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همرسوبی بدون استفاده از عنصر حامل برای پیش تغلیظ یون‌های منگنز، کبالت، نیکل، کادمیم و مس از نمونه‌های آبی، چای دم شده و تنباکو

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Carrier Element-Free Coprecipitation for Preconcentration of Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} Ions from Water, Brewed Tea and Tobacco Samples

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چکیده

یک روش پیش تغلیظ بر اساس همرسوبی یون‌های منگنز، کبالت، نیکل، کادمیم و مس با استفاده از رسوب‌دهنده آلی جدید با نام ۲-(۴-{ [(۴-{۵-اکسو – ۴- [۱-(۲-تینیل) متیلیدن]-۵،۴-دی هیدرو-۳،۱- اکسازولو-۲-ایل}فنیل) ایمینو]متیل}فنیل)-۴-[۱-فنیل متیلیدن]۳،۱- اکسازولو-۵ (H4) اون بدون استفاده از هر گونه عنصر حامل توسعه داده شد. عناصر تغلیظ شده حاصل با استفاده از طیف سنج جذب اتمی شعله تعیین شدند. تاثیر بعضی از پارامترهای تجزیه ای شامل pH، مقدار رسوب‌دهنده، زمان توقف، سرعت و زمان سانتریفیوژ، حجم نمونه و حضور یون‌های مختلف روی بازیابی کمی یون‌های آنالیت بررسی گردید. تحت شرایط بهینه، نمودارهای درجه بندی برای یون‌های آنالیت بررسی گردید. انحراف استاندارد نسبی برای هفت تعیین تکراری مخلوط ۰/۱ میکروگرم بر میلی لیتر از یون‌های منگنز، کبالت، نیکل، کادمیم و مس در محلول اولیه به ترتیب ۲/۵، ۲/۴، ۲/۲، ۲/۱ و ۲/۵ درصد بدست آمد. حدود تشخیص براساس Sb/m۳ برای یون‌های منگنز، کبالت، نیکل، کادمیم و مس در محلول اولیه به ترتیب ۱/۲، ۱/۳، ۱/۲، ۰/۶ و ۱/۵ نانوگرم برمیلی لیتر بدست آمد. روش پیشنهاد شده برای تعیین مقادیر ناچیز یون‌های آنالیت در نمونه‌های استاندارد، آب، دم‌کرده چایی و تنباکو بکار برده شد و نتایج رضایت‌بخشی بدست آمد.

واژه‌های کلیدی

پیش تغلیظ؛ همرسوبی بدون عنصر حامل؛ نمونه‌های زیست محیطی .

Abstract

A preconcentration procedure, based on the coprecipitation of Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} ions using a new organic coprecipitant, (2-(4-{[(4-{5-oxo-4-[1-(2-thienyl) methylidene]- 4,5-dihydro- 1,3- oxazole-2-yl} phenyl) imino] methyl} phenyl) methylidene] amino} phenyl) -4-[1-phenyl methylidene] -1,3-oxazole-5(4H)-one (OTMDO) without adding any carrier element has been developed. The resultant concentrated elements were determined by using flame atomic absorption spectrometer. The influences of some analytical parameters including pH, amount of the coprecipitant, standing time, centrifugation rate and time, sample volume and diverse ions were investigated on the quantitative recoveries of analyte ions. Under the optimized experimental conditions, the calibration curves for the analyte ions were studied. The relative standard deviations for seven replicate determinations of a mixture of 0.1 $\mu g\ mL^{-1}$ Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} ions in the original solution were 2.5, 2.4, 2.2, 2.1 and 2.5%, respectively. The detection limits based on $3S_b/m$ for Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} ions in the original solution were 1.2, 1.3, 1.2, 0.6 and 1.5 ng mL^{-1}, respectively. The proposed method has been applied for determination of trace amounts of the analyte ions in the standard, water samples; brewed tea; tobacco samples and satisfactory results were obtained.

Keywords

Preconcentration; Carrier Element-Free Coprecipitation; Environmental Samples.

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1. INTRODUCTION

Heavy metals, in environment are one of the major sources of pollution. Small amounts of these elements are common in our environment and actually necessary for good health but large amounts of them may cause acute and chronic toxicity. Heavy metals toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, damage the blood composition, lung, kidneys, liver and other vital organs [1]. Because of these reasons determination of metal ion concentrations in environmental samples is one of the most important fields of the analytical chemistry [2-3]. The determination of trace heavy metal ions in environmental samples by flame atomic absorption spectrometry (FAAS) is directly difficult even with background correction and chemical modification; not only because of the presence of many trace metals at concentrations near or below detection limit, but also because the analyzed sample matrix may cause serious interference [4-6].

In order to solve these problems, various separation/preconcentration procedures, including solvent extraction [7], solid phase extraction (SPE) [8,9], cloud point extraction [10], membrane filtration [11,12], coprecipitation [13-15], ion exchange [16], electroanalytical techniques [17,18], etc. can be used.

Coprecipitation has also an important place in the preconcentration and separation methods due to its some advantages including simplicity, high preconcentration factors, low consumption of organic solvent and short analysis time period for the procedures [19-20]. In the coprecipitation procedure, a precipitate was occurred by the combination of a carrier element and a suitable inorganic or organic ligand.

In the present work, a coprecipitation method, which has been called carrier element-free coprecipitation (CEFC) [20], (2-(4-{[(4-{5-oxo-4-[1-(2-thienyl) methylidene]- 4,5-dihydro- 1,3-oxazole-2-yl} phenyl) imino] methyl} phenyl) methylidene] amino} phenyl) -4-[1-phenyl methylidene] -1,3-oxazole-5(4H)-one (OTMDO) without adding any carrier element was developed for the separation and preconcentration of Mn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions. It is a great advantage due to there is no contamination and interference risk for analytes from a carrier element.

The influences of analytical parameters such as amount of coprecipitant, sample volume, diverse ions, etc. were investigated. The proposed method was applied to several environmental samples for determination of trace metal contents.

2. EXPERIMENTAL

2.1. Instrumentation

A SensAA GBC atomic absorption spectrometer (Dandenong, Australia) equipped with deuterium background correction and air–acetylene burner was used for absorbance measurements. Manganese, cadmium, cobalt, nickel and copper hollow cathode lamps were used as light sources. The operating parameters of elements were set according to the manufacturer recommendations. The acetylene flow rate and burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution. A Metrohm 692 pH meter (Herisau, Switzerland) was used for pH measurements. A Centurion scientific centrifuge model 1020 D.E. (West Sussex, United Kingdom) was used to accelerate the phase separation.

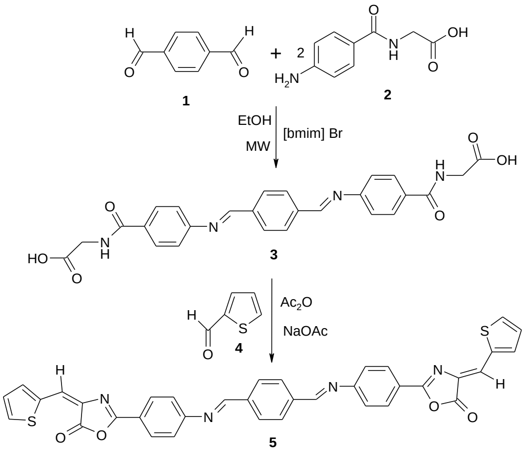
2.2. Reagents and Solutions

De-ionized water was used throughout the experimental work. The stock solutions of manganese, cadmium, cobalt, nickel and copper were purchased from (Merck, Darmstadt, Germany). Working standard solutions were obtained by appropriate dilution of the stock standard solutions by serial dilution with de-ionized water. The laboratory glassware were kept overnight in a 1.4 mol L^{-1} HNO_3 solution. Before using, all of the glassware were washed with de-ionized water and dried. The solutions of alkali metals salt (1% w/v) and various metal salts (0.1% w/v) were used to study the interference of anions and cations, respectively. Diluted HNO_3 and NaOH solutions were used for pH adjustments. A solution of 0.5% (w/v) OTMDO in dimethyl sulfoxide-ethanol (1:4 v/v) was prepared.

2.3. Synthesis of OTMDO

At first compound 3 was synthesized. For this purpose, 1 mL ethanol was added to a mixture of terephthalaldehyde (1 mmol), 4-aminohippuric acid (2 mmol) and ionic liquid [bmim]Br (0.3 g). The mixture was irradiated in a microwave oven at a power output of 500 w for 10 min. After completion of the reaction, the resulting solid residue, 4-[(4-{[4-(carboxymethyl-carbamoyl)-phenylimino]-methyl}-benzylidene)-amino]-benzoylamino}-acetic acid (compound 3) is washed with cold water (2×10 mL) and is crystallized from N,N-dimethylformamide, water and hydrochloric acid (2:1:1) (Scheme I).

Then, OTMDO (compound 5) was synthesized using compound 3 (Scheme I). For this purpose, compound 3 (1 mmol), thiophene-2-carbaldehyde (2 mmol), acetic anhydride (1 mL) and sodium acetate (2 mmol) are introduced into a beaker. The mixture is irradiated in a microwave oven at a power output of 500 w for 15 min. After irradiation, the paste is cooled to room temperature then washed with cold ethanol 96% and N,N-dimethylformamide. The precipitate formed (OTMDO) was separated and dried (Scheme I).



Scheme 1. Steps for synthesis of OTMDO

2.4. Coprecipitation procedure

The coprecipitation procedure was optimized with aqueous solutions prior to its application to the real samples. First, 40.0 mL portions of aqueous solution containing 10 µg of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) were given and pH adjusted to 10.0. Then, 2.0 mL 0.5 % OTMDO was poured into the tube. After 10 min, the solution was centrifuged at 3500 rpm for 15 min and the supernatant was removed. After this, the precipitate was dissolved with 3.0 mL of HNO_3 3 mol L^{-1}. The final solution was aspirated directly into the flame of FAAS.

2.5. Sample preparation

All water samples and Hookah's water samples were collected in acid leached polyethylene bottles. Before the analysis, the organic content of the water samples was oxidized in the presence of 1% H_2O_2 and then was acidified to pH 2 with nitric acid. Before the analysis, the samples were filtered before analyses through a cellulose membrane of 0.45 µm pore size (Millipore). For preparation of brewed tea, 1.0 g of Blake tea was weighed accurately into a beaker containing 100 mL of deionized water and heated on a water bath for 20 min. The solution was cooled and filtered. Then, the filtrate was made up to 250.0 mL with deionized water in a calibrated flask.

For preparation of Hookah's and Cigarette's tobacco, 2.0 g of these materials were weighed accurately into two beakers and dissolved in concentrated nitric acid (ca. 10 mL) with heating on a water bath [21]. The solutions were cooled, diluted to 20 mL with deionized water and filtered. Then, the filtrate was made up to 250.0 mL with deionized water in two calibrated flasks.

3. RESULT AND DISCUSSION

3.1. Synthesis of coprecipitant agent

The obtained results about of compound 3: m.p. 234-237 °C; Yield: 85%; Anal. Calcd. for $C_{26}H_{22}N_4O_6$: C, 64.19; H, 4.56; N, 11.52. Found: C, 64.45, H, 4.81, N, 11.35; FT-IR (KBr, cm^{-1}): 2400-3500, 1699, 1652, 1603, 1501 ; ^1H NMR (500 MHz, DMSO-d6, δ / ppm): 3.41 (s, 4H, $2CH_2$), 7.31-8.43 (m, 16H, CH imin, ArH, NH), 10.54 (s, 2H, acid); Mass spectrum, *m/z* (%)*:* 484 $[M-2H]^+$ (4), 368 (4), 280 (100), 237 (95), 137 (41), 92 (16).

The obtained results about of compound 5 (OTMDO): m.p. (decomposed): 318-319 °C; Yield: 92%; Anal. Calcd. for $C_{36}H_{22}N_4O_4S_2$: C, 67.70; H, 3.47; N, 8.77. Found: C, 67.28, H, 3.61, N, 8.49; FT-IR (KBr, cm^{-1}): 1791, 1647, 1503; ^1H NMR (500 MHz, DMSO-d6, δ / ppm): 6.93 (s, 2H, Vinyl), 7.51-8.33 (m, 18H, ArH), 8.61(s, 2H, imin); Mass spectrum, *m/z* (%)*:* 638 $[M]^+$ (4), 368 (10), 298 (14), 162 (20), 120 (100).

3.2. Effects of pH

The influence of the pH on the recovery of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions were investigated at the range of 3–12 because pH is one the most important factor on the quantitative recoveries of analytes. For that purpose, 2 mL of OTMDO were added to test solutions containing 10 µg of analyte ions, then pH of these solutions were adjusted by the addition of NaOH and HNO_3 solutions. As can be seen from Fig. 1, the recovery of all elements increased with increase of pH and quantitative results were obtained for all studied elements at pH range 10-11. For further experiments, pH 10.5 was chosen as optimum pH.

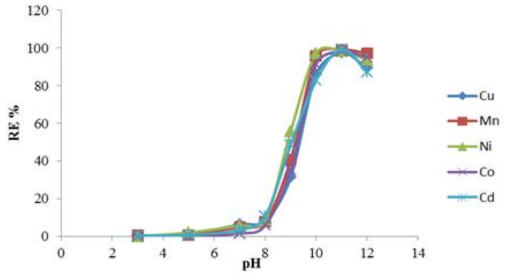


Fig. 1: Effect of pH on the recovery of the analyte ions. Conditions: Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions, 10.0 µg; OTMDO 0.5 %, 2 mL; Standing time, 10 min; Centrifuge speed, 3500 rpm; Centrifuge time, 15 min; Final solution, 3.0 mL of HNO_3 3 mol L^{-1}.

3.3. Effects of OTMDO amount

The influence of amount of OTMDO on the recovery of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions were also investigated in the range of 0–15 mg. The results showed that the recoveries were not quantitative without OTMDO. The recoveries of the analyte ions increased with increasing amount of OTMDO. The results showed that for the quantitative and simultaneous recoveries of the analyte ions, OTMDO was necessary. Quantitative recoveries for all the analytes were obtained at 5 mg. Therefore, 2 mL 0.5% OTMDO was used in all subsequent works.

3.4. Effects of standing time, centrifugation time and rate

The standing time, centrifugation time and rate for precipitate formation was also optimized because these are the important factors influencing the quality of coprecipitate. For this purpose 2 mL of OTMDO were added into a series of solutions (40 mL) containing analyte ions after pH was adjusted to 10.5. Then, the solutions were kept standing from 0 to 20 min. The results were showed that after 7 min, quantitative recoveries were obtained. Therefore, 10 min was selected as optimum standing time for all subsequent experiments. This period was long enough for the formation of precipitate and adsorption of trace metal ions on the precipitate.

The effect of the centrifuge rate was examined in the range of 2000–4500 rpm at the optimal conditions. The optimum centrifugation rate was determined as 3000 rpm for all studied metal ions. Therefore, 3500 rpm was selected as optimum the centrifuge rate for all subsequent experiments.

Also, the influence of centrifugation time on the recovery of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions were investigated in the range of 5–20 min at 3500 rpm. The results were showed that, quantitative recoveries were obtained for analyte ions in the range of 10–20 min. Therefore, all the other works were performed at 3500 rpm for 15 min.

3.5. Effect of sample volume

The sample volume used for the coprecipitation procedure influences the preconcentration factor. In order to, a series of sample solutions, containing 10 µg of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions were prepared in the volume range 25 to 300 mL and recoveries of the analyte ions measured at the optimum conditions. The results showed that Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions were quantitatively recovered when the sample volume was less than 250 mL. When the sample volume exceeded 250 mL, the recovery of the analyte ions decreased. Consequently, by considering the final elution volume (5.0 mL) and a breakthrough volume of 250 mL, a preconcentration factor of 50 was easily achievable.

3.6. Effect of foreign ions

One of the main problems in the atomic absorption spectrometric determination of the heavy metal ions is interference from matrix. Therefore the effect of interfere ions on the coprecipitation efficiency of the analyte ions was examined. For this, various amounts of interfering ions were added to a solution containing 10 µg of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions and the coprecipitation procedure was followed. The results are shown in Table 1. The results showed that large number of anions and cations used have no considerable effect on the determination of the analyte ions. Also some transition metals at mg L^{-1} levels were not interfered on the recoveries of the analyte ions. As a result, the coprecipitation procedure could be applied to the highly saline samples and the samples that contain some transition metals at tolerable level given in Table 1.

Table 1. Tolerance limit of foreign ions.

Foreign ions	Interference/Analyte ions(II) ratio				
	Mn(II)	Co(II)	Ni(II)	Cd(II)	Cu(II)
$H_2PO_4^-$, HPO_4^{2-}	>5000	> 5000	> 5000	> 5000	> 5000
Ca^{2+}	2000	2500	2500	2500	2000
Mg^{2+}	2500	2000	2000	2500	2000
Al^{3+}	300	250	200	200	250
Ag^+	400	400	300	400	300
Ba^{2+}	250	300	200	200	200
Cr^{3+}	400	350	300	300	400
Zn^{2+}	250	200	200	250	250
Fe^{3+}	250	300	250	200	300
Pb^{2+}	400	350	400	400	500

3.7. Analytical performance

Under the optimized conditions, calibration curves were constructed by co-precipitation 40.0 mL of a sample solution containing of known amounts of the analyte ions. Seven replicate determinations of a mixture of 0.1 μg mL^{-1} Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions in the original solution gave a mean absorbance of 0.068, 0.057, 0.061, 0.088 and 0.067 with relative standard deviations 2.5%, 2.4%, 2.2%, 2.1% and 2.5%, respectively. The detection limits based on $3S_b/m$ for Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions in the original solution were 1.2, 1.3, 1.2, 0.6 and 1.5 ng mL^{-1}, respectively. The analytical parameters are given in Table 2.

3.8. Analysis of Certified Reference Material

The standard reference material (CRM-TMDA 54.4 fortified lake water) was also used for the method validation. Good agreement was obtained between analytical values and certified values (Table 3). The statistical comparison by t-test ($p < 0.05$) showed no significant difference between the certificated values and the experimental results.

3.9. Applications

After being verified the accuracy of the present coprecipitation procedure, this procedure was applied to the determination of manganese, cobalt, nickel, cadmium and copper content in different water samples, Brewed tea and Hookah's water samples. Also, the recovery of the analyte ions from water samples spiked with Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions were studied. The results are given in Table 4. According to these results, the added Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions can be quantitatively recovered from the water samples by the coprecipitation procedure. These results demonstrate the applicability of the procedure for manganese, cobalt, nickel, cadmium and copper determination in different water samples, Brewed tea and Hookah's water samples.

Also, the applicability of the coprecipitation procedure was evaluated in two tobacco samples. For this purpose, an aliquot of these prepared solutions were taken individually and the analyte ions were determined by the coprecipitation procedure. The recovery of the analyte ions from tobacco samples spiked with analyte ions was also studied. The results are given in Table 5. According to this Table, the added analyte ions can be quantitatively recovered from the tobacco samples by the coprecipitation procedure.

Table 2. Analytical parameters of the method.

Statistical parameters	Mn	Co	Ni	Cd	Cu
Linear ranges (ng mL^{-1})	5.0-800.0	5.0-1000.0	5.0-1000.0	2.5-500.0	5.0-800.0
Regression equations	A=0.673X+0.003	A=0.582X+0.004	A=0.601X+0.004	A=0.893X+0.003	A=0.674X+0.004
Correlation coefficient (R^2)	0.998	0.997	0.998	0.997	0.998
RSD%	2.5	2.4	2.2	2.1	2.5
Detection limit (ng mL^{-1})	1.2	1.3	1.2	0.6	1.5

Conditions: Volume of the original solution, 40 mL, Volume of the final solution, 3.0 mL, and other conditions were the same as Fig. 1.

Table 3. Determination of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) in CRM samples.

Sample	Certified value (ng mL^{-1})	Found[a] (ng mL^{-1})
TMDA 54.4 fortified lake water	Mn : 275	Mn : 273.2±6.5
	Co : 309	Co : 314.6±7.1
	Ni : 337	Ni : 332.5±6.8
	Cd : 158	Cd : 163.1±4.9
	Cu : 443	Cu :448.0±9.2

[a] Mean±standard deviation (n=3)

Table 4. Determination of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) in water samples.

Sample	Found[a] (ng $\mathrm{mL^{-1}}$)	Added (ng $\mathrm{mL^{-1}}$)	Found (ng $\mathrm{mL^{-1}}$)	Recovery (%)
Well Water (Payame Noor University of Kerman)	Mn: 9.4±0.3	Mn:20.0	Mn: 28.7±0.9	96.5
	Co: 7.3±0.3	Co:20.0	Co: 28.0±0.8	103.5
	Ni: 8.0±0.2	Ni:20.0	Ni: 28.4±0.8	102.0
	Cd: 4.2±0.2	Cd:20.00	Cd: 24.5±0.7	104.0
	Cu: ND[b]	Cu:20.00	Cu: 21.2±0.6	106.0
River Water (Kohpayeh, Kerman)	Mn: 7.1±0.3	Mn:20.0	Mn: 26.7±0.8	98.0
	Co: 8.0±0.4	Co:20.0	Co: 27.4±0.8	97.0
	Ni: 7.3±0.3	Ni:20.0	Ni: 28.2±0.8	104.5
	Cd: ND	Cd:20.00	Cd: 20.8±0.7	104.0
	Cu: 6.3±0.3	Cu:20.00	Cu: 27.0±0.6	103.5
River Water (Shahdad, Kerman)	Mn: 7.7±0.4	Mn:20.0	Mn: 26.8±0.8	95.5
	Co: 7.4±0.3	Co:20.0	Co: 28.1±0.8	103.5
	Ni: 8.0±0.3	Ni:20.0	Ni: 28.7±0.8	103.5
	Cd: ND	Cd:20.00	Cd: 20.7±0.7	103.5
	Cu: 8.6±0.4	Cu:20.00	Cu: 27.9±0.6	96.5
Brewed tea	Mn: ND	Mn:20.0	Mn: 20.67±0.78	103.4
	Co: ND	Co:20.0	Co: 19.59±0.81	98.0
	Ni: 7.08±0.25	Ni:20.0	Ni: 27.54±0.91	102.3
	Cd : ND	Cd:20.0	Cd: 20.77±0.76	103.8
	Cu: 6.25±0.22	Cu: 20.0	Cu:26.82±0.85	102.8
Hookah's water	Mn: ND	Mn:20.0	Mn: 19.82±0.85	99.1
	Co: ND	Co:20.0	Co: 20.62±0.76	103.1
	Ni: 8.23±0.25	Ni:20.0	Ni: 27.45±0.82	96.1
	Cd: 4.34±0.76	Cd:20.0	Cd: 25.18±0.90	104.2
	Cu:8.73±0.22	Cu: 20.0	Cu:28.05±0.88	96.6

[a] Average of four determination±standard deviation, [b] Not Detected

Table 5. Determination of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) in Tobacco samples.

Sample	Found[a] (μg $\mathrm{g^{-1}}$)	Added (μg $\mathrm{g^{-1}}$)	Found (μg $\mathrm{g^{-1}}$)	Recovery (%)
Hookah's Tobacco	Mn: 2.28±0.09	Mn:20.0	Mn: 22.83±0.83	102.8
	Co: 2.35±0.11	Co:20.0	Co: 22.59±0.74	101.2
	Ni: 6.63±0.23	Ni:20.0	Ni: 26.20±0.91	97.8
	Cd: 3.58±0.12	Cd:20.0	Cd: 22.95±0.76	96.8
	Cu:6.48±0.24	Cu: 20.0	Cu:25.88±0.85	97.0
Cigarette's Tobacco	Mn: 2.93±0.12	Mn:20.0	Mn: 23.15±0.90	104.2
	Co: 2.66±0.09	Co:20.0	Co: 22.42±0.69	98.8
	Ni: 6.92±0.32	Ni:20.0	Ni: 26.58±0.86	98.3
	Cd: 3.27±0.11	Cd:20.0	Cd: 23.84±0.77	102.8
	Cu: 7.58±0.37	Cu: 20.0	Cu:28.23±0.84	103.2

[a] Average of four determination±standard deviation

3.10. Comparison of coprecipitation procedure with the other methods

A comparison of the coprecipitation procedure with other reported preconcentration methods, for Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) extraction from water samples, is given in Table 6 [21-25]. Based on the results shown in Table 6, the detection limits obtained, using the coprecipitation procedure, was better than some of the other reported preconcentration methods [24] and comparable with the other references [21-23,25]. Also, the relative standard deviation of the present procedure was lower than some of the other reported preconcentration methods [22,23,25].

Table 6. Comparison of the coprecipitation procedure with other reported methods for preconcentration of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) ions.

System	Analysis method	RSD (%)	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	Ref.
SPE	FAAS	Cu:1.9 Ni:2.3 Co:2.6 Cd:2.1	Cu:2.0-900.0 Ni:5.0-1700.0 Co:5.0-1700.0 Cd:1.0-400.0	Cu:0.4 Ni:1.0 Co:1.2 Cd:0.2	21
SPE	ICP-OES	2.7-5.9	--------	Co: 0.41 Ni: 0.41 Cd: 0.30	22
Coprecipitation	FAAS	≤10	Mn: ------ Ni: ------ Cd:-----	Mn: 0.45 Ni: 0.06 Cd:0.34	23
Coprecipitation	FAAS	----	-----	Ni: 3.0 Cd:2.0	24
SPE	FAAS	Cu: 4.31 Ni: 5.80 Cd: 3.83	Cu:0.4-2600 Cd:0.2-1000 Ni:1.0-5000	Cu:0.86 Ni:0.92 Cd: 0.65	25
Coprecipitation	FAAS	Mn:2.5 Co:2.4 Ni:2.2 Cd:2.1 Cu:2.5	Mn: 5.0-800.0 Co:5.0-1000.0 Ni:5.0-1000.0 Cd:2.5-500.0 Cu:5.0-800.0	Mn:1.2 Co:1.3 Ni:1.2 Cd:0.6 Cu:1.5	Present work

4. CONCLUSIONS

The present coprecipitation procedure using OTMDO as coprecipitating agent offers a useful preconcentration method for environmental and tobacco samples. In this study, we used an organic coprecipitant. This agent provides effective and quantitative collection of trace metal ions on itself without adding any carrier metal for the formation of insoluble complexes or salts which may cause interference risk for analytes. The procedure has been successfully applied to the real samples for the determination of Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) levels with acceptable accuracy and precision. The coprecipitated analyte ions can be sensitively determined by atomic absorption spectrometry without any influence of coprecipitant agent. The method is simple, low cost and fast.

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