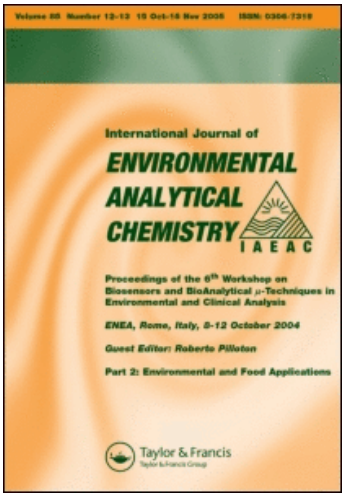

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The use of electrothermal vaporization ICP-OES for the determination of trace elements in human hair using slurry sampling and PTFE as modifier

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A procedure for the determination of trace elements in human hair has been proposed by electrothermal vaporization inductively coupled plasma optical emission spectrometry (ETV-ICP-OES) with slurry sampling. Slurry was prepared by immersing human hair with conc. HNO_3 and then adding a polytetrafluoroethylene (PTFE) slurry, which was used as a chemical modifier for the improvement of vaporization characteristic of analyte. The slurry was homogenized with an ultrasonic vibrator before the measurement. The vaporization behaviour of the analytes in slurry and solution and the main influence factors for the determination were studied with the addition of PTFE systematically. Detection limits for this method varied from $0.033\,\mu g\,g^{-1}$ (Cu) to $3.21\,\mu g\,g^{-1}$ (Zn) with the relative standard deviations (RSDs) of 2.8–7.1%. The proposed method was successfully applied for the determination of trace elements (Cu, Mn, Cr, Fe, Zn, Cd and Pb) in human hair with minimum chemical pretreatment and aqueous calibration. The accuracy was checked by comparing the results of this method with those using pneumatic nebulization (PN) ICP-OES after a conventional acid decomposition of the same sample. In addition, the standard reference material of human hair (GBW 07601) was analysed with good agreement between the results from the proposed method and the certified values.

Keywords: Human hair; Trace elements; Slurry sampling; Electrothermal vaporization; Inductively coupled plasma optical emission spectrometry; Polytetrafluoroethylene midifier

1. Introduction

The effect of trace elements, particularly heavy metals, on the environment, ecosystem and the health of human beings can be evaluated to a certain extent by studying the content, speciation and distribution of the trace elements in human fluids and tissues such as whole blood, urine, serum, hair, liver, kidney and brain, etc. [1,2]. Of these, human hair has received increasing attention owing to the following advantages over the other specimens: higher trace-element concentrations, easy and non-invasive collection, convenient shipment and storage, and relatively stable components [3–5].

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Therefore, it is essential to develop a simple, rapid, sensitive and accurate method with minimum chemical pretreatment for the determination of trace elements in human hair.

To date, inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) involving previous sample dissolution still represent the most important routine methods for the determination of trace elements in human fluids and tissues [6–12]. Liquid nebulization has become the most popular sample introduction technique for ICP-OES, ICP-MS and AAS because of its convenient operation and high precision. However, this technique often suffers from a low efficiency of sample transport, high sample consumption, and a time-consuming and sometimes hazardous dissolution technique prior to analysis, which can lead to a risk of contamination and loss of analytes. Although some solid sampling techniques, which are based on a fine powder, have been developed for ICP-OES, ICP-MS and AAS for a direct analysis of trace element in biological samples [13–18], problems resulting from matrix interference, particle size effect, calibration difficulty and sample inhomogeneity must be considered. Compared with the conventional solution sample introduction technique, slurry sampling combined with electrothermal vaporization (ETV) as a means of sample introduction for ICP-OES has demonstrated distinct merits of a high sampling efficiency, low contamination risk, small sample and reagent consumption, low absolute detection limit, and direct analysis of solid sample for avoiding hazardous pollutants from sample decomposition. Furthermore, the application of various chemical modifiers in ETV-ICP-OES for changing the volatility of analytes could significantly improve the analytical performances of methods. Among these, representative examples are the application of fluorinating reagents [19–21], chelating reagents [22] and alkylating reagents [23].

The purpose of this work was to develop a simple and rapid method for the determination of trace elements in human hair by slurry sampling ETV-ICP-OES with calibration against aqueous standards. A PTFE slurry was used as a chemical modifier to convert the analytes into the fluorides with various volatilities in a high-temperature graphite furnace to improve the analytical performance. The main factors affecting the determination, including homogeneity and stability of slurry, vaporization characteristics of analytes, optimization of temperature programme and matrix effects, were investigated in detail. The proposed method has been successfully used to determine Cu, Mn, Cr, Fe, Zn, Cd and Pb in human hair with only minimal chemical pretreatment prior to the measurements.

2. Experimental

2.1 *Instrumentation*

A power of 2 kW, a 27 ± 3 MHz ICP spectrometer (Beijing Second Broadcast Equipment Factory, Beijing) and a conventional plasma silica torch were used. A WF-1 type heating cycle together with a graphite furnace vaporizer was used as a vaporization device equipped with a pyrolysis graphite tube (Beijing Second Optics, Beijing). Two ends of a Teflon tube (0.5 m long, 4 mm i.d.) are respectively connected to ETV and ICP. The radiation from the plasma was focused as a 1 : 1 straight image on the entrance slit of a WDG-500-1A monochromator (Beijing Second Optics) with

Table 1. ETV-ICP-AES operation parameters.

Incident power (kW)	1.1
Carrier gas (Ar) flow rate ($L\,min^{-1}$)	0.5 for ETV, 0.9 for PN
Coolant gas (Ar) flow rate ($L\,min^{-1}$)	18
Observation height (mm)	12
Entrance slit width (μm)	25
Exit slit width (μm)	25
Drying temperature (°C)	100, ramp, 10 s, hold, 20 s
Pyrolysis temperature (°C)	700, ramp, 10 s, hold, 30 s
Vaporization temperature (°C)	2400, 4 s
Clear-out temperature (°C)	2700, 3 s
Sample volume (μL)	20

a reciprocal linear dispersion of 1.6 nm/mm. The evolved components were swept into the plasma excitation source through the Teflon tube by a stream of carrier gas. The transient signals were detected with a R456-type photo-multiplier tube (Hamamatsu, Japan) and a home-made d.c. amplifier, and recorded using a U-135 recorder (Shimadzu, Japan). The instrumentation and operation conditions are listed in table 1.

2.2 *Reagents*

The stock standard solutions ($1\,mg\,mL^{-1}$) for Cu, Mn, Cr, Fe, Zn, Cd and Pb were prepared from their specpure oxides (Shanghai, China) by conventional methods. A 60% (m/v) PTFE slurry ($d < 1\,\mu m$; viscosity, 7×10^{-3} to 15×10^{-3} Pa s) was purchased from the Shanghai Institute of Organic Chemistry, China. All other chemicals used in this work were of specpure grade or analytical grade (Shanghai, China). Twice-distilled water was used throughout.

2.3 *Sample preparation*

Human hair was washed, dried and chopped into smaller pieces (2 mm) [18]. A portion (100 mg) of this was accurately weighed into a test tube with graduation and immersed with 0.5 mL of concentration HNO_3 for 2 h to form a suspension solution by non-complete digestion. Then, 0.1 mL of 60% (m/v) PTFE slurry and 0.05 mL of 0.1% Triton X-100 were added and diluted to 1.0 mL with twice-distilled water for analysis. The sample for PN-ICP-OES was prepared according to the literature [6]. The aqueous standard solutions containing 6% (m/v) PTFE were used for calibration. The slurry samples were dispersed with an ultrasonic vibrator for 20 min, and then the micro-test tubes were shaken prior to sampling.

2.4 *Procedures*

After ICP had been stabilized, a 20 μL sample was pipetted into the furnace. After being dried and ashed, analytes were vaporized and carried into the plasma by argon gas under the selected operating conditions. A peak-height measurement was used for calibration.

3. Results and discussion

3.1 *Sample requirement*

In ICP-OES, the most common sample introduction technique is pneumatic nebulization (PN) of a liquid by a concentric nebulizer. Because of the introduction of less than 10% of sample solution into ICP-OES with most of the sample being wasted, its application is often limited for only very small amounts of biological sample available for analysis (usually at milligram or microlitre levels). Compared with PN, ETV is considered to be one of the most effective methods of introducing a micro-size sample into the plasma. In this work, although 100 mg of sample was used for the study, the minimum amount of sample required for the proposed method in a real analysis could be as little as 10 mg because of the very small sample volume (10–20 μL), which is much lower than that for PN-ICP-OES after wet-chemical sample decomposition (often more than 0.5 g).

3.2 *Study of slurry homogeneity and stability*

Because of the important effect of slurry homogeneity and stability on the precision and accuracy, the dependence of the laying time of slurry on the signal intensities of the analytes was examined. The results demonstrated that the signal intensities of the analytes remain constant within at least 2 h of testing. It was confirmed that the slurry prepared by the proposed method was able to meet the requirements of the measurement.

3.3 *Selection of ICP operation parameters*

The ICP operation parameters were established on the basis of signal–background ratios (S/B) by using the standard analyte solution containing 6% (m/v) PTFE. The results showed that there were no obvious differences in the power and observation height between PN-ICP-OES and ETV-ICP-OES, but the effects of carrier-gas flow rate on S/B in ETV-ICP-OES were greater than that in PN-ICP-OES. In this work, a carrier gas using a power of 1.1 kW, 0.5 L min^{-1} flow rate and 12 mm observation height was used for subsequent measurements.

3.4 *Comparison of analyte vaporization behaviour*

The typical signal profiles of Cr in slurry and solution, which were prepared from the same sample, were investigated with and without PTFE. The results shown in figure 1 indicate that in the absence of PTFE, the signal intensity of Cr in slurry or solution was very weak, and a broad signal profile with tailing was recorded. Furthermore, the residue signals of Cr were almost the same as the original signals. With the addition of PTFE, however, the sharper, more intense and symmetrically shaped peaks without trailing were detected, and there were no memory effects for slurry or solution. Similar results were also observed for Cu, Mn and Fe, but the intense signals for the readily volatile elements Zn, Cd and Pb could be recorded in both cases because they do not form the thermally stable oxide or carbide. In addition, it should be noted from figure 1 that the appearance time, height and profile of the emission signals from the slurry were very similar to those of the solution. This suggests that

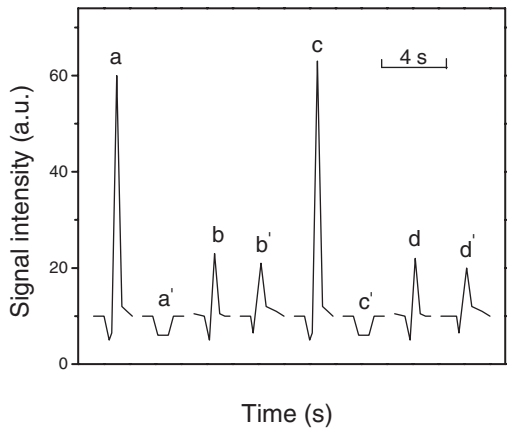

Figure 1. Emission signal profiles of Cr in the slurry and the solution prepared from the same sample with or without PTFE. a: Cr in the solution with PTFE; b: Cr in the solution without PTFE; c: Cr in the slurry with PTFE; d: Cr in the slurry without PTFE; a′, b′, c′ and d′: their residual signals recorded during the second heating period.

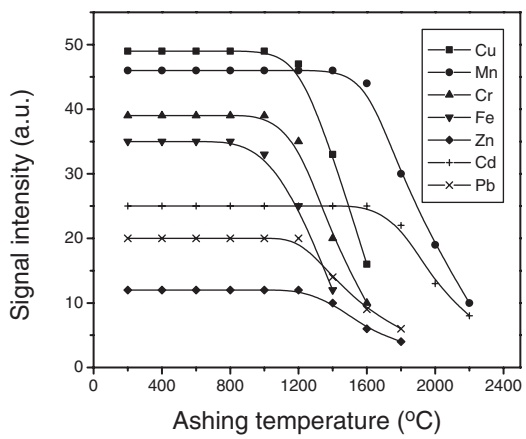

Figure 2. Influences of ashing temperature on signal intensity with PTFE. Cu, Mn and Cr: 0.5 μg mL^{-1}; Fe: 1.0 μg mL^{-1}; Cd: 10 μg mL^{-1}; Pb and Zn: 20 μg mL^{-1} for the standard solution.

the vaporization behaviours of analytes in slurry and solution are very similar in the presence of PTFE. Hence, the standard solutions can be used for the calibration of slurry samples. From the above experimental results, it can be concluded that the addition of PTFE not only greatly promotes the release of analytes from the slurry to eliminate any differences in the chemical species in which samples exist, but also remarkably enhances the vaporization and transportation efficiencies, thus leading to great improvements in analytical sensitivity.

3.5 *Optimization of ashing temperature*

Figure 2 shows the dependences of analyte signal intensities on ashing temperature. It can be seen that with the addition of PTFE, the emission signal losses of the analytes

occur at above 1000°C. The reason for this is that the PTFE slurry can convert the analytes into the corresponding fluorides to improve their volatilities. For the easier volatile elements (Cd, Zn and Pb), the tolerable ashing temperatures were greatly increased owing to the formation of the more stable fluorides with higher boiling points. The boiling points of the corresponding fluorides are listed in table 2. To completely remove organic matrix in human hair without signal losses, an ashing temperature of 700°C was selected for the analysis of real samples in this work.

3.6 *Effect of ashing time*

The experimental results show that the signal intensities of the analytes do not increase by increasing the ashing time beyond 30 s. Therefore, an ashing time of 40 s was chosen throughout the experiment.

3.7 *Influence of vaporization temperature*

The influences of vaporization temperature on the signal intensities of the analytes were investigated in the addition of PTFE. From figure 3, the following conclusions can be drawn: (1) the higher the vaporization temperature, the stronger the signal intensity; (2) the signal increment reaches a plateau above a proper temperature (2400°C) owing to the formation of fluorides with similar vaporization characteristics. In this study, a vaporization temperature of 2400°C was used to ensure complete vaporization of the elements of interest.

Table 2. Boiling points of fluorides for interesting elements.

Fluoride	CuF_2	MnF_2	CrF_3	FeF_3	ZnF_2	CdF_2	PbF_2
Boiling point (°C)	1449	1820	1291	927	1497	1750	1293

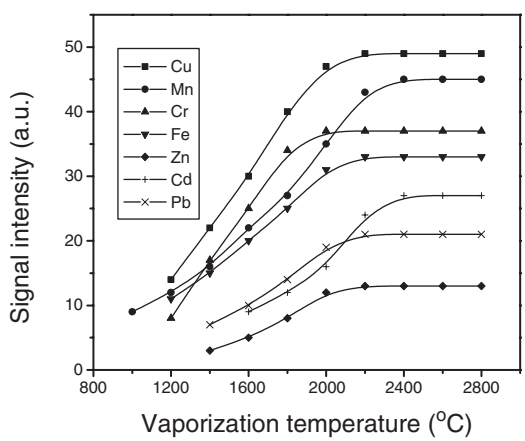

Figure 3. Signal intensity *versus* vaporization temperature with PTFE. Cu, Mn and Cr: 0.5 μg mL^{-1}; Fe: 1.0 μg mL^{-1}; Cd: 10 μg mL^{-1}; Pb and Zn: 20 μg mL^{-1} for the standard solution.

3.8 *Investigation of matrix interference*

With PTFE, the effects of the main coexisting components (Na, K, Ca and Mg) in human hair on the signal intensities of the analytes were examined. The permissible excesses of matrix elements, which gave errors of less than 10% for the determination of the analytes, were evaluated. The results show that the tolerable amounts of the aforementioned matrix elements were in the range of 2–5 $mg\,mL^{-1}$. However, once the concentrations of the matrix elements surpass the tolerable amounts, the signal intensities of the analytes decrease remarkably. This could be attributed to the two 'competition reactions', one between the analytes and PTFE, and the other between the matrix elements and PTFE, which lead to incomplete analyte vaporization.

3.9 *Choice of PTFE concentration*

The experimental results shows that the signal intensities for Cu, Mn, Cr and Fe were accentuated at a PTFE concentration up to about 4%, and their maximum signal intensities were achieved with this concentration, remaining constant up to the highest amounts tested. However, the PTFE does not affect the signal intensities for Zn, Cd and Pb, owing to their easier volatilities. In the work, a higher PTFE concentration of 6% was used because of the consumption of matrix in the real sample analysis.

3.10 *Detection limits and precision*

An aqueous standard series containing the analytes with 6% (m/v) PTFE was used for calibration. The linear dynamic range of the calibration curves covers three orders of magnitude. The detection limits of the interesting elements in the sample analysed as slurry (3σ) and relative standard deviations (RSDs) for the nine replicate measurements are listed in table 3 and compared with those obtained by PN-ICP-OES [6]. As can be seen from table 3, with the exception of Zn, the detection limits of the interesting elements are improved greatly.

3.11 *Sample analysis*

The proposed method was applied for the determination of Cu, Mn, Cr, Fe, Zn, Cd and Pb in real sample (human hair). The same sample was also analysed by a dissolution-based PN-ICP-OES [6]. The analytical results obtained are in good

Table 3. Detection limits and relative standard deviations ($n = 9$).

		Detection limits ($\mu g\,g^{-1}$)		
Element	Wavelength (nm)	ETV-ICP-OES	PN-ICP-OES [6]	RSD (%)
Cu	324.754	0.033	2	2.8
Mn	259.370	0.047	1	3.0
Cr	267.716	0.061	–	3.5
Fe	259.940	0.078	2	5.0
Zn	334.502	3.21	2.5	7.1
Cd	228.567	0.092	2	4.2
Pb	220.353	0.61	2.5	6.3

Table 4. Analytical results of the trace elements in human hair ($n = 5$).

Element	ETV-ICP-OES			PN-ICP-OES
	Calibration curve method[a] ($\mu g\,g^{-1}$)	Analyte addition technique[a] ($\mu g\,g^{-1}$)	Calibration curve method[b] ($\mu g\,g^{-1}$)	Calibration curve method[b] ($\mu g\,g^{-1}$)
Cu	15.4 ± 2.1	14.9 ± 1.9	16.0 ± 2.3	15.5 ± 1.2
Mn	4.35 ± 0.63	5.40 ± 0.72	4.56 ± 0.57	5.72 ± 0.45
Cr	0.69 ± 0.12	0.62 ± 0.11	0.57 ± 0.09	0.71 ± 0.08
Fe	65.7 ± 8.3	60.4 ± 6.5	71.2 ± 9.0	65.9 ± 4.5
Zn	187 ± 12	175 ± 15	180 ± 13	170 ± 8
Cd	0.32 ± 0.06	0.40 ± 0.08	0.38 ± 0.05	0.30 ± 0.04
Pb	7.35 ± 1.02	8.17 ± 1.15	6.84 ± 0.98	7.22 ± 0.64

[a]Direct analysis with slurry sampling.
[b]Analysis after digestion with $HNO_3 + H_2O_2$.

Table 5. Analytical results of the trace elements in standard reference material of human hair (GBW 07601) ($n = 5$).

Element	Found[a] ($\mu g\,g^{-1}$)	Certified ($\mu g\,g^{-1}$)
Cu	11.5 ± 1.2	10.6 ± 0.7
Mn	5.8 ± 0.7	6.3 ± 0.5
Cr	0.45 ± 0.08	0.37 ± 0.05
Fe	49 ± 7	54 ± 6
Zn	205 ± 15	190 ± 5
Cd	0.16 ± 0.03	0.11 ± 0.02
Pb	9.5 ± 1.3	8.8 ± 0.9

[a]Calibration curve method with slurry sample.

agreement (seen in table 4). To confirm the accuracy of the proposed method, the standard reference material of human hair (GBW 07601) was also analysed by ETV-ICP-OES. The results listed in table 5 were averages of five measurements. The determined values are identical to the certified values.

4. Conclusions

The addition of PTFE in ETV-ICP-OES could enhance the signal intensities of the refractory (Cr) and the medium volatile elements (Cu, Mn and Fe) due to the formation of the easier volatile fluorides. Although PTFE shows no effect on the signal intensities of the easy volatile elements (Zn, Cd and Pb), their tolerable ashing temperatures increase greatly (above 1200°C) without the losses of the analytes. In this case, the interferences of the matrix components in biological sample could be decreased significantly. In addition, the proposed method offers the following advantages: (1) simple sample preparation; (2) small sample requirement; (3) convenient and rapid operation; (4) reduction in sample contamination; (5) calibration with standard solutions without matrix matching.

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