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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

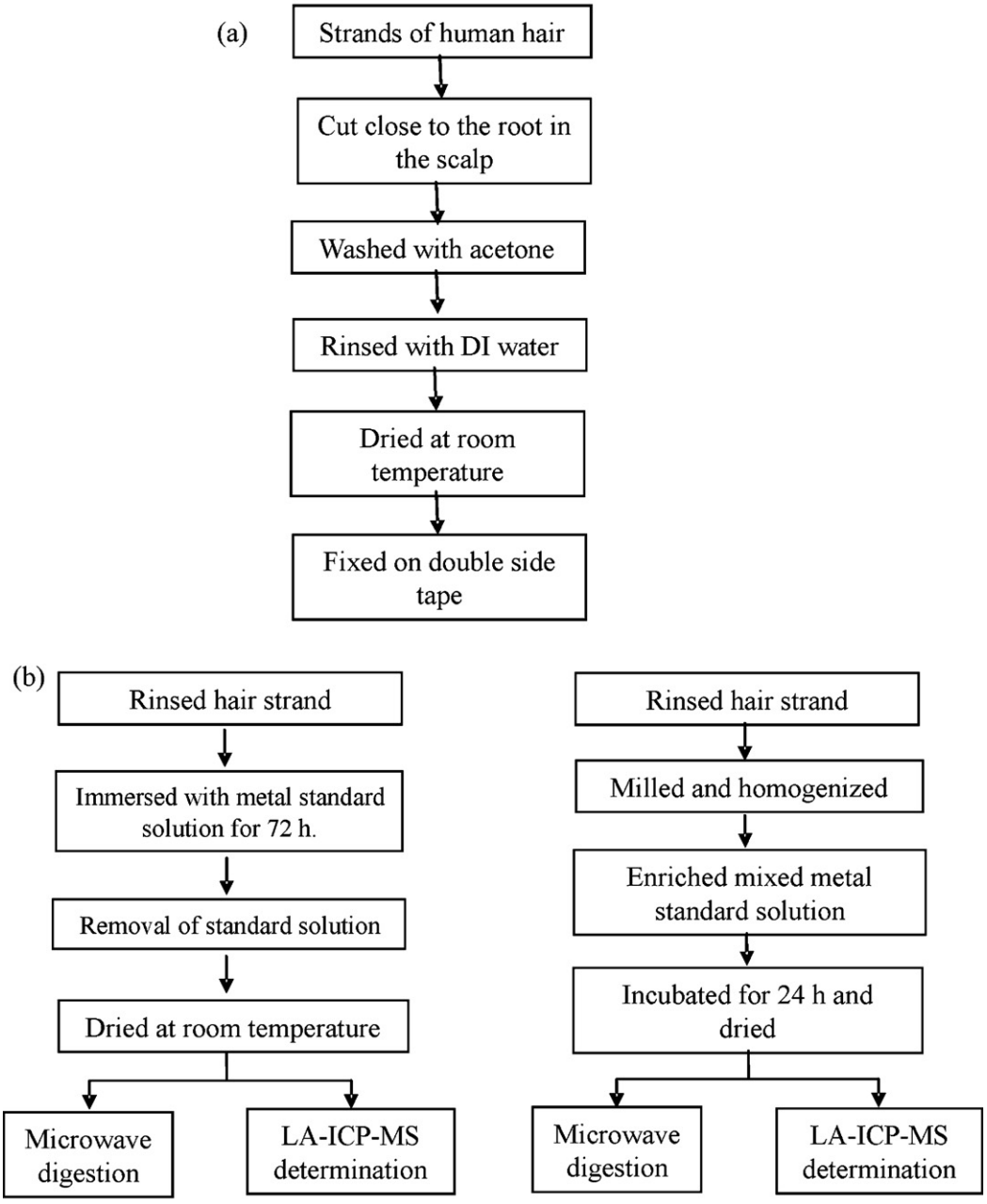

Fig. 1. Experimental workflow of hair analysis using LA-ICP-MS: (a) schematic of the sample preparation of hair strands for LA-ICP-MS determination. (b) Preparation of metal immersed hair strand standards and of metal enriched hair powder standards.

from 0.5 to 100 $\mu g\,L^{-1}$. The incubation time was varied between 15 min and 10 h in order to probe its effect.

3. Results and discussion

3.1. Quantification strategy using metal enriched hair powder standards

For quantification of LA-ICP-MS data of elemental distributions in hair samples, a set of metal-enriched hair powder standards was prepared. The homogenous hair powder was spiked with defined concentration of analytes from 0.5 to 400 $\mu g\,g^{-1}$. The calibration curves obtained showed good linearity with correlation coefficients between 0.985 and 0.999 for Mg, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Mo, Cd, Ba, Hg, Pb, and U as summarized in Table 2. The respective limits of detection (LOD) ranged from 0.3 to 7.8 $\mu g\,g^{-1}$. This standard addition quantification procedure was validated by IAEA 085 reference materials using one point calibration. The measured concentrations of some elements of IAEA 085 are shown in Fig. 2 and were in good agreement with the certified values. No significant difference was observed at the 95% confidence level. Metal-enriched hair powder standard was easy to prepare in the laboratory and could be used for multielement detection in hair samples using LA-ICP-MS.

3.2. Quantification strategy using metal immersed hair strand standards focussing on As

The mixed metal-immersed hair strands and As-immersed hair strands were fixed one by one on double-sided adhesive tape and analyzed directly by line scanning using LA-ICP-MS. The ion intensity ratios of $^{75}As^{+}/^{34}S^{+}$ obtained along As-immersed hair strands

Table 2
Linear regression equations and limits of detection (LOD) of LA-ICP-MS applied to metal enriched hair powder standard; x is concentration/$\mu g\,g^{-1}$ and y the analyte signal normalized to ^{34}S.

Analyte	Linear regression equation	R	LOD ($\mu g\,g^{-1}$)
^{24}Mg	$y = 0.017x - 0.3536$	0.9869	7.8
^{48}Ti	$y = 0.0179x + 0.4293$	0.9968	3.2
^{51}V	$y = 0.0208x + 0.1012$	0.9995	0.4
^{52}Cr	$y = 0.0213x + 0.2365$	0.9995	2.5
^{55}Mn	$y = 0.0265x - 0.0264$	0.9851	0.4
^{56}Fe	$y = 0.0174x + 0.102$	0.9903	0.8
^{59}Co	$y = 0.0211x + 0.0279$	0.9993	0.6
^{60}Ni	$y = 0.0016x + 0.014$	0.9989	6.5
^{63}Cu	$y = 0.0115x - 0.0212$	0.9997	0.5
^{64}Zn	$y = 0.0072x + 0.086$	0.9896	6.1
^{71}Ga	$y = 0.0137x - 0.0026$	0.9956	0.7
^{75}As	$y = 0.0022x - 0.0036$	0.9910	0.6
^{85}Rb	$y = 0.0198x + 0.0002$	0.9993	1.7
^{88}Sr	$y = 0.0253x + 0.0333$	0.9997	0.9
^{95}Mo	$y = 0.004x - 0.0008$	0.9998	1.2
^{111}Cd	$y = 0.0012x - 0.0019$	0.9976	0.6
^{138}Ba	$y = 0.0163x + 0.1688$	0.9954	7.7
^{140}Ce	$y = 0.0247x + 0.0945$	0.9986	0.8
^{202}Hg	$y = 0.0017x - 0.0002$	0.9935	0.7
^{208}Pb	$y = 0.0168x - 0.1155$	0.9967	0.3
^{209}Bi	$y = 0.0162x + 0.0105$	0.9987	0.9
^{238}U	$y = 0.0173x + 0.0315$	0.9998	1.1

are plotted in Fig. 3a. The As signal was homogeneously distributed along the hair strands. Similar stable signals of the respective elements were obtained along the hair strands immersed in multi-element standards.

The As species primarily affine to proteins are As(III) compounds such as H_3AsO_3. Especially As(III) covalently binds to disulfide groups as abundantly present in keratin, the major constituent of hair [2,4,15]. The redox potential of H_3AsO_4/H_3AsO_3 and $H_2AsO_4^-/H_3AsO_3$, respectively at the present pH 2.5 is 0.4 V [15]. As can be read from the respective Pourbaix diagrams the redox potential of the multielement solution at pH 2.5 will be significantly higher (e.g. Pb(II)/Pb(IV) 1.4 V; Fe^{2+}/Fe^{3+} 0.8 V; Cr(III)/Cr(VI) 1.3 V; Hg(I)/Hg(II) 0.8 V) in the sense of higher oxidative conditions. The availability of H_3AsO_3 in the multielement solution will be decreased by several decades. To stabilize As(III) in a multielement milieu the addition of reducing agents would be necessary. For these reasons we preferred a separate mono-element standard for As.

Apparently, binding of As under the present conditions was a slow process, as after 10 h but not after 15 min of incubation measurable As binding to hair was observed, which is in congruency with previous reports [14]. The calibration line ($R^2 = 0.9928$) obtained for the ion intensity ratio of $^{75}As^+/^{34}S^+$ from immersed hair strand standard is plotted in Fig. 3b. The limit of detection

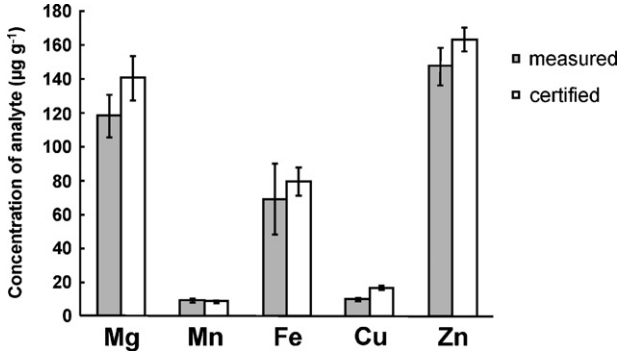

Fig. 2. Comparison of analyte concentration in IAEA 85 standard reference material measured by LA-ICP-MS (via the calibration curve obtained from metal enriched hair powder standards) with the certified values.

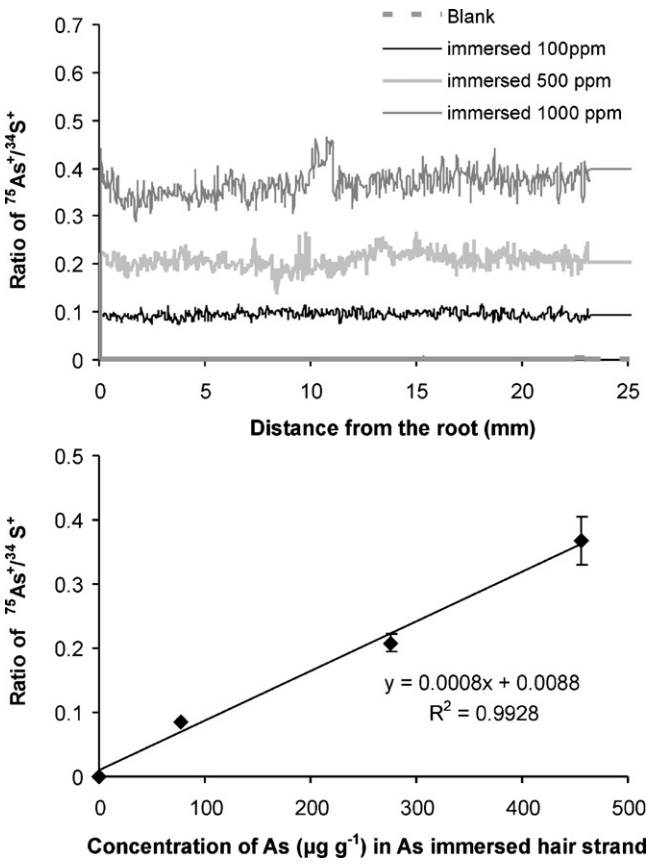

Fig. 3. Calibration of LA-ICP-MS using As immersed hair strand standards. (a) Ratio of ion intensities $^{75}As^+/^{34}S^+$ along immersed hair strand standards of different concentration. (b) Calibration curve and respective parameters obtained using As immersed hair strand standards.

(LOD) was determined at 1.19 $\mu g\,g^{-1}$. It was calculated by ablation of 10 washed strands from an unexposed subject. Thus, immersion of hair strands into standard solution seems a suitable calibration strategy. Care should be taken on the element species used, their compatibility and sufficient incubation time.

3.3. Metal distribution along a single hair strand

3.3.1. Hair strand phantoms with segmental As profile and a case of suspected environmental As exposition

In order to determine the ability of this method to provide spatial distribution of As along the hair strands, some hair strands were only partially immersed in As standard solution along a segment spanning 2.0 cm from the root and analyzed by LA-ICP-MS. The hair samples were entirely ablated from root to tip. As shown in Fig. 4, informative As-distribution profiles of hair strands were obtained. As-exposed segments were clearly demarked from non-immersed segments. Deviations of the As length profile from an ideal step function can be explained by candle-wick effects and dripping effects. The highest ion intensity of $^{75}As^+$ was found at the position nearly to the hair root. This study demonstrates that LA-ICP-MS and hair analysis be used for time resolved exposition monitoring of As at higher concentration. The very strong and virtually covalent attachment of external As implies that hair analysis cannot discriminate between external and internal As deposition. This issue had already been addressed by Hindmarsh [14] who further showed that even the study of a hair cross section did not allow this discrimination. Finger nail after careful abrasion of the superficial

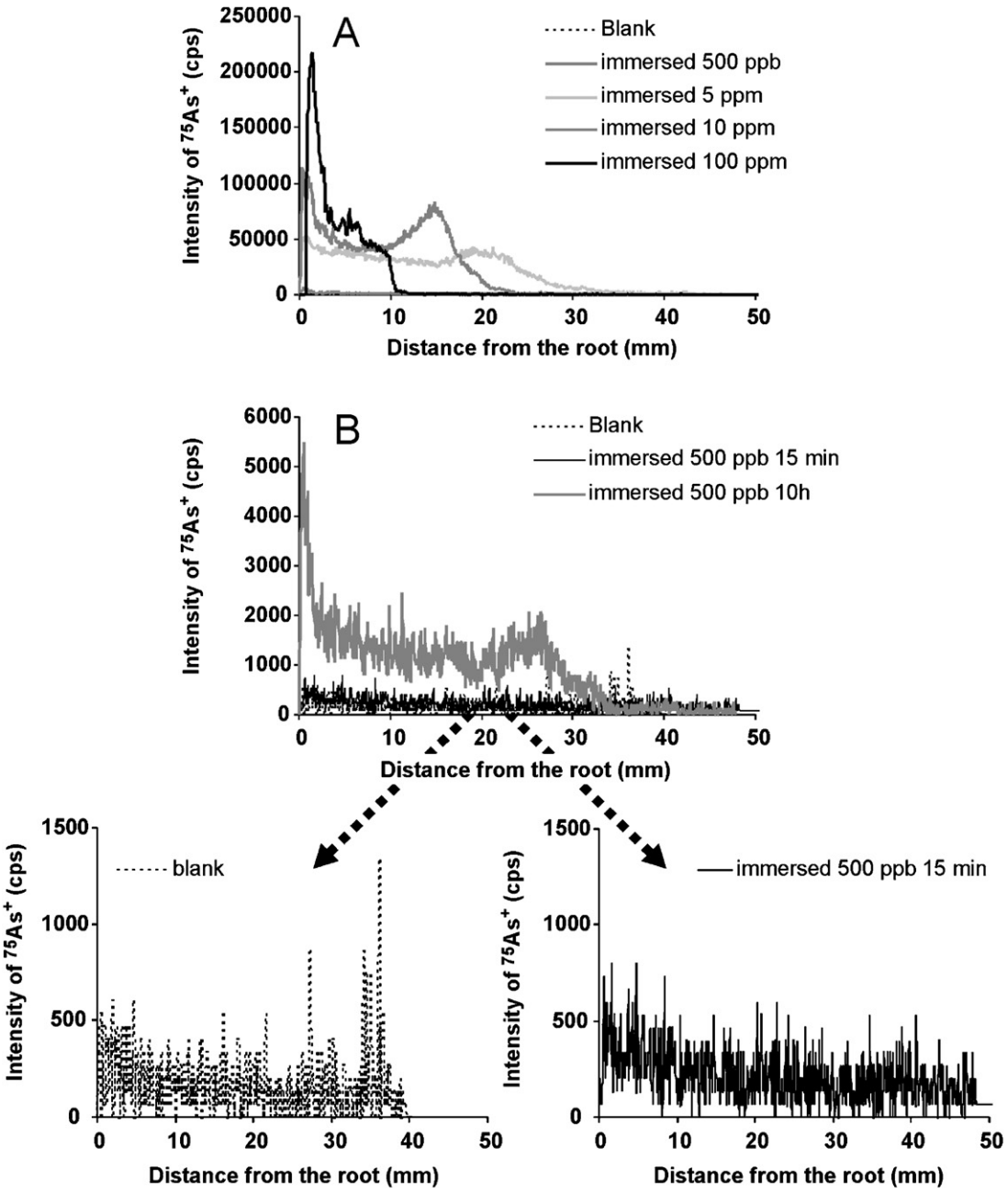

Fig. 4. As distribution of a hair strand only partially immersed into the As solution at a given segment. (a) The ion intensity of As in hair strands immersed in As standard solution with different concentrations. (b)The intensity of As in hair strands immersed in the 500 $\mu g\,g^{-1}$ As standard solution with different incubation times.

layers therefore might be better bio-indicators of internal exposition.

In this study, the As distribution profile in hair strands collected from a volunteer who lived near an open pit gold mine were not detectable. The metabolism and detoxification of arsenic have been extensively studied by Vahter [16]. In the early phase following a single exposure, arsenic distributes to liver and kidney; in the later phase, e.g. 24 h after the exposure event, little of the original amount remains in these organs, and the greatest amounts can be found in tissues that accumulate arsenic more readily, such as skin, hair and nails [6,17,18]. Concentration of arsenic in hair ranged from 0.08 to 0.25 $\mu g\,g^{-1}$ in an unexposed population. In contrast, in chronically exposed populations, concentrations ranging from 1 to greater than 9 $\mu g\,g^{-1}$ have been reported [14,19–21].

3.3.2. Five cases of element monitoring in hair strands

Hair samples from five volunteers were analyzed in order to study the exposition history of the recent months. The length profiles of detected analytes (Mg, Fe, Zn, Cu, Ba, Mn Rb, Sr, Mo and Pb) along the hair strands are shown in Fig. 5. The signal intensity of each element was normalized to (^{34}S) as internal standard to compensate for variations of the amount of ablated material per acquisition cycle. Note, that the length profiles are plotted starting from the hair root to the tip; the live-time axis proceeds in the inverse direction and 10 mm approximately equal 1 month. All hair samples show a quite different distribution pattern. Clear signals of Cu, Zn Mg, Fe and the others were obtained in all of samples. In samples (a–d) Cu was constant along the hair but hair sample (e) displayed high and variable Cu concentration with a large maximum in the younger portion of the strand. Sharp Fe peaks very

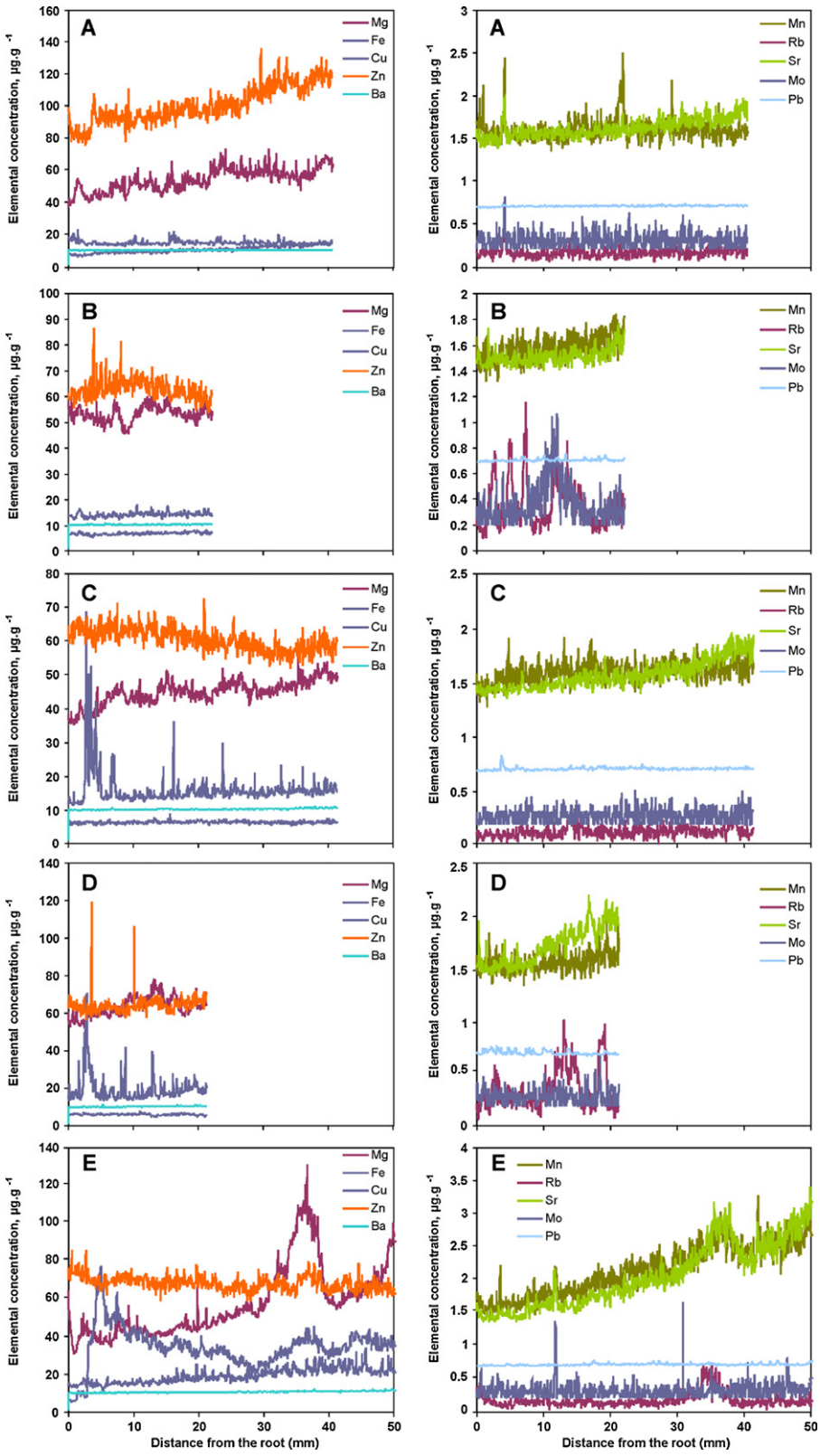

Fig. 5. Elemental length profile along hair strands collected from five volunteers measured by LA-ICP-MS. Metal enriched hair powder standard was used for calibration propose.

close to the root-near end may be external contaminations from dirty and edgeless scissors. The elemental profiles of Cu, Zn, Fe and Mg in sample (a) were in good agreement with values obtained on this sample using solution based calibration and LA-ICP-MS reported previously [8]. Sample (e) is exemplary for the possibilities of treatment monitoring. This subject took two times high doses of Mg supplementation for a couple of days. One peak was recorded entirely with a relatively sharp increase, a plateau during 1–2 weeks followed by an exponential decrease. An exponential decrease phase from a previous Mg intake was recorded on the

same hair cut. Apparently Mn and Sr were accompanying ingredients of this Mg preparation. The decrease of Mg to half the peak value took place on about 3 mm of hair length corresponding to 10 days of life time. A biological elimination half live of Mg of about 10 days was also observed in radiotracer studies using ^{28}Mg [22].

4. Conclusions

Analysis of single hair strands using LA-ICP-MS is an emerging tool for the quantitative time-resolved exposition monitoring of metals and trace elements. This technique requires only a minimal sample preparation, a washing step and a very small amount of sample and is easy to implement in routine work. The measurement is rapid and easy to perform with convenient sampling. Two different quantification strategies can be used, enriched metal hair powder standards and hair strands immersed in metal solution standards. The fields of application include therapeutic drug monitoring (such as As_2O_3, in leukemia; VO_4^{3-} in diabetes, Pt-compounds in cancer), occupational exposure, nutritional and toxicological controls and the study of environmental contamination.

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