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RESEARCH ARTICLE

Flame Atomic Absorption Determination of Ni^{2+}, Cu^{2+} and Co^{2+} Ions in Some Water and Food Samples After Cloud Point Extraction Using a Thio Schiff-Base as a New Complexing Agent

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Abstract: *N*(2-Thiophenyl)-1-(2-hydoxyphenyl)Imine (NTPHPI) was used as a proper complexing agent for the preconcentration by cloud point extraction followed by atomic absorption spectrometric to determine of Ni^{2+}, Cu^{2+} and Co^{2+} ions in real samples. NTPHPI and Triton X-114 were used as hydrophobic ligand and non-ionic surfactant respectively and the pH of 8 was chosen as optimum. Under the optimized experimental conditions, the selective preconcentration and determination of low concentration of Ni^{2+}, Cu^{2+} and Co^{2+} ions as 1, 5 and 6 ng mL^{-1} can be made respectively. The proposed method was successfully applied to the preconcentration and low-level determination of the cited ions in different water, chocolate and honey samples.

Keywords: Ni^{2+}, Cu^{2+} and Co^{2+} ions, Cloud-point extraction, *N*(2-Thiophenyl)-1-(2-hydoxyphenyl) imine

Introduction

While copper and cobalt are essential nutrients, nickel has no known beneficial health effects. However, these metals may be harmful if taken in excessive amounts. The most common harmful health effect of nickel in humans is an allergic reaction. Cobalt can be beneficial for humans because it is part of Vitamin B12. However, it can also be harmful, because exposure to high levels of cobalt can result in lung and heart effects and dermatitis[1].

Food saves the main route of these elements intake from foods. Copper, nickel and cobalt can natural be present in foods, as a result of pollution, or from the storage or processing of foods, such as when tin migrates from cans into the contained foods[2,3]. These metals normally occur at very low levels in the environment, so sensitive methods are needed to detect them in most environment and food samples. The determination of copper, nickel and cobalt in these matrices is usually carried out by flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS)[4] spectrophotometry[5,6] inductively coupled optical emission spectrometry (ICP OES)[7,8] chemiuminescence and electrochemical methods[9]. FAAS is a powerful detection technique to determine trace amounts of metal ions with well-known interferences. It also requires low operator skill for operation and comparatively low cost instrumentation and operation. However, there are some drawbacks. For instance, most of environmental samples cannot be directly processed with FAAS because this technique has not enough sensitivity. Therefore, preconcentration and separation of analyte are needed before measuring. Successful preconcentration can be achieved by various methods, such as precipitation[10,11] liquid–liquid[12] solid-phase[8,13,14] or cloud-point extraction[15-17].

Cloud-point extraction is based on the property that a solute present in aqueous solution of non-ionic surfactant is distributed between two phases. Recently great attention has been paid to its great potentials in separating toxic solutes from several matrices[18,19]. Procedures for preconcentration of metal ions using CPE have been based on the extraction of these metallic substances as low water-soluble chelate complexes[20].

Several categories of ligands have been widely employed for cloud point extraction of metal ions but the schiff base ligands and specially thioschiff bases were less used for this purpose[21,22]. The aim of this work is to apply a thioschiff base *N*(2-thiophenyl)-1-(2-hydoxyphenyl) imine (NTPHPI) as a good complexing agent in CPE procedure to determine of copper, nickel and cobalt in food samples.

Experimental

Analytical-grade methanol, acids, and other chemicals used in this study were obtained from Merck Company. A 1.0% (w/v) Triton X-114 from E. Merck (Darmstadt, Germany) was prepared by dissolving 1.0 g of Triton X-114 in 100 mL volumetric flask with stirring. All chemicals such as Cu(II), Ni(II), Co(II) and other cations nitrate were purchased from Merck Company. All solutions were prepared with two time distilled water. The *N*(2-thiophenyl) - 1-(2-hydroxy phenyl) imine(NTPHPI) was synthesized according to the literature[23]. NTPHPI (Figure 1) was dissolved in alkaline ethanol solvent.

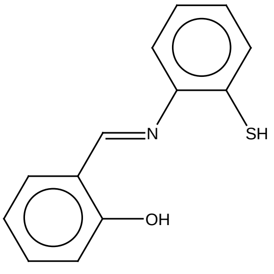

Figure 1. Structure of *N*(2-thiophenyl)-1-(2-hydoxyphenyl)Imine

Instrumentation

A Perkin-Elmer Model 97 AAnalyst 300 (Shelton, CT, USA) atomic absorption spectrometer equipped with deuterium background correction and copper, nickel and cobalt hollow-cathode lamps as the radiation source was used for absorbance measurements at wavelength of 324.8, 232.0 and 240.7 nm respectively. The instrumental parameters were adjusted according to the manufacturer’s recommendations .A30 E 148 centrifuge was used to accelerate the phase of separation process. A Metrohm 744 pH meter furnished with a combined glass-saturated calomel electrode was used for pH measurements.

General procedure

A typical cloud point experiment required the following steps: an aliquot of 15 mL of a solution containing 133.3 µg L^{-1} Ni^{2+}, Cu^{2+} and Co^{2+} ions, 0.17% (w/v) Triton x-114 and (NTPHPI) (0.13 mM) was adjusted to pH 8 by adding NaOH. The mixture was shaken for 1 min and left to stand in a thermo-stated bath at 60 °C, for 25 min. Separation of the phases was achieved by centrifugation at 3500 rpm for 15 min. The whole system was cooled in an icebath for 5 min when the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved to 0.5 mL in 1.0 M HNO_3 in methanol and the Ni^{2+}, Cu^{2+} and Co^{2+} ions content was readily evaluated by FAAS.

Application of real samples

Water samples

Analysis of water samples for determining of analyte contents was performed as follows: About 500 mL of sample was passed through a sintered glass funnel and 1 mL concentrated HNO_3 was added to eliminate and decompose organic matter. The water samples were stored in polyethylene bottles. Then 5 mL of sample was added to centrifuge tube and the analysis was done according to the general procedure section.

Honey samples

For the microwave digestion of honey sample, 1.0 g of sample from Shafi brand was digested with 4 mL of concentrated HNO_3 and 2 mL of concentrated H_2O_2 in microwave system. After digestion, the volume of the digested sample was made up to 100 mL with distilled water. 2.0 mL of prepared sample was added to centrifuge tube and the analysis was carried out in line with general procedure section[24].

Chocolate samples

The general procedure for preparation of chocolate sample was as following. The chocolate sample was weighted into a crucible and heated on a heater until fuming ceased. Then the crucible was transferred into a furnace at 400 °C for 3 h to ash the sample. After cooling, the residue was treated with 2 mL 1:1 nitric acid solution and gently heated on the heater to dryness. The crucible was transferred to the furnace again to remove traces of black residues. Then it was treated with 2-3 mL 1:1 nitric acid solution and cooled, filtered and made up to 25 mL in a volumetric flask. 3.0 mL of prepared sample was added to centrifuge tube and the analysis was carried out in line with general procedure section[25].

Results and Discussion

The aim of this paper is was to develop a simple, sensitive and available method for the preconcentration and determination of trace amounts of Ni^{2+}, Cu^{2+} and Co^{2+} ions in various real samples using flame atomic absorption spectrometry coupling with CPE. In this regard, the influence of various effective parameters including, pH, surfactant and ligand concentrations, heating time and temperature, centrifuge time and rate and the effect of electrolyte on absorbance were investigated.

Effect of pH

The formation of the metal-chelate and its chemical stability are two important factors which influence CPE. The pH plays a unique role in metal-chelate formation and subsequent extraction and proved to be the main parameter for CPE. The pH is a key parameter for obtaining high extraction yield, because complex formation yield strongly depends on pH strength. In this view, a set of similar experiments in the pH range of 2.0-11.0 were accomplished according to the described procedure in experimental section and the results are shown in Figure 2. The maximum sensitivity for CPE was obtained at pH 8. In more acidic solutions, deterioration of the signal occurs due to the ligand protonation, while at pH > 8, the signal decreases and the recovery reduces due to formation of charged hydroxyl – M – (NTPHPI) mixed complexes or precipitation of metal ions in the form of hydroxides. Consequently, pH = 8 was selected for the subsequent studies.

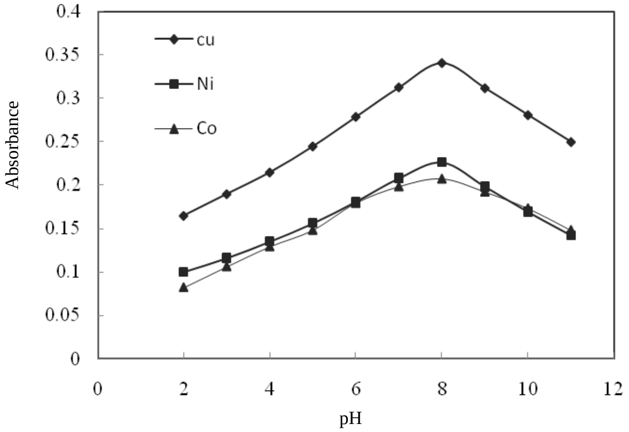

Figure 2. Effect of pH of test solution on the CPE of Ni^{2+}, Cu^{2+} and Co^{2+} ions
Conditions: 133.3 μg L^{-1} Ni^{2+}*,* Cu^{2+} *and* Co^{2+} *ions, 0.17% (w/v) Triton x-114 and NTPHPI 0.13 mM*

Effect of ligand concentration

The absorbance of extracted metal ions as a function of the concentration of ligand is shown in Figure 3. As can be seen, increasing ligand concentration up to a 0.13 mM causes absorbance increases. Thus, the ligand concentration of 0.13 mM was chosen to optimize other variables. At lower than 0.13 mM of ligand, insufficient concentration caused which the complexation wasn't completely. A possible explanation for the decrease with higher concentrations may be attributed to the formation of charged complexes with excess ligand in the medium or remaining of excess of ligand in aqueous solution and competitive with surfactant-rich phase for formation of complex with metal ions in aqueous phase.

Effect of Triton x-114 concentration

Type and concentration of surfactant are important factors, in cloud point extraction. Triton x-114 was chosen as a proper surfactant due to it's physicochemical characteristics, low cloud point temperature, commercial availability, relatively low price, low toxicity, it's high density in the surfactant-rich phase and facilities phase separation. The variation in absorbance of extracted Ni^{2+}, Cu^{2+} and Co^{2+} ions within the Triton x-114 concentration range of 6.6×10^{-3}- 0.2% (w/v) was examined and the results are shown in Figure 4. It can be seen that quantitative extraction was obtained with an optimum Triton x-114 concentration of 0.166% (w/v), where the highest absorbance for extracted Ni^{2+}, Cu^{2+} and Co^{2+} ions was obtained. For lower than 0.166% (w/v), the preconcentration efficiency of the formed complexes was very low, since the assemblies at low concentration were probably inadequate to preconcentrate trace amounts of Ni^{2+}, Cu^{2+} and Co^{2+} ions. The decreasing of absorbance in concentration higher than 0.166% (w/v), is due to the remaining of some parts of Triton x-114 and ligand in the aqueous solution. Therefore this phase can compete with surfactant-rich phase to draw analyte ions. Also, at high concentration of surfactant, the viscosity of the enrichment phase was increased and the efficiency of the aspirating was decreased.

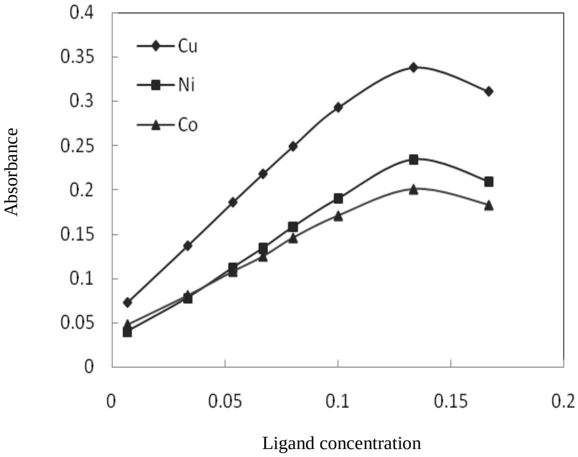

Figure 3. Effect of NTPHPI concentraction on the CPE of Ni^{2+}, Cu^{2+} and Co^{2+} ions *Conditions: 133.3 µg L^{-1} Ni^{2+}, Cu^{2+} and Co^{2+} ions, 0.17% (w/v) Triton x-114 and pH, 8.0*

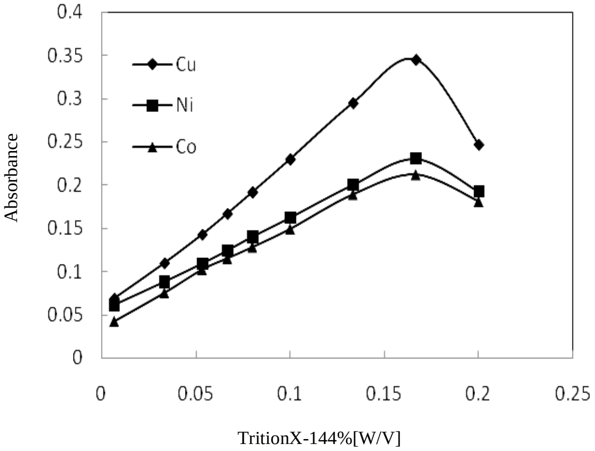

Figure 4. Effect of Triton x-114 concentration on the CPE of Ni^{2+}, Cu^{2+} and Co^{2+} ions *Conditions: 133.3 µg L^{-1} Ni^{2+}, Cu^{2+} and Co^{2+} ions, NTPHPI 0.13 mM pH 8.0*

Effect of ionic strength

It is known that ionic strength of the solution is one of the effective factors in cloud point extraction. In this work, the effect of KNO_3 salt as an electrolyte, on the process was investigated. It is observed that the increasing concentration of salt to the 0.1 M is not effective on the process, but more concentration caused decreasing in absorbance of extracted surfactant-rich phase. This effect might be explained by the additional surface charge when the salt concentration is very high.

Effect of temperature and equilibrium time on CPE

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and separation of phases. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range of 30–70 ^{o}C and 5–30 min were thoroughly optimized, respectively. It was found that holding the sample solutions for 25 min at 60 ^{o}C was quite satisfactory to achieve small volume of the surfactant-rich phase, quantitative extraction and experimental convenience.

Effect of centrifuge time and rate

It is required to preconcentrate trace amounts of Ni^{2+}, Cu^{2+} and Co^{2+} ions with high efficiency in short time. Therefore, CPE on a set of experiments of 15 mL sample at optimum condition by heating 60 ^{o}C and centrifuging in various rate and time further cooling in 5 min has been carried out. It was found that centrifugation at 3500 rpm for 15 min separates the two phases completely. The enrichment phase did not separate completely, in less than centrifugation rate and time.

Characteristics of the method

Calibration graph was obtained by preconcentrating of 15 mL of several solutions under optimum condition, containing various concentration of analyte. The process was completed according to the general procedure section and the absorbance of final solution was measured by FAAS. Linear relationship between the measured absorbance and concentration of Ni^{2+}, Cu^{2+} or Co^{2+} ions in the range 0.007-0.330 ppm was obtained. Table 2 gives the calibration parameters for the purposed CPE method including the linear ranges, the relative standard deviation obtained for 3 analyte samples subjected to the complete procedure, volume ratio and the limit of detection. Also, a calibration graph was obtained without preconcentration in order to calculate the enrichment factor. The enrichment factor was calculated as the ratio of the slopes of calibration curve with and without preconcentration, The obtained factor for Ni^{2+}, Cu^{2+} and Co^{2+} ions were obtained, 70.4, 74.65 and 85.7, respectively.

Interference study

In the view of high selectivity provided by CPE-FAAS, the interferences were almost related to preconcentration step, *i.e.*, cations may react with ligand and anions may form complexes with Ni^{2+}, Cu^{2+} or Co^{2+} ions. Therefore extraction efficiency decreases. The possible interference cationic species were given in Table 2 in two ratios including 1:500 and 1:1000 of analyte to interfere cation. As it is obvious from the results in Table 2, there was no significant interference at a 1:500 or 1:100 ratio of Ni^{2+}, Cu^{2+} or Co^{2+} to the cations.

Real samples-Evaluation of method

The proposed method was applied for the determination of Cu^{2+}, Ni^{2+} and Co^{2+} ions by spiking technique in chocolate, honey and two different water samples including well and tap water as mentioned in experimental section. The results of well and tap water samples are summarized in Table 3. The results of the determination of Cu^{2+}, Ni^{2+} and Co^{2+} ions in honey and chocolate samples are listed in Table 4. As it can be seen, the determination of Cu^{2+}, Ni^{2+} and Co^{2+} ions in real samples is noticeably accurate by the purposed method.

Table 1. Characteristics performance of the presented CPE method

Analyte Conditions	Concentration range, ppm	Slope	Intercept	r^2	RSD%[a]	LOD, ppm[b]	Enrichment and preconcentration factor
Cu^{2+} Without preconcentration[c]	1-10	0.029±0.003	0.007±0.004	0.996	2.6(2.000)	0.330	
Cu^{2+} With preconcentration (0.166% Triton X-114)[d]	0.007-0.33	2.165±0.008	0.043±0.008	0.999	2.44(0.066)	0.001	PF[e]=30 EF[f] =74.65
Ni $^{2+}$ Without preconcentration[c]	1-10	0.021±0.002	0.001±0.004	0.998	1.2(2.000)	0.490	
Ni^{2+} With preconcentration (0.166% Triton X-114)[d]	0.007-0.33	1.480±0.025	0.030±0.001	0.999	1.00(0.066)	0.005	PF=30 EF=70.5
Co^{2+} Without preconcentration	1-10	0.0189±0.002	0.008±0.004	0.983	4.70(2.000)	0.595	
Co^{2+} With preconcentration (0.166% Triton X-114)[d]	0.007-0.33	1.200±0.025	0.003±0.001	0.997	1.06 (0.066)	0.006	PF=30 EF=63.5

[a] *Values in parentheses are the Ni^{2+}, Cu^{2+} and Co^{2+} concentrations (ppm) for which the RSD was obtained.* [b] *Limit of detection, calculated as eight times the standard deviation of the blank signal.* [c] *Standard solutions of Ni^{2+}, Cu^{2+} and Co^{2+} ions in 0.1 mol L^{-1} HNO_3 medium.* [d] *Dilution of the surfactant-rich phase to 500 μL of 0.1 mol L^{-1} HNO_3 in MeOH* [e] *Enrichment Factor* [f] *Preconcentration Factor*

Table 2. Effect of the interference ions on the determination of the analytes

Analyte	Ion	Analyte
Cu^{2+}	Li^{+}, K^{+}, Na^{+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+}, Cr^{3+}	1000
	Zn $^{2+}$, Mn^{2+}, Cd^{2+}, Fe^{3+}, Al^{3+}	500
Ni^{2+}	Li^{+}, K^{+}, Na^{+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+}, Cr^{3+}	1000
	Cu^{2+}, Mn^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}	500
Co^{2+}	Li^{+}, K^{+}, Na^{+}, Cu $^{2+}$, Pb^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cr^{3+}	1000
	Mn^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}	500

Table 3. Determination of analytes in water samples without and after spiking

Analyte	Sample	Added, ppm	Founded, ppm	Recovery%
Cu^{2+}	Well water	0	0.092	-
		1.00	1.13	103.5
	Tap Water	0	nd	-
		1.00	0.88	88
Ni^{2+}	Well water	0	0.038	-
		1.00	1.18	114
	Tap Water	0	0.17	-
		1.00	1.17	99.8
Co^{2+}	Well water	0	nd	-
		1.00	1.03	103
	Tap Water	0	0.25	-
		1.00	1.31	106

Table 4. Determination of analytes in chocolate and honey samples without and after spiking

Analyte	Sample	Added, µg/g	Founded, µg/g	Recovery%
Cu^{2+}	Chocolate	0.00	1.50	-
		8.33	9.75	99.0
	Honey	0.00	nd	-
		33.30	31.30	94.0
Ni^{2+}	Chocolate	0.00	nd	-
		8.33	8.40	100.1
	Honey	0.00	nd	-
		33.30	30.30	91.0
Co^{2+}	Chocolate	0.00	nd	-
		8.33	8.13	97.6
	Honey	0.00	nd	-
		33.30	31.60	94.9

Conclusion

The purposed cloud point extraction method using ligand as a stable and fairly selective complexing agent offers a simple, rapid, inexpensive and environmentally benign methodology for preconcentration and separation of Cu^{2+}, Ni^{2+} and Co^{2+}in aqueous solutions. This method gives very low LOD, good RSD and it was applied to determine trace amounts of Cu^{2+}, Ni^{2+} and Co^{2+} ions in various real samples. In a full comparison of presented results in this paper with those previously reported, it is found that this method is superior in terms of linear range, detection limits and selectivity.

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