nebulizer and a radial spray chamber, and a Thermo Scientific hydrofluoric acid resistant kit consisting of a polymeric Burgener MiraMist nebulizer, polymeric cyclonic spray chamber and a torch with a ceramic centre tube. The former kit was used for the introduction of solutions derived using slurry approach and the later one was used for HF containing sample solutions derived through microwave digestion of PM10 samples. Each target element was measured using two wavelengths in order to overcome spectral interferences caused from simultaneously introduced matrix constituents. Background corrected emission signals were used for signal quantification. Sample flow rate and instrumental parameters such as RF power, nebulizer flow, auxiliary and cooling gas flow rate were optimized in order to obtain optimum sensitivity and reproducibility. Optimized instrumental parameters applied in the present study are shown in Table 1. Each element has been measured using two emission lines, the first line (λ 1) was

selected for analyte quantification and the second one (λ 2) was used for quality control purpose. In case of the elements Ca and Mg it has to be mentioned that less sensitive emission lines were used.

A Multiwave 3000 digestion system (Anton Paar, Austria) equipped with a 16MF100 Rotor and MF 100 digestion vessels was used for microwave assisted digestion of PM10 samples. On the other hand, Bernas type Teflon-lined bombs were used for preparation of aerosol slurry solutions which were heated in an indigenously developed refractory oven with a temperature controller.

2.2 *Standards and reagents*

All used chemicals were of analytical reagent grade. Nitric acid (65%), hydrofluoric acid (48%), perchloric acid ($HClO_4$, 70%) and hydrogen peroxide (30%) were purchased from Merck (Darmstadt, Germany). High purity water was obtained by double distillation of previously deionized water (reverse osmosis/ion exchange combination Euro 20 plus, SG Water Systems, Germany) and used throughout. Metal standard solutions were prepared by diluting a 100 mg/l custom assurance multielement standard solution (Ba, Ca, Mg, Mn, Fe, Cu, Sr and Ti in 5% HNO_3) from SPEX Certiprep (NJ, USA) and adding single element standards (Al, Zn, Si, Na, and K, 1000 mg/l in 1% HNO_3) purchased from Merck. The prepared standard solutions were kept refrigerated at $4^{\circ}C$ in pre-cleaned polypropylene tubes till the further use. Reaction vessels and tubes were decontaminated prior to use by soaking them for at least 24 hours in 5% HNO_3 followed by another 24 hours in high purity water, rinsing them again with high purity water and drying them under a VFT 1525 ultraclean laminar flow hood (WEISS Technik GesmbH, Austria). Standard reference material® 2709 (San Joaquin Soil) from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to verify the accuracy of microwave digestion procedure.

2.3 *Sample collection and pre-treatment*

Sampling of size segregated airborne particulate matter samples (PM10) was performed at the site Getreidemarkt in downtown Vienna (16° 24′ E, 48° 12′ N), right next to a heavy traffic road with stop and go traffic during 7th June to 22nd July 2008. The sampling site was located on the balcony of the institute building, in a distance of approximately 2 m to the traffic lane and 5 m above the road level. For method validation, an additional set of eight PM10 aerosol samples was also collected at the site Hartberg, Styria from 21st April to 5th May 2005. This site represents a rural sampling location with less traffic intensity. Collection of PM10 samples was performed using an automated sampling device (Leckel, Germany) containing a PM10 pre-separation head

with an intake volume of 2.3 m^3 h^{-1} (being equivalent to 40 l min^{-1}). Filter holders were equipped with GN-4 Metricel$^®$ mixed cellulose ester filters (diameter: 47 mm, pore size: 0.8 µm, PALL Life-sciences, Michigan, USA) as sampling substrates. The filter samples were automatically changed after a collection period of 24 h, the air volumes collected within these sampling intervals varied between 50–55 Nm^3 (standard temperature pressure, 273 K and 1013 hPa). To exclude any contamination from the sampling procedure itself field blanks were collected by purging sample air for 30 s through the filter. The collected PM10 samples were stored in Petri dishes with seal of Parafilm M until analysis. Handling of filter samples (e.g. insertion of filters in filter holders) and all other manual operations (e.g., cutting of filter samples into two equal halves) were conducted in a particle free environment inside a laminar flow hood (Weiss VFT 1525) using ceramic scissor (IEDA Trading Cooperation, Japan) and ceramic forceps (Rubis Switzerland). Gravimetric analysis of the cellulose filters was performed by weighing sample filters before and after sampling on a Sartorius MC 210P (USA) weighing balance, the determined mass difference has been attributed to the amount of collected particulate matter (PM10).

For analysis, the collected PM10 aerosol samples were divided into two equal halves. One half of each PM10 sample was treated by newly developed approach. For this purpose, prepared filter halves were placed in pre-cleaned Bernas type Teflon-lined bombs followed by addition of defined amounts of oxidants and mineral acids. The Teflon-lined bombs were then placed in refractory oven, which allowed simultaneous treatment of 32 samples, where samples were treated for 60 min. (reaction time including cooling time) at elevated temperature to ensure a complete mineralization of the filter substrate. After treatment the samples were allowed to cool down and derived solutions including undissolved particles were transferred to polypropylene tubes and diluted to final volume of 10 ml with bi-distilled water. The prepared slurry solutions were stored in refrigerator at 4$^°$C until analysis. For quality control the remaining halves were digested using a conventional microwave procedure with subsequent ICP-OES analysis of the mineralized solution. The filter halves were treated in MF100 digestion vessels with 5 ml conc. nitric acid and 100 µl of hydrofluoric acid. Microwave assisted digestion was carried out at a maximum temperature of 190$^°$C and a maximum pressure of 20 bars using a Multiwave 3000 digestion system equipped with a 16HF100Rotor (Anton Paar, Austria) enabling the simultaneous treatment of 16 samples. The conversion of filter halves into clear solutions using above microwave conditions was accomplished in 80 min. (including sample cooling), the

derived solutions were transferred into polypropylene vessels and diluted with high purity water to a final volume of 50 ml, and were stored in the refrigerator at 4°C until analysis.

3. Results and discussion

3.1 *Optimization of sample pre-treatment procedure*

The complete mineralization of filter material used for collection of aerosol samples as well as homogenous suspension of residual particles in the derived solution is prerequisite for a slurry procedure [20]. Furthermore, stable slurry is required in order to achieve a representative aerosol for introduction into the plasma, in order to produce precise and accurate analytical results [22]. For the oxidation/dissolution of the sampling substrate, oxidizing agents like perchloric acid and hydrogen peroxide were used. In a first series of experiments, a mixture of 500 µl conc. HNO_3 and 300 µl $HClO_4$ (70%) was used for decomposition of filter halves from blank samples as well as PM10 test samples from Vienna. After a pre-treatment time of 1 h at 130°C, the derived reaction products were allowed to cool down, transferred into polypropylene tubes and afterwards diluted to a volume of 10 ml with bi-distilled water. After this type of sample pre-treatment, some elements were expected to be completely dissolved (e.g., Ca, Mg, Zn, Sr, Na and Fe) but for some elements (e.g., Al, Si and Ti) quantitative dissolution is impossible with the used conditions. So a part of the sample is still remaining in particulate form. Finally the resulting slurry solutions were measured using described ICP-OES conditions, and compared to the results derived from the analysis of the second filter halves pretreated using conventional microwave digestion and ICP-OES analysis. For validation of the microwave digestion procedure, approximately 50 mg of dried SRM 2709 (San Joaquin Soil) were digested using the same conditions as described for PM10 samples. After dilution with bi-distilled water the resulting solutions were measured using ICP-OES under optimized conditions. The derived results for SRM 2709 were in good agreement with the certified values confirming that microwave digestion procedure yielded accurate results for studied elements as shown in Table 2. Signal quantification was performed in all experiments using a calibration function derived from the analysis of aqueous standard solutions. For most elements (Al, Fe, Si, Ba, Cu, Mn and Ti), the results derived using developed procedure underestimated the microwave results distinctly, furthermore a poor reproducibility was observed. The reason which accounts for this outcome was the open treatment of PM10 samples at a temperature of 130°C for increased time of 1 h which may cause losses of analyte during sample boiling in open vessels. Furthermore, sedimentation of particles in the prepared slurries was observed as carbonaceous fraction was not

completely oxidized and black carbon was still visible in the residues, which indicates unstable slurries. So in order to overcome these problems $HClO_4$ was replaced by H_2O_2 (30%) for oxidation of filter substrate and other constituents of PM10 samples, and the pre-treatment temperature and time were reduced to 110°C and 30 min. respectively. Furthermore, the volume of the used acid was increased to improve the dispersion of resulting slurries as it has already been reported that final contents of 5-10% acid solution facilitates the suspension of particles[22]. For this purpose, a mixture of 1000 µl of conc. HNO_3 and 500 µl H_2O_2 was used for sample pre-treatment. In addition, the Bernas type Teflon-lined bombs were covered with caps during pre-treatment in order to avoid sample losses. Application of this procedure resulted in colorless solutions after dilution with bi-distilled water with no obvious sedimentation of particles (e.g., black carbon). Furthermore, it was also found that the applied acid content (HNO_3) was sufficient for formation of stable slurry solutions, thus avoiding the use of ultrasonic treatment and slurry stabilizing agents like Triton-X etc. This improved approach yielded comparable results to those derived after microwave digestion procedure for the same set of PM10 filter samples except for Al, Si and Ti. Additionally, an improved reproducibility was observed for replicate analysis of the same PM10 sample.

3.2 Comparison of new approach and microwave digestion procedure

Suitability of the proposed procedure for the analysis of various elements in airborne particulate matter was investigated by analysis of two sets of PM10 samples. One was collected from Hartberg, Styria and other was collected at Getreidemarkt, Vienna. Each set consisted of 8 PM10 samples which were analyzed using microwave digestion procedure with subsequent ICP-OES measurement of the diluted digest as a standard method and comparing the derived results with the findings derived for the same sample with the newly developed procedure.

Comparing the results obtained for the investigated elements excellent microwave to new approach ratios ranging from 1.00±0.07 (Fe) to 1.09±0.08 (Na) were found, except for Al, Si and Ti which showed ratios of 1.50±0.19, 1.80±0.10 and 1.93±0.18 respectively. This outcome indicates that the slurry approach underestimated the results of the reference measurement distinctly for these elements. A result which could be explained with the increased occurrence of these elements in the particulate form, since most siliceous compounds will remain undissolved after pretreatment with the new approach. Furthermore it has to be considered that Al, Si and Ti were reported to be dominant in the so called coarse mode of the investigated PM10 samples. Especially for larger particles differences in the sample introduction efficiency as well as a different behavior in the plasma could be expected than for introduced droplets of liquid standard

solution, causing differences in the signal intensities observed for so-called slurry samples and aqueous standard solutions.

Interpreting the results derived for Al, Si and Ti in PM10 samples from Hartberg and Vienna it is obvious that both investigated sites showed ratios in the same order, in fact for all three elements a linear correlation between microwave results and the findings derived with the proposed approach was found. Figure 1 presents the results derived for Si with a correlation coefficient (r^2) of 0.98, similarly Al and Ti showed a correlation (r^2) greater than 0.95 and 0.91 respectively. This outcome confirms that differences in the sample composition, which were expected for the rural site Hartberg and the urban site Vienna, have no significant influence on the microwave digestion to new approach concentrations ratios. To overcome possible differences in sample transportation, evaporation, dissociation, atomization and excitation in the plasma with respect to aqueous solutions the use of correction factors for slurry procedures has been recommended in literature [23-25]. Considering the findings derived with the microwave approach as true results, correction factors of 1.5, 1.80 and 1.93 for Al, Si and Ti were calculated, which are in the same order as reported by Darke et al. [26] for the slurry ICP-OES analysis of geochemical materials.

3.3 *Analytical figures of merit*

Analytical characterization of developed slurry procedure was performed by multiple analysis of PM10 samples using the optimized pre-treatment procedure. Comparing the results derived for the two different emission lines, it was observed that both spectral lines used for each element produced almost identical results except from Al 167.079, K 769.896, Na 818.326, Si 251.611, Sr 421.552 and Ti 308.802 which resulted in signals associated with distinctly higher uncertainty. However, throughout the whole manuscript only the results derived for the first line (λ 1) were used for analyte quantification. For determination of reproducibility, it was necessary to divide one PM10 sample into several parts, since it is not possible to collect a set of identical PM10 aerosol samples. The relative standard deviation (RSD %) obtained from six replicate determinations of a PM10 sample which has been divided into six equal parts, ranged from 3.2% (Ca) to 9.1% (Zn). When comparing the RSD values of the investigated elements, it was observed that the elements Zn and Ti showed relatively enhanced results (RSD % being 9.1 and 7.9 respectively), an outcome which could be explained with the low concentrations of these elements in PM10 (especially when compared to e.g., Ca or Fe). Thus with the use of 1/6 parts of the filter sample the prepared slurry solutions contained only very low contents of the investigated trace elements leading to increased uncertainties in ICP-OES analysis. With the use

of filter halves instead of 1/6 filter parts improved RSD values were expected for these elements since a three times higher sample intake leads to increased concentrations of these metals in the resulting slurry solutions.

A set of ten blank filter halves was used to determine the limit of detection (LOD) for developed slurry ICP-OES procedure. The LOD was calculated as 3 times the standard deviation (3σ) of the signal derived from filter blank samples. Considering the air volume of the collected PM10 samples the determined instrumental detection limits were converted into method detection limits. Derived results for LOD values of measured elements are presented in Table 3, which are for most elements in the same order as observed for the conventional microwave digestion procedure. A result which indicates that the less effective sample introduction of the slurry samples with the high solid kit is compensated by avoiding unnecessary sample dilution as required in case of the microwave procedure. For some elements a slightly improved sensitivity was observed, an outcome which results from the distinctively reduced consumption of reagents for sample preparation, lowering the risk of sample contamination and thereby reducing the analyte signals of pretreated filter blanks. Derived LOD values are sufficient for investigation of ambient trace elements concentrations in PM10 (Table 3).

3.4 *Analysis of PM10 samples*

The developed ICP-OES procedure was applied for the analysis of selected crustal and trace elements in the PM10 samples collected from down town in Vienna. PM10 mass concentrations of the investigated samples varied between 20.7 and 46.6 µg m^{-3} with an average value of 34.4±6.5 µg m^{-3} (n=31) which is within the limit of 50 µg m^{-3} according to EU standards [27]. For element specific analysis each PM10 sample has been divided into two halves. One half of each filter sample was treated using proposed procedure whereas other half was digested using microwave digestion procedure for quality control purpose. When the results obtained via developed procedure were compared with that of microwave digestion procedure, a good agreement was observed for Ba, Ca, Cu, Fe, K, Mg, Mn, and Na. After application of the correction factors presented in the previous chapters for Al, Si and Ti, even for these elements a good agreement was found. In case of Sr and Zn, it was not possible to compare results because for these elements the microwave digestion procedure yielded concentrations below the respective detection limits. The concentrations of the investigated crustal elements varied between some hundred ng m^{-3} and few µg m^{-3} with highest concentrations for Fe and Si, distinctly reduced concentrations ranging from some ng m^{-3} (Sr) to more than hundred ng m^{-3}(K) were found for trace elements (for details see Table 4).

The concentration ranges observed for crustal elements (Al, Ca, Fe, Mg, and Si) are comparable to the results reported for other urban sites in Europe. For example, Limbeck et al. [28] have found that concentrations of these elements vary from 0.26 ± 0.34 µg m^{-3} (Mg) to 2.08 ± 1.82 µg m^{-3} (Si) in PM10 samples collected in Vienna. Slezakova et al. [29] reported that the concentration of the crustal elements Al, Ca, Fe, Mg and Si ranged from 0.11 ± 0.05 µg m^{-3} (Mg) to 2.43 ± 1.60 µg m^{-3} (Si) in PM10 samples collected from Oporto, Portugal. Similarly, Gietl et al. [30] have found that PM10 samples collected from Marylebone road London with heavy traffic show similar values of crustal elements (Al, Ca, Fe, Mg and Na) ranging from 0.08 ± 0.05 µg m^{-3} (Al) to 1.21 ± 0.72 µg m^{-3} (Fe). Comparable results for these elements were also reported for PM10 samples from a heavy traffic site in down town Budapest by Salma et al. [31] ranging from 0.79 ± 1.20 µg m^{-3} (Al) to 2.59 ± 0.51 µg m^{-3} (Si). Vecchi et al. [32] have reported comparable concentrations of crustal elements (Al, Ca, Si and Fe) in PM10 samples collected from an urban site in Milan ranging from 0.84 µg m^{-3} (Al) to 2.40 µg m^{-3} (Si). Alleman et al. [33] have also found that the concentrations of crustal elements (Al, Ca, Fe, Mg, Na and Si) were varied from 0.27 ± 0.16 µg m^{-3} (Al) to 2.04 ± 3.07 µg m^{-3} (Si) in PM10 samples collected from Dunkirk region of France.

The results reported for trace elements (Ba, Cu, Mn, K, Sr, Ti and Zn) were also found to be in good accordance to literature findings. For example, Limbeck et al. [28] reported that concentration of the trace elements, Ba, Cu, Mn, Ti and Zn varied from 12.0 ± 6.8 ng m^{-3}(Ba) to 48 ± 26 ng m^{-3}(Zn) in PM10 samples collected from down town Vienna. Slezakova et al. [29] have found that concentration of the trace elements Cu, Mn, Ti and Zn ranged from 13.4 ± 5.8 ng m^{-3} (Mn) to 172 ± 104 ng m^{-3} (Zn) in PM10 samples collected from Oporto, Portugal. Similarly, Gietl et al. [30] have reported that concentrations of the trace elements, Ba, Cu, Ti and Zn varied from 3.1 ± 1.9 ng m^{-3} (Ti) to 53 ± 34 ng m^{-3} (Cu) in PM10 samples from Marylebone road London. The concentrations of trace elements (Cu, Mn, K, Ti and Zn) in PM10 samples collected from a site in down town Budapest [31] were also comparable with above findings and ranged from 22 ± 4 ng m^{-3} (Mn) to 93 ± 14 ng m^{-3}(Zn). Comparable concentrations of trace elements Cu, Mn, Ti and Zn have been reported in PM10 samples from an urban site in Milan [32] ranging from 45 ng m^{-3} (Mn) to 180 ng m^{-3} (Zn). Similar results for trace elements (Ba, Cu, Mn, K, Sr, Ti and Zn) ranging from 3.1 ± 1.8 ng m^{-3} (Sr) to 674 ± 1129 ng m^{-3} (K) have been reported in PM10 samples collected from Dunkirk region of France [33].

Based on the derived results the contribution of crustal and trace elements to total PM10 mass has been calculated, yielding an average contribution of 13.9 ± 2.48 % of total PM10 mass

concentrations for crustal elements whereas trace elements contributed not more than 1% to PM10 mass, a result which confirms that crustal elements are major contributors to ambient PM10 concentrations. However, since the mineral components Si, Ca, Fe, Al and Mg were assumed to be present rather in the form of oxides than in elemental form, it is recommended to convert the measured element concentrations into the respective mass concentrations of the most common oxides for PM10 mass balances [32]. Using this approach mean contributions of 32.6±5.8 % were obtained for the mineral fraction (considering the oxides SiO_2, Al_2O_3, CaO, MgO and Fe_2O_3). This outcome is in accordance to findings of Limbeck et al. [28] who have found that mineral fraction of these oxides contributed 31.7±16% (Kendlerstraße), 27.8± 14% (Rinnböckstraße) and 22.3±17% (Schafberg) to PM10 mass for three different sites in Vienna.

Finally an investigation was also carried out to study the difference in concentrations of measured elements in PM10 samples collected from urban site (Getreidemarkt, Vienna) and rural site (Hartberg, Styria) which is less influenced by traffic intensity. The concentration of crustal elements (Al, Ca, Mg, and Si) in PM10 samples collected from Hartberg, Styria ranged from 0.22±0.12 μg m^{-3} (Mg) to 1.42±1.01 μg m^{-3} (Ca) which was found to be in the same order as reported for PM10 samples collected from urban site, Getreidemarkt (Table 4). However, distinct differences were observed for the crustal element Fe which showed a concentration of 0.46±0.21 μg m^{-3} in PM10 samples collected from Hartberg, whereas the concentration of Fe in PM10 samples collected from urban site Vienna was approximately 4 times higher. An outcome which could be credited to occurrence of heavy traffic at urban site since Fe is known to be an important contributor of traffic emission [6]. The concentration of trace elements Mn, Sr, Ti and Zn in PM10 samples from Hartberg varied from 3±2 ng m^{-3} (Sr) to 38±13 ng m^{-3} (Zn) which were in the same order as observed for urban site, however the concentration of Ba and Cu in urban PM10 samples was found to be 4.6 and 5.2 times higher respectively than at the rural site. These findings could be attributed to the difference of traffic intensity at two sites because in literature it has been reported that motor vehicles are well known sources for Ba and Cu and lead to enhanced levels of these elements at traffic influenced sites [6, 29-30].

4. Conclusion

A procedure for the determination of major and some minor inorganic aerosol constituents has been developed which avoids the use of hazardous reagents such as HF and expensive instruments such as microwave digestion system for sample pre-treatment. In combination with ICP-OES measurement, the proposed approach allows accurate determination of selected crustal

and trace elements in PM10. Al, Si and Ti were not completely dissolved with the proposed approach, in contrast to elements such as Ca, Fe or Mg, thus correction factors were applied for accurate quantification of these elements with aqueous standard solutions. Applicability of correction factors was determined for samples with a crustal load up to 2.4 µg m^{-3}(Si). Since the PM10 samples from drier regions with higher concentration of crustal materials can be expected to carry more coarse particles, so correction factors for such samples might differ from the proposed ones.

The procedure is found to be advantageous over traditional microwave digestion procedure in terms of sensitivity and time consumption. Increased sensitivity was obtained by avoiding the sample dilution step usually required after microwave digestion to adjust an appropriate level of acid content. Furthermore the developed procedure reduces the risk of contamination due to decreased reagent consumption and manipulation steps. Improvements in the time demand for sample could be achieved by an increased sample throughput, with the Multiwave 3000 digestion system used in this work 16 samples could be pretreated within 80 minutes, whereas the proposed procedure requires only 60 minutes for 32 samples. However, it is recommended to investigate the applicability of presented sample introduction technique for analysis of some toxic trace metals like As, Cd, Ni and Pb in PM10 samples in future studies which was not possible in present work due to limited sensitivity of ICP-OES.

Application of this procedure for the analysis of crustal elements and selected trace metals in PM10 samples collected in Vienna (Austria) has revealed comparable concentrations to other Central European cities. The cumulated mass of SiO_2, Al_2O_3, CaO, MgO and Fe_2O_3 accounted for 32.6 ± 5.8 % of the PM10 mass, confirming that crustal elements were major contributors to ambient PM10 concentrations.

Acknowledgements

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Table 1 Instrumental parameters and analytical wavelengths (nm) used for ICP-OES analysis

Parameter	Value	Parameter	Value
Rf power	1200 W	Nebulizer flow	0.65 l min^{-1}
Sample flow	0.75 ml min^{-1}	Auxiliary flow	1.0 l min^{-1}
Read delay	60 s	Coolant flow	12 l min^{-1}
Integration time	10 s	Number of replicates	5
Background correction	constant shift from analytical line		

Element	Wavelength [nm] λ 1*	λ 2	Element	Wavelength [nm] λ 1*	λ 2
Al	308.215	167.079	Mn	257.610	259.373
Ba	455.403	233.527	Na	589.592	818.326
Ca	315.887	422.673	Si	212.412	251.611
Cu	324.754	224.700	Sr	407.771	421.552
Fe	234.349	259.940	Ti	334.941	308.802
K	766.490	769.896	Zn	202.548	213.856
Mg	285.213	202.582			

λ 1* is used for quantification of the analyte whereas λ 2 is applied for quality control purpose.

Table 2 Measured contents of NIST SRM 2709 using microwave
digestion procedure

Elements	Measured values [% contents]	Certified values [% contents]
Al	7.61±0.20	7.50±0.06
Ba	993±19*	968±40*
Ca	1.83±0.13	1.89±0.05
Cu	33.1±3.0*	34.6±0.7*
Fe	3.65±0.11	3.50±0.11
K	2.09±0.07	2.03±0.06
Mg	1.57±0.06	1.51±0.05
Mn	555±24*	538±17*
Na	1.22±0.08	1.16±0.03
Si	28.70±1.16	29.66±0.23
Sr	241±24*	231±2*
Ti	0.347±0.02	0.342±0.024
Zn	114±8*	106±3*

*results given in μg/g unit

Table 3 Limit of detection (LOD) values for various elements derived using proposed approach and microwave digestion procedure along with PM10 concentration ranges for European cities

Elements	Proposed method			Microwave procedure			PM10 conc. ranges for European cities†
	Instrumental LOD$	Method LOD$^{\Delta}$		Instrumental LOD$	Method LOD$^{\Delta}$		
	[ppb]	[ppb]	[ng m^{-3}]	[ppb]	[ppb]	[ng m^{-3}]	[ng m^{-3}]
Al	7	109	27	0.9	40	50	570±530 to1350±941
Ba	12	BDL	1*	0.5	1	2	12±6$^{\varnothing}$
Ca	40	195	71	0.6	122	234	889±555 to 1880$^{\varepsilon}$
Cu	21	BDL	2*	0.4	10	14	20±10 to 87±40
Fe	16	26	16	0.8	12	17	740±440 to 1830$^{\varepsilon}$
K	42	BDL	4*	3.1	22	27	257±75 to 834±461
Mg	16	35	13	0.9	12	14	111±54 to 310±91
Mn	20	BDL	2*	0.7	1	1	13±6 to 45$^{\varepsilon}$
Na	47	88	37	3.3	54	66	293±83$^{\varnothing}$
Si	35	74	27	2.1	313	350	2080±1920 to 2586±507
Sr	10	BDL	1*	0.8	2	2	3±2$^{\varnothing}$
Ti	7	BDL	1*	0.9	2	2	20±21to 91±47
Zn	15	36	14	0.3	61	31	48±26 to 180$^{\varepsilon}$

$ derived from the analysis of aqueous standard solutions, * calculated using ½ of the instrumental LOD
Δ derived from the analysis of 10 pre-treated filter blank samples
BDL= below detection limit, $^{\varepsilon}$ values are reported without standard deviations,
† Data taken from the PM10 studies in Vienna, Oporto, Budapest and Milan, $^{\varnothing}$ data available from only one study

Table 4 Mean concentrations of measured elements in PM10 samples using proposed procedure and ratios obtained between results derived using microwave and proposed procedure

Elements	Concentrations of PM10 samples (n=31) Proposed method		Ratios microwave to proposed procedure
	Conc. range	Mean±SD	
conc. in µg m^{-3}			
Al	0.17-0.64	0.29±0.12	0.92±0.11
Ca	0.54-2.04	1.02±0.33	1.06±0.12
Fe	1.27-2.66	1.89±0.43	1.00±0.07
Mg	0.10-0.33	0.19±0.06	1.04±0.09
Na	0.10-0.52	0.20±0.11	1.10±0.08
Si	0.54-2.41	1.40±0.59	1.07±0.11
conc. in ng m^{-3}			
Ba	19-42	28±5	0.98±0.06
Cu	64-130	94±20	1.03±0.08
Mn	14-43	22±6	0.99±0.08
K	85-277	139±50	1.07±0.14
Sr*	2-7	3±1	-
Ti	11-42	23±7	0.95±0.10
Zn*	34-70	51±10	-

*For Sr and Zn, the concentrations for PM10 samples were below than LOD in case of microwave digestion procedure, so it was not possible to calculate ratios. Al, Si and Ti concentrations have been corrected by applying the determined correction factors
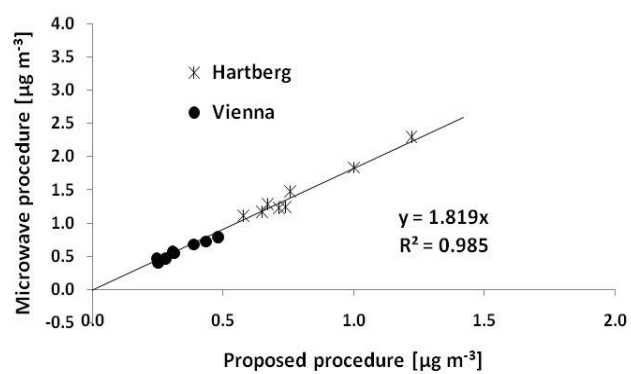
Fig. 1: Relationship of Si concentrations obtained using proposed and microwave digestion procedure for PM10 samples collected at Hartberg (Styria) and Getreidemarkt (Vienna)

P 3

6.3 On-line determination of water-soluble zinc in airborne particulate matter using a dynamic extraction procedure coupled to flame atomic absorption spectrometry

On-line determination of water-soluble zinc in airborne particulate matter using a dynamic extraction procedure coupled to flame atomic absorption spectrometry

Azam Mukhtar and Andreas Limbeck*

In this work a flow injection procedure with FAAS detection for the on-line determination of water-soluble Zn in airborne particulate matter samples is presented. The method is based on a preliminary extraction of samples with water under dynamic conditions and the subsequent on-line FAAS measurement of the dissolved fraction of Zn. As compared to traditional batch-wise systems, the developed on-line extraction procedure offers enhanced sensitivity and sample throughput, reduced risk of sample contamination and the absence of metal redistribution or readsorption processes. With the use of two filter punches (diameter 9 mm) for analysis an instrumental detection limit of 2 ng Zn was obtained, which translates to a method detection limit of approximately 0.4 ng m^{-3} when considering the volumes of air collected per investigated aerosol sample. The reproducibility of analysis given as the relative standard deviation was 2.6% ($n = 6$). The procedure was applied for analysis of water-soluble Zn in aerosol samples from two urban sites in Austria. Accuracy of derived results was confirmed by analysis of the same sample set with a traditional batch-wise extraction approach as well as mass balance determination.

Introduction

Airborne particulate matter (APM) contains a variety of metals. These metals are either contributed by natural sources such as crustal weathering, sea-salt aerosol generation, volcanism or anthropogenic processes such as fossil fuel combustion, industrial activity, incineration.[1] The high metal concentrations reported for contaminated sites such as urban areas can pose serious human health risks.[2–4] The toxicity of metal depends upon its species present in airborne particulate matter and their bio-accessibility. However, most of the studies dealing with determination of trace elements in APM focus on the determination of total metal concentration without distinguishing the various species that are present.[5] But for risk assessment of metal toxicity, it is important to determine bio-accessible concentrations instead of total metal contents.[6] Determination of the water-soluble fraction could be used as an upper level estimate for the bio-accessible fraction as it can easily be dissolved in the lung fluid and imparts toxicity to human beings and other living organisms.[7]

In order to determine the water-soluble fraction, particulate samples are generally extracted with leaching agents such as sodium chloride (1% m/v solution), phosphate buffered saline or potassium citrate.[5,8,9] In recent years, water is chosen as the simplest and most universal extraction solvent for estimation of the bio-accessible fraction of trace metals in APM, for example extraction of APM samples is routinely used by USEPA workers

for toxicity testing.[10–12] The procedures reported so far were based on the batch-wise extraction of various metals in APM,[13–15] which are based on the extraction of the sample with different leaching agents and reaction times in the range of 30–90 min.[16] However, such batch-wise extraction procedures were found to be time consuming, troublesome, laborious and there are also chances of contamination as well as analyte losses. Additionally, there are problems of adsorption of dissolved species on remaining particulate matter due to long exposure times.[17,18] On the other hand, on-line extraction techniques are fast, exclude troublesome sample handling steps and reduce the possibility of sample contamination as well as analyte losses.[19,20] Another benefit of on-line dynamic extraction procedures is that they give comprehensive knowledge about the kinetics of the extraction process.[21] Furthermore, automation of on-line extraction procedures is possible with the use of flow-injection systems which enhances sensitivity and precision of the analysis.[22]

Although there are many studies reporting on-line extraction procedures for various metal fractions in samples like soil, sediments, fly ash, rocks, sea food *etc.*,[23–27] but until now no work has been reported for the dynamic extraction of airborne particulate matter. In contrast to the above mentioned environmental samples it is not possible to investigate APM with conventional micro-extraction columns, rotating coils or stirred flow chambers, since APM is collected on filter substrates and usually only available with total sample amounts in the order of few mg. Thus a new approach is required which enables dynamic extraction of such small sample amounts with element specific on-line detection. The present study describes a novel approach for on-line determination of water-soluble zinc in airborne particulate matter with an aerodynamic diameter ≤ 10 μm

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(PM10) using a flow injection procedure coupled with flame atomic absorption spectrometry (FAAS). Zinc is an essential element which is required for living organism's body systems in optimum quantity but zinc imbalance can result to severe diseases,[28] e.g., C. Prieditis et al.[29] reported the comparative pulmonary toxicity of various soluble metals found in urban dust by instilling them into mouse lung and animals. The determination of bio-accessible Zn in airborne particulate matter samples is therefore of great concern.

Experimental

Reagents and materials

High purity water was obtained by distillation of de-ionized water derived from a reverse osmosis/ion exchange combination (Euro 20 plus-SG water system, Germany) using in house quartz apparatus. Nitric acid (Merck, Germany) used was of analytical reagent grade. A certified stock solution of Zn (1000 mg l^{-1}) was procured from Merck (Germany) and various working standard solutions were prepared by dilution with 1% HNO$_3$ (vol/vol). Standard solutions as well as prepared sample solutions were kept refrigerated at 4 °C in pre-cleaned polypropylene tubes till the further use. On-line as well as batch-wise extractions were performed using high purity water as leaching agent. Standard reference material® 2709 (San Joaquin Soil) from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to verify the accuracy of total Zn measurements.

Instrumentation

A Perkin-Elmer flame atomic absorption spectrometer 5100 ZL employed with a hollow-cathode lamp for zinc as specific light source has been used for analysis. Measurement of zinc was conducted at a wavelength of 213.9 nm using a slit width of 0.7 nm and a lamp current of 15 mA. Deuterium underground correction has been used to overcome interferences caused from undissociated matrix molecules. A standard air-acetylene stainless steel nebulizer was operated at an airflow rate of 10 l min^{-1} and acetylene flow rate of 2 l min^{-1}. For sample introduction the self-aspirating mode of the nebulizer has been used. The burner height was adjusted to provide optimum sensitivity for conventional sample measurement using a read time of 5 s and four replicates for analysis.

FI-Procedure

The applied flow-injection system consisted of a peristaltic pump (SPETEC, Germany) for continuous transfer of the leaching agent and a six port injection valve (VICI, USA) equipped with a sample cartridge for insertion of PM10 filter samples. A schematic diagram of the FI-manifold used for on-line extraction of PM10 samples is presented in Fig. 1a. Peristaltic pump and six port injection valve were connected using inert peristaltic pump tubes (I.D. 1.2 mm), whereas FAAS detection system, sample cartridge and the individual positions of the injection valve were connected with PTFE tubings (I.D. 0.3 mm). The sample cartridge was prepared from a commercially available Chromafix® SPE column (Macherey-Nagel, Germany, diameter 12 mm,
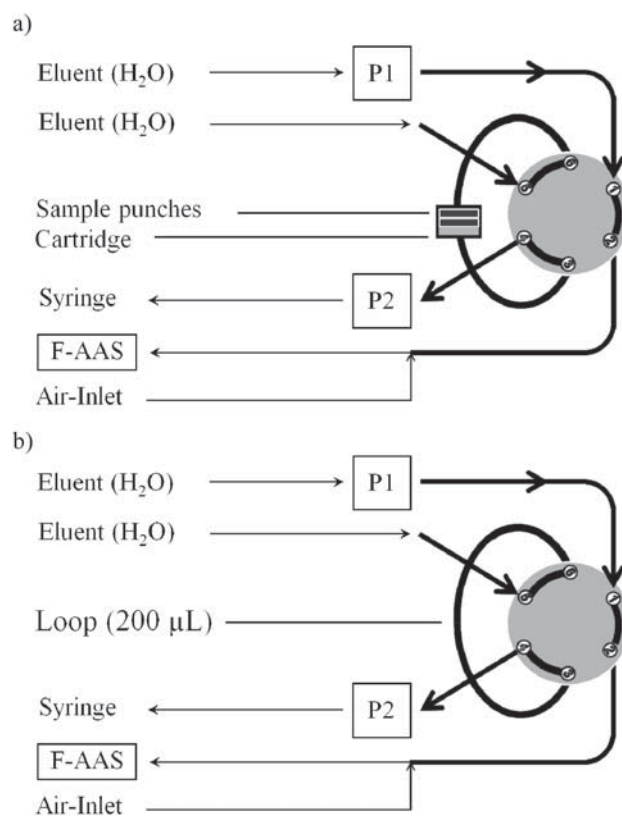
Fig. 1 a) Manifold for analysis of PM10 samples. b) Manifold for injection of standard solutions.

length 14 mm) by removing upper frit and sorbent material. The remaining porous frit at the bottom of the cartridge has been used as sample holder. The cartridge has been connected to FI-system using luer-fittings which allowed an easy and fast replacement of sample cartridge.

Measurement of PM10 samples

For on-line extraction of PM10 samples, two aliquots with a diameter of 9 mm were punched out of each sample and packed into pre-cleaned sample cartridges. After insertion of the sample cartridge into the FI-manifold, the valve was switched into inject position thus allowing the leaching solution to pass through the cartridge prior to the introduction into the FAAS and thereby extracting the water-soluble zinc in PM10 filter samples. The eluent was then directed to the detection unit where the transient elution profile was recorded. On-line FAAS measurement was started with switching of valve position. Total measurement time was 100 s with an interval of two seconds per data point.

Measurement of standard solutions

Quantification of the extraction profiles was based on a calibration function which has been determined using aqueous zinc standards. For this purpose the sample cartridge used for analysis of PM10 samples has been replaced with a 200 µl loop (Fig. 1b), which was filled with zinc standard solutions of varying concentrations and then injected into the carrier stream of the leaching agent. The defined volume of standard solution was

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then transported to the detection unit (FAAS) thereby a transient signal was created which has been measured using the conditions described for analysis of PM10 samples.

Batch-wise extraction procedure and determination of residual/total zinc contents

For method validation the water-soluble fraction of zinc in PM10 samples has also been determined using a conventional batch-wise extraction procedure. The aqueous extraction was performed by treating three punches of filter samples (diameter 9 mm) in 10 ml polypropylene tubes with 3 ml of high purity water. The closed polypropylene tubes were placed in ultrasonic bath (Sonorex TK30, Bandelin, Germany) and extracted for 90 min using ultrasonic agitation. In a next step, samples were centrifuged (Hettich, Zentrifugen-EBA 20) at 4000 rpm for 10 min for separation of filter substrate and undissolved material. The supernatant clear sample solutions were transferred to new 10 ml polypropylene tubes and stored until further analysis, which has been conducted by conventional FAAS measurement.

Determination of total zinc contents was performed by treatment of three aerosol filter punches (diameter 9 mm) with 400 μl of conc. nitric acid in closed polypropylene tubes using ultrasonic agitation. After an interaction time of 90 min the derived digests were diluted with high purity water to a final volume of 3 ml. After separation of filter residue and undissolved sample constituents through centrifugation, 2 ml of derived clear solution from each sample were transferred into new sample tubes and stored inside a refrigerator until analysis by FAAS.

For mass balance demonstration (*i.e.*, comparison of total zinc contents with the sum of water-soluble zinc and zinc remaining after sample leaching), residual zinc contents of filter punches after on-line extraction were also determined. For this purpose the sample cartridge was detached from FI-system after sample leahing and filter punches were taken out of sample cartridge with the help of ceramic forceps. These filter punches were then transferred to pre-cleaned polypropylene tubes followed by addition of 400 μl of conc. nitric acid and treated in the same way as described above for the determination of total zinc contents and finally measured by FAAS.

Sample collection

Sampling of size segregated airborne particulate matter samples (PM10) was performed at three urban sites in Austria (Don-Bosco, Graz in December 2003; Rudolfsplatz, Salzburg in January 2005 and Neue Welt, Linz in March 2006). These sites were located close to major roadways with occasional stop and go traffic conditions, furthermore, these sites were affected by industrial activities and emissions related to civil populations. Collection of PM10 samples was performed using an automated sampling device (Leckel, Germany) containing a PM10 pre-separation head with an intake volume of 2.3 m³ h⁻¹ (being equivalent to 40 l min⁻¹). Filter holders were equipped with GN-4 Metricel® mixed cellulose ester filters (diameter: 47 mm, pore size: 0.8 μm, PALL Life-sciences, Michigan, USA) as sampling substrates. The filter samples were automatically changed after a collection period of 24 h, the air volumes collected within these sampling intervals varied between 50–55 Nm³ (standard temperature pressure, 273 K and 1013 hPa). To exclude any contamination from the sampling procedure itself field blanks were collected by purging sample air for 30 s through the filter. Handling of filter samples (*e.g.* insertion of filters in filter holders) and all other manual operations (*e.g.*, preparation of filter punches) were conducted in a particle free environment inside a laminar flow hood (Weiss VFT 1525) using indigenously developed quartz puncher, ceramic forceps (Rubis Switzerland) and other metal free tools.

Results

Optimization of the FI-procedure

In a first set of experiments, the nebulizer of the FAAS was directly connected to the outlet position of the six port valve. The flow rate of the leaching agent was adjusted to 1 ml min⁻¹. The results achieved with this arrangement for aerosol test samples showed a sudden increase in the Zn absorption, which decreased with increased extraction time and reached the baseline level after approximately 60 s, as expected for the leaching profile. Nevertheless, these first results were not satisfying since the signal showed fluctuations with time and flame extinguished from time to time. These problems could be explained with the operating conditions of the FAAS. The flow rates used for fuel gas and oxidant caused a flow rate of approximately 3 ml min⁻¹ in the self-aspirating mode of the nebulizer. Since the FI-system delivered the leaching agent only with a flow rate of 1 ml min⁻¹, an under pressure was created in the transfer line which caused the formation of air bubbles in the liquid flow and thus preventing a continuous introduction of leaching agent in the FAAS.

In order to overcome this problem, a T-shaped junction was introduced into the transfer line with an additional inlet for the introduction of air. This air inlet allowed a pressure compensation *via* suction of a respective air flow into the transfer line, disabling the formation of an under pressure in the FI-manifold. With this improved set up it was possible to measure extraction profiles without sudden and unexpected disappearance of the flame, but for the first data points always a disturbed baseline with high signal variations was observed. Furthermore the elution peaks showed sometimes sudden signal drops disabling repeatable measurements. The reason for this outcome was the air introduced into the FI-system with each change of the sample cartridge. To minimize the volume of air remaining in the cartridge after insertion of porous frit and sample punches, the Chromafix SPE columns were cut in length to reduce the inner volume of the cartridge from 1500 μl to approximately 700 μl. However after insertion of frit and PM10 filter punches, a small volume remained in the cartridge which led still to the introduction of air bubbles into the FI-system. This problem was overcome by filling of cartridge with leaching agent prior to the start of the leaching process and FAAS measurement. For this purpose a syringe has been connected to the FI-system, which allowed in the load position to fill the cartridge partially with high purity water. Analysis has been started immediately after filling of the cartridge by switching the valve into the inject position.

Influence of flow rate

A set of experiments was conducted to study the effect of leaching agent flow rate on extraction of water-soluble zinc. The

flow rate of leaching agent has been varied in the range from 0.6 to 1.2 ml min^{-1}. With decreasing flow rate, a shift in the shape of elution profile from sharp and high signals to broad and low peaks was observed. For determination of the optimum flow rate replicate measurements of the same sample using the mentioned conditions were performed. For quantitative evaluation of resulting transient signals, an adequate baseline correction was applied to the recorded data set. The peak area of obtained peaks was then determined using OriginPro 8, data analysis and graphing software from OriginLab Corporation (Northampton, USA). Comparison of derived peak areas was difficult since reproducibility of FI-analysis (calculated in percent relative standard deviation) was observed to be influenced by the flow rate of leaching agent disabling accurate quantification at low flow rates. Best results were obtained for a flow rate of 1.0 ml min^{-1}, therefore all further experiments were conducted at this flow rate of 1.0 ml min^{-1}. Examples for elution profiles of PM10 samples from different sites in Austria using the optimized conditions for analysis are shown in Fig. 2.

Quantification of elution profiles

The on-line calibration of aqueous standards was performed by replacing the sample cartridge with a 200 µl sample loop which allowed reproducible injection of a defined value of Zn standard solutions into the carrier stream of the leaching agent. The peak area of the obtained transient signal corresponds to the injected mass of analyte. Each standard was measured three times during each measurement cycle. Calibration with aqueous Zn standard solutions performed *via* on-line FI-procedure was linear throughout the investigated range (varied between 0 and 1000 ng of Zn) exhibiting a correlation coefficient (r^2) exceeding 0.995. The relative standard deviation obtained by insertion of 200 µl of 1000 µg l^{-1} aqueous zinc standard was found to be 1.2% ($n = 6$).

After aqueous calibration, the effect of co-eluted matrix which might interfere FAAS measurement of Zn was studied by a matrix matched calibration. For this purpose, PM10 filter punches with a diameter of 9 mm were spiked prior to analysis with defined amounts of Zn, (*e.g.*, 20 µl of a 10 mg l^{-1} Zn standard solution resulted in an addition of 200 ng of zinc). After

Fig. 2 Extraction profiles of urban PM10 samples and filter blank.

evaporation of the solvent with a gentle stream of nitrogen the filter punches were inserted into the sample cartridge and analyzed using the FI-system. The results obtained from these experiments showed an excellent recovery for spiked zinc amounts. The slope of matrix matched calibration was found to be 0.0088 which was nearly identical to the slope obtained from calibration with aqueous standard solutions (0.0090), although other soluble sample constituents such as ionic species and organic acids were co-eluted with the analyte and simultaneously introduced into the detection unit. This outcome proved that aqueous calibration could be used for quantification of PM10 aerosol samples.

Analytical figures of merit

Reproducibility of the developed on-line FI-procedure for the analysis of water-soluble zinc in airborne particulate matter was performed by analyzing six replicates from the same PM10 sample. The relative standard deviation was found to be 2.6% ($n = 6$) showing good reproducibility of the FI-procedure. The effect of any contamination during sample treatment such as filter punching and insertion into sample cartridge was investigated by analyzing field blank filters. The signals for collected field blanks were found to be identical to those of aqueous blanks derived from analysis of a cartridge in the absence of filter punches, confirming contamination free sample pretreatment. The result of a typical field blank signal is depicted in Fig. 2. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as 3 times the standard deviation (3σ) and 10 times the standard deviation (10σ) of the filter blank signals and were found to be 2 ng of Zn and 7.2 ng of Zn respectively. Considering the volumes of air typically collected for the investigated PM10 samples these instrumental limits correspond to a method detection limit of 0.4 ng m^{-3} and a method quantification limit of 1.6 ng m^{-3}.

For validation of the on-line procedure, a set of eighteen PM10 samples was processed in triplicate using the proposed method and a conventional batch-wise extraction procedure. Analysis of PM10 samples was performed in accordance to the description presented in the experimental section using the optimized on-line extraction procedure. The conditions used for batch-wise extraction of PM10 samples were comparable to the procedures reported in literature for extraction of various soluble metals in APM.[5,14] The LOD (3σ) and LOQ (10σ) for batch-wise extraction procedure were found to be 5 µg l^{-1} and 24 µg l^{-1} respectively. These LOD and LOQ values correspond to a method detection limit of 2.4 ng m^{-3} and a method quantification limit of 11.5 ng m^{-3}. The relative standard deviation for batch-wise procedure was found to be 3.3%. Comparison with the on-line procedure indicates that the batch-wise approach is comparatively less sensitive. Furthermore, the on-line procedure is much faster and excludes troublesome sample handling steps which impart risks of sample contamination as well as analyte losses. However, results observed for water-soluble zinc concentrations in PM10 have shown a good agreement between on-line and batch-wise approach (Fig. 3), confirming that the developed on-line extraction procedure is applicable for the determination of water-soluble Zn in APM. Excellent correlations ($r^2 < 1.04$) between on-line and batch-wise results were found for
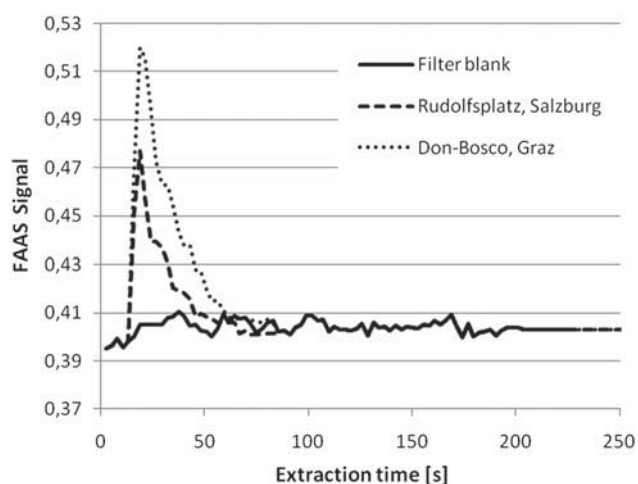
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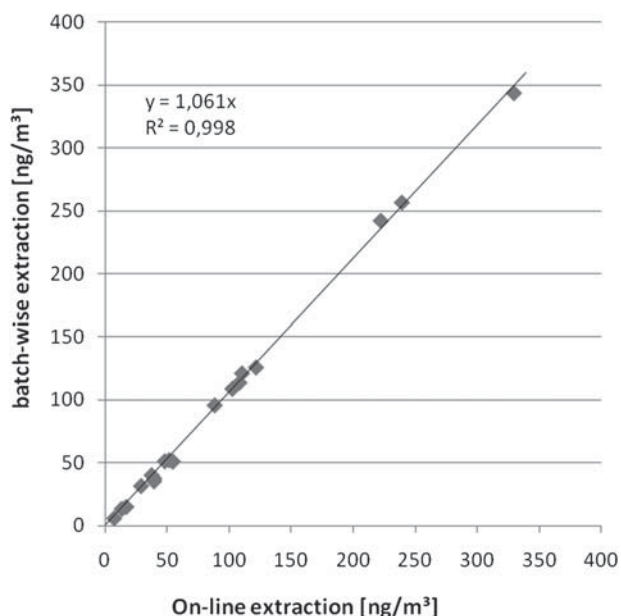*J. Anal. At. Spectrom.*, 2010, **25**, 1056–1062 | 1059

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Fig. 3 Correlation between on-line extraction results for water-soluble Zn in PM10 and the findings derived *via* batch-wise extraction of the same sample set (number of samples 18).

water-soluble Zn concentrations below 200 ng m^{-3}, for higher concentrations the on-line approach delivered slightly reduced concentrations, which are a result of the high absorbance values derived for these samples exceeding the linear calibration range marginally.

Furthermore the accuracy of the extraction procedure has been demonstrated by calculating the mass balance of water-soluble and insoluble fractions of Zn in PM10 and comparison with the total Zn contents of the investigated samples. For this purpose, a third set of twelve PM 10 samples from the site Neue Welt (Linz, Austria) was analyzed using the presented on-line extraction procedure with subsequent measurement of the residual Zn contents remaining on the filter punches after leaching of water-soluble Zn. Total Zn contents of these samples were determined *via* analysis of another set of filter punches. The accuracy of the procedure applied for measurement of residual and total zinc contents was evaluated by digestion of the NIST standard reference material SRM 2709 (San Joaquin Soil). Approximately 20 mg of SRM 2709 were taken in 10 ml polypropylene tubes and 1 ml of conc. nitric acid was added. The tubes were treated in ultrasonic bath for 90 min, the contents were diluted to 10 ml with high purity water and centrifuged at 4000 rpm for 10 min. The tubes were decanted off and the extracted samples were then measured with FAAS. A good agreement was found between the certified value of 106 ± 3 μg g^{-1} and observed value 111 ± 8 μg g^{-1} ($n = 4$) which ensures the reliability of total Zn determination in APM samples. Based on the results derived for water-soluble, residual and total Zn concentrations (all experiments were performed in triplicate) a mass balance has been calculated for each APM sample. The excellent correlation found between cumulated fractions and total concentrations ($n = 12$, see Fig. 4) indicates that artifacts such as sample contamination or analyte losses during sample pretreatment, extraction and digestion were negligible.

Analysis of PM10 samples

Concentrations of water-soluble zinc in PM10 aerosol samples varied from 13 ± 3 to 329 ± 4 ng m^{-3} with an average value of 124 ng m^{-3} ($n = 10$) and 33 ± 1 to 430 ± 8 ng m^{-3} with an average value of 170 ng m^{-3} ($n = 12$) for samples collected at the sites Don-Bosco, Graz and Neue Welt, Linz respectively. On the other hand, the samples collected at Rudolfsplatz, Salzburg showed distinctly decreased concentrations for water-soluble Zn ranging from 7 ± 2 to 108 ± 4 ng m^{-3} with an average value of 51 ng m^{-3} ($n = 8$). Results derived for the individual PM10 samples are listed in Table 1.

Calculation of the water-soluble fraction of Zn in PM10 requires information about the total Zn contents of the investigated samples, which have been determined from another set of punches. The total Zinc in PM10 samples collected from Graz Don-Bosco was found to be in the range of 95 ± 8 to 484 ± 3 ng m^{-3} and from 85 ± 1 to 626 ± 7 ng m^{-3} in samples collected from Neue Welt, Linz, whereas the total zinc contents of PM10 samples from Rudolfsplatz, Salzburg varied from 97 ± 1 to 166 ± 8 ng m^{-3} (Table 1). These results are in accordance to literature findings. For example Voutsa *et al.*[30] and Smichowski *et al.*[31] reported for different urban sites Zn concentrations in PM10 ranging from 25 to 814 ng m^{-3} for sampling sites in Greece and 6.1 to 130.2 ng m^{-3} for urban sites in Argentina. Moreno *et al.*[32] have reported mean annual Zn concentrations in PM10 ranging from 14.5 to 417.4 ng m^{-3} for different urban sites in Spain.

The percentage of water-soluble fraction of Zn for Don-Bosco, Neue Welt and Rudolfsplatz ranged from 14 to 76%, 39 to 84% and 7 to 84% respectively, indicating a high variability for the water-soluble Zn fraction in PM10 (Table 1). An outcome which is confirmed by literature, *e.g.*, Karthikeyan *et al.*[9] have reported an average value of 77 ± 14 ng m^{-3} for water-soluble zinc at an
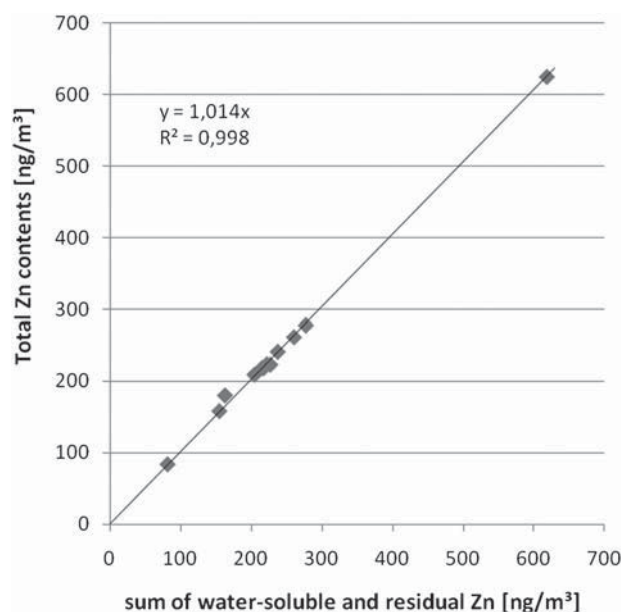

Fig. 4 Mass balance demonstration: correlation between water-soluble plus residual Zn in PM10 and the total Zn concentrations (number of samples 12).

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Table 1 Water-soluble and total Zn concentrations in PM10 samples from the sites Don-Bosco (Graz, No. 1–10), Rudolfsplatz (Salzburg, No. 11–18) and Neue Welt (Linz, No. 19–30), as obtained by application of the on-line extraction technique for water-soluble contents along with acid digestion for total contents

Sample No.	Date of collection	Water-soluble Zn/ng m^{-3}	Total Zn/ng m^{-3}	Water-soluble fraction (%)
1	16-12-2003	13 ± 3	95 ± 8	14
2	17-12-2003	121 ± 24	339 ± 3	35
3	18-12-2003	29 ± 9	129 ± 12	22
4	23-12-2003	37 ± 8	147 ± 4	25
5	24-12-2003	102 ± 5	142 ± 7	72
6	25-12-2003	110 ± 3	238 ± 3	46
7	26-12-2003	222 ± 2	392 ± 8	57
8	27-12-2003	329 ± 4	484 ± 3	68
9	28-12-2003	239 ± 2	314 ± 7	76
10	29-12-2003	39 ± 2	117 ± 11	33
11	01-01-2005	48 ± 7	157 ± 2	30
12	03-01-2005	39 ± 2	148 ± 5	26
13	04-01-2005	51 ± 2	119 ± 7	43
14	05-01-2005	54 ± 1	129 ± 3	42
15	07-01-2005	7 ± 2	97 ± 1	7
16	08-01-2005	17 ± 1	166 ± 8	10
17	09-01-2005	88 ± 3	147 ± 5	60
18	10-01-2005	108 ± 4	129 ± 7	84
19	09-03-2006	167 ± 13	241 ± 4	69
20	10-03-2006	33 ± 1	85 ± 1	39
21	12-03-2006	183 ± 3	219 ± 6	84
22	14-03-2006	212 ± 5	262 ± 3	81
23	16-03-2006	105 ± 4	159 ± 2	66
24	19-03-2006	133 ± 5	225 ± 2	59
25	21-03-2006	134 ± 3	224 ± 4	60
26	23-03-2006	167 ± 2	219 ± 3	76
27	24-03-2006	141 ± 4	210 ± 2	67
28	25-03-2006	430 ± 8	626 ± 7	69
29	27-03-2006	215 ± 3	279 ± 3	77
30	29-03-2006	116 ± 1	181 ± 2	64

urban site in Singapore with water solubilities ranging from 45 to 100%. Similar results were reported for the contribution of water-soluble Zn in PM10 samples from Tokyo (Japan), which was found to be in the order of 80–90%.[13] Birmili *et al.*[15] have also reported that most of the Zn in PM7.2 samples collected from Birmingham was present as water-soluble fraction with an average value of 33 ng m^{-3} ($n = 9$).

Conclusion

In this work, a method for the on-line determination of bio-accessible Zn in airborne particulate matter is presented. The developed extraction procedure is based on the implementation of a sample packed micro-cartridge into the conduits of a FI-system. Sample-leaching was performed by pumping extracting agent through the cartridge for assessment of the respective soluble metal fraction. On-line detection of the released Zn was conducted by direct coupling of the extraction manifold with a continuously operating FAAS. Hence, time-resolved information on the ongoing leaching process was obtained.

Compared to conventional batch-wise extraction the developed FI-procedure led to an improved sensitivity, since the on-line approach enabled measurement of the derived transient elution signals, whereas the off-line procedure determines only averaged species concentrations in the prepared eluate.

Furthermore it was observed that on-line coupling of the FI-system to the nebulizer of the FAAS minimized sample losses as well as contamination risks since troublesome sample handling steps such as filtration or centrifugation could be avoided. Thus in addition to an enhanced sample throughput also improvements in the reproducibility could be achieved, resulting in drastically decreased limits of detection and quantification respectively for water-soluble Zn in PM10 when compared to corresponding data of batch-wise procedures.

To demonstrate the applicability of the developed method, PM10 samples collected at three different urban sites in Austria were analyzed. The content of water-soluble Zn determined for these PM10 samples varied from 7 to 430 ng m^{-3}, results which are in good agreement with the findings obtained by conventional batch-wise extraction and off-line FAAS measurement of the same samples. However, the results derived for water-soluble Zn in PM10 have to be considered as an estimation for bio-accessible Zn only, since leaching experiments with artificial lung fluid at body temperature may lead to increased results due to the enhanced dissolution of Zn in the presence of organic complexing agents. Future studies should be therefore focused on a detailed comparison of the two leaching approaches.

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6.4   Development of an ETV-ICP-OES procedure for assessment of bio-accessible trace metal fractions in airborne particulate matter

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TECHNICAL NOTE

Development of an ETV-ICP-OES procedure for assessment of bio-accessible trace metal fractions in airborne particulate matter

Azam Mukhtar and Andreas Limbeck*

The present study describes an ETV-ICP-OES procedure for determination of bio-accessible fractions of Ba, Co, Cu, Mn, Ni and Pb in airborne particulate matter. The method is based on the preliminary extraction of trace metals with synthetic gastric juice using a physiologically based extraction test and the subsequent measurement of gastric extracts with ETV-ICP-OES. Signal quantification was based on external calibration with aqueous standard solutions using In as internal standard. The limits of detection (LOD) calculated as three times the standard deviation (3σ) of the signal derived from filter blank samples ranged from 1.8 ng (Mn) to 12.2 ng (Cu) for analyzed aliquots of 40 µl sample extracts which translates to a method detection limit of 0.11 ng m^{-3} (Mn) to 0.75 ng m^{-3} (Cu). The reproducibility of analysis is given as the relative standard deviation varied from 1.9% (Cu) to 5.7% (Ni). Compared to conventional ICP-OES measurement of sample extracts, the developed ETV-ICP-OES procedure was found to offer enhanced sensitivity. The accuracy of the developed method was assessed by analysis of the same sample set with the conventional ICP-OES procedure using liquid sample introduction as well as by comparison of total metal contents and the cumulated sum of extractable metal contents and those remaining after sample extraction, showing good recoveries for all investigated elements. Finally the developed procedure was applied for determination of bio-accessible trace metal fractions in PM10 samples collected from Graz-Süd (Austria) indicating that mean bio-accessible metal fractions varied between 32 ± 14% (Ni) and 97 ± 36% (Pb).

Introduction

In recent years, many epidemiological studies have shown that airborne particulate matter (APM) has a serious impact on human health.[1–4] Toxicological studies have implicated metal contents as a possible harmful component of APM[5] since they can be absorbed into human tissues during breathing especially particles with an aerodynamic diameter less than 10 microns (PM10). The toxicity of metal depends upon its species that are present. For risk assessment of metal toxicity, it is important to determine bio-accessible concentrations instead of total metal contents.[6] 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-vitro* surrogates of body fluid or juices, whereas bioavailability is the amount that is actually taken across the cell membranes.[7,8] Most of the studies dealing with estimation of the bio-accessible fraction of trace metals in APM have used water as the leaching agent for toxicity testing.[9–12] But water-soluble metal

fraction may not represent bio-accessible fraction since water does not mimic the conditions of human body fluid.

Particles in the 2.5 to 10 µm size fraction are in most cases deposited in the tracheal and the bronchial region after inhalation, from where they are transported within hours by the so-called mucociliary clearance adoral and are mainly swallowed. This fraction reaches the gastrointestinal tract (GIT), where it comes into contact with gastric juice.[7] On the other hand, particles less than 1 µm can enter into the alveolar region of lungs where they interact with the lung fluid.[13–15] However, since the fraction with an aerodynamic diameter <1 µm is usually only a minor contributor to total PM10 concentrations the majority of inhaled PM10 mass will arrive at the gastrointestinal tract. Furthermore it has to be considered that gastric juice contains pepsin and a comparatively higher acidity[7] than neutral lung fluid,[16] which can considerably increase the solubility of metals in the digestive tract, thereby increasing the bio-accessible fraction. Thus for risk assessment of trace metal contents in PM10 it is more significant to use synthetic gastric juice instead of lung fluid. Nowadays an *in-vitro* physiologically based extraction test (PBET) is recommended for estimating bio-accessible metal fractions, where APM is extracted with the help of synthetic gastric juice and ultrasonic agitation, subsequently prepared extracts were analyzed using element specific detection

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techniques such as ICP-OES or ICP-MS.[17–19] Application of this approach improves risk assessment but hampers analysis,[20] since the organic matrix used for sample extraction causes spectral and non-spectral interferences during ICP-OES or ICP-MS measurement. A common way to reduce the influence of an interfering matrix is sample dilution. But in the case of PM10 investigations, where only limited sample amounts of less concentrated samples are available, this simple approach may lead to insufficient sensitivity for trace metal analysis, thus accurate quantification of toxic trace metals is difficult.

In the present study, an alternative method is presented in which an *in-vitro* physiologically based extraction test (PBET) has been performed with APM followed by subsequent measurement of resulting extracts using electrothermal vaporization inductively coupled plasma optical emission spectrometry (ET-ICP-OES). The developed procedure allows us to separate the organic matrix prior to element specific detection, enabling highly sensitive measurement of trace elements in APM up to a level of some hundred pg m^{-3}. Furthermore, there is no need to digest or dilute sample extracts containing pepsin, thereby saving time and reducing the risk of sample contamination.

Experimental

Reagents and materials

Nitric acid (HNO$_3$, 65%), hydrochloric acid (HCl, 37%), perchloric acid (HClO$_4$, 70%) and sodium chloride (NaCl) were of analytical reagent grade and were procured from Merck (Darmstadt, Germany). Pepsin from porcine stomach mucosa (456 units mg^{-1} solid) was purchased from Sigma Aldrich (Chemie GmbH, Steinheim, Germany). High purity water was obtained by distillation of de-ionized water derived from a reverse osmosis/ion exchange combination (Euro 20 plus-SG water system, Germany) using in house quartz apparatus. Certified multielement standard solutions of In, Ba, Co, Cu, Mn, Ni and Pb (1000 mg L^{-1}) were purchased from Merck (Darmstadt, Germany) and diluted with 1% HNO$_3$ (v/v) in order to prepare various working standard solutions. The prepared standard solutions were kept refrigerated at 4 °C in pre-cleaned polypropylene (PP) tubes until further use. The synthetic gastric juice was prepared according to a US Pharmacopeia methodology[7] by dissolving 2 g NaCl in 50 ml of high purity water followed by addition of 7 ml of conc. HCl in order to maintain the pH of the resulting solution at 2–2.5. To this solution, 3.2 g of pepsin were added, dissolved well and finally the volume was made up to 1 litre using bi-distilled water. Indium at the level of 1 mg l^{-1} was also added to the prepared synthetic gastric juice as an internal standard in order to overcome non-spectral interferences as well as errors related to manual sample handling steps (*e.g.*, pipetting of gastric extracts as only 40 μl were used for analysis). The prepared synthetic gastric juice was stored in refrigerator at 4 °C until further use. Standard reference material® 1648a (urban particulate matter) from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to verify the accuracy of procedure used for measurement of residual and total metal contents in PM10 samples. All used reaction vessels and polypropylene (PP) tubes were decontaminated prior to use by soaking them for at least 24 h in 5% HNO$_3$ followed by another 24 h in high purity water, rinsing them again with high purity water and drying them under a VFT 1525 ultraclean laminar flow hood (Weiss Technik GesmbH, Austria).

Instrumentation

An iCAP 6500 series ICP-OES spectrometer (Thermo Scientific, USA) was used for simultaneous multielement analysis. The ICP-OES was equipped with a standard extended torch and a ceramic injector tube. Background corrected emission signals were used for signal quantification. For sample introduction by electrothermal vaporization, an ETV system model 4000A ETV (Spectral Systems, Fürstenfeldbruck, Germany) was corresponding in essence to a longitudinally heated graphite tube furnace. The ETV 4000 unit consists of a commercially available graphite-tube furnace, power supply, gas supply and water cooler. The heating cycle of the ETV was completely computer controlled and the temperature could be ranged from room temperature up to about 2600 °C. During the heating cycle, argon gas flow removes all vapors in the graphite tube. The elements are generally transformed into more volatile compounds by the addition of halogen containing reaction gas (CHClF$_2$, 1.5 ml min^{-1}). Chlorides and fluorides produced were easily vaporized from the graphite furnace because the boiling points of these compounds are much lower than carbides or oxides of the same elements.[21,22] A second argon gas flow was introduced after the evaporation tube. Rapid cooling of atoms and molecules formed enhances the formation of a stable and transportable aerosol.[23–25] In the present study, an ETV heating program of 60 s consisting of a matrix removal step at 300 °C (hold time 10 s) and a final analyte vaporization step at 2100 °C was used. The carrier and bypass argon gas flow rates were 0.38 and 0.14 l min^{-1} respectively whereas the Freon flow rate was 1.5 ml min^{-1}. The ETV unit was interfaced to the ICP *via* 40 cm long and 4 mm internal diameter PTFE tubing. The sample aerosol was transported directly into the plasma. Time synchronization between the starting of the resistance heated ETV furnace system and the ICP spectrometer was performed with the help of Thermo ITEVA software. Optimized

Table 1 Instrumental parameters and analytical wavelengths used for ICP-OES analysis along with thermal cycle of ETV

Parameters	Value	Element	Wavelength
Rf power (W)	1250 W	Ba	233.527
Auxilliary flow	0.8 l min^{-1}	Co	228.616
Coolant flow	12 l min^{-1}	Cu	224.700
Measurement Time	60 s	Mn	294.920
Integration time	10 s	Ni	231.604
Plasma viewing height	12 mm	Pb	220.353
Cumulative ETV gas flow	0.52 l min^{-1}	In	230.606
Background correction	Constant shift from analytical line		

Thermal cycle of ETV

Program step	Temperature/°C	Ramp/s	Hold time/s
Pyrolysis	300	30	10
Vaporization and cleaning	2100	—	20

instrumental parameters of ETV-ICP-OES and the heating program of ETV used in the present study are summarized in Table 1.

Collection of PM10 samples

Sampling of size segregated airborne particulate matter samples (PM10) was performed at five sites in Styria, Austria (Graz-Süd, during Jan–Feb 2007, Köflach, Peggau, Donawitz and Göβ, during Jun to Sept, 2006) representative for mid-European rural and urban locations. Collection of PM10 samples was performed using an automated sampling device (Leckel, Germany) containing a PM10 pre-separation head with an intake volume of 2.3 m^3 h^{-1} (being equivalent to 40 l min^{-1}). Filter holders were equipped with GN-4 Metricel® mixed cellulose ester filters (diameter: 47 mm, pore size: 0.8 μm, PALL Life-sciences, Michigan, USA) as sampling substrates. The filter samples were automatically changed after a collection period of 24 h, and the air volumes collected within these sampling intervals varied between 50 and 55 N m^3 (standard temperature pressure, 273 K and 1013 h Pa). To exclude any contamination from the sampling procedure itself field blanks were collected by purging the sample air for 30 s through the filter. The collected PM10 samples were stored in Petri dishes with a seal of Para film M until analysis. Handling of filter samples (*e.g.* insertion of filters in filter holders) and all other manual operations (*e.g.*, preparation of filter punches) were conducted in a particle free environment inside a laminar flow hood (Weiss VFT 1525) using an indigenously developed quartz puncher, ceramic scissors (IEDA Trading Cooperation, Japan) and ceramic forceps (Rubis Switzerland).

In-vitro physiologically based extraction test (PBET) and determination of residual/total metal contents

For determining the bio-accessible trace metal fraction present in APM, an *in-vitro* physiologically based extraction test was performed. For this purpose, seven aliquots with a diameter of 12 mm were punched out from each collected PM10 sample. Four punches from each PM10 sample, which corresponds to a collected sample volume of approximately 14.4 m^{-3} and an absolute sample intake in the order of some hundred μg APM, were taken into pre-cleaned polypropylene tubes followed by addition of 700 mg of synthetic gastric juice. The tubes were closed and treated in ultrasonic bath (Sonorex TK30, Bandelin, Germany) at 37 °C for 1 h in order to extract soluble trace metal fractions. After cooling down the sample solutions at room temperature, the derived gastric extracts were centrifuged (Hettich, Zentrifugen-EBA 20) at 5000 rpm for 10 min for separation of the filter substrate and undissolved material. The supernatant clear sample solutions were transferred to new 3 ml polypropylene tubes and stored until further analysis.

Accuracy of analysis has been demonstrated by comparison of total metal contents with the sum of extractable metal contents and those remaining after sample extraction. For determination of residual trace metal contents, 1 ml of high purity water was added to the filter punches remaining in the PP tubes after gastric extraction followed by centrifugation at 5000 rpm for 10 min in order to wash out the remaining gastric extract. After removal of the separated solutions, the remaining filter punches were

transferred to pre-cleaned Bernas type Teflon lined bombs followed by addition of 1 ml conc. HNO_3, 1 ml HCl and 50 μl of $HClO_4$. The Teflon lined bombs were then placed in an indigenously developed refractory oven and treated at 130 °C for 1 h in order to mineralize the filter substrate and to dissolve residual metal contents. Finally, the temperature of the refractory oven was increased to 150 °C and maintained for another 30 min for evaporation of excessive amount of HNO_3 and HCl. The small droplet of $HClO_4$ remaining in the Teflon lined bombs was then cooled down to room temperature. Finally the derived digests were diluted to a final mass of approximately 2 g in PP tubes with 1% (v/v) HCl and a defined amount of In as internal standard was added.

The remaining three aerosol filter punches with a diameter of 12 mm (which is equal to 10.8 m^{-3} sample volume) were used for determination of total trace metal contents. The sample digestion and dilution steps were identical as described above for determination of residual metal contents with the exception of the wash out step. All prepared sample solutions were kept refrigerated at 4 °C until analysis.

Analysis of standard solutions and PM10 samples

For analysis, 40 μl of sample and standard solution were pipetted into graphite boats and dried inside the laminar flow box using an infrared (IR) lamp (TYP-LT 150, Germany) until dryness. During this process, the graphite boats were kept covered with Petri dishes in order to avoid contamination from surroundings. The step of external drying of liquid samples was preferred in order to avoid the plasma load because the formed vapours when directed to the plasma could cause sudden extinguishing of plasma, since the ETV furnace was not provided with a diverting valve in order to remove the formed vapours prior to the vaporization step. For analysis, the graphite boats were inserted into the graphite furnace tube which was closed at one end using a shutter. The ETV furnace program was started by the ICP-OES software and the emission spectra of the vapor introduced into the plasma were measured. The ETV-ICP produced a transient signal of analyte for which the peak area was integrated using Thermo ITEVA software. For signal quantification, a set of multi-element standard solutions with concentration levels of 0.5, 1.0 and 1.5 mg l^{-1} in 1% HCl containing In at 1 ppm level was prepared. Results derived for the investigated standards were used to construct a calibration curve.

For assessing the method accuracy, the bio-accessible fraction of trace metals in APM was also measured using the conventional ICP-OES procedure. In this case, similar to the ETV procedure, seven aliquots with a diameter of 12 mm were punched out from each collected PM10 sample. Four punches from each PM10 sample were taken into pre-cleaned PP tubes followed by addition of 2 g of synthetic gastric juice and treated as described above. For conventional ICP-OES measurement, sample introduction into plasma was accomplished using a high solid kit consisting of an aerosalt nebulizer and a cyclonic spray chamber. The nebulizer and sample flow rates were 0.6 l min^{-1} and 0.8 ml min^{-1} respectively. All other used parameters were similar as presented in Table 1 for ETV-ICP-OES measurements. A set of matrix matched multi-element standard solutions ranging from 0 to 200 ppb was used for construction of the

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calibration curve and the derived calibration curves were used for quantification of each element present in measured PM10 samples. Furthermore, In was also used as internal standard for conventional ICP-OES measurements in order to overcome non-spectral interferences caused from a simultaneously introduced sample matrix.

Results and discussions

Optimization of ETV parameters

Particulate matter (PM) is a complex mixture of various compounds that consist of carbonaceous species (organic carbon, elemental and carbonate carbon), mineralic components and certain trace metals.[26] Extracts of PM samples are therefore made up of a mixture of different soluble species and the constituents of the used synthetic gastric juice. ETV-ICP-OES analysis requires therefore optimization of the temperature furnace program to achieve complete removal of interferences and maximum signal to noise ratios. The temperature program of ETV consists of three steps *i.e.*, pyrolysis, vaporization and cleaning out. So the first step was the optimization of pyrolysis temperature in order to remove the organic matrix from the samples. For this purpose, a gastric pool solution was prepared from ten different gastric extracts of PM10 samples by combining 500 µl from each solution. From this pool extract, a volume of 40 µl was pipetted into graphite boats and measured using a pyrolytic temperature ranging from 300 °C to 800 °C. It was found that with the increase of pyrolytic temperature, the resulting peak areas for target elements decreased, as shown in Fig. 1. In the case of Pb, the signal was decreased to the order of blank samples at pyrolytic temperatures of 700 °C and 800 °C (Fig. 1). Maximum peak areas were observed at pyrolytic temperatures of 300 °C and 400 °C. At the pyrolytic temperature of 300 °C, an improved reproducibility of measurement was obtained as compared to 400 °C. So the optimum pyrolytic temperature was chosen to be 300 °C.

In a second step, the vaporization temperature was optimized. Since the target elements (Ba, Co, Cu, Mn, Ni and Pb) have different vaporization temperatures, compromise conditions have to be selected for multielement analyses. For this purpose, the influence of vaporization temperatures ranging from 1900 °C to 2300 °C on the analyte signals was investigated. The peak areas increased linearly for Ba, Co, Cu and Ni up to a temperature of 2100 °C and then almost constant at 2200 °C and 2300 °C, as shown in Fig. 1. In the case of Mn and Pb, almost a constant peak area was observed at all selected temperatures, an outcome which accounts for the differences in volatility and thermal behavior of these elements. So a temperature of 2100 °C was selected as an optimum vaporization temperature for target elements. It was also found that a temperature of 2100 °C with a hold time of 20 s was sufficient for complete removal of analyte as the re-measurement of graphite boats after optimization of vaporization temperature yielded signals similar to blank samples.

An investigation was also carried out in order to study the relationship between the volumes of gastric juice extract applied for ETV-ICP-OES analysis and the obtained corresponding peak areas. Sample volumes of 20 µl, 30 µl and 40 µl were used in order to maximize the analyte signal and to study the separation of organic sample matrix. It was found that with increasing volume of up to 40 µl, the signal was enhanced for target elements with best signal/blank ratios for the highest investigated volume, so a sample volume of 40 µl was selected for analysis of APM extracts and digests.

Analytical figures of merit

Reproducibility of the developed ETV-ICP-OES procedure for analysis of bio-accessible trace metal fractions in APM was performed by replicate analyses of a set of six PM10 samples. Since it is not possible to collect a set of identical aerosol samples, the preparation of a pooled PM10 sample was necessary. In order to prepare an identical set of PM10 samples, six PM10 test samples were selected and six aliquots with a diameter of 12 mm were punched out from each PM10 sample. One punch from each PM10 sample was taken and combined in one polypropylene tube. Similarly five other pooled PM10 samples were prepared by taking one punch from each selected PM10 samples. The prepared set of pooled samples was measured using optimized procedure and derived relative standard deviations were found to be varied from 1.9% (Cu) to 5.7% (Ni). The effect of any contamination during sample treatment such as filter punching and insertion into sample cartridge was investigated by analyzing field blank filters. The signals for collected field blanks were found to be identical to those of aqueous blanks, confirming contamination free sample pre-treatment.

For signal quantification, the use of aqueous as well as matrix matched calibration was investigated. For this purpose aqueous and matrix matched standard solutions (including synthetic gastric juice) were prepared, and measured using the optimized ETV-ICP-OES procedure. The derived results indicated that the calibration slopes for selected elements were almost identical for aqueous and matrix matched calibration, an outcome which could be explained with the removal of volatile organic sample matrix before vaporisation of the analyte, the use of a modifier gas (Freon R12) and an internal standard for signal correction. So aqueous calibration was used in all further experiments for quantification of derived signals.

For determination of limit of detection (LOD), another set of eight blank filters was used. From each field blank aliquots with a diameter of 12 mm were punched and extracted with 700 mg of gastric juice solution in pre-cleaned PP tubes as described previously for preparation of gastric extracts of PM10 samples. The extracted gastric blanks were measured using optimized ETV-ICP-OES conditions. The limit of detection was calculated as 3 times the standard deviation (3σ) of the signals derived from
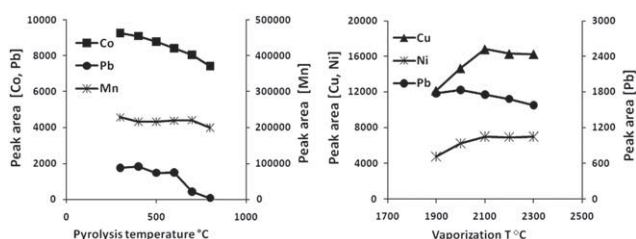

Fig. 1 Optimization of temperature program.

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Table 2 LOD values for ETV-ICP-OES and ICP-OES procedures

| Elements | ETV-ICP-OES | | ICP-OES |
	Instrumental LOD[a]/ng	Method LOD[b]/ng m^{-3}	Method LOD[b]/ng m^{-3}
Ba	0.32	0.20	4
Co	0.15	0.30	6
Cu	0.27	0.75	12
Mn	0.29	0.11	11
Ni	0.12	0.23	10
Pb	0.21	0.11	38

[a] With the use of 40 µl sample extract for ETV-ICP-OES analysis.
[b] Derived from the analysis of filter blanks, calculated considering the collected air volumes.

filter blanks. The obtained LOD values were converted into method detection limits by using the volume of collected air (approximately 55 m^3) per sample. The LOD values derived for the investigated elements are shown in Table 2.

For demonstrating the method accuracy, a set of 25 PM10 samples collected from different sites in Styria, Austria were analyzed using the ETV-ICP-OES method and the conventional ICP-OES procedure. The limits of detection for the conventional ICP-OES procedure were also determined in the same way as described above for the ETV-ICP-OES method with the exception that a volume of 2 ml gastric juice was used for extraction of filter blanks. This is because the minimum volume required for replicate measurements of a sample was 2 ml using the conventional ICP-OES procedure with liquid sample introduction. Table 2 presents the method detection limits derived for conventional ICP-OES measurements. Comparing the derived results, it is obvious that the LOD values for the ETV-ICP-OES method are far better than the conventional ICP-OES procedure.

The results obtained for bio-accessible contents of Ba, Co, Cu, Mn, Ni and Pb in the investigated sample set of 25 PM10 samples showed a good agreement, indicating that the proposed procedure is applicable for the determination of bio-accessible trace metals in APM. Fig. 2 depicts the results derived for Ba, Cu and Mn. However, due to limited sensitivity of the conventional ICP-OES procedure, it was not possible to quantify all elements in

measured samples. For example, the conventional ICP-OES procedure yielded all results below LOQ for Co and Ni; only four samples showed concentrations above LOQ for Pb in measured 25 samples. In contrast, for the ETV-ICP-OES procedure seven (Ni), seventeen (Co) and twenty five (Pb) out of 25 samples showed results above corresponding LOQ values. The concentrations for Ba, Cu and Mn were found to be above the respective quantification limits for all measured 25 samples. This outcome demonstrates clearly the main advantage of the developed ETV-ICP-OES approach when compared to the conventional ICP-OES procedure.

The accuracy of the developed procedure has been demonstrated by calculating the mass balance of bio-accessible and residual fractions of trace elements and comparison with the total metal contents of the PM10 samples. For this purpose, a set of 14 PM10 samples collected at the urban site Graz-Süd, Austria was analyzed. The bio-accessible, residual and total contents of these PM10 samples were determined as described in the Experimental section. The suitability of the procedure applied for measurement of residual and total metal contents was evaluated by digestion of the NIST standard reference material SRM 1648a (urban particulate matter). For this purpose, approximately 20 mg of dried SRM 1648a were taken into Teflon lined bombs and treated in the same way as described above for determination of residual and total metal contents. After addition of In as internal standard and dilution with 1% HCl (v/v) to a final mass of 10 g, the resulting solutions were measured using

Table 3 ETV-ICP-OES results for SRM® 1648a

| Elements | Results for SRM® 1648a/mg kg^{-1} | |
	Certified values	Measured values
Ba	no value	546 ± 49
Co	17.93 ± 0.68	19.1 ± 0.97
Cu	610 ± 70	620 ± 48
Mn	790 ± 44	793 ± 22
Ni	81.1 ± 6.8	85.3 ± 6.9
Pb	0.655 ± 0.033[a]	0.659 ± 0.015[a]

[a] Results are presented in terms of percentage composition.
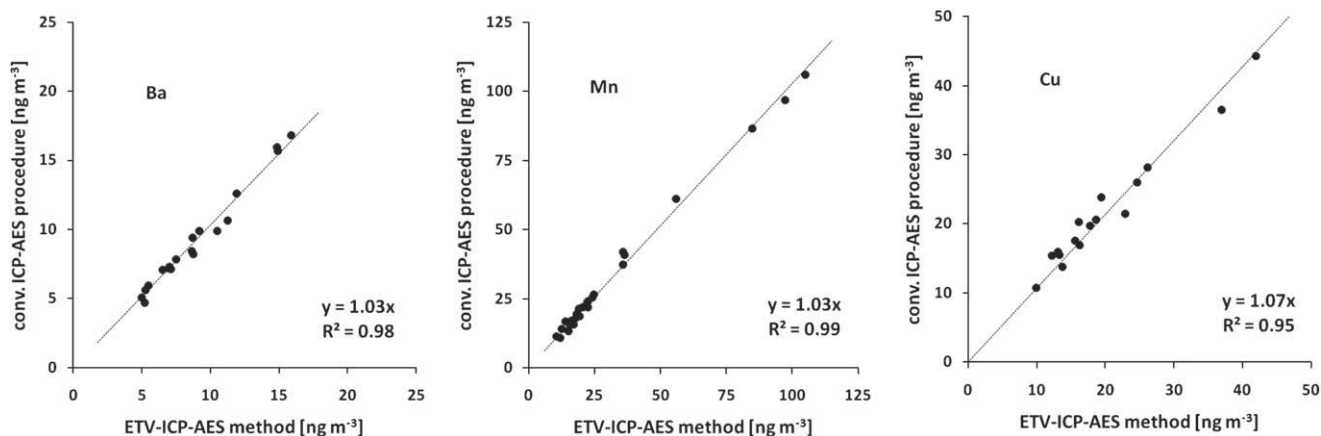
Fig. 2 Agreement between the conc. of extractable target elements in PM10 samples derived via ETV-ICP-OES and conventional ICP-OES procedure (n = 25).

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ETV-ICP-OES under optimized conditions. The derived results for SRM 1648a (Table 3) were in good agreement with the certified values confirming that sample pre-treatment and ETV-ICP-OES measurement yielded accurate results for studied elements.

Based on the results derived for bio-accessible, residual and total trace metal concentrations, a mass balance was calculated for each element and all investigated PM10 samples. For all elements, a good agreement was found between the cumulated fractions and total contents (Fig. 3), in particular when considering that absolute analyte masses of only some hundred ng were compared, confirming the suitability of this approach for analysis of PM10 samples. Derived results demonstrate furthermore that errors such as sample contamination or analyte losses during sample pre-treatment, extraction and digestion were negligible.

Analysis of PM10 samples

The developed ETV-ICP-OES procedure was applied for determination of bio-accessible trace metal fractions in the set of PM10 samples collected at the site Graz-Süd which is an urban residential area with middle to high pollution level. The total concentrations of the investigated metals varied between few ng m^{-3} (Co) and hundred ng m^{-3} (Cu), as shown in Table 4. Over the whole sampling period a good correlation between the concentrations of Ba, Cu and Pb was observed ($r^2 > 0.8$), a result which could be explained with similar emission sources (e.g. motor vehicle emissions), whereas remaining elements were correlated with a lesser extent only ($r^2 < 0.6$). The concentration

ranges observed for investigated elements (Ba, Co, Cu, Mn, Ni and Pb) are comparable to the results reported for other urban sites in Europe. For example, Limbeck et al.[27] have found that concentrations of these elements varied from 1.8 ± 1.1 ng m^{-3} (Co) to 21 ± 15 ng m^{-3} (Cu) in PM10 samples collected from Vienna. Similarly, Alleman et al.[28] reported that concentrations of these trace elements were varied from 0.5 ± 0.43 ng m^{-3} (Co) to 147 ± 275 ng m^{-3} (Mn) in PM10 samples collected from Dunkirk harbor (France). Vousta et al.[29] have reported trace metal concentrations (Co, Cu, Mn, Ni and Pb) ranging from 3.8 ng m^{-3} (Ni) to 78 ng m^{-3} (Pb) in PM10 samples collected from an urban area in Thessaloniki, Greece. Comparable results have been reported by Karthikeyan et al.[12] in PM10 samples collected from an urban site in Singapore for elements Co, Cu, Mn, Ni and Pb ranging from 0.9 ± 0.2 ng m^{-3} (Co) to 15.6 ± 9.2 ng m^{-3} (Pb). Similarly Fernandez et al.[10] found that metal contents (Co, Cu, Mn, Ni and Pb) in PM10 samples collected from the city of Seville, Spain varied from 0.30 ng m^{-3} (Ni) to 43.7 ng m^{-3} (Pb).

The metal concentrations extractable with synthetic gastric juice were found to be generally lower than the respective total concentrations, indicating that the investigated metals were only partially soluble in this solvent. The mean contents of extractable metal fractions in analyzed PM10 samples varied between 0.6 ± 0.2 ng m^{-3} (Co) and 32.8 ± 28.2 ng m^{-3} (Cu), as shown in Table 4. The greater values for standard deviation indicate that the bio-accessible metal contents were varied largely during the sampling period. A fairly good correlation was found between the elements Ba, Cu, Mn and Pb ($r^2 > 0.8$), which indicates that these metals undergo similar atmospheric transformations.
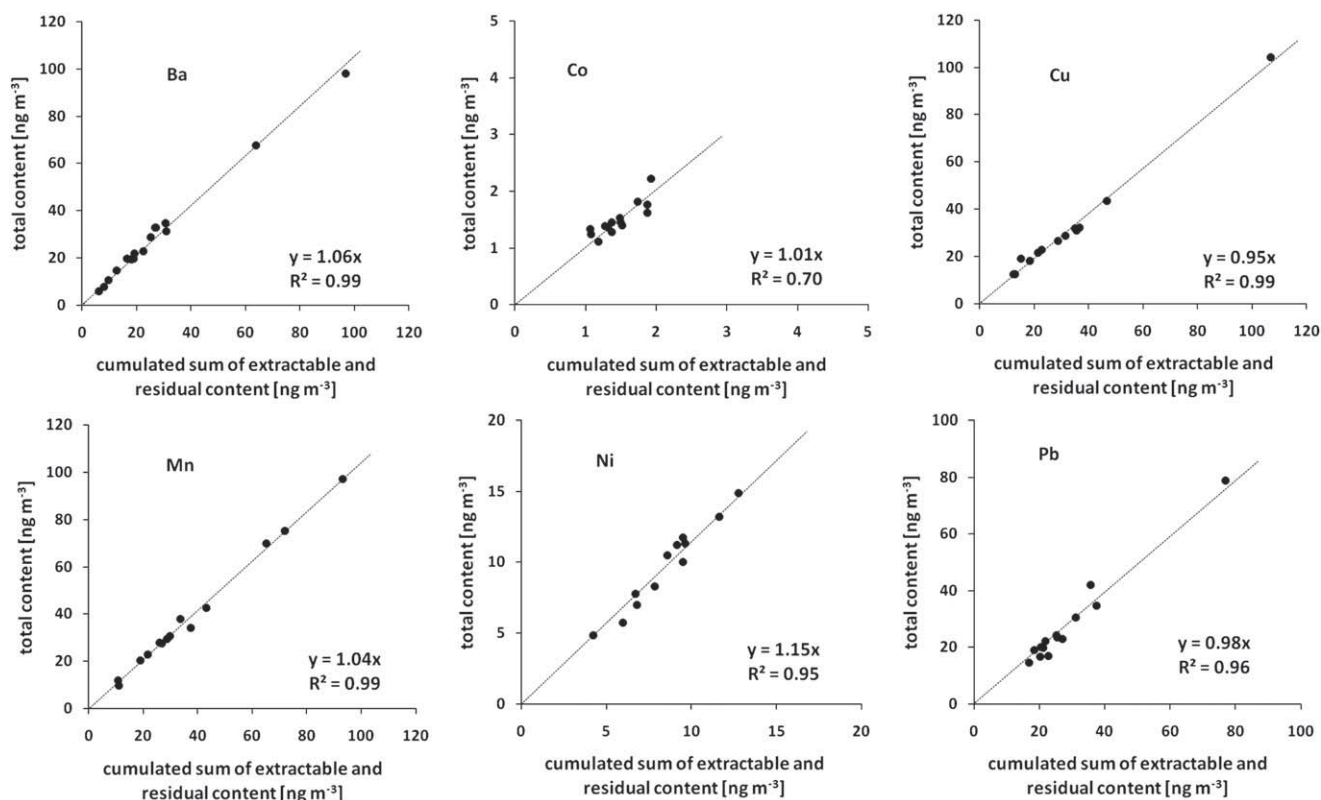

Fig. 3 Mass balance demonstration, agreement between bio-accessible plus residual metal contents and the total metal concentrations for PM10 samples from Styria, Austria ($n = 14$).

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Table 4 Concentration ranges and averages of bio-accessible and total metal contents in PM10 samples collected at Graz-Süd ($n = 14$)[a]

Elements	Total contents (ng m^{-3})		Extractable contents (ng m^{-3})		Bio-accessibility (%)	
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
Ba	7.7–98.2	29.3 ± 22.7	5.6–54.7	22.0 ± 11.3	33–97	78 ± 23
Co	1.1–1.8	1.5 ± 0.3	0.3–1.1	0.6 ± 0.2	24–65	38 ± 13
Cu	12.4–118.5	37.8 ± 29.5	8.9–114.0	32.8 ± 28.2	27–96	80 ± 36
Mn	9.7–97.2	37.4 ± 23.9	4.8–59.6	22.6 ± 16.7	31–81	55 ± 21
Ni	4.8–20.1	10.8 ± 3.9	1.4–10.7	3.7 ± 2.2	9–53	32 ± 14
Pb	14.5–78.8	26.7 ± 15.7	11.3–80.9	26.2 ± 16.2	43–100	97 ± 36

[a] For samples with extractable contents below LOQ the corresponding data for LOD have been used for calculation of bio-accessible fractions.

Based on the results derived for total and extractable metal concentrations in airborne PM, percentage bio-accessibility of each studied trace metal was calculated. Interpreting the results presented in Table 4 it is obvious that leachabilities of the investigated metals differ significantly, and lowest solubility was observed for Co and Ni, indicating that these metals are associated with less soluble phases than the elements Ba, Cu and Pb, which showed higher solubilities approaching mean values in the order of 78 to 97%. Comparison of bio-accessible fractions in PM10 samples reported in the present study with literature data is not simple, since there are many parameters (investigated size fraction, composition of the extraction fluid, extraction time, meteorological conditions, etc.) which differ with respect to conditions used in the present study. Falta et al.[20] have used comparable parameters to study the bio-accessible fraction in APM and found that the percentage of bio-accessible trace metal fractions varied from 44 (Co) to 86 (Pb) in PM10 samples from an urban site in Vienna which is in accordance to the present study where the percentages of bio-accessible fractions of Co and Pb are found to be 38 and 97 respectively. Fernandez et al.[10] have used water as the leaching agent for extraction of leachable metal fraction and found that bio-accessible (%) fraction of trace metals (Co, Cu, Mn, Ni and Pb) is varied from 3.9 (Pb) to 39.5 (Ni) in PM10 samples collected from Seville, Spain whereas Karthikeyan et al.[12] reported 11% (Co) to 41% (Cu) bio-accessible metal contents in PM10 samples collected from an urban site in Singapore using water as the leaching agent. Jianjun et al.[13] used 0.01 M ammonium acetate solution for extraction of soluble trace metals in particles below 1 μm and have found that % bio-accessibility of trace metals is varied from 29 (Pb) to 54 (Cu).

These bio-accessible (%) contents found in the literature are comparatively smaller than those reported in the present study because water was used as a solvent of extraction in these studies, since the synthetic gastric juice being acidic in nature and having complex composition (pepsin) mimic the conditions as human body fluid, thus facilitating leaching of trace metals better than water.[10,11]

Conclusion

The present study describes an ETV-ICP-OES procedure for determination of bio-accessible trace metal fractions obtained after applying an in-vitro PBET to APM using synthetic gastric juice. Careful optimization of the temperature program allowed removal of organic matrix compounds and interference free measurement of target analytes as well as enabled external calibration with aqueous standards to be used for quantification of derived signals. Compared to conventional ICP-OES measurement of derived sample extracts a distinctly improved sensitivity could be achieved, which allows the measurement of toxic trace metals such as Co, Ni and Pb up to a level of some hundreds of pg m^{-3} in PM10 samples.

Applicability of the proposed method has been demonstrated by the analysis of a set of PM10 samples from Graz-Süd (Austria). Bio-accessible (%) fractions of the investigated trace metals were found to be varied from 32 ± 14% (Ni) to 97 ± 36% (Pb) indicating that APM is contaminated with potentially toxic fractions of metals as this fraction is supposed to be accessible to the human physiological system.

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7 List of abbreviations

APM	….	Airborne particulate matter
AED	….	Aerodynamic diameter
BC	….	Black carbon
CC	….	Carbonate carbon
CCN	….	Cloud condensation nuclei
DMS	….	Dimethyl sulphide
EC	…	Elemental carbon
ETAAS	….	Electrothermal atomic absorption spectrometry
ETV-ICP-OES	….	Electrothermal vaporization inductively coupled plasma optical emission spectrometry
FAAS	….	Flame atomic emission spectrometry
FIA	….	Flow injection analysis
GIT	….	Gastrointestinal tract
HC	….	Hydrocarbons
IN	….	Ice nuclei
INAA	….	Instrumental neutron activation analysis
ICP-OES	….	Inductively coupled plasma optical emission spectrometry
ICP-MS	….	Inductively coupled plasma mass spectrometry
PM	….	Particulate matter
PBAP	….	Primary biological aerosol particles
PBET	….	Physiologically based extraction test
PANs	….	Peroxy acylnitrates
PM10	….	Particulate matter with an aerodynamic diameter less than 10 microns
PM2.5	….	Particulate matter with an aerodynamic diameter less than 2.5 microns
PM1	….	Particulate matter with an aerodynamic diameter less than 1 micron
PIXE	….	Particle induced X-ray emission

ROS	….	Reactive oxygen species
SOA	….	Secondary organic aerosols
SIA	….	Secondary inorganic aerosols
USEPA	….	United States Environment Protection Agency
XRF	….	X-ray fluorescence

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9 Curriculum vitae

E U R O P E A N
C U R R I C U L U M   V I T A E
F O R M A T

PERSONAL INFORMATION

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WORK EXPERIENCE

• Dates (from – to)	12.2007 – present	10.2005 – 11.2007
• Name and address of employer	Institute for Chemical Technologies and Analytics, Vienna University of Technology, Austria.	University of Education, Campus Faisalabad, Pakistan
• Type of business or sector	PhD	Education
• Occupation or position held	Research Assistant	Lecturer
• Main activities and responsibilities	Aerosol Characterization inorganic fraction, bioavailability of trace elements in airborne particulate matter, development of new methods and automation for analysis of metallic fractions	Teaching Chemistry at graduation level
• Dates (from – to)	01.2004 – 06.2005	09.2002 – 01.2004
• Name and address of employer	Coates Lorilleux (Dainipon Ink Chemicals), Pakistan	Dawchem Industries (pvt) Limited, Pakistan
• Type of business or sector	Industry – Printing Inks	Industry- Texile and paint chemicals
• Occupation or position held	Chemist (R&D)	Technical Officer
• Main activities and responsibilities	Development of new products, quality control and customer service	Development and quality control of Textile auxiliaries

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EDUCATION AND TRAINING			
• Dates (from – to)	01.2007 - present	10.1999 - 03.2002	09.1993 – 08.1999
• Name and type of organization providing education and training	Vienna University of Technology, Institute for Chemical Technologies and Analytics, Vienna, Austria.	University of Punjab, Institute of Chemistry, Lahore, Pakistan	Govt. Forman Christian College, Lahore Pakistan
• Principal subjects/occupational skills covered	Field: Environmental Analytical Chemistry	Specialization: Organic Chemistry	Field: Chemistry, Zoology, Botany
• Title of qualification awarded	Doctorate	Graduate master	Bachelor
• Level in national classification (if appropriate)	Doctorate	M.Sc. Chemistry	B. Sc. Pre-medical

PERSONAL SKILLS
AND COMPETENCES
Acquired in the course of life and career
*but not necessarily covered by formal
certificates and diploma*

Perseverance
Objectivity
Avaibility to requirements
Aspiration for improvement
Determined to achieve goals

MOTHER TONGUE

Punjabi,

OTHER LANGUAGES

	English	German
• Reading skills	excellent	Good
• Writing skills	excellent	satisfactory
• Verbal skills	fluent	satisfactory

SOCIAL SKILLS
AND COMPETENCES
*Living and working with other people, in
multicultural environments, in positions
where communication is important and
situations where teamwork is essential
(for example culture and sports), etc.*

Very good relations with public and colleagues
Honesty in work
Stimulating non-conflicting atmosphere
Team work
Respect for co-workers and facilitating them for achievement of cumulative goal
Flexibility to any kind of undesired environment

ARTISTIC SKILLS
AND COMPETENCES
Music, writing, design, etc.

N.A.

ORGANISATIONAL SKILLS
AND COMPETENCES
*Coordination and administration of
people, projects and budgets; at work, in
voluntary work (for example culture and
sports) and at home, etc.*

Organization ability
Professional conscience
Accurate execution of duties
Dedicate to work
Class representative during M.Sc.
President Speers Chemical Society at Graduation level

TECHNICAL SKILLS AND COMPETENCES *With computers, specific kinds of equipment, machinery, etc.*	Word, PowerPoint, Origin, ICP-OES, Laser ablation-ICP-MS, AAS, GC-MS, Multiwave digestion apparatus, Excellent Pedagogical skills
OTHER SKILLS AND COMPETENCES *Competences not mentioned above.*	Participation in Europass Workshop held on 19th May 2010 in Vienna. Lead Trainer, Intel Teach to Future Program, 2006. Certification in Customer Relationship Management ISO 9001 Certification
DRIVING LICENSE(S)	
ADDITIONAL INFORMATION	Prof. Dr. Andreas Limbeck, Vienna University of Technology Institute for Chemical Technologies and Analytics, Vienna, Austria
ANNEXES	List of Publications and Research area

Dated: 07.07.2011   Signature

Chaudhary Azam Mukhtar

List of Publications

1. *"Development of an ETV-ICP-OES procedure for assessment of bio-accessible trace metal fractions in airborne particulate matter"*, Azam Mukhtar and Andreas Limbeck, J. Anal. At. Spectrom., 2011, 26, 2081.

2. *"A new approach for determination of crustal and trace elements in airborne particulate matter"*, Azam Mukhtar and Andreas Limbeck, International Journal of Environmental Analytical Chemistry, DOI number: 10.1080/03067319.2011.620709.

3. "*On-line determination of water-soluble zinc in airborne particulate matter using a dynamic extraction procedure coupled to flame atomic absorption spectrometry*", Azam Mukhtar and Andreas Limbeck, J. Anal. At. Spectrom., 2010, 1056-1062.

4. *"A new approach for the determination of silicon in airborne particulate matter using electrothermal atomic absorption spectrometry"*, A. Mukhtar and A. Limbeck, Analytica Chimica Acta, 2009,646,17-22.

5. *"Fatty acid composition of tobacco seed oil and synthesis of alkyd resin"*, Mukhtar Azam, Ullah Habib, Mukhtar Hamid, Chinese Journal of Chemistry, 2007,25, 705-708.

6. *"Extraction and Characterization of Tobacco Seed Oil"*, Azam Mukhtar, Habib Ullah and Hamid Mukhtar, Asian Journal of Chemistry, 2006, 18, 20-24.

7. *"Improving the Coating Properties of Alkyd Resin by blending with Epoxy Resin"*, Azam Mukhtar, Habib Ullah and Hamid Mukhtar, International Journal of applied Chemistry, 2006, 2, 13-20.

8. *"2-(2-Iodobenzenesulfonamido)acetic acid"*, M. N. Arshad, I. U. Khan, M. Shafiq and A. Mukhtar, *Acta Cryst.,* 2009, E**65**, O 549.

9. *"Effect of the canopy cover on the organic and inorganic content of soil in Cholistan desert"*, Basit Karim, Azam Mukhtar, Hamid Mukhtar, and Makshoof Athar, *Pak. J. Bot*., 2009, 41(5): 2387-2395.

10. *"Determination of Arsenic, mercury and copper in the organ meat of beef, mutton and poultry"*, Azam Mukhtar, Shabir Ahmad and Hamid Mukhtar, Biologia, 2005, 51 (82), 71-75.

11. *"Optimization of culture medium for the production of alpha amylase by Aspergillus oryzae"*, Mukhtar, Hamid; Ikram-Ul-Haq; Mukhtar, Azam. Biologia, 2007, 53(2), 149-155.

Conference Publications

1. **A. Mukhtar**, A. Limbeck

   "Slurry sampling ICP-OES procedure for fast and accurate determination of crustal and trace elements in airborne particulate matter";
   Talk: 36th International Symposium on Environmental analytical Chemistry, Rome, Italy, 5th to 09th October, 2010.

2. A. Limbeck, **A. Mukhtar**

   "*Development of a dynamic extraction procedure with on-line ICP-OES detection for fast and accurate determination of soluble trace metal fractions in airborne particulate matter*";
   Talk: 2010 Winter Conference on Plasma Spectrochemistry, Fort Myers/Florida, 4th to 9th January, 2010.

3. A. Limbeck, E. Herincs, **A. Mukhtar**

   "Development of a dynamic extraction procedure with on-line ICP-OES detection for fast and accurate determination of soluble trace metal fractions in airborne particulate matter";
   Talk: Euroanalysis, Innsbruck, Austria, 6th to 10th September, 2009.

4. A. Limbeck, **A. Mukhtar**:

   "*Slurry ETAAS procedure for the accurate determination of Silicon in airborne particulate matter*";
   Talk: European Symposium of Atomic Spectroscopy (ESAS08), Weimar, Germany; 28th Sept. to 1st October, 2008; in: "*ESAS08 - Book of Abstracts*", (2008), 33.

5. **A. Mukhtar**, A. Limbeck:

   "*Development of a slurry ICP-OES procedure for determination of mineral components in airborne particulate matter*";
   Talk: ANAKON 2009, Berlin; 17th to 20th March, 2009; in: "*Documentation*", (2009), 70.

6. E. Herincs, **A. Mukhtar**, A. Limbeck:

   "*A new approach for determination of soluble trace metal fractions in airborne particulate matter using a dynamic extraction procedure coupled to ICP-OES*";

   Poster: Colloquium Spectroscopicum Internationale XXXVI, Budapest; 30th August to 3rd Sept., 2009; in: "*Scientific Program & Book of Abstracts*", (2009), 225.

7. **A. Mukhtar**, A. Limbeck:

   "*Fractionation of Zinc in Airborne Particulate Matter using a dynamic extraction procedure coupled to Flame Atomic Absorption Spectroscopy*";

   Poster: ANAKON 2009, Berlin; 17th to 20th March, 2009; in: "*Documentation*", (2009), 164.

8. **A. Mukhtar**, A. Limbeck:

   "*Slurry sampling ICP-OES procedure for fast and accurate measurement of crustal elements in airborne particulate matter*";

   Poster: Junior Scientist Conference 2008, Vienna; 16th to 18th November, 18-2008; in: "*Junior Scientists Conference 2008 Proceedings*", (2008), ISBN: 978-3-200-01612-5; 261 - 262.

9. A. Limbeck, **A. Mukhtar**:

   "*Development of an ETV-ICP-OES procedure for assessment of bio-accessible trace metal fractions in airborne particulate matter*"

   Poster: Winter Plasma Conference 2011, Zaragoza, Spain; 30th January to 4th February, 2011.

10. **A. Mukhtar**, A. Limbeck:

    "*Comparison of extraction efficiencies of various leaching solutions for assessment of bio-accessible trace metal fractions in airborne particulate matter*".

    Poster: Euroanalysis 2011, Belgrade, Serbia, 11th to 15th, September, 2011.

11. **A. Mukhtar**, A. Limbeck:

    "*Direct analysis of trace metals in airborne particulate matter using electrothermal vaporization in combination with inductively coupled plasma atomic emission spectroscopy*".

    Poster: Euroanalysis 2011, Belgrade, Serbia, 11-15 September, 2011.

Seminars

1. Modern Analytical Chemistry: "*New approaches for determination of bio-accessible trace metal fractions in airborne particulate matter*" 6th May, 2011 at Institute of Chemical Technologies and Analytics, Vienna University of Technology, Austria.

2. Applied modeling approaches: atmospheric science *"Radiative forcing of green house gases"* at International Institute for Applied Systems Analysis (IIASA), Laxenburg, Austria.