# A new coprecipitation method without carrier element for separation and preconcentration of some metal ions at trace levels in water and food samples

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## ARTICLE INFO

## ABSTRACT

A new simple and sensitive preconcentration, separation and environmentally friendly method based on carrier element free coprecipitation (CEFC) was developed using 4-(2-hydroxybenzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one (APSAL) as a new organic co-precipitant to precipitate $Cr^{3+}$, $Cu^{2+}$, $Fe^{3+}$, $Pb^{2+}$ and $Zn^{2+}$ ions from water and food samples. The levels of the studied elements were detected by flame atomic absorption spectrometry (FAAS). The impact of several analytical parameters, such as pH, sample volume and coprecipitant amount as well as centrifugation rate and time was investigated to recover the examined metal ions. The influence of matrix ions was also tested, and no interferences were observed. The recovery values of the analyte ions were calculated and found to be in the range of 95–101%. The detection limits, corresponding to three times the standard deviation of the blank ($N=10$), were found to be in the range of 0.2–1.2 µg L$^{-1}$. The relative standard deviation (RSD) was calculated to evaluate the precision of the proposed method and was found to be $\leq 5.0\%$. The calculated preconcentration factor was 100. The proposed method was successfully applied to separate and preconcentrate trace amounts of ions in several water and food samples. To confirm the accuracy and validate the proposed method, certified reference materials were analyzed with satisfactory results.

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## 1. Introduction

Heavy metals have hazard and harmful impacts on human health and the environment because they are toxic even at very low concentrations. Thus accurate detection of metal ions at trace concentration levels in environmental, food and water samples is very important in analytical chemistry and environmental pollution monitoring [1,2].

Flame atomic absorption spectrometry (FAAS) has been a useful technique to detect trace heavy-metal ions in various environmental, food and water samples because of its high selectivity, speed, easy instrument usage and low costs [3]. Two main limitations in FAAS detections of heavy-metal ions are lower levels of analyte ions than the detection limits of FAAS and high interfering influences of matrix ions on the signal of the analytes [1,4].

To overcome these limitations, several technologies have been widely used to pre-concentrate and separate trace metals, such as liquid–liquid extraction [5,6], cloud point extraction [7,8], solid phase extraction [9–13], membrane filtration [14,15] and electroanalytical [16,17] techniques.

Co-precipitation is an important pre-concentration and separation technique for trace metal ions because of its simplicity, rapidity, short analysis time, low consumption of organic solvent and high pre-concentration factor. Other advantages of the co-precipitation method are that separation and preconcentration can be completed in the same step, and several analyte ions can be separated and preconcentrated from the matrix using different inorganic or organic co-precipitants [1]. Metal hydroxides such as zirconium, aluminum, gadolinium, erbium and dysprosium [18–29] have been used as inorganic coprecipitants. Organic coprecipitants that are able to form neutral chelates with metallic species such as 8-hydroxyquinoline, pyrrolidine dithiocarbamate, Rubens acid, dibenzyldithiocarbamate, 5-methyl-4-(2-thiazolylazo) resorcinol and violuric acid [30–42] have been used to preconcentrate trace metal ions from various samples.

Co-precipitation involves incorporating trace impurities from a soluble liquid phase into a precipitate. The ability of precipitates to capture special impurities may be used to concentrate or enrich

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trace elements [43]. Co-precipitation mechanisms may include surface adsorption, ion exchange, surface precipitation, and occlusion [44]. In recent years, a new coprecipitation method without the need for a carrier element has been established, and thus this method has been called "carrier element free coprecipitation" (CEFC) [1]. The CEFC method has significant importance for separating and preconcentrating heavy metals because it does not have contamination or background adsorption risks for metal ions from a carrier element [1,45–54].

In the present study, a new, simple and sensitive co-precipitation method using 4-(2-hydroxybenzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one (APSAL) as an organic coprecipitant without a carrier element was established to separate and preconcentrate $Cr^{3+}$, $Cu^{2+}$, $Fe^{3+}$, $Pb^{2+}$ and $Zn^{2+}$ ions from food and water samples prior to FAAS detection. The influences of various analytical parameters, such as pH, APSAL coprecipitant amount, centrifugation rate, time and sample volume, were investigated.

## 2. Experimental

### 2.1. Apparatus

A Shimadzu model AA-640-13 atomic absorption spectrometer (Tokyo, Japan) with deuterium background corrector equipped with a flame burner was used in this study. All measurements were conducted with an air/acetylene flame. A 10 cm long slot-burner head, a lamp and an air–acetylene flame were used. The instrumental parameters for the working elements were those recommended by the manufacturer's manual book. The pH measurements were made on a Hanna pH-meter equipped with a combined glass–calomel electrode (Portugal) (HI: 9321). A centrifuge (Isolab, Germany) was employed. A Milestones Ethos D closed vessel microwave system (Milestone Inc./Italy) (maximum pressure 1450 psi, maximum temperature 300 °C) was used to digest food samples. Laboratory glassware was immersed in a 10% (v/v) $HNO_3$ solution overnight and then rinsed and cleaned with bidistilled water. Polypropylene bottles were used to store samples prior to analysis.

### 2.2. Reagents and solutions

All of the chemicals used in this work were of analytical grade and were obtained from Merck (Darmstadt, Germany) or Fluka (Bunch., Switzerland) and bidistilled/deionized water was used in all experiments. The standard stock solutions of metal ions (1000 mg L$^{-1}$) were prepared by dissolving nitrate salts of the metals in 0.5 mol L$^{-1}$ $HNO_3$. The standard solutions used for calibration were prepared by diluting the metal stock solutions with 0.5 mol L$^{-1}$ $HNO_3$ before use.

In this study, APSAL was used as a coprecipitating agent for the first time and was synthesized according to the procedure provided in the literature [55]. A 0.2% (w/v) APSAL solution was prepared in ethanol.

Buffer solutions were prepared to adjust the solution pH values. Sodium dihydrogen phosphate/phosphoric acid buffer was used to adjust solutions to pH 2.0. Acetate buffer was prepared by mixing different amounts of 1.0 mol L$^{-1}$ $CH_3COONa$ and 1.0 mol L$^{-1}$ $CH_3COOH$ to maintain the pH range from 4.0 to 6.0. A di-sodium hydrogen phosphate/sodium dihydrogen phosphate buffer solution was used to adjust solutions to pH 7.0. Ammonia/ammonium chloride buffer solutions (0.1 mol L$^{-1}$) were prepared by adding an appropriate amount of $NH_3$ to $NH_4Cl$ solutions to result in solutions of pH from 8.0 to 10 [56]. The accuracy of the method was verified by analyzing certified reference materials GBW 07605 Tea

(Institute of Geophysical and Geochemical Exploration, Langfang, China) and SRM 1515 Apple leaves (National Institute of Standard and Technology, Gaithersburg, MD, USA).

### 2.3. Coprecipitation procedure

In the present study, the CEFC method was applied to model solutions to separate and preconcentrate analyte ions. For this purpose, 1.5 mL of the co-precipitating agent APSAL solution (0.2% w/v) was added to 50-mL of an aqueous solution containing 25 µg of $Cr^{3+}$, $Cu^{2+}$ and $Fe^{3+}$, 20 µg of $Pb^{2+}$ and 10 µg of $Zn^{2+}$. The pH values of the solutions were adjusted to 7.0 using buffer solution. After standing for 10 min, the solution was centrifuged at 3500 rpm for 15 min, and then the supernatant was removed. Finally, the precipitate that adhered to the centrifuge tube was dissolved in 1.0 mL of conc. $HNO_3$. The final volume was filled to 5.0 mL with deionized water, and then the contents of the analyte ions were detected and analyzed by FAAS.

### 2.4. Applications to water and food samples

The presented preconcentration procedure was applied to detect chromium, copper, iron, lead and zinc ions in different water samples. The tap and mineral water samples were from Zagazig city, the Nile river water samples were from Shobra Al-Keima, Egypt and the seawater samples were from the Red Sea, Egypt and were collected and stored in prewashed polyethylene bottles. The samples were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size before trace metal analysis and were acidified with 1.0% (v/v) nitric acid. The organic content of the water samples was oxidized with 1.0% (w/v) $H_2O_2$ and concentrated nitric acid. The pH of the samples was adjusted to 7.0 with a buffer solution. Then, the preconcentration procedure given above was applied to study the water samples. The levels of the studied analyte concentrations in the samples were determined by FAAS.

Another application of the presented procedure was performed using certified reference materials [NIST, SRM 1515 Apple leaves (0.25 g) and GBW 07605 Tea (0.25 g)] and some food samples (black tea, green tea, coffee, tobacco, flour and rice) (1.0 g) which were purchased from a supermarket in Zagazig, Egypt. Afterward, they were placed in small mesh and dried in an oven at 90 °C to constant weights. The samples were digested with 10 mL of concentrated $HNO_3$ (65%) and 3.0 mL of $H_2O_2$ (30%) in the microwave digestion system and evaporated to near dryness. After evaporation, 10 mL of deionized water was added and the samples were mixed. The resulting mixture was filtered through filter paper and then diluted to 50 mL with deionized water. All of the samples were stored in polyethylene bottles. The blanks were prepared in the same way as the sample [49]. The preconcentration procedure given above was applied to the samples. The analytes in the final solution were determined by FAAS.

## 3. Results and discussion

### 3.1. Effect of pH

The influences of the aqueous solution pH values on the recoveries of the analytes were investigated in the range from 2.0 to 10 because pH is a very important factor that affects the quantitative recoveries of analytes using the co-precipitating agent (APSAL). The pH values were adjusted by adding related buffer solutions. Next, the coprecipitation procedure given above was applied to these solutions. The obtained results of this study are given in Fig. 1. According to the results, the analyte ions were quantitatively