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Biomonitoring for arsenic, toxic and essential metals in single hair strands by laser ablation inductively coupled plasma mass spectrometry

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ABSTRACT

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been developed as reliable analytical technique for the quantitation of metal distributions at micrometre resolution. In this work a novel microanalytical strategy for biomonitoring of arsenic, toxic and essential metals in single hair strands is proposed. Two different calibration strategies in LA-ICP-MS were developed using either certified hair standard reference material (IAEA 086) or prepared matrix-matched laboratory hair standards doped with analytes of interest at defined concentration. Powdered hair standards and human hair strands mounted on a sticky tape in the LA chamber were analyzed under the same experimental conditions by an optimized LA-ICP-MS technique. The use of hair powder standard allows calibration curves to be obtained by plotting the analyte ion (M^+) intensity normalized to $^{34}S^+$ (the ratio $M^+/^{34}S^+$) as a function of the concentration determined by ICP-MS of acidic digests. The linear correlation coefficients (R) of calibration curves for analytes As, Ba, Cd, Ce, Co, Cr, Cu, Fe, Ga, Hg, Mg, Mo, Ni, Pb, Rb, Sr,Ti and U were typically between 0.985 and 0.999. The limit of detection (LOD) was 0.6 $\mu g\,g^{-1}$ for As and ranged from 0.3 to 7.8 $\mu g\,g^{-1}$ for the other analytes. Distinct elemental exposition time profiles were observed in hair samples from five volunteers.

1. Introduction

Trace analysis of toxic and essential elements in hair, nail and other biological tissues is of increasing importance in studies related especially to medicine, forensic, archaeology and nutrition. The effect of the deficiency or excess of essential (nutritional) trace metals such as Fe, Cu, Zn and/or toxic metals (e.g., Pb and Hg) at the ultratrace level on our health and their contribution to the development of different diseases can thus be studied [1]. Especially hair samples can be used for sensitive biomonitoring of trace elements and offer a precise time profile reflecting the history of exposition as most trace elements are continuously incorporated into the growth zone of the hair constantly growing about 1 cm per month. Metals at trace concentration levels have been quite often determined in the bulk of samples of biological materials after their homogenization and acidic digestion using inductively coupled plasma mass spectrometry (ICP-MS). However, this does not provide information on spatial distribution of metals in the analyzed hair strands [2–6]. The distribution analysis of the metals in biological tissue requires powerful quantitative imaging techniques, like laser ablation inductively coupled mass spectrometry (LA-ICP-MS) or secondary ion mass spectrometry (SIMS). In previous studies sensitive analytical procedures for monitoring of uranium as environmental contamination and of therapeutic platinum in single hair strands by LA-ICP-MS was described by Becker's group [7,8]. In the latter work transient peaks of Pt along the hair strands were detected by LA-ICP-MS which corresponded to single doses of cisplatin that the subject received every 3 weeks. Time resolved monitoring of Pt and Hg was also used to determine the time point of intoxication in two forensic cases [9].

Several quantification strategies have been developed for element distribution analysis using LA-ICP-MS in human hair including certified reference materials (CRM) or matrix-matched laboratory standards [7]. Recently, we developed a solution-based calibration method [8] that was applied to human hair and mouse hair. Solution based calibration in LA-ICP-MS is an elegant analytical calibration technique that requires two different introduction systems for the aerosol gas stream from the laser ablation chamber for the solid hair sample and for the aerosol gas stream from

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Table 1
Optimized experimental conditions of LA-ICP-MS for hair analysis.

ICP-MS (X Series 2)	
Rf-power (W)	1400
Carrier gas (L min^{-1})	0.92
Isotopes measured	^{7}Li, ^{24}Mg, ^{33}S, ^{34}S, ^{48}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{66}Zn,^{71}Ga, ^{75}As, ^{85}Rb, ^{88}Sr, ^{98}Mo,^{111}Cd, ^{137}Ba, ^{140}Ce, ^{202}Hg, ^{208}Pb, ^{238}U
Dwell time (ms)	100
Laser ablation	
Method	Single line scan
Repetition frequency (Hz)	20
Spot size (μm)	300
Scanning speed (μm s^{-1})	50
Pulse energy (mJ)	0.084

a nebulizer for aqueous standard solutions. An easier approach is the calibration strategy with the aid of solid hair standards because only one sample introduction system is required. Several authors used certified human hair (in powder form) pressed into solid flat pellets [10] or pressed on carbon tabs [11]. Hair strands were glued on glass slides or attached to a two side tape and directly ablated. In summary, trace element monitoring in hair strands remains an attractive method in toxicology and surveillance of nutritional status. The assessment of suspected occupational, environmental or accidental exposure to toxic elements (Hg, Pb, As) was described [6,10,12–14].

The aim of this work was to develop matrix matched hair standards and a LA-ICP-MS technique for determination of especially As, toxic metals (such as Pb, Cd, Hg) but also nutrient elements in single human hair for biomonitoring of environmental exposure.

2. Experimental

2.1. Instrumentation

An ICP-MS spectrometer (XSeries 2 from Thermo Scientific, Bremen, Germany) operating at standard mode was coupled with a laser ablation system UP 266 New Wave – wavelength of Nd:YAG laser: 266 nm (Cambridge, UK). LA-ICP-MS uses a laser beam to ablate sample material in an argon atmosphere under normal pressure in the laser ablation chamber. The ablated sample was transported into ICP-MS by an argon gas stream. Optimization of experimental parameters was performed by ablating of certified hair standard fixed on double-sided adhesive tape. For optimization, laser parameters were varied in order to obtain the highest analyte ion intensities. The experimental parameters (the rf power of 1400 W and carrier gas flow rate of 0.87 L min^{-1}) of the LA-ICP-MS measurements were optimized in order to obtain maximum analyte ion (M^+) intensity and minimum intensity of oxide (MO^+) and double charged (M^{2+}) ions. Sulphur (via measurement of $^{34}S^+$) was used as the internal standard element. The optimized experimental parameters for all measurements are summarized in Table 1.

2.2. Samples and sample preparation

Hair samples provided by five volunteers from three different countries (Brazil, France and Thailand) were analyzed in order to check the applicability of the proposed method. Strands of the human hair were cut close to the root in the scalp, washed with acetone and deionised water, and dried at room temperature. Single hair strands were fixed one by one on a double sided adhesive tape and analyzed by LA-ICP-MS. A schematic of hair sample preparation is shown in Fig. 1a.

2.3. Reagents and certified hair standard

ICP multielement standard solution IV, HNO_3, HCl and H_2O_2 from Merck were used. They were of Suprapur® grade; the HNO_3 and HCl were further purified by sub-boiling distillation. All chemicals used were analytical reagent grade. Acetone, HPLC grade (Merck), was used for hair washing prior to analysis. High purity deionised water (18.2 MΩ cm) obtained from a Milli-Q system was used for all dilution of mixed metal standard solution and digested samples. A series dilution of ICP multi-element standard stock solution IV (Merck) was immediately prepared prior to use. Certified hair standard reference material (IAEA 086) from the International Agency Energy Atomic (IAEA), Vienna, Austria was employed for validation of metal concentration in metal enriched hair powder standard.

2.4. Preparation of matrix matched laboratory hair standards

Two different types of standards were prepared, hair strands immersed into solutions of defined element concentrations and metal enriched hair powder. The experimental workflow is given in Fig. 1b. Hair samples were taken from a volunteer without any history of arsenic exposure and cleaned according to the procedure described above. Thereafter, the some hair strands were immersed in 10 mL of a multielement aqueous solution containing 0.5–50 mg L^{-1} of Li, Mg, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Mo, Co, Cd, Ba, Hg, Pb and U for 24 h. The other hair strands were immersed in As standard solutions of different concentrations (0.5–1000 μg g^{-1}) for 72 h. Then the solutions were removed and the hair was left to dry at room temperature.

Metal enriched hair powder standard was prepared from rinsed hair by milling with a SPEX6799 FREEZER/MILL (SPEX Industries, Inc., Metuchen, NJ, USA). Aliquots of the homogeneous powder were spiked with a mixed metal standard solution (ICP multielement standard solution IV, Merck) in the concentration range of 0.5–400 mg L^{-1} and incubated for 24 h. The metal enriched hair powders were dried in the oven at 55 °C. The final element concentrations in the standard materials were controlled in microwave induced acidic digests (Microwave Accelerated Reaction Systems, MARS-5, CEM Microwave Technology Ltd.). The digested samples were made up to 10 mL with DI water and 2%, (v/v) HNO_3 analyzed by ICP-MS (Agilent 7500).

2.5. Calibration strategy and sample analysis

^{34}S was used for internal standardization of LA-ICP-MS measurements to compensate for ablation variation in the ablation process and instrumental drifts. The calibration curve was obtained by plotting the observed ratio of analyte ion intensities to $^{34}S^+$ intensities versus the accurate metal concentration determined by ICP-MS. Each point of the calibration curve was the average signal obtained by ablating at least three lines of 2 cm. Ion intensities and concentrations were plotted as function of the length position on the hair strand obtained as the product of ablation speed and ablation time. The limit of detection (LOD) was calculated by the ablation of 10 washed native unexposed hair strands.

2.6. Creation of hair sample phantoms with segmental As contamination

In order to check the limits of length resolved As distribution analysis in hair strands using LA-ICP-MS, rinsed hair strands were only partially incubated in a defined As solution (3 strands for each concentration). Only a segment of the hair strands about 2 cm from the root was immersed. The concentration of the As solution ranged