Determination of 28 selected elements in textiles by axially viewed inductively coupled plasma optical emission spectrometry

Iva Rezić [a,b,*], Michaela Zeiner [b], Ilse Steffan [b]

[a] Laboratory of Analytical Chemistry, Department of Applied Chemistry, Faculty of Textile Technology, University of Zagreb, Croatia
[b] Department of Analytical and Food Chemistry, Faculty of Chemistry, University of Vienna, Austria

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ABSTRACT

A simple, robust and reliable analytical procedure for the determination of 28 selected elements, namely Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Hg, Mg, Mn, Mo, Na, Ni, Pb, Sc, Si, Se, Sn, Sm, Sr, Tl, V, and Zn in textile materials by inductively coupled plasma optical emission spectrometry (ICP-OES) after microwave digestion of samples was optimized and validated in this work. The total amount of elements present in textile samples was determined after microwave digestion of materials in 7 mol/L nitric acid within the optimal working program: 5 min at 150 °C (power 250 W), 15 min 180 °C (300 W) and 20 min at the maximum temperature of 200 °C (350 W). For the quality control reasons, which were ascertained by analysis of the certified cotton trace elements reference material IAEA-V9, the ICP-OES method was optimized through several parameters: by comparing Meinhard and Gemcone Low Flow nebulizers efficiency, ranging nebulizer gas flows from 0.6 to 1.0 L/min, ranging sample flows from 0.8 to 1.2 mL/min, testing RF power from 1200 to 1400 W, detecting data acquisition time (read time) from 0 to 527 s, ranging washing (delay) time from 0 to 408 s, as well as by checking the occurring interferences for the optimal line selection. Validation included determination of linearity, selectivity, accuracy, reproducibility, precision and limits of detection calculated for all 28 selected elements of interest. The developed analytical procedure was successfully applied on textile fibers (cotton, flax and hemp) as well as on standard knitted textile sample materials (cotton and wool).

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1. Introduction

Raw textile materials like cotton, flax or hemp may contain different elements. Their metal content varies significantly between years and between climate growth areas [1,2]. According to current investigations, cotton, flax and hemp sometimes adsorb very large amounts of elements from the environment [3,4], and for this reason they can be used as bio-absorbers [5]. The average elemental composition of plants is H, C, O, N, K, Ca, Mg, P, S, Cl, Fe, B, Mn, Zn, Cu and Mo. As it can be seen from this data, even raw and unprocessed textile fibers originating from plants may contain significant amounts of elements, which depends on environment and the origin of the materials. According to Moore et al. [6] several other elements (such as Cot) are present in trace amounts or are important only for some plant species (like Na, Se and Si). Other elements that can occasionally be found in plants (Au, Al, Pb, Hg, Sr, Ni, F and U) are absorbed from the soil. Those elements are often toxic for plant organisms. Phytotoxicity associated with high levels of heavy metals has been well documented. Levels of 1–5 mg/kg of Cr present in the bioavailability form in soil solution are critical for a number of plant species [7].

Elements present in cotton or similar cellulose textiles contribute to problems in textile industry (yarn manufacturing, bleaching, dyeing, and textile processing quality). High levels of heavy metals cause problems in rotor spinning and needle wear in knitting [1]. K, Ca and Mg influence fiber processing friction: increasing metal level causes a decrease of friction properties [8]. Problems reported from dyeing processes are related with metal contribution to the light-induced yellowing of whitewashed denim. Mn and Fe ions are readily air-oxidized to compounds that cause yellowing. In addition, transition metals catalyze organic reactions and strongly bond many organic compounds to cotton [9]. For those reasons the textile materials should be monitored for the presence of different elements like Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Hg, Mg, Mn, Mo, Na, Ni, Pb, Si, Se, Sn, Tl, V, and Zn [10]. All of those elements are extensively used in the textile processing industry.

Toxicity of heavy metals on textiles and their impact on human health has to be monitored according to different ecological textile standards: Markenzeichen schadstoffgeprüfter Textilien, Öko Tex Standard, Clean fashion and others [11]. According to the prescribed

* Corresponding author at: Faculty of Textile Technology, Prilaz Baruna Filipovića 30, 10000 Zagreb, Croatia. Tel.: +385 1 3712 593; fax: +385 1 3712 599.
E-mail addresses: iva_rezic@net.hr, iva.rezic@ttf.hr (I. Rezić).

Table 1
Raw textile fibers (cotton, flax, hemp) and standard cotton and wool materials.

Sample	Description
A1	Pure cotton fiber
A2	Pure flax fiber
A3	Pure hemp fiber
B1	Standard cotton material adsorptive
B2	Standard cotton non-adsorptive
B3	Standard wool fabric

Table 2
Specification of the spectrometer, ICP source and operating conditions.

Spectrometer	Perkin Elmer Optima 3000 XL, Axial view
View	Axial view
Optical system	Echelle
Wavelength range	165–782 nm
Practical spectral bandwidth	At 200 nm–6 pm, 400 nm–10 pm, at 600–16 pm
Vacuum ultraviolet region	With a nitrogen generator
Detector	High performance solid state detector, the segmented array charge coupled device detector (SCD, U.S. patent No 4,820,048)
RF generator	40 MHz free running generator with <0.1% variation in output power stability and true power control
RF frequency (MHz)	40.68
Power output (W)	From 750 W to 1500 W
Plasma gas flow (L min^{-1})	15.0
Nebulizer chamber	Cyclone
Nebulizer(s)	Meinhard concentric glass (Low-Flow GemCone)
Spray chamber	Cyclone
Plasma torch	One-piece standard quartz torch with a 2.0 mm alumina injector
Pump	Peristaltic
Operating conditions	
Incident power (W)	1300
Outer argon flow rate (l min^{-1})	15
Auxiliary gas flow (L min^{-1})	0
Sheath gas flow rate (L min^{-1})	0.5
Liquid uptake rate (sample flow) (mL min^{-1})	2.0 – Meinhard concentric glass nebulizer 0.8 – Low-Flow GemCone nebulizer
Carrier gas flow rate (L min^{-1})	20
Read time	60 s
Delay time	35 (30) s

limits, textiles need to be tested for the presence of chemicals, dyes and metals [12].

For the determination of many different elements in textiles, an appropriate analytical method has to be developed and applied. One of the most widely used analytical technique for different elements determination in biological and environmental materials is ICP-OES due to its advantages over other analytical methods: before all a possibility of simultaneous determination of many elements of interest, freedom from different chemical interferences and high detection power. The biggest disadvantage of this method is the line richness that can cause spectral interference. Example of particular line-rich elements are: Ce 5250 lines, Fe 4400 lines, W 3800 lines, Mo 3400 lines and Cr 3000 lines [13]. At the same time this property offers the advantage of great number of choices of potential analytical lines.

All the measurements in this work have been performed with the axially viewed configuration. The axial viewed torch system was chosen due to many advantages, such as improving the detection limits and linear dynamic range [14]. Silva et al. [15] found that the sensitivity attained with the axially viewed arrangement was approximately 20 times better that the one obtained with the radially viewed configuration, which is a confirmation of the previous reports from Ivaldi and Tyson [14] and Brenner and Zander [16]. In this work axially viewed ICP-OES method was developed, validated and applied for the determination of 28 different elements namely Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Co, Cu, Fe, K, Hg, Mg, Mn, Mo, Na, Ni, Pb, Sc, Si, Se, Sn, Sm, Sr, Tl, V, and Zn in textile materials (cotton, flax and hemp).

2. Experimental

2.1. Samples

Investigated textile samples (cotton, flax, hemp and wool) are presented in Table 1. Pure cellulose fibers as well as textile materials were analyzed. The most important material was cotton: it was chosen since this is the most important textile material and the most significant textile fiber in the world (when comparing to all other natural and man-made polymer fibers).

2.2. Chemicals and standard solutions

All the chemicals and standards used were of p.a. grade, supplied by Merck, Darmstad, Germany. Calibration standards for all 28 elements were supplied as stock standard solutions of 1000 mg/L, from which the working mixed standard in ranges of 0–40 mg/L were prepared. For the method development, IAEA V-9 (cotton trace element analysis) certified reference material was analyzed after microwave digestion in 7 mol/L nitric acid. The chosen CRM material was chosen so that it meets the required properties, and so that the matrix of the reference sample is as similar to the matrix of the unknown sample, as possible. For this reason the same source error would be encountered when analyzing a CRM and the unknown samples.

2.3. Instrumentation

A closed-vessel microwave digestion system MLS 1200 Mega (produced by Milestone) equipped with the temperature control was used for the sample digestion. The inductively coupled plasma-optical emission spectrometer used was a Perkin Elmer Optima 3 000 XL. Within this configuration, instrument was equipped with a standard one piece extended torch with a quartz injector tube, a cyclone spray chamber and a concentric nebulizer, as it is presented in Table 2.

2.4. Sample preparation

Textile samples and raw plant materials were dried for 48 h at 60 °C before analysis, then cut and weighed. 0.5 g of dried samples were put into the digestion vessels of the microwave oven and completely digested with 8 mL of 7 mol/L nitric acid. The temperature program was as follows: 5 min at 150 °C (power 250 W), 15 min 180 °C (300 W) and 20 min at the maximum temperature of 200 °C (350 W). The resulting solutions were cooled, filled up to 10 mL with 7 mol/L nitric acid and analyzed by ICP-OES. The certified reference material for cotton trace element analysis IAEA V-9 was digested and analyzed in the same way.

3. Results and discussion

3.1. Optimization of ICP-OES working parameters

Instrument optimization was performed by changing nebulizers (Meinhard and Gemcone Low Flow), ranging nebulizer gas flows from 0.6 to 1.0 L/min (0.6, 0.7, 0.8, 0.9, 1.0, and 1.0 L/min), ranging sample flows from 0.8 to 1.2 mL/min (0.8, 0.9, 1.0, 1.2, and
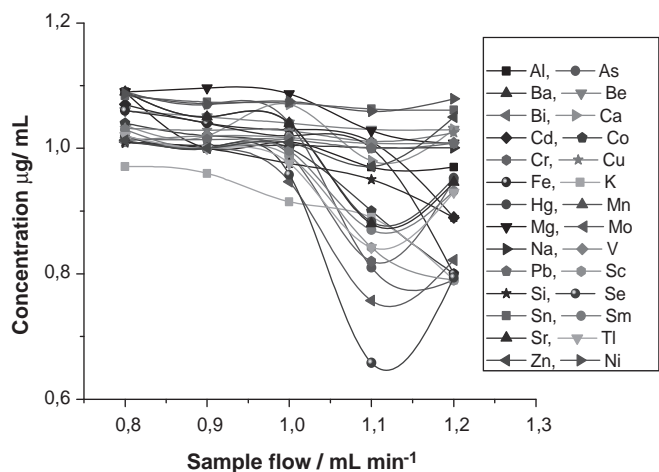
Fig. 1. Sample flow optimization (Low flow Gemcone nebulizer).
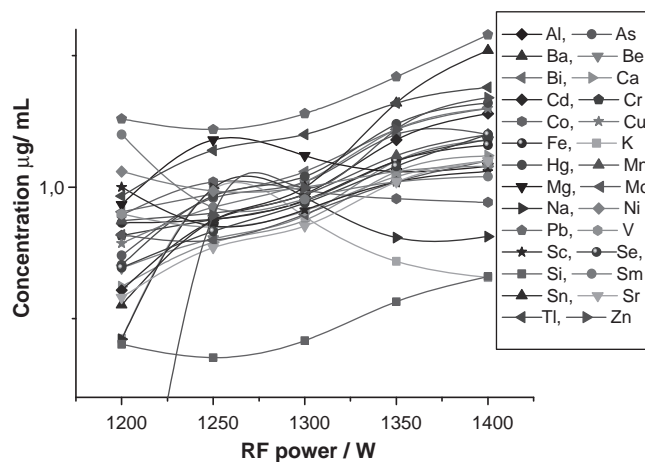

Fig. 3. RF power optimization (Low flow Gemcone nebulizer).

1.3 mL/min), testing RF power from 1200 to 1400 W (1200, 1250, 1300, 1350, and 1400 W), detecting data acquisition time from 0 to 527 s, ranging washing (delay) time from 0 to 408 s; as well as by checking the occurring interferences for the optimal line selection.

Sample flow (Fig. 1) was optimized by Low flow Gemcone nebulizer for 1 µg/mL CALs (standard mixed solutions of elements) and IAEA V-9 CRM (certified reference materials). Result of the nebulizer gas flow optimization is presented in Fig. 2, from which it is obvious that the optimal nebulizer gas flow is the 0.8 mL/min for few elements (K, Ba and Sr) while for all the other elements tested the optimal flows are below this value, at 0.7 mol/LL/min. RF power optimization (Fig. 3) showed that after 1250 W the intensity of easily ionized elements which are important for biological materials (like Ca, K, Mg, and Na) drops significantly. For this reason 1300 W was chosen as the optimal working RF power. The summary optimization results of all parameters shown for one chosen example element (aluminum) are presented in Fig. 4.

LowFlow and Meinard nebulizers were compared, and those results are presented in Fig. 5. The Gem Cone Low – flow nebulizer was chosen for the purpose of this work due to its numerous advantages. For the measurements of textile digests, in which there was a big possibility of having small non digested particles, this was a very useful property. Although the Meinhard nebulizer may clog due to the incomplete digestion, this was not observed in this work, since the digestion procedure was optimized to be complete. Nevertheless, there is a limitation with the applied optimizing procedure: since the three parameters studied (sample flow rate, nebulizer gas
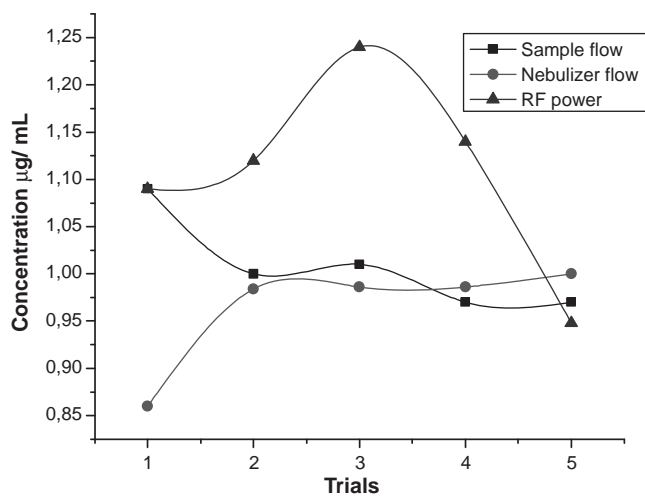

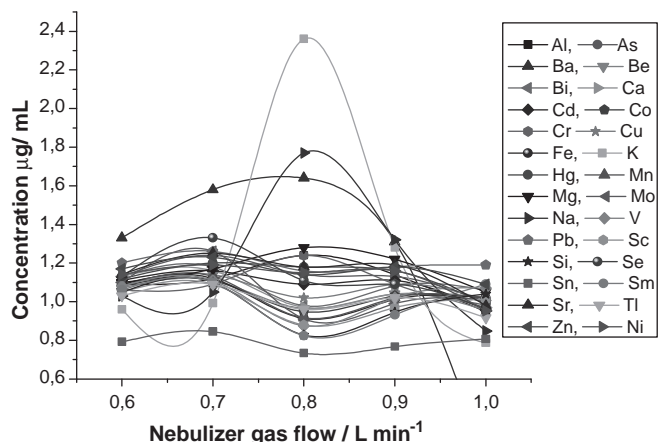Fig. 4. Summary optimization data of aluminum.

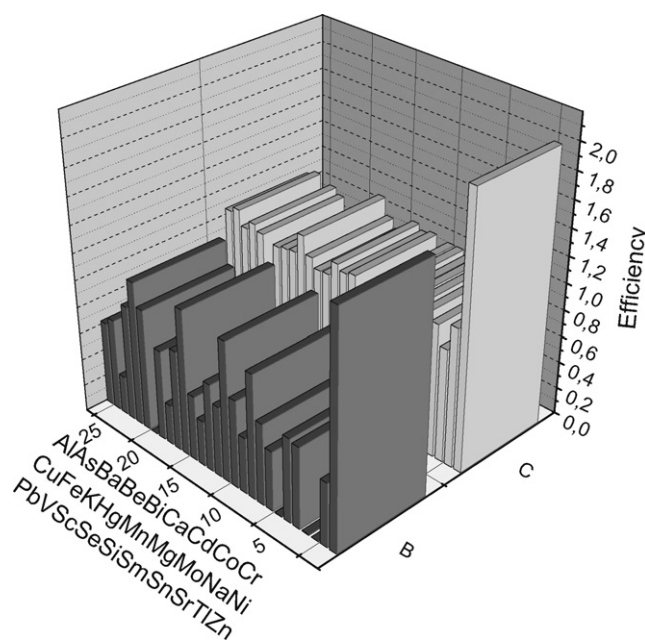Fig. 2. Nebulizer gas flow optimization (Low flow Gemcone nebulizer).

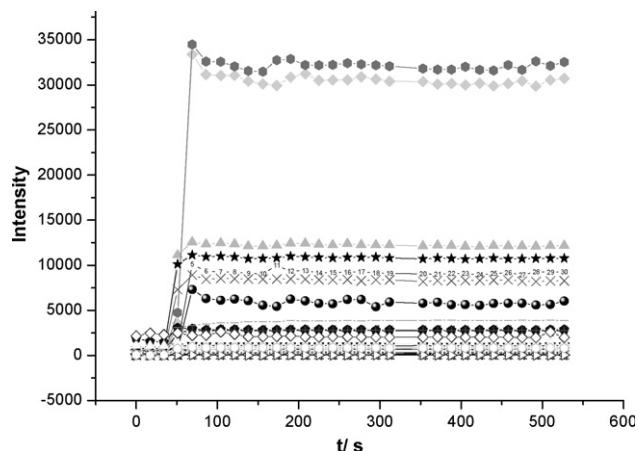Fig. 5. Comparison of *Gemcone* (B) and *Meinhard* (C) nebulizers.

Fig. 6. Read time optimization.

flow rate and RF power) were treated as independent parameters (and therefore were optimized separately), the current optimization is only a local optimization but not a global one. This could be further improved if taken into consideration that the effects of RF power and nebulizer gas flow are dependent, so different RF power would have different optimized nebulizer gas flow, and vice versa (Figs. 6 and 7).

3.2. Interferences and the plasma robustness

In order to determine possible interferences, spectral overlapping and shifting, each investigated element was separately measured in concentrations of 1 and 10 mg/L. It was important to determine the interfering elements or compounds by the *ICP WinLab* software data [17] and the literature data [18–22]. For example, the emission line of Al at 308.215 nm was strongly affected by other nearby emission lines of Mn, Gd, or –OH. The influence was stronger when lower concentrations of Al were observed, for blank and low concentrations of standard solutions. The *ICP WinLab32* software offered a possibility to easily compensate this interference: it was done by subtracting the line value of the blank solution from all the other lines. In more complicated cases, background corrections in 1 and 2 points were performed. In the worst cases, emission lines were not used for measurements, but others had to be selected.

The absence of excitation interference was indicated by the plasma robustness and for it's calculations the ionic-to-atomic line

ratio of two magnesium emission lines (atomic and ionic transition) was used: the atomic emission line (285.213 nm) and the ionic emission line (280.271 nm) [23], with their background equivalent concentrations of 0.05 and 0.01 mg/L, respectively. Since in our measurements the ratio was much bigger than 10 (intensitiy of Mg, 280.270 = 14575207.3 arbitrary units; intensity of Mg, 285.213 = 2840025.1 arbitrary units), the plasma was considered to be robust so that plasma parameters did not have to be further optimized.

3.3. Line selection and limits of detection

Biological materials (plants used as raw textiles like cotton, flax or hemp) are rich in Ca, K, Mg and K which affect the plasma according to Chan, Daskalova and Boevski, Iglésias et al. and Masson [24–28]. Multi-element standard solutions in the investigated matrix system and different certified reference materials solutions after digestion were scanned by ICP-OES over the selected wavelength range of interest to monitor the line interferences. The most important criteria for line selection was accessibility of wavelengths with the used instrument Optima 3 000 XL, appropriate elements concentration according to their expected concentration ranges, and possible interference (spectral or others) occurrences. The line selection was based on the fact that the easy ionisable elements are present as major constituents, while other elements are present as minor or trace elements. Therefore the fact that by increasing the RF power the intensity of the major elements drops significantly was very advantageous. Line selection was done by testing certified reference material (IAEA V-9). The lines chosen were those that gave results in the best agreement to the certified values. The limits of detection calculated by 0.6 μg/mL mix standard solution in 7 mol/L nitric acid for 28 different elements of interest are listed in Table 3, together with the recommended and chosen lines. The lines recommended for biological material according to Nölte [13] are compared to chosen lines and those results are also presented in Table 3.

3.4. Calibration, statistics, validation and quality control

The validation was performed with the purpose of assuring the accuracy of the measurements. For this purpose mix standard solutions were prepared from the stock standard solution of 1000 mg/L by dilution in the 7 mol/L nitric acid. The ranges of the calibration curves (7 points) were selected to match the expected concentrations of the investigated elements in natural plant materials. The limits of detection were calculated as the concentrations equivalent to three times the standard deviations of a series of 11 successive measurements of the signals of the blank solutions. The results are presented in Table 3 and are in the range from 0.3 to 105 μg/L which corresponds to ranges reported in the literature [22,29–32].

3.4.1. Linearity

The ICP-OES has extremely good linearity, which covers much broader concentration range than majority of other analytical instrumental methods (for instance UV/vis spectrometry). Linearity was checked in ranges of 0–40 μg/mL for all elements of interest. The correlation coefficients were all beyond 0.996 except for Ca, Hg, and Na.

3.4.2. Analyte losses during microwave digestion

Microwave digestion of calibration standard solutions was performed for the purpose of determination of analyte loses during microwave digestion. Therefore 0.2, 0.4, 0.6, 1.0, and 2.0 μg/mL were digested in the microwave oven under the same digestion program as all the materials. After the digestion, solutions were diluted up to 10 mL and measured by ICP-OES. R^2 of all elements
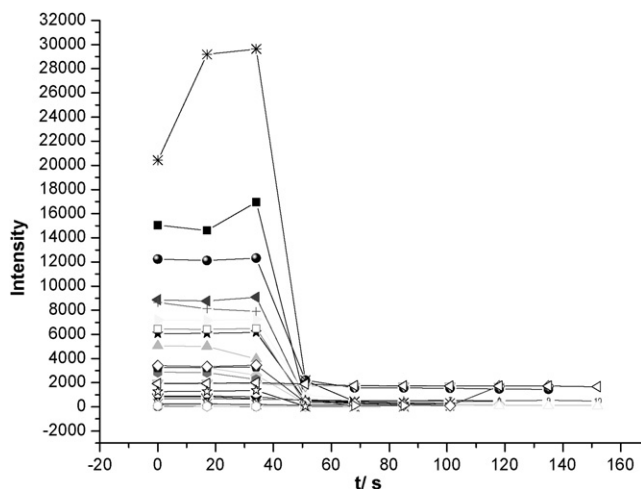

Fig. 7. Delay (washing) time optimization.

Table 3
Limits of detection, recommended lines [13], the most prominent lines (italic) and selected lines (bold values).

Element	λ$_{recommended}$ (nm)	Limits of detection µg/L in 7 mol/L nitric acid (λ (nm))
Al	396.152, 167.022	**16.6 (308.215)**, *5.85 (237.312)*, 8.75 (396.152)
As	197.197, 188.979	*13.5 (188.979)*, **28.8 (193.696)**, 26.2 (197.197)
Ba	455.403	**1.0 (230.424)**, *0.5 (233.527)*, 4.9 (413.066)
Be	313.107	*0.2 (234.861)*, **4.3 (265.045)**
Bi	–	19.8 (190.178), 33.9 (222.825), ***0.5 (206.170)***
Ca	317.933, 396.847	**9.6 (315.887)**
Cd	228.802, 226.502	0.6 (226.502), 0.8 (228.802), ***0.4 (214.438)***
Co	228.616,	*1.0 (228.616)*, 1.2 (230.786), **1.7 (238.892)**
Cr	267.716, 205.552	0.6 (205.560), *0.4 (267.716)*, 2.7 **(357.896)**
Cu	327.396, 324.754	**3.2 (224.700)**, *1.7 (324.754)*, 4.6 (327.396)
Fe	259.940, 238.204	2.6 (238.204), 0.6 (239.562), ***0.3 (259.940)***
Hg	–	***4.0 (194.168)***, 25.8 (253.652), –(435.835)
K	766.490	–(404.721), –(310.205), ***8.4 (766.491)***
Mg	285.213, 279.079	**28.9 (202.582)**, *3.2 (279.079)*, –(279.553)
Mn	257.610	**13.3 (257.610)**, 35.9 (260.569), –(279.482)
Mo	202.030	*2.1 (202.030)*, **6.0 (203.844)**, 5.1 (204.598)
Na	589.592, 330.237	–(288.114), ***105.1 (330.237)***
Ni	231.604, 221.648	*2.2 (221.647)*, 2.6 (231.604), 6.3 (232.003), **31.31 (341.476)**
V	–	5.6 (270.412), **2.5 (292.402)**, *1.3 (309.311)*, –(310.230)
Pb	220.353	**30.3 (216.999)**, 6.9 (220.353), –(261.418)
Sc	–	1.2 (337.215), 0.62 (357.253), ***0.3 (361.384)***
Se	196.026	***21.2 (196.026)***, –(203.985), –(235.435)
Si	251.611	5.1 (212.412), 32.6 **(221.667)**, *4.0 (251.611)*, 11.3 (288.158)
Sm	–	***12.9 (359.260)***, 15.4 (363.429)
Sn	–	***6.0 (189.933)***, 40.5 (242.170), 10.6 (283.999)
Sr	407.771, 421.552	**11.9 (232.235)**, *0.1 (407.771)*, 0.1 (421.552)
Tl	334.941	**15.2 (190.800)**, 57.5 (276.787), 54.0 (351.924)
Zn	206.200, 213.856	*0.5 (202.548)*, **0.8 (206.191)**, 0.6 (213.856)

was in the range of 0.9927–0.9997. Therefore we can conclude that during the microwave digestion, all the elements are preserved for the analysis, which makes this procedure much more appropriate for textile fibers digestion than other digestion methods (like dry mineralization or open vessel digestion). No analyte loss was found for all elements investigated.

3.4.3. Accuracy, precision and repeability

The accuracy of the microwave digestion was checked by digesting the certified reference material IAEA-V-9 (for trace elements in cotton cellulose) 11 times under the same microwave digestion program parameters. The results of the accuracy measurements presented in Table 4 show that for majority of the elements tested, measured and the certified values were in a good agreement. In all experiments the precision of the ICP-OES measurements was specified with a relative standard deviation (RSD) of the line signals within 0.2–2%. RSD of the certified reference material IAEA V-9 digestion procedure ($n = 14$ digestions) was in the range from 1.8 to 30.9% for majority of elements with exception of Pb.

Table 4
Accuracy data for *IAEA-V-9* after microwave digestions, $n = 14$.

Element	Certified (µg/g)	95% confidence interval	Found (µg/g)	Difference (%)
Al	44	13–53	43.49	−1.2
As	–	–	3.84	–
Ba	9	6–12	8.31	−7.7
Be	–	–	0.08	–
Bi	–	–	0.23	–
Ca	240	220–260	275	14.6
Cd	0.002	0.001–0.006	0.002	0.0
Co	–	–	–	–
Cr	0.11	0.08–0.14	0.12	9.1
Cu	0.59	0.47–0.94	0.65	10.2
Fe	11	7–15	10.75	−2.3
K	–	–	34.88	–
Hg	0.06	0.04–0.08	0.08	40
Mg	53	46–67	50.66	−4.4
Mn	0.15	0.12–0.21	0.15	0.0
Mo	0.034	0.030–0.049	0.029	−14.7
Na	56	49–64	34.68	−38.1
Ni	0.09	0.07–0.18	0.06	−33.3
Pb	0.25	0.22–0.33	0.40	60.0
V	0.09	0.07–0.10	0.09	0.0
Sc	0.009	0.007–0.01	0.009	0.0
Se	0.015	0.008–0.018	0.022	46.7
Si	–	–	69.25	–
Sn	–	–	–	–
Sm	0.003	0.002–0.004	0.003	0.0
Sr	0.65	0.54–0.96	0.65	0.0
Tl	–	–	–	–
Zn	–	–	1.60	–

Table 5
Elements found in cotton, flax, hemp and wool textile samples ($n = 3$), results are presented in mg/g.

	Cotton	RSD (%)	Flax	RSD (%)	Hemp	RSD (%)	Wool	RSD (%)
Al	13.9	2.4	76.1	3.1	86.8	2.9	25.2	4.2
Ba	<LOD	–	<LOD	–	<LOD	–	4.8	7.5
Be	0.4	25.7	<LOD	–	<LOD	–	<LOD	–
Ca	230	21.4	310	19.9	540	20.3	660	28.9
Cr	4.2	2.4	<LOD	–	<LOD	–	3.1	2.9
Cu	<LOD	–	9.6	5.6	0.8	30.1	<LOD	–
Fe	14.4	3.3	33.0	4.2	34.8	3.7	19.3	4.5
K	1170.2	19.7	64.1	9.6	67.8	15.4	16.9	11.2
Mg	397.3	16.2	86.6	14.9	82.1	14.3	<LOD	–
Na	<LOD	–	<LOD	–	365	27.7	<LOD	–
Ni	3.0	4.5	<LOD	–	<LOD	–	2.3	3.9
Pb	<LOD	–	<LOD	–	<LOD	–	0.7	30.9
Sc	<LOD	–	<LOD	–	<LOD	–	5.6	15.9
Sn	17.4	28.9	<LOD	–	<LOD	–	31.6	30.9
Zn	14.2	4.3	7.2	3.8	1.1	5.2	<LOD	–

*As, Bi, Cd, Co, Hg, Mn, Mo, V, Se, Sm, Sr and Tl were in all samples present below limits of detection.

3.5. Application of developed method on cotton, hemp and flax

Many different problems related to biological sample preparation prior the ICP-OES determination have been reported in the literature [33–36]. The importance of this investigation covers broad field from agricultural sector and botanical research [37] to environmental concerns [38,39]. The novelty of this work is the microwave sample digestion associated with the axial view ICP detection. The method was developed by using the certified reference material for cotton trace elements analysis. Such material was the most appropriate, since it had the most similar matrix to the investigated textiles [40–42]. Samples of textile materials made of natural fibers (Table 1) were digested under the same microwave digestion program as was the CRM IAEA-V-9, and afterwards analyzed by ICP-OES. The results are presented in Table 5. As those results show, the methods of microwave digestion and ICP-OES which were developed in this work for determination of different macro, micro and trace elements in textile materials can be successfully applied on cotton, flax, hemp and wool samples.

4. Conclusions

The ICP-OES measurements of elements present in raw textile materials (cotton, flax, hemp and wool) were validated through several parameters: limits of detection, linearity, selectivity, accuracy, precision and reproducibility that were determined by using certified reference material IAEA-V-9. The validation proved that the developed ICP-OES method can be applied for 28 elements determination in textile materials like cotton, flax and hemp. Optimal working conditions of ICP-OES are presented in Table 2. It was found that the Low-Flow Gem Cone nebulizer offered several advantages over the concentric Meinhard nebulizer. The biggest disadvantage of Meinhard nebulizer over LowFlow GemCone is the possibility of clogging, which might occur if the digestion procedure would not be complete. Since raw textile materials contain large amounts of heavy metals, which creates problems during textile processing and may have a negative impact on human health and the environment, elements have to be determined with the highly precise analytical method such is the proposed ICP-OES.

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