Micro near infrared spectroscopy (MicroNIRS) based on on-line enrichment: determination of trace copper in water

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Introduction

In recent years, near infrared spectroscopy (NIRS) has gained widespread attention and acceptance in different fields by virtue of its advantages over other analytical techniques. However, there are two main problems for the determination of trace amounts of heavy metal ions: the low sensitivity, and no absorption of metal ions.

Only a few reports^{1,2} refer to the use of NIRS to determine low-concentration metal ions. In these articles, a few kinds of enrichment methods were used to improve sensitivity for the determination of low-concentration metal ions. For example, Sheng *et al.*¹ used macroporous styrene iminodiacetic acid chelating resin D401 to adsorb copper (Cu²⁺), cobalt (Co²⁺)and nickel (Ni²⁺), and then measure resin by near-infrared diffuse reflectance spectroscopy. Zixia Huang *et al.*² used D401 chelating resin as an enrichment material that was assembled into a glass column, and the diffuse reflection NIR spectra were measured on the side of the column after the enrichment procedure. These methods can detect ppm-level metals.

In the present study, a micro near infrared spectroscopy (MicroNIRS) technique was proposed that aims to develop novel methods for determining micro or trace analytes by NIRS. An on-line enrichment technique was developed using a special enrichment material of Glycidyl methacrylate-Ethylene dimethacrylate-Iminodiacetic acid (GMA-EDMA-IDA) monolithic material, and applied to MicroNIRS. Compared with particulate materials, such as D401 chelating resin, this material allowed the enrichment device to be designed more easily, with improved stability and repeatability. The measurement of diffuse NIR spectra was carried out on the surface of the material where the analytes were concentrated. Interference from the solvent was reduced largely because it had been removed when enrichment was applied. The new technique is expected to improve greatly the sensitivity of NIRS.

Experimental

The Cu concentration in solutions was detected with an ICP optical emission spectrometer (Varian 710-ES, USA) as reference data. A Near-Infrared Rapid Content Analyzer (FOSS XM-1100 Series, Sweden) was used to measure NIR spectra. The enrichment procedure was carried out by the specially-designed enrichment device (Figure 1).

The GMA-EDMA-IDA monolithic material was synthesized^{3–5} and assembled inside a matched plastic/glass tube. A solution containing Cu ions was passed through the column, the metal ions were enriched on the surface of the material where diffuse reflection NIR spectra were measured.

All calculations including spectra pretreatment and PLS modeling were carried out by selfediting programs in Matlab (Ver. 7.1: The MathWork, USA).

Results and discussion

Aqueous solutions were prepared containing five concentration ranges of Cu, i.e., $0.10-1.0 \text{ mg} L^{-1}$, $0.05-0.50 \text{ mg} L^{-1}$, $0.01-0.10 \text{ mg} L^{-1}$, $0.001-0.010 \text{ mg} L^{-1}$, $0.0001-0.001 \text{ mg} L^{-1}$. A total of 21 solutions were prepared. The diffuse reflectance spectra were recorded by touching the diffuse reflection probe onto the surface of the monolithic material after the enrichment procedures for all Cu solutions. Every sample was scanned three times, so that 63 spectra were obtained for each concentration range, and three blank spectra were recorded before the enrichment procedure. Multiplicative scatter correction (MSC)⁶ was used to treat the original spectra for the following data analysis.

Correlation between spectra and concentrations is the basis of quantitative analysis. Linear correlation coefficient r in every wavelength point of the MSC-pretreated NIR spectra against the



Figure 1. The enriched equipment.



Figure 2. Correlation coefficients at all spectral points for the range $0.10-1.0 \text{ mg L}^{-1}$ (a), $0.05-0.50 \text{ mg L}^{-1}$ (b), $0.01-0.10 \text{ mg L}^{-1}$ (c), $0.001-0.010 \text{ mg L}^{-1}$ (d), and $0.0001-0.0010 \text{ mg L}^{-1}$ (e).

Cu concentrations was calculated for every concentration range. Values of r across all wavelength points are shown in Figure 2.

Strong negative correlations were apparent in the spectral region of 900~1350 nm in all the correlation plots. Nearly all values of |R| were above 0.8, and the maximum correlation coefficient came up to 0.9985 for the concentration range of 0.10–1.0 mg L⁻¹. These were interpreted to be associated with O-H second overtone and combination bands,⁷ because the concentration of O-H groups in -N (CH₂COOH)₂ of the monolithic column is reduced with increasing Cu content. In addition, it was clear that the r plots had a similar shape for all concentration coefficients were found in the spectral regions of 1450–1480 nm and 2000–2080 nm. These were interpreted as C-H stretch first overtone and combination of $-CH_2$ -group in -N (CH2COO-)₂Cu, where carboxyl H was replaced by Cu when Cu was chelated with -N(CH2COOH)₂. This was related to the variation of Cu concentration.

Partial Least Squares (PLS) regression was performed as a multivariate calibration method for predicting the concentrations of Cu from the NIR spectra over a broad spectral region including both positive and negative correlation areas. For the PLS modeling, segmental cross-validation was used to find the number of PLS factors that gave minimum root mean squares error of cross validation (*RMSECV*). For segmental cross validation, the calibration set was divided into several segments, and one segment was used for validation while others for PLS calibration. This procedure was done for each segment respectively to obtain the average *RMSECV* for different latent

Concentration range (mg L ⁻¹)	Number of LVs	$RMSEP (mg L^{-1})$	RE
0.10–1.0	7	2.29×10^{-2}	4.32%
0.05-0.50	6	1.20×10^{-2}	4.83 %
0.01–0.10	7	3.60×10^{-3}	6.81 %
0.001-0.010	7	4.86×10^{-4}	9.65 %
0.0001-0.0010	7	2.42×10^{-5}	4.44%

Table 1. PLS models and the results of Monte Carlo segmental cross-validation.

variable numbers. To assure the stability of the model, the segments were divided in a random way, and the calculation of segmental cross validation and PLS calibrations were repeated 200 times, using the Monte-Carlo algorithm.⁸

Before modeling and cross validation, a test set was selected randomly with 13 samples from all 63 spectra, and the 50 remaining samples were divided into five segments for segmental cross validation. The test set was evaluated with the PLS model. The root mean squared error of prediction (*RMSEP*) was calculated with the predicted concentrations of the 13 samples in the test set and the relative error (RE) was computed by dividing the actual concentration by the *RMSEP*. All the error values of the five concentration ranges were listed in Table 1.

Table 1 shows that the *RE* values were below 10% for all ranges with the minimum value of 4.32%. Generally, the values of *RE* enlarged gradually with the decreasing concentration range. Even though the *RE* is close to 10% for the 0.001–0.010 mg L⁻¹ range, it is still acceptable considering that the concentrations had reached the ppb-level. This work has demonstrated that the micro-NIRS technique, based on on-line enrichment, has high potential in trace metal determination.

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