

# Application of ICP-MS for the determination of trace metals in textiles

**Birutė Pranaitytė\***,

**Audrius Padarauskas and**

**Evaldas Naujalis**

*Laboratory for Metrology in  
Chemistry, Semiconductor Physics  
Institute, A. Goštauto 11,  
LT-01108 Vilnius, Lithuania*

A sector field high-resolution inductively coupled plasma mass spectrometry (ICP-MS) was developed for the determination of total amount of trace metals (Cd, Cr, Cu, Ni and Pb) in textiles after microwave-assisted acidic digestion of samples at 300 °C for 28 min. Spectral interferences arising from the plasma gases or the major components of the samples were identified and removed. Detection limits of the studied analytes were between  $0.5 \times 10^{-11}$  g/g for  $^{208}\text{Pb}$  and  $8.5 \times 10^{-11}$  g/g for  $^{110}\text{Cd}$ . The method was applied to determine Cd, Cr, Cu, Ni and Pb in four textile samples using standard addition calibration technique. The accuracy of the proposed technique was checked against certified comparative reference material. Good agreement between the certified values and the concentrations measured was obtained.

**Key words:** inductively coupled plasma mass spectrometry, heavy metals, textile products

## 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 the textiles during the production, dyeing process or via the protection agents used for the storage of these textiles. Furthermore, cotton, flax and hemp sometimes adsorb very 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 heart, blood and blood producing organs, skin diseases and some others. Due to the toxicity of some heavy metals, the guidelines for tolerable amounts of these metals in textile products have been provided and are being adopted by countries all over the world [4].

Determination of the metal content of different textile materials is very important not only for the safety of consumers, but also for the textile industry. It is known that some metals present in cotton may contribute to problems in yarn manufacturing, bleaching and dyeing, and processing quality [5]. Problems reported from dyeing processes are related to metal contribution to the light-induced yellowing of whitewashed denim. Transition metals catalyze organic reactions and function as mordants that strongly bind many organic compounds to cotton. The use of chromium-based dyes is essential for fast black-dyeing of wool

and nylon [6]. For this reason the textiles treated in those processes should be monitored for the presence of different metals, and their presence has to be reduced by applying different production methods [7].

Hence, much attention should be devoted to the development of a fast, reliable and sensitive method for the determination of toxic metals in textile materials. Several analytical techniques, such as anodic stripping voltammetry [8], spectrophotometry [9], atomic absorption spectrometry [10] and X-ray fluorescence spectrometry [11] have been proposed for the determination of total or extractable amounts 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 the measurement of ultratrace metals in a wide range of sample types [12]. Virtually, all the 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 set of elements takes only about few minutes per sample. Recently, laser ablation ICP-MS technique has been proposed for the examination of the metal content in historical textiles [13], but this non-destructive method permits only a semi-quantitative and comparative (the comparison of the intensity of peaks) analysis.

This paper describes the application of sector field high-resolution ICP-MS technique for the determination of total amounts of cadmium, chromium, copper, lead and nickel in textile products.

## EXPERIMENTAL

A double-focusing sector field ICP mass spectrometer Element2 of high resolution (Thermo Finnigan AB, Germany) was used

\* Corresponding author. E-mail: pranaityte@pf.lt

for the measurements. Typical routine operating conditions are given in Table 1. The instrument has the capability to use three different resolution settings,  $m/\Delta m$  (10% valley definition): 300 (low-resolution mode); 4000 (medium-resolution mode) and 10000 (high-resolution mode).

Table 1. Element2 instrument settings for the 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

A closed-vessel microwave digestion system (Anton Paar GmbH, Austria) equipped with a temperature control was used for the sample digestion.

All the solutions were prepared with polyethylene laboratory ware using Milli-Q deionized water. High purity  $\text{HNO}_3$  (65% v/v, SuprapurR, Merck) was used as received. Standard solutions were prepared from ICP-MS multi-element standard solution VI CertiPUR (Merck). A certified comparative reference material for cotton trace element analysis IAEA-V-9 was used to validate the sample preparation and analysis procedure.

## RESULTS AND DISCUSSION

### Isotopic interferences

As a rule, in the case of multi-isotopic elements, the strategy for the selection of the isotope was to choose the most abundant and at the same time the least interfered one. Whenever possible, it is desirable to perform the analysis in a low-resolution mode because of the higher ion transmission attainable in this way. On the other hand, this mode is affected by mass interferences to a large extent. Spectral interferences are caused by atomic ions and/or polyatomic ions with the same nominal mass of the analyte. The latter type of interferences is more serious and come

from ions of the plasma gas and/or the major elements in the sample matrix. In order to obtain higher accuracy, two or three most abundant isotopes of each metal were selected for the determination. Only Ni was determined from one  $^{60}\text{Ni}$  isotope because the most abundant  $^{58}\text{Ni}$  isotope can not be resolved from  $^{58}\text{Fe}$  even in the high-resolution mode. A list of known and possible interferences for the selected isotopes of the metals studied are given in Table 2, along with the resolution selected to spectrally resolve most of them from the analyte isotopes.

In this case, only Pb isotopes were analysed in the low-resolution mode ( $m/\Delta m = 300$ ). Although not measured, the concentration of Er, Os, Ir, Yb and Pt in textiles is expected to be very low. Furthermore, the formation of the polyatomic ions for these metals is relatively low. It appears, therefore, that these interferences can be totally neglected.

In the case of the determination of Cr, Cu and Ni isotopes, the most important interferences deriving from C, O, Cl, Ca, Cd, Mg, Ba, Sb, Na polyatomic ions can be resolved in a medium-resolution mode ( $m/\Delta m = 4000$ ). All other potentially interfering elements can be neglected, either because of scarce abundance of the involved polyatomic species or their extremely low concentration in textile samples. As regards Cd isotopes, most of the interferences are resolved only in a less sensitive high-resolution mode ( $m/\Delta m = 10000$ ).

### Microwave-assisted sample digestion

A complete dissolution of solid samples requires a digestion step to be performed most times, which can be accelerated using high temperature and pressure, microwaves, or ultrasound assistance. Among these auxiliary energies, microwaves are the most widely used, both in closed-multimode and open-focused devices.

Nitric acid was used singly as a digestion reagent in our preliminary experiments. The digestion procedure was optimized with the certified reference material (IAEA-V-9) by varying the most significant experimental conditions: digestion time (5–50 min), sample size (0.1–1.0 g), oxidant concentration (1–10 mL  $\text{HNO}_3$ ) and applied microwave power (100–1000 W). Textile samples were completely dissolved after a digestion of 0.300–0.500 g of textile with 5–6 mL of 65%  $\text{HNO}_3$  at 300 °C for 28 minutes. The optimized digestion program consisted of five power stages: 400, 600, 700, 800 and 900 W for a duration of 6,

Table 2. Potential spectral interferences of the isotopes studied

Element	Isotope	Isotopic abundance, %	Mass	Interferent	Resolution required
Pb	$^{206}\text{Pb}$	24.10	205.9745	$^{166}\text{Er}^{40}\text{Ar}$ , $^{190}\text{Os}^{16}\text{O}$ ;	300
	$^{207}\text{Pb}$	22.10	206.9759	$^{167}\text{Er}^{40}\text{Ar}$ , $^{191}\text{Ir}^{16}\text{O}$ ;	
	$^{208}\text{Pb}$	52.40	207.9766	$^{168}\text{Er}^{40}\text{Ar}$ , $^{168}\text{Yb}^{40}\text{Ar}$ , $^{192}\text{Pt}^{16}\text{O}$ , $^{192}\text{Os}^{16}\text{O}$ .	
Cr	$^{52}\text{Cr}$	83.79	51.9405	$^{103}\text{Rh}^{++}$ , $^{104}\text{Pd}^{++}$ , $^{104}\text{Ru}^{++}$ , $^{12}\text{C}^{40}\text{Ar}$ , $^{36}\text{Ar}^{16}\text{O}$ , $^{105}\text{Pd}^{++}$	4000
	$^{53}\text{Cr}$	9.50	52.9407	$^{105}\text{Pd}^{++}$ , $^{106}\text{Pd}^{++}$ , $^{106}\text{Cd}^{++}$ , $^{37}\text{Cl}^{16}\text{O}$ , $^{13}\text{C}^{40}\text{Ar}$ , $^{35}\text{Cl}^{18}\text{O}$ , $^{36}\text{Ar}^{16}\text{O}^1\text{H}$ , $^{107}\text{Ag}^{++}$	
Ni	$^{60}\text{Ni}$	26.10	59.9308	$^{119}\text{Sn}^{++}$ , $^{44}\text{Ca}^{16}\text{O}$ , $^{120}\text{Sn}^{++}$ , $^{120}\text{Te}^{++}$ , $^{24}\text{Mg}^{36}\text{Ar}$ , $^{20}\text{Ne}^{40}\text{Ar}$ , $^{121}\text{Sb}^{++}$	4000
Cu	$^{63}\text{Cu}$	69.17	62.9296	$^{125}\text{Te}^{++}$ , $^{47}\text{Ti}^{16}\text{O}$ , $^{27}\text{Al}^{36}\text{Ar}$ , $^{126}\text{Te}^{++}$ , $^{126}\text{Xe}^{++}$ , $^{23}\text{Na}^{40}\text{Ar}$ , $^{45}\text{Sc}^{18}\text{O}$ , $^{23}\text{Na}^{23}\text{Na}^{16}\text{O}^1\text{H}$ , $^{15}\text{N}^{16}\text{O}^{16}\text{O}^{16}\text{O}$ , $^{14}\text{N}^{17}\text{O}^{16}\text{O}^{16}\text{O}$ , $^{127}\text{I}^{++}$	4000
	$^{65}\text{Cu}$	30.83	64.9278	$^{129}\text{Xe}^{++}$ , $^{49}\text{Ti}^{16}\text{O}$ , $^{25}\text{Mg}^{40}\text{Ar}$ , $^{130}\text{Xe}^{++}$ , $^{130}\text{Te}^{++}$ , $^{130}\text{Ba}^{++}$ , $^{23}\text{Na}^{23}\text{Na}^{18}\text{O}^1\text{H}$ , $^{131}\text{Xe}^{++}$	
Cd	$^{110}\text{Cd}$	12.49	109.9030	$^{70}\text{Ge}^{40}\text{Ar}$ , $^{70}\text{Zn}^{40}\text{Ar}$ , $^{74}\text{Ge}^{36}\text{Ar}$ , $^{94}\text{Mo}^{16}\text{O}$ , $^{94}\text{Zr}^{16}\text{O}$ , $^{110}\text{Pd}$	10000
	$^{111}\text{Cd}$	12.80	110.9042	$^{71}\text{Ga}^{40}\text{Ar}$ , $^{75}\text{As}^{36}\text{Ar}$ , $^{95}\text{Mo}^{16}\text{O}$ , $^{93}\text{Nb}^{18}\text{O}$	
	$^{112}\text{Cd}$	24.13	111.9028	$^{72}\text{Ge}^{40}\text{Ar}$ , $^{96}\text{Mo}^{16}\text{O}$ , $^{96}\text{Ru}^{16}\text{O}$ , $^{96}\text{Zr}^{16}\text{O}$ , $^{112}\text{Sn}$	

4, 4, 4 and 10 min, respectively. The digested sample was cooled, diluted to 100 g with deionized water, yielding a clear solution without any detectable formation of a precipitate. Consequently, in all the further experiments the resulting sample solutions were subjected to ICP-MS without filtration.

### Analytical performance

Several analytical performance characteristics important for the quantitative analysis were measured. For calibration curves, the standard solution mixture was diluted step-wise with 2% nitric acid, and solutions for nine points including the blank test solution were prepared. Three replicates were prepared for each analyte concentration.

The detection limits were calculated as three 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 the three replicate measurements. The blank consisted of deionized water with 2%  $\text{HNO}_3$ .

These results have been summarized in Table 3. As can be observed, the detection limits of the studied isotopes lie between  $0.5 \times 10^{-11}$  g/g for  $^{208}\text{Pb}$  and  $8.5 \times 10^{-11}$  g/g for  $^{110}\text{Cd}$ . Slightly higher detection limits for the three 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 the trace metals in textiles. The linearity of the calibration curves was considered to be satisfactory in the wide concentration range with correlation coefficients  $r \geq 0.996$  for all the isotopes.

### Sample analysis

Finally, the concentrations of Cd, Cr, Cu, Ni and Pb were determined in four textile samples obtained from a market-place in

Vilnius. All the samples were processed in the Chinese textile industry. In order to evaluate the accuracy of the sample preparation and analysis procedures, a certified reference material for cotton trace element analysis IAEA-V-9 was used. All measurements were performed using multiple standard addition technique. As an example, Figure shows the standard addition curve obtained for Cu isotopes in the certified reference material sample. The obtained results, together with the certified values are reported in Table 4. It can be seen that they are in good agreement with the certified concentrations. A comparison of the means using a  $t$ -test has shown that there is no statistically significant difference between them at 95% confidence level. Although the concentration of Cd in the reference material was found to be below the quantification limit, this result also corresponds to the certified value.

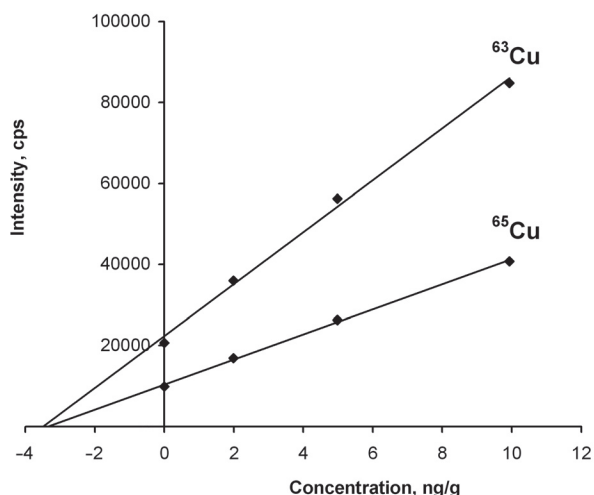


Figure. Standard addition curves obtained for two Cu isotopes in certified reference material sample

Table 3. Method performance characteristics

Isotope	Linearity range, g/g	Correlation coefficient ( $r$ )	Detection limit, g/g
$^{206}\text{Pb}$	$0.3 \times 10^{-10} - 5.0 \times 10^{-6}$	0.998	$1.1 \times 10^{-11}$
$^{207}\text{Pb}$	$0.3 \times 10^{-10} - 5.0 \times 10^{-6}$	0.998	$0.8 \times 10^{-11}$
$^{208}\text{Pb}$	$0.1 \times 10^{-10} - 5.0 \times 10^{-6}$	0.998	$0.5 \times 10^{-11}$
$^{52}\text{Cr}$	$1.5 \times 10^{-10} - 5.0 \times 10^{-6}$	0.999	$4.5 \times 10^{-11}$
$^{53}\text{Cr}$	$2.7 \times 10^{-10} - 5.0 \times 10^{-6}$	0.999	$8.2 \times 10^{-11}$
$^{60}\text{Ni}$	$2.2 \times 10^{-10} - 5.0 \times 10^{-6}$	0.999	$6.7 \times 10^{-11}$
$^{63}\text{Cu}$	$0.5 \times 10^{-10} - 5.0 \times 10^{-6}$	0.997	$2.2 \times 10^{-11}$
$^{65}\text{Cu}$	$0.9 \times 10^{-10} - 5.0 \times 10^{-6}$	0.996	$2.8 \times 10^{-11}$
$^{110}\text{Cd}$	$2.8 \times 10^{-10} - 1.0 \times 10^{-3}$	0.999	$8.5 \times 10^{-11}$
$^{111}\text{Cd}$	$2.7 \times 10^{-10} - 1.0 \times 10^{-3}$	0.999	$8.2 \times 10^{-11}$
$^{112}\text{Cd}$	$1.5 \times 10^{-10} - 1.0 \times 10^{-3}$	0.999	$5.0 \times 10^{-11}$

Table 4. Determination of some heavy metals in textile samples by ICP-MS ( $n = 3$ )

Sample	Element concentration $\pm$ standard deviation (mg/kg)				
	Cd	Cr	Cu	Ni	Pb
No 1 (blue)	– <sup>a</sup>	$0.17 \pm 0.01$	$23.57 \pm 0.86$	$0.09 \pm 0.01$	$0.34 \pm 0.02$
No 2 (red)	– <sup>a</sup>	$0.10 \pm 0.01$	$0.88 \pm 0.03$	$0.09 \pm 0.01$	$0.06 \pm 0.01$
No 3 (cherry)	– <sup>a</sup>	$0.25 \pm 0.02$	$12.16 \pm 0.45$	$0.17 \pm 0.02$	$0.18 \pm 0.01$
No 4 (black)	– <sup>a</sup>	$0.31 \pm 0.02$	$1.07 \pm 0.04$	$0.47 \pm 0.04$	$0.36 \pm 0.02$
Reference material IAEA-V-9	– <sup>a</sup> (0.002) <sup>b</sup>	$0.13 \pm 0.01$ (0.11)	$0.66 \pm 0.04$ (0.59)	$0.10 \pm 0.01$ (0.09)	$0.26 \pm 0.01$ (0.25)

<sup>a</sup> Below the quantification limit.

<sup>b</sup> Values in parentheses are certified concentrations.

From the presented results it can be concluded that ICP-MS technique is well suited for rapid and sensitive monitoring of trace metals in textile samples.

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#### References

1. H. W. Nurnberg (Ed.). *Pollutants and their Ecotoxicological Significance*. Wiley, Chichester (1985).
2. D. Purves. *Trace Element Contamination of the Environments*. Elsevier Science Publishers B. V., Netherlands (1985).
3. P. Linger, J. Mussig, H. Fischer and J. Korbort, *Ind. Crops Prod.*, **16**, 33 (2002).
4. S. Kirin and R. Eunko, *Tekstil*, **48**, 299 (1999).
5. D. E. Brushwood, *Am. Assoc. Text. Chem. Color.*, **5**, 20 (2002).
6. J. W. Rucker, H. S. Freeman and W. N. Hsu, *Text. Chem. Color.*, **24**, 66 (1992).
7. J. W. Rucker, H. S. Freeman and W. N. Hsu, *Text. Chem. Color.*, **24**, 21 (1992).
8. D. Katovic, I. Piuac and I. Soljagic, *Text. Research J.*, **55**, 20 (1985).

9. Z. Grabaric, L. Bokic and B. Stefanovic, *J. AOAC Int.*, **82**, 683 (1999).
10. A. V. Raghunath, G. Srinivasan and S. Durani, *Indian J. Chem. Technol.*, **7**, 35 (2000).
11. M. Dogan, M. Soylak, L. Elci and A. Von Bohlen, *Microchim. Acta*, **138**, 77 (2002).
12. J. S. Becker, *Spectrochim Acta Part B*, **57**, 1805 (2002).
13. M. I. Szyrkowska, K. Czerski, T. Paryjczak, E. Rybicki and A. Wlochowicz, *Fibres and Textiles in Eastern Europe*, **14**, 87 (2006).

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#### PĖDSAKINIŲ METALŲ NUSTATYMAS TEKSTILĖJE INDUKTYVIAI SUŽADINTOS PLAZMOS MASIŲ SPEKTROMETRIJOS METODU

##### Santrauka

Optimizuotas induktyviai sužadintos plazmos masių spektrometrijos metodas kai kuriems sunkiesiems metalams (Cd, Cr, Cu, Ni ir Pb) tekstilėje nustatyti. Tekstilės mėginiai buvo mineralizuojami veikiant azoto rūgštimi (28 min) mikrobangų krosnelėje 300°C temperatūroje. Identifikuoti galimi plazmos dujų ir mėginių matricos komponentų spektriniai trukdžiai. Išmatuotos pagrindinės metodo analizinės charakteristikos. Metalų aptikimo ribos yra intervale nuo  $0,5 \times 10^{-11}$  g/g  $^{208}\text{Pb}$  iki  $8,5 \times 10^{-11}$  g/g  $^{110}\text{Cd}$ . Atlikta keturių tekstilės gaminių analizė. Metodo teisingumas įvertintas analizuojant paliudytąją pamatinę medžiagą. Nustatyta, kad išmatuoti ir deklaruoti metalų kiekiai statistiškai nesiskiria.