Analytical Methods for the Determination of Heavy Metals in the Textile Industry

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Heavy metals in textile wastewater represent a major environmental problem, and are a potential danger to human health when present on textiles. Furthermore, the presence of some metals influences the production of textiles. Heavy metals are often used as oxidizing agents, as metal complex dyes, dye stripping agents, fastness improvers, and finishers. Thus, they act as hazardous sources throughout entire textile processing. Toxic effects of heavy metals on humans are well documented. Therefore, it is important to monitor heavy metals throughout the entire production. Today, maximum permissible values for metals in textiles are given by different regulations, according to which the heavy metals have to be determined both qualitatively and quantitatively. Several analytical procedures for the determination of heavy metals were tested for their application on textiles. The advantages and disadvantages of TLC, UV-VIS, GF-AAS, ICP-OES, and ICP-MS methods are discussed.

Key words: *Textile materials, heavy metals, analytical methods, textile production, wastewater*

Introduction

The major chemical pollutants present on textiles are dyes containing carcinogenic amines, toxic heavy metals, pentachlorophenol, chlorine bleaching, halogen carriers, free formaldehyde, biocides, fire retardants, and softeners. Because heavy metals are often used as oxidizing agents, as metal complex dyes, dye stripping agents, fastness improvers, and finishers (water repellents, flame retardants, anti-fungal and odor-preventive agents) they act as sources of contamination throughout the entire textile processing.

When present in/on textile materials, heavy metals represent a major environmental problem in textile industry, as well as a potential danger to human health. Heavy metals can be very dangerous to the human population and nowadays their toxic effects are the subject of many scientific studies.[1] Damages of organs, disorders in the respiratory tract and lung diseases, dysfunction of the heart, of blood and blood producing organs, disorders in the nervous system, skin diseases, and abnormalities in fertility and pregnancy are reported. A summary is given in Table 1.

It has been proved that accumulation of heavy metals in body tissue and their binding to enzymes disrupt the functioning of cells, which also leads to tumors or cancers.[2] For this reason, it is important to monitor heavy metals in/on textile materials. Today different standards are in use prescribing the analysis of textile materials and indicating the maximum permissible values. According to standards, such as MST *(Markenzeichen schadstoffgeprüfter Textilien),* Öko Tex Standard *(Internationale Gemeinschaft für Forschung und Prüfung auf dem Gebiet der Textilökologie),* Clean fashion, Steilman, Commitextile, EC Approach, EPG *(The European Product Guarantee),* and *Ecomarc Scheme,* textile materials must fulfill high ecological requirements in low concentrations of allergenic, toxic and carcinogenic metals for which purpose appropriate analytical methods must be applied. The mass fraction limits of several metals are listed in Table 2.[3–6]

According to these regulations, heavy metals should be extracted from textile materials and determined subsequently both qualitatively and quantitatively.

Besides the effect on human health, high concentrations of heavy metals in textile wastewater have a negative impact on the environment, on water quality itself, as well as on the biota living in the waterbodies.[7] Several techniques are applied for the removal of heavy metals from textile wastewaters.[8] Nevertheless, certain amounts of toxic elements resulting from the textile industry are found in surface and groundwater.[9,10]

It is known that some metals present in cotton may contribute to problems in yarn manufacturing, bleaching and dyeing, and in the processing quality.[11] Problems reported for dyeing processes are related to metal contribution to the light-induced yellowing of whitewashed denim. Manganese and ferrous ions are readily air-oxidized and form compounds causing yellowing. In addition, transition metals catalyze organic reactions and function as mordant that strongly binds many organic compounds to cotton.[12] For this reason, the textiles treated by those processes should be monitored for the presence of different metals (alumi-

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T a b l e   1   – *Health hazard effects induced by metals from textiles on different biological systems*[1]

T a b l i c a   1   – *Štetni učinci metala s tekstilnih materijala na različite biološke sustave*[1]

Metals Metali	Nervous System Nervni sustav	Cardiovascular Kardiovaskularni	Gastroenteral Probavni	Endocrine Endokrini	Immune System Imunosni sustav	Kidney Bubreg	Liver Jetra	Lungs Pluća	Blood Krv	Skin Koža
Al	+							+		
As	+		+	+			+	+	+	+
Cd	+	+	+			+		+		
Co	+	+	+	+	+			+		+
Cr			+		+	+		+		+
Cu	+		+						+	
Fe	+		+				+	+		
Hg	+		+			+		+		
Mn	+			+	+			+		
Ni					+			+		+
Pb	+	+	+	+	+	+			+	+
Tl	+		+	+		+		+		
Zn			+					+		

T a b l e   2   – *Limits for heavy metals suggested by different environmental standards*[3–6]

T a b l i c a   2   – *Granične vrijednosti teških metala propisane različitim eko-standardima*[3–6]

Heavy metals w/mg g^{-1} Teški metali w/mg g^{-1}	Öko Tex	EPG	Eco-tex	TOX PROOF	M. S. T.
Sb	–	–	–	0.2	–
As	0.2–1.0	0.01	0.01	0.2	–
Cd	0.1	0.005	0.005	0.1	–
Cr	1.0–2.0	0.1	0.1	1.0	0.5
Cr	0.0	–	0.0	0.0	0.1
Co	1.0–4.0	0.2	0.2	1.0	–
Cu	25–50	3.0	3.0	20.0	0.5
Pb	0.2–1.0	0.04	0.04	0.8	–
Hg	0.02	0.001	0.001	0.02	–
Ni	1.0–4.0	0.2	0.2	1.0	0.5
Zn	–	5.0	3.0	20.0	2.0

num, calcium, copper, iron, magnesium, manganese, and titanium) and their amounts have to be reduced by applying different production methods.[13]

Metals are most frequently used in textile wet processing, although some of them are extremely toxic to many organisms. The use of chromium-based dyes is essential for the fast black dyeing on wool and nylon. In future, these dyes will probably be replaced by newly developed ones containing less toxic metals like iron.[14] Cobalt, chromium and occasionally copper and nickel form part of the most commonly used dyes, especially dyes for leather materials, nylon and wool. While chromium is generally used, cobalt has found selected applications only. As a group, the metal-complex dyes offer good overall fastness properties.[15] Because of their widespread application, metals are present in textile dyeing wastewaters as free ionic or complex metals, which contribute to environmental concerns.[16] Cobalt and chromium are applied particularly in dyes for wool: almost every wool mordant dye uses chromium compounds. The chromium containing C.I. Mordant Black 11 is one of the most widely used dyes in the world.[17] Copper salts are used to fix direct dyes and to enhance the light fastness on nylon. Antimony improves wash fastness properties on nylon fibers.[18] Cationic dyes contain zinc as well as trace concentrations of mercury, cadmium and arsenic as impurities. Not only zirconium and aluminum, but also salts of many other metals are used extensively in textile processing.[19] Usual mass fraction of heavy metals in dyes are (in μg g^{-1}): w = 1.0 to 1.4 (As), up to 1.0 (Cd), 3.0 – 83.0 (Cr), 1.0 – 3.2 (Co), 33.0 – 110.0 (Cu), 6.0 – 52.0 (Pb), 0.5 – 1.0 (Hg), and 3.0 – 32.0 (Zn).[20]

Different analytical methods can be applied for the determination of heavy metals present in and on textile materials, in textile wastewaters, as well as in different reagent solutions used in textile processing. In this study, several analytical procedures for the determination of heavy metals were tested. The advantages and disadvantages of thin layer chromatography (TLC), UV-VIS spectrometry, graphite furnace and flame atomic absorption spectrometry (GFAAS, FAAS), inductively coupled plasma – optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) are presented.

Analysis of heavy metals

Qualitative and quantitative analyses of (heavy) metals in textile industry are a challenging field due to the wide range of analytical tasks. First, the determination of heavy metals does not only comprise final analyses, but is very complex. Usually it is not possible to analyze the whole specimen depending on the kind and amount of the sample. Therefore, only a part (or portion) of the system under study is selected for the following analysis procedure in a laboratory or directly on the site. Some common steps involved in the analytical process are: sampling, sample preservation, sample preparation, analysis, and data evaluation.

Sampling

The first step of an analytical procedure is *sampling*. Thereby the sample is drawn from the object to be analyzed, collected in such a way that it can be considered representative for the original object. All factors that may result in differences in the elemental concentrations, i. e. losses or contaminations, must be taken into consideration.

Since wastewater analyses are not only a concern in textile industry, but also in other kinds of industrial activity as well as in environmental investigations, standard analytical pro-

cedures and sampling guidelines describing the manner of conducting an appropriate sampling for metal analyses[21–23] are applied.
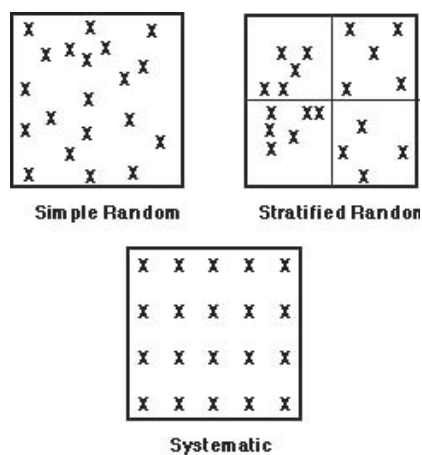

F i g. 1 – *Sampling plans (X represents an individual soil core location)*
S l i k a 1 – *Planiranje uzorkovanja (X predočuje pojedino mjesto uzimanja uzorka)*

Since textile products are heterogeneous materials it is not sufficient to analyze only one sample spot of fabric, but various parts have to be tested in order to estimate the entire population of possible results. Uniform textiles can be sampled in an analogous way to soil samples, i.e. in a simple random, stratified random or systematic pattern. With an increasing number of sampling points, the chance of obtaining an inaccurate estimate of the average metal concentration in the fabric decreases. The three above-mentioned sampling plans are presented in Fig. 1.[24] With a simple random system each fabric sample is selected separately, randomly and independently of previously drawn units. A stratified random sample is taken from a textile material having been divided into several subunits or quadrants from which simple random cores are obtained. This increases the precision of the data obtained for the entire fabric. The systematic sampling is a further progression in an attempt to ensure complete textile coverage, similar to the change from the simple random to the stratified random. Samples are taken at regularly spaced intervals in all directions. Usage of a systematic sampling plan has been widely accepted, because it is straightforward and potentially increases the accuracy of analyses of heterogeneous materials.

Sample preservation

The next step of great importance is *sample preservation*, as there is usually a delay in time between sample collection and analysis. Sample preservation should ensure that the sample retains its physical and chemical characteristics so that the analysis performed truly represents the object under study.

Changes of the composition of a sample after its collection may be due to physical, chemical, and biological processes. The first involve volatilization, diffusion, and adsorption on surfaces. Possible chemical changes are photochemical reactions, oxidation, and precipitation, whereas biological processes include biodegradation and enzymatic reactions. Commonly used steps in sample preservation are temperature control, addition of preservatives, the choice of proper containers, and the observance of recommended storage time, which depends on the analyte of interest as well as on the sample matrix. Some typical preservation methods for metal analyses are listed in Table 3.

T a b l e 3 – *Sample preservation techniques in metal analysis*
T a b l i c a 3 – *Metode čuvanja uzoraka u analizi metala*

Sample Uzorak	Metals Metali	Preservation Method / Metoda konzerviranja	Container type / Vrsta spremnika	Storage time / Vrijeme čuvanja
aqueous solution vodena otopina	dissolved otopljeni	filter on-site, acidify to pH 2 with HNO_3 odmah filtrirati te dušičnom kiselinom podesiti pH na 2	plastic plastika	6 months 6 mjeseci
	total ukupni	Acidify to pH 2 with HNO_3 dušičnom kiselinom podesiti pH na 2	plastic plastika	6 months 6 mjeseci
	Cr(VI)	cool to 4 °C hladiti do 4 °C	plastic plastika	24 hours 24 sata
	Hg	acidify to pH 2 with HNO_3 dušičnom kiselinom podesiti pH na 2	plastic plastika	28 days 28 dana
solid sample (fabrics) čvrsti uzorak (tkanina)	total ukupno	exclude moisture and air contact izbjeći kontakt s vlagom te zrakom	plastic plastika	years godinama

Any contamination with other metals, losses of volatile analytes or even enrichment due to evaporation of the solvent have to be avoided throughout the entire analytical process. Table 4 gives an overview of possible contamination during all steps of the analytical process.

Sample preparation

Sample preparation is the following and last step prior to analysis, as most samples are not ready for direct introduction into analytical instruments. In some cases, the analytes have to be released from the matrix by extraction or digestion in order to obtain a clear solution. The kind of sample preparation applied depends on the sample, the matrix, and the concentration level of the analytes. For instance, trace analysis requires more stringent sample preparation than major component analysis.

T a b l e   4   – *Sources of sample contamination*
T a b l i c a   4   – *Izvori kontaminiranja uzoraka*

Step of Analytical Process Koraci analitičkog procesa	Source of Contamination Izvor kontaminacije
sampling uzorkovanje	sample collection equipment oprema za uzorkovanje containers spremnici preservation reagents (e.g. acids) reagensi sample handling rukovanje uzorkom ambient contamination okoliš
transport and storage transport i skladištenje	containers spremnici cross-contamination of other samples drugi uzorci sample handling rukovanje ambient contamination okoliš
sample preparation priprema uzorka	sample handling rukovanje sample preparation equipment laboratorijski pribor carry-over in instruments unošenje u instrument Cross-contamination of other samples drugi uzorci dilutions razrjeđenja homogenization homogenizacija reagents reagensi ambient contamination okoliš
analysis analiza	carry-over in instrument unošenje u instrument Instrument memory effects instrument reagents reagensi syringes, tubes laboratorijski pribor ambient contamination okoliš

Extraction procedures

For many purposes it is not necessary to know the total amount of an element in a sample. Especially for risk estimations the determination of the extractable amounts of heavy metals is of importance, since they reflect their possible impact on human health. Therefore, commonly used extraction media are artificial sweat (pH 5.5 as well as pH 8.0) or saliva solutions. Due to their extensive contact with the human skin extraction samples are commonly performed with leather samples.[25, 26]

Extraction is not only a simple preparation step, but can also be used as a pre-concentration procedure. If the concentrations of analytes in a liquid sample or in a digest solution are below the detection limits of the analytical procedure used, this additional step is required. A commonly used method is solid-phase extraction (SPE).[27]

Digestion procedures

Usually, for all the analytical methods mentioned above, the sample should be present in a liquid form, best as a dilute aqueous solution. Total matrix dissolution is common and ensures complete availability of the analytes for analyses, but is time and labor intensive. Acid digestion usually renders all metal species into the same form and therefore cannot be used for speciation analyses. A less time-consuming method is slurry sampling, where the finely powdered sample is taken up in a slurry fluid.

Commonly used methods for dissolving samples prior to metal analyses are digestion in an open container, digestion in a pressurized, sealed container, as well as microwave assisted decomposition. Usually the samples are prepared by digesting the matrix using a strong acid.

To destroy organic matrices (cotton, wool, synthetic fibers) oxidizing agents are used. This procedure leads to a clear digest solution.[1, 28] Nitric acid is usually applied[29] because there is a minor chance of forming insoluble salts as might be the case with HCl or H_2SO_4. Hydrogen peroxide may be added to increase the oxidizing power of the digestion mixture.

Microwave-assisted digestion in a closed system has several advantages over open container dissolution methods. Teflon containers usually release less metal contaminants than glass or ceramic beakers or crucibles. In addition, the sealed container eliminates the chance of airborne dust contamination and reduces evaporation, so that less digestion solution is required. Losses of volatile metal species can also be eliminated. In comparison with an open vessel decomposition step, a microwave-assisted digestion procedure is less time-consuming.

Total matrix dissolution of samples is the basis for the determination of the total metal content of a certain specimen.[1, 29] Based on this information the fraction of extracted metal amounts can be calculated. Investigations in this field are usually performed with leather samples or dyed fabrics.[25, 26]

Methods for the determination of heavy metals

After sampling followed by an appropriate sample preparation step, different analytical methods can be applied for qualitative and quantitative determination of heavy metals, in e.g. wastewater samples, textile materials and reagent solutions.

Thin layer chromatography

Thin layer chromatography is a simple, rapid procedure usually applied as a screening method for the determination of heavy metals present on textile materials. In our previous experiments[31] optimization of the separation and the identification of heavy metals present on cotton material was performed by TLC–densitometry, after microwave di-

gestion of cotton samples. The best separation was achieved on microcrystalline cellulose pre-coated layers with an acetonitrile / HCl (conc.) / water developer and by visualization with a quercetine / dimethylglyoxime / NH_3 reagent. A highly sensitive 3CCD color video camera was used to capture the chromatograms under white light. Optimization of the composition of the ternary mobile phase was performed using the experimental design software package Design – Expert 6. This method was developed for separating and determining Mn^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Fe^{3+}, and Zn^{2+} ions in their mixtures.[31]

Another application of TLC is the qualitative and semi-quantitative determination of different metal-containing textile dyes.[32] Since many dyes are carcinogenic, a simple method for fast screening is advantageous.

The greatest advantage of this method is its ability to separate and simultaneously identify a number of metal components present in or on the sample. Because it demands small sample amounts and low amounts of chemical reagents, this method is both economically and ecologically favorable. The disadvantage of this method is the relatively high limit of detection (LOD) for certain metals and its poor quantitative reproducibility.

UV-VIS

UV-VIS spectrometry is also a relatively fast and simple method for the determination of heavy metals. For the application of this method metals should however be converted to colored complexes prior to analysis using different chemical reagents. This analytical method is mainly used to obtain quantitative or structural information about a substance. Commonly applied inorganic reagents for metals are: thiocyanate for Fe, Co and Mo, hydrogen peroxide for Ti, V and Cr, and iodide for Bi, Pa and Th. The organic reagents usually applied for the determination of the metals covered by textile standards such as Öko Tex are listed in Table 5.

T a b l e 5 – *Characteristics for the determination of selected heavy metals by UV-VIS-spectrometry*[33]
T a b l i c a 5 – *Karakteristike UV-VIS spektrofotometrijskog određivanja odabranih teških metala*[33]

Metal Metal	Reagent Reagens	Wavelength λ/nm Valna duljina λ/nm	Linear range γ/mg L^{-1} Linearno područje γ/mg L^{-1}
As	Heteropoly Blue	840	0.3–3
Cd	Cadion	560	0.05–0.5
Co	Nitroso-R-Salt	420	0.1–1
Cr	4–Methyl-2-Pentanone	540	0–1.7
Cu	2,2'-Biquinoline	545	0.5–4
Fe	1,10-Phenanthroline	510	0.5–5
Hg	Dithizone	610	0.3–3
Ni	Dimethylglyoxime	460	0.2–5
Pb	Dithizone	510	0.4–3
Zn	Zincon	620	0.3–2

Applying UV-VIS-spectrometry, nickel present in aqueous solution has to be extracted with CCl_4 after conversion with dimethylglyoxime into a red organic complex. The resulting sample solutions are then placed into a cuvette and exposed to ultraviolet and/or visible light. The unabsorbed light is focused onto a photomultiplier tube detection system using a double beam design. The measured absorbance is proportional to the metal concentration present. The advantages of this method are:

– broad area of applicability
– high sensitivity (LOD in the mg l^{-1} range)
– high selectivity
– simple and rapid automatic method

Some disadvantages that have to be taken into account are:

– time-intensive sample preparation and measuring procedure (binding to complexes, adjusting of the pH-value, special extraction procedures) to obtain colored metal complexes which can be determined by UV-VIS
– interferences by other colored substances in the sample.

In addition to its application as a single method, UV-VIS-spectrometry can also be used as detector after capillary electrophoresis separation of the analytes. The applicability of capillary electrophoresis speciation of chromium in leather tanning liquor using UV-detection was demonstrated by Pobozy and colleagues.[34] Using the 1,5-diphenyl carbazide method for the determination of chromium in tannery effluents after acid digestion gave better results than applying FAAS or ICP-OES.[28]

AAS

Atomic absorption spectrometry (AAS) is widely used for the determination of trace and ultra trace elements in all kinds of samples. In AAS, a beam of light passes the sample. Depending on the concentration of the element, a certain amount of the light is absorbed. Comparing the intensity of the original beam and of the beam after passing the sample, the concentration of the element can be calculated. Since each element absorbs light of a defined wavelength, the AAS instruments have individual sources of light for each element. Commonly, AAS is a method for the determination of only one single element per analysis. The advantage is that this analytical method allows the determination of elements in very low mass concentrations (μg L^{-1}-range). Depending on the mass concentration range expected and the sample amount available, analysis can be performed either by flame AAS (FAAS) or graphite furnace AAS (GFAAS). For the first, a sample volume of some mL is required, for the latter only small amounts of samples (10–30 μL) are necessary. Therefore, GFAAS enables much lower limits of detection than FAAS. Further, with GFAAS an enrichment of the analyte is possible by pipetting the sample into the graphite tube repeatedly. By changing the pipetting speed of the autosampler device, the effects of physical interferences due to higher viscosity of solutions such as saliva or sweat solutions can be minimized. In order to avoid chemical inferences, chemical modifiers may be applied. Standard conditions, regarding pyrolysis and atomization temperature as well as the kind and amount of a chemical modifier for the selected elements are listed in Table 6.

T a b l e 6   – *Standard conditions for the GFAAS determination of selected heavy metals*[30]

T a b l i c a 6   – *Standardni uvjeti određivanja odabranih teških metala pomoću GF-AAS*[30]

Metal Metal	λ/nm	Pyrolysis ϑ/°C Piroliza ϑ/°C	Atomization ϑ/°C Atomizacija ϑ/°C	Modifier Modifikator m/µg	Characteristic masses Karakteristične mase pg/0.0044 As
As	193.7	1200	2000	3 µg Mg(NO$_3$)$_2$ 5 µg Pd	40
Cd	283.3	700	1400	3 µg Mg(NO$_3$)$_2$ 50 µg (NH$_4$)$_2$HPO$_4$	1.3
Co	242.5	1400	2400	15 µg Mg(NO$_3$)$_2$	17
Cr	357.9	1500	2300	15 µg Mg(NO$_3$)$_2$	7
Cu	324.8	1200	1900	3 µg Mg(NO$_3$)$_2$ 5 µg Pd	17
Fe	247.3	1400	2100	15 µg Mg(NO$_3$)$_2$	12
Ni	232.0	1100	2300	………	20
Pb	228.8	850	1500	3 µg Mg(NO$_3$)$_2$ 50 µg (NH$_4$)$_2$HPO$_4$	30
Zn	213.9	700	1800	5 µg Mg(NO$_3$)$_2$	1.0

AAS is a single-element method, working in a sequential mode. It is appropriate for monitoring studies of a certain element, such as Cd, Cr, As, and Pb, which exhibit negative effects on human health even when present in very low mass concentrations. AAS is, in contrast to TLC and UV-VIS, a fully automated procedure and thus less labor-intensive. The disadvantage of GFAAS is the long analysis time per sample (10–15 min for 3 or 4 replicates).

One important application of this method is monitoring of wastewaters.[35] Manzoor and colleagues used FAAS for analysis of trace metals in textile effluents as well as in soil and groundwater. These three media were analyzed for Cr, Pb, Ni, Co, Fe, Ca, Na, K, and Zn.[36] AAS was also applied by a Turkish research group for the investigation of industrial wastewater. The concentrations found for some metal ions in textile wastewater exceeded the values given in the Water Pollution Control Regulation of Turkish Authorities.[10]

Especially in extraction solutions, such as artificial sweat, the expected concentrations of toxic metals, e. g. lead or cadmium, are very low, so that GFAAS provides some advantages compared with other methods proposed for the analysis of metals in textiles.[29] Nevertheless, pre-concentration steps might be necessary to ensure the detectability of trace elements in an artificial sweat solution. Applying solid-phase extraction or co-precipitation procedures prior to GFAAS measurements, Co, Ni, Cu, Fe, Pb, Cd, Sb, as well as As can be determined quantitatively at µg L^{-1}-levels in sweat solutions without significant influences by matrix effects.[27]

ICP-OES

In optical emission spectrometry (OES) the sample is exposed to a source of high energy, such as an inductively coupled plasma (ICP). At temperatures of T = 5000 to 10000 K, elements emit light of a spectrum being characteristic for each element. This emitted light is collected by photomultipliers or LEDs. Since the intensity of the emitted light is directly proportional to the concentration of the element in the sample, quantification by calibration is possible. Modern ICP-OES instruments may analyze up to 70 elements in one step.

Since Inductively coupled plasma – optical emission spectrometry (ICP-OES) is a multi-element method, it is ideal for scanning liquid samples in order to obtain overall information on the inorganic composition of the sample under study. The sample need is higher than for GFAAS (1–2 mL). The limits of detection achievable for ICP-OES are higher than those obtained by GFAAS. The time per sample required using ICP-OES is much lower than for GFAAS. The method is applied for a wide variety of analytical tasks.[1, 25, 26] An overview of lines and detection limits for the quantitative determination of the selected metals in textile digest solutions is given in Table 7.

T a b l e 7   – *Detection limits calculated for 7 mol L^{-1} nitric acid – digest solutions*[1]

T a b l i c a 7   – *Granice detekcije određene za 7 mol L^{-1} dušičnu kiselinu – otopine nakon digestije*[1]

Element Element	Limits of detection [µg L^{-1}] in c = 7 mol L^{-1} nitric acid (λ/nm) Granice detekcije [µg L^{-1}] u c = 7 mol L^{-1} dušičnoj kiselini (λ/nm)
Al	28.3 (308.215), 171.3 (394.401), 37.9 (396.152)
As	5.4 (188.979), 8.9 (193.696), 10.8 (197.197), 1.3 (228.812)
Be	0.3 (234.861), 9.2 (265.045), 0.4 (313.042), 0.2 (313.107)
Bi	7.3 (190.178), 8.6 (222.825), 3.2 (223.061), 42. 9 (406.772)
Co	3.0 (228.616), 0.2 (230.786), 1.5 (231.160), 0.5 (238.892)
Cr	0.7 (205.560), 1.7 (206.149), 0.1 (267.716), 0.4 (357.896)
Cu	8.2 (213.598), 86.6 (224.700), 121.8 (324.754), 110.5 (327.396)
Fe	1.0 (234.349), 0.3 (238.204), 0.5 (239.562), 0.1 (259.940)
K	32.0 (310.179), 116.7 (310.205), 0.4 (766.491)
Mg	11.6 (202.582), 0.5 (279.079), 0.3 (279.553), 0.3 (280.270), 0.3 (285.213)
Mn	0.1 (257.610), 0.1 (260.569), 0.6 (279.482), 0.9 (294.920)
Mo	0.8 (203.844), 2.4 (204.598), 1.6 (281.615)
Ni	2.2 (221.647), 2.0 (231.604), 2.6 (232.003), 1.1 (341.476)
Si	0.6 (212.412), 0.5 (251.611), 4.1 (252.851), 0.8 (288.158)
Sn	12.3 (189.933), 31.7 (235.484), 33.7 (242.170), 33.2 (283.999)
Tl	3.5 (190.800), 2.7 (276.787), 10.6 (351.924)
Zn	0.5 (202.548), 2.8 (206.191), 0.6 (213.856)

The following advantages distinguish ICP-OES from AAS:

– both simultaneous and sequential analysis of multiple elements is possible
– the calibration function is spread over a wide dynamic range
– the number of measurable elements is high.

One of the disadvantages of the ICP-OES method is the high argon consumption.

Many applications of ICP-OES in the textile field are reported in literature. This method can be used to obtain an overview of the inorganic composition of various textile samples, such as cotton, flax, wool, silk, viscose, and polyester materials. Not only digested fabrics may be analyzed by ICP-OES, but also sweat extracts in order to determine the amount of leachable metals.[1] Another important topic regarding heavy metals and textiles is the investigation of detergents for domestic use. They were analyzed formerly by GFAAS. For this purpose, ICP-OES ensures accurate data, due to minimization of background interferences. The results of both methods were found to be in good agreement.[37]

For evaluation of the influence of the textile industry on the environment, an investigation of industrial effluents as well as groundwater and soil samples was carried out. A wide range of metals was determined using ICP-OES and flame-photometry.[28, 38] The determination of total chromium in digests of tannery effluents showed interferences caused by high concentrations of mineral acids and electrolytes resulting in higher values' than obtained by UV-VIS spectrophotometry.[28] The fraction of copper, cobalt and chromium in textile mill wastewater was determined using ICP-OES after a previous separation by cation exchange and reverse phase chromatography.[39]

ICP-MS

Another analytical method uses the radiation of an ICP source: by exposing a sample to the high temperatures of the plasmas, not only light is emitted but also ions are formed. These can be analyzed by a mass spectrometer (MS). Mass spectrometers use the difference in mass-to-charge ratio (m/z) of ionized atoms or molecules for separation from each other. Mass spectrometry can be used for quantification of atoms or molecules. By applying ICP-MS it is possible to analyze almost all elements of the periodic system in one analysis step with very low limits of detection.

ICP-MS is characterized by the following features:

– high sensitivity analysis – lower detection limits of most elements (ppt or ppq-range)
– simultaneous multi-element analysis
– wide dynamic range
– isotope composition

The disadvantage of ICP-MS are the high operational costs because of the high amount of argon used and the high susceptibility to high salt concentrations present in digest solutions or in sweat and saliva extraction solutions, resulting in interfrences of the mensurements.

Thus, ICP-MS is mostly used for analysis of wastewater. The determination of isotopes and their percentage in natural fibers gives information of their provenience.

The interest in using ICP-MS for analysis of organic and environmental samples, including raw materials and finished textiles, has grown over the last decade. Due to the low limit concentrations of certain metals given in various eco-standards, this analytical method is of great importance for analysis of samples from textile industry.[40] ICP-MS is further described as a tool for the identification of mordants and dyes on ancient textile samples. Not only mordants containing copper, iron, tin, aluminium or uranium could be successfully investigated, but also organic dyes with substitutional bromine.[41]

Using Laser Ablation ICP Time of Flight Mass Spectrometry (LA-ICP-TOF-MS) solid samples can be analyzed. This is of great importance for ancient textile samples in order to obtain the maximum amount of information on its inorganic composition with negligible damage of the samples.[42] The application of LA-ICP-MS using different instrumentation, e.g. quadruple (LA-ICP-QMS) and double-focusing sector field mass spectrometer (LA-ICP-SFMS), for technical textile quality control was reported by Becker and colleagues.[43]

Coupling ion chromatography with ICP-MS allows the speciation of chromium in wastewaters.[44]

Discussion

For choosing the most appropriate method for the determination of heavy metals present in or on textile material, different parameters should be considered. The most important are costs of the analyses, time required and amount of samples available. Furthermore, limits of detection, sensitivity and selectivity of the method should be considered, as well as possible interferences caused by the sample matrix.

A combination of at least two of the analytical methods mentioned is normally used for analysis of the metals in and on textile materials as well as in various samples from textile processing.

Conclusion

The best results for sample analysis are usually achievable by combining different methods. For instance, simple and rapid thin layer chromatography can be applied as a fast screening method prior to ICP-OES or GFAAS measurements. In the first step, the metals should be determined qualitatively and their concentration ranges estimated. Thereupon, the method for an exact quantification may be chosen depending on the analytical task.

References
Literatura

1. *I. Rezić, I. Steffan*, Microchem. J. **85** (2007) 46.
2. *H. Marquadt, S. S. Schäfer, R. O. McClellan, F. Welsch* (Eds), Toxicology, Academic Press, New York, 1999.
3. *R. Čunko*, Tekstil **45** (1996) 1.
4. *S. Kirin, R. Čunko*, Tekstil **48** (1999) 299.

5. Internationale Gemeinschaft für Forschung und Prüfung auf dem Gebiet der Textilökologie: Öko Text Standards 100, 200, 1000, (2005).

6. *E. Nieminen-Kalliala*, Aut. Res. J. **3** (2003) 206.

7. *T. Ohe*, *T. Watanabe, K. Wakabayashi*, Mutat. Res. **567** (2004) 109.

8. *S. R. Shukla,* Heavy metals, Colourage **53** (2006) 74.

9. *Z. M. Siddigi, D. Pathania*, Indian Journal of Environmental Protection **22** (2003) 201.

10. *M. Soylak, A. Uzun, L. Elcj*, Kuwait Journal of Science and Engineering **28** (2001) 149.

11. *D. E. Brushwood,* Am. Assoc. Textile Chem. Col. **5** (2002) 20.

12. *J. W. Rucker, H. S. Freeman, W. N. Hsu*, Textile Chem. Col. **24** (1992) 66.

13. *J. W. Rucker, H. S. Freeman, W. N. Hsu,* Textile Chem. Col. **24** (1992) 21.

14. *H. S. Freeman,* Textile Chem. Col. **27** (1995) 13.

15. *N. E. Houser,* Textile Chem. Col. **18** (1986) 11.

16. *W. E. Hill, S. Perkins, G. S. Sandlin*, Textile Chem. Col. **25** (1993) 26.

17. *J. R. Aspland,* Textile Chem. Col. **3** (1993) 55.

18. Delaware Valley Section, Textile Chem. Col. **22** (1990) 23.

19. *K. K. Leonas, L. Michael,* Am. Dyestuff Rep. **3** (1994) 26.

20. *S. Barclay, C. Buckley,* Waste Minimization Guide for the Textile Industry, A Step Towards Cleaner Production, Volume 1, The Pollution Research Group.

21. *S. Magdalena, K. Agata, N. Jacek,* Crit. Rev. Environ. Sci. Technol. **33** (2003) 31.

22. *M. Radojevic, N. Vladmir,* Practical Environmental Analysis 1, The Royal Chemical Society of Chemistry, 1999, 288–356.

23. APHA, AWWA, WPC, Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, AWWA, WPC, Washington DC, USA, 1998.

24. *J. S. Jacobsen,* MT 8602 Agriculture (http://www.montana.edu/wwwpb/pubs/mt8602.html; 12. 4. 2007).

25. *M. Zeiner*, *I. Rezić, I. Steffan*, Toxicology Letters **164** (2006) S187.

26. *B. Basaran*, *M. Iscan, B. O. Bitlisli, A. Aslan*, J. Soc. Leather Technol. Chemists **90** (2006) 229.

27. *S. Saracoglu, U. Divrikli, M. Soylak, L. Elci, M. Dogan,* Journal of Trace and Microprobe Techniques **21** (2003) 389.

28. *S. Balasubramanin, V. Pugalenthi*, Talanta **50** (1999) 457.

29. *M. Dogan, M. Soylak, L. Elci, A. von Bohlen,* Mikrochimica Acta **138** (2002) 77.

30. Perkin Elmer, B3111.06. Empfohlene Standardbedingungen für transversal beheizte Graphitrohröfen (THGAs). Ausgabe 1.4, March 1992.

31. *I. Rezić, Lj. Bokić, A. J. M. Horvat*, J. Plan. Chrom. **17** (2004) 305.

32. *M. Zeiner*, *I. Rezić, I. Steffan,* Toxicology Letters **164** (2006) S184.

33. *P. Patnaik,* Dean's Analytical Chemistry Handbook, McGraw-Hill, New York, 2004, 625–630.

34. *E. Pobozy, M. Knell, K. Kilian, R. Kataky, M. Trojanowicz*, Electrophoresis **24** (2003) 2259.

35. *I. Rezić, M. Zeiner, I. Steffan,* unpublished data.

36. *S. Manzoor, Munir H. Shah, N. Shaheen, A. Khalique, M. Jaffar*, Journal of Hazardous Materials A **137** (2006) 31.

37. *C. Ruffo, A. Bruno, D. Mariani*, Tinctoria **100** (2003) 34.

38. *V. S. Shrivastava, S. S. Patil*, Indian Journal of Environmental Protection **25** (2005) 1021.

39. *J. S. Crain, A. M. Essling, J. T. Kiely, E. A. Huff, D. R. Huff, D. G. Graczyk*, Technical Report http://www.osti.gov/bridge/product.biblio.jsp?osti_id=501517 [17.4.2007].

40. *A. Pizzala,* Tinctoria **100** (2003) 49.

41. *L. Dussubieux, M. W. Ballard*, Mater. Res. Soc. Symp. Proc. **852** (2005) 291.

42. *M. I. Szynkowska, K. Czerski, T. Paryjczak, E. Rybicki, A. Wlochowicz*, Fibres and Textiles in Eastern Europe **14** (2006) 87.

43. *J. Su. Becker, C. Pzikhardt, N. Hoffmann, H. Höcker, J. Sa. Becker*, Atomic Spectrometry **23** (2002) 1.

44. *ZL. Chen, M. Megharaj, R. Naidu*, Talanta **72** (2007) 394.

List of symbols
Popis kratica

GF-AAS	– graphite furnace absorption spectrometry – atomska apsorpcijska spektrometrija s grafitnom kivetom
FAAS	– flame atomic absorption spectrometry – plamena atomska apsorpcijska spektrometrija
ICP-OES	– inductively coupled plasma – optical emission spectrometry – induktivno spregnuta plazma – optička emisijska spektrometrija
ICP-MS	– inductively coupled plasma – mass spectrometry – induktivno spregnuta plazma – masena spektrometrija
LOD	– limit of detection – granica detekcije
SPE	– solid-phase extraction – ekstrakcija čvrstom fazom
TLC	– thin layer chromatography – tankoslojna kromatografija
UV-VIS	– ultraviolet and visible spectrometry – ultraljubičasta i vidljiva apsorpcijska spektroskopija
c	– concentration, mol L^{-1} – koncentracija, mol L^{-1}
m	– mass, µg – masa, µg
T	– absolute temperature, K – apsolutna temperatura, K
w	– mass fraction, mg g^{-1} – maseni udjel, mg g^{-1}
γ	– mass concentration, µγ Λ^{-1} – masena koncentracija, µg L^{-1}
ϑ	– temperature, °C – temperatura, °C
λ	– wave length, nm – valna duljina, nm

SAŽETAK

Analitičke metode za određivanje teških metala u tekstilnoj industriji

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Teški metali u otpadnim vodama tekstilne industrije čine ogroman problem za okoliš, a kada se nalaze na tekstilnim materijalima iskazuju potencijalnu opasnost po ljudsko zdravlje. U tekstilnoj industriji teški se metali vrlo često rabe kao oksidansi, bojila te sredstva za poboljšavanje svojstava postojanosti. S obzirom na to da su toksični učinci teških metala na ljudsko zdravlje danas veoma dobro poznati (Tablica 1), vrlo je važno kontrolirati njihovu prisutnost tijekom proizvodnje i prerade tekstilnih materijala. Maksimalno dopuštene količine teških metala koje se nalaze na tekstilnim materijalima, pa se tijekom uporabe mogu ekstrahirati znojenjem i tako štetno utjecati na zdravlje ljudi, regulirane su različitim standardima (Tablica 2). Prema njima, potrebno je određivati i pratiti metale na materijalima, za što je moguće primijeniti nekoliko različitih analitičkih metoda. U ovom radu razmatrani su prednosti i nedostaci metoda TLC, UV-VIS, GF-AAS, ICP-OES i ICP-MS.

Prije analize udjela teških metala na tekstilnim materijalima, uzorke je potrebno pripremiti za analizu. Velika važnost uzorkovanja (Slika 1), pripreme i čuvanja uzoraka (tablice 3–4) naglašene su u poglavljima 2.1 – 2.3. Metoda tankoslojne kromatografije opisana u poglavlju 2.4. može se jednostavno i brzo primijeniti za učinkovito razdvajanje i dokazivanje različitih teških metala. Nedostatak te metode su visoke granice detekcije. UV-VIS spektroskopija je također jednostavna analitička metoda za određivanje metala koja zahtijeva pažljivu pripravu uzoraka. Karakteristike UV-VIS određivanja odabranih teških metala prikazane su u Tablici 5. Atomska apsorpcijska spektroskopija (FAAS i GF-AAS) jedna je od najviše upotrebljavanih metoda u analizi metala koja ima niske granice detekcije. Osnovni nedostatak te metode je nemogućnost istodobnog određivanja više elemenata u istom uzorku, kao što je to moguće kod induktivno spregnute plazme. Stoga je i priprava uzorka za analizu AAS-om dugotrajnija te iziskuje veće troškove. Zbog toga danas najprikladnije metode za analizu metala postaju upravo ICP-OES i tehnike ICP-MS, koje imaju mnoge prednosti nad ostalim analitičkim metodama: izrazito niske granice detekcije (Tablica 7), vrlo široko linearno područje (čak i do nekoliko stotina mg kg^{-1}) te mogućnost simultanog određivanja velikog broja elemenata u istom uzorku. Nedostatak je visoka cijena instrumenata te visoki troškovi analize. Kao zaključak pregleda analitičkih metoda za određivanje teških metala na tekstilnim materijalima, iznesena je činjenica da se najbolji rezultati postižu kombinacijom različitih metoda odabranih i validiranih za namijenjenu svrhu.

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