Analytical Methods

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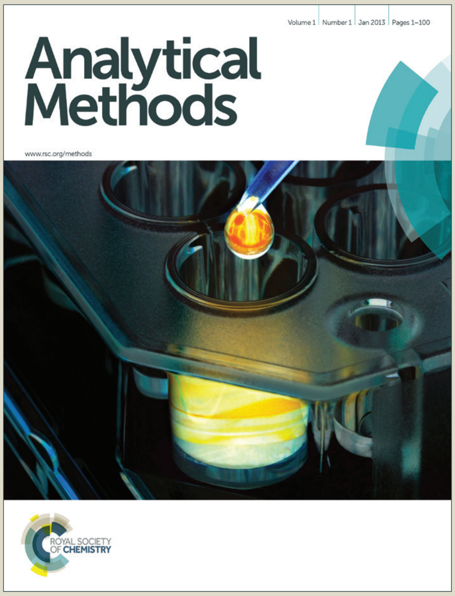

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Simple and rapid method for simultaneous pre-concentration of eight trace-heavy-metals in water using 1-(2-pyridylazo)-2-naphthol and yttrium for X-ray fluorescence spectrometry

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A simple and rapid pre-concentration technique was proposed for the simultaneous determination of eight trace heavy metals in water by energy-dispersive X-ray fluorescence (EDXRF) spectrometry. Yttrium was added as a carrier ion to a sample solution containing Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The metals were collected on a membrane filter as precipitates or co-precipitates with 1-(2-pyridylazo)-2-naphthol at pH 10. The metals on the filter were determined by EDXRF spectrometry. Yttrium improved the collection efficiency of Cr(III) drastically and also expanded the pH ranges for quantitative recoveries of the metals. Only fifteen min was required to prepare the membrane filter retaining the metals. Linear calibrations were obtained from μg L^{-1} to mg L^{-1} levels of the metals in 50 mL sample solution. The limits of detection were as follows: Cd, 1 μg L^{-1} ; Cr, 0.3 μg L^{-1}; Cu, 1 μg L^{-1}; Fe, 1 μg L^{-1}; Mn, 0.3 μg L^{-1}; Ni, 2 μg L^{-1}; Pb, 2 μg L^{-1}; Zn, 2 μg L^{-1}. The sensitivities were enough for monitoring drinking water. The proposed method was applied to river water and underground waters. The analytical results were agreed with those obtained by GF-AAS for the detected metals. The recoveries of the spiked metals in the waters were quantitative. This method was advanced to the separation and determination of Cr(III) and Cr (VI). The proposed system of pre-concentration and EDXRF spectrometry has high potential for routine monitoring of trace heavy metals because of its simplicity and rapidity besides cost-effectiveness.

Introduction

Simultaneous determination of multi trace-heavy-metals in drinking water and environmental water is strongly required for water quality control. For routine analysis, the analytical method should be simple, rapid and cost-effective besides produce reliable results. Of many instrumental methods, X-ray fluorescence (XRF) spectrometry satisfies such requirements. This method is suitable for solid samples because of its high potential for surface analysis. Usually XRF is, however, not applied directly to liquid samples due to its poor sensitivity. Many pre-concentration techniques have been proposed to overcome the demerit. Recently, Pytlakowska proposed micro-extraction technique for silicate by XRF spectrometry. [1] Membrane filtration is a simple, rapid and cost-effective pre-concentration technique. The technique has been developed by many researchers. They were reviewed by Marguí *et al.*.[2] In the membrane technique, trace metals in aqueous samples were converted into inorganic or organic compounds, and they were collected on a membrane filter by filtration. The metals on the filter were determined by XRF spectrometry. The technique has enhanced the potential of XRF for trace elements in water. The outstanding merit of XRF measurement is no requirement of expensive consumables such as gas, reagents, and appliances besides its simplicity and rapidity. Moreover, once the metals are collected on a membrane filter, it is very easy to preserve the filter and transport it to a laboratory before XRF measurement. The essential things in the membrane technique are to find out a suitable reagent or an adsorbent and to set up the sample conditions to collect the focused metals quantitatively and simultaneously. In this study, eight heavy metals, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, were focused. Most of them were designated on the WHO guidelines for drinking water quality and regulated in the drinking water quality standards (DWQSs) of Japan. Co-precipitation of the metals with iron(III) hydroxide is very simple, but iron is always a primary element to be determined in water.[3,4] Co-precipitation with zirconium hydroxide was proposed for several metals.[5,6] But recovery of iron was seriously decreased by Zr. Some chelating reagents have been proposed as precipitant for multi-metals. Of these reagents, carbamates such as pyrrolidinedithiocarbamate (PDTC or APDC), diethyldithiocarbamate (DDTC) and dibenzyldithiocarbamate (DBDTC), were applied to several metals.[7-17] However, the recovery of Mn was very low with any carbamates reported. Püschel proposed 1-(2-pyridylazo)-2-naphthol (PAN) for Mn, Fe, Co, Ni, Cu and Zn.[18] In that report, however, Pb, Cd and Cr were not included. M.G.Vanderstappen *et al.* also proposed PAN for many metals including Cr, Mn, Ni, Cu, Zn, Hg and Eu.[19] The sample solution from 0.5 to 4 L was heated at 70-80^o for 10 min, and allowed to cool from 3 hours up to 3 days before filtration. Soylak *et al.* also reported PAN for atomic absorption spectrometry of Cu and Pb.[20] Activated carbon and cation-selective membrane were proposed for Se [21] and Hg [22]. Marguí *et al.* proposed chelating disc for several metals but not including Mn, Cr and Fe.[23] Hagiwara *et al.* also proposed miniature solid-phase extraction discs for As in drinking water.[24] Zawisza *et al.* proposed multi-walled carbon nanotubes (MWCNTs) for eight heavy metals. [25] Marguí *et al.* applied MWCNTs to river water samples.[26] The recoveries of some metals were not quantitative under the recommended conditions. In most of the proposed membrane techniques, the retention mode was single such as precipitation, co-precipitation or adsorption under the proposed conditions. In some cases, combination of different retention modes drastically improved the recoveries of trace elements. Luke recommended Cu or Fe(III) as the co-precipitant to improve the recovery of Mn by DDTC.[7] Watanabe *et al.* recommended Ni as a carrier to improve the recovery of iron by PAN.[8] Thus the combination of precipitation and co-precipitation has high potential to improve the recoveries of the metals. Unfortunately, Cu, Fe and Ni are often target ions in environmental analysis. We have proposed membrane techniques for trace analysis by instrumental [27-32] and visual methods [33]. In our preliminary experiments, the seven metals, Cd, Cu, Fe, Mn, Ni, Pb and Zn were collected on a membrane filter with PAN quantitatively at room temperature in a short time. However, the recovery of Cr(III) was very low. Heating a sample solution was reported for the quantitative recovery of Cr^{3+}.[19] Slow-reaction-rate of hydrated Cr^{3+} with PAN probably requires such time consuming procedure. Fortunately, we found the addition of yttrium in a sample solution drastically improved the recovery of Cr(III) with PAN. Moreover, the pH ranges for quantitative recoveries of the target ions were expanded one or more pH units to produce easy pH adjustment. In this paper, the conditions of rapid and simultaneous collection of the eight metals on a membrane filter using PAN and Y, and determination of them by energy-dispersive X-ray fluorescence (EDXRF) spectrometry are described. Applications of the proposed method to river water and ground waters, and an advanced technique for the separation and determinations of Cr(III) and Cr(VI) are also described. The purpose of this study is to develop a simple pre-concentration technique for routine monitoring of trace heavy metals by EDXRF spectrometry.

Experimental

Apparatus

Energy-dispersive X-ray fluorescence (EDXRF) instrument, MiniPal4 (PANalytical Co. Inc.), equipped with Rh tube anode and silicon drift detector cooled by thermoelectric means was used for XRF measurement. Tube filter was changed appropriately for each metal to obtain precise results. The filter and the operation conditions were as follows: Kapton (30 kV, 300 μA), Al (20kV, 450 μA), Al_thin(12 kV, 750 μA), Ag (30 kV, 300 μA) ; live time :100 s; medium: air. A typical EDXRF spectrum will be shown in the section of results and discussion together with the list of instrumental parameters and conditions. A polyethylene thin film was placed on the side of membrane filter retaining the metals. Another plastic plate of polypropylene was placed at the reverse side of the membrane. The sandwiched filter was fixed between two metal rings of sample holder. X-Ray was irradiated from downward direction to the membrane-face retaining the metals. Measurement was performed for 100 s. The result was obtained from the average count of 5 measurements for each sample. Atomic absorption instrument equipped with carbon graphite furnace, Z-8000 (Hitachi Co. Ltd.) was used for GF-AAS measurement. D-24 pH meter (Horiba Co. Ltd.) was used for pH measurement. An aspiration apparatus KG-25 (Advantec Co. Ltd.) equipped with 150 mL funnel (17 mm effective filtration diameter) was used for filtration.

Reagents and materials

The standard solutions of heavy metals were prepared as follows. The nitrates of Cd, Cr(III), Ni and Pb, sulfates of Cu, Mn and Zn, chlorides of Fe(II, III), and potassium chromate of analytical grade (Wako Pure Chemical Industries Ltd.) were dissolved in 0.1 M nitric acid to make 1000 mg L^{-1} solutions. Yttrium standard solution for AAS (1000 mg L^{-1}) was purchased from Wako Pure Chemical Industries Ltd. The metal solutions were diluted to appropriate concentrations with 0.1 M nitric acid. PAN solution was prepared by dissolving 1 g of 1-(2-pyridylazo)-2-naphthol (Dojin Chem. Co. Inc.) in 100 mL of ethanol. Tetramethylammonium hydroxide (TMAH) (AA-grade, Tama Pure Chem. Co. Inc.) was diluted with water to make 12.5% (v/v). Sodium *p*-phenolsulfonate solution was prepared by dissolving the reagent (Tokyo Kasei Kogyo Co. Ltd.) with water to make 0.5 M solution. Hydrazinium sulfate of analytical grade (Wako Pure Chemical Industries Ltd.) was dissolved in water to make 5 M solution. Nitric acid and ethanol of analytical grade were purchased from Wako Pure Chemical Industries Ltd. Water was obtained by Direct-Q 3UV (Millipore Co. Inc.). A sheet of membrane filter comprised of mixed-cellulose-ester, pore-size 0.45 μm (Advantec Toyo A045A304C) was cut to suitable square sizes before use.

Pre-concentration procedure

The schematic flow diagram of entire procedure from pre-concentration to XRF measurement is shown in Fig.1

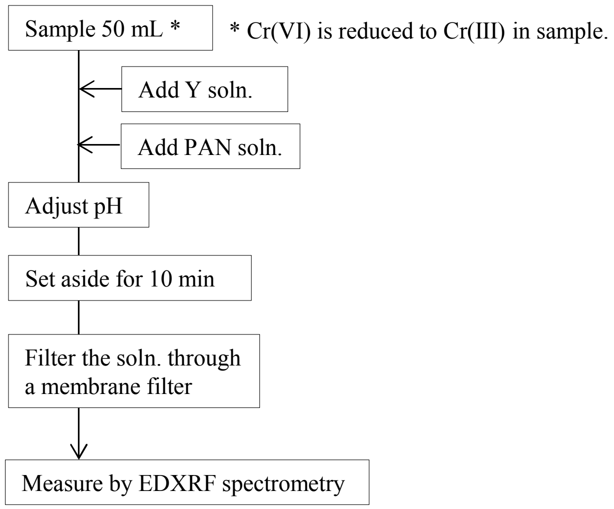

Fig.1 Schematic flow diagram of the proposed method.

Take sample solution (50 mL, acidified to pH 2 with nitric acid) in a beaker. Add the Y solution (25 µL of 1,000 mg L^{-1} solution) and the PAN solution (1.3 mL). Add the sodium *p*-phenolsulfonate solution (1.0 mL), and adjust the pH to *ca.*10 with the TMAH solution. After setting aside for 10 min, filter the solution through the membrane by aspiration. Mount the membrane to the XRF instrument as described in the previous section. For the determination of total Cr (Cr(III) plus Cr(VI)), the hydrazinium sulfate solution (1 mL) was added to the sample solution, and set aside for 3 min to reduce Cr(VI) to Cr(III) before addition of PAN. The concentration of Cr(VI) was obtained by subtracting the Cr(III) from the total Cr.

Results and discussion

Chelating reagents

Shirkhanloo *et al*. proposed a mixed cellulose ester membrane column for the pre-concentration of Cu, Pb and Cd without any chelating reagent at pH 8.[34]In our preliminary experiments, without any chelating reagent some metals were collected on the membrane filter partially but not quantitatively. As described in introduction, many chelating reagents have been proposed to convert heavy metals into membrane-collectable forms. In this study, at first the suitability of APDC, DDTC and DBDTC were inspected. Most of the metals were collected on the filter from acid medium by the reagents. But the recovery of Mn was very poor at any pH by the reagents. Next, pyridylazo-type chelating reagents were investigated. 2-(5-Bromo-2-pyridiylazo)-5-[N-n-propyl-N-(3-sulfopropyl)amino] phenol (5Br-PAPS) forms soluble chelate anions with heavy metals in alkaline medium. And the anionic chelates were collected as ion-pairs with cationic surfactant. More than *ca.* 80% recoveries were obtained by this method for the eight metals but not quantitative. PAN forms precipitates with many heavy metals in alkaline medium. In our preliminary experiments, seven metals were collected quantitatively, but the recovery of Cr(III) was lower than 80%. Therefore, the improvement of the recovery of Cr(III) was investigated at first.

Effect of yttrium as carrier

The recovery of Cr(III) was, however, quantitative in the presence of other metals. Probably such recovery-enhancement for Cr(III) was caused by co-precipitation with PAN-chelates of other metals. The recovery coefficients of other seven metals were not so different both in the presence and absence of other metals. In this study, addition of foreign metal was investigated for quantitative recovery of Cr(III). At first Al was inspected. Aluminum at 0.5 mg L^{-1} was effective for quantitative recoveries of 0.1 and 0.5 mg L^{-1} Cr(III), but of little use for lower concentrations than 0.05 mg L^{-1} Cr(III). Moreover, Al occurs commonly in environmental water at various concentrations. Therefore, setting up the Al concentration in sample solution is very difficult. Next, Y was investigated. Yttrium is very rare in environmental water. Therefore it is very easy to set up its concentration in sample solution. The recoveries of Cr(III) at 0.05, 0.1 and 0.5 mg L^{-1} in the presence of Y at various concentrations is shown in Fig.1. More than 0.4 mg L^{-1} of Y was enough to obtain constant recoveries of Cr(III) at the concentrations. Then, 0.5 mgL^{-1} of Y was recommended in this study. Yttrium did not give any undesirable results on the collection of the focused metals. As described later, Y presented another advantage of expending the pH ranges for quantitative recoveries of other metals. Probably, not only Y but also other metal-PAN precipitates play as scavengers for co-precipitation of Cr-PAN chelates. But the exact mechanism is not clear so far.

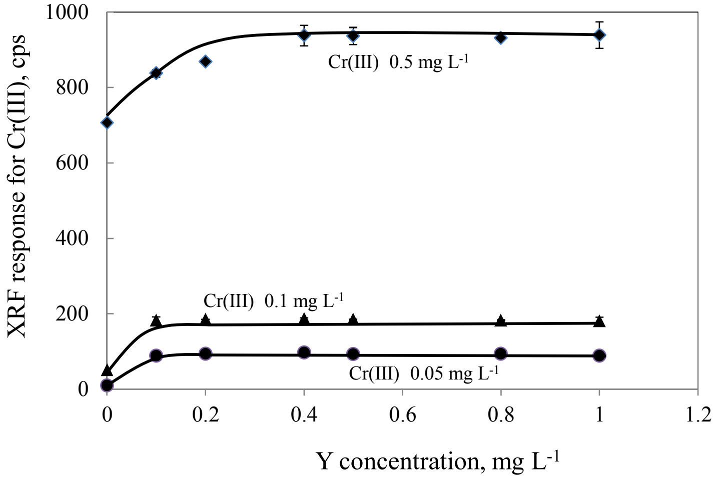

Fig. 2 Effect of Y on the collection of Cr(III).

Effect of pH

pH is one of the most important parameters for the collections of the metals with PAN. The recovery tests for each metal were performed in the presence of Y (0.5 mg L^{-1}) at various pHs. The metal concentrations were set up to give comparable precision, because XRF sensitivity for each metal is quite different. The results for each metal are shown together in Fig.3

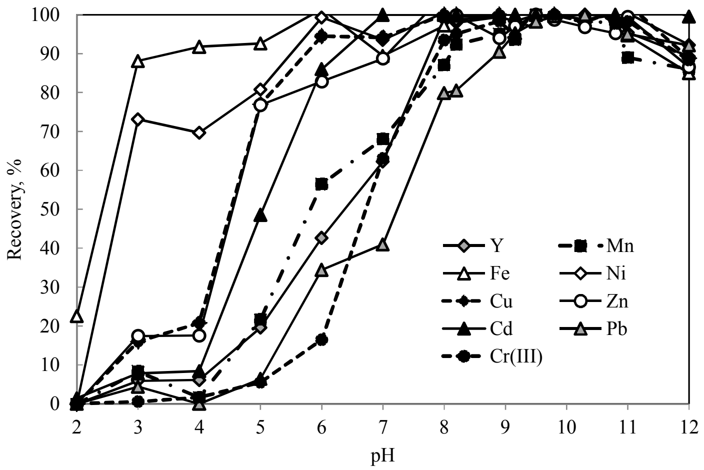

Fig. 3 Effect of pH on the recoveries of metals. Fe, Mn, Ni: 0.05 mg L^{-1}; Cr ,Cu, Zn: 0.1 mg L^{-1} ; Cd, Pb,Y: 0.5 mg L^{-1}

The recovery of Y is also shown in Fig.3. More than 95% recoveries were obtained for each metal over the pH range from 9.2 to 10.8. It was found that the pH ranges for the quantitative recoveries of Cd and Cu were expanded to acid side for *ca.* one pH unit and those of Fe, Mn, Ni, Pb and Zn were expanded to alkaline side for *ca.*0.5 pH unit by the addition of Y. Thus the pH ranges for quantitative recoveries are affected by other heavy metals. Addition of an unfocused metal such as yttrium at constant concentration is very effective to improve the pH ranges for quantitative recoveries and to obtain reproducible results besides brings us easy pH adjustment.

Amount of PAN

The effect of the amount of PAN on the recoveries of the metals was examined. The PAN solution, 0.5, 1.0, 1.2, 1.3, 1.5 and 2 mL, was added to the mixtures of various metal concentrations, 0.01-0.05 mg L^{-1} for Fe, Mn, Ni, 0.01-0.1 mg L^{-1} for Cr(III), Cu and Zn, 0.01-0.5 mg L^{-1} for Cd, Pb in 50 mL sample solution. More than 1 mL of the PAN solution gave quantitative recoveries for all the metals at any concentrations. In this study, 1.3 mL (13 mg) was recommended. Too much addition of PAN caused clogging of filtration due to the precipitation of PAN itself.

Time setting aside before filtration

The effect of the elapsed time before filtration after pH adjustment from 0 to 20 min with 5-min interval was examined. More than 10 min gave satisfactory recoveries for all the metals.

Effect of sample volume

The sample volume is important, because it concerns the sensitivity, the filtration time and the amount of reagents. The XRF response was examined at different sample volume from 10 to 80 mL with 10-mL interval. A linear XRF response was obtained for every metal in proportional to the amount of them at less than 70 mL. Fifty mL was adopted in this study. The filtration required only a few minutes.

Filtration area

Filtration area also concerns the sensitivity and filtration time in this technique. Two funnels with different filtration diameters of 17 and 37 mm, corresponding effective filtration areas are 227 and 1075 mm^2, respectively, were investigated under various sample volumes. The smaller one gave higher sensitivity than the larger one at the same concentration and sample volume. In this study, the smaller one was adopted. We can estimate the volume of the membrane retaining the metals to be *ca.* 33 μL from the thickness of the filter 145 μm and the effective filtration area 227 mm^2. If whole amount of the metals is trapped in the construction of the filter, the concentration factor becomes *ca.* 1500 when 50 mL sample is supplied. In practice, the metals are retained in much smaller space of the surface of the filter to give higher concentrations. Probably high sensitivity of this method partly came from such high enrichment factor.

Separation and determinations of Cr(III) and Cr(VI)

Z.Bahadir *et al*. proposed modified multiwalled carbon nanotubes (MWCNTs) for the determination of Cr(VI) in drinking water by total reflection XRF spectrometry.[35] In our study, Cr(VI) was not retained at all even in the presence of PAN and Y. Probably, Cr(VI) does not form collectable complex with PAN as well as does not co-precipitate with Y-PAN chelate. It was found that Cr(VI) did not interfere with the determination of Cr(III). Therefore, if Cr(VI) is reduced to Cr(III) quantitatively before pre-concentration, we can determine the sum of Cr(III) and Cr(VI). Ultimately we can determine Cr(VI) by subtracting the concentration of Cr(III) from that of Cr(III) plus Cr(VI). Several reducing reagents were investigated to convert Cr(VI) into Cr(III). Ascorbic acid was of little use as reducing reagent. Sodium thiosulfate gave only 50% recovery of Cr(VI) as Cr(III), and lower recoveries for other metals wrongly. Hydroxyl ammonium gave quantitative recovery for Cr(VI), but lower for Pb. Hydrazinium sulfate was most suitable, because it gave quantitative recovery of Cr(VI) without any influence on the recoveries of other metals. The effects of the concentration of hydrazinium sulfate and elapsing time for reducing Cr(VI) was examined. Reducing time for 3 min using 0.10 M hydrazinium sulfate gave the same linear calibration for 0.05-0.2 mg L^{-1} of Cr(VI) as that for Cr(III). At lower concentrations of 0.05 M hydrazinium sulfate, the recoveries reached only 86% at the very most. The recovery tests of Cr(III) and Cr(VI) spiked to a river water sample will be described in the section of application. The sensitivity of present method for Cr(VI) was comparable to the MWCNTs method.[35]

Calibration and precision

Liner calibration ranges for individual metals in 50 mL sample solutions were as follows: Cd, 0.005-1.0 mg L^{-1}; Cr, 0.001-0.5 mg L^{-1}; Cu, 0.005-1.0 mg L^{-1}; Fe, 0.005-1.0 mg L^{-1}; Mn, 0.001-1.0 mg L^{-1}; Ni, 0.01-1.0 mg L^{-1}; Pb, 0.01-1.0 mg L^{-1}; Zn, 0.01-1.0 mg L^{-1}. The coefficient of determination (= R^2) was larger than 0.995 for every calibration. The limits of detection based on 3 times of standard deviation of reagent blank obtained from the solution consisted of water, nitric acid (pH 2) and Y (0.5 mg L^{-1}) by the recommended procedure were as follows: Cd, 1 μg L^{-1} ; Cr, 0.3 μg L^{-1}; Cu,1 μg L^{-1}; Fe, 1 μg L^{-1}; Mn,0.3 μg L^{-1}; Ni, 2 μg L^{-1}; Pb, 2 μg L^{-1}; Zn, 2 μg L^{-1}. The WHO guidelines[36] and the quality standards in Japan[37] for drinking water are as follows: Cd,0.003(W) and 0.001(J) mg L^{-1}; Cr,0.05 as total (W) and 0.05 as Cr(VI) (J) mgL^{-1} ; Cu, 2 (W) and 1(J) mg L^{-1} ; Fe, none(W) and 0.3(J) mg L^{-1} ; Mn, 0.4(W) and 0.05 (J) mgL^{-1}; Ni, 0.07 (W) and 0.01(J) mg L^{-1}; Pb,0.01(W) and 0.01 (J) mg L^{-1}; Zn, 3 (W) and 1.0 (J) mg L^{-1}. Where, W and J in round brackets mean the WHO guidelines and the standard of Japan, respectively. Table 1 is the precisions of the proposed method for two kinds of mixtures with different concentrations of the metals. The metals in both mixtures were determined within 10% RSD.

Table 1 Precisions of the proposed method for two kinds of mixtures prepared at various concentrations.

Mixture 1

	Cd	Cr(III)	Cu	Fe	Mn	Ni	Pb	Zn
Conc., mg L^{-1}	0.050	0.010	0.050	0.050	0.010	0.010	0.050	0.010
RSD, %	6.4	2.7	5.7	5.2	5.4	7.1	6.7	8.8

Mixture 2

	Cd	Cr(III)	Cu	Fe	Mn	Ni	Pb	Zn
Conc., mg L^{-1}	0.10	0.050	0.10	0.10	0.050	0.050	0.20	0.050
RSD, %	5.4	5.9	7.5	7.0	5.8	4.8	5.4	6.6

Sample volume was 50 mL. RSDs were obtained from 5 determinations.

An example of typical EDXRF spectrum obtained by the proposed method is shown in Fig.4 together with the list of instrumental parameters and measurement conditions.

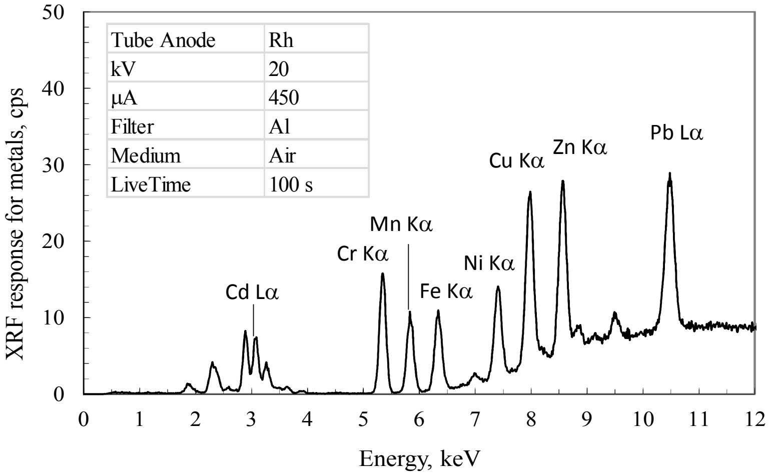

Fig. 4 EDXRF spectrum by the proposed method. Cd, 50 μg L^{-1} ; Cr, 10μg L^{-1}; Cu,10 μg L^{-1}; Fe, 5 μg L^{-1}; Mn,7 μg L^{-1}; Ni, 10 μg L^{-1}; Pb,50 μg L^{-1}; Zn, 100 μg L^{-1}

Effect of diverse ions

The effects of diverse ions on the determination of the metals are shown in Table 2. Most of the common species in natural waters did not affect the recoveries even at high concentrations. Phosphate and silicate at very high concentrations gave lower recoveries for several metals.

Table 2 Effect of diverse ions on the determination of the heavy

Ions	Added as	Added, mg L^{-1}	Recovery and remarks
Na^+	NaCl	1000	>90% for every heavy metal
K^+	KF	2100	>90% for every heavy metal
Ca^{2+}	$Ca(NO_3)_2$	1000	>90% for every heavy metal
Mg^{2+}	$MgSO_4$	100	>90% for every heavy metal
NH_4^+	NH_4NO_3	1000	>90% for every heavy metal
NO_3^-	NH_4NO_3	3400	>90% for every heavy metal
F^-	KF	1000	>90% for every heavy metal
Cl^-	NaCl	1500	>90% for every heavy metal
SO_4^{2-}	$MgSO_4$	400	>90% for every heavy metal
PO_4^{3-}	NaH_2PO_4	1000	Cd(85%), Cr(3.5%), Fe(57%), Pb(10%) *
		100	Cd(110%), Cr(88%), Fe(90%)*
		10	>90% for every heavy metals
Silicate	Prepared from SiO_2	100 as SiO_2	Cr(12%), Fe(43%), Mn(73%), Pb(14%)*
		50 as SiO_2	Cr(36%), Fe(83%), Pb(73%)*
		10 as SiO_2	>90% for every heavy metal

The concentration of every heavy metal was 0.10 mg L^{-1}. *More than 90% recoveries for other metals.

Application to river and underground waters

The proposed method was applied to river water and underground waters. Table 3 shows the analytical results for river water and also the recoveries of the metals spiked to the water. Iron and Mn were detected in the sample with satisfactory precision. Other metals were under their detection limits. The recoveries of the spiked metals were almost quantitative within 10% variation. The effect of foreign components in the river water was negligible.

Table 3 Analytical results and recovery tests for river water.

Added, mg L^{-1}	Found, mg L^{-1}							
	Cd	Cr(III)	Cu	Fe	Mn	Ni	Pb	Zn
0	ND	ND	ND	0.038 ±0.001	0.0166 ±0.0004	ND	ND	ND
0.0100	0.012 ±0.001	0.0100 ±0.0003	0.011 ±0.001	0.048 ±0.002	0.027 ±0.001	0.010 ±0.002	0.009 ±0.002	0.010 ±0.001
0.100	0.091 ±0.007	0.105 ±0.007	0.100 ±0.004	0.140 ±0.007	0.118 ±0.006	0.105 ±0.005	0.100 ±0.008	0.105 ±0.007
0.200	0.202 ±0.002	0.178 ±0.001	0.208 ±0.001	0.250 ±0.002	0.223 ±0.001	0.200 ±0.002	0.212 ±0.002	0.204 ±0.002

Sample was obtained from Joganji River in Toyama, Japan. The results were obtained from 3 determinations. ND means not detected. ± Means the variation range calculated from the standard deviation.

Recovery test of the spiked Cr(III) and Cr(VI) to the river water was also performed. A couple of spiked samples with different concentrations of Cr(III) and Cr(VI) were prepared for the examination. Table 4 is the results of recovery tests. The recoveries of both Cr(III) and total Cr (= Cr(III) + Cr(VI)) were almost satisfactory.

Table 4 Recovery-tests for Cr(III) and Cr(VI) spiked to river water

	Cr added, mg L^{-1}		Cr found, mg L^{-1}	
	Cr(III)	Cr(VI)	Cr(III)	Cr(III)+Cr(VI)
Recovery test 1	0.010	0.010	0.010 ± 0.001	0.020 ± 0.001
Recovery test 2	0.050	0.050	0.050 ± 0.004	0.098 ± 0.007

Table 5 is the comparison of the analytical results for two underground waters by the proposed method and GF-AAS. The groundwater of Toyama City was used for drinking and other domestic purposes. The groundwater of Toyama Univ. obtained in the campus was used for sanitary, cooling and other various purposed. GF-AAS was performed for acidified samples without any pre-concentration procedure. Iron, Cu and Zn were detected in the samples by both methods. Other heavy metals were not detected by the methods. Both analytical results were in good agreement for Fe, Cu, Zn detected in the samples. The recoveries of the spiked metals to the samples are also shown in the Table 5. The recovery coefficients were almost satisfactory for every metal. The proposed method is useful to judge the quality of water for drinking water.

Table 5 Comparison of the analytical results obtained by the proposed method and GF-AAS for ground waters and recovery tests for the proposed method

Sample	Method	Metal added, mg L^{-1}	Found, mg L^{-1}							
			Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Toyama City	GF-AAS	0	<0.008	<0.01	<0.02	0.055	-----	<0.05	<0.01	<0.02
	XRF (Present Method)	0	ND	ND	0.018 ± 0.001	0.035 ± 0.002	0.0018 ± 0.0002	0.001 ± 0.001	0.002 ± 0.001	0.004 ± 0.001
		0.0050	0.007 ± 0.002	0.005 ± 0.001	0.023 ± 0.001	---	0.0122 ± 0.0004	0.005 ± 0.001	0.007 ± 0.004	0.008 ± 0.001
		0.010	0.007 ± 0.001	0.010 ± 0.001	0.029 ± 0.001	0.050 ± 0.002	0.013 ± 0.002	0.010 ± 0.001	0.013 ± 0.002	0.014 ± 0.003
		0.050	0.048 ± 0.005	0.045 ± 0.002	0.068 ± 0.002	0.098 ± 0.003	0.053 ± 0.002	0.052 ± 0.001	0.053 ± 0.001	0.053 ± 0.002
		0.100	0.098 ± 0.002	0.090 ± 0.003	0.117 ± 0.005	0.160 ± 0.004	0.105 ± 0.004	0.100 ± 0.002	0.102 ± 0.004	0.104 ± 0.006
		0.200	0.196 ± 0.005	0.196 ± 0.008	0.22 ± 0.01	0.23 ± 0.03	0.204 ± 0.009	0.21 ± 0.01	0.20 ± 0.01	0.20 ± 0.01
Toyama Univ.	GF-AAS	0	<0.008	＜0.01	0.045	＜0.02	----	＜0.05	＜0.01	0.222
	XRF (Present Method)	0	ND	ND	0.039 ± 0.001	0.008 ± 0.001	0.0005 ± 0.0003	0.019 ± 0.001	0.005 ± 0.001	0.223 ± 0.005
		0.0050	0.009 ± 0.001	0.005 ± 0.001	0.044 ± 0.002	----	0.0058 ± 0.0006	0.023 ± 0.001	0.010 ± 0.001	0.24 ± 0.01
		0.010	0.013 ± 0.001	0.011 ± 0.001	0.048 ± 0.005	0.018 ± 0.001	0.0112 ± 0.0006	0.028 ± 0.001	0.016 ± 0.002	0.25 ± 0.02
		0.050	0.051 ± 0.001	0.045 ± 0.001	0.087 ± 0.004	0.058 ± 0.001	0.052 ± 0.002	0.068 ± 0.004	0.055 ± 0.003	0.27 ± 0.01
		0.100	0.099 ± 0.004	0.094 ± 0.004	0.141 ± 0.004	0.107 ± 0.004	0.106 ± 0.005	0.123 ± 0.007	0.104 ± 0.005	0.33 ± 0.01
		0.200	0.193 ± 0.008	0.20 ± 0.01	0.24 ± 0.01	0.213 ± 0.005	0.20 ± 0.01	0.22 ± 0.02	0.21 ± 0.02	0.43 ± 0.02

Results were obtained from 3 determinations. ---- Means not performed. The determination by GF-AAS was performed without any pre-concentration procedure.

Conclusions

Simultaneous and quantitative collection of eight heavy metals on a membrane filter under the same conditions was successfully performed using PAN and Y. The collection of heavy metals through precipitation or co-precipitation on a filter is greatly influenced by the presence of other metals. Therefore, addition of an unfocused metal such as yttrium at constant concentration is very effective to obtain quantitative and reproducible recoveries of the trace metals. Small sample volume in this pre-concentration technique brings us small amount of reagent consumption and rapid sample treatment. This technique could be performed on-site for environmental waters. Once the metals are collected on a filter, it is very easy to preserve the filter and transport it to a laboratory before EDXRF measurement. Moreover, EDXRF spectrometry requires no expensive consumables such as gas, reagent, and appliances. Therefore, this method is simple, rapid and cost-effective, ultimately convenient for routine analysis. This pre-concentration technique could be applied to other instrumental analysis such as AAS and ICP-AES, if the metals on the filter could be eluted with acid or other solvent.

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