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On-line solid phase extraction system using 1,10-phenanthroline immobilized on surfactant coated alumina for the flame atomic absorption spectrometric determination of copper and cadmium

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ABSTRACT

An on-line solid phase extraction (SPE) preconcentration system coupled to flame atomic absorption spectrometer (FAAS) was developed for determination of copper and cadmium at $\mu g\,L^{-1}$ level. The method is based on the on-line retention of copper and cadmium on a microcolumn of alumina modified with sodium dodecyl sulfate (SDS) and 1,10-phenanthroline and subsequent elution with ethanol and determination by FAAS. The effect of chemical and flow variables that could affect the performance of the system was investigated. The relative standard deviation ($n = 6$) at 20 $\mu g\,L^{-1}$ level for copper and cadmium were 1.4 and 2.2% and the corresponding limits of detection (based on 3σ) were 0.04 and 0.14 $\mu g\,L^{-1}$, respectively. The method was successfully applied to determination of copper and cadmium in human hair and water samples.

1. Introduction

In recent years, the toxicity and effect of heavy metals on human health and environment has received considerable attention [1,2]. Copper is an essential micronutrient. This element is needed by plants and animals at very low concentration and is toxic at higher levels [3,4]. Cadmium is a toxic element even at low concentration. It can be accumulated in several organs, producing carcinogenic effects [5]. The kidney is a critical target organ for cadmium, and the half-life of the element in this tissue is about 30 years [6]. It is therefore important to accurately determine the concentration of these elements in water and biological samples.

In order to detect the low copper and cadmium concentration in different samples, very sensitive techniques are required. Inductively coupled plasma mass spectrometry (ICP-MS) [7] and electrothermal atomic absorption spectrometry [8] have enough sensitivity to allow determination of these elements at trace level. However, the sensitivity obtained with flame atomic absorption spectrometry (FAAS), an available instrument in most laboratories, is not sufficient for detection of these elements at low levels. Thus for trace determination with FAAS a preconcentration step is required.

Flow injection on-line separation and preconcentration with a microcolumn of appropriate sorbent, has been utilized to enhance sensitivity and selectivity in analytical determination of trace metals [9,10]. This method exhibits some extremely favorable features compared to batch counter parts, such as: higher efficiency, simple operation, rapidity, low reagent and sample consumption and freedom from contamination. Microcolumns containing chelating ion exchangers [11], activated carbon [12], C_{18} octadecyl bonded silica gel [13], polyurethane foam [14] and various other materials [15–20] have been used for FI on-line preconcentration of analyte prior to the determination with AAS. Activated alumina is one of the most commonly used substrate in FIA-SPE procedures [21–23]. Recently modified alumina by surfactant and hydrophobic chelating agent has also been used for this purpose [24–26].

1,10-Phenanthroline is known to be one of the effective chelating reagents for some metal ions [27]. It has been used as a complexing agent for on-line preconcentration of copper, cadmium, and cobalt on a microcolumn of RP-C_{18} with a flow injection-flame atomic absorption spectrometry system [28]. Silica gel modified with 1,10-phenanthroline has also been used in batch preconcentration of Fe(II), Cu(II), and Ag(I) [29]. In the present work, an on-line procedure for the preconcentration and determination of copper and cadmium at low concentration levels by atomic absorption spectrometry incorporating a microcolumn of 1,10-phenanthroline immobilized on surfactant coated alumina is reported.

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2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). Doubly deionized water was used throughout for dilutions.

A stock standard solutions of (1000 mg L^{-1}) copper(II) was prepared by dissolving 0.3802 g $Cu(NO_3)_2{\cdot}3H_2O$ in 1 mL nitric acid in a 100 mL volumetric flask and diluting to the mark with water. A 1000 mg L^{-1} cadmium(II) solution was prepared by dissolving 0.2744 g $Cd(NO_3)_2{\cdot}4H_2O$ in 1 mL nitric acid and diluting to 100 mL with water. Working solutions were prepared daily from the stock solutions by appropriate dilution with water.

Alumina (γ-form 10–50 μm, chromatographic grade) was purified prior to use by shaking with 5 mol L^{-1} nitric acid and washing with water. Sodium dodecyl sulfate (SDS) and 1,10-phenanthroline were used without further purification. A 0.5% solution of 1,10-phenanthroline was prepared by dissolving 500 mg of reagent in 100 mL ethanol.

2.2. Preparation of the solid sorbent

1.5 g of alumina particles was suspended in 50 mL of water and was mixed with 100 mg of SDS. Then, 5 mL of 0.5% solution of 1,10-phenanthroline was added and the pH was approximately adjusted to 2.5 with 1 mol L^{-1} hydrochloric acid. The suspension was stirred for 15 min with a mechanical shaker. The mixture was then filtered, washed, air-dried, and stored in a closed brown bottle for subsequent use

2.3. Preparation of microcolumn

The microcolumn used for preconcentration of analyte was prepared by packing ~60 mg of 1,10-phenanthroline immobilized on surfactant coated alumina in a PTFE (Teflon) tube with 1.5 mm i.d. and 3.5 cm length. A little glass wool was placed at the both ends to retain the sorbent in the tube.

2.4. Preparation of hair sample

The human hair sample was rinsed with acetone, chloroform and doubly distilled water and then was dried at 60 °C. An exact weight of sample (0.5 g) was treated with 12 mL of concentrated HNO_3 and 2 mL concentrated $HClO_4$ and was heated on a hot plate at 150 °C for 30 min. Finally, about 5 mL of 30% H_2O_2 solution were gradually added until the solution turned colorless and was heated nearly to dryness at 200 °C to yield a whitish residue. Approximately 5 mL of 0.1 mol L^{-1} HNO_3 was added to the baker and the contents were heated at 100 °C for 15 min. The pH of solution was adjusted to ~4.5 with ammonia solution and was diluted to 100 mL in a conical flask.

2.5. Preparation of certified lead sample

To 0.1 g of lead sample (BCR No 288), 5 mL of concentrated nitric acid was added, the solution was heated over a water bath for few minutes, and 3 mL H_2O_2 was added. The solution was further heated for few minutes, diluted with water and was filtered. The pH was adjusted to approximately 4.5 by ammonia solution (0.1 mol L^{-1}) and was diluted to 100 mL in a volumetric flask.

2.6. Instrumentation

A Buck Scientific Model 210 VGP flame atomic spectrometer, equipped with single element hollow cathode lamps and air-acetylene flame was used for Cu and Cd measurements. Copper and cadmium hollow cathode lamps were used as the radiation source at the wavelength of 324.7 and 228.8 nm, respectively. The flow injection manifold was consisted of peristaltic pump (Ismatic, MS-REGLO/8-100, Switzerland), rotary injection valve (Rheodyne, CA, USA) and microcolumn of 1,10-phenanthroline immobilized on surfactant-coated alumina (PTFE tube 3.5 cm × 1.5 mm i.d.). A Linseis x-t chart model L-250 was used for monitoring the absorbance time response.

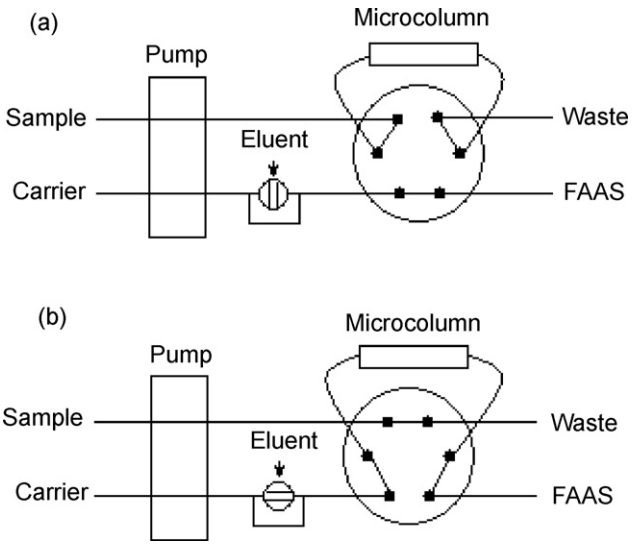

Fig. 1. Schematic diagram of the flow system for preconcentration and determination of analytes: (a) sample loading; (b) eluent injection.

2.7. Flow system operation

The manifold of the flow system is shown schematically in Fig. 1. Its operation can be divided into two steps: preconcentration and elution; in the first stage 20 mL of the sample at pH 4.5, was passed through the microcolumn of 1,10-phenanthroline immobilized on surfactant-coated alumina at a flow rate of 5 mL min^{-1}. Simultaneously the eluent loop (250 μL) was filled up with the eluent solution (ethanol) and the baseline was set by pumping the carrier into the instrument nebulizer.

In the second stage, the valve was switched and elution process started; the content of the elution loop was displaced by the carrier stream to the microcolumn and so the retained analytes were desorbed from the sorbent, and sample plug was driven to the spectrometer where absorbance measurements were made. The peak heights of the transient signals obtained were used for quantification.

3. Results and discussion

The anionic surfactant, SDS, is effectively sorbed on the positively charged alumina surfaces in acidic solution, forming aggregates termed hemi-micelles and ad-micelles [30], which present high potential as the sorbent materials for SPE. 250 mg of SDS is completely adsorbed on 1.5 g of γ-alumina over a wide range of pH (1–6) whereas the sorption of SDS on α-alumina is very slight, probably because of its chemically inert surface [31]. Thus, The use of γ-alumina is essential for the preparation of chelating sorbent. When SDS and alcoholic solution of 1,10-phenanthroline is added to the acidified suspension of alumina particles, the ligand is trapped homogeneously on the hemi-micelles and ad-micelles formed by SDS on alumina surface. By mixing 1.5 g of alumina with 100 mg of SDS and 5 mL of 0.5% 1,10-phenantrhroline solution at pH 2.5, approximately 25 mg of 1,10-phenanthroline immobilized on alu-

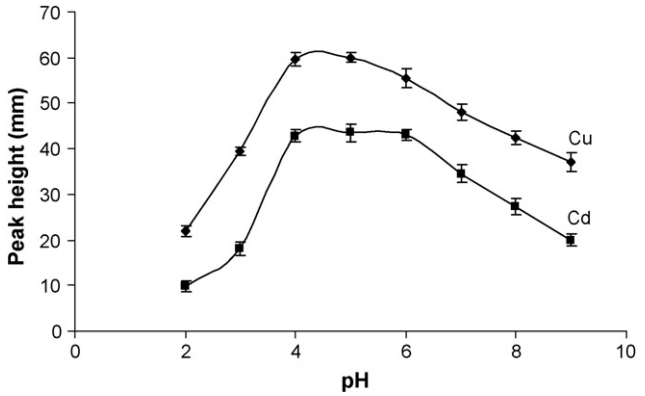

Fig. 2. Effect of sample pH on analyte response. Copper and cadmium samples, 40 μg L^{-1}; sampling volume, 10 mL; eluent, ethanol (250 μL).

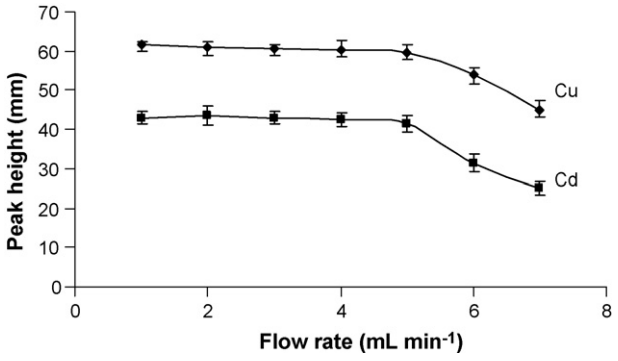

Fig. 3. Effect of flow rate on copper and cadmium deposition. Copper and cadmium concentration, 40 μg L^1; sample volume, 10 mL; eluent, ethanol (250 μL).

mina. The chelating sorbent was stable for several weeks and was used for preparation of the microcolumn.

The experimental procedure was optimized by univariable method to establish the best chemical and FI conditions for the retention and elution of the analytes. Solutions containing 40 μg L^{-1} of each analyte were employed for these studies.

The pH value of the solutions has a critical role on the overall performance of the SPE method. So the effect of pH on the retention of copper and cadmium was studied in the range of 2–9. According to the results shown in Fig. 2, the optimum pH range for copper and cadmium were 4–5 and 4–6, respectively. The progressive decrease in the retention of analytes at low pH is due to competition between the hydrogen ions and analytes for the chelating sorbent. Therefore, pH 4.5 was selected for subsequent work.

The length of microcolumn was found to have significant effect on peak height of analytes. The effect of length of the microcolumn on efficiency of analytes deposition was investigated; a 3.5 cm

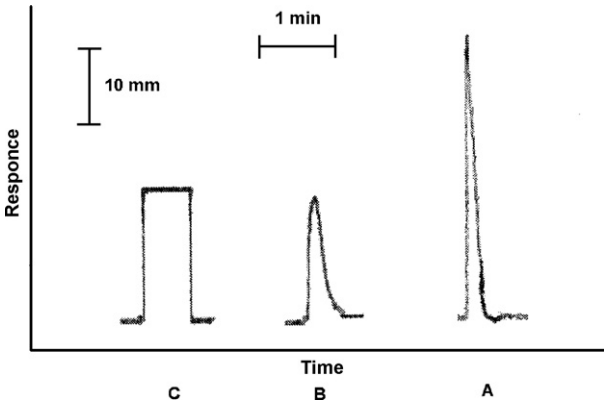

Fig. 4. Absorbance versus time for: (A) sequential injection of Cu (II) solution (250 μL, 1 mg L^{-1} Cu, pH ~4.5) and ethanol (250 μL); (B) direct injection of ethanolic copper solution (250 μL, 1 mg L^{-1} Cu); (C) conventional nebulization of ethanolic copper solution (1 mg L^{-1}).

Table 1
Effect of diverse cations and anions on the recovery of copper and cadmium: analyte concentration, 10 μg L^{-1}; concentrated volume, 20 mL; pH~4.5; flow rate, 5 mL min^{-1}.

Ion	Mole ratio	Recovery %	
		Cu	Cd
Na^+	1000	100	97
K^+	1000	101	98
Ca^{2+}	1000	96	100
Mg^{2+}	1000	98	100
Ba^{2+}	1000	97	102
Pb^{2+}	1000	100	96
Al^{3+}	1000	97	100
Fe^{3+}	200	96[a]	102[a]
Co^{2+}	20	100	98
Ag^+	50	98	97
Ni^{2+}	20	100	100
Cl^-	1000	97	98
Br^-	1000	100	100
F^-	1000	100	98
SO_4^{2-}	1000	99	101
PO_4^{3-}	1000	103	96
CO_3^{2-}	1000	98	99

[a] Masked with F^- (2 mL 5% NaF).

microcolumn was found to be sufficient for deposition of 0.8 μg of each analyte from 20 mL solution.

The effect of the sample loading rate in the range of 1 to 7 mL min^{-1} on the preconcentration process was checked. Results demonstrated (Fig. 3) that depositions of analytes were independent of flow rate up to 5 mL min^{-1}; but a further increase in flow rate cause a graduate decrease in the response, suggesting the possibility of impaired uptake efficiency as a consequence of short contact time.

Table 2
Determination of copper and cadmium in hair and water samples: concentrated volume, 20 mL; pH ~4.5; flow rate, 5 mL min^{-1}.

Sample	Added (μg L^{-1})		Found (μg L^{-1})		Recovery (%)		GF-ASS (μg L^{-1})	
	Cu	Cd	Cu	Cd	Cu	Cd	Cu	Cd
Tap water	–	–	12.5 ± 0.3	–			12.8 ± 0.6	–
	10	10	22.7 ± 0.5	10.3 ± 0.5	102	103		
Sea water	–	–	8.4 ± 0.6	3.9 ± 0.3			8.63 ± 0.35	4.11 ± 0.12
	10	10	18.5 ± 0.9	13.6 ± 0.7	101	97		
River water	–	–	5.2 ± 0.3	–			5.23 ± 0.17	–
	10	10	15.1 ± 0.7	9.6 ± 0.5	99	96		
Human hair (μg g^{-1})	–	–	14.41 ± 0.35	0.37 ± 0.01			14.39 ± 0.41	0.39 ± 0.01
	2	2	16.37 ± 0.32	2.35 ± 0.07	98	99		

Table 3
Determination of Cd and Cu in certified lead sample (BCR No 288): concentrated volume, 20 mL; pH ~4.5; eluent, 250 μL ethanol.

Analyte	Found[a] (μg g^{-1})	Certified (μg g^{-1})
Cu	19.1 ± 0.5	19.3 ± 0.4
Cd	32.6 ± 0.8	33.3 ± 0.9

[a] Mean and standard deviation of three determinations.

The elution of analytes from the microcolumns was studied by using different eluents such as nitric acid; hydrochloric acid; pure, dilute, and acidified ethanol. With pure ethanol signal enhancement was observed and therefore was chosen as the most effective eluent.

The influence of the ethanol flow rate (1–7 mL min^{-1}) on the analyte desorption from the microcolumn was also studied by varying the flow rate between 1 to 6 mL min^{-1}. The results showed that the analytical signal was increased with increasing the flow rate up to 3 mL min^{-1} and then leveled off. The decreased in analytical signal at flow rates less than 3 mL min^{-1} is due to incompatibility between the elution and nebulization flow rates. Thus, in subsequent studies a flow rate of 4 mL min^{-1} was selected to match aspiration flow rates of the instrument.

The effect of eluent volume was studied using several eluent loops with volumes between 100 and 400 μL. The smallest volume of eluent, sufficient for complete recovery of retained analytes, was 200 μL. Therefore, a volume of 250 μL of eluent was chosen for subsequent work.

The absorption capacity of 1,10-phenanthroline coated alumina for Cu(II) and Cd(II) was studied with batch method. The capacity of the sorbent was found to be 1.28 and 1.13 mg g^{-1} of packing material for Cu(II) and Cd(II), respectively. The high capacity of microcolumn permitted large sample volumes to be preconcentrated without degradation in performance. Quantitative recovery was obtained from preconcentration of 40 mL of a 20 μg L^{-1} solution of copper and cadmium (eluent volume 250 μL).

A typical absorbance time response for the sequential injection of the sample (250 μL of 1 mg L^{-1} copper) and ethanol (250 μL) is given in Fig. 4A, and for comparison the equivalent transient signals for direct injection and conventional nebulization of ethanolic solution of copper are also included (Fig. 4B and C). A dispersion coefficient of 0.42 Cu was calculated from consideration of peak height of AAS signals for conventional nebulization and sequential injection with microcolumn. The relatively narrow and intense elution response (Fig. 4A) relative to the signal for direct injection (Fig. 4B) indicates a degree of preconcentration for microcolumn sample processing, even though the same volume (250 μL) of solutions were used in the deposition-elution steps. Furthermore, the relatively sharp elution peak is an indication of fast exchange kinetics for the elution process. By comparing the area of the signals of direct injection (Fig. 4B) and microcolumn elution peak (Fig. 4A) a recovery of more than 98% was obtained with a single injection of eluent.

3.1. Analytical performance

Under the optimum conditions with the use of 20 mL sample solution, the calibration graphs were linear in the concentration ranges of 0.2–50 and 0.5–60 μg L^{-1} of copper and cadmium, respectively. Equation of calibration graphs were $H = 2.974\,C + 0.361$ ($r = 0.9991$) and $H = 2.083\,C + 0.052$ (where H is peak height and C is the concentration) with correlation coefficient of 0.9991 and 0.9991 for copper and cadmium, respectively.

The detection limits of Cu and Cd defined as $3S_b/m$ (where S_b and m are the standard deviation of the blank and slope of the calibration graph, respectively) were 0.04 and 0.14 μg L^{-1}, respectively.

Table 4
A comparison of the analytical characteristics of the present method against some of the reported on-line preconcentration procedures for Cd and Cu determinations by FAAS.

Solid matrix	Ligand	Analyte	pH	EF[a]	LOD[b] (μg L^{-1})	RSD[c] (%)	Sample	Reference
Multi-walled carbon nanotube	–	Cu	5.0–7.5	25	0.11	2.4	Environmental and biological	[32]
		Cd	4.5–6.5	24	0.3	2.1		
Amberlite XAD-4	1-(2-pyridylazo)-2-naphthol	Cu	6.0–9.0	30	0.06	1.2	Sea water	[33]
Amberlite XAD-2	2-(2-thiazolylazo)-5-dimethylaminophenol	Cu	7.5	62	0.23	3.7	Food	[34]
Microcrystalline naphtalline	Ammonium pyrrolidine dithiocarbamate	Cd	1–9	53	3.2	3.6	Water, human blood	[35]
SDS-coated Alumina	1,5-Diphenylcarbazone	Cu	5.5–7.5	100	1.4	3.5	Water, stainless steel	[36]
Polyurethane foam	2-(2-benzothiazolylazo)-2-*p*-cresol	Cd	6.5–9.25	41	0.27	1–5	Biological reference material	[37]
Activated carbon	Methyl thymol blue	Cd	9.0	1000	1.0	4.2	Water, sewage sludge	[38]
RP-C_{18}	1,10-Phenanthroline	Cu	5.0–6.0	32	0.3	3	Sea water, mussel	[28]
		Cd	5.0–6.0	32	0.5	1.4		
Poly(octadecyl diitaconate)	Ammonium pyrrolidine dithiocarbamate	Cd	1.1	110	0.08	2.1	Biological reference material	[17]
Acrylic acid grafted PTFE fiber	–	Cd	3.5–6.5	73	0.1	0.9	Biological reference material	[39]
Chromosorb 105	Pyrocatechol violet	Cu	5.0–8.0	55.5	0.02	1.1	Drinking water sample	[40]
SDS-coated Alu-mina	1,10-Phenanthroline	Cu	4–5	175	0.04	1.4	Water and human hair	This work
		Cd	4–6	116	0.14	2.2		

[a] EF: enhancement factor.
[b] LOD: limit of detection
[c] RSD: relative standard deviation.

The relative standard deviations (RSD) for six replicate measurements at 20 μg L^{-1} of copper and cadmium with sample volume of 20 mL were 1.4 and 2.2%, respectively. The experimental enrichment factors (EF) obtained for a sample volume of 20 mL, based on the ratio of the slopes of the calibration graphs with and without preconcentration [9], were 175 and 116 for copper and cadmium, respectively. For 20 mL sampling volume, the analytical throughput of 14 h^{-1} was achieved. The concentration efficiencies (CE) of copper and cadmium defined as CE = EF × (f/60) [9] (where EF is the enrichment factor and f is sampling frequency expressed in samples analyzed per hour) were 41 and 27, respectively.

3.2. Effect of various ions

Some experiments were carried out to examine the effects of coexisting ions on the adsorption of copper and cadmium on microcolumns. In these experiments, various coexisting ions were added to the solution containing 10 μg L^{-1} of copper and cadmium, and the recommended procedure was applied. The results are shown in Table 1. The ions considered at the mole ratio given in the table, did not show any interference in the measurement of analytes.

3.3. Applications

The method was applied to the determination of copper and cadmium in tap, river, and sea water. The water samples were filtered through a Millipore 0.45 μm pore-size membrane into previously cleaned polyethylene bottles. The pH was adjusted to 4.5 by addition of hydrochloric acid and the samples were analyzed according to the procedure. The reliability of method was checked either by spiking the sample or comparing the results with data obtained by graphite furnace atomic absorption analysis. Furthermore, the method was applied for determination of Cu and Cd in human hair sample. The results are shown in Table 2. As can be seen, the recovery of spiked sample is good, and there is satisfactory agreement between the results and data obtained by graphite furnace atomic absorption analysis.

The procedure was also applied to the determination of copper and cadmium in a certified lead sample (BCR No 288). The results of this investigation together with accepted value are given in Table 3 and indicate the suitability of the method for this type of sample. Thus, the procedure is reliable for determination of Cu and Cd in a wide range of samples.

4. Conclusion

It has been demonstrated that preconcentration and matrix separation with a microcolumn of immobilized 1,10-phenanthroline combined with FAAS can be used for the determination of trace amounts of copper and cadmium. The main advantages of the method are: ease and simplicity of sorbent preparation, high stability of microlcolumn, low cost, enhanced sensitivity of FAAS, and speed of analysis. The proposed method allows the determination of copper and cadmium with detection limits of 0.04 and 0.14 μg L^{-1}, respectively that are lower or comparable to the previously reported FI-FAAS (Table 4). The method has adequate accuracy and selectivity and it can be used for determination of copper and cadmium in hair and water samples

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