Talanta 99 (2012) 918–923

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Carbon nanotubes as a solid sorbent for the preconcentration of Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb prior to wavelength-dispersive X-ray fluorescence spectrometry

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ARTICLE INFO

Article history:
Received 2 April 2012
Received in revised form
19 July 2012
Accepted 23 July 2012
Available online 31 July 2012

Keywords:
Solid-phase extraction coupled to WDXRF
Multiwalled carbon nanotubes
Trace element preconcentration
Natural water analysis

ABSTRACT

The preconcentration of trace elements on multiwalled carbon nanotubes (MWCNTs) followed by a wavelength-dispersive X-ray fluorescence analysis (WDXRF) has been investigated. The proposed preconcentration procedure is based on the sorption of trace elements on MWCNTs dispersed in analyzed solution. After sorption, the MWCNTs with the metal ions were collected onto the filter, and then the preconcentrated elements were determined directly by WDXRF. The preconcentration method was optimized, and in consequence, in order to obtain satisfactory recoveries using 100 mL of samples, the sorption process was performed with 1 mg of MWCNTs within 5 min. Some conditions of the preconcentration process such as the pH of analyte solution, amounts of MWCNTs, the volume of the sample, the contact time between analytes and MWCNTs (stirring time), and the effects of foreign metals are discussed in detail in the paper. Adsorption onto raw and oxidized MWCNTs was also studied. The proposed procedure allows obtaining the detection limits of 0.6, 0.6, 1.0, 0.7, 0.6, 0.5, 0.9 and 1.9 ng mL^{-1} for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II), respectively. The recoveries of determined elements were about 100%. Because the analytes are not eluted from the sorbent before WDXRF analysis, the risk of contamination and loss of analytes is reduced to minimum. Moreover, because the samples are analyzed as a thin layer, the matrix effects can be neglected. The proposed preconcentration method using MWCNTs coupled with WDXRF spectrometry was successfully applied to determine trace elements in natural water samples.

1. Introduction

Several preconcentration methods for determination of trace elements are applied prior to X-ray fluorescence spectrometry (XRF). Because the XRF allows the solid samples to be analyzed, the precipitation and solid phase extraction (SPE) methods are willingly applied [1]. One of the most appropriate method is preconcentration of trace elements via direct precipitation with inorganic reagents such as MnO_2, $Mg(OH)_2$ [2] $Fe(OH)_3$, CaC_2O_4 [3] and organic reagents such as thioacetamide [4], 8-hydroxyquinoline [5], dithiocarbamate [6] or more selective sodium 3-hidroxy-4-((1-hidroxy-2-naphtalenyl)azo)-7-nitro-1-naphtalensulfonate (EBT) [7]. The following step of the procedures using the aforementioned organic compounds was the filtration of the formed complexes and the deposition of the solid on the membrane. A simple method for the preconcentration of trace elements is also applied specially prepared filters, such as paraffin-treated cellulose filters [8], the iminodiacetate extraction disk (IED) [9], the filters with zinc sulfide layer [10], impregnated membranes and polymer inclusion membranes contained an anionic exchanger, Aliquat 336 [11,12]. There are also known methods using Aliquat 336 in combination with activated carbon [13] or using only activated carbon as a sorbent prior XRF analysis [14].

Carbon nanotubes (CNTs) – another allotropic form of carbon – have been recently applied willingly in analytical chemistry for the preconcentration of trace elements [15]. Both single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) are particularly useful for analytical application because of their unique properties. They are ideal as a solid-phase extraction adsorbent, because of their large specific sorbing surface areas and the hexagonal arrays of carbon atoms, which are profitable for strong interaction with organic compounds and metal ions. CNTs are usually used as a sorbent before flame atomic absorption spectrometry (FAAS) [16–18], electrothermal (ET) AAS [19–22], inductively coupled plasma atomic emission spectrometry ICP-OES [23–25]. There are also papers in which

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http://dx.doi.org/10.1016/j.talanta.2012.07.059

CNTs were used before flow injection (FI) AAS [26], and hydride generation atomic fluorescence spectrometry (HG-AFS) [27]. CNTs are almost always used to fill the microcolumns. The flow rate of a sample solution is usually 1–5 mL min^{-1}. The volumes of the filtered samples are commonly in the range of 50–1000 mL. Thus, in case of large volumes, sample preparation using the micro-columns can be really time-consuming. Moreover, the analytes retained on CNTs have to be eluted. Elution procedures involve

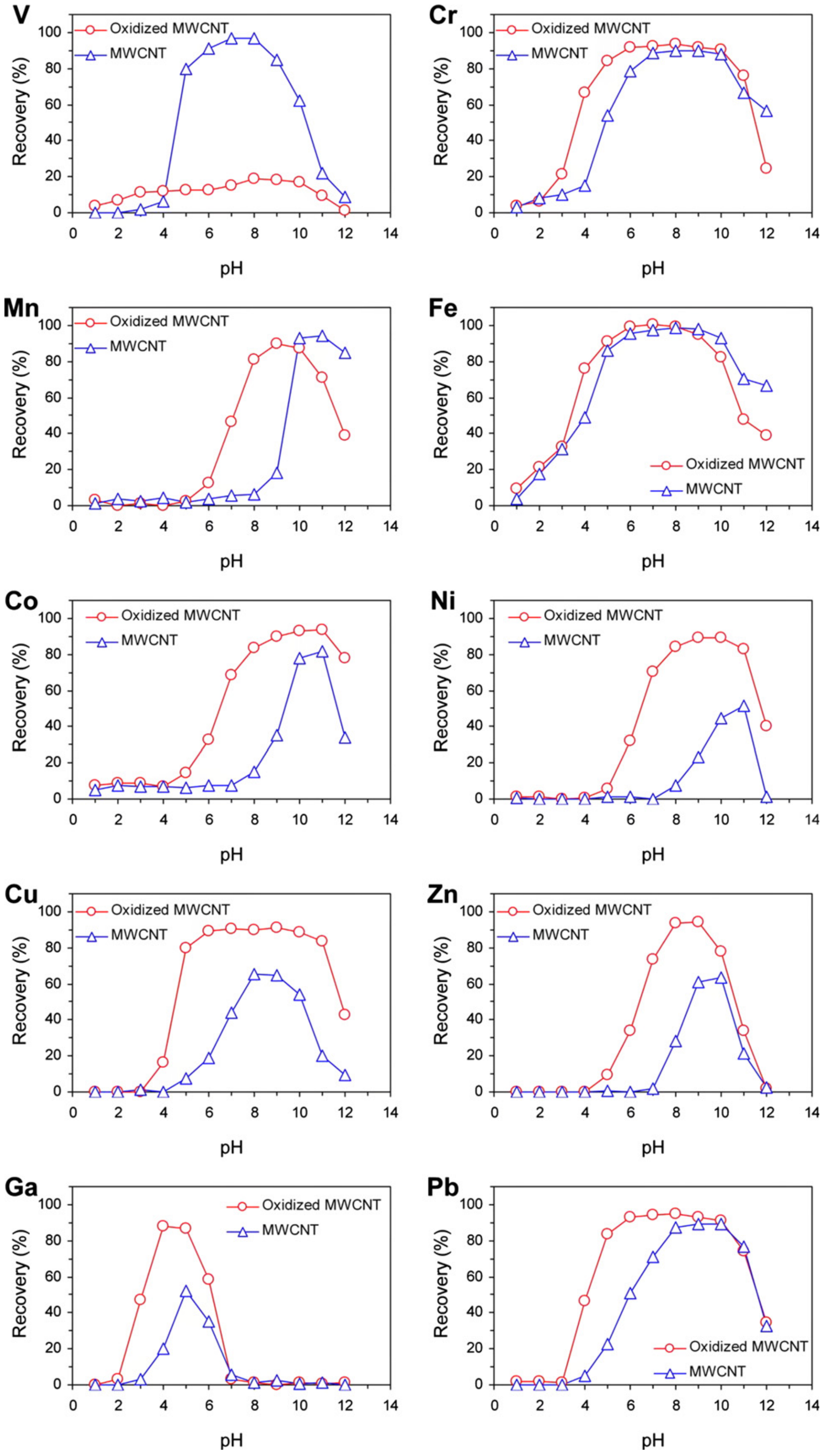

Fig. 1. The influence of pH on the recovery of determined elements.

the use of additional reagents. The serious problems of the elution process can be also the loss of determined elements and/or contamination of samples.

The application of MWCNTs to preconcentrate trace elements prior to WDXRF analysis is described in this paper. This favorable combination of group preconcentration and multielemental determination compared to other techniques offers the following important advantages: the analytes do not have to be eluated from MWCNTs before XRF analysis; the samples can be stored and analyzed many times; the sample preparation is easy and not time-consuming; the matrix effects, risk of contamination and loss of analytes are reduced to the minimum. The proposed combination of sorption of trace elements on MWCNTs and WDXRF spectrometry was proved to be appropriate for the determination of trace amounts of chromium, manganese, iron, cobalt, nickel, copper, zinc and lead ions in aqueous solutions and to be an alternative to other techniques commonly used in the analysis of liquid samples.

2. Experimental

2.1. Materials

Stock solutions (1 mg mL^{-1} of V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III) and Pb(II)), nitric acid (65%, Suprapur®), ammonium hydroxide solution (25%, Suprapur®) were purchased from Merck (Darmstadt, Germany), MWCNTs were purchased from Sigma Aldrich (Steinheim, Germany). The pH of the analyzed solutions was adjusted with 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} NH_3. A multielement standard solution (50 μg mL^{-1} of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga and Pb) was prepared from the stock solutions (1 mg mL^{-1}). All reagents were dissolved and diluted with high purity water obtained from the Milli-Q system.

2.2. Apparatus

A wavelength-dispersive X-ray spectrometer Rigaku ZSX Primus with rhodium target X-ray tube was used for the measurements. The X-ray tube was operated at 50 kV and 40 mA. A LiF analyzing crystal and a scintillation counter were used. The measurements were performed in the vacuum. The time of measurement of each element was 100 s.

2.3. Preparation of the suspension of raw and oxidized MWCNTs

The MWCNTs were oxidized using HNO_3 [28]. 250 mg of the raw or oxidized MWCNTs were put into 50 mL flasks and filled with water up to the mark. Directly before use the suspension of the MWCNTs was dispersed for 30 min in an ultrasonic bath in order to homogenize the suspension.

2.4. Preconcentration procedure

100 μL of 50 μg mL^{-1} multielemental solution of V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III) and Pb(II) and 200 μL of 5 mg mL^{-1} suspension of MWCNTs were added to 100 mL of water. The pH of the solution was adjusted to 9. Next, the mixture was stirred by a magnetic stirrer for 5 min. After that, the sample was filtrated and MWCNTs with adsorbed elements were collected onto the Whatman filter. The loaded filter was dried under an IR heater, protected using a 0.5 mL of 0.5% (m/V) solution of polystyrene in carbon tetrachloride and measured by WDXRF spectrometer.

2.5. Preparation of water samples

The water samples were collected from an industrial district of Poland. The samples were filtered through membrane filters (pore size 0.45 mm, Millipore) and acidified with nitric acid. Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) were adsorbed onto 1 mg of oxidized MWCNTs from 100 mL of water with pH adjusted to 9.

3. Results and discussion

In order to achieve the best performance, the preconcentration procedure was optimized for various analytical parameters, such as the pH of the sample solution, the amounts of MWCNTs, the volume of the solution, the time of contact of the analytes solution with MWCNTs. The matrix effect was also investigated in detail.

3.1. The effect of the solution pH

The pH of the solution affects the surface charge of the adsorbent and the degree of ionization of the adsorbates. The effect of pH on the recovery of determined element ions was investigated for both the raw and the oxidized MWCNTs.

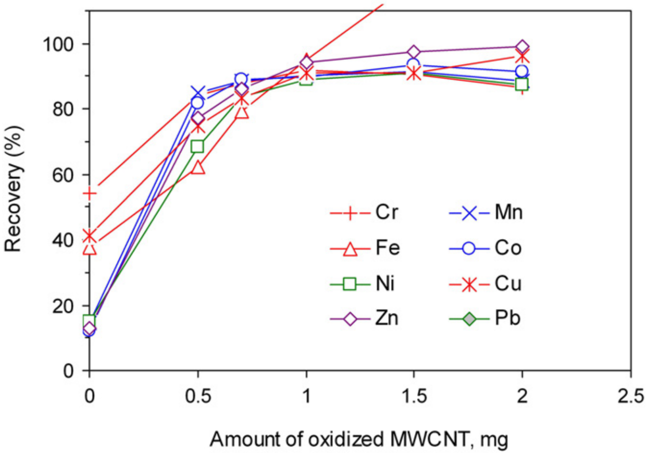

Fig. 2. The influence of oxidized MWCNTs mass on the recovery of determined elements.

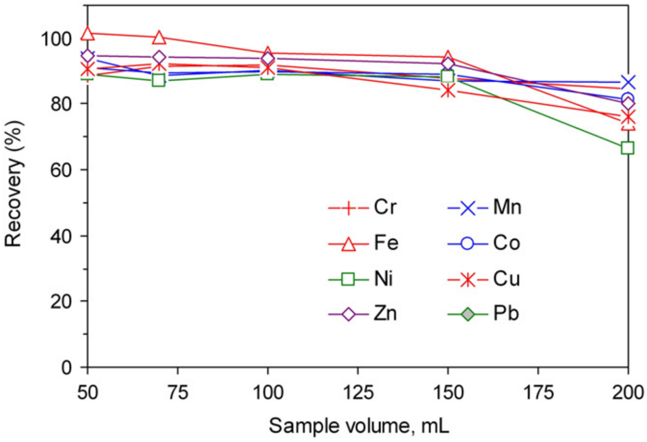

Fig. 3. The influence of analyte solution volume on the recovery of determined elements.

The effect of pH values on the recoveries of V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III) and Pb(II) was studied in the range of 1–12. As shown in Fig. 1, quantitative recoveries (ca. $>90\%$) were obtained for the majority of the studied ions at the pH range of 8–10. Only in case of Ga the best recovery was obtained at pH=4. Generally better recoveries for oxidized MWCNTs in comparison with raw ones were observed. The carboxyl and hydroxyl groups introduced during oxidization on MWCNTs surface are essential features, which are attractive for the preconcentration of trace elements. In subsequent experiments sorption process was performed using oxidized MWCNTs at pH=9. Nevertheless, the preconcentration of vanadium onto oxidized MWCNTs cannot be recommended due to the low recovery of ca. 20%, and definitely better result can be achieved when preconcentration is performed onto raw MWCNTs (pH=7–9). As a consequence of this investigation, vanadium and gallium were not considered in the next studies.

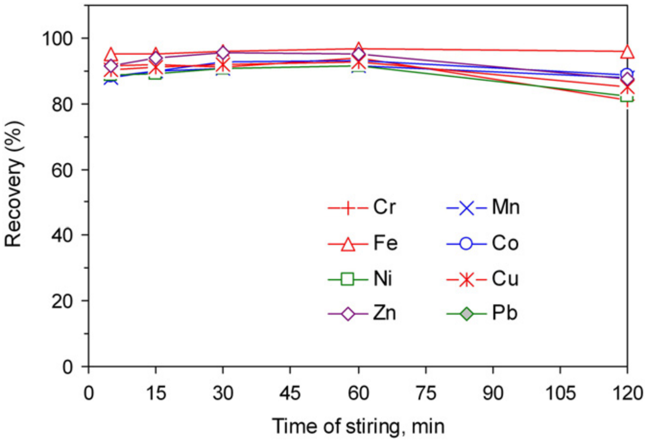

Fig. 4. The influence of stirring time of analyte solutions with oxidized MWCNTs on the recovery of determined elements.

Table 1
The maximum concentrations of matrix elements for which the relative error resulting from neglecting matrix effects is 5%.

Analyte	Matrix element (μg mL^{-1})							
	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb
Cr	–	25	21	19	16	15	14	3
Mn	37	–	28	25	21	20	18	4
Fe	5	41	–	32	27	25	23	6
Co	6	6	45	–	34	32	28	7
Ni	8	7	7	50	–	40	35	9
Cu	10	9	8	7	52	–	43	11
Zn	12	11	10	9	9	61	–	13
Pb	21	19	17	15	14	13	12	–

3.2. *The effect of the mass of oxidized MWCNTs*

Various amounts of oxidized MWCNTs ranging from 0 to 2000 μg were examined to obtain the best recoveries of analytes. The amount of oxidized MWCNTs is an important parameter because this amount should be sufficient to adsorb the determined elements quantitatively, and to form the thin homogeneous samples appropriate for XRF analysis. The results obtained for solutions of pH=9 are presented in Fig. 2. As can be observed, the recovery of metal ions increases with the mass of the oxidized MWCNTs. It can be explained by the increase in the number of the active sites of the oxidized MWCNTs available for binding the metal ions. The recoveries were more than 90% for most analytes when the mass of MWCNTs was larger than 700 μg. In the case of iron, the recovery increased in direct proportion to the mass of MWCNTs. It results from the contamination of MWCNTs with trace amounts of iron. The precipitation of trace elements can assist their sorption via electrostatic interactions. When the preconcentration was performed without MWNCTs, the recoveries were low, e.g. below 40% for Cu, Fe and Pb below 20% for Mn, Co, Ni and Zn and ca. 50% for Cr. Generally, the results indicated that both precipitation (co-precipitation) and sorption via binding metal ions through sharing an electron pair of functional groups of oxidized MWCNTs (–OH, –C=O, –COOH) were present.

In consequence of this discussion, only 1 mg of oxidized MWCNTs was used in the subsequent stage of the procedure.

3.3. *The effect of sample volume*

The effect of the sample volume on the recovery of metals was studied in the range of 50–200 mL using 1 mg of oxidized MWCNTs. The results are shown in Fig. 3. It can be observed that in case of Cr(III) and Mn(II) the sample volumes in the studied range did not have influence on their high recoveries. In case of other determined elements the obtained recoveries were never worse than 90% for the solutions of volume up to 150 mL. The application of the larger sample volumes for the preconcentration can improve the detection limits, but unfortunately it leads to the decrease in the analytes recoveries. When the sample volume was 200 mL, the recoveries of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) were not quantitative, i.e. 75%, 81%, 66%, 76%, 80% and 68% respectively. The lower recoveries for large sample volumes (e.g. 200 mL) can be explained by the limited contact between the metal ions and the active sites of the MWCNTs if only 1 mg of sorbent was used. This problem can be easily solved by using bigger mass of MWCNTs.

Nevertheless, in the subsequent stage of the procedure 1 mg of oxidized MWCNTs was used for the preconcentration of trace elements from 100 mL of the solution in order to optimize the method.

3.4. *The effect of stirring time*

The stirring time of an analyte solution with oxidized MWCNTs can influence the efficiency of the preconcentration of

Table 2
The influence of Na, K, Ca, Mg, Al and Cl on the recovery of the studied elements.

Matrix	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb
20 μg mL^{-1} Na, K, Mg, 100 μg mL^{-1} Ca, 250 μg mL^{-1} Cl	99 ± 4	98 ± 5	102 ± 7	100 ± 1	97 ± 3	98 ± 4	97 ± 6	100 ± 5
50 μg mL^{-1} Na, K, Mg, 250 μg mL^{-1} Ca, 600 μg mL^{-1} Cl	98 ± 5	97 ± 4	95 ± 6	98 ± 2	96 ± 2	97 ± 5	99 ± 7	101 ± 6
100 μg mL^{-1} Na, K, Mg, 500 μg mL^{-1} Ca, 1200 μg mL^{-1} Cl	96 ± 4	99 ± 4	98 ± 5	98 ± 3	103 ± 4	96 ± 6	99 ± 6	96 ± 5
200 μg mL^{-1} Na, K, Mg, 1000 μg mL^{-1} Ca, 2400 μg mL^{-1} Cl	100 ± 4	95 ± 5	104 ± 5	94 ± 4	98 ± 3	101 ± 4	95 ± 4	99 ± 7
0.5 μg mL^{-1} Fe, Al, 5 μg mL^{-1} NO$_3^-$	99 ± 6	98 ± 6	–	99 ± 4	101 ± 5	100 ± 4	97 ± 6	97 ± 8
1.0 μg mL^{-1} Fe, Al, 10 μg mL^{-1} NO$_3^-$	96 ± 6	101 ± 5	–	102 ± 3	97 ± 4	97 ± 5	95 ± 6	98 ± 6
5.0 μg mL^{-1} Fe, Al, 51 μg mL^{-1} NO$_3^-$	97 ± 5	97 ± 4	–	102 ± 5	94 ± 5	99 ± 6	96 ± 8	100 ± 5

analytes. As shown in Fig. 4, the stirring time of the solution in the range of 5–60 min does not play a significant role in the preconcentration of the determined metal ions using the proposed procedure. The recoveries of analytes are close to 100% even after 5 min of stirring, which can indicate that the adsorption process is very quick and the reaction between metal ions and functional groups of oxidized MWCNTs is immediate. Furthermore, in case of stirring time longer than 60 min, desorption is observed. The biggest loss of recovery (to 70%) is observed for Pb(II) when the stirring time is 120 min. In case of other elements the impact of 120 min stirring time is smaller; ca. 10% fall in recovery is observed.

3.5. *The effect of matrix elements*

The preparation of samples is one of the most important steps of the analysis. In case of XRF spectrometry the thickness of samples has a fundamental meaning in regard to obtaining reliable results. In this research samples were prepared as thin layers. It means that the thickness of the samples and the amounts of elements are low enough to neglect the errors resulting from matrix effects. Table 1 shows the maximum concentrations of matrix elements for which the relative errors resulting from neglecting matrix effects are not bigger than 5%. These concentrations were calculated for the procedure using 100 mL of the analyte solution. It is worth noting that the concentrations of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) in natural water samples do not exceed the values presented in Table 1. Nevertheless, in some types of water, the concentration of Fe(III) can be very high and the problem of matrix effects can be observed, especially when trace concentrations of Ni(II), Cu(II) and Zn(II) are determined. In this case, the Fe effect cannot be neglected. Even 7, 8 and 10 µg mL^{-1} of Fe(III) can generate the 5% error resulting from neglecting the matrix effects in case of the determination of Ni(II), Cu(II) and Zn(II), respectively.

Table 3
The parameters characterizing the method.

Analyte	Maximum concentration (µg mL^{-1})	Sensitivity (mL µg^{-1} s^{-1})	LOD (ng mL^{-1})		RMS (µg mL^{-1})
			10 s	100 s	
Cr	0.20	3012 ± 68	2.0	0.6	0.0042
Mn	0.15	3213 ± 12	1.9	0.6	0.0028
Fe	2.00	3914 ± 115	3.1	1.0	0.055
Co	0.15	4421 ± 104	2.2	0.7	0.0031
Ni	0.15	5537 ± 167	1.8	0.6	0.0038
Cu	0.20	5969 ± 158	1.6	0.5	0.0048
Zn	2.00	5284 ± 154	2.8	0.9	0.054
Pb	0.20	1957 ± 39	5.9	1.9	0.0034

The recovery of the determined elements was also investigated from the solutions containing additionally alkali metal ions such as Na(I), K(I), Mg(II) at concentration of 20–200 µg mL^{-1}, Ca(II) at concentration of 100–1000 µg mL^{-1}, Al(III) and Fe(III) at concentration of 0.1–5.0 µg mL^{-1}. The elements were chosen due to their common occurrence in various types of water. As shown in Table 2, all determined elements can be quantitatively preconcentrated on oxidized MWCNTs under optimized conditions, even from solutions with high concentration of alkali metals. It can be seen that matrix metals which can be found in natural water have no obvious influence on the recoveries of determined elements under the selected conditions. The recoveries of all determined elements on oxidized MWCNTs were never worse than 95%. It is probably because the alkali metals may have low ability for binding sites on the surfaces of oxidized MWCNTs.

3.6. *Analytical performance*

The proposed procedure provided linear analytical curves for Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Pb(II) up to 0.20 µg mL^{-1} and for Fe(III) and Zn(II) up 2.00 µg mL^{-1} with correlation coefficients better than 0.99 (100 mL sample volume and 1 mg of oxidized MWCNTs). The root of the mean square of the sum (RMS) characterizing the dispersion point around the straight line ranged from 0.0028 to 0.054 µg mL^{-1}. All discussed values are given in detail in Table 3. The detection limits (DL) were calculated from $DL=(3/k)(B/t)^{1/2}$, where k is the sensitivity of the method, B is the background count rate in counts per second and t is the counting time. If counting time was 10 s, DLs for most elements were found to be ca. 2.5 ng mL^{-1}. But if the counting time was lengthened to 100 s, DLs were significantly better i.e. ca. 0.8 ng mL^{-1}. Such detection limits are similar or even better to those obtained by F-AAS commonly applied after preconcentration with MWCNTs [15]. Moreover, application of WDXRF allows performing multielemental analysis and prepared samples can be stored and measured many times.

The carried out method was used to analyze water from an industrial region of Poland. The exemplary results of WDXRF and ICP-OES (comparative method) analysis are presented in Table 4. The analytical procedure was verified by using the water sample spiked with the known amounts of the elements to be determined. The samples were spiked with 20 and 50 ng mL^{-1} of Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Pb(II) and with 200 and 500 ng mL^{-1} of Fe(III) and Zn(II). The results presented in Table 4 show that the recoveries of the determined elements range from 92% to 107%.

Table 4
The WDXRF analysis of water and samples spiked with 20 and 50 ng mL^{-1} of Cr, Mn, Co, Ni, Cu and Pb and with 200 and 500 ng mL^{-1} of Fe and Zn.

Element	Water sample (ng mL^{-1})	Spiked water sample				ICP-OES (ng mL^{-1})	Relative difference (%)
		Sample[a] (ng mL^{-1})	Recovery (%)	Sample[b] (ng mL^{-1})	Recovery (%)		
Cr	7.3 ± 0.3	26 ± 1	94	60 ± 2	105	7.8 ± 0.2	6.4
Mn	55 ± 2	74 ± 3	95	101 ± 3	92	53 ± 2	3.8
Fe	510 ± 31	728 ± 24	109	978 ± 33	94	500 ± 23	2.0
Co	3.0 ± 0.4	23 ± 1	100	51 ± 2	96	3.4 ± 0.2	11.8
Ni	< DL	19 ± 1	95	48 ± 2	96	< DL	–
Cu	3.4 ± 0.1	25 ± 1	108	50 ± 2	93	3.6 ± 0.1	5.6
Zn	148 ± 4	357 ± 12	105	637 ± 19	98	144 ± 4	2.8
Pb	6.7 ± 0.9	25 ± 1	92	60 ± 2	107	< DL	–

[a] Water spiked with 20 ng mL^{-1} of Cr, Mn, Co, Ni, Cu, Pb and 200 ng mL^{-1} of Fe and Zn.

[b] Water spiked with 50 ng mL^{-1} of Cr, Mn, Co, Ni, Cu, Pb and 500 ng mL^{-1} of Fe and Zn.

4. Conclusions

The combination of WDXRF analysis and the preconcentration of trace elements on MWCNTs dispersed in analyzed solution is developed. A great advantage of the proposed method is group and fast quantitative sorption of trace elements coupled with a nondestructive multielemental analysis. The elements sorbed on MWCNTs were determined directly by WDXRF. It means that the analytes do not have to be eluated from the sorbent before the measurement. In consequence, the risk of contamination and loss of analytes during sample preparation for XRF analysis is reduced to the minimum. The obtained samples are durable, can be stored and analyzed multiple times. Moreover, the proposed sample preparation is not time-consuming and it is cost-efficient. The proposed method allows for matrix effects to be neglected. The method is characterized by good recovery within 90–110% and low detection limit 0.5–1.9 ng mL^{-1}. The proposed combination can be an alternative to other techniques commonly used in the analysis of liquid samples. The method was successfully applied to determine Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) by WDXRF in water samples. It is worth emphasizing that the proposed method can be applied even in the analysis of high salinity water.

References

[1] M. Schmeling, R.E. Van Grieken, Sample preparation for X-ray fluorescence, in Handbook of X-ray Spectrometry, in: R.E. Van Grieken, A.A. Markowicz (Eds.), Second Edition,Marcel Dekker, NewYork, Basel, 2002.
[2] B. Zawisza, R. Sitko, J. Anal. At. Spectrom. 19 (2004) 995–999.
[3] P. Lam Ramos, D.J. Frías Fonseca, M.A. González Garcia, D.E. Aguiar Lambert, J.R. Estévez Alvarez, I. Pupo González, D.R.López Sánchez, J. Radioanal. Nucl. Chem. 247 (2001) 583–587.
[4] V. Jánošová, M. Sýkorová, O. Štroffeková, E. Havránek, J. Anal. Chem. 65 (2010) 56–63.
[5] F.L. Melquiades, P.S. Parreira, M.J. Yabe, M.Z. Corazza, R. Funfas, C.R. Appoloni, Talanta 73 (2007) 121–126.
[6] A. Efendioglu, M. Yagan, B. Bati, J. Hazard. Mater 149 (2007) 160–165.
[7] M. Vega, M. Augusto, M.C. Talío, L.P. Fernández, Microchem. J. 99 (2011) 425–428.
[8] V.P. Gordeeva, M.A. Statkus, G.I. Tsysin, Yu.A. Zolotov, Talanta 61 (2003) 315–329.
[9] W. Abe, S. Isaka, Y. Koike, K. Nakano, K. Fujita, T. Nakamura, X-Ray Spectrom. 35 (2006) 184–189.
[10] R. Sitko, B. Zawisza, Z. Mzyk, At. J. Anal. Spectrom. 21 (2006) 13–18.
[11] C. Fontàs, I. Queralt, M. Hidalgo, Spectrochim. Acta Part B 61 (2006) 407–413.
[12] C. Fontas, E. Margui, M. Hidalgo, I. Queralt, X-Ray Spectrom. 38 (2009) 9–17.
[13] P.R. Aranda, S. Moyano, L.D. Martinez, I.E. De Vito, Anal. Bioanal. Chem. 398 (2010) 1043–1048.
[14] S. Latv, S. Peräniemi, M. Ahlgrén, Anal. Chim. Acta 478 (2003) 229–235.
[15] R. Sitko, B. Zawisza, E. Malicka, Trends Anal. Chem. 37 (2012) 22–31.
[16] A. Stafiej, K. Pyrzynska, Microchem. J. 89 (2008) 29–33.
[17] C.G. Yuan, Y. Zhang, S. Wang, A. Chang, Microchim. Acta 173 (2011) 361–367.
[18] H.-D. Liang, D.-M. Han, Anal. Lett. 39 (2006) 2285–2295.
[19] R.A. Gil, P.H. Pacheco, P. Smichowski, R.A. Olsina, L.D. Martinez, Microchim. Acta 167 (2009) 187–193.
[20] M. Savio, B. Parodi, L.D. Martinez, P. Smichowski, R.A. Gil, Talanta 85 (2011) 245–251.
[21] H. Costa, G. Lima, L. Nacano, C. Tarley, Water Air Soil Pollut. 217 (2011) 557–565.
[22] R.A. Gil, Silvia N. Goyanes, G. Polla, P. Smichowski, R.A. Olsina, L.D. Martinez, J. Anal. At. Spectrom. 22 (2007) 1290–1295.
[23] P. Liang, Y. Liu, L. Guo, Spectrochim. Acta Part B 60 (2005) 125–129.
[24] P. Liang, Y. Liu, L. Guo, J. Zeng, H. Lu, J. Anal. At. Spectrom. 19 (2004) 1489–1492.
[25] M.A. Salam, M.S.I. Makki, M.Y.A. Abdelaal, J. Alloys Compd. 509 (2011) 2582–2587.
[26] X. Zhao, N. Song, Q. Jia, W. Zhou, Microchim. Acta 166 (2009) 329–335.
[27] H. Wu, H. Wen, B. Han, B. Du, J. Lu, J. Tian, Microchim. Acta 166 (2009) 41–46.
[28] A.B. González-Guerrero, E. Mendoza, E. Pellicer, F. Alsina, C. Fernández-Sánchez, L.M. Lechuga, Chem. Phys. Lett. 462 (2008) 256–259.