Ultrasound-assisted emulsification–microextraction and spectrophotometric determination of cobalt, nickel and copper after optimization based on Box-Behnken design and chemometrics methods

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A fast, simple, and economical method for extraction, preconcentration and determination of cobalt, nickel and copper as their 1-(2-pyridilazo) 2-naphthol (PAN) complexes based on ultrasound-assisted emulsification–microextraction (USAEME) and multivariate calibration of spectrophotometric data is presented. Various parameters affecting the extraction efficiency were optimized both with univariate and Box–Behnken design. The resolution of ternary mixtures of these metallic ions was accomplished by using partial least-squares regression (PLS), orthogonal signal correction- partial least-squares regression (OSC-PLS), and orthogonal signal correction- genetic algorithms-partial least-squares regression (OSC-GA-PLS). Under the optimum conditions, the calibration graphs were linear in the range of 2.0–150.0, 2.0–120.0 and 2.0–150.0 ng mL^{-1} for Co^{2+}, Ni^{2+}, and Cu^{2+}, respectively, with a limit of detection of 0.14 (Co^{2+}), 0.13 (Ni^{2+}) and 0.14 ng mL^{-1} (Cu^{2+}) and the relative standard deviation was <2.5%. The method was successfully applied to the simultaneous determination of these cations in different samples.

Keywords: ultrasound-assisted emulsification–microextraction, chemometrics, cobalt, nickel, copper.

INTRODUCTION

Heavy metals are sometimes called "trace elements". The determination of heavy metals at trace levels in environmental samples is an important part of chemistry due to their positive or negative effects on the human body[1]. Industrial processes can release heavy metals into their wastewater streams, resulting in potential contamination of the environment. Among those cobalt, nickel and copper are metals, which appear together in many real samples. So, it is very important to determine their concentrations[2].

Sample preparation represents a major challenge and a very important step in the development and application of an analytical method. In general, this step consists of an extraction and preconcentration procedure of target compounds from a sample matrix[3]. Various sample preparation methods including solid-phase microextraction (SPME) fibers[4], hollow fiber solid phase microextraction (HF-SPME)[5], micro-solid phase extraction (μSPE)[6], dispersive liquid–liquid microextraction (DLLME)[7, 8], Ionic liquids (ILs) applied in liquid-phase microextraction (LPME)[9], and surfactant-assisted emulsification dispersive liquid–liquid microextraction (SAE–DLLME)[10] have been developed for this purpose. Regueiro et al.[3] coupled two well-known procedures, namely dispersive liquid–liquid microextraction (DLLME)[11] and ultrasound-assisted liquid–liquid microextraction (USALLE)[12], and developed the so-called ultrasound-assisted emulsification–microextraction (USAEME) procedure. This procedure differs slightly from that used in conventional DLLME, the difference being that instead of a disperser solvent, US energy is applied as a means of dispersing the extraction solvent, meaning the disperser solvent can be omitted from the extraction procedure[13].

Several spectrometric techniques such as flame graphite furnace atomic absorption spectrometry (GFAAS)[14], flame atomic absorption spectrometry (FAAS)[15], inductively coupled plasma optical emission spectrometry (ICP-OES)[16], inductively coupled plasma mass spectrometry (ICP–MS)[17] and spectrophotometric[10, 18] have been widely used for determination of trace amounts of heavy metal ions in environmental samples.

A derivatization is an important tool for analysis; especially complex-forming reactions are widely used for separation and/or preconcentration before spectrophotometric determination. Different Chelating agents have been proposed, such as 2-(2'–Thiazolylazo) p-cresol (TAC), 1-(2-thiazolylazo) 2-naphthol (TAN), 1-(2-pyridylazo) 2-naphthol (PAN)[19–21]. PAN forms highly colored and stable complexes with a number of metals. The simultaneous determination of these ions by use of the UV-Vis spectrophotometry techniques and conventional metallochromic indicators in aqueous solution is difficult because, generally, the absorption spectra overlap and the curves are not suitable for quantitative evaluation[22].

Nowadays quantitative spectrophotometry has been greatly improved by the use of a variety of multivariate statistical methods, particularly partial least squares regression (PLS). It has been shown that PLS is a reasonable choice for the resolution of overlapping signals and quantitative analysis over a wide range of conditions[23–26].

Orthogonal signal correction (OSC) is a preprocessing technique used for removing the information unrelated to the target variables based on constrained principal component analysis. OSC is a suitable preprocessing method for partial least squares calibration of mixtures without loss of prediction capacity using the spectrophotometric method.

Among the different variable selection strategies, genetic algorithms (GAs) is an interesting, flexible and widely used alternative[27–30]. Genetic algorithms is a stochastic method for optimization based on the evolution process of living beings in which simplicity and effectiveness have been applied to the various types of optimization problems in many scientific fields[31].

This work presents the use of genetic algorithms in combination with an orthogonal signal correction–partial least squares (OSC–PLS) method for the variable selec-

tion process to determine ternary mixtures of nickel, cobalt and copper in water samples. A Box–Behnken design was used in order to find the optimum conditions for the method through response surface methodology.

PREPARATION AND CHARACTERIZATION

Reagents and chemicals

All reagents were of an analytical reagent grade. The water utilized in all studies was double-distilled and deionized. The 1-(2-pyridylazo) 2-naphthol (PAN) (Sigma, Shanghai, China) was used as chelating agent. All solvents, such as chloroform, carbon tetrachloride, dichloromethane, chlorobenzene and ethanol, were purchased from Merck (Darmstadt, Germany). Stock solutions (1000 mg L^{-1}) of copper, nickel and cobalt were purchased from Merck (Darmstadt, Germany). The working standard solutions were made by an appropriate dilution daily as required. A stock PAN solution (2.0×10^{-3} M) in Ethanol was prepared by dissolving the solid reagent. This solution was spectrophotometrically stable for at least a week. Universal buffer solutions were prepared by Lurie[32].

Apparatus

All absorbance measurements were obtained using a Hewlett–Packard 8453 diode array spectrometer controlled by a Hewlett-Packard computer, between 400 and 700 nm digitized every 1 nm. A model 780 digital Metrohm pH meter equipped with a combined glass–calomel electrode was used for the pH adjustments. The centrifuge was performed by a Sigma 3K30). An ultrasonic (VGT–1740QTD, Taiwan) water bath with a temperature control and a digital timer was used to emulsify the extraction solvent. OSC and PLS models were performed with the PLS Toolbox, Version 4.0 (Eigenvector Technologies). The GAs program was written in MATLAB by Leardi. Box-Behnken design was accomplished with Minitab Version 16.

Ultrasound-assisted emulsification–microextraction (USAEME)

10.0 mL standard solution containing different concentration of Co^{2+}, Ni^{2+} and Cu^{2+}, 2.0 mL of the buffered solution (pH 5.5), 1.0 mL of PAN solution (2.0×10^{-3} M) were placed in a 12 mL screw cap glass test tube with a conical bottom. In this step, metal ions reacted with PAN to form related complexes. After 15 min, the tube was placed into the ultrasonic water bath in such a way that the level of both liquids (bath and sample)

was the same. Then 300 μL of a mixture of CCl$_4$ and CHCl$_3$ (extraction solvents 1:2 v/v%) were injected into the sample solution by using a syringe. The extraction was completed under ultrasound in 3.5 min at the predetermined temperature (~32°C). Then, the emulsion was disrupted by centrifugation at 3000 rpm for 3.5 min and thus the organic phase was sedimented at the bottom of the tube. The upper aqueous phase was removed with a syringe. The sedimented phase dried by passing nitrogen gas. Finally, the residue was dissolved in 0.5 mL EtOH and was analyzed by UV–Vis spectrophotometric. The experimental setup used in this investigation is illustrated in Figure 1.

Real samples preparation before USAEME

In this experiment, water samples and synthetic samples were selected for validating the proposed method. Wastewater samples were collected from Arak city. Prior to the preconcentration procedure, all the water samples were filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter, then adjusted to pH 5.5 and then stored in 4°C.

RESULTS AND DISCUSSION

Preliminary experiments

In the USAEME method, there are several factors that would significantly affect the extraction efficiency, such as the types and volumes of extractant, ultrasonic time, the pH of the solution, ionic strength, concentration of ligand, centrifugation speed and time.

The selection of the extraction solvent is very important. The solvents with higher density than water, immiscibility with water, good solubility toward the chelate of the analytes and forming a stable emulsion system were considered for the extraction. Carbon tetrachloride (CCl$_4$), chloroform (CHCl$_3$), chlorobenzene (C$_6$H$_5$Cl), dichloromethane (CH$_2$Cl$_2$) were examined. Then an appropriate mixture of extraction solvents was tested. The results show that the highest absorbance was obtained with carbon tetrachloride and chloroform with ratio 1:2 v/v%. The combined use of CHCl$_3$ and CCl$_4$ as extractant solvent together allowed the effective extraction of these ions from the selected samples.

The Volume of extraction solvent is a crucial parameter that has an important effect on the extraction efficiency. Repeatability of results, extraction efficiencies and volume of deposited organic phase are affected by the volume of extraction solvent used. Concentrations of analytes in the organic phase deposit were reduced as
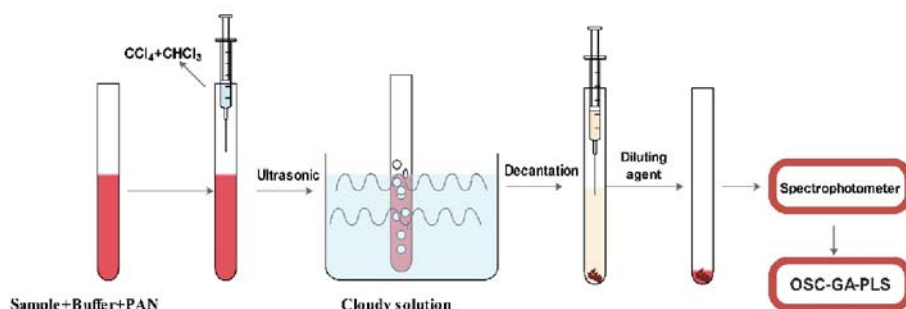

Figure 1. Schematic USAEME and chemometrics procedure

the volume of extraction solvent increased as an effect of dilution; nevertheless, the amount of extracted analyte was increased. To study the effect of extraction solvents, different volumes of carbon tetrachloride and chloroform with ratio 1:2 v/v% in the range of 100–500 μL were subjected to the extraction procedure. The results show that absorbance increased with the volume of extraction solvent increasing to 400 μL and then nearly constant.

Metal complexation with PAN is very dependent on the pH of the solution. The effect of pH on the absorption of PAN complexes of Co^{2+}, Ni^{2+} and Cu^{2+} was studied in the range of 3.0–7.0 using a universal buffer. It can be seen that when pH value is nearly 5, the absorbance of all complexes increased. The progressive decrease in extraction at low pH is due to the competition of the hydrogen ion with the analyte for reaction with PAN. At higher pH values, the hydrolysis of cations occurs.

Dispersion is the key step in determining whether extraction is successfully carried out or not. Sonication produces fine droplets of organic solvent into the aqueous bulk and results in the generation of a high contact area between the aqueous phase and the extraction solvent. Sonication time was optimized in the range of 1–10 min under constant experimental conditions. The results show that absorbance increased by increasing the extraction time up to 3.5 min. After 3.5 min, the absorbance remained nearly constant.

Extraction time is one of the most important factors in the extraction procedure. In USAEME, extraction time is defined as the time between injection of the extraction solvent and the end of the sonication stage. In this work, the extraction time was varied using the values of 4–20 min for sample solution. Results revealed that the time, in the range studied, does not obviously affect the efficiency of USAEME.

The influence of PAN volume on the extraction was evaluated in the range of 300–1500 μL of PAN. The absorbance was increased by increasing PAN volume, which was well expected. It seems that after addition 1000 μL of ligand, slight reduction of extraction in high concentration of PAN is due to the extraction of PAN itself, which can easily saturate the small volume of extraction solvent. Therefore, the volume of 1000 μL was chosen as the optimum amount of the determination of the heavy metal ions.

The rate of complex formation of PAN with Co^{2+}, Ni^{2+} and Cu^{2+} was low, and at room temperature, the color of complexes reached a maximum in 15 min. So reaction time was considered 15 minutes.

Generally, addition of salt can decrease the solubility of analytes in the aqueous phase and promote the transfer of the analytes towards the organic phase. The influence of ionic strength on USAEME performance was evaluated by adding various amounts of sodium chloride in the range 0–10% (w/v) while the other parameters were kept constant. There was no significant effect on the extraction efficiency of target compounds.

A major parameter in USAEME that affects the formation of microdroplets from the extraction of solvent in the aqueous phase is centrifugation. The rate of centrifugation was adjusted between 1000 to 5000 rpm for 5–2 minutes. The results showed that a clear upper phase was created, and phase separation was complete when the centrifugation time was 3.5 min and speed was 3000 rpm. Thus, these values were selected as optimal conditions for further testing.

Optimization of significant variables using Box-Behnken design

The traditional optimization procedure varying "one-variable-at-a-time", is a strategy based on experience that does not guarantee the attainment of a true optimum of the extraction conditions. The one-at-a-time design is a classical univariate method which consists of investigating the response for each factor while all other factors are held at a constant level[33]. Conversely, the chemometrics approach relies on a rational experimental design, which allows the simultaneous variation of all experimental factors, saving time and materials. The Box–Behnken design (BBD)[34] is probably the most widely used experimental design applied for fitting a second-order response surface.

An optimization procedure was applied in order to find out the exact values of the most important factors. The design consisted of 27 sets of experiments carried out according to the Box–Behnken technique as shown in Table 1. The experimental ranges selected for independent variables were: volume of ligand (X_1: 800–1200 μL), sample pH (X_2: 4–7), extracting agent volume (X_3: 200–400 μL), sonication time (X_4: 1–5 min). These ranges were selected based on a prior experiment about the system under study. The factor levels were coded as –1 (low), 0 (central point) and +1 (high). The design of experiments of Box–Behnken and the values of response Y under the different experimental combinations are presented in Table 1.

After obtaining the model and analyzes, it was found that the number of terms such as X_1X_2, X_1X_3, X_2X_4, X_3X_4, X_1^2, X_4^2 did not give significant effect on response. Therefore, to reduce the complexity and increase the accuracy, the second time modeling was performed by omitting these in significant terms. The improved equation is as Equation (1).

$$Y = 0.771 + 0.145X_1 + 0.136X_2 + 0.091X_3 + 0.042X_4 - \\ -0.051X_2X_3 + 0.048X_2^2 + 0.055X_3^2 \qquad (1)$$

The positive values for the measured responses in regression equation indicated the synergistic effect (optimization), while the negative values represent the inverse relationship/antagonistic effects[35]. The derivatization of this general equation as (pH), sonication time, (V_{ext}) and (V_{ligand}) results in four new equations: $\frac{\partial Y}{\partial X_1}, \frac{\partial Y}{\partial X_2}, \frac{\partial Y}{\partial X_3}$ and $\frac{\partial Y}{\partial X_4}$ were each equated to zero and the resulting four equations were solved simultaneously to obtain the values of X_1, X_2, X_3 and X_4 corresponding to the maximum of Y. The optimum values of the tested parameters were obtained as follows: X_1 = 1000, X_2 = 5.5, X_3 = 300 and X_4 = 3.5.

Statistical analysis

According to the results of Table 2, the analysis of variance (ANOVA) was used to evaluate the significance of the model equation and related terms.

Table 1. Factors and their levels in Box-Behnken design and observed response

Run No.	Actual level of factors				Absorbance
	X_1	X_2	X_3	X_4	
1	1200	5.5	300	1	0.850
2	800	5.5	300	1	0.575
3	1000	5.5	200	5	0.810
4	1200	5.5	200	3	0.858
5	1000	4	400	3	0.869
6	1200	5.5	400	3	0.989
7	1000	7	400	3	1.086
8	1000	4	200	3	0.547
9	800	5.5	200	3	0.528
10	1000	7	300	5	0.923
11	1200	5.5	300	5	0.085
12	1200	4	300	3	0.882
13	1200	7	300	3	1.114
14	1000	5.5	300	3	0.748
15	800	4	300	3	0.482
16	1000	4	300	5	0.709
17	1000	7	300	1	0.890
18	1000	7	200	3	1.017
19	800	5.5	400	3	0.791
20	1000	5.5	400	5	0.970
21	1000	4	300	1	0.673
22	800	5.5	300	5	0.691
23	1000	5.5	400	1	0.897
24	800	7	300	3	0.814
25	1000	5.5	200	1	0.701
26	1000	5.5	300	3	0.835
27	1000	5.5	300	3	0.783

Table 2. Analysis of variance (ANOVA) evaluation of linear, quadratic and interaction terms for each response variable

Variables	DF[a]	SS[b]	MS[c]	F-values	*p*-value
Model	14	0.6605	0.0471	22.05	0.000
X_1	1	0.2696	0.2696	125.97	0.000
X_2	1	0.2218	0.2218	103.68	0.000
X_3	1	0.0993	0.0992	46.39	0.000
X_4	1	0.0209	0.0209	9.80	0.009
X_1^2	1	0.0022	0.0014	1.04	0.329
X_2^2	1	0.0093	0.0095	4.35	0.059
X_3^2	1	0.0126	0.0001	5.93	0.031
X_4^2	1	0.0002	0.0098	0.10	0.761
X_1X_2	1	0.0025	0.0000	1.18	0.300
X_1X_3	1	0.0043	0.0024	2.05	0.178
X_1X_4	1	0.0001	0.00037	0.05	0.828
X_2X_3	1	0.01026	0.0042	4.79	0.049
X_2X_4	1	0.00004	0.0000	0.0000	0.967
X_3X_4	1	0.00034	0.0021	0.16	0.696
Residual	12	0.02568	0.0023		
Lack-of-Fit	10	0.0219	0.0026	1.16	0.548
Pure Error	2	0.0037	0.00081		
Total	26	0.6862			

R^2 = 96.26; Predicted R^2 = 89.05; Adjusted R^2 = 91.89. [a]DF: Degree of freedom, [b]SS = Sum of squares, [c]MS: Mean squares.

The experimental data were evaluated with various descriptive statistical analyses such as *p*–value, degrees of freedom (DF), the sum of squares (SS), determination coefficient (R^2) and adjusted determination of coefficient (R^2_a). The model equation and related terms were considered to be significant if *p*-values were less than 0.05 (*p*-value at 95% confidence level). The goodness of fit of the model was checked by the correlation coefficient (R^2). The R^2 value of 0.9626 indicated that 96.26% of the variability was explained by the model and only 0.374 was as a result of chance. The value of R^2 (96.26%) also indicates good agreement between the experimental and predicted values of response. The lack-of-fit measures the failure of the model to represent data in the experimental domain at points which are not included in the regression[36]. The *p*-value of lack of fit

0.548 indicated that the quadratic model is statistically significant for the response.

Interference study

The influence of various species on the absorbance of a solution mixture containing 20.0 ng mL^{-1} of Ni^{2+}, 10.0 ng mL^{-1} of Co^{2+} and 20.0 ng mL^{-1} of Cu^{2+} was investigated. An ion was considered as interference when its presence produced a variation in the absorbance of the sample greater than 5%. Among the interfering ions tested; the ions Na$^+$, Li$^+$, K$^+$, No$_3^-$ and Br$^-$ did not interfere at concentrations 1000 times higher than those of the analytes. The ions Mg^{2+}, Ca^{2+} did not interfere up to 500 times higher than those of the analytes. The ion Cd^{2+} did not interfere up to 20 times higher and the ion Pb^{2+} 10 times higher than those of the analytes.

The ions Zn^{2+}, Fe^{2+} did not interfere up to 5–fold excess over analytes.

However, PLS calibration can implicitly model some interference, whenever the calibration solutions and samples have similar compositions and interferences are included in variable concentrations in the calibration set. This allows the interference to be overcome without previous separation and makes the method more robust.

Analytical performance of the method

Under the optimal conditions, calibration curves were constructed for the determination of Ni^{2+}, Co^{2+} and Cu^{2+} ions, according to the mentioned procedure. Linearity was within the range of 2.0–120.0 ng mL^{-1} for Ni^{2+}, 2.0–150.0 ng mL^{-1} for Co^{2+} and 2.0–150.0 ng mL^{-1} for Cu^{2+} in the initial solution. The correlation of determination (r^2) was 0.997 for Ni^{2+}, 0.996 for Co^{2+} and 0.997 for Cu^{2+} ions. The limit of detection is defined as LOD=3S_b/m, where S_b is the standard deviation of 10 replicates blank signals and m is the slope of the calibration curve after preconcentration. For a sample volume of 10 mL, it was found to be 0.13 ng mL^{-1} for Ni^{2+}, 0.14 ng mL^{-1} for Co^{2+} and 0.14 ng mL^{-1} for Cu^{2+} ions. The preconcentration factor was 200, as the original volume used in the present experiment was 10 mL and a final extract volume of approximately 50 μL. In order to test the reproducibility of the proposed method Intra and inter-day precision was performed by measuring the absorbance of spiked water samples (40.0 ng mL^{-1} each of ions) at five different times during the single day and on five subsequent days respectively. The percent relative standard deviation (RSD) was calculated 1.6–2.2%.

Table 3 compares the proposed method with the other methods for the determination of ions.

Multivariate calibration and Prediction set

The first step in the simultaneous determination of Co^{2+}, Ni^{2+} and Cu^{2+} in mixtures by multivariate methods involved constructing the calibration matrix. The multivariate calibration requires a careful experimental design of the standard composition of the calibration set for providing the best predictions. When working with three components (in this case cations), the experimental domain corresponds to a triangle. In our case, the range of variation of each cation was defined by a univariate calibration step[23]. A training set of 21 samples was taken (Table 4).

In PLS model, the cross– validation (leave–one–out) method was used for selecting the number of factors and the predicted residual error sum of squares (PRESS) is calculated. One reasonable choice for the optimum number of factors would be that number which yielded the minimum PRESS.

In order to select the mixtures for prediction set, their compositions were randomly designed. For the evaluation of the predictive ability of a different model, the root mean square error of prediction (RMSEP) Equation (2) and relative standard error of prediction (RSEP) Equation (3) can be used:

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{n}(y_{i,pred} - y_{i,obs})^2}{n}} \qquad (2)$$

Table 3. Comparison of USAEME with other reported preconcentration techniques for Co^{2+}, Ni^{2+} and Cu^{2+} determination

Analytes	Method	Detection system	Chelating agent	PF[a] or EF[b]	LOD[c] [μg L^{-1}]	RSD[d] [%]	Ref.
Co^{2+}	DLLME	FO–LADS	PAN	165	0.2	< 4	37
Pd^{2+}				162	0.25		
Ni^{2+}	SPE	FAAS	PAN	70	1.18	< 1	38
Co^{2+}	DLPME	GFAAS	PAN	101[b]	0.021	7.5	14
Ni^{2+}				200[b]	0.033	8.2	
Co^{2+}	DLLME	UV–Vis	PAN	125[b]	0.5	2.5	39
Co^{2+}	CPE	FO–LADS	PAN	198	0.2	< 4	40
Ni^{2+}				199	0.04		
Co^{2+}	USAEME	UV–Vis	PAN	200[a]	0.14	2.3	This work
Ni^{2+}					0.13	1.7	
Cu^{2+}					0.14	1.2	

[a] Preconcentration factor. [b] Enrichment factor. [c] Limit of detection. [d] Relative standard deviation. GFAAS graphite furnace atomic absorption spectrometry. DLPME dispersive liquid phase microextraction. DLLME dispersive liquid–liquid microextraction. FO–LADS fiber optic-linear array detection spectrophotometry. SPE solid phase extraction. CPE cloud point extraction. USAEME ultrasound assistant emulsification microextraction.

Table 4. Concentration data of the different mixtures used in the calibration set for the determination of Cu^{2+}, Ni^{2+} and Co^{2+} (ng mL^{-1})

Mixture	Cu^{2+}	Ni^{2+}	Co^{2+}	Mixture	Cu^{2+}	Ni^{2+}	Co^{2+}
M1	2.0	2.0	150.0	M12	2.0	96.0	30.0
M2	30.0	20.0	120.0	M13	2.0	72.0	60.0
M3	60.0	2.0	90.0	M14	2.0	48.0	90.0
M4	90.0	2.0	60.0	M15	2.0	24.0	120.0
M5	120.0	2.0	30.0	M16	30.0	24.0	90.0
M6	150.0	2.0	2.0	M17	60.0	24.0	60.0
M7	120.0	24.0	2.0	M18	90.0	24.0	36.0
M8	90.0	48.0	2.0	M19	30.0	48.0	60.0
M9	60.0	72.0	2.0	M20	60.0	48.0	30.0
M10	30.0	96.0	2.0	M21	30.0	72.0	30.0
M11	2.0	120.0	2.0				

$$RSEP(\%) = 100 \times \sqrt{\frac{\sum_{i=1}^{n}(y_{i,pred} - y_{i,obs})^2}{\sum(y_{i,obs})^2}} \qquad (3)$$

where $y_{i,\ pred}$ is the predicted concentration using different model, $y_{i,\ obs}$ is the actual concentration and n is the number of compounds in the prediction set.

Preprocessing by orthogonal signal correction

Methods that find and extract variation with the property outlined above were originally called orthogonal signal correction (OSC) methods, or filters[41]. OSC is a preprocessing method for PLS regression to find variation in a descriptor matrix that is unrelated to that in a response matrix, and which therefore can be extracted and analyzed separately.

The results show that score plots have better results when OSC–PLS is used. Moreover, the OSC–filtered data give much simpler calibration models with fewer components than the ones based on the original data (Table 5).

OSC–GA–PLS

Variable selection is a critical step for increasing the predictive ability of multivariate analysis, and should ideally eliminate both uninformative and/or highly correlated data.

The OSC application to the calibration data implied that the OSC–PLS presents better results than PLS. In the other hand, GA can select suitable wavelengths. The results show that GA–PLS is a good method for the use of lower data, demonstrating more enhanced results in comparison with PLS. According to the above data, we decided to apply both OSC and GA in order to gain satisfactory results in the PLS application. Combining OSC and GA variable selection led to slightly better modeling and increased predictability. For calibration set, three OSC components were used for filtering. Evaluation of the prediction errors for the validation set reveals that the OSC–GA treated data give substantially lower the root mean square error of prediction (RMSEP) values prediction values than OSC–PLS data (Table 6).

Real water sample analysis

To validate the applicability of the method for simultaneous extraction and determination of Co^{2+}, Ni^{2+} and Cu^{2+} in aqueous samples, waste water, well water and tap water were collected and analyzed with the proposed method. The results were shown in Table 7. The results indicated that there were no Co^{2+}, Ni^{2+} and Cu^{2+} found in the samples. These samples were then spiked with Co^{2+}, Ni^{2+} and Cu^{2+} at a different concentration to investigate the effect of sample matrices. As can be seen from Table 6, the spiked recoveries were satisfied in the range of 97.4–104.3% with the precisions of 0.9–1.7% (RSD), which indicated that USAEME combined with OSC–GA–PLS method was reliable and could be used for the trace analysis of Co^{2+}, Ni^{2+} and Cu^{2+} in aqueous samples.

CONCLUSIONS

A novel and simple method based on ultrasound-assisted emulsification–microextraction (USAEME) combined with the spectrophotometric and OSC–GA–PLS was evaluated for the preconcentration and the determination of trace Cu^{2+}, Ni^{2+} and Co^{2+} from water samples. The USAEME method offered benefits such as low cost and no need for specialized instruments. In addition, it is important to point out that USAEME is

Table 5. Concentration data for prediction set mixtures of Cu^{2+}, Ni^{2+}, Co^{2+} and their predicted values [ng mL^{-1}]

Mixture	True			Predicted [PLS]			Predicted [OSC–PLS]			Predicted [OSC–GA–PLS]			Recovery [%]		
	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}
M22	40.0	60.0	100.0	47.8	76.2	82.4	45.2	71.2	88.4	39.6	61.2	96.5	99.0	102.0	96.5
M23	100.0	20.0	40.0	106.0	16.8	43.3	102.1	17.2	42.3	102.3	20.3	39.9	102.3	101.5	99.7
M24	140.0	60.0	80.0	126.1	68.2	89.3	132.2	64.5	85.2	138.6	59.2	81.2	99.0	98.6	101.5
M25	20.0	40.0	60.0	26.1	43.7	69.3	24.1	42.6	65.2	21.0	39.1	61.2	105.0	97.7	102.0
M26	80.0	120.0	20.0	75.1	145.2	18.5	76.2	129.8	18.9	81.2	122.6	19.8	101.5	102.2	99.0
M27	120.0	40.0	10.0	123.3	44.1	12.5	115.2	35.8	12.0	120.8	38.9	10.2	100.6	97.2	102.0
M28	60.0	60.0	40.0	66.5	41.3	36.9	65.2	53.2	38.1	60.2	58.6	39.1	100.3	97.7	97.8

Table 6. Statistical parameters obtained by applying the three methods

Methods	PLS			OSC–PLS			OSC–GA–PLS		
	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}
NF[a]	5	5	5	4	4	4	3	3	3
PRESS	5.14	9.67	9.94	4.38	2.73	3.06	2.39	1.08	1.79
RMSEP	7.61	14.07	8.55	4.9	6.79	5.37	1.24	1.45	1.51
RSEP%	8.54	21.93	14.69	5.56	10.58	9.23	1.37	2.25	2.62

[a] Number of factor.

Table 7. Determination of Cu^{2+}, Ni^{2+} and Co^{2+} in real water samples

	Added [ng mL^{-1}]			Found [ng mL^{-1}]			Recovery [%]			RSD [%]		
	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}
Waste water	0.0	0.0	0.0	ND[a]	ND	ND	–	–	–	–	–	–
	80.0	80.0	80.0	82.2	83.4	81.1	102.8	104.3	101.4	0.9	1.5	1.4
Well water	0.0	0.0	0.0	ND	ND	ND	–	–	–	–	–	–
	60.0	40.0	60.0	61.1	41.6	59.8	101.8	104.1	99.7	1.1	1.6	1.3
Tap water	0.0	0.0	0.0	ND	ND	ND	–	–	–	–	–	–
	60.0	100.0	40.0	58.9	102.3	38.9	98.2	102.3	97.4	1.6	1.3	1.5

[a] Not detection.

a low organic solvent consuming extraction technique, which turns it into an environmentally friendly technique. In this method, the consumption of the toxic organic solvent (at μL level) was minimized without affecting the method sensitivity. The application of a Box–Behnken matrix became the possible, rapid, economical and efficient way of an optimization strategy of the proposed procedure. The Cu^{2+}, Ni^{2+} and Co^{2+} mixture based on their complexation with the common reagent PAN, due to the high spectral overlapping observed between the absorption spectra, is a complex system. For overcoming the drawback of spectral interferences, PLS multivariate calibration method is applied. Also, the present study shows that the GAs can be a good method for feature selection in spectral data sets. Analysis of the results for mixtures showed that the use of GA–PLS leads to the better prediction compared to the PLS method. The predicted values are obtained by the application of OSC–GA–PLS model for absorbance data showed the prediction ability of the OSC–GA–PLS method much improvement compared to the GA–PLS method. The method can be successful offers a good selectivity for the simultaneous determination of Co^{2+}, Ni^{2+} and Cu^{2+} in the presence of a variety of metal ions in real water samples.

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