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Simultaneous determination of mercury, lead and cadmium ions in water using near-infrared spectroscopy with preconcentration by thiol-functionalized magnesium phyllosilicate clay

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ABSTRACT

Analysis of metal ions in environment is of great importance for evaluating the risk of heavy metal to public health and ecological safety. A method for simultaneous determination of metal ions in water samples was developed by using adsorption preconcentration and near-infrared diffuse reflectance spectroscopy (NIRDRS). A high capacity adsorbent of thiol-functionalized magnesium phyllosilicate, named Mg-MTMS, was prepared by co-condensation for preconcentration of Hg^{2+}, Pb^{2+} and Cd^{2+} in aqueous solutions. After adsorbing the analytes onto the adsorbent, NIRDRS was measured and PLS models were established for fast and simultaneous quantitative prediction. Because the interaction of the ions with the functional group of the adsorbent can be reflected in the spectra, the models built with the samples prepared by river water were proven to be efficient enough for precise prediction. The determination coefficients (R^2) of the validation samples for the three ions were found as high as 0.9197, 0.9599 and 0.9861, respectively. Furthermore, because the high adsorption efficiency of Mg-MTMS, the detected concentrations are as low as milligrams per liter for the three ions, and the concentration can be further reduced. Therefore, the feasibility of quantitative analysis metal ions in river water by NIRDRS is proven and this may provide a new way for fast simultaneous determination of trace metals in environmental waters.

1. Introduction

Water contamination with heavy metals is an issue of global concern since the accumulation of heavy metals is one major risk factor for public health and ecological safety. Some well-known diseases such as minamata disease, itai-itai disease, and saturnism are among the examples to address the toxicity of mercury, cadmium and lead ions. It is therefore vital to develop effective approaches to rapidly analyze these metal ions in different real samples, although there have been various methods based on spectroscopic, electrochemical, or chromatographic techniques. Great efforts have been made in recent years on the separation and preconcentration techniques for quantitative analysis of metal ions in environmental or biological water samples due to the low level of concentration and matrix interferences [1–5]. Meanwhile, effective adsorbents [6–12] with high selectivity and super loading capacity have been prepared through conjugating with metal complexing groups. Among these adsorbents, Mg-MTMS, a kind of thiol-functionalized magnesium phyllosilicate, has attracted particular attention due to its unique structure and concentrated thiol group, and it was proven to be a high effective absorbent for Hg^{2+}, Pb^{2+} and Cd^{2+} [6].

Near-infrared spectroscopy (NIRS) is a kind of fast and nondestructive analytical method, which has been proven to be a green tool for multi-component analysis [13]. Compared with conventional analytical methods, NIRS is more convenient, eco-friendly and cost-effective for complex sample analysis [14,15]. Besides its application in the qualitative and quantitative analysis of organic matters in the fields of agriculture, food, textiles, petrochemicals and pharmaceuticals, the technique has also been recently used to quantitatively analyze metals such as Pb, Cu, Ni, Mn, Zn, Cr, Cd, Co, etc. in sediment [16–18], soil [19–23] and water samples [24–26]. However, it is hard to see the NIR responses of metal ions in solution or in adsorbed states [16,19,25], although NIR signals of Fe^{2+} and Cu^{2+} in minerals were detected by Frost et al. [27,28]. Generally, the flexibility of NIRS in the quantitative determination of trace metals are accounted for by the "indirect analysis" in two different ways, i.e., either the organic groups combined with the metal ions [16,21,24,25] or the organic matters whose concentrations are proportional to the metal ions [18,19] can be quantitatively determined by NIRS.

In this study, an approach for simultaneous determination of metal ions in dilute solution by using near-infrared diffuse reflectance spectroscopy (NIRDRS) was proposed. Adsorbent was

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used for gathering the metal ions, NIRDRS was adopted for fast measurement and chemometric modeling was applied for simultaneously determination of the specified analyte. Therefore, Mg-MTMS was prepared as a high efficient adsorbent to preconcentrate the trace Hg^{2+}, Pb^{2+}, and Cd^{2+} from water samples. Then, a partial least squares (PLS) regression model was built by using the diffuse reflectance NIR spectra of the Mg-MTMS with the adsorbates, and the performance of the model was investigated by cross validation and external validation. It was proven that the sensitivity of NIRS can be improved due to the high capacity of adsorbent and quantitative determination can be achieved by the interaction of the metal ions and the thiol group in the adsorbent.

2. Experimental

2.1. Reagents and apparatus

All chemical reagents, including sodium hydroxide, magnesium chloride, nitric acid, mercury nitrate, lead nitrate and cadmium nitrate are of analytical purity grade. (3-mercaptopropyl) trimethoxysilane was purchased from Alfa Aesar (USA).

NIR spectra of the samples were measured on a Vertex 70 near infrared spectrophotometer (Bruker, Ettlingen, Germany) with near infrared integrating sphere diffuse reflection accessory (Bruker, Ettlingen, Germany). Tungsten–halogen lamp is used as light source and PbS detector is used. ICP-9000 (N + M) inductively coupled plasma–atomic emission spectrometry (ICP–AES) (Thermo Jarrell-Ash Corp., Franklin, USA) was used for detection of the metal ions in the solvent (river water) and z180-180 atomic absorption spectrophotometer (Hitachi, Tokyo, Japan) was used for detection of the remained analytes (Hg^{2+}, Pb^{2+}, Cd^{2+}) in the solutions after adsorption. D/max-2500 X-ray diffraction spectroscopy (Rigaku, Tokyo, Japan) and MAGNA-560 FT-IR spectrophotometer (Nicolet, Madison, USA) were used for characterization of the synthesized material.

2.2. Preparation and characterization of Mg-MTMS

The thiol-modified magnesium phyllosilicate material was prepared in a one-step silylation process as reported in the literature [29]. 16.5 mmol (3.40 g) of magnesium chloride hexahydrate was dissolved in 100 mL of methanol at first. Then 22.0 mmol (4.33 mL) of mercaptopropyltri-methoxysilane (MTMS) (Mg/Si molar ratio = 0.75), 400 mL 0.05 mol L^{-1} sodium hydroxide solution was added subsequently to the solution, resulting a cloudy suspension. After stirred overnight, a white precipitate can be isolated by centrifugation. After thoroughly washed with de-ionized water (5 times, 40 mL) and ethanol (2 times, 40 mL), and dried at 65 °C in air, a white powder (Mg-MTMS) can be obtained. The product was characterized by powder X-ray diffraction (XRD) and infrared spectroscopy (IR). Powder X-ray diffraction patterns were collected by Cu Kα radiation ($\lambda = 1.5405$ Å), and infrared spectrum was recorded with KBr pellet in 4000–400 cm^{-1} wavenumber range.

2.3. Samples preparation

The nitrate salts of mercury, lead and cadmium were dissolved with de-ionized water as stock solutions, concentrated 0.5360 g L^{-1}, 0.4927 g L^{-1} and 0.4927 g L^{-1}, respectively. 38 mixture samples of Hg^{2+}, Pb^{2+} and Cd^{2+} were prepared by diluting their stock solutions with river water. The concentration ranges of the three ions were 2.680–50.91 mg L^{-1}, 3.942–49.27 mg L^{-1} and 3.942–49.27 mg L^{-1}, respectively. The river water as solvent was filtered to remove the laurel-green suspended solids, and its pH was adjusted from 8.7 to ca. 5.0 with nitric acid before use. The contents of metal ions in the river water measured by ICP–AES were Na^{+} – 198.5 mg L^{-1}, K^{+} – 9.09 mg L^{-1}, Ca^{2+} – 33.74 mg L^{-1} and Mg^{2+} – 54.01 mg L^{-1}, respectively, but Hg^{2+}, Pb^{2+} and Cd^{2+} ions were not found.

100 mL of the aforementioned mixture samples and 0.20 g Mg-MTMS were added in a conical flask with a horizontal shaking bath at room temperature (ca. 25 °C) for 120 min at shaking frequency of 150 rpm. After that, the solutions were filtered with vacuum pump and the solids were further air-dried. Then, the adsorbents with the analytes were used for the spectral measurement. These spectra were used as calibration set to build the PLS models. In the experiments, the amount of Mg-MTMS was optimized, because a less amount of the adsorbent is in favor of the sensitivity, but goes against the reproducibility. It was found that the spectral reproducibility can be ensured when 0.20 g Mg-MTMS was used.

Under the same procedures and conditions, 15 samples of the three ions were prepared and their spectra were measured as validation set. The concentration ranges were 4.288–50.38 mg L^{-1}, 4.927–48.78 mg L^{-1} and 5.912–48.78 mg L^{-1}, respectively. The concentrations in both calibration set and validation set were designed by D-optimal experimental design to minimize the correlation among the analytes.

2.4. Spectral measurements

All samples were scanned over a wavenumber range from 4000 to 10,000 cm^{-1} using the near infrared spectrophotometer in diffuse reflectance mode. During the measurements, a reference spectrum was taken with the gold-coated background provided with the instrument before the measurements. To increase signal to noise ratio, both reference and sample spectra were measured with scan number 128, resolution 4 cm^{-1} and the average spectrum of three parallel measurements was used. The spectrophotometer was kept balance at 25 °C ambient for 60 min before use.

It is worthy of note that the Mg-MTMS with these metal ions cannot be thrown in the atmosphere directly due to the toxicity. The samples should be collected and treated after experiment.

2.5. Quantitative calculation

PLS regression has been the most commonly used tool for modeling the relationship of NIR spectral matrix (predictors) and concentration (observations). It can be known as a generalization form of multiple linear regression (MLR), but both the two matrices are projected to a new space of latent structure. In PLS modeling, therefore, the latent factors accounting for as much of the variation as possible are adopted relate the two matrices. Because it models not only the relationship but also the structure of two data matrices, data with many, noisy, collinear, and even incomplete variables can be accurately analyzed [30].

In this study, OPUS-QUANT program, which is based on PLS regression, in the OPUS 6.0 software package (Bruker, Ettlingen, Germany) provided with the instrument was used for quantitative analysis. 38 samples were used as calibration set for building the partial least squares (PLS) models for the three ions, respectively. The performance of calibration models were evaluated by the determination coefficients (R^2) and root mean squared errors of cross validation (RMSECV). In addition, residual predictive deviation (RPD), the ratio of standard deviation (SD) to standard error of prediction (SEP) in cross validation, was also used to indicate the robustness and predictive accuracy of the models. Generally, a model with RPD over 3.0 is considered suitable for screening and process control and over 5.0 for accurate quantitative analysis [16].

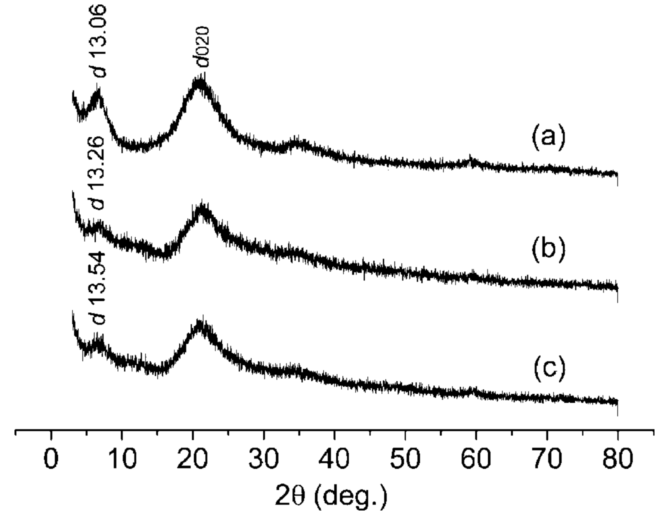

Fig. 1. Powder X-ray diffraction pattern of Mg-MTMS (a), Mg-MTMS with Pb^{2+}, Cd^{2+} (b) and Mg-MTMS with Hg^{2+}, Pb^{2+}, Cd^{2+} (c).

The latent variable numbers for the PLS models were determined by leave-one-out cross validation (LOO-CV) with *F*-test [31].

3. Results and discussion

3.1. Adsorbent characterization

The structure of Mg-MTMS had been well studied by XRD, TEM, FTIR and solid state ^{29}Si and ^{13}C NMR spectroscopy [6,34]. The molecular formula of the material is $Si_8R_8Mg_6O_{16}(OH)_4$, and $R = SH(CH_2)_3$ and it has a layered structure. SiO_4 forms the framework sheets of material, mercaptopropyl binds to SiO_4 as organic layer, and Mg^{2+} layer combines with oxygen of SiO_4 and hydroxy by electrostatic interaction. Furthermore, when metal ions react with SH at the edges of the layer, a hydrophilic porthole for the entry of additional ions will be created and the interlayer space that facilitates the inserting of more ions will be enlarged. Therefore, the adsorbent owns excellent uptake capacity for metal ions [6,34].

For verification of the synthesized adsorbent, XRD patterns of the material before and after adsorption was measured as shown in Fig. 1. Fig. 1(a) shows the XRD pattern of the synthesized material. The two peaks at 2θ 20.720° and 6.760° correspond to the (0 2 0) and (0 0 1) reflections. From the latter peak the interlayer distance (d_{001}) can be calculated as 13.06 Å. The value is consistent with that described in the literatures [29,32,33]. Fig. 1(b and c) shows the XRD pattern after loading Pb^{2+}, Cd^{2+} and Pb^{2+}, Cd^{2+}, Hg^{2+}, respectively. The layer space is expanded to 13.26 Å ($2\theta = 6.660°$) and 13.54 Å ($2\theta = 6.520°$) due to the ligation of the ions. The results are also consistent with the fact that the interlayer distance can be enlarged by loaded metal ions, and Hg^{2+} has a significant effect on the change of interlayer distance [6].

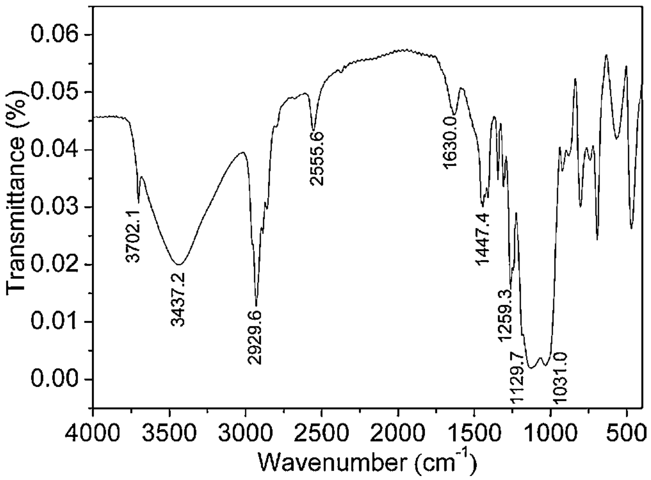

Fig. 2. FT-IR spectrum of the synthesized Mg-MTMS.

Fig. 2 shows the infrared spectrum of the material. The groups S–H (2555.6 cm^{-1}), Si–O–Si (1031.0 cm^{-1}), Si–C (1129.7 cm^{-1}), C–H (2929.6, 1447.4 cm^{-1}), O–H (3437.2, 1630.0 cm^{-1}) can be found in the spectrum, and this is in accordance with that of the talc-like structure [29], confirming that the thiol group is bonded to the substrate.

3.2. Enrichment efficiency

In order to evaluate the enrichment efficiency of the synthesized adsorbent for Hg^{2+}, Pb^{2+}, and Cd^{2+}, 100 mL solution with 51.32 mg L^{-1} Hg^{2+}, 49.18 mg L^{-1} Pb^{2+} and 50.74 mg L^{-1} Cd^{2+} was added into conical flask with 0.2004 g Mg-MTMS for the adsorption. After the enrichment procedures as described in the experimental section, the sample was centrifuged and the upper solution was analyzed by atomic absorption spectrophotometer. It was found that the residual concentrations of Hg^{2+}, Pb^{2+} and Cd^{2+} in the solution are 0.16, 0.023 and 0.016 mg L^{-1}, respectively. Therefore, the 99.69%, 99.95% and 99.97% of the three ions are immobilized on the Mg-MTMS. The results ensure that the three ions in river water can almost completely be adsorbed to the adsorbent, and at the same time, the coexisting ions K^+, Na^+, Ca^{2+}, and Mg^{2+} in river water seems not to interfere the adsorption efficiency of

Table 1
PLS models and the results of cross validation.

Analyte	Preprocessing	Factors	Wavelength regions (cm^{-1})	R^2	RMSECV	RPD
Hg^{2+}	No spectral preprocessing	14	6074.8–5453.8 4557.1–4246.6	0.9495	3.18	4.45
	Straight line subtraction	11	6074.8–5453.8 4557.1–4246.6	0.9615	2.78	5.10
	First derivative	11	6074.8–5453.8 4557.1–4246.6	0.9501	3.16	4.48
	Multiplicative scattering correction	11	6074.8–5453.8 4557.1–4246.6	0.9455	3.30	4.29
	Constant offset elimination	13	6074.8–5453.8 4557.1–4246.6	0.9454	3.31	4.28
Pb^{2+}	No spectral preprocessing	12	6074.8–5453.8 4557.1–4246.6	0.9766	2.22	6.53
	Straight line subtraction	11	6074.8–5453.8 4557.1–4246.6	0.9856	1.74	8.34
	First derivative	12	6074.8–5453.8 4557.1–4246.6	0.9747	2.31	6.29
	Multiplicative scattering correction	10	6074.8–5453.8 4557.1–4246.6	0.9684	2.58	5.63
	Constant offset elimination	12	6074.8–5453.8 4557.1–4246.6	0.9781	2.15	6.75
Cd^{2+}	No spectral preprocessing	12	6074.8–5453.8 4557.1–4246.6	0.9877	1.60	9.02
	Straight line subtraction	11	6074.8–5453.8 4557.1–4246.6	0.9884	1.55	9.29
	First derivative	11	6074.8–5453.8 4557.1–4246.6	0.9849	1.77	8.16
	Multiplicative scattering correction	10	6074.8–5453.8 4557.1–4246.6	0.9843	1.81	7.99
	Constant offset elimination	11	6074.8–5453.8 4557.1–4246.6	0.9850	1.77	8.16

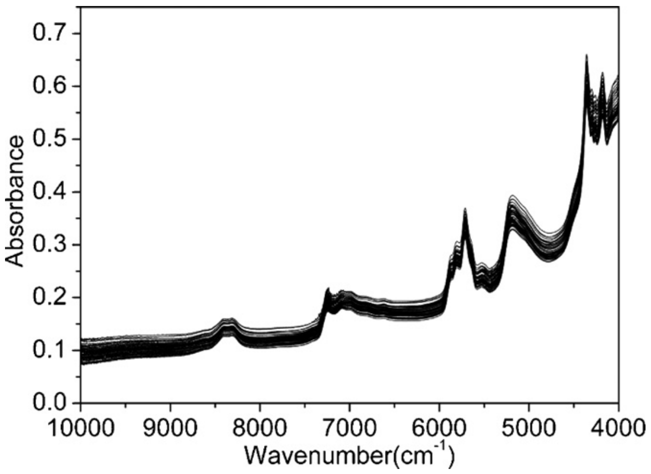

Fig. 3. NIR spectra of the adsorbent with different amount of the analytes.

the adsorbent for the three analyzing ions. Such results may be accounted for by the high content of the complexing thiol group and the synergistic mechanism of the adsorption [6].

In addition, when the same amount of Hg^{2+}, Pb^{2+}, and Cd^{2+} was diluted in 1000 mL, the enrichment can also be performed almost completely. This indicates that the excellent enrichment efficiency can be achieved in further diluted solution. In other words, the method may have high potential for analyzing the low concentration samples when large amount of the samples are available, because the sensitivity or the detection limit is determined by the absolute amount of the analytes adsorbed on the adsorbent.

3.3. Quantitative analysis

Fig. 3 shows the NIR spectra of the adsorbent with the adsorbates. Although it is generally difficult to analyze the peaks in an NIR spectrum of a complex sample, the absorption bands around 7251, 5190, 5718, 4359 and 5808 cm^{-1} can be attributed to the O–H first overtone, O–H combination, C–H first overtone, C–H combination and S–H first overtone, respectively. The O–H signal may be produced by H_2O adsorbed in the adsorbent. However, it is hard to see the difference between the spectra although different amount of the metal ions are adsorbed. The reason may be that only a very small part (around 7%) of the S–H is coordinated with the ions. Therefore, the changes in the spectra caused by the adsorbates cannot be analyzed by visual inspection. With the same reason, it is impossible to perform quantitative analysis by the commonly used univariate calibration.

As one of the most commonly used multivariate calibration technique, PLS was used in this study for quantitative determination of the three ions. In order to obtain optimal PLS models, signal preprocessing techniques, including straight line subtraction, derivative calculation, constant offset elimination and multiplicative scatter correction (MSC) were applied to correct the background of the spectra, and the optimal wavenumber regions were also selected by using the OPUS software. The results obtained by LOO-CV with different signal processing techniques and different wavenumber regions were summarized in Table 1. From the parameters of R^2, RMSECV, and RPD in the table, it is clear that the models can be improved by preprocessing and wavenumber selection, and most of the models are acceptable for quantitative determination, because their R^2 values are above 0.95 and RPDs are above 5 [35,36]. In the following studies, however, the best model with straight line subtraction, latent variable number 11, and wavenumber regions 6074.8–5453.8 cm^{-1} and 4557.1–4246.6 cm^{-1} was used.

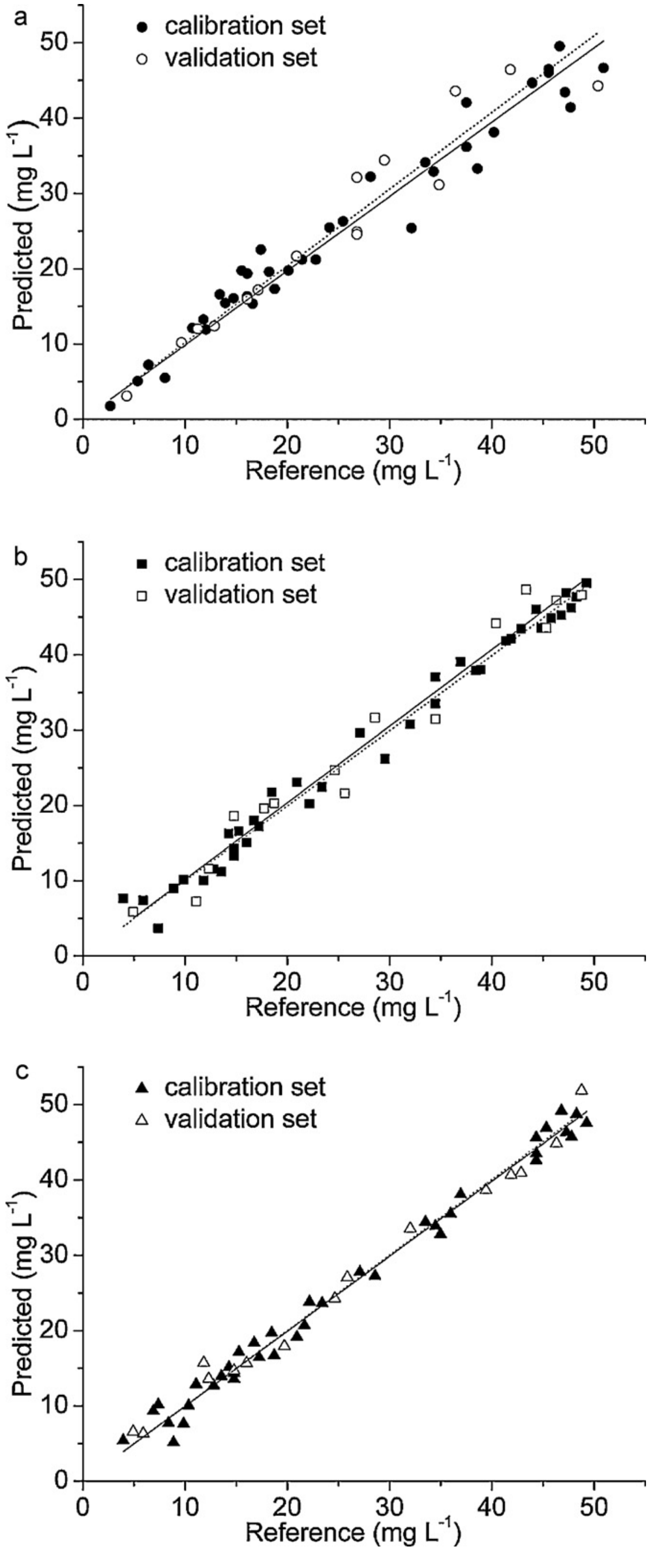

Fig. 4. Relationship of the predicted concentrations of Hg^{2+} (a), Pb^{2+} (b), and Cd^{2+} (c) with the reference values of the calibration(●, ■, ▲) and validation (○, □, △) samples. The solid and dot lines are obtained by the linear regression of points for calibration and validation set, respectively.

Table 2
Validation results of the best PLS models for the three metal ions.

Analyte	Recovery range (%)	RMSEP	R^2
Hg^{2+}	87.92–119.9	3.54	0.9197
Pb^{2+}	84.22–125.6	2.81	0.9599
Cd^{2+}	90.93–133.2	1.72	0.9861

To test the feasibility of the PLS models, the 15 validation samples were used for investigating the prediction capability. The results were displayed in Table 2 and the relationship of the predicted and reference values for Hg^{2+}, Pb^{2+} and Cd^{2+} were shown in Fig. 4(a–c), respectively. It can be seen that the recoveries of the three ions are between 87.92 and 119.9%, 84.22 and 125.6%, and 90.93 and 133.2%, respectively, and good linearities are obtained within the concentration range of 4.288–50.38 mg L^{-1} for Hg^{2+}, 4.927–48.78 mg L^{-1} for Pb^{2+} and 5.912–48.78 mg L^{-1} for Cd^{2+}, respectively. All the data demonstrate that accurate predictions can be obtained by the PLS models, and the proposed method may be a flexible way for determination of the metal ions in water samples. It is worthy of noting that there is no well accepted parameter for evaluation of the detection limit for a multivariate calibration model. However, it can be expected that the detection limit or sensitivity of the proposed method can be further improved due to the high enrichment efficiency of Mg-MTMS, because the parameters are dependent on the amount of the analytes adsorbed onto the adsorbent.

It may be necessary to further investigate the rationality of the method, because it is too hard to analyze the difference between the NIR spectra of the samples. Generally, NIR spectra are composed of weak and broad peaks, thus the changes caused by small variation of a sample cannot be examined visually. However, as reported in tremendous works [15–26], the small change can be detected quantitatively by multivariate models. In this study, the selected spectral regions are 6074.8–5453.8 cm^{-1} and 4557.1–4246.6 cm^{-1}, which should be attributed to the spectral information of $-CH_2-CH_2-CH_2-SH$. On the other hand, according to the work by Lagadic et al. [6], there are different interaction mechanism between Hg^{2+}, Pb^{2+}, Cd^{2+} and SH group. Hg^{2+} coordinates with the SH on the adsorbent in a bidentate manner, but Pb^{2+} and Cd^{2+} are captured in a different way. The different interaction strength may also bring different changes to the spectra. Therefore, adsorbents like Mg-MTMS can be used as a mediating sensor for the adsorbed metal ions, and the information should be reflected in NIR spectra.

4. Conclusions

A method for quantitative analysis of metal ions in dilute solution at the concentration level of milligrams-per-liter was proposed by using NIRS with the high efficiency adsorbent (Mg-MTMS) and chemometrics. The adsorbent was proven to be high efficient for adsorbing Hg^{2+}, Pb^{2+} and Cd^{2+} in dilute solution, thus it is a suitable material for metal ions enrichment. Furthermore, the adsorbent with the three metal ions was measured directly by NIRS in diffuse reflection mode, and the spectra was found to be informative enough for building a quantitative PLS model. With the samples prepared with real river water, the feasibility of the method was proven. The concentration that can be correctly determined was found to be as low as 4.288, 4.927 and 5.912 mg L^{-1} for Hg^{2+}, Pb^{2+} and Cd^{2+}, respectively, and the concentration can be further reduced. Therefore, the proposed method may be a good alternative for determination of low concentration metal ions in environmental water samples.

Acknowledgments

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