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Application of double-focusing sector field ICP-MS for determination of ultratrace constituents in samples characterized by complex composition of the matrix

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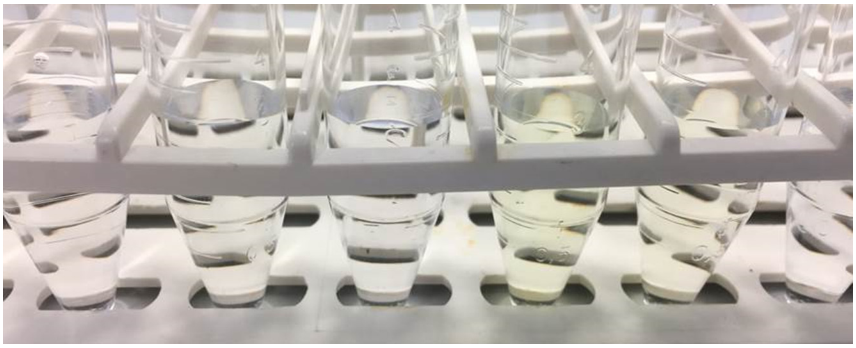
HIGHLIGHTS

- Determination of ultra-trace elements in snow, waters and clinical samples by ICP-SFMS.
- Combination of pre-concentration and matrix separation
- Concentration ranges of a variety of TCEs and other elements at ultra-trace levels in environmental sample matrices.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of double focusing, sector field mass spectrometry (ICP-SFMS) for determination of analytes, including technology critical elements (TCE), at ultra-trace levels in environmental and clinical matrices was critically evaluated. Different configurations of the ICP-SFMS introduction system as well as various sample preparations, pre-concentration and matrix separation methods were employed and compared. Factors affecting detection capabilities and accuracy of data produced (instrumental sensitivity, contamination risks, purity of reagents, spectral interferences, matrix effects, analyte recovery and losses) were discussed. Optimized matrix-specific methods were applied to a range of reference and control materials (riverine, brackish and seawaters; whole blood, serum and urine) as well as tap water and snow samples collected in the area of Luleå city, northern Sweden; brackish and seawater from the Laptev Sea; venous blood samples with a special emphasis on determination of Au, Ag, Ir, Os, Pd, Pt, Re, Rh, Ru, Sb and Te. Even though these low abundant elements are relatively under-documented, the results produced were compared with published data, where available.

1. Introduction

The need to accurately measure concentrations of an ever broader range of elements in environmental and clinical samples is constantly

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growing. This interest stems from socio-economic factors, technological advances, environmental and public health concerns which increasingly focus on previously less studied, emerging contaminants such as technologically critical elements (TCE) (Cobelo-Garcia et al., 2015; Fairbrother et al., 2007; Kamala et al., 2016; Karn, 2011; Ravindra et al., 2004; Schäfer et al., 1999) presented in natural matrices at trace and ultra-trace levels. Global production of these low abundance elements has increased dramatically over the last few decades due to new emerging application areas, most notably in advanced electronics and the introduction of car catalysts worldwide (Johnson-Matthey, 2003, 2004).

The increased use of these elements has resulted in a significant discharge into our environment at both local and global scales (via long range transport of aerosols) causing changes in the elemental background even in remote areas as demonstrated by studying temporal concentration patterns recorded in dated ice, peat bog and sediment cores where concentrations have increased worldwide since the 1970s (Barbante et al., 2001; Rauch et al., 2005; Soyol-Erdene et al., 2011b; Tuit et al., 2000; Van De Velde et al., 2000). This increased anthropogenic load together with occupational and other pathways for human exposure, such as the use in contrast agents (Gd), drugs (Pt, Ir, Au, Os), implants (e.g. Ag, Pt) and dental alloys (Ag, Au, Pd), has led to the inclusion of biological matrices to the range of samples to be analysed. The general pathways and behavior of these elements are under-documented and their low abundances in environmental and clinical matrices present an analytical challenge.

In spite of significant progress in instrumental and method developments, reliable measurements of element concentrations at or below ng L^{-1} in liquids and μg kg^{-1} in solids still represent a significant analytical challenge requiring the use of extremely sensitive and selective techniques often combined with matrix separation and/or analyte pre-concentration. Moreover, the need for meticulous contamination control at all stages of sampling, transport and analysis cannot be overemphasized (Boutron, 1990; Planchon et al., 2001; Rodushkin et al., 2010).

Among modern analytical techniques, double focusing, sector field mass spectrometry (ICP-SFMS) has been extensively used for determination of TCE in a variety of matrices due to unique combination of high sensitivity and relative freedom from spectral interferences offered by high resolution capabilities. Moreover, the technique provides isotopic information that is required for quantification using isotope dilution (ID) and can provide valuable information on elemental sources and accumulation pathways (Rodushkin et al., 2013). The outstanding merits of ICP-SFMS in the field of ultra-trace analysis are reflected in a significant number of research papers and reviews (e.g. Becker, 2005; Jakubowski et al., 1998). The majority of publications though are focused on a very limited number of analytes (often a single one) which is somehow surprising considering the multi-elemental capabilities of the technique and the additional value of complimentary information for better understanding of systems/objects studied.

Over the last two decades we have reported on numerous ICP-SFMS uses for analyses of a wide range of elements in different matrices, including natural fresh and saline waters (Rodushkin et al., 2005; Rodushkin and Ruth, 1997), food and biota (Rodushkin et al., 2008, 2007) as well as body fluids (Rodushkin et al., 2004, 2000; Rodushkin and Odman, 2001) to mention but a few. The aim of this work is to present a range of ICP-SFMS-based, matrix-specific analytical methods for high throughput ultra-trace analysis. Previously published approaches were used as a starting point, they were adopted and optimized with respect to the determination of Au, Ag, Ir, Os, Pd, Pt, Re, Rh, Ru, Sb and Te (representing most challenging analytes among TCE) and were successfully used by the laboratory in numerous screening, monitoring and exposure assessment programs. The analytical performance of ICP-SFMS for determination of these low-abundance elements are demonstrated for the analysis of snow, fresh and saline waters, whole blood, human urine and serum. Though these methods can be used (either directly or after minor modifications) for determination of rare earth elements (REE) and high field strength elements (HFSE), detailed discussion concerning those analytes is omitted and the reader is directed to relevant publications in the field (e.g. Bayon et al., 2009; Lu et al., 2007).

2. Material and methods

2.1. Instrumentation

Instrumental analysis was performed using two single-collector ICP-SFMS instruments (ELEMENT XR and ELEMENT 2, Thermo Fisher Scientific, Bremen, Germany) which can operate in three pre-defined resolution modes: low-resolution mode (LR, $m/\Delta m$ approximately 350), medium-resolution mode (MR, $m/\Delta m$ approximately 5400) and high-resolution mode (HR, $m/\Delta m$ approximately 12,000) and with different configurations of the sample introduction system (Table 1). The first of the instruments was equipped with the standard introduction system including Peltier-cooled spray chamber, FAST autosampler and operates with methane addition to the plasma (Rodushkin et al., 2005). The second is coupled to a high efficiency/sensitivity desolvating system Aridus II (Teledyne CETAC technologies, Omaha, Ne, USA), with PFA spray chamber and micro-concentric nebulizer. Details of the instrumental operating and data acquisition parameters are summarized in Table 2.

A laboratory UltraCLAVE single reaction chamber microwave digestion system (Milestone, Sovisole, Italy) was used for digestions of clinical samples.

2.2. Chemicals and reagents

Nitric acid (HNO_3, 69–70%) and thiourea (CH_4N_2S), both from Sigma-Aldrich Chemie GmbH, Munich, Germany, used in this work were all of analytical grade. The former acid was purified further by sub boiling distillation in quartz stills directly into 1 L Teflon bottles. Hydrochloric acid (HCl, 30%, Sigma-Aldrich Chemie GmbH) and hydrogen fluoride (HF, 48%, Merck, Darmstadt, Germany) was of Ultrapur grade.

The distilled, de-ionized water (DDIW) used for dilution of samples and preparation of blanks, spike solutions and standards, was de-ionized Milli-Q water (Millipore, Bedford, MA, USA) purified by reverse osmosis followed by ion-exchange cartridges and finally sub-boiling distillation in Teflon stills (Savillex, Minnetonka, MN, USA).

AG 50W-X8 cation-exchange resin (200–400 dry mesh size, 63–150 μm wet bead size, Bio-Rad Laboratories AB, Solna, Sweden) was cleaned by soaking in 14 M HNO_3 overnight followed by several rinses with Milli-Q water and loading as slurry into 2 mL low-density polyethylene (LDPE) columns. Loaded columns were additionally cleaned by passing 4 mL of 14 M HNO_3 and 8 mL of Milli-Q water, followed by pre-conditioning with 4 mL 9.5 M HCl and finally 10 mL of DDIW.

Calibration standards and spike solutions were prepared by gradual dilutions of 1000 mg L^{-1} individual single element stocks (Ultra Scientific, Analytical Solutions, N. Kingstown, USA and Inorganic Ventures, Christiansburg, USA) in 0.7 M HNO_3/0.5 M HCl and were checked against quality control samples prepared from 10 mg L^{-1} multi-element standard (IV-stock-28, Inorganic Ventures). Initial dilutions of concentrated stocks were performed in a dedicated fume hood located far from laboratory areas used for preparation of samples.

2.3. Samples

Snow samples ($n > 50$) were collected into 2 L zip-lock plastic bags in the city and suburbs of Luleå (northern Sweden), a medium sized town (population approximately 75,000) located in the province of Norrbotten during February and March 2017. The area surrounding Luleå is heavily industrialized, with steelworks as the dominant local industry. Samples represent freshly fallen snow (taken during or directly after heavy snowfalls) and snow cores (accumulation period of approximately 3 months) collected away from roads or local industries as well