



Analytical proposal for trace element determination in human hair. Application to the Biscay province population, northern Spain



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ABSTRACT

The proposed methodology was applied to 114 donors aged 0–90 years old from various geographical areas of the Biscay province (northern Spain) which were characterized by differing environmental conditions and dietary habits. 22 trace elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, V and Zn) were determined by inductively coupled plasma techniques (ICP) with mass spectrometry (MS) and optical emission (OES) detections. Analytical steps were deeply discussed including pre-treatment (washing) and acid treatment (microwave system). Additionally, the pre-treated and non pre-treated human hair samples were studied by scanning electron microscope coupled to an energy dispersive X-ray spectrometer (SEM-EDX). This microscale characterization was found essential to assess the proposed human hair washing step prior to the analytical determinations.

The essential chemical elements found were Al, Ca, K, Sr, Na and Zn with concentrations higher than 100 mg kg⁻¹. Trace metals exceeding 10 mg kg⁻¹ level were Mg, Fe and Cu (Fe > Cu). Other trace metals with concentrations greater than 1 mg kg⁻¹ were, in order of abundance, Hg > Ni > Ti. The lowest concentration values were found for Mn, Pb, Cr, Cd and As as minor elements.

Results revealed that the trace metal contents generally increased with the tap water consumption and environmental conditions. Specifically, smokers showed lower metal concentration levels than nonsmokers and Hg level directly increased with the fish consumption.

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1. Introduction

Concern about the effects of environmental exposure to trace metals on human health has driven the scientific community to find reliable tools and methods for assessing the impact of emissions of toxic metals from anthropogenic activities. Biological monitoring has been extensively employed with this end in view, and blood, urine, feces, hair and nails are the biological materials most frequently analyzed to ascertain the levels of many metals [1–4]. According to this, human hair can provide a permanent record of trace and toxic elements associated with normal and abnormal metabolism as well as their assimilation from the environment than other biological matrices as blood and urine. In addition, hair is easily collected, conveniently stored, and easily treated.

A hair can be defined as a slender, thread-like outgrowth from a follicle in the skin of mammals. Composed mainly of keratin, it has three morphological regions: the cuticle, medulla, and cortex. The high affinity of hair for metals is mainly due to the presence of cystine, which makes up approximately 14% of human hair. Many metals

found in hair are bound to sulfur atoms in cystine or to sulfhydryl groups (SH) present in other amino acids [5]. Moreover, melanin pigments can bind cations by ionic interaction at physiological pH since melanins are polyanionic polymers containing negatively charged carboxyl groups and semiquinones [6]. Besides, uncharged metals, as elemental Hg, may also bind to the hydrophobic core of the melanin polymer in the hair structure [7]. All of these chemical interactions make the trace metals persistent in human hair for a long time.

Human hair has been frequently used for different purposes and in different fields of application [8–14]. However, some problems related with its use, as biomonitor of environmental pollution could appear, including the difficulties related with the interpretation of the results and the elaboration of reference values. The difficulties in establishing normal or reference ranges are due to the natural variance of hair composition as a possible consequence of age, sex, hair color, ethnical and geographical origin, dietary factors, etc. [15–18]. Apart from that, the lack of standardized methodology, including the pre-treatment procedure (i.e. washing), makes not possible to differentiate between the *exogenous* and *endogenous* sources for trace elements in human hair. *Endogenous* quantities of metals are those incorporated into the hair proteins and *exogenous* quantities are those attached by the direct

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environmental contact after the hair has been formed. In this sense, washing procedures are widely employed by laboratories to remove *exogenous* contaminants in order to obtain only the one corresponding to *endogenous* source.

An ideal washing procedure would remove only external contaminants and leave *endogenous* elements intact. However, in practice, this is very difficult to obtain and standardized washing procedures become a fundamental requirement so as to compare different experimental data from inter-laboratory studies. Moreover, analytical methodology choices can also introduce biases and variability, which can result from volatilization losses, contamination and/or interferences during analysis. In order to overcome this variability, microwave assisted digestion has been recommended as most suitable sample preparation method for standardization [19] and inductively coupled plasma-mass spectrometry (ICP-MS) and optical emission spectrometry (ICP-OES) were proven to be the best technique for ultra-trace multi-element analysis [20]. All these instrumentation upgrades resulted in improved precision, accuracy, reliability, and detection limits. The main advantage of microwave-assisted acid digestion is the small amount of mineral acids required and the low production of nitrous vapors. Furthermore, microwave systems keep blank levels low due to the employment of small volumes of reagents and it allows processing more samples per hour than conventional digestion systems. In addition, ICP techniques can simultaneously determine many elements of interest and they are free from chemical interferences and have high detection power.

In this study, new data regarding trace elements in human scalp hair samples are presented by using an analytical method based on an optimized microwave acid digestion prior to the ICP-MS and ICP-OES analyses. The survey was aimed to apply the analytical proposal for trace elements in scalp hair from inhabitants in various geographical areas of the Biscay province (northern Spain), characterized by differing environmental conditions, to test whether human hair is valuable to reflect environmental exposure and contamination from dietary habits by trace elements. In addition, various washing procedures used in the sample pre-treatment process have been examined and discussed in order to establish a standardized method capable of explaining the variability and accuracy of the analytical data. The washing step was finally implemented from the experimental data obtained by using ICP techniques and microscope spectrometry (SEM-EDX) in quantitative and semi-quantitative analyses, respectively. In addition, acid digestion of human hair samples was also optimized to obtain the maximum recovery of the trace metals by considering the more significant variables in a microwave system.

2. Materials and methods

2.1. Reagents and solutions

All reagents were of analytical-reagent grade and ultrapure water (18.2 M Ω cm at 25 °C) obtained from a Milli-Q® Element A10 system (Millipore™, Bedford, USA) was used throughout the work. Concentrated nitric acid (69%, Tracepur) was obtained from Merck (Darmstadt, Germany), and checked for possible trace metal contamination. The volumetric glassware was grade A and was calibrated at laboratory temperature. All glassware and plastic materials used were previously soaked for 24 h in 5.0% v/v nitric acid, washed with distilled water and finally rinsed with ultrapure water, dried and stored.

Working standard solutions of Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, V and Zn were prepared immediately prior to their use, by stepwise dilution of certified standard multi-element solution (100 mg L⁻¹) (Merck, Darmstadt, Germany) with HNO₃ 1.0% v/v. Hg standard solutions were prepared from the mono-element 1000 mg L⁻¹ solution (Merck, Darmstadt, Germany). Additionally, a 10 mg L⁻¹ multi-element standard solution (Sc, Y, Rh, Ho) from Inorganic Ventures (Equilab, Madrid, Spain) was also used as internal standard in direct ICP-MS analysis.

For the accuracy of methodology, the certified reference material (CRM) of human hair IAEA-086 (LGC Standards, Barcelona, Spain) was used.

2.2. Apparatus

The qualitative analysis was carried out by scanning electron microscope (SEM) using an EVO40 scanning electron microscope (Carl Zeiss STS, Germany) coupled to an X-Max energy-dispersive X-ray spectrometer (EDX, Oxford Instruments, Abingdon, Oxfordshire, UK). First of all, samples were coated with gold with an Emitech K550× sputter-coater equipped with a film thickness monitor (Quorum Technologies LTD, UK). The coated specimens were observed in the scanning electron microscope to obtain morphological information in order to evaluate the presence of particulate matter and/or structural damages in hair treated under different conditions. For that purpose, experimental conditions were: high vacuum mode, wolfram hot electron emission and acceleration voltage of 30 kV. Moreover, the elemental composition of some particles was measured by employing EDX analysis. In this case, probe current varying between 180 pA and 400 pA, work distance of 8.5 mm, X-ray acquisition time of 250 s and the same conditions described above were used.

The quantitative analysis of trace metals was performed by using ICP-MS and ICP-OES. Operating conditions are shown in Table 1. ICP-MS (7700×, Agilent Technologies, Palo Alto, USA) was used for trace metal determinations using a MicroMist micro-uptake glass concentric nebulizer (Glass Expansion, West Melbourne, Victoria, Australia). In order to reduce MO⁺ formation in the plasma, the spray chamber was peltier cooled at 2 °C. A standard quartz torch with 2.5 mm internal diameter injector was used. Finally, standard nickel cones (sample and skimmer) were used. The optimization of the ICP-MS conditions was achieved by adjusting the torch position and tuning for reducing oxide and doubly charged ion formation with a standard tuning solution containing 1.0 μg L⁻¹ of ⁷Li, ²⁴Mg, ⁵⁹Co, ⁸⁹Y, ¹⁴⁰Ce and ²⁰⁵Tl in 1.0% HNO₃. This equipment includes a collision cell (He gas, ORS3 system, Agilent Technologies©) for discriminate spectral interferences with high performance for all the trace metals considered in here. ICP-OES (Horiba Jobin Yvon, Activa) was used with a quartz Meinhard concentric nebulizer, a Scott-type spray chamber and a standard quartz sheath connection between the spray chamber and the torch. Daily, the ICP-OES was checked by using a 5.0 mg L⁻¹ standard solution containing Al, Cd, K, Mg and Zn. The plasma robustness (intensity ratio for Mg 280.270 and 285.213 lines) was verified to be higher than 6.0. The peak resolution was checked by using Cd 226.502 and K 766.490 lines (peak width lower than 12 and 22 pm for Cd and K, respectively). Finally, the stability of the system was determined by using the following lines: Al 396.152, Cd 226.502, Pb 220.353 and K 766.490 nm to be % RSD lower than 3.0% in two hour measurements.

The microwave-assisted digestion was carried out in a close microwave device Mars 5 (CEM, Vertex, Barcelona, Spain) equipped with 8–24 teflon vessels and temperature controllers.

2.3. Sample collection and pre-treatment

Human hair samples were collected from 114 donors, 0–90 years old, of both genders living in different environmental contexts and habits of the Biscay province (northern Spain). Biscay province (43°15'00"N 2°59'00"O) has a powerful steel industry, chemical processing and refinery. Moreover, the capital of the province is Bilbao City along which including its metropolitan area account for about 1.2 million people.

A questionnaire was administered to them in order to collect details concerning physical data, ethnic origin, dietary habit, gender and age. The details related to donor's identity, residence, health condition, smoking, alcohol drinking and fish consumption were also recorded.

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