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Determination of metals in textiles by ICP-MS following extraction with synthetic gastric juice

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A sector field high-resolution inductively coupled plasma mass spectrometry (ICP-MS) was applied for the determination of trace metals (Cd, Cr, Cu, Ni and Pb) in textiles after extraction of samples with synthetic gastric juice (aqueous 0.07 mol/l HCl solution). Effects of the stirring rate, the extraction time and the extractant-to-sample mass ratio on the extraction performance of metals were investigated. Detection limits of the analytes studied were between 0.5×10^{-11} g/g for Pb and 8.5×10^{-11} g/g for Cd. The extractable fraction of Cr, Cu, Ni and Pb has been estimated for certified reference material and for four textile samples. The amount of extractable Cd was found to be below the quantification limit. Two of the metals, Cr and Ni, showed a relatively low extractability which ranged from 15 to about 25%. In contrast, Cu and Pb were estimated to be approximately 60% extractable.

Key words: ICP-MS, heavy metals, extraction, gastric juice, textiles

INTRODUCTION

The major chemical pollutants on textiles are dyes containing carcinogenic amines and toxic heavy metals [1, 2]. Heavy metals can exist in natural structures of textiles or they can penetrate into textiles during their production, dying process or via the protection agents used for the storage of textiles. Furthermore, cotton, flax and hemp sometimes adsorb relatively large amounts of metals from the environment [3].

The basic requirements deciding whether textile products may be successfully commercialised are health and safety for the user, and harmlessness for the environment. People are often exposed to different allergenic and toxic chemicals coming from textiles due to daily contact with clothes, bed linen and similar products. Toxic effects of heavy metals on human health are very well known: damages of organs, disorders in the respiratory tract and lung diseases, dysfunction of the heart, blood and blood producing organs, skin diseases and some others. Due to the toxicity of some heavy metals, guidelines for tolerable amounts of these metals in textile products have been provided and are being adopted by countries all over the world [4].

Textile is categorized according to its utilization into products for babies, products with direct contact to skin, products without direct contact to skin, and decorative materials [5]. For risk estimations, the determination of the extractable amounts of heavy metals is of importance, since they reflect their possible impact on human health. To date, the commonly used extraction media have been synthetic artificial sweat and saliva [6–8]. According to the recently introduced regulation [9], common heavy metals extractable with synthetic gastric juice from textile used in baby clothes and toys should also be monitored. This method simulates contact with gastric juice when a material has been swallowed. However, the extractability of heavy metals from textiles with gastric juice as an extractant has not been studied.

Several analytical techniques such as anodic stripping voltammetry [10], spectrophotometry [11], atomic absorption spectrometry [12] and X-ray fluorescence spectrometry [6] have been proposed for the determination of heavy metals in textiles. Each method has its own merits, but generally they are laborious, time-consuming, not selective enough and often lack sensitivity.

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique for measuring ultratrace metals in a wide range of sample types [13]. Virtually, all elements can be measured, high sensitivity and low background signals combine to give very low detection limits (ng/l in most cases), and the measurement of a full suite of elements takes only a few minutes per sample. The laser ablation ICP-MS method has been proposed to examine the metal content in historical textiles [14], but this non-destructive method permits only a semi-quantitative and comparative (comparison of the intensity of peaks) analysis. In our previous work

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[15], the high resolution double-focusing sector field ICP-MS technique was developed for the determination of common heavy metals in textiles. However, the paper was focused only on the determination of the total amount of metals after microwave-assisted acidic digestion of textile materials.

The main objective of this study was the further investigation of the applicability of the ICP-MS method for the determination of extractable cadmium, chromium, copper, lead and nickel in textiles. For this purpose, the extraction procedure employing synthetic gastric juice as an extractant was optimized. The applicability of the method to textile samples was also demonstrated.

EXPERIMENTAL

A high resolution double-focusing sector field ICP mass spectrometer Element2 (Thermo Finnigan AB, Germany) was used for the measurements. The typical routine operating conditions are given in Table 1. The instrument has the capability to use three different resolution settings, m / Δm (10% valley definition): 300 (low-resolution mode), 4000 (medium-resolution mode) and 10000 (high-resolution mode).

All solutions were prepared with polyethylene laboratory ware using Milli-Q deionized water. High purity HNO_3 (65% v/v) and HCl (37% v/v) were used as received (SuprapurR, Merck). Standard solutions were prepared from ICP-MS multi-element standard solution VI CertiPUR (Merck) by appropriate dilution in 2% (v/v) HNO_3. A certified comparative reference material IAEA-V-9 for cotton trace element analysis was used to validate sample preparation and analysis procedure.

Textile samples were dried for 48 h at 60 °C and cut. Then 0.2 g of a sample was weighed, transferred to a 25 ml beaker and 10 ml of synthetic gastric juice (aqueous 0.07 mol/l HCl solution) was added. The mixture was heated at 37 °C for 60 min on a magnetic stirrer (1200 rpm) and then filtered through a 0.2 μm membrane filter, diluted with HNO_3 up to 10 ml in a volumetric flask to achieve 2% HNO_3 in the final solution and analysed. Each extraction was performed in triplicate.

Table 1. **Instrument settings for ICP-MS measurements**

Parameter	Value
Cool gas (Ar) flow	14 l/min
Auxiliary gas (Ar) flow	0.7 l/min
Nebuliser gas (Ar) flow	1 l/min
RF power	1100 W
Torch type	Fassel
Nebuliser	Meinhard
Spray chamber	Scott type (double pass)
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.8 mm orifice diameter

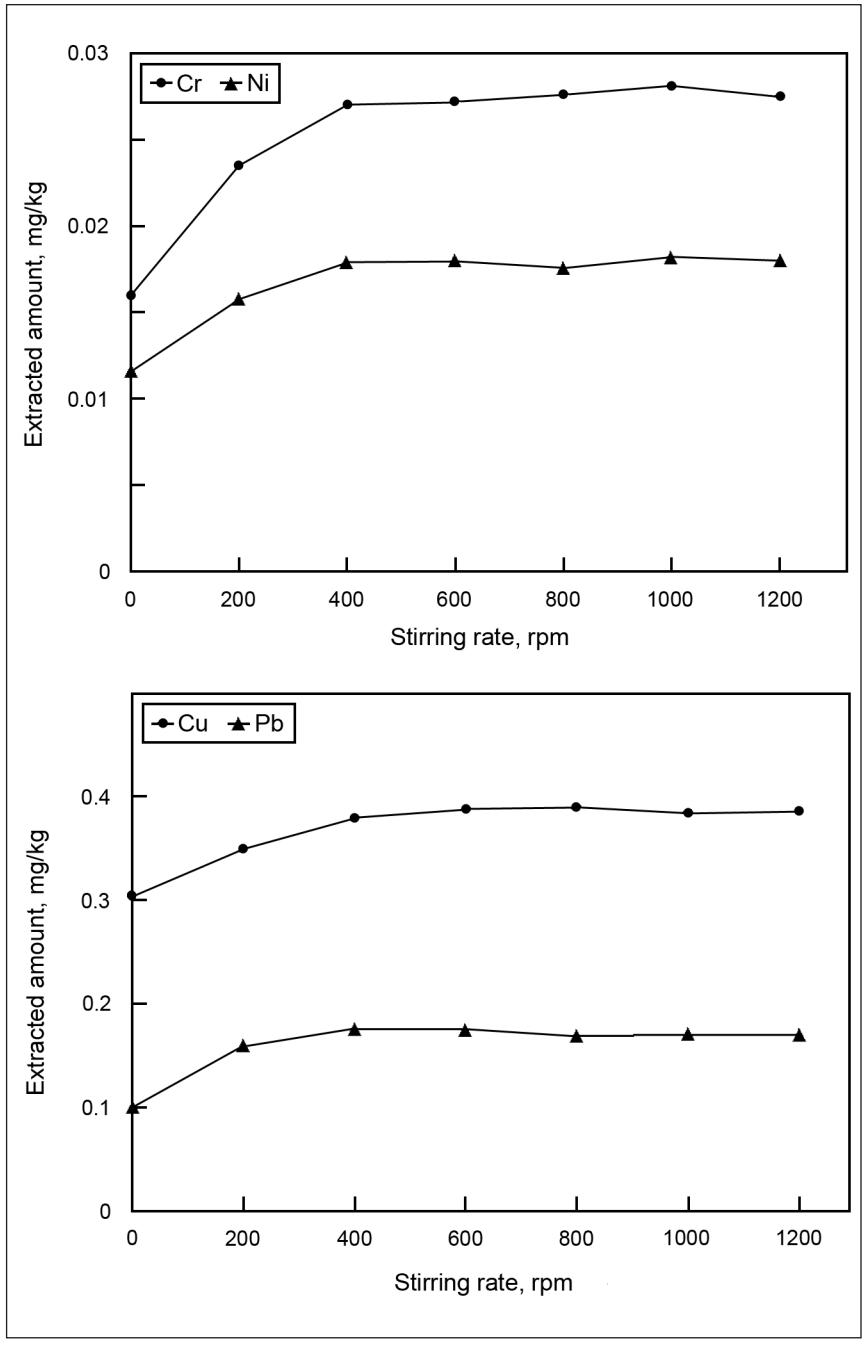

Fig. 1. Effect of stirring rate on the extraction efficiency of metals from certified reference material IAEA-V-9 for cotton trace element analysis. Sample mass 0.2 g, extractant volume 10 ml, extraction time 60 min

RESULTS AND DISCUSSION

Optimization of the extraction procedure

The extraction procedure was optimized with a certified reference material for cotton trace element analysis (IAEA-V-9) by varying most significant experimental conditions: stirring rate, extraction time and the extractant-to-sample mass ratio. All the extractions were performed using synthetic gastric juice (aqueous 0.07 mol/l HCl solution) as an extractant at body temperature (37 °C).

Sample stirring reduces the extraction time by enhancing the convective–diffusive mass transfer rate. To investigate the effect of the stirring rate on extraction efficiency, textile samples (0.2 g) were extracted for 60 min with 10 ml of gastric juice at various stirring rates. The results are shown in Fig. 1. The amount of extractable Cd was found to be below the quantification limit. As is seen, the increase in stirring rate from zero to about 400 rpm improved significantly the extraction efficiency. At higher stirring rates, the amount of metals extracted did not change significantly. Although the stirring rates higher than 400 rpm did not enhance the extractability of metals, to guarantee an effective extraction from different textile samples (e. g. with larger metal concentrations, etc.) the maximum stirring rate was chosen for the following experiments.

The second factor considered was the effect of extraction time. As is shown in Fig. 2, the extraction efficiency of the metals gradually increased with increasing extraction time up to 40–50 min and then reached plateau. Based on these results, an extraction time of 60 min was selected for the sample analysis.

Finally, the effect of the extractant-to-sample-mass ratio was investigated. In this experiment, the extraction efficiency of metals with different gastric juice amounts (2, 5, 10 and 20 g) used for extraction was measured. Reference material mass (0.2 g), extraction time (60 min) and stirring rate (1200 rpm) were kept constant in all these experiments. The variability in metal extractability of the reference material across the range of extractant-to-sample-mass ratios is shown in Table 2. There was no statistically significant difference in the extractable amount of Cr, Cu, Ni and Pb measured for each ratio. In addition, the solubility of each metal for the extractant-to-sample ratios employed was independent of the textile sample masses (0.2 and 0.5 g) used, suggesting that the synthetic gastric juice releases the metal uniformly from the textile over this range. The extractant mass of 10 g was chosen providing an adequate extraction performance from higher (at least up to 1 g) sample amounts.

Analytical performance

Several analytical performance characteristics important for quantitative analysis were measured. For calibration curves, the standard solution mixture was diluted stepwise with 2% nitric acid, and solutions for nine points including the blank test solution were prepared. Three replicates were carried out for each analyte concentration. Detection limits were calculated as three

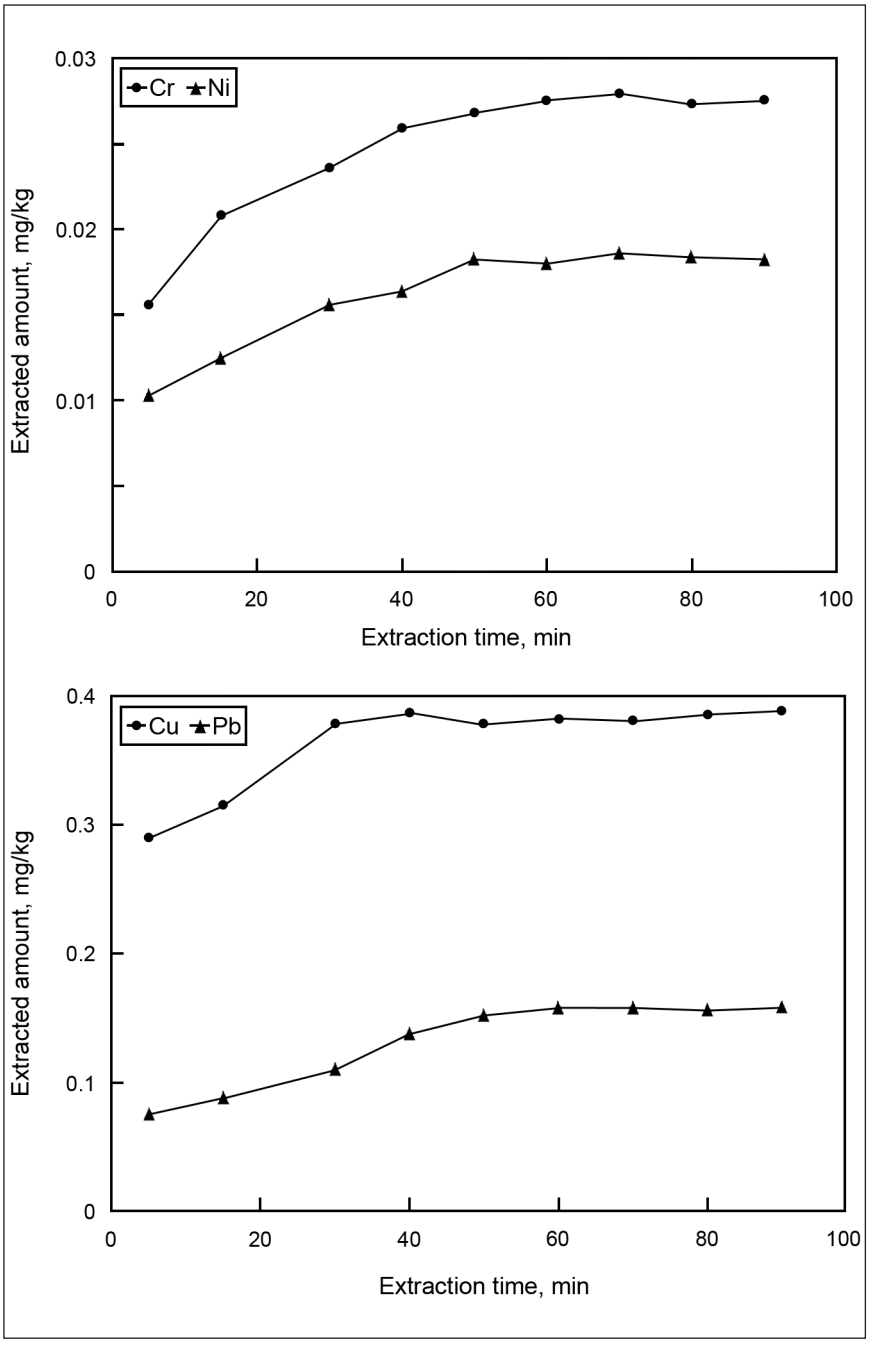

Fig. 2. Effect of extraction time on the extraction efficiency of metals from certified reference material IAEA-V-9 for cotton trace element analysis. Sample mass 0.2 g, extractant volume 10 ml, stirring rate 1200 rpm

Table 2. **Effect of extractant-to-sample-mass ratio on the extractability (mg/kg) of metals (n = 3, textile sample mass 0.2 g)**

Metal	Extractant-to-sample-mass ratio			
	10	25	50	100
Cr, mg/kg	0.027	0.029	0.028	0.028
Cu, mg/kg	0.392	0.380	0.376	0.395
Ni, mg/kg	0.019	0.021	0.020	0.019
Pb, mg/kg	0.164	0.172	0.178	0.173

Table 3. **Determination of extractable heavy metals in certified IAEA-V-9 reference material (n = 3)**

Metal	Certified total amount, mg/kg	Extractable amount, mg/kg	Extractable fraction, %
Cd	0.002	–[a]	–
Cr	0.11	0.03	27.3
Cu	0.59	0.40	67.8
Ni	0.09	0.02	22.2
Pb	0.25	0.17	68.0

[a] Below the quantification limit.

times the standard deviation of the intensities of the blank signals at *m/z* for each isotope. The average values and the standard deviation of the blank signals were obtained by using the results of three replicate measurements. The blank consisted of deionized water with 2% HNO_3.

The detection limits of the isotopes studied lie between 5.0×10^{-12} g/g for Pb and 8.5×10^{-11} g/g for Cd. Slightly higher detection limits for Cd isotopes can be explained by higher instrumental backgrounds obtained in the high-resolution mode. The detection limits are low enough for the method to be useful for the monitoring of trace metals in textiles. The linearity of the calibration curves was considered as satisfactory in the wide concentration range (up to 5.0×10^{-6} g/g for Cr, Cu, Ni and Pb and up to 1.0×10^{-3} g/g for Cd) with the correlation coefficients $r \geq 0.996$ for all isotopes.

Sample analysis

In order to evaluate the sample preparation and analysis procedures, the certified reference material IAEA-V-9 for cotton trace element analysis was analysed under optimized conditions. The extractable fraction was determined by dividing the mass of metal recovered from the gastric juice extraction by the certified value of the total metal content in a sample. The obtained results are reported in Table 3.

Finally, the concentrations of total and extractable Cr, Cu, Ni and Pb were determined in four baby textile samples obtained from the market in Vilnius. All the samples were processed by the Chinese textile industry. The total concentrations of the metals were measured after microwave-assisted acidic digestion of textile materials according to the procedure reported in our previous study [15]. All measurements were performed using the multiple standard addition technique. The results are presented in Table 4. Cadmium was not quantifiable in the textile samples.

There was no statistically significant difference in the extractable fraction of metals measured in the certified reference material and in the textile samples. The solubility of individual metals in synthetic gastric juice varied from 14.9

Table 4. **Determination of extractable metals in textile samples by ICP-MS (n = 3)**

Metal	Metal determined	Sample			
		No. 1 (blue)	No. 2 (red)	No. 3 (cherry)	No. 4 (black)
Cr	Total, mg/kg	0.17	0.10	0,25	0.31
	Extractable, mg/kg	0.04	0.02	0.05	0.07
	Extractable, %	23.5	20.0	20.0	22.6
Cu	Total, mg/kg	23.6	0.88	12.2	1.07
	Extractable, mg/kg	12.3	0.49	7.91	0.70
	Extractable, %	52.0	55.7	64.8	65.4
Ni	Total, mg/kg	0.09	0.09	0.17	0.47
	Extractable, mg/kg	0.02	0.02	0.03	0.07
	Extractable, %	22.2	22.2	17.6	14.9
Pb	Total, mg/kg	0.34	0.06	0.18	0.36
	Extractable, mg/kg	0.19	0.04	0.11	0.18
	Extractable, %	55.9	66.7	61.1	50.0

to 66.7%. Two of the metals, Cr and Ni, showed a relatively low extractability. In contrast, Cu and Pb were estimated to be approximately 60% extractable. The results indicate that each metal has a different physical and/or chemical binding capacity to the textile.

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METALŲ NUSTATYMAS TEKSTILĖS IŠTRAUKOSE SINTETINĖMIS SKRANDŽIO SULTIMIS INDUKTYVIAI SUŽADINTOS PLAZMOS MASIŲ SPEKTROMETRIJOS METODU

S a n t r a u k a

Optimizuotas induktyviai sužadintos plazmos masių spektrometrijos metodas kai kurių metalų (Cd, Cr, Cu, Ni and Pb) ištraukoms sintetinėmis skrandžio sultimis (vandeninis 0,07 mol/l HCl tirpalas) iš tekstilės nustatyti. Ištirta mėginio maišymo greičio, ekstrakcijos trukmės bei ekstrahento ir mėginio masių santykio įtaka ekstrakcijos efektyvumui. Metalų aptikimo ribos yra intervale nuo $0{,}5 \times 10^{-11}$ g/g Pb iki $8{,}5 \times 10^{-11}$ g/g Cd. Išsiekstrahuojančių Cr, Cu, Ni ir Pb kiekiai buvo įvertinti paliudytajai pamatinei medžiagai ir keturiems tekstilės mėginiams. Cd koncentracijos gautuose ekstraktuose buvo mažesnės už metodo nustatymo ribą. Nustatyta, kad iš tekstilės mėginių skrandžio sultimis išsiplauna 15–25% Cr ir Ni bei maždaug 60% Cu ir Pb.