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Development of efficient method for preconcentration and determination of copper, nickel, zinc and iron ions in environmental samples by combination of cloud point extraction and flame atomic absorption spectrometry

Research Article

Mehrorang Ghaedi*[a], Ardeshir Shokrollahi[a], Khodabakhsh Niknam[b], Ebrahim Niknam[a], Mustafa Soylak[c]

[a] *Chemistry Department, Yasouj University, 75914-353 Yasouj Iran*

[b] *Chemistry Department, Bushehr University, Bushehr Iran*

[c] *Chemistry Department, University of Erciyes, 38039 Kayseri, Turkey*

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Abstract: A cloud point extraction procedure for the preconcentration of copper, nickel, iron and zinc ions in various samples has been described. Analyte ions in aqueous phase are complexed with 3-((indolin-3-yl)(phenyl)methyl)indoline (IYPMI) and following centrifugation quantitatively extracted to the aqueous phase rich in Triton X-114. The surfactant-rich phase was dissolved in 2.0 mol L^{-1} HNO_3 in methanol prior to metal content determination by flame atomic absorption spectrometry (FAAS). The effects of some parameters including, the concentrations of IYPMI, Triton X-114 and HNO_3, bath temperature, centrifuge rate and time were investigated on the recoveries of analyte ions. At optimum conditions, the detection limits of (3 SDb m^{-1}) of 1.6, 2.8, 2.1 and 1.1 ng mL^{-1} for Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+} along with preconcentration factors of 30 and enrichment factor of 48, 39, 34 and 52 for Cu^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+} respectively, were obtained. The proposed cloud point extraction has been successfully applied for the determination of metal ions in real samples with complicated matrix such as biological, soil and blood samples with high efficiency.

Keywords: *3-((indolin-3-yl)(phenyl)methyl)indoline (IYPMI) • Cloud Point Extraction • Triton X-114 • Flame Atomic Absorption Spectrometry*

1. Introduction

Monitoring trace element concentrations in biological materials, particularly biological fluids, might be considered a difficult analytical task [1,2], mostly due to the complexity of the matrix and the low concentration of these elements, which requires sensitive instrumental techniques and often a preconcentration step [4,5]. The traditional liquid–liquid extraction and other conventional separation methods are time-consuming and labor-intensive approaches; require relatively large amounts of high-purity and frequently toxic solvents, which have to be disposed of properly. Cloud point extraction (CPE) is based on the phase behavior of surfactants in aqueous solutions, which exhibit phase separation after an increase in temperature or the addition of a salting-out agent [3,4]. Trace elements can be extracted to the surfactant- rich phase usually after formation of a hydrophobic complex with an appropriate chelating agent [5]. This approach has been successfully employed to extract and pre-concentrate several trace elements from a variety of matrices [6-14]. The technique is based on the property of most surfactants in aqueous solutions to form micelles and to separate into a surfactant-rich phase of a small volume and a diluted aqueous phase when heated to a temperature known as the cloud point temperature. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simpler, cheaper, more highly efficient and more environmentally friendly than those extractions that use organic solvents. Cloud point methodology practical application of surfactants in analytical chemistry has been used to separate and preconcentrate analyte compounds as a step prior to their determination after the formation of sparingly water-soluble complexes [15-22].

* E-mail: m_ghaedi@mail.yu.ac.ir

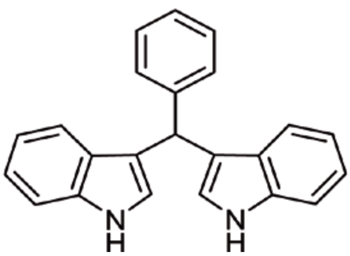
The efficiency of the CPE depends on the hydrophobicity of the ligand and the complex, their apparent equilibrium constants in the micellar medium and the kinetics of the formation of the complex and their transference between the phases. Triton X-114 was chosen as the non-ionic surfactant because of its low cloud- point temperature and high density of the surfactant rich phase as well as its low cost, commercial availability and lower toxicity.

Since, our survey through literature did not show any application of 3-((indolin-3-yl)(phenyl)methyl)indoline (IYPMI) as complexing agent in CPE, therefore, we decided to use it in the presence of Triton X-114 in CPE as clean and simple procedure for preconcentration and determination of Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions.

2. Experimental Procedures

2.1. Reagents

All solutions were prepared with deionized water. Analytical-grade of acids, bases and other chemicals used in this study were obtained from Merck, Darmstadt, Germany. The calibration curve was established using standard solutions prepared in 2 M HNO_3 by dilution from 1000 mg L^{-1} stock solutions (E. Merck, Darmstadt, Germany). A 1% (w/v) Triton X-114 (E. Merck, Darmstadt, Germany) was prepared by dissolving 1.0 g of Triton X-114 in 100-mL volumetric flask with stirring. The ligand, 3-((indolin-3-yl)(phenyl)methyl)indoline (IYPMI) (scheme 1) was synthesized according to literature [22].



Scheme 1. The structure of ligand

2.2. Instrumentation

A Shimadzu 680-AA-atomic absorption spectrometer equipped with deuterium background correction and copper, zinc, iron and nickel hollow-cathode lamp as the radiation source using the resonance wavelength of 324.8 nm for copper, 248.3 nm for iron, 213.9 nm for zinc, 232.0 nm for nickel. The instrumental parameters were adjusted according to the manufacturer's recommendations. A Hettich centrifuge was used to accelerate the phase separation process. A Metrohm 692 pH/ion meter furnished with a combined glass-saturated calomel electrode was used for pH measurements.

2.3. Test Procedure

A typical cloud point experiment has been carried out according to following procedure. An aliquot of 15 mL of an aqueous solution containing 0.26 μg mL^{-1} of Cu^{2+}, Ni^{2+}, Fe^{3+} and 0.13 μg mL^{-1} of Zn^{2+}, 0.13 % (w/v) of Triton X-114 and 0.66 mM of IYPMI in pH 5.5 was prepared. The mixture was shaken for 1 min and left to stand for 20 min in a thermo-stated bath at 50°C. Separation of the phases was achieved by centrifugation at 3500 rpm for 15 min. The whole system was cooled in an ice bath for 15 min so that the surfactant-rich phase would regain its viscosity and the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 0.5 mL of 2.0 M HNO_3 in methanol and then the analyte contents were determined by FAAS.

2.4 Application

The real samples were treated according to our previous publication [23-27] as following.

The certified liver sample was also digested in the manner described below. Triplicate samples (weight of 10 mg) were weighed in glass flasks and 5 – 10 mL of concentrated HNO_3 was added. The flasks were capped and then digested at 60 – 70ºC for 1 – 2 h until semi-dryness. The digests were treated with 5 mL nitric acid and a few drops of H_2O_2, heated on a hot plate at approximately 80°C until the color of the digestion solution became bright yellow. Then the sample was cooled, and diluted to a volume of 25 mL in volumetric flasks with distilled water. Then the procedure given in Section 2.3 was applied.

For digestion of orange juice samples, 5.0 g of the orange juice samples were accurately weighed and added with 5 mL of concentrated HNO_3 in the digestion vessel and a heating program was executed. After that, 1 mL of H_2O_2 (30% w/v) was added and heated for 2 h in 650ºC. The residue was cooled and filtered and then the procedure given in Section 2.3 was applied.

A 5 g of homogenized soil sample or 10 mL of blood sample was weighed accurately in a 200-mL beaker. In the digestion procedure, 10 mL concentrated HNO_3 and 2 mL $HClO_4$ 70% were added and then heated for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250-mL calibrated flask and its pH was adjusted to desired value and diluted to mark with deionized water. Then the procedure given in Section 2.3 was performed.

Lotus trees sample was purchased from Gachsaran, Iran. Afterwards, they were taken in small mesh. A 40-g sample was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to a furnace for overnight heating at 650ºC. The residue was cooled and treated with 10.0 mL concentrated nitric acid and 3 mL 30% (w/v) H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 2 – 4 mL 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved and filtered and the pH was adjusted to 10.0 by addition of KOH and diluted to 25 mL. Then, the procedure given in Section 2.3 was performed.

3. Results and Discussion

Since the IYMPI ligand possesses nitrogen donor atoms and a conjugated π system, it should form stable complexes with Cu^{2+}, Ni^{2+}, Fe^{3+}, and Zn^{2+} ions. Thus, we decided to examine its capability as a suitable reagent for sensitive and extractive CPE of copper, nickel, iron and zinc ions.

3.1. Effect of pH

The influence of pH on method sensitivity was carried out by conducting a set of similar CPE experiments by changing the pH of aqueous solution of sample in the range of 2.0 to 9.0. Fig. 1 shows the effect of pH on the sensitivity of the method. It was found that maximum sensitivities were achieved at pH 5.5. Therefore, a pH of 5.5 was selected for subsequent work. In acidic medium, a weak complexation and uptake occurs; which is explained by competition between metal ions and hydrogen ions for the binding to the ligand. On the other hand, by increasing the pH the potential of active sites of ligand for metal ion binding and consequently the metal ions uptake were increased. The uptake capacities increased with increasing pH, reaching plateau values at around pH 5.5 (Fig. 1).

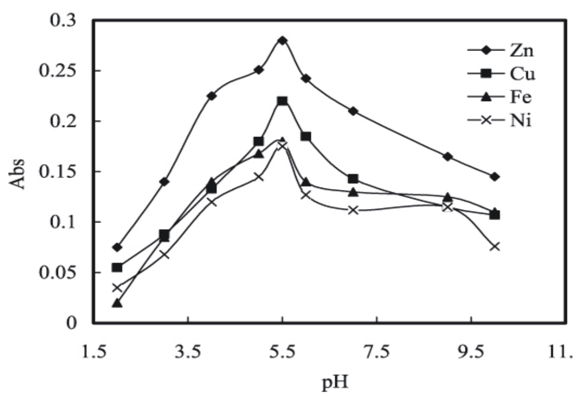


Figure 1. Effect of pH on cloud point extraction of analyte ions

3.2. Effect of IYPMI concentration

The concentration of IYPMI was evaluated over the range 0.3 - 2.7 mM. The sensitivity of system as a function of the IYPMI concentration is shown in Fig. 2. At 0.66 mM of IYPMI concentration, the maximum sensitivity of method was obtained. Therefore, 0.66 mM of an IYPMI concentration was chosen for subsequent experiments. At higher concentration of IYPMI, probably due to formation of charge complexes, the sensitivity of method will be reduced.

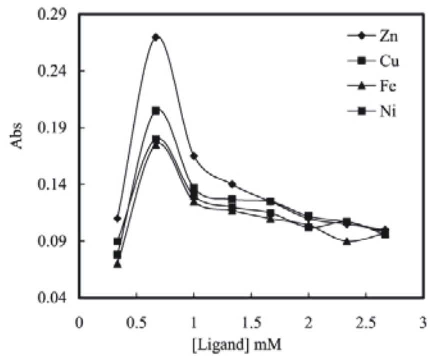


Figure 2. Effect of ligand concentration on CPE of analyte ions

3.3. Effect of Triton X-114 concentration

The presence of active groups in the surfactant molecule can be considered advantageous under certain circumstances when electrostatic interactions are favorable. The non-ionic surfactants, poly(-oxyethylene)-7,5-(p-tert-octylphenyl)ether (Triton X-114) and PONPE-7.5 are the most frequently used surfactant to perform CPE experiments.

The preconcentration efficiency was evaluated using Triton X-114 concentrations ranging from 0.04% to 0.27% (w/v). The results are demonstrated in Fig. 3. The highest signal was obtained with 0.13% (w/v) Triton X-114. By decreasing the surfactant concentration to 0.04% (w/v) the recovery was reduced. The method sensitivity also decreased for a higher Triton X-114 concentration (0.27% w/v). This result might be related to the presence of the high amount of surfactant, resulting in an increase in the volume of the surfactant-rich phase. In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity [28,29]. At lower Triton X-114 concentrations (below 0.04% w/v), the preconcentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex [31,32]. A surfactant concentration of 0.13% (w/v) for Triton X-114 was selected for all subsequent experiments.

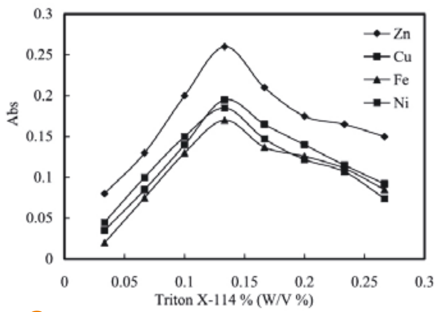


Figure 3. Effect of surfactant concentration on CPE of analyte ions

3.4. Effect of NaCl concentration

The effects of NaCl as electrolyte were investigated in the concentration range of 0.0 to 0.27 M (Fig. 4). High sensitivity of method for Cu^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+} ions were obtained at 0.15 M NaCl concentration. This effect might be explained by salting-out effect or the additional surface charge when the NaCl concentration is high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process [31-35]. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. In this way, 0.15 M of NaCl was used in all further experiments.

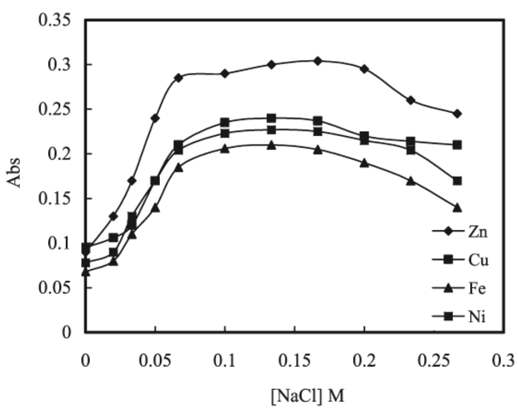


Figure 4. Effect of salt concentration on CPE of analyte ions

3.5. Effect of methanol volume

Since the surfactant-rich phase obtained after the cloud point preconcentration contains a high concentration of Triton X-114 and, at the same time, the volume obtained is rather small, 0.5 mL various concentration of HNO_3 in methanol was added to the surfactant-rich phase after phase separation in order to facilitate its introduction into the nebulizer of atomic absorption spectrometer. There is an optimum volume of 0.5 mL of 2.0 M HNO_3 in methanol. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated tubes and measuring the absorbance. For larger volumes of acidified methanol, a dilution was clearly the major reason for a gradual absorbance reduction. A 0.5 mL of 2.0 M HNO_3 in methanol was therefore used throughout the remaining experiments.

3.6. Effect of temperature

The cloud point temperature of Triton X-114 is 23 - 26ºC (approximately room temperature), which is preferred for carrying out CPE procedure especially for thermally labile compound and other analytical purposes. In order to decrease the cloud point temperature of micellar solution of Triton X-114, addition of NaCl solution is required. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which cooperate for completion of the reaction and efficient separation of phases. It was observed that a temperature of 50ºC is adequate for analyte ions. Higher temperatures lead to the decomposition of IYPMI-ions complexes and the reduction of analytical signal. At lower temperatures, the separation of the two phases is not complete. The dependence of method sensitivity upon equilibration time was studied for a heating time of 5 - 25 min. An equilibrium time of 20 min was chosen as the optimal to achieve quantitative extraction.

3.7. Effect of centrifuge time and rate

For the best efficiency of the method, it is required to preconcentrate trace amount of metal ions with high sensitivity and in a short time. To test the influence of centrifugation on the met hod sensitivity, CPE has been carried out for a series of experiments, in which a 15-mL aqueous sample containing 0.66 mM IYMPI, 0.26 μg mL^{-1} of Cu^{2+}, Ni^{2+}, Fe^{3+} and 0.13 μg mL^{-1} of Zn^{2+}, and 0.15 M NaCl has been heated to 50°C for 20 min and centrifuged at various rates and for different lengths of time. The results indicate that at the optimized reagent concentration, the best conditions for sample centrifuging were 15 min at 3500 rpm.

3.8. Effect of foreign ions

In view of high selectivity attributed to flame atomic absorption spectrometry, the only source of low sample recovery must be the preconcentration step. This problem may be attributed to the fact that cations may react with ligand and anions may form stable complex with metal ions and resulting in a decrease in extraction efficiency. CPE procedures for Cu^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+} ions determination in the high salt content samples can be strongly affected by the matrix constituents of the sample. To perform this study, 15 mL of solution containing 0.26 μg mL^{-1} of Cu^{2+}, Ni^{2+}, Fe^{3+} and 0.13 μg mL^{-1} of Zn^{2+}, and interferents ion in different interferents-to-analyte ratios in the presence of 0.13% (w/v) Triton X-114, were subjected to the complete procedure.Table 1 shows the tolerance limits of the interferent's ions (error < 5%). A relative error of less than 5% was considered to be within the range of experimental error. At the given level no significant interference was observed in the determination of these ions. Thus, the interference-free determination level of present system indicates that high concentration of matrix salts, have minimal effect on ions species relative to matrix ions

Table 1. Effects of the interferences ions on the recoveries of the examined metal ions

Interfering Ions	Interfering ion to analyte weight ratio			
	Ni	Fe	Cu	Zn
Li^{+}, Na^{+}, K^{+}, Al^{3+}, Ti^{+}, NO_3^{-}, NO_2^{-}, Cl^{-}	1000			
Ba^{2+}, Mg^{2+}, Ca^{2+}	600			
Mn^{2+}, SO_4^{2-}	350			
Co^{2+}, Cd^{2+}	250			
Ag^{+}	150	150	250	200
Pb^{2+}	450			
CH_3COO^{-}	900			
Hg^{2+}	100	100	150	200

3.9. Characteristics of the method

Calibration graphs were obtained by preconcentrating 15 mL of a sample containing known amounts of Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+} ions under the experimental conditions. Under the specified experimental conditions the calibration curves Zn^{2+} ion were linear from 0.01 – 0.20 mg L^{-1} and for, Ni^{2+}, Fe^{3+} and Cu^{2+} ions from 0.01 – 0.30 mg L^{-1}. Limits of detection according to IUPAC are also included. The limit of detection (LOD) of a method is the lowest analyte concentration that produces a response detectable above the noise level of the system. The limits of detection (LOD) based on three times the standard deviations of the blank (N = 20, LOD = Xb +3s, where Xb is the blank value and s is the standard deviation (SD) of the blank (n = 10), were found to be (3 SDb/m) of 1.6, 2.8, 2.1 and 1.1 ng mL^{-1} for Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+} along with preconcentration factors of 30 and enrichment factor (slope of calibration curve after preconcentration to slope of calibration curve before preconcentration) of 48, 39, 34 and 52 for Cu^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+} respectively.

The limit of quantification (LOQ) is the lowest level of analyte that can be accurately and precisely measured. The limits of quantification, defined as 10 times the standard deviation (s) of the blank (n = 10), were found to be 6.6, 11.8, 8.9 and 5.1 ng mL^{-1} for Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+}. The precision of the proposed method was evaluated by ten successive CPE with 0.26 μg mL^{-1} of Ni^{2+}, Fe^{3+} and Cu^{2+} ions and 0.13 μg mL^{-1} of Zn^{2+} ion in 15 mL of sample solutions. The relative standard deviations (RSD) were 3.6%, 2.0%, 2.7%, 2.1% for these ions, respectively.

3.10. Accuracy and applications

We have explored the feasibility of the CPE methodology using preconcentration with IYMPI ligand in surfactant media for the determination of concentration of Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+} ions in different matrices. A wide variety of samples were tested by our method and these included natural water, soil, blood, orange juice and lotus tree leaves samples by addition method. Spiking experiments checked reliability. The results are presented in Table 2, 3 and 4. The quantitative recoveries of spiked samples were satisfactory and were confirmed using standard addition method. This indicates the robustness of the system in the determination of analytes in real samples.

4. Conclusion

The micellar extraction of Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+} ions with IYPMI into the phase of non-ionic surfactant Triton X-114 has been investigated. The present cloud-point extraction offers a simple, rapid, economical methodology for preconcentration and separation of analyte ions in real samples prior to their analysis by flame atomic absorption spectrometry (FAAS). The present method has numerous advantages over reported methods [35-42]. Ligand used in this work is distinct in terms of sensitivity, selectivity towards metal ions. Optimum volume of the surfactant-rich phase and low consumption of chemical reagents obtained by using the present cloud-point methodology permitted to design an extraction strategy presenting robustness, low cost, good extraction efficiency and lower toxicity than those using organic solvents. The proposed method gives very low detection limits and good standard deviations.

Table 2. Recovery of trace elements from spiked blood and lotus samples after application of presented procedure, samples (N = 3)

Ion	Blood				Lotus tree		
	Added	Found	RSD	Recovery	Found	RSD	Recovery
	μg g^{-1}	μg g^{-1}	%	%	μg g^{-1}	%	%
Fe	0.0	0.496	1.7	-	0.268	1.7	-
	0.2	0.690	1.3	97.0	0.473	1.3	102.5
Cu	0.0	0.169	1.6	-	0.266	1.8	-
	0.2	0.373	1.2	102.0	0.474	1.3	104.0
Zn	0.0	0.156	1.8	-	0.153	1.9	-
	0.2	0.362	1.3	103.0	0.358	1.4	102.5
Ni	0.0	0.105	1.9	-	0.135	1.8	-
	0.2	0.311	1.4	103.0	0.340	1.3	102.5

Table 3. Recovery of trace elements from spiked environmental samples after application of presented procedure

Ion	Added, μg mL^{-1}	Found, μg mL^{-1}	RSD, %	Recovery, %
BCR 185 R liver certified reference material (mg kg^{-1})^{a}				
Fe	0	-	---	----
Cu	0	274.9	1.5	99.2
Zn	0	134.8	1.7	97.3
Ni	0	-----	---	---

Certified value is 277 mg kg^{-1} for copper and 138.6 mg kg^{-1} for zinc.

Table 4. Recovery of trace elements from spiked spinach and soil samples after application of presented procedure

Ion	Added, μg g^{-1}	Found, μg g^{-1}	RSD, %	Recovery, %
Spinache				
Zn	0	68.6	1.2	-
	100	170.1	0.9	101.5
Ni	0	74.9	1.3	-
	100	177.6	0.8	102.7
Cu	0	78.6	1.2	-
	100	180.1	0.9	101.5
Fe	0	89.6	1.2	-
	100	192.3	0.9	102.7
Soil				
Zn	0	0.256	1.4	-
	0.4	0.662	1.0	101.5
Ni	0	0.374	1.4	-
	0.4	0.618	1.1	102.8
Cu	0	0.249	1.3	-
	0.4	0.654	0.8	101.3
Fe	0	0.284	1.3	-
	0.4	0.693	1.0	102.3
Orange Juice				
Zn	0	0.157	1.7	-
	0.2	0.361	1.4	102.0
Ni	0	0.310	1.6	-
	0.2	0.506	1.3	98.0
Cu	0	0.705	1.4	-
	0.2	0.911	1.2	103.0
Fe	0	0.041	2.1	-
	0.2	0.247	1.8	103.0

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