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DETERMINATION OF COPPER, ZINC, CADMIUM AND LEAD IN WATER USING CO-PRECIPITATION METHOD AND RAMAN SPECTROSCOPY

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Mn co-precipitation method combined with Raman spectroscopy were used to determine trace heavy metals (copper, zinc, cadmium and lead) in water sample. Different concentrations of heavy metals including copper, zinc, cadmium and lead in water samples were separated and enriched by Mn^{2+}-phen-SCN- ternary complex co-precipitation procedure. The Raman spectra of co-precipitation sediments were collected using confocal micro-Raman spectrometry. Different preprocessing treatments and regression calibration methods were compared. The best models using partial least squares regression (PLS) of copper, zinc, cadmium and lead were built with a correlation coefficient of prediction (R_p) of 0.979, 0.964, 0.956 and 0.972, respectively, and the root mean square error of prediction (*RMSEP*) of 6.587, 9.046, 9.998 and 7.751 μg/kg, respectively. The co-precipitation procedure combined with Raman spectroscopy method are feasible to detect the amount of heavy metals in water.

Keywords: Raman spectroscopy; co-precipitation; heavy metals; partial least squares regression.

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1. Introduction

Heavy metals in food and environment are important risk factors for environmental pollution.[1] Accurate determination on heavy metals in environment is the main research field in analytical chemistry. High levels of matrix components are influenced in the determination of heavy metal ions. Separation methods like solid phase extraction, cloud point extraction, solvent extraction, etc. have been widely used.[2,3] The characterization of heavy metals in water is an important requirement for sewage disposal because of its toxic elements accumulating in the environment.

It is common that the total concentrations of metals in water are not a good indicator of bioavailability, for the different and complex distribution patterns of metals.[4,5] There are many reports on the single extraction procedures with different chemical agents, for available metals.[6] Co-precipitation is widely applied to separation and pre-concentration of analysis from a liquid matrix and/or purified extracts for heavy metal ions.[7] Co-precipitation could be preconcentrated and separated from the matrix simultaneously. It has many advantages, such as simple and fast. Several kinds of ion can be pre-concentrated and separated from the matrix simultaneously. Several inorganic or organic co-precipitants can be used as efficient collectors of trace elements. Co-precipitation by phenanthroline of various metal ions including copper, zinc, cadmium and lead were reported for the pre-concentration-separation of trace elements from various media like water.[8]

Raman spectroscopy is a useful analytical technique based on the interaction of an incident monochromatic radiation with vibration energy levels of molecules. The technique has been reported for many years in combination with optical fibers.[9–12] It enables someone to analyze both qualitative and quantitative information for various chemical mixtures *in situ*. Raman spectra of heavy metals complex possibly provide bonding structures of heavy metals complexation. Raman spectroscopy was applied to obtain the heavy metal complex samples.[13,14] A better understanding on these aspects of the adsorption process is helpful to detect the heavy metals concentration and to eventually optimize strategies for the removal of heavy metals from contaminated water.

In our research work, Mn phen co-precipitation procedure combined with Raman spectroscopy method were investigated for the determination of trace quantities of heavy metals (copper, zinc, cadmium and lead) in the water. Different concentrations of copper, zinc, cadmium and lead heavy metals in the water samples were conducted by separation and enrichment with the Mn^{2+}-phen-SCN- ternary complex co-precipitation procedure.

2. Materials and Methods

2.1. *Samples preparation*

All chemical reagent used in this work were analytical grade. Deionized water (TAOSHI Water Equipment Engineering Co., Ltd, $18.2\,M\Omega \cdot cm^{-1}$ resistivity) was used for all dilutions. Laboratory glassware was kept overnight in the 10% v/v HNO_3 solution, and then rinsed with ultra pure water. Standard solution of copper, zinc, cadmium and lead ions were national secondary standard material, medium 2% HNO_3 stock metal solutions, $100\,mg\ L^{-1}$ Sigma were diluted daily for obtaining reference and working solutions. Standard solutions used for the calibration procedures were prepared before using by diluting the stock solution with $1\,mol\ L^{-1}$ HNO_3. Each working solution was added by the four solutions in the following procedure: a certain amount of $0-120\,mg\,L^{-1}$ of ions, $1\,g\,L^{-1}$ of manganese ion solution 9 mL, $3\,g\,L^{-1}$ phenanthroline solution of 14 mL and $10\,g\,L^{-1}$ KSCN solution of 6 mL, respectively. HCl and sodium hydroxide were used for pH adjustment. Centrifugation was carried out using a TDL-80-2B low-speed centrifuge (0−6000 rpm, 0−60 min, 220/50 Hz). The precipitates were obtained after drying naturally for 5 h.

2.2. *Apparatus*

Confocal Raman micro-spectra (SENTERRA, Bruker Tech. and Serv. Co., Ltd, Ettlingen, Germany) equipped with a TE cooled Si CCD detector and a 14 mW maximum power diode laser was used in the research. The waveband of 780 nm line, provided by a visible laser was used as excitation line. The system has an OLYMPUS optical microscope with 10, 20, 50 and 100 times power objectives and a high spatial resolution ($<1\,\mu m$). The resolution of confocal depth reach to $2\,\mu m$ and the Raman system was controlled by software OPUS (Bruker Tech. and Serv. Co., Ltd, Ettlingen, Germany).

2.3. *Statistical analyses and interpretation*

Calibration models between the contents of heavy metals and Raman spectra were developed by PLS and MLR regressions methods. To obtain the optimized calibration model, the pretreatment methods including transform baseline, first derivative calculation, multiplicative scatter correction (MSC) and standard normal variate (SNV) were compared. The data were analyzed using Unscrambler 10.0 (CAMO AS, Trondheim, Norway) and Origin Pro 8.5 (OriginLab Corporation, Hampton, U.S.A.) statistical package.

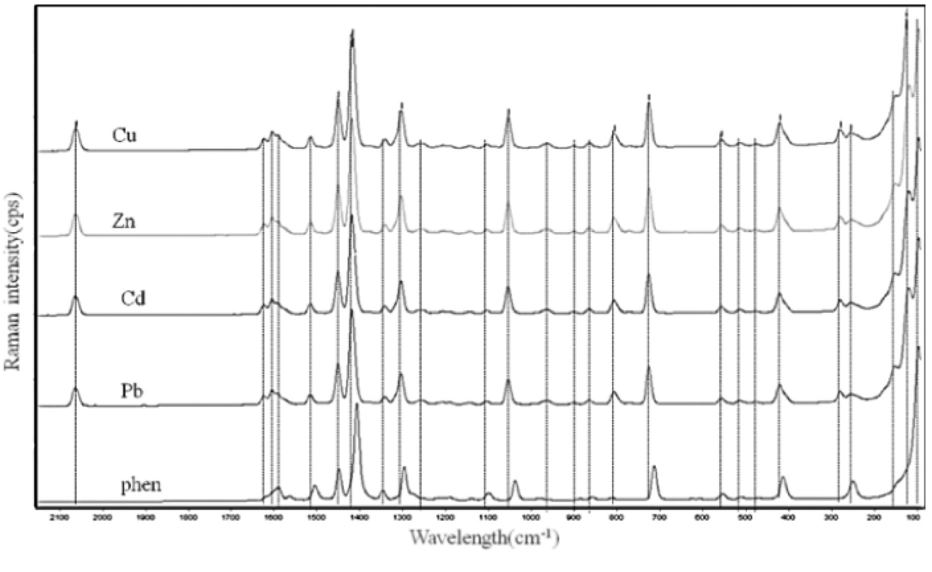
The performance of the PLS calibration models was evaluated in terms of the correlation coefficients (r) and root mean square error (RMSE), which was determined by leave-one-out cross-validation (LOO-CV). The factor number for PLS model was determined by using the LOO-CV with F-test.

3. Results and Discussion

3.1. *Raman spectra band analysis*

Raman spectrum included a lot of molecular structure information. After metal ions combined with Mn^{2+}-phen-SCN^- complexity, C−N bond was coordinated with the vibration frequency of the C−C bond and C−H bond in the Raman spectra of great changes. Figure. 1 shows the Raman spectra of different heavy metals (copper, zinc, cadmium and lead) complexity. Phenanthroline ν (C−C) at $1503\,\mathrm{cm}^{-1}$ Chu vesting ν (C−N) composite vibration peak, after the formation of complexes all moves to higher wavenumber of $1514\,\mathrm{cm}^{-1}$. Phenanthroline attributed to the ν (C−C) vibration peak at $1617\,\mathrm{cm}^{-1}$, after the formation of complexity and all move to higher wavenumber of $1622\,\mathrm{cm}^{-1}$. Which peaks shifted to higher wavenumber is phenanthroline ν (C−C) peak at $1035\,\mathrm{cm}^{-1}$ vesting 17 wave number shifts to higher wavenumber after the formation of complexes. In Fig. 1, phenanthroline in the 809, 980, 1205 and $1345\,\mathrm{cm}^{-1}$ are assigned to the ω (CH), τ (C−H), ν (C−C) δ (C−H) and ν at (C−N) vibration, in the formation of complexes the red shifted to 805, 960, 1204 and $1340\,\mathrm{cm}^{-1}$ place, respectively. The reasons for the changes in the Raman spectra is mainly a result of the effects of heavy metal ions to form a complex system of space and phenanthroline space symmetry greatly changed before and after the complexation.

Table 1 shows the comparison of different heavy metals complex observed in Raman spectra. Compared with phenanthroline, the Raman spectra of Cu^{2+}-Mn^{2+}-phen-SCN^-, Zn^{2+}-Mn^{2+}-phen-SCN^-, Cd^{2+}-Mn^{2+}-phen-SCN^- and Pb^{2+}-Mn^{2+}-phen-SCN^- complex presented new characteristic peaks at 147, 769, 1259, 1375 and $1603\,\mathrm{cm}^{-1}$, respectively. It suggests that a new coordination bond is existed and a complex system in the experiment is successfully formed. The peaks position and peak shape of four



cps: count per second

Fig. 1. The Raman spectrum of different heavy metals complex.

Table 1. Comparison of different heavy metals complex observed in Raman spectra.

	Raman wavenumber (cm^{-1})						
No.	KSCN	phen	Cu	Zn	Cd	Pb	Peak position
1	98	93	93	94	93	93	
2	123		115	116	117	116	
3			147	147	148	149	
4		247	252	252	252	252	
5			276	276	277	276	
6		410	418	418	418	418	
7	484	466	474	474	474	474	out-of-plane laud ring
8		508	511	511	512	511	ring deform
9		551	554	554	554	554	ring deform and out-of-plane
10	747	711	724	724	724	724	Ring deform
11			769	769	769	769	ω C−H
12		809	805	805	806	805	
13		855	863	863	863	863	Ring deform
14		882	899	899	900	899	τ C−H
15	968	980	960	961	961	961	
16		1035	1052	1052	1052	1052	ν C−C
17		1097	1102	1102	1103	1102	δ C-H
18		1137	1141	1141	1141	1141	
19		1188	1188	1189	1189	1188	
20		1205	1204	1204	1205	1205	ν C−C δ C−H
21			1259	1260	1258	1260	
22		1294	1302	1302	1302	1302	ν C−N
23		1345	1340	1340	1341	1341	
24			1375	1376	1376	1377	ν C−C
25		1405	1416	1417	1417	1417	ν C−C ν C−H
26		1447	1449	1449	1449	1449	ν C−C
27		1503	1514	1514	1514	1514	ν C−C ν C−N
28		1589	1591	1591	1591	1591	
29			1603	1603	1603	1603	ν C−C
30		1617	1622	1622	1622	1622	
31	2004	2015	2015	2015	2014	2014	
32	2050		2062	2062	2063	2062	SCN
33		3063	3070	3070	3071	3070	

kinds of complexes are extremely similar, it shows that though the four kinds of complexes have different ligands, they have the same spatial configuration.

Influence of different heavy metals on phenanthroline ligand in complexes can be observed in the Raman spectra. The lines of phenanthroline vibrations were identified easily by comparison of Raman spectra with different heavy metals.

The latter spectrum was formed mostly by phenanthroline vibrations excluding the line at $1035\,\mathrm{cm}^{-1}$ due to totally symmetric vibration $\nu_2(\mathrm{NO}_{-3})$. Some phenanthroline lines shift (assigned to ν(C=C, C=N), ν(C=C) + δ (CH), ring breathing, δ(C−H) out-of-plane vibrations) by $2{-}4\,\mathrm{cm}^{-1}$ to high-frequency side at transition. These shifts witness about increasing the polarizing influence of heavy metal ions on heterocyclic molecule and strengthening the heavy metal ions−N bonds in the above-mentioned rows of compounds. The weakest bond heavy metal ions molecule should be in other complexes, the strongest one should be in nitrates, and similar symptoms were observed by G. Brehm for $\mathrm{Fe(phen)_2(NCS)_2}$ complexes. Therefore, the application of Raman spectroscopy can be measured by small changes in vibrations in the sensitive band of the heavy metal complexes, to determine the vibration frequency of the metal coordination bond.

3.2. *Quantitative analysis*

The co-precipitation of Mn^{2+}-phen-SCN^- ternary complex systems for copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb) in the water was studied. The heavy metal complexes were collected, before Raman spectroscopy method and were used to analyze heavy metal complexes of Cu, Zn, Cd and Pb in the water, respectively. The calibration models were developed of the heavy metal concentrations in the water. The procedure was involved as follows: the Raman spectra of heavy metal complexes were pretreated with different methods including smoothing, first derivative, second derivative, MSC, SNV, baseline correction and de-trending, and the best methods using PLS calibration models were compared for the heavy metal concentrations of Cu, Zn, Cd and Pb, respectively.

The pretreatment methods were attempted to eliminate the interference of Off-target factors. Tables 2, 3, 4 and 5 show the results of PLS calibration models with different spectral pretreatments, the number of each heavy metal complex samples are the same, with the number of calibration set and validation set are 56 and 28, respectively.

As shown in Tables 2 and 3, both the background removal (transform baseline) and the background

Table 2. Comparison results for Cu concentrations developed by PLS with different preprocessing methods.

		Calibration set		Validation set	
Preprocessing method	PCs	R_C	*RMSEC* (μg/kg)	R_P	*RMSECV* (μg/kg)
Origin	5	0.984	6.260	0.981	6.998
1st D	4	0.982	6.726	0.979	7.246
2nd D	8	0.987	5.792	0.981	6.969
SNV	3	0.981	6.846	0.979	7.245
MSC	3	0.981	6.849	0.979	7.248
Baseline	5	0.983	6.537	0.981	6.912
de-trending	4	0.982	6.796	0.979	7.323

Table 3. Comparison results for Zn concentrations developed by PLS with different preprocessing methods.

		Calibration set		Validation set	
Preprocessing method	PCs	R_C	*RMSEC* (μg/kg)	R_P	*RMSECV* (μg/kg)
Origin	10	0.983	6.586	0.957	10.306
1st D	7	0.983	6.566	0.969	8.826
2nd D	10	0.983	6.473	0.971	8.886
SNV	9	0.978	7.385	0.949	11.192
MSC	9	0.979	7.312	0.948	11.394
Baseline	10	0.984	6.394	0.955	10.592
de-trending	9	0.980	7.071	0.956	10.462

Table 4. Comparison results for Cd concentrations developed by PLS with different preprocessing methods.

		Calibration set		Validation set	
Preprocessing method	PCs	R_C	*RMSEC* (μg/kg)	R_P	*RMSECV* (μg/kg)
Origin	10	0.974	7.089	0.943	11.807
1st D	9	0.988	5.449	0.952	10.916
2nd D	12	0.956	10.488	0.889	16.347
SNV	9	0.987	5.708	0.958	10.188
MSC	9	0.987	5.716	0.953	10.868
Baseline	10	0.984	6.241	0.957	10.353
de-trending	9	0.988	5.462	0.961	9.896

Table 5. Comparison results for Pb concentrations developed by PLS with different preprocessing methods.

		Calibration set		Validation set	
Preprocessing method	PCs	R_C	*RMSEC* (μg/kg)	R_P	*RMSECV* (μg/kg)
Origin	7	0.982	6.746	0.973	8.216
1st D	7	0.992	4.446	0.977	7.548
2nd D	9	0.964	9.436	0.937	12.405
SNV	6	0.983	6.609	0.975	7.973
MSC	6	0.981	6.835	0.973	8.231
Baseline	7	0.982	6.718	0.973	8.145
de-trending	6	0.981	6.966	0.972	8.387

correction (SNV and MSC) techniques can improve the performance of the PLS calibration models.

As shown in Tables 4 and 5, both the background removal (transform baseline) and the background correction (SNV and MSC) techniques can improve the performance of the PLS calibration models besides second derivative. It shows that the Raman spectra of Cd and Pb complex related information were retained in a certain degree by either of pretreatment. The principal components (PCs) of calibration models of Cd was larger than the others, may be due to physical traits and grain structure complicated when the Cd complex generated. The best preprocessing methods corresponding to the best calibration models for the heavy metal concentrations of Cd and Pb were de-trending and first derivative, respectively, with the correlation coefficients of cross calibration (R_c) of 0.988 and 0.992, respectively, the correlation coefficients of cross validation (R_{cv}) of 0.961 and 0.977, respectively, while the root mean squared error of cross calibration (*RMSEC*) of 5.462 and 4.446 μg/kg, respectively, the root mean squared error of cross validation (*RMSECV*) of 9.896 and 7.548 μg/kg, respectively.

When the Raman spectra of heavy metal complexes were pretreated, the best preprocessing methods corresponding to the best calibration models for the heavy metal concentrations of Cu, Zn, Cd and Pb were linear baseline correcting, first derivative, SNV, MSC and first derivative, respectively.

The Raman spectra with pretreatment were used as the inputs of PLS and MLR to develop prediction models, and the models were evaluated by predicting the 28 unknown samples. The MLR input variable for Table 1 listed 33 Raman peaks. Compared with PLS and MLR model prediction result is the worst, the root mean squared error of prediction (*RMSEP*) is 1.6 times above. In spite of this, MLR modeling variable is only 5% of the full spectrum of modeling variables.

The results in Table 6 showed that modeling by PLS was better than by MLR for the heavy metal concentrations of Cu, Zn, Cd and Pb in the water. The R_p were 0.979, 0.964, 0.956 and 0.972, respectively, while the *RMSEP* were 6.587, 9.046,

Table 6. Prediction results of values of heavy metal concentration by PLS models with Raman spectral data.

			Calibration set		Prediction set	
Heavy metal	Model	PCs	R_{cv}	RMSECV (μg/kg)	R_p	RMSEP (μg/kg)
Cu	PLS	5	0.981	6.912	0.979	6.587
	MLR	–	0.959	10.420	0.951	11.012
Zn	PLS	7	0.969	8.826	0.964	9.046
	MLR	–	0.8064	13.449	0.965	15.315
Cd	PLS	10	0.961	9.896	0.956	9.998
	MLR	–	0.858	19.003	0.815	20.164
Pb	PLS	8	0.977	7.548	0.972	7.751
	MLR	–	0.947	11.454	0.842	17.272

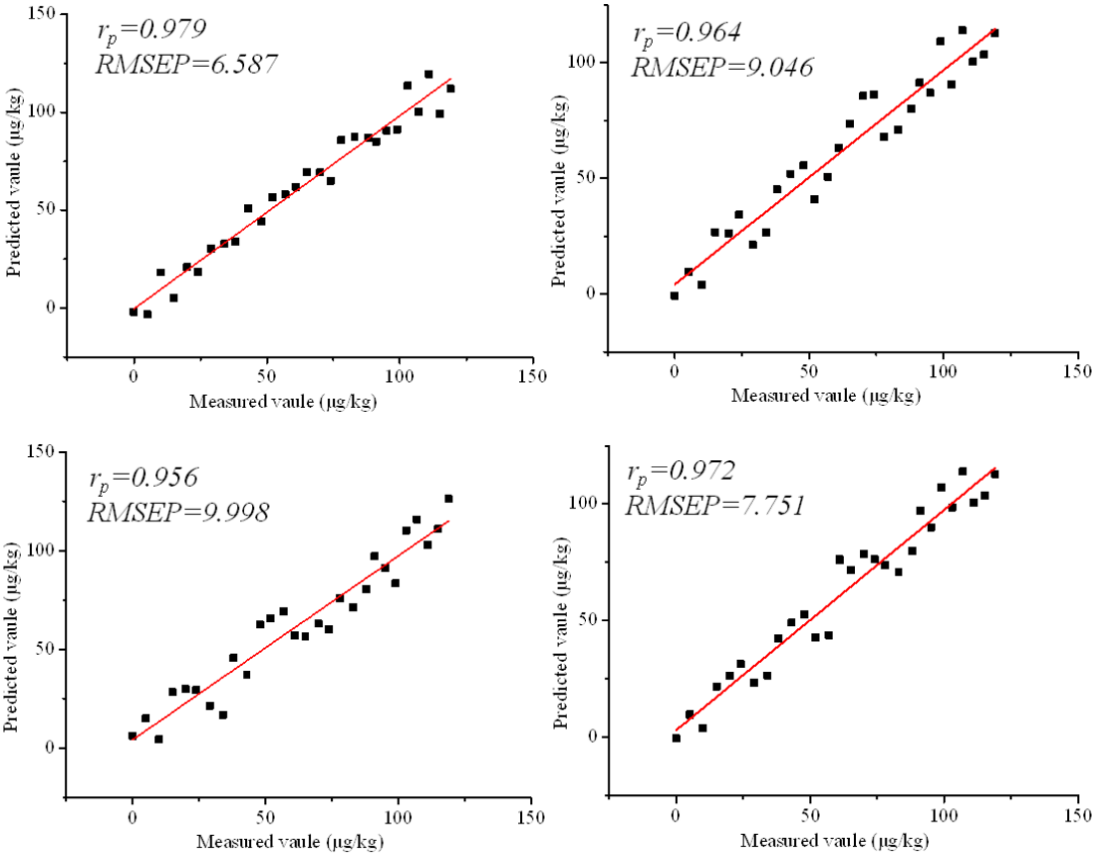


Fig. 2. The predicted result of prediction set of heavy metals by PLS.

9.998 and 7.751 μg/kg, respectively, as shown in Fig. 2.

The results indicate that Raman spectroscopy technique combined with co-precipitation method can be used for the quantitative analysis of the concentrations of Cu, Zn, Cd and Pb in water. The methods offer a reference to determine the heavy metal concentrations, such as Cu, Zn, Cd and Pb.

4. Conclusion

Confocal micro-Raman spectroscopy combined with co-precipitation method was applied to detect the heavy metals, such as copper, zinc, cadmium and lead in water. In addition, the Raman spectra preprocessing methods and modeling methods were compared. Different concentrations of copper, zinc, cadmium and lead heavy metals in the water samples were enriched by using coprecipitation method with the Mn^{2+} phen-SCN-ternary complex. The Raman spectra of generated sediment were preprocessed and compared with different preprocessing methods. The Raman spectra with pretreatment were used as the inputs of PLS to develop prediction models, and the models were evaluated by predicting the 28 unknown samples. The results showed the correlation coefficients of prediction (R_p) were 0.979, 0.964, 0.956 and 0.972, respectively, while the RMSEP were 6.587, 9.046, 9.998 and 7.751 μg/kg, respectively.

The presented work shows the possibility of the usage of precipitate for determination of trace Cu, Zn, Cd and Pb ions, and application of the procedure prior to their Raman spectroscopy determination of them in environmental samples.

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