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Biomonitoring of essential and toxic metals in single hair using on-line solution-based calibration in laser ablation inductively coupled plasma mass spectrometry

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ABSTRACT

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been established as a powerful and sensitive surface analytical technique for the determination of concentration and distribution of trace metals within biological systems at micrometer spatial resolution. LA-ICP-MS allows easy quantification procedures if suitable standard references materials (SRM) are available. In this work a new SRM-free approach of solution-based calibration method in LA-ICP-MS for element quantification in hair is described. A dual argon flow of the carrier gas and nebulizer gas is used. A dry aerosol produced by laser ablation (LA) of biological sample and a desolvated aerosol generated by pneumatic nebulization (PN) of standard solutions are carried by two different flows of argon as carrier or nebulizer gas, respectively and introduced separately in the injector tube of a special ICP torch, through two separated apertures. Both argon flows are mixed directly in the ICP torch. External calibration *via* defined standard solutions before analysis of single hair was employed as calibration strategy. A correction factor, calculated using hair with known analyte concentration (measured by ICP-MS), is applied to correct the different elemental sensitivities of ICP-MS and LA-ICP-MS. Calibration curves are obtained by plotting the ratio of analyte ion $M^+/^{34}S^+$ ion intensities measured using LA-ICP-MS in dependence of analyte concentration in calibration solutions. Matrix-matched on-line calibration in LA-ICP-MS is carried out by ablating of human hair strands (mounted on a sticky tape in the LA chamber) using a focused laser beam in parallel with conventional nebulization of calibration solutions. Calibrations curves of Li, Na, Mg, Al, K, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Mo, Ag, Cd, I, Hg, Pb, Tl, Bi and U are presented. The linear correlation coefficients (R) of calibration curves for analytes were typically between 0.97 and 0.999. The limits of detection (LODs) of Li, V, Mn, Ni, Co, Cu, Sr, Mo, Ag, Ba, Cd, I, Hg, Pb, Bi and U in a single hair strand were in the range of 0.001–0.90 $\mu g\,g^{-1}$, whereas those of Cr and Zn were 3.4 and 5.1 $\mu g\,g^{-1}$, respectively. The proposed quantification strategy using on-line solution-based calibration in LA-ICP-MS was applied for biomonitoring (the spatial resolved distribution analysis) of essential and toxic metals and iodine in human hair and mouse hair.

1. Introduction

Analysis of body fluids, hair, nail and other biological tissues for essential and toxic metals is of increasing importance in studies related especially to medicine, forensic, archaeology and nutrition. Metals at trace concentration levels have been quite often determined in the bulk of samples of biological materials after their homogenization and acid digestion using inductively coupled plasma mass spectrometry (ICP-MS) [1]. However, this analytical approach may not provide enough information because it ignores the spatial distribution of metals in the analyzed specimens. For imaging of metals on biological samples or on tissue sections, secondary ion mass spectrometry (SIMS) [2] and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [1] are the most common sensitive mass spectrometric techniques. SIMS

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can directly produce spatial resolved ion images of metals [3] and organic compounds [4] in thin tissue sections with a lateral resolution in the low μm and sub-μm range. The main drawbacks of SIMS are huge matrix effects and a high formation rate of polyatomic ions that make the quantification of analytical data difficult. Due to significantly lower matrix effects and lower formation rate of polyatomic ions, quantification of metal ions using LA-ICP-MS is relatively simple if suitable matrix-matched standard reference materials are available. However, the quantification of analytical data using LA-ICP-MS can be difficult if adequate matrix-matched standard reference materials are not available. Therefore, matrix-matched laboratory standards have been prepared and employed for calibration of LA-ICP-MS [5,6].

In the last years, LA-ICP-MS has been established as a suitable technique for quantitative imaging of metals in biological tissues, which has already been demonstrated in several studies [5–13].

Several quantification strategies have been developed for element distribution analysis in human hair using LA-ICP-MS, such as the use of certified reference materials (CRM) or the preparation of matrix-matched laboratory standards [9]. Certified human hair (in powder form) pressed into solid flat pellets [10,14] or pressed on carbon tabs [11] has been applied to obtain the calibration curve, whereas strands of the hair sample were glued on a glass slide [15] or attached to a two side tape and directly ablated [11]. However, when hair in the powder form is used for calibration the precision of the calibration curve may be low because of the highly variable ablation/sampling process [16]. In another approach [17], single hair strands with known concentration of As (of people from an area contaminated with the toxic metalloid) were used to obtain a calibration curve. In that case, hair strands of the standards and samples were simply mounted on tape and ablated. A different strategy was used by other authors [9] for quantification of Pt in hair. Standards consisting of Pt-enriched hair strands (prepared in the laboratory) were used for calibration in order to quantify the concentration of Pt along the hair of a patient who had been treated with cisplatin. The thiol and amino groups present in protein are the main binding sites for the covalent attachment of metals in the hair, enriched and used as standard for calibration. However, not all elements can do it, and their enrichment in the hair can be achieved just by adsorption or deposition.

To compensate for density and thickness differences throughout the analyzed section as well as interference correction, the analyte signal is usually normalized to an internal standard element, which needs to be homogeneously distributed in the sample matrix. In the case of hair, sulphur is recommended due to its presence in several amino acids such as cysteine, methionine and cysteic acid in the hair. The ^{34}S isotope has preferentially been used in LA-ICP-MS [9,10,14–16] for standardization.

An attractive calibration strategy is the solution-based one in which the dry aerosol generated by laser ablation of the sample is combined with the aerosol generated by solution nebulization of an aqueous standard [10,18–20]. Calibration has been carried out by passing the aerosol produced in ultrasonic nebulizer (USN) through laser ablation (LA) chamber or by passing the aerosol produced in the LA chamber through the spray chamber of the USN [18], or by directly coupling of micro-flow nebulizer [19] or USN [10] with the LA chamber. A bulb positioned between the gas flow from the LA and from the nebulizer has been used as a mixing tool [21], or a Y or T connector [22,23] has been employed to combine both gas flows before introduction into the ion source of ICP-MS. In another approach a self-aspirating micro-flow nebulizer and a cyclonic spray chamber admixed to the LA-aerosol transport tube right in front of the ICP-MS spectrometer [24] has been used.

In the present study we propose a solution-based calibration method using a dual flow of carrier gas directly mixed in the injector tube. The dry aerosol generated by laser ablation of biological sample and that produced by pneumatic nebulization (PN) are carried by two different argon flows and introduced separately in the injector tube through two different apertures in the torch. By mixing both aerosols inside the injector tube it is expected that the solution-based calibration can be more easily performed because of the possibility of using a wide variety of nebulizers. This approach has not been used so far. Hair with known analyte concentration is used to correct for the differences between sampling rate and aerosol transport efficiency among ICP-MS and LA-ICP-MS. The pneumatic nebulizer chosen has a desolvation system that improves sensitivity and reduces polyatomic ions formation.

2. Experimental

2.1. Instrumentation

For the experiments 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). For solution introduction into the plasma a high-efficiency nebulizer ESI APEX-Q (ESI, Omaha, NE, USA) equipped with a PFA microconcentric nebulizer, a heated cyclonic spray chamber and a Peltier-cooled multipass condenser [1] was used. The experimental parameters of the ICP-MS measurements using the APEX-Q nebulizer with desolvator were optimized in order to obtain maximum ion (M^+) intensity and minimum intensity of oxide (MO^+) and double charge (M^{++}) ions. Then, the laser was connected to the ICP-MS spectrometer. There was the entry of two carrier gas flows in the injector tube and a compromise condition was established for the nebulizer gas. It was reduced from 0.88 to 0.50 L min^{-1} and the gas flow passing through the LA chamber was manually adjusted in order to obtain the highest M^+ intensity ($^{238}U^+$ and $^{115}In^+$ were monitored). To do so, the analyte was continuously introduced into the plasma by pneumatic nebulization using the APEX-Q nebulizer. The carrier gas passing through the LA chamber was adjusted and fixed using a mass flow controller (MKS PR 3000). Fig. 1 shows the schematic of the system used, while the main operational conditions are summarized in Table 1.

2.2. Reagents

Supra-pure nitric acid, HCl and H_2O_2 from Merck were used after a further purification of the acids by sub-boiling distilla-

Table 1
Optimized experimental conditions for solution-based calibration of LA-ICP-MS for single hair analysis.

ICP-MS (X Series 2)	
Rf-power, W	1400
Carrier gas, L min^{-1}	0.88 (nebulizer gas + LA carrier gas)
Analyte ions monitored	$^{7}Li^+$, $^{23}Na^+$, $^{25}Mg^+$, $^{27}Al^+$, $^{34}S^+$, $^{39}K^+$, $^{51}V^+$, $^{53}Cr^+$, $^{55}Mn^+$, $^{57}Fe^+$, $^{58}Ni^+$, $^{59}Co^+$, $^{63}Cu^+$, $^{65}Cu^+$, $^{64}Zn^+$, $^{66}Zn^+$, $^{85}Rb^+$, $^{98}Mo^+$, $^{107}Ag^+$, $^{111}Cd^+$, $^{127}I^+$, $^{202}Hg^+$, $^{137}Ba^+$, $^{208}Pb^+$, $^{88}Sr^+$, $^{205}Tl^+$, $^{208}Pb^+$, $^{209}Bi^+$, $^{238}U^+$
Dwell time, ms	100
Laser ablation	
Method	Single line scan
Repetition frequency, Hz	20
Spot size, μm	300
Scanning speed, μm s^{-1}	30
Pulse energy, mJ	0.089
APEX nebulizer	
Sample uptake rate, mL min^{-1}	0.7
Heater temperature, °C	140
Cooler temperature, °C	2

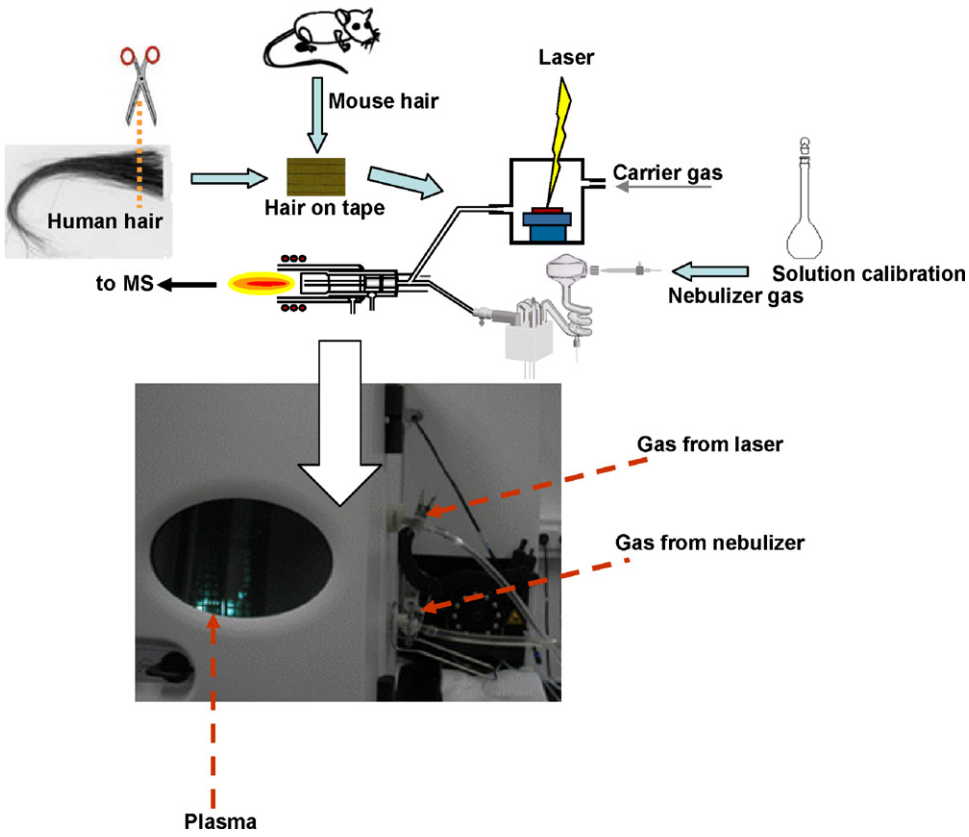

Fig. 1. Workflow of hair analysis by LA-ICP-MS using solution-based calibration, coupling of laser and pneumatic nebulizer to torch and photograph showing the two gas entrances into the spectrometer. Note that a special ICP torch and injector tube with two apertures are used.

tion. All dilutions were made with high purity deionised water (18.2 MΩ cm), obtained from a Milli-Q system. Calibration solutions in 2% (v/v) HNO_3 were prepared from serial dilutions of a monoelement standard solutions (Merck CertiPrep). Acetone (from Merck) was used for hair washing.

2.3. Samples and sample preparation

Hair samples provided by two healthy volunteers from two different countries (Brazil and Thailand), and one mouse hair sample 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 water, dried at room temperature and analyzed (Fig. 2(b)). For the mouse, hair strands were just pulled out and directly washed and dried the same way as human hair. Additionally, hair of a volunteer person was used in order to correct the difference of elemental sensitivities among ICP-MS and LA-ICP-MS (the sequence of analysis is summarized in Fig. 2(a)). This sample hair was taken from the scalp, rinsed with acetone, twice with Milli-Q water and left in contact with 10 mL of a multielement aqueous solution containing 30 mg L^{-1} of Li, Na, Mg, K, Al, V, Cr, Mn, Fe, Ni, Co, Cu, Sr, Mo, Co, Ag, Cd, I, Ba, Hg, Pb, Tl, Bi and U for a period of 24 h. Then, the solution was removed and the hair was left to dry at room temperature.

Three 50 mg-aliquots of the enriched hair were microwave-digested (Microwave Accelerated Reaction Systems, MARS-5, CEM Microwave Technology Ltd.), using 500 μL HNO_3, 300 μL HCl and 200 μL H_2O_2. Digestion of hair was performed with the following heating program: 150 W for 10 min, cooling for 2 min, 300 W for 10 min and cooling for 30 min. The digested sample was then transferred to graduated polypropylene vials and made up to 15 mL with water. When necessary, the hair solution was further diluted with 2% (v/v) HNO_3. The analyte concentration in the hair solution was determined using ICP-MS.

Strands of the human hair samples were separated and sections of about 2 cm long were cut. These 2 cm-human hair sections and mouse hair were mounted (one by one in parallel) on two-side tape fixed on the sample holder of the LA chamber and inserted into the LA chamber (Fig. 1). One part of one of the human hair samples was digested as above described and employed to investigate the total trace elements contents using ICP-MS.

2.4. Calibration strategy and sample analysis

The element concentrations in the hair were determined by LA-ICP-MS using solution-based calibration. Calibration curves were obtained by using pneumatic nebulization (PN) of standard solutions and LA of hair strands simultaneously in order to arrange matrix-matching. While a human hair strand was ablated the calibration solution or 2% (v/v) HNO_3 was nebulized and both aerosols introduced in the injector tube (Fig. 1). The solution-based calibration was performed using 5–6 calibration solutions, which were prepared in 2% (v/v) HNO_3. The element concentrations in standard solutions for calibration ranged from 0.2 to 4.0 μg L^{-1}, with the exception of K, Mg and Na; the calibration curve of these elements were in the range of 2.0–20 μg L^{-1}. The ratios of different analyte ion intensities to that of $^{34}S^{+}$ intensity were plotted as a function of the solutions calibration concentrations. The measured time-dependent ion intensity raw data of analytes were uploaded into the Excel software for further data analysis. Correction factors were calculated for each analyte using the ratio of the concentration found using ICP-MS to concentration found using LA-ICP-MS.

The analyte concentration measured by LA-ICP-MS along the hair strands was determined through the linear regression equation of the calibration curve, which was obtained *via* solution-based

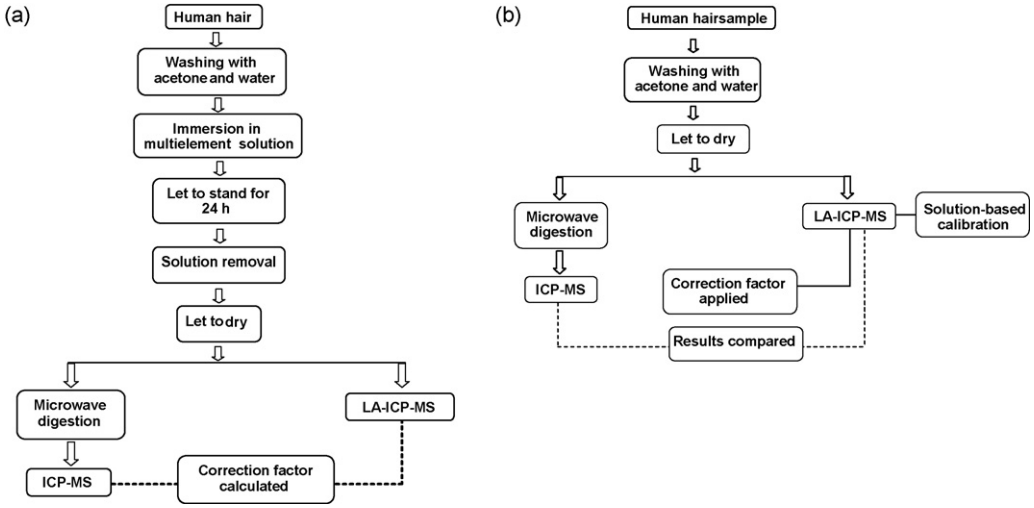

Fig. 2. Experimental workflow of the hair analysis using LA-ICP-MS: (a) enriched hair is analyzed in order to correct the differences in sensitivity among ICP-MS and LA-ICP-MS and (b) a human hair sample is analyzed by LA-ICP-MS and ICP-MS in order to check the accuracy of the LA-ICP-MS method.

calibration. Since the sensitivity of ICP-MS was higher than that of LA-ICP-MS, the element concentration in hair measured by LA-ICP-MS was multiplied by the correction factor calculated for each element. The time domain data were converted to distance by multiplying the scan speed and time used during laser ablation.

The limits of detection (LODs) were calculated by ablating 10 different parts of the two-side tape used, in parallel with nebulization of 2% (v/v) HNO_3. The average signal + 3 s (s is the standard deviation of the measurements) was then transformed in concentration by using the linear regression equation of the calibration curve.

3. Results and discussion

3.1. Solution-based calibration and limits of detection

The pneumatic nebulizer used in the present investigation provides aerosol desolvation and high sensitivity [25]. Compared with the dry aerosol generated by laser ablation the aerosol produced by conventional pneumatic nebulization is wet. This results in changes in plasma temperature, analyte ion sensitivity and polyatomic ion formation. In the present study, we observed that the ion sensitivity was in general about 3 times higher when the ablated aerosol was analyzed under wet plasma conditions, compared to a dry aerosol introduced in the plasma. This indicates that, in doing the calibration with aqueous standards, the dry aerosol of the ablated sample must be introduced into the plasma in conjunction with wet aerosol produced by nebulization (of the same solvent used for the aqueous standards).

To obtain quantitative data in a solution-based calibration, different element sensitivity in ICP-MS and LA-ICP-MS must be considered. Transport efficiency and sample amount introduced into the plasma is different for LA-ICP-MS and ICP-MS; the difference varies with the type of material analyzed, instrumental parameters and the experimental arrangement used. For example, in the case of a 30 μm-thick brain homogenate, we observed the signal per 1 ng g^{-1} of Cu in the ablated solid was 30,000 lower than that in nebulized aqueous solution.

Becker et al. [26] proposed the insertion of a micronebulizer directly into a cooled-laser ablation chamber for calibration of LA-ICP-MS using aqueous standard solution. The wet aerosol produced by nebulization and that from the ablated material (thin section of human brain) were mixed in the LA chamber and a mono flow of the carrier gas was used to transport them to the plasma. For the correction of different element sensitivities in ICP-MS and LA-ICP-MS a correction factor (ratio of concentration of internal standard element homogeneously distributed in the sample determined by solution-based calibration by LA-ICP-MS/true concentration of internal standard element in the sample) was used. A similar experimental arrangement for on-line isotope dilution was employed by Pickhardt et al. [19]. Differences of sensitivity in LA-ICP-MS and ICP-MS were corrected by applying a correction factor defined as the true concentration of internal standard element in the sample (certified apple leaves and glass) divided by the concentration determined *via* on-line isotope dilution in LA-ICP-MS. In the present study, the correction factor was obtained by dividing the concentration of the analyte measured by ICP-MS by that found by LA-ICP-MS. The element concentrations determined in the hair samples (measured *via* calibration curves obtained by use of standard solutions) were then multiplied by the respective correction factor, to take into account the different sensitivities in LA-ICP-MS and ICP-MS. In the case of hair, the main difference in sensitivity observed between ICP-MS and LA-ICP-MS is mainly due to the lower amount of sample introduced into the inductively coupled plasma using laser ablation. There is a much greater signal contribution from the aqueous standards than from the laser ablated aerosol.

The linear regression coefficient of the calibration (R) curves and the LODs experimentally determined using solution-based calibration and LA-ICP-MS are summarized in Table 2. It shows that the values of the linear correlation coefficient are typically between 0.97 and 0.999, being those of Na, Mg, Al and K the worst ones. The quantification of these in nature abundant metals at low concentration levels is difficult in ICP-MS, because of the relatively high signal of blank and/or interference from polyatomic ions on the most abundant isotopes. Still, it is possible to quantify these elements in hair by LA-ICP-MS according to the proposed method. According to Table 2, the LODs of Na, Mg, Al and Fe are much higher than those of other elements. The main reason for the elevated LODs of these elements was the contamination of the tape used for fixing the hair.

3.2. Elements concentration in single human hair and mouse hair samples

The developed method was employed for biomonitoring (distribution analysis) of essential and toxic metals and iodine in several hair samples. The concentrations of several elements along the hair

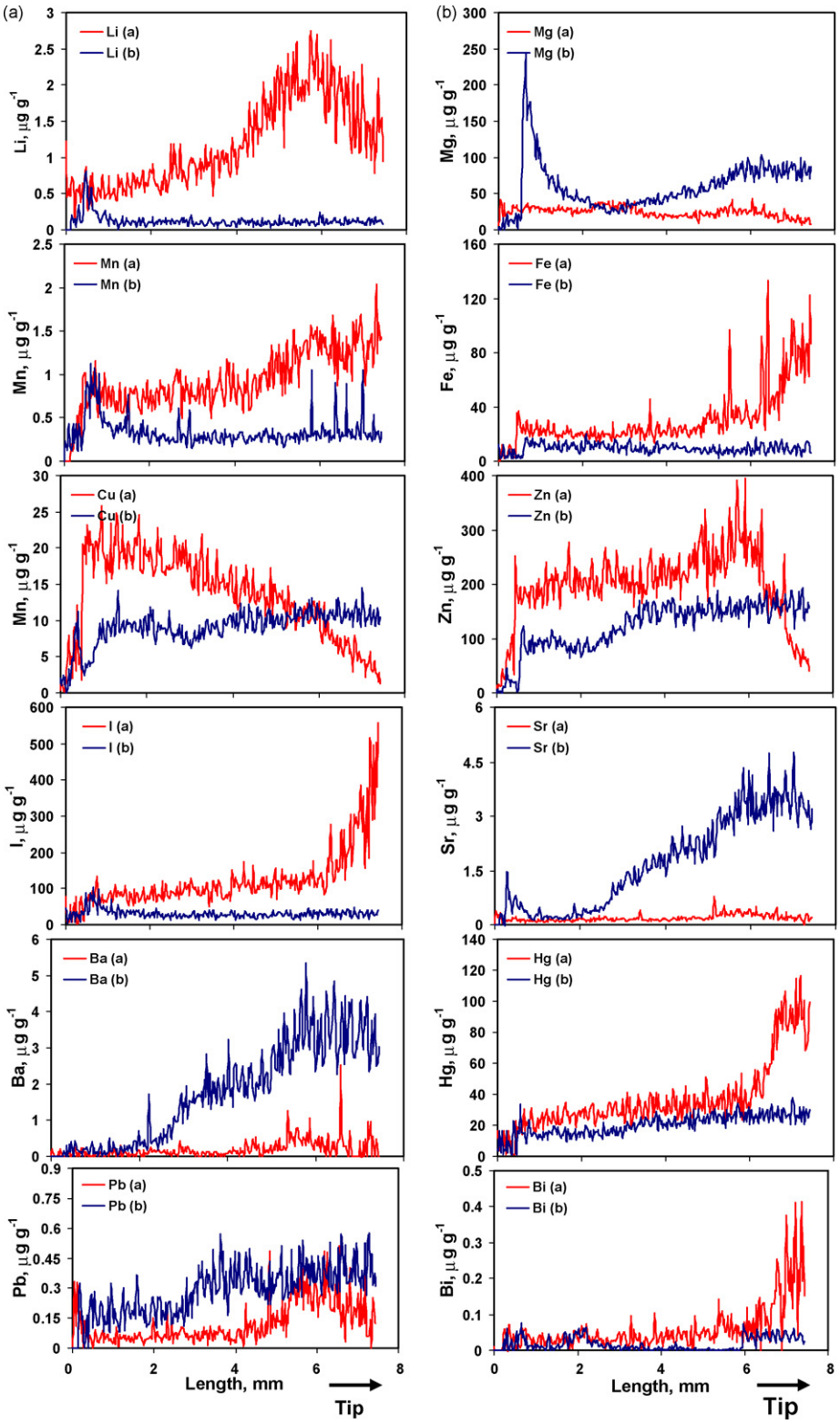

Fig. 3. Concentration of elements along of hair strands of individuals from different countries (a) and (b). Solution-based calibration was used for quantification (see the text for more details).

strands that constituted the analyzed samples are shown in Fig. 3 (for human hair) and Fig. 4 (for mouse hair). The signal intensity of each element was normalized to ($^{34}S^{+}$) as internal standard ($^{34}S^{+}$) to compensate the hair heterogeneity, mainly with respect to thickness. According to Fig. 3, the hairs of people from different countries can be distinguished by the profile of the element concentration. The variation of element concentrations along the hair and the differences among the samples can be attributed to the change of environment (people have moved from their countries of origin), the type of food and drinking water intake. Both hair samples show a quite different distribution pattern. For example, sample (a) was taken from a person who had usually eaten fish (contaminated with

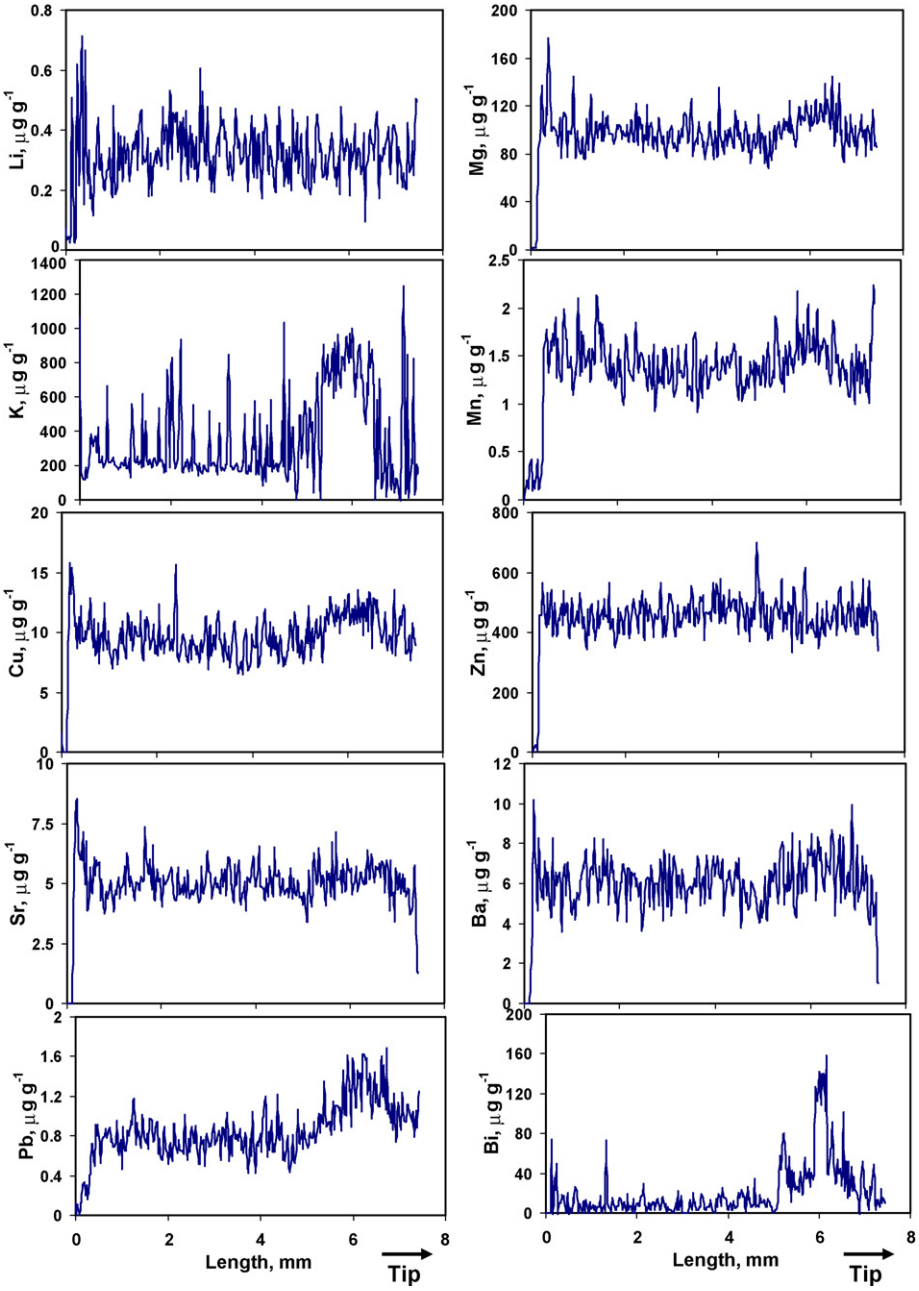

Fig. 4. Concentration of elements along of hair of mouse. Solution-based calibration was used for quantification (see the text for more details).

Hg, which is detected by LA-ICP-MS with a serious high Hg concentration (up to 120 $\mu g\,g^{-1}$ in human hair)) when living in the country of origin. This person had moved 4 weeks before the hair sampling; this can explain why the concentration of Hg is higher in the tip of the hair. A correlation of the significant Hg enrichment in the tip of hair with Fe and I was found, whereas Zn and Cu in this part of hair were depleted. Pb at low concentration range was detected in both human hair samples [(a) and (b)] with different distribution pattern. For human hair sample (b) an enrichment of Ba and Sr with length was observed.

The mouse (whisker) hair was analyzed with the purpose to verify the applicability of the method and also find the possibility of using hair for biomonitoring of metals in studies involving mice. It is expected that if a mouse is exposed to a given environment, drug and food, the target elements absorbed by its organism will be reflected in the hair. According to Fig. 4, the variation of element concentrations along the mouse hair (like a local enrichment of Pb and Bi in the older part of mouse hair) can be observed. The enrichment was accidental because the mouse was not purposely intoxicated with these elements. These results of element distribution analysis by LA-ICP-MS indicate the possibility to apply the new solution-based calibration method as an easy quantification strategy of biomonitoring of metal distribution in single hair strands to detect possible contamination (intoxication) or treatment with metal-containing drugs.

In order to check the accuracy of the developed LA-ICP-MS method for element quantification in hair, one of the human hair samples was digested in a microwave oven and the analytes measured by ICP-MS. The same section along the hair was analyzed by both ICP-MS and LA-ICP-MS (the concentration along the hair strand was averaged). Good agreement was found between the results obtained by LA-ICP-MS and ICP-MS for the same elements,

Table 2
Linear regression equation and linear correlation coefficient (R) of calibration curves, and limit of detection (LOD) using solution-based calibration and LA-ICP-MS; x is in ng g^{-1} and the analyte signal was normalized to $^{34}S^{+}$ signal in order to obtain the calibration curves.

Analyte	Linear regression equation	R	LOD μg g^{-1}
^{7}Li	$y = 0.0877x + 0.0029$	0.9999	0.091
^{23}Na	$y = 0.1231x + 0.6865$	0.9746	34
^{25}Mg	$y = 0.0165x + 0.0191$	0.9798	67
^{27}Al	$y = 0.107x + 0.1034$	0.9916	37
^{39}K	$y = 0.0718x + 0.8366$	0.9817	182
^{51}V	$y = 0.1186x + 0.0034$	0.9998	0.11
^{53}Cr	$y = 0.0128x + 0.0008$	0.9999	3.4
^{55}Mn	$y = 0.2028x + 0.0156$	0.9994	0.051
^{57}Fe	$y = 0.0038x + 0.004$	0.9962	19
^{58}Ni	$y = 0.0559x + 0.0086$	0.9995	0.90
^{59}Co	$y = 0.124x + 0.0044$	0.9995	0.056
^{63}Cu	$y = 0.0656x + 0.1189$	0.9961	0.18
^{65}Cu	$y = 0.0316x + 0.0567$	0.9997	0.19
^{64}Zn	$y = 0.0366x + 0.4411$	0.9963	15
^{66}Zn	$y = 0.0220x + 0.2631$	0.9985	5.1
^{88}Sr	$y = 0.2598x + 0.0245$	0.9998	0.086
^{98}Mo	$y = 0.036x + 0.0011$	0.9998	0.027
^{107}Ag	$y = 0.0115x - 0.0004$	0.9953	0.005
^{111}Cd	$y = 0.0307x + 0.0007$	0.9988	0.048
^{127}I	$y = 0.0013x + 0.004$	0.9951	0.12
^{137}Ba	$y = 0.0432x + 0.0054$	0.9998	0.13
^{202}Hg	$y = 0.0036x + 0.0077$	0.9940	0.15
^{203}Tl	$y = 0.1896x + 0.0049$	0.9999	0.001
^{208}Pb	$y = 0.336x + 0.0377$	0.9997	0.043
^{209}Bi	$y = 0.5417x + 0.0037$	0.9999	0.026
^{238}U	$y = 0.769x - 0.0269$	0.9997	0.001

as shown in Table 3. The concentrations measured are also in accordance with the range quoted in the literature. The concentrations of Li and I found in one of the samples are markedly higher than the values reported. This could be due to the sort of drinking water and dietary intake by the individual (mainly addition of iodine to sodium chloride used in food). According to Table 3, several elements were not detected in hair analyzed by LA-ICP-MS, but could be measured by ICP-MS. The LODs of ICP-MS are lower due to higher elemental sensitivity, mainly because the mass of hair introduced into the plasma is higher, as previously discussed. Moreover, the standard deviation observed for LA-ICP-MS is in general larger than that observed for ICP-MS. This occurs because the element concentration varies along the hair, which is not detected in the analysis using ICP-MS.

4. Conclusions

A new analytical strategy of solution-based calibration in LA-ICP-MS to quantify the concentration of trace, minor and major elements in hair was created. This calibration by using pneumatic nebulization of standard solution and aerosol desolvation combined with laser ablation of biological sample is possible for a multitude of elements in a large concentration range. In addition, the sample throughput is high and the LODs of trace elements are from μg g^{-1} to ng g^{-1} range. It was demonstrated that the proposed method can be applied to measure the concentration of elements in different sort of hair such as human hair and mouse hair. This may facilitate researche using tests with mice because they would not be sacrificed. Sample collection would be easier and non-invasive, requiring little sample preparation (only washing) and very small amounts of sample (1–3 single hair strands). The proposed method can be employed in routine analysis, which can extend the use of hair analysis for therapy, occupational exposure, nutritional and toxicological controls but also for imaging studies of thin slices of biological tissues.

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Table 3
Element concentrations in human hair determined by ICP-MS after sample decomposition, by LA-ICP-MS directly, compared to published values. Results are the average and standard deviation of three replicates (high standard deviation are due to inhomogeneous metal distribution in hair samples). The limits of detection are summarized in Table 2. nd: non-detected.

Analyte	Human hair				
	Sample A (μg g^{-1})		Sample B (μg g^{-1})		
	ICP-MS	LA-ICP-MS	LA-ICP-MS	Published (μg g^{-1}) [27–29]	
Li	0.12 ± 0.01	0.12 ± 0.09	1.18 ± 0.61	0.005–0.046	0.006–0.46
Na	170 ± 8	296 ± 108	1640 ± 532	344 ± 31	0.04–2100
Mg	52.6 ± 7.9	60.6 ± 33.8	24.4 ± 7.1	163 ± 17	36.9 ± 35.9
Al	57.9 ± 11.6	nd	nd	0.1–191	8.49 ± 7.31
K	127 ± 11	210 ± 60	549 ± 167	146 ± 14	4–1100
V	0.28 ± 0.02	nd	nd	0.005–0.134	0.02 ± 0.02
Cr	1.92 ± 0.02	nd	nd	6.33 ± 0.68	0.03–33
Mn	0.25 ± 0.01	0.33 ± 0.16	0.98 ± 0.29	2.29 ± 30	0.62 ± 0.76
Fe	75.6 ± 8.3	nd	31.9 ± 20.3	88.2 ± 6.7	12.5 ± 5.7
Ni	12.9 ± 0.9	nd	nd	0.002–28	0.41 ± 0.55
Co	0.23 ± 0.01	nd	nd	0.071 ± 0.005	0.02 ± 0.03
Cu	12.9 ± 0.6	9.45 ± 1.85	14.1 ± 5.4	8.5–96	22.6 ± 15.6
Zn	75.1 ± 3.5	101 ± 33	207 ± 57	154 ± 3	189 ± 53
Sr	4.5 ± 0.1	3.74 ± 1.26	0.18 ± 0.09	45.7 ± 3.5	0.14–5.54
Mo	0.029 ± 0.003	nd	nd	0.021–0.165	0.03 ± 0.02
Ag	nd	nd	nd	0.025–1.96	0.26 ± 0.61
Cd	0.405 ± 0.001	nd	nd	0.010–0.356	0.17 ± 0.30
I	30.2 ± 3.3	29.9 ± 10.1	129 ± 82	0.13–3.31	0.03–33
Ba	3.5 ± 0.5	2.66 ± 0.93	0.23 ± 0.28	6.33 ± 0.68	1.99 ± 2.67
Hg	18.0 ± 1.8	21.0 ± 6.1	30.3 ± 7.6	0.07–106	1.44 ± 1.84
Tl	0.004 ± 0.000	nd	nd	0.0002–0.0016	–
Pb	0.38 ± 0.09	0.29 ± 0.12	0.12 ± 0.11	0.22–7.26	6.41 ± 3.23
Bi	0.021 ± 0.002	0.058 ± 0.062	0.018 ± 0.019	0.002–0.255	<0.03
U	0.029 ± 0.030	nd	nd	0.1–0.25	0.006–0.436

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