

J. A. Salonia · R. G. Wuilloud · J. A. Gásquez
R. A. Olsina · L. D. Martinez

On-line complexation of zinc with 5-Br-PADAP and preconcentration using a knotted reactor for inductively coupled plasma atomic emission spectrometric determination in river water samples

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Abstract An on-line zinc preconcentration and determination system implemented with inductively coupled plasma atomic emission spectrometry (ICP-AES) associated with flow injection (FI) was studied. The zinc was retained as zinc-2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol (Zn-(5-Br-PADAP)) complex at pH 9.2. The zinc complex was removed from the knotted reactor (KR) with 30% v/v nitric acid. An enrichment factor of 42 was obtained for the KR system with respect to ICP-AES using pneumatic nebulization. The detection limit for the preconcentration of 10 mL of aqueous solution was 0.09 µg/L. The precision for 10 replicate determinations at the 5 µg/L Zn level was 2.3% relative standard deviation (RSD), calculated with the peak heights obtained. The calibration graph using the preconcentration system for zinc was linear with a correlation coefficient of 0.9997 at levels near the detection limits up to at least 100 µg/L. The method was successfully applied to the determination of zinc in river water samples.

Introduction

Zinc is the 24th most abundant element in the Earth's crust, and its concentration averages about 70 µg/g in most rock-forming minerals. Zinc is an essential element for plant and animal life, and lack of adequate zinc intake appears to be a far greater threat to human health than overexposure [1, 2]. In mineral deposits of base and precious metals, zinc is associated with Cu, Pb, Ag, Au, Sb, As and Se, and is an excellent indicator of such deposits as well as a good pathfinder. Thus, Zn is widely used for geochemical prospective studies [3]. The average concentration of Zn in river water is in the order of 20 µg/L, which

is taken as the base value for prospective studies [3]. The use of Zn in prospective studies of river water is limited to the determination of low concentrations close to the base value. This is to say that follow-up studies must be carried out in such a way that concentrations as low as, or even lower than 20 µg/L [3, 4] can be determined. Therefore, powerful techniques are required, and only a few of them show sufficient sensitivity. Among these are electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma mass spectrometry (ICP-MS).

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is one of the most used techniques for the determination of zinc traces. The most sensitive line for Zn is at 213.856 nm. However, this line exhibits spectral interferences from elements such as Fe, Ni, and Cu. The second most sensitive line, at 206.200 nm, does not exhibit such interferences. However, the determination limit that can be reached (approximately 40 µg/L) is not enough for Zn determination in river water.

In order to achieve accurate, reliable and sensitive results, preconcentrations and separations are needed when the concentrations of analyte elements in the sample are too low to be determined directly by ICP-AES. Many preconcentration techniques [5–12] for the determination of Zn have been proposed, including chelation and extraction, precipitation, coprecipitation, and ion-exchange resins. However, many of these methodologies are performed in batch, thus requiring great sample volumes in order to reach low detection limits. Besides, these systems present higher contamination risks. When preconcentration techniques are applied in batch mode, the time of analysis increases and the operations are usually too tedious to be compatible with the ICP-AES measurements. Furthermore, these procedures are not practical for application in routine analysis. This situation has been significantly improved utilizing flow injection (FI) associated with ICP-AES [13, 14], such that general drawbacks of batch preconcentration procedures have been largely eliminated, and currently the preconcentrations can be achieved almost as efficient as a simple ICP-AES determination. Reagent consumption is usually reduced to a

J. A. Salonia · R. G. Wuilloud · J. A. Gásquez · R. A. Olsina
L. D. Martinez (✉)
Area de Química Analítica, Facultad de Química,
Bioquímica y Farmacia, Universidad Nacional de San Luis,
Chacabuco y Pedernera, 5700 San Luis, Argentina

minor percent of that in batch procedures, and sample contamination is reduced, which becomes important when trace concentrations are determined. In fact, to date the most dramatic improvements achieved in FI-ICP-AES have been in the field of on-line preconcentration.

Flow injection on-line preconcentration based on the sorption of metallic complexes on the inner walls of a PTFE knotted reactor (KR) has been successfully applied [15]. The use of the KR as a collector for precipitates [16] has been found feasible in FI on-line precipitation-preconcentration systems.

So far, in most of the work in which KRs have been used, they have been coupled to flame atomic absorption spectrometry (FAAS) [17, 18] or to ETAAS [19–23]. ICP-AES also constitutes an interesting alternative for coupling with KR in order to perform preconcentrations and determinations of metal traces, besides exhibiting a sensitivity similar to that of ETAAS. Additionally, KR has the advantage of a low hydrodynamic back-pressure, permitting high load sample rates and elevated throughput of sample.

The most widely used reagents for metal preconcentration in KR have so far been diethyldithiocarbamate (DDTC) [19, 21] and ammonium pyrrolidine dithiocarbamate (APDC) [20, 23]. Pyridylazo reagents form insoluble chelates with numerous metallic ions. However, we have not found any reference in the literature to the use of these reagents in KR preconcentration. 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) has been used as a reagent in the spectrophotometric determination of numerous metallic ions [24–26], although precautions had to be taken in order to avoid the precipitation of the corresponding chelate, such as the addition of surfactant agent. This fact suggested to us that, in absence of a surfactant, 5-Br-PADAP could be a suitable reagent for preconcentration of zinc on KR.

In the present work, a method for preconcentration and determination of zinc using a KR is proposed. Zinc was retained under the form of Zn-(5-Br-PADAP) complex. The determination was performed using ICP-AES associated with a FI methodology.

Experimental

Reagents

A solution of 5-Br-PADAP (Aldrich, Milwaukee, WI, USA) 10^{-2} mol/L was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution.

Working standard solutions were prepared by stepwise dilution from 1000 mg/L Zn stock standard solution (Merck) immediately before use.

A buffer solution was prepared by diluting a 3.0 mol/L ammonium hydroxide solution adjusted to pH 9.2 with a hydrochloric acid solution.

Ultrapure water (18 M Ω /cm) was obtained from an EASYpure RF (Barnstedt, Iowa, USA).

All the reagents were of analytical-reagent grade and the presence of zinc was not detected in the working range.

Table 1 ICP instrumental parameters^a and operating conditions

ICP conditions	
RF generator power	0.8 kW
Frequency of RF generator	40.68 MHz
Plasma gas flow rate	8.5 L/min
Auxiliary gas flow rate	1 L/min
Carrier gas flow rate	0.8 L/min
Observation height (above load coil)	15 mm
Analytical line: Zn	206.200 nm
Preconcentration conditions	
pH of loading solution	9.2
5-Br-PADAP concentration	5×10^{-5} mol/L
Loading flow rate 5-Br-PADAP	2.5 mL/min
Loading flow rate sample	5 mL/min
Loading time	120 s
KR length	200 cm
Ethanol concentration	10% (v/v)
Eluent concentration (HNO ₃)	30% (v/v)
Eluent flow rate	1.5 mL/min

^a A concentric glass nebulizer was used

Instrumentation

The measurements were performed with a sequential ICP spectrometer [Baird (Bedford, MA, USA) ICP 2070]. The 1 m Czerny-Turner monochromator had a holographic grating with 1800 grooves/mm. The ICP operating conditions are listed in Table 1. The FI system used is shown in Fig. 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bell, France)] was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. For sorption of the complex, a KR was made from a 2 m length of PTFE tubing of 0.5 mm internal diameter by tying interlaced knots of approximately 5 mm diameter loops. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent and eluent. The 206.200 nm spectral line was used and FI system measurements were expressed as peak-height emission, which was corrected against the reagent blank.

Sample preparation

The river water samples were filtered through 0.45 μ m pore size membrane filters immediately after sampling, and were acidified to pH 2 with nitric acid and stored at 4 °C in bottles (Nalgene; Nalge, Rochester, NY, USA).

All the instruments used were previously washed with a 10% v/v HNO₃/water solution and then with ultrapure water.

Procedure

Preconcentration step. The aqueous sample solution (0.01 mol/L nitric acid) containing zinc, at a flow rate of 5.0 mL/min, and 5-Br-PADAP 5×10^{-5} mol/L (at a flow rate of 2.5 mL/min) buffered to pH 9.2, were mixed on-line to form the metal complex. This mixture was then loaded on the KR during 120 s, valve V in load position (a) (Fig. 1). After the loading time, a further washing with buffer diluted solution served to remove the sample still present in the line and in the KR. Finally, the peristaltic pump P₁ was stopped, the injection valve V was switched to the injection position (b) and the retained metal complex was eluted with nitric acid 30% v/v at a flow rate of 1.5 mL/min, directly into the pneumatic nebulizer and ICP-AES. Since the metal complex Zn-5-Br-

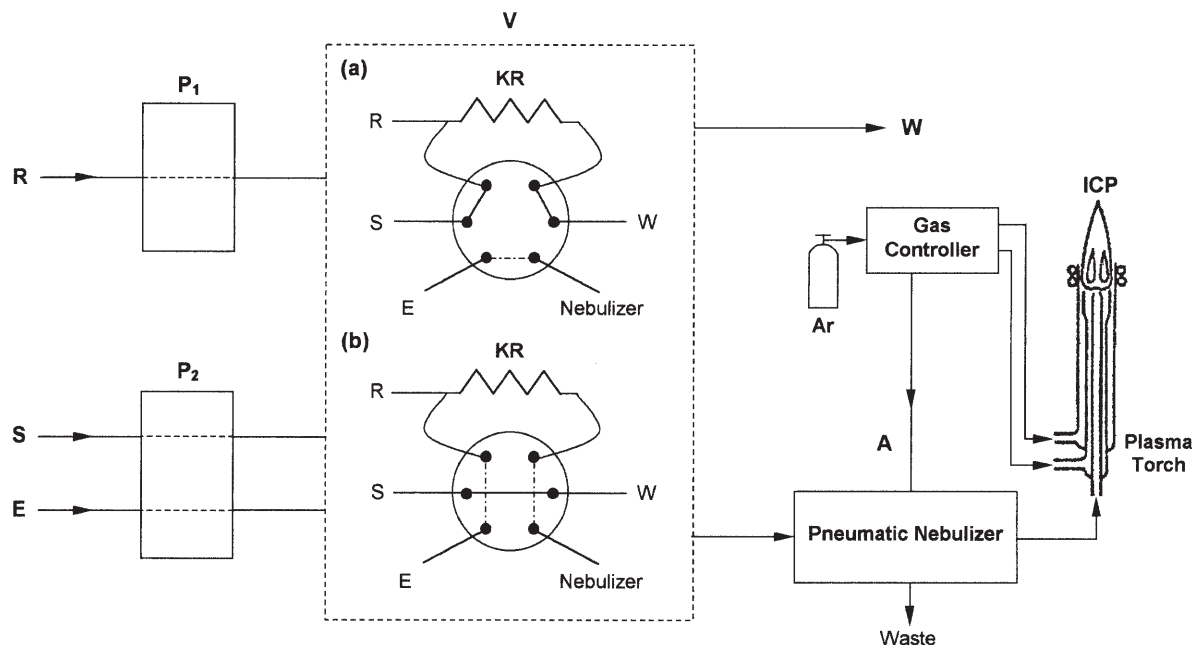


Fig. 1 Schematic diagram of the instrumental setup. *R*: 5×10^{-5} mol/L 5-Br-PADAP solution (2.5 mL/min) *S*: sample (flow rate: 5.0 mL/min), *E*: eluent (flow rate: 1.5 mL/min), *A*: Ar (flow rate: 0.8 L/min), *W*: waste, *P*₁, *P*₂: peristaltic pumps, *V*: injection valve, *KR*: knotted reactor. Valve positions: (a) sample loading; (b) injection

PADAP is not totally retained on the KR, the standard solution must also be passed through the KR. The operating conditions were established and the determination was carried out.

Results and discussion

Optimization of the loading variables

pH, flow rate and loading time conditions. In order to optimize the sorption conditions for the retention of the metal complexes, the zinc signal was monitored by measuring it with ICP-AES while changing the pH of the solution that passes through the KR. The optimal pH values were in the range of 8 – 9.9. This phenomenon is understandable, since a better on-line complexation occurs within this range. According to these results, the selected pH was 9.2. All other conditions as in Table 1.

The sample flow rate through the KR is a very important parameter, since this is one of the steps that controls the time of analysis. We could verify that the optimum sample loading flow rate was achieved at 5 mL/min, which in optimum conditions allows to reach an enrichment factor (EF) value of 42. At higher flow rates, the response decreases. A sample loading time of 120 s was used for preconcentration. All other conditions as in Table 1.

The flexibility of adopting different sample loading times to attain different enrichment factors is one of the advantages of the proposed method. A preconcentration time of 120 s allows to obtain an acceptable EF as well as

elevated sample throughput, which in turn leads to good concentration efficiency (CE).

KR length. An important parameter to be optimized was the KR length. Good results were obtained for a length of 200 cm, and further increases in length did not show any improvement in the enrichment factors. All other conditions as in Table 1.

Effect of solvent concentration. In order to avoid the precipitation of the reagent 5-Br-PADAP in aqueous medium, the solution of the complexing reagent was prepared in the presence of ethanol. It was observed that with 10% v/v of ethanol, 5-Br-PADAP remained in solution up to concentrations in the order of 10^{-4} mol/L. Subsequently, the influence of ethanol concentration on the preconcentration of the complex Zn-5-Br-PADAP was assessed. The preconcentration decreases when ethanol concentrations above 25% v/v are used in the 5-Br-PADAP solution. This behavior was to be expected since increasing solvent concentration leads to higher solubility of the Zn-5-Br-PADAP complex, which hinders its precipitation and adsorption on the KR walls. The ethanol concentration was set at 10% v/v, which enabled to achieve both stability of the complexation reagent solution and efficiency of the system for preconcentration of the Zn-5-Br-PADAP complex. All other conditions as in Table 1.

Concentration and flow rate of 5-Br-PADAP solution. The concentration and loading flow rate of the 5-Br-PADAP solution were optimized. The minimum reagent/metal ratio necessary to achieve optimum preconcentration was 5:1. However, the maximum possible concentration of 5-Br-PADAP was 10^{-4} mol/L, since at higher values the preconcentration capacity of the system is de-

creased, which could be attributed to the fact that the complexing reagent and the Zn-5-Br-PADAP complex compete for adsorption on the KR inner walls. The 5-Br-PADAP concentration selected for the present work was 5×10^{-5} mol/L. The optimum load rate of the 5-Br-PADAP solution was 2.5 mL/min. All other conditions as in Table 1.

Optimization of the elution conditions

The selection of an eluent for the complex was critical. In most of the reported works, determination is performed using ETAAS and therefore the use of an organic solvent does not cause any difficulties. This was not possible in this case, however, since organic solvents generate strong turbulence in the ICP which can eventually lead to its extinction. Nitric acid turned out to be a good eluent for the Zn-5-Br-PADAP complex with 25% v/v as the minimum concentration necessary to obtain the best response. A concentration of 30% v/v nitric acid was adopted for the remainder of this work.

The effect of the flow rate of the eluent was also investigated and it was found that the best response was achieved at 1.5 mL/min. A typical elution profile for Zn after complete optimization of the FI system is shown in Fig. 2. All other conditions as in Table 1.

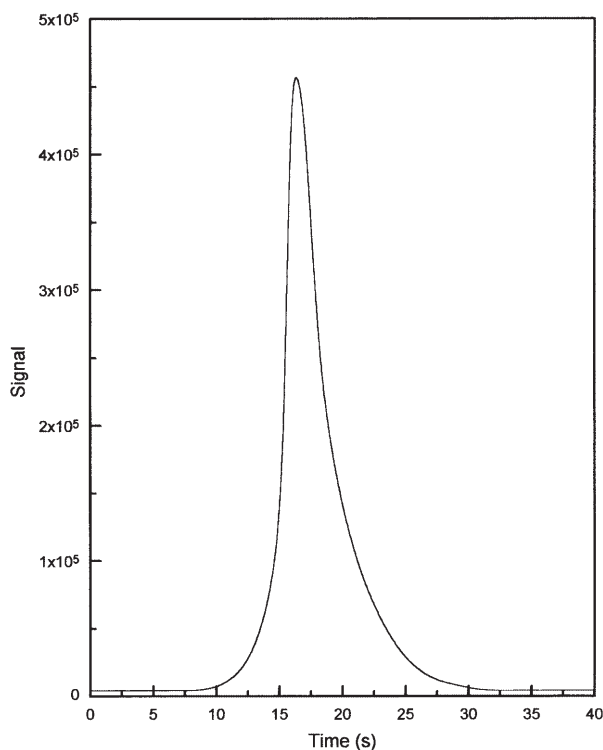


Fig. 2 Peak profile obtained by preconcentration of 10 mL of Zn solution using the system depicted in Fig. 1. Sample loading flow rate was 5 mL/min; the elution flow rate was 1.5 mL/min; Zn concentration was 50 $\mu\text{g/L}$; 5-Br-PADAP concentration was 5×10^{-5} mol/L

Table 2 Effect of interferents on the recovery of Zn under the corresponding optimum preconcentration conditions. The concentration of Zn was 5 $\mu\text{g/L}$ and all results are the average of triplicate measurements

Interferent	Concentration ($\mu\text{g/L}$)	Recovery (%)
Fe ³⁺	30,000	99.0
Ni ²⁺	3,000	98.5
Cu ²⁺	3,000	99.4
Ca ²⁺	50,000	100.0
Mg ²⁺	15,000	99.6
K ⁺	8,000	100.0
Na ⁺	21,000	100.0
Al ³⁺	3,000	98.9

Interferences

The effects of representative potential interferent species (at the concentration levels at which they may occur in the sample concerned) were tested under the corresponding optimum preconcentration conditions. The results are presented in Table 2. Thus, these analytes could tolerate up to at least 3 times the concentration values normally found in river water. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not retained on the KR.

Performance of the preconcentration system with KR

The overall time required for preconcentration of 10 mL of sample (2 min, at flow rate of 5 mL/min), washing (0.2 min, at flow rate of 1.5 mL/min) and elution (approx. 0.5 min, at flow rate of 1.5 mL/min) was about 2.7 min; the throughput was about 22 samples per hour. An enrichment factor (EF) of 42 was obtained with respect to ICP-AES using pneumatic nebulization. EF is defined as the ratio of the slopes of the linear section of the calibration curves after and before the preconcentration [27].

The reproducibility of the preconcentration method was evaluated by passing through the KR 10 mL of standard solution of zinc (5 $\mu\text{g/L}$) and repeating this procedure 10 times. The relative standard deviation (RSD) was 2.3%, calculated with the peak heights obtained. The calibration graph using the preconcentration system for zinc was linear with a correlation coefficient of 0.9997 at levels near the detection limit up to at least 100 $\mu\text{g/L}$. The detection limit (DL) was calculated as the amount of zinc required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ). The value of DL obtained for the preconcentration of 10 mL of aqueous solution was 0.09 $\mu\text{g/L}$.

Method validation

In order to demonstrate the validity of this method, 1 L of river water was collected and divided into 10 portions of 100 mL each. The proposed method was applied to six

Table 3 Method validation

Ali- quots	Base value ($\mu\text{g/L}$)	Quantity of Zn added ($\mu\text{g/L}$)	Quantity of Zn found ($\mu\text{g/L}$)	Recovery (%) ^a
1	–	0.00	2.35 ± 0.15	–
2	2.35	1.00	3.33	97.8
3	2.35	3.00	5.32	98.9
4	2.35	5.00	7.33	99.6
5	2.35	8.00	10.37	100.2

^a $100 \times [(\text{found}-\text{base})/\text{added}]$

Table 4 Concentrations of zinc in river water samples (95% confidence interval; $n = 6$)

Sample	Zn concentration ($\mu\text{g/L}$)
1	2.35 ± 0.15
2	1.52 ± 0.20
3	2.34 ± 0.14
4	10.60 ± 0.10
5	4.30 ± 0.10
6	7.80 ± 0.10

portions and the average quantity of zinc obtained was taken as a base value. Then, increasing quantities of zinc were added to the other aliquots of the sample and zinc was determined by the same method (Table 3). Additionally, the proposed method was applied to a standard reference material, NIST SRM 1640 Trace Elements in Natural Water, with a zinc content of $53.2 \pm 1.1 \mu\text{g/kg}$. The density of this SRM at 22°C is $1.0015 \pm 0.0005 \text{ g/mL}$. Using the proposed method the content of zinc determined in this SRM was $52.9 \pm 0.10 \mu\text{g/kg}$.

Finally, the results of the method applied to zinc determination in river water samples are shown in Table 4.

Conclusions

The on-line coupling of a FI sorption preconcentration system with a knotted reactor to FI-ICP-AES increases the speed of the preconcentration and analysis process and reduces sample consumption and contamination risks. The results in this work demonstrate the possibility of using 5-Br-PADAP for the preconcentration of zinc, since the Zn-5-Br-PADAP complex was effectively adsorbed on the inner surface of a KR made of PTFE. The manifold presented provided an enrichment factor of 42 with respect to ICP-AES using pneumatic nebulization. This system of

preconcentration permits zinc determinations in river water samples in concentrations of the order of $\mu\text{g/L}$. The determination shows good reproducibility and accuracy.

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