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Trace Elements Determination in Human Scalp Hair by Inductively Coupled Plasma Mass Spectrometry and Its Application to Health Status Assessment

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ABSTRACT

In this paper, elements including Al, Cr, Mn, Fe, Cu, Zn, As, Se, Cd and Pb in scalp hair samples from five male adults in the age of 50 – 55 were accurately quantified by inductively coupled plasma mass spectrometry (ICP-MS). The ICP-MS quantification results were analyzed according to the recommendation from the Trace Element Research Council of China. It was found that the contents of Cr, As, Cd, and Pb were within the permitted ranges, while the concentrations of Mn, Fe, and Cu differentiated individually. It was worth noting that Fe contents in two samples were over 200 μg·g^{-1}, which were higher than the highest permitted value of 130 μg·g^{-1}. Interestingly, these two specimens also exhibited relatively higher concentrations of Mn and Cu. For Se, all five specimens showed slightly higher than the upper permitted value of 0.6 μg·g^{-1}. But Al far exceeded the allowed 7.0 μg·g^{-1}, yielding a ratio up to approximately 26-fold. It was also found that the content of Zn in one sample was out of the permitted range, giving about 13.5% lower than the least required concentration. It can thus be deduced that the participants having an accumulation of Mn, Fe, Cu, Se or Al were suggested to control the daily ingestion of these elements from foodstuff and/or medicine, while the participant showing Zn deficiency was recommended to take a reasonable amount of Zn supplements. From this study, all these participants were highly recommended to take a detailed check-up for the further health status assessment.

Keywords: Human scalp hair, trace element quantification, health status evaluation, acidic digestion, ICP-MS.

INTRODUCTION

Trace elements in biochemistry are known as the dietary minerals required in minute amounts for proper growth, development, and physiology of organs [1]. The inorganic trace elements in human bodies have diverse roles in a range of biological activities, such as immune system effectiveness, tissue development/maintenance, and cell metabolic rate optimization [2, 3].

Among various inorganic trace elements, some metal elements such as Zn, Cu, Fe, Mn, Cr and Se exhibit unique physiological properties and indispensable for human, which are called essential

and/or nutrition elements [4, 5]. For example, element Zn usually functions as a cofactor for certain enzymes involved in metabolism and cell growth [6, 7]. It is also known that element Cu is not only a pivotal constituent in a series of enzymes, but also helpful for bone's growth/formation, and the iron absorption/transferring [8, 9]. Similarly, the element Cr in form of Cr (III) can increase enzyme activities, and show important functions in carbohydrate metabolism, stimulation of fatty acid, and cholesterol synthesis [10, 11]. However, some other trace elements involving As, Cd and Pb are regarded as xenobiotics due to no clear body functions and well-known harmful effects at trace levels [12-14]. Such elements exert biological toxicities causing health problems from neural to genetic systems [15]. For instance, Pb was shown to result in behavior abnormalities, and learning/hearing disorders [14], while Cd can inhibit the repairs of DNA mismatch [14, 16]. Also, the element As was found to correlates to hyperpigmentation, keratosis, various types of cancer and vascular diseases [12, 13, 17]. The element Al, which can cross the blood-brain barrier and accumulate into glial and neuronal cells [18], is highly neurotoxic and thus proposed to be involved in Parkinsonism, dementia, and Alzheimer's disease [19]. In fact, the excessive essential/nutrition trace elements can become toxic for body health and might cause fatal diseases [20-22]. On the other side, the deficiency of essential/nutrition trace elements could make the involving biological functions impaired and result in severe malfunctions [23, 24]. Islam et al. [25] comprehensively summarized the relationships between trace elements and human health. Hence, the concentration level evaluation of trace elements is of importance in both the identification of the excess or deficiency of specific nutrients and the prediction of the undesired exposure to contaminants from environment.

Trace element concentration levels in human beings are usually assessed using blood and urine. However, both blood and urine samples reflect the xenobiotic exposure for a very short or limited period, and the analytical results from such matrices fluctuate with any changes in physiological or environmental condition. Human hair, which grows at a rate of approximately 1 cm per month and exhibits high affinity to most inorganic elements, has been proved to provide a more permanent and historic record of trace elements assimilated from human medium [26]. Furthermore, hair sample is characterized by non-invasive collection, convenient storage, and less hazardous handling [27]. The hair matrix has thus become an attractive biological material in studies related to pollutant exposure [28], medicine [29], forensics [30], archaeology [31], nutrition [32], and effect of lifestyle on human health [33], etc. For example, scalp hair as an efficient biomarker was used in the monitoring of heavy metals on large cohorts [34], occupational exposure determination [35] and the exposure observation of local habitants in polluted areas [36-38]. Many analytical approaches were employed to determine trace elements in human hair samples. Atomic absorption spectrophotometry (AAS) was the most frequently utilized technique in trace element determination of human hair samples [39-43]. Other techniques including inductively coupled plasma atomic emission spectrometry (ICP-AES) [44-46], atomic fluorescence spectrometry [47], spectrofluorimetric [48], anodic stripping voltammetry [49], particle-induced X-ray emission [50] and X-ray fluorescence [51] were also developed for the quantification of trace elements in hair samples. ICP mass spectrometry (ICP-MS) is a sophisticated technique for multi-element determination at trace levels, showing merits of low detection limits, high sensitivities, wide dynamic ranges, and excellent element resolution [52]. By using ICP-MS technique, trace elements in human hair samples were studied and applied to therapeutic treatment identification [53], health risk

assessment in mining affected area [36, 44, 54]/electronic waste recycling area [55], long-term safety monitoring of environmental exposure to pollutants [56, 57], and screening tests in different diseases [58].

In this work, human scalp hair sample as a biomarker for health risk assessment was evaluated *via* trace element concentration levels. The scalp hair samples from five male adults between 50 and 55 years old were decomposed by a low-pressure closed wet digestion pattern using concentrated HNO_3. Ten trace elements including Al, Cr, Mn, Fe, Cu, Zn, As, Se, Cd, and Pb, in the scalp hair samples were then quantified by ICP-MS. The potential health risks of the participants were discussed in detail according to the permitted values set by the Trace Element Research Council of China (TERCC).

EXPERIMENTAL

Reagents and Standard Solutions

High purity acids and ultra-pure water were used throughout in this work. To remove metallic or cationic impurities, the commercially available acid of HNO_3 (68% v/v, AR grade) was treated by a sub-boiling distillation system (Savillex DST-1000-PFA, USA) using a middle mode prior to usage. Ultra-pure water with a resistivity of 18.2 MΩ·cm was obtained by passing deionized water through a Milli-Q water purification system (Millipore, Bedford, MA, USA). Here, five solutions containing elements Al, Cr, Mn, Fe, Cu, Zn, As, Se, Cd, and Pb (5, 20, 50, 80 and 100 $ng \cdot g^{-1}$) in 2% HNO_3 (v/v), which were used as the external calibrators, were prepared by gravimetric dilution from a Multi-element Calibration Standard solution of 10 $\mu g \cdot g^{-1}$ (Agilent Technologies, Tokyo, Japan).

Instrumental Apparatus

In this work, the element quantification was carried out on a Thermofisher Scientific X series ICP-MS instrument (Waltham, MA, USA). The configuration of this ICP-MS was described in detail in our previous work [63]. The ICP-MS was optimized daily by mass calibration to obtain stable and relative maximum signal intensities for elements Li, Co, In, and U by using a tuning solution of 10 $ng \cdot mL^{-1}$. Before optimization, the mass resolution was adjusted to achieve a 10% peak width of 0.7 – 0.8 amu. During the optimization, the ratios for oxide formation, hydroxide formation and doubly charged species were controlled less than 2.0%. The details of parameter optimization were discussed below. Before element determination, the pulse/analog factors of the detector were calibrated using a multi-element tuning solution of 500 $ng \cdot mL^{-1}$. A 10 $ng \cdot mL^{-1}$ of Rh solution, which was prepared using 1.0 $mg \cdot mL^{-1}$ of single-element standard solution (the National Institute of Standards and Technology, Beijing, China), was aspirated online as an internal standard element to correct any signal drift from the organic matrix effect of hair samples. In addition, the quantification quality was controlled by repeatedly analyzing a standard solution using an SSB (standard-sample bracketing) strategy. The typical operating conditions and optimum instrumental parameters were summarized in TABLE 1.

Table 1: Operating parameters for the utilized Thermofisher X series ICP-MS instrument. [1]

Instrument parameters	Operating conditions	Instrument parameters	Operating conditions
Spray chamber	Cone chamber at 2 °C	Extraction*	−561 v

Sample/skimmer cone	Nickle/Xi, 1.1/0.75 mm	Focus*	22 v
Scan type	Peak jumping	Lens 1*	−10.0 v
Output power	1250 W	Lens 2*	−39.2 v
Nebulizer inserting depth*	3.0 cm	Lens 3*	−182.7 v
Plasma Ar*	14.5 L·min^{-1}	D1*	−36.5 v
Auxiliary Ar*	0.80 L·min^{-1}	D2*	−145 v
Nebulizer Ar*	0.80 L·min^{-1}	DA*	−35.3 v
Sampling depth*	100	Pole bias*	2.8 v
Dwell time*	10 ms	Hexapole*	2.0 v
Sweeps*	20	Horizontal position*	70
Sample introduction rate*	1.0 L·min^{-1}	Vertical position*	400
Mass resolution	Standard	Analog voltage*	1950 v
Detector mode	Dual	Pulse counting voltage*	2670 v

[1] The parameters marked with a star are the default values that can be optimized daily.

Hair Sample Collection and Handling

Here, the study associated to hair sample collection and analysis were performed according to the legal provisions and rules of the Hospital of Chang'an University. Informed consent was also obtained from all the individual participants involved in this study. Additionally, the experimental protocol of the present investigation including hair sample digestion and application of trace elements to health status assessment was approved by the Local Ethics Committee.

Five local male residents, who were in the age of 50 – 55, voluntarily joined this study and declared that there had been no usage of hairspray and hair dyes at least one year before sampling. The collected hair samples, approximately 2.0 cm, were taken from the occipital region of the participants. After sampling, the hair samples were stored in air-tight sealed plastic bags and transferred to a thousand-clean room in the Laboratory of Mineralization and Dynamics, Chang'an University. The collected hair samples were thoroughly washed with detergent and subsequent ultra-pure water to eliminate the absorbed mud and dust particles, and then cut into 1 – 2 mm by a scissor which is made of polytetrafluoroethylene (PTFE) to avoid potential elemental contamination. Thereafter, the hair samples were rinsed with ultra-pure water and dried at 80 °C in an oven for 4 h before subsequent digestion.

In this work, the hair samples were directly decomposed by using concentrated HNO_3 via a low-pressure acidic digestion method. In brief, the samples with weight of about 0.70 g were transferred into PTFE vessels, and the concentrated HNO_3 with a volume of 5 mL was carefully added. After been continually heated at 125 °C for 15 min, the samples in the sealed vessels were evaporated until incipient dryness. Then, the samples were fortified with 2.0 mL of ultra-pure water and heated to reach incipient dryness again. Thereafter, 2.0 mL of 2% HNO_3 (v/v) were introduced into the samples, and the sample solutions were naturally cooled down to ambient temperature. Finally, the digested samples were diluted using 2% HNO_3 (v/v) to the 10.0-mL calibrated mark. Here, to reduce the possible effect from the decomposed proteins on sample introduction system in particular the nebulizer device of the ICP-MS, the decomposed

sample solutions were then filtrated through the Sartorius ash-free qualitative filter paper (0.22 μm, Goettingen, Germany). Thereafter, the samples were directly taken for trace element determination by the optimized ICP-MS.

Spiking Procedures

The repeatability of the ICP-MS detector in this work was tested with calibration procedures carried out on three different days. The quantification precision was assessed *via* repetitive measurements for all the analytes in standard solutions and digested hair samples with RSDs studied. The standard reference material (SRM) GBW09101 was applied to accuracy evaluation of this proposed approach. In brief, the SRM GBW09101 was decomposed as above, and known quantities of standard solutions which contained elements Al, Cr, Mn, Fe, Cu, Zn, As, Se, Cd, and Pb were fortified. After the mixture became homogeneous, the trace elements were then assayed by ICP-MS, and the spiked recoveries were studied.

RESULTS AND DISCUSSION

Experimental Condition Optimization for ICP-MS

Considering the operation property of the quadrupole ICP-MS, a daily instrumental optimization was done before any element quantification. Here, the effects of nebulizer/plasma/auxiliary gas flow rate, and sampling depth were discussed in detail for this utilized ICP-MS. The influence of nebulizer gas flow rate from 0.6 to 1.2 L·min^{-1} on oxide formation (CeO^+/Ce^+), hydroxide formation ($CeOH^+/Ce^+$) and doubly charged species (Ce^{2+}/Ce^+) was checked, with results graphically shown in FIGURE 1. It can be seen from FIGURE 1 that the formation of oxides and hydroxides exhibited a close relationship with nebulizer gas flow rate. Generally, the obtained ratios of $CeOH^+/Ce^+$ and CeO^+/Ce^+ were lower than 1.1% with a nebulizer gas flow rate less than 0.8 L·min^{-1}. But an exaggerating increment of oxide formation and hydroxide formation with ratio values over 3.0% was observed. On the other hand, the ratio of Ce^{2+}/Ce^+ first went up to 3.3% and then declined obviously with nebulizer gas flow rate higher than 0.75 L·min^{-1}. It was obvious that these observed phenomena were similar with those in our previous work [59], in which the optimal nebulizer gas was 0.85 L·min^{-1}. We assumed that such slight differentiation might come from the compromise of the parameters of this ICP-MS configuration, or the status of the nebulizer/quartz torch devices for human hair sample matrix.

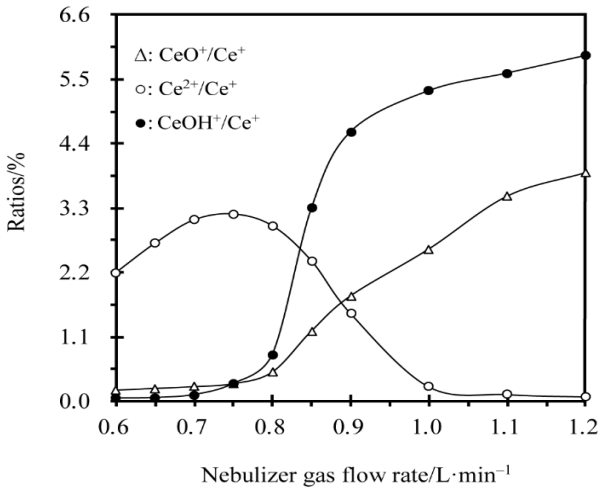

Figure 1: The effect of nebulizer gas flow rate on analyzing the accuracy of ICP-MS [59].

To further assure the optimal nebulizer gas flow rate, the signal intensities of low- to high-mass elements were studied when applying 0.65 – 0.95 L·min^{-1} of nebulizer gas flow rate. The results were given in FIGURE 2, where a 10 ng·mL^{-1} of the tuning standard solution was used. As shown in FIGURE 2, the signal intensities from low- to high-mass including Li, Co, In, and U were found to increase steadily with the increasing nebulizer gas flow rate up to 0.80 L·min^{-1}. After that, the signal intensities of Co, In, and U slightly declined, while the signal intensity of low mass element Li presented a staggering decrement. Thus, 0.80 L·min^{-1} of nebulizer gas flow rate was chosen as optima in this work. Here, the effects of plasma and auxiliary gas flow rates on the m/z counting rate were tested within 11.0 – 16.0 and 0.60 – 0.85 L·min^{-1}, respectively. Under the optimized nebulizer gas flow rate, results showed that 14.5 L·min^{-1} of plasma gas flow rate and 0.80 L·min^{-1} of auxiliary gas flow rate yielded relatively high and stable signal intensities for Li, Co, In and U.

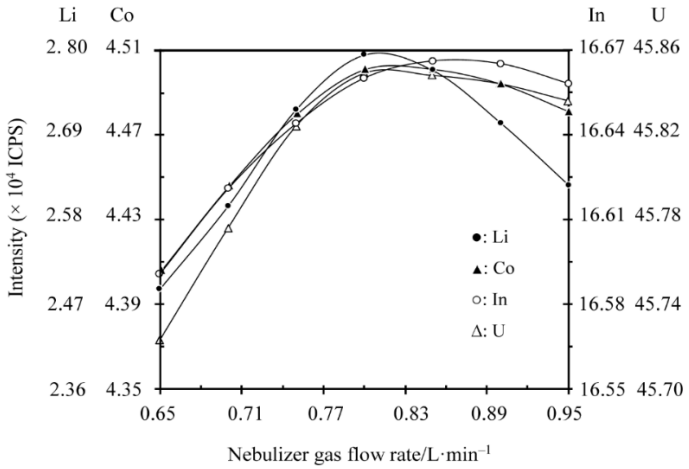

Figure 2: Relationship of element counting intensity versus nebulizer gas flow rate.

To enhance the signal sensitivity and improve the determination precision, the sampling depth in a range from 80 to 120 was examined in this work, and the results were graphically given in FIGURE 3. It was observed that the element signal sensitivities varied differently with sampling depth. As shown in Figure 3, the signal intensity of low-mass Li increased with the increasing sampling depth, but the signal intensity of mid-mass Co was found to increase first and then decline from 100 of sampling depth. It was worth noting that the signal intensity of high-mass U had small variations with the sampling depth less than 100, and then exhibited a prominent decrement. For element In, the signal intensity presented a steady decline from 80 to 110 of sampling depth and then became stabilized. Considering the compromise of the stability of signal intensity and element sensitivities, a sampling depth of 100 was selected in the subsequent work. The optimum values of nebulizer inserting depth and sample introduction rate, and the typically default values of dwell time, sweeps, lens voltages, torch position and RF power were collected in TABLE 1.

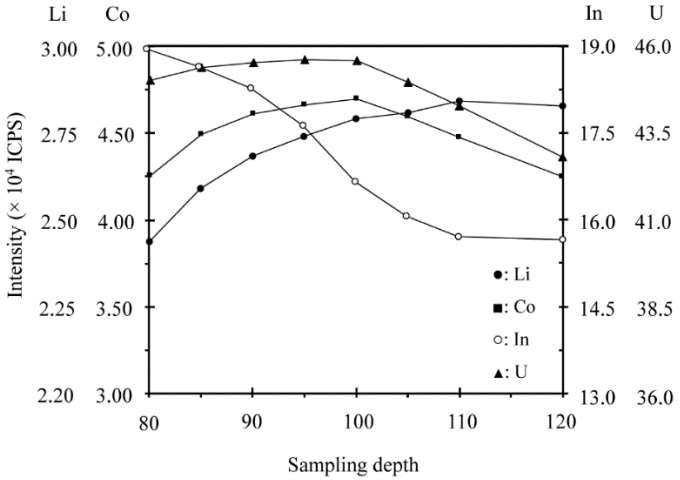

Figure 3: The influence of sampling depth on the element counting intensity. Here, the effect of sampling depth was studied by continuous aspirating a 10 ng·mL^{-1} of tuning standard solution into the ICP-MS, with relative signal intensities of Li, Co, In and U recorded.

Repeatability and Accuracy Study of Element Analysis in Hair Sample by ICP-MS

To evaluate the repeatability of this approach, a series of standard solutions (5, 50, 100 ng·g^{-1}) and digested human hair samples were repetitively quantified in three consecutive days under the proposed optimum operating conditions given in Table 3 with the determination RSDs studied. Results showed that the RSDs for intra- and inter-day measurements were less than 4.0% (n = 5), which indicated the capability of this current method for trace element determination in hair samples.

It is known that the accuracy of a method is typically verified by comparing quantification results of the SRM from the proposed method and the certified values with the absolute or the relative errors assayed. Here, the hair SRM GBW09101 was applied to the accuracy study of this ICP-MS approach. By taking the concentration differences for the elements in this hair standard material into consideration, 1.0 g of this hair SRM sample was digested as mentioned above and the solution was then split into three parallel batches. For these three batches, one was directly introduced to the ICP-MS for trace element measurement, and the other two were diluted 10 and 10^2-fold before element analysis, respectively. The concentration levels of trace elements Al, Cr, Mn, Fe, Cu, Zn, As, Se, Cd, and Pb in the SRM sample were quantified by ICP-MS using the spiked-recovery protocol. The analytical results including RSDs, determination recoveries, and element concentrations were collected in TABLE 2.

Table 2: Accuracy study results for SRM GBW09101 by the proposed ICP-MS method. [1]

Elements	Added ng·g^{-1}	Found ng·g^{-1}	RSDs %	Recovery %	Content μg·g^{-1}	Referred value μg·g^{-1}
Al	20	43.5	2.7	102.5	23.0 ± 1.2	23.2 ± 2.0
	30	52.6	2.8	97.1	23.5 ± 1.5	
Cr	70	158.2	1.6	101.4	8.72 ± 0.25	8.74 ± 0.97
	100	185.4	1.3	97.9	8.75 ± 0.24	
Mn	30	68.1	2.3	100.6	3.79 ± 0.33	3.83 ± 0.38

	50	89.2	2.0	103.4	3.75 ± 0.26	
Fe	100	263.4	1.6	98.4	165 ± 3.8	160 ± 16
	200	361.8	1.1	97.9	166 ± 1.9	
Cu	20	52.5	2.2	93.5	33.8 ± 1.2	33.6 ± 2.3
	30	63.0	3.2	97.7	33.7 ± 2.0	
Zn	100	292.5	2.3	105.1	189 ± 6.7	191 ± 16
	200	391.6	2.5	100.8	190 ± 9.8	
As	10	29.5	1.2	96.5	0.199 ± 0.011	0.198 ± 0.023
	20	39.7	1.5	100.6	0.196 ± 0.060	
Se	10	68.6	2.2	96.4	0.59 ± 0.06	0.59 ± 0.04
	20	77.8	2.8	102.0	0.57 ± 0.04	
Cd	10	17.4	1.1	103.2	0.071 ± 0.014	0.072 ± 0.010
	20	27.2	1.9	99.5	0.073 ± 0.012	
Pb	30	68.7	2.3	101.1	3.84 ± 0.16	3.83 ± 0.18
	50	89.6	1.8	102.0	3.86 ± 0.16	

[1] Elements Al, Mn, Fe, Cu, and Zn were analyzed in the batch sample with a dilution index of 10^2; Cr, As, Se, and Pb are analyzed in the batch sample with a dilution index of 10; Cd is analyzed in the batch sample without further dilution. Results were given as the average of five repetitions.

Apparently, the concentration results of the studied trace elements in this hair SRM highly agreed with the certified values, giving the determination recoveries ranging from 93.5% to 105.1% and RSDs less than 2.8% (n = 5). Hence, it can be deduced that this proposed method was capable of accurately quantifying the trace element in hair samples.

Trace Element Determination Results in Human Scalp Hair Samples

The scalp hair samples from five male adults (50 – 55 years old) were decomposed as described in sample handling section. Under the optimized conditions of ICP-MS system, the elements including Al, Cr, Mn, Fe, Cu, Zn, As, Se, Cd, and Pb in the hair samples were measured with RSDs lower than 3.2% (n = 5), and the determination results which were given in the form of 95% confidential level were summarized in TABLE 3. It can be seen from TABLE 3 that the concentration levels of the ten elements varied in different degrees for the studied hair samples. It was clear that the contents of Al, Mn, and Fe for the five specimens were in a wide range of 8.45 ± 0.19 to 181.7 ± 2.1 μg·g^{-1}, 2.74 ± 0.08 to 15.73 ± 0.28 μg·g^{-1}, and 28.30 ± 0.57 to 230.1 ± 7.4 μg·g^{-1}, respectively. The other seven elements including Cr, Cu, Zn, As, Se, Cr, and Pb showed corresponding concentration ranges of 0.58 ± 0.01 ~ 1.09 ± 0.03 μg·g^{-1}, 12.48 ± 0.52 ~ 22.88 ± 0.79 μg·g^{-1}, 103.8 ± 2.3 ~ 151.9 ± 2.9 μg·g^{-1}, 0.23 ± 0.01 ~ 0.61 ± 0.04 μg·g^{-1}, 0.81 ± 0.03 ~ 0.93 ± 0.08 μg·g^{-1}, 0.05 ± 0.01 ~ 0.23 ± 0.01 μg·g^{-1}, and 2.39 ± 0.11 ~ 7.95 ± 0.23 μg·g^{-1}, respectively.

Table 3: Analytical results for trace elements in scalp hair samples. [1]

Elements	Sample 1 μg·g^{-1}	Sample 2 μg·g^{-1}	Sample 3 μg·g^{-1}	Sample 4 μg·g^{-1}	Sample 5 μg·g^{-1}	TERCC permitted value μg·g^{-1}
Al	8.45 ± 0.19	17.13 ± 0.45	70.35 ± 1.6	90.25 ± 1.4	181.7 ± 2.1	≤ 7.0
Cr	0.58 ± 0.01	0.64 ± 0.05	0.82 ± 0.03	0.94 ± 0.03	1.09 ± 0.03	0.3 ~ 1.2
Mn	2.74 ± 0.08	2.79 ± 0.08	7.34 ± 0.22	10.57 ± 0.28	15.73 ± 0.28	0.8 ~ 2.8

Fe	28.30 ± 0.57	46.87 ± 1.69	46.66 ± 0.61	230.1 ± 7.4	216.9 ± 8.7	20 ~ 130
Cu	16.06 ± 0.29	12.48 ± 0.52	20.62 ± 0.43	18.01 ± 0.62	22.88 ± 0.79	8.0 ~ 20
Zn	130.4 ± 2.2	148.9 ± 3.9	103.8 ± 2.3	145.2 ± 2.8	151.9 ± 2.9	120 ~ 210
As	0.46 ± 0.04	0.23 ± 0.01	0.61 ± 0.04	0.28 ± 0.03	0.54 ± 0.07	≤ 1.0
Se	0.88 ± 0.05	0.93 ± 0.08	0.81 ± 0.03	0.86 ± 0.06	0.83 ± 0.07	0.2 ~ 0.6
Cd	0.05 ± 0.01	0.09 ± 0.01	0.16 ± 0.01	0.12 ± 0.01	0.23 ± 0.01	≤ 0.6
Pb	3.90 ± 0.11	2.39 ± 0.11	7.95 ± 0.23	5.46 ± 0.13	2.65 ± 0.01	≤ 10

[1] The RSDs were less than 3.2% (n = 5), and the results were given in 95% confidential level.

Assessment of Potential Health Risk Based on The Trace Element Analysis

To further evaluate the concentration levels of the studied elements in the hair samples, the quantification results were compared to the permitted values from the TERCC which were compiled in TABLE 3. it was found that the elements Cr, As, Cd, and Pb in the five hair samples were well within the suggested ranges, which revealed that the daily intakes of these trace elements were reasonable. It was also observed that the concentration levels of element Mn, Fe, and Cu differentiated individually. For element Fe in sample 4 and sample 5, the contents were found to reach 230.1 ± 7.4 and 216.9 ± 8.7 $\mu g \cdot g^{-1}$, respectively. It was clear that they were over the highest Fe permitted value of 130 $\mu g \cdot g^{-1}$. Since the excess Fe can cause direct intestine damage, oxidative stress and/or pathogen growth [60], these two participants were specifically suggested to lower down the iron enriched foodstuff. It was worth noting that these two sample specimens also exhibited relatively higher concentrations of Mn and Cu, which might reveal that there existed potential health risks associated to synaptic dysfunction and interruption of axonal transport [61]. When came to element Se, all the five specimens were found to be slightly higher than the upper permitted value of 0.6 $\mu g \cdot g^{-1}$. But element Al far exceeded the allowed 7.0 $\mu g \cdot g^{-1}$, showing 1.2 – 26-fold higher than the upper limit. The sample 5 in particular had the concentration of Al high up to 181.7 ± 2.1 $\mu g \cdot g^{-1}$, yielding a ratio to the highest suggested value of approximately 26-fold. It can thus be deduced that there might be a slight burden of Mn, Fe, and Cu for some participants, but a relatively heavy burden of Se and Al to different degrees for all the five participants. Thus, the daily ingestion of these elements from foodstuff and/or medicine should be controlled stringently, and a detailed routine check-up for these participated males was highly recommended. For element Zn, it was found that only the content in sample 3 was out of the permitted range, showing about 13.5% lower than the least required concentration which demonstrated there might exist deficiency of this element. This suggested that a reasonable intake of Zn supplements was necessary for this participant due to the possible health risks from Zn deficiency [62].

CONCLUSION

In this paper, trace elements including Al, Cr, Mn, Fe, Cu, Zn, As, Se, Cd, and Pb in human scalp hair samples were accurately quantified by the proposed ICP-MS approach, with determination recoveries in a range of 93.5 – 105.1% and RSDs less than 2.8% (n = 5). The data analysis

according to the recommendations from the TERCC revealed that elements Cr, As, Cd, and Pb in the participants lay within the suggested ranges. However, the concentrations of Mn, Fe, and Cu in some participants were found to be higher than the upper permitted values, which revealed that there might be health risks such as synaptic dysfunction and interruption of axonal transport. Furthermore, all the participants showed concentration levels of Se and Al over the allowed highest values. It was worth noting that the content of element Al in sample 5 were 26-fold higher than the upper limit of 7.0 $\mu g \cdot g^{-1}$. It can thus be deduced that there might be a relatively heavy burden of element Al to some degree for the participated male adults, who might have potential health risks associated to Al excess. It was also observed that element Zn contents in the studied hair samples expect sample 3 were in the permitted concentration range, showing there might be Zn deficiency for this participant.

By this current trace element analysis in scalp hair samples, it was highly recommended that the routine ingestion of Al and Se from daily diet and/or medicine must be regulated strictly for all the participants, while the daily intake of foodstuff which enrich in Mn, Fe and Cu should be carefully controlled for some participants. Additionally, a reasonable intake of Zn supplements was suggested for the participant who showed the deficiency of Zn. Collectively, a detailed routine check-up for these participants was highly recommended based on the analytical results of trace elements in scalp hair matrix. Our study clearly assured the practical value of scalp hair as a biomarker for nutrition status and health risk evaluation *via* trace element analysis, promising an alternative strategy in merits of convenience and non-invasive sampling for mass health status investigation.

Conflicts of Interest

The authors declare no conflict of interest.

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