

On-line system for preconcentration and determination of metals in vegetables by Inductively Coupled Plasma Optical Emission Spectrometry

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Abstract

A procedure has been developed for the simultaneous determination of trace amounts of cadmium, copper, chromium, nickel and lead in digested vegetable samples. The method involves solid-phase extraction of the metals using a minicolumn of Amberlite XAD-4 modified with dihydroxybenzoic acid (DHB) and detection by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The elution of the metals from minicolumn was performed with 1.0 mol L⁻¹ hydrochloric acid. Variables associated with flow preconcentration system performance, such as pH, buffer concentration, eluent concentration and sampling flow rate, were optimized. The developed procedure provides enrichment factors of 100, 72, 16, 91 and 53, for cadmium, copper, chromium, nickel and lead, respectively. Detection limits ($3\sigma_B$) were 0.02 (Cd), 0.23 (Cu), 0.58 (Cr), 0.060 (Ni) and 0.54 (Pb) $\mu\text{g L}^{-1}$. The procedure was applied for determination of metals in samples of guarana and cabbage. The accuracy of the method was checked by the analysis of a certified reference material (NIST 1571, Orchard leaves). Results found were in agreement with certified values.

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1. Introduction

The content of trace elements in different samples is important and of great interest due to human exposure and environment parameters. Essential trace elements are those compounds that need to be present in the human diet to maintain normal physiological functions. Risk assessment of trace elements has examined two ends of the toxicity aspect: (1) that associated with intakes that are too high and the resulting toxicity and (2) that associated with intakes that are too low and result in nutritional problems [1,2]. Vegetable samples can contain toxic metals from their presence in the soil, water or air. High levels can be found when agricultural expedients are used, such as fertilizers and

pesticides [3]. People are exposed to toxic metals mainly by eating foods containing them, breathing contaminated workplace air or drinking contaminated water [4,5].

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is widely recognized as a suitable technique for the determination of metals [6]. However, the low level of some metals in some samples is not compatible with the LOD of this technique. In order to achieve accurate, reliable and sensitive results, preconcentration and separation are needed when the concentrations of analyte elements in the original material or the prepared solution are too low to be determined directly by ICP-OES.

Preconcentration is an effective means for extending the LODs of ICP-OES technique. However, when practiced manually in the batch mode, the operations are usually too tedious to be compatible with the ICP-OES measurements. Stringent control of the laboratory environment is also required to avoid

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Table 1
Instrumental conditions for ICP-OES measurements

Parameter	Cd	Cu	Cr	Pb	Ni
Analytical wavelengths (nm)	226.502	327.395	267.7160	220.353	230.299
Power (kW)	1.2	1.2	1.2	1.2	1.2
Nebulizer pressure (kPa)	200	200	200	200	200
Plasma gas flow (L min ⁻¹)	15.0	15.0	15.0	15.0	15.0
Nebulizer gas flow (L min ⁻¹)	0.7	0.7	0.7	0.7	0.7
Auxiliary gas flow (L min ⁻¹)	1.5	1.5	1.5	1.5	1.5

sample contamination if ultra-trace determinations in the $\mu\text{g L}^{-1}$ range are to be attempted. This situation has been improved significantly by utilizing on-line system coupled with ICP-OES [7–9]. Some methodologies used for metal preconcentration have been developed with ionic exchanger resins [10], precipitation [11], cloud point extraction [12–14], knotted reactors [15–17] and solid-phase extraction [18–22].

In the present work, an on-line procedure for simultaneous preconcentration and determination of Cr, Cu, Ni, Pb and Cd at low concentration levels using ICP-OES is proposed. It is based on sorption of these metals in a minicolumn packed with Amberlite XAD-4 modified with dihydroxybenzoic acid (DHB) and elution with a solution with hydrochloric acid.

2. Experimental

2.1. Instrumentation and apparatus

A Varian (Mulgrave, Australia) Vista simultaneous Inductively Coupled Plasma Optical Emission Spectrometer with axial viewing and a Charge Coupled Device (CCD) detector was used. The spectrometer was operated in the module of acquisition of transient signals. A cyclonic spray chamber and a concentric nebulizer were used. The metal determinations were realized under manufacturer recommended conditions listed in Table 1.

An Alitea C-6 XV (Stockholm, Sweden) peristaltic pump equipped with Tygon tubes were used to propel all the solutions. A Rheodine model 5041 (Cotati, CA, USA) four-way manual valve was used to select the preconcentration/elution steps. All the connections, i.e., fittings and two and three-way joints were made of plastic and PEEK materials. The manifold was made of a PTFE tube with a 0.5 mm i.d. An analytical balance (Sartorius Ag Gottingen, Germany) was used to weigh the vegetable samples. A Digimed DM20 (São Paulo, Brazil) pH meter was used to measure the pH.

2.2. Reagents and solutions

All reagents were of analytical grade unless otherwise stated. Ultrapure water was obtained from an EASY pure RF (Barnstedt, Dubuque, IA, USA). Nitric acid and ethanol were of Suprapur quality (Merck). Laboratory glassware was kept overnight in 10% nitric acid solution. Before use, the glassware was rinsed with deionised water and dried in a dust free environment.

Metal solutions were prepared by diluting $1000 \mu\text{g mL}^{-1}$ standard solutions (Merck, Germany) which were prepared in 1% hydrochloric acid solution.

Borate buffer solution (pH 8.0) was prepared by dissolving 38.1 g of sodium tetraborate (Merck) in 1000 mL of deionized water and pH was adjusted with hydrochloric acid.

Standard Reference Material (SRM) Orchard leaves NIST 1571 with reference content for Cd, Cr, Cu, Ni and Pb obtained from the National Institute of Standard and Technology (NIST, Gaithersburg, MD, USA) was used to check the accuracy and precision of the proposed method.

2.3. Synthesis of DHB XAD-4 resin and minicolumn preparation

The synthesis of DHB/XAD-4 resin was made in a similar way with having procedure described previously [23]. Amberlite XAD-4 bead (5 g) were treated with 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 and the mixture stirred at 60°C for 1 h on a water bath. Thereafter, the reaction mixture was poured into an ice–water mixture. The nitrated resin was filtered, washed repeatedly with water until free from acid and thereafter treated with a reducing mixture of 40 g of SnCl_2 , 45 mL of concentrated HCl and 50 mL of ethanol. The mixture was refluxed for 12 h at 90°C . The solid precipitate was filtered and washed with water and 2 mol L^{-1} NaOH. The amino resin was first washed with 2 mol L^{-1} HCl and finally with distilled water to remove the excess of HCl. It was suspended in an ice–water mixture (150 mL) 1 mol L^{-1} HCl and 1 mol L^{-1} NaNO_2 . The diazotized resin was filtered, washed with ice-cold water and reacted with DHB (3.3 g in 250 mL of 10% w/v NaOH solution) at $0\text{--}3^\circ\text{C}$ for 24 h. The resulting brown colored resin was filtered, washed with water and dried in air. The minicolumn was made with 3.50 cm length and internal diameter of 4.0 mm, contains about 100 mg of DHB-XAD-4. A syringe was used to put the sorbent inside the minicolumn.

2.4. Sample preparation

For the decomposition [24] of the sample and certified reference material, about 0.4 g of the material were treated with 4.0 mL of 1:1 (v/v) nitric acid solution and kept overnight in a Teflon vessel. Afterwards, the Teflon vessel was closed and put into a pressurized digestion system. The thermal heating was carried out in a stove at 170°C for 16 h. After cooling at room temperature, the obtained solution was adjusted to pH 8.0 with a

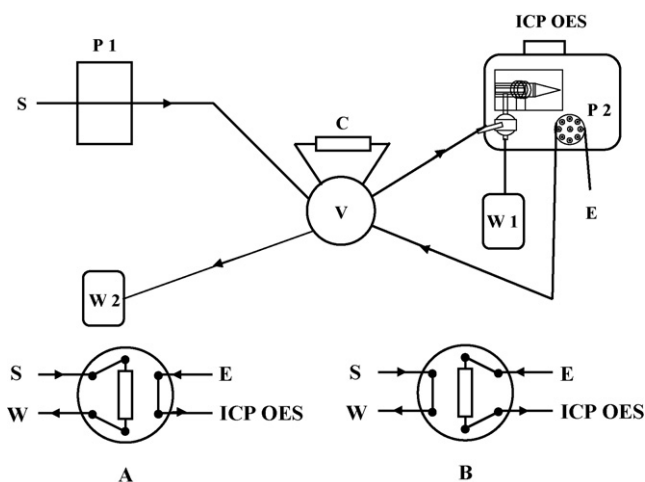


Fig. 1. Schematic diagram of the flow system used for the preconcentration and determination of metals by FI-ICP-OES. S, sample; E, eluent ($\text{HCl } 1 \text{ mol L}^{-1}$); P1, peristaltic pump 1 (8.0 mL min^{-1}); P2, peristaltic pump 2 (2.5 mL min^{-1}); C, Amberlite XAD-4/DHB minicolumn; V, four-way valve; ICP-OES, Inductively Coupled Plasma Optical Emission Spectrometer; W1, waste of ICP-OES nebulizer and W2, waste of on-line system. A, four-way valve in the preconcentration step and B, four-way valve in the elution position.

10% w/v sodium hydroxide, a borate buffer solution was added and made up to desired volume. Analytical blanks (2.0 mL of deionized water) were prepared in the same way.

2.5. On-line preconcentration system

The diagram of the on-line preconcentration system is shown in Fig. 1. The flow system was carried out using one peristaltic pump fitted with tygon tubes, one four-way valve and a minicolumn packed with DHB/XAD-4, coupled to an Inductively Coupled Plasma Atomic Emission Spectrometry [25]. The flow system was operated in the time-based mode. In the preconcentration step, the sample solutions buffered properly at pH 8.0 (S) were continuously passed through the column (C) pumped for 2 min at 8.0 mL min^{-1} . In this step, the metal ions were adsorbed on the sorbent minicolumn and the sample matrix sent to waste (W). During this step, a flow of eluent (E) 1.0 mol L^{-1} hydrochloric acid that flow at 2.5 mL min^{-1} , was being aspirated from the containers by the pump (P) to stabilize the plasma. By switching the valve to the injection position, a stream of 1.0 mol L^{-1} hydrochloric acid that flows at 2.5 mL min^{-1} displaces the metals complexed. This eluate is directly transported to the nebulizer of ICP-OES. Transient signals were measured as peak height mode by using instrument software. It was not necessary to recondition the minicolumn at the end of each cycle since samples were buffered before preconcentration.

3. Results and discussion

To determine the optimal conditions for maximum extraction of Cd, Cr, Cu, Pb and Ni on Amberlite XAD-4 modified with DHB and its determination by ICP-OES, several parameters were assessed using a standard solution containing a $20.0 \mu\text{g L}^{-1}$ concentration of metals. The eluent flow rate was

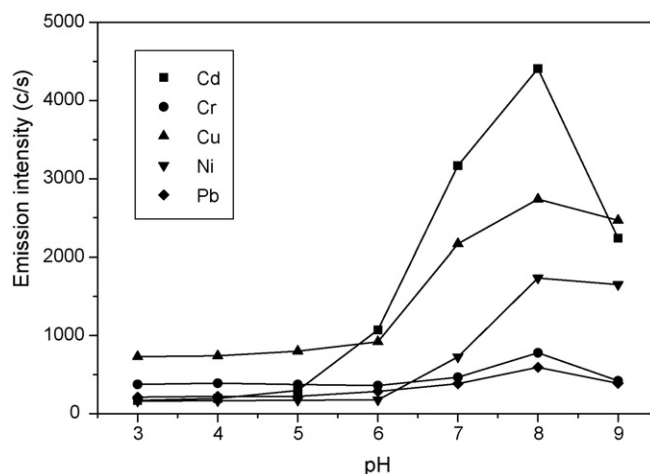


Fig. 2. Effect of pH on the retention of metals in the column. Conditions: sample flow rate 5.0 mL min^{-1} , buffer concentration 0.002 mol L^{-1} , eluent flow rate 2.5 mL min^{-1} and HCl concentration 0.5 mol L^{-1} .

set at 2.5 mL min^{-1} , which is the condition required by the spectrometer nebulizer.

3.1. Effect of pH

The effect of pH on the sorption of studied metals on resin inside the minicolumn was studied within a pH ranging from 3.0 to 9.0, as indicated in Fig. 2. The retention conditions of the metals were optimized and their analytical signals were monitored by measuring it with ICP-OES while changing the pH of the solution that passes through the sorption minicolumn. Fig. 2 shows that the maximum signal is obtained when pH attain the value 8.0 for all studied metals. For pHs lower than 6, a competition between protons and the analyte for the adsorption sites is shown, while at pHs higher than pH 9.0 the analytical signal begins to decrease. Considering these results, the borate buffer pH 8.0 was suggested since this solution provides a higher analytical signal.

3.2. Effect of sampling flow rate and aqueous volume

The effect of the sample flow rate on the metals extraction through the minicolumn was studied by varying the flow rate from 3.0 to 8.8 mL min^{-1} at the optimal pH established in the previous experiment. The results in Fig. 3 indicate that the efficiency of metal retention on the solid-phase reached its maximum at a flow rate of 8.0 mL min^{-1} .

3.3. Effect of the eluent concentration

The effect of the eluent concentration, which was a hydrochloridric acid solution, was evaluated. In this system, where the minicolumn is not reconditioned, this factor is very important because the HCl solution must provide fast elution of metal from the solid-phase in order to produce a well-defined and reproducible peak. On the other hand, a highly acidic eluent reduces the ability of the pH in the column to

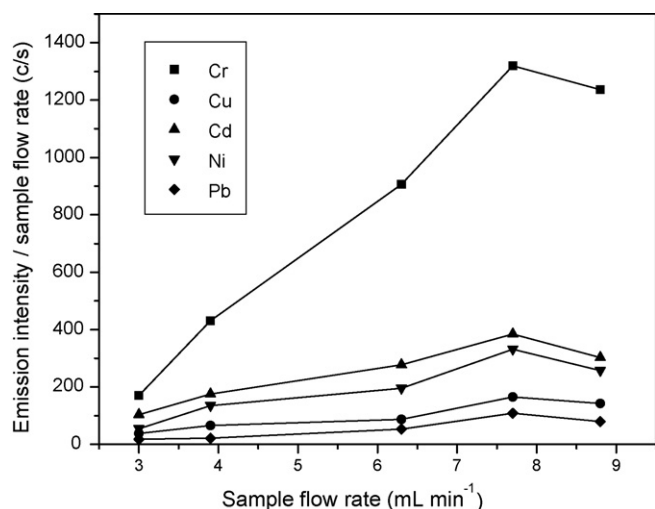


Fig. 3. Effect of sample flow rate on the retention of metals in the column. Conditions: pH 8.0, buffer concentration 0.002 mol L^{-1} , eluent flow rate 2.5 mL min^{-1} and HCl concentration 0.5 mol L^{-1} .

recover in the sampling step. This high acidity diminishes ion sorption on the resin, thus, reducing the extraction efficiency. As indicated in Fig. 4, the optimum eluent concentration achieved, which satisfied all studied metal was 1.0 mol L^{-1} HCl. Nitric acid also was tested in the elution of cadmium from minicolumn.

3.4. Effect of final buffer concentration

The final concentration of borate buffer (pH 8.0) in the sample solutions was studied. An adequate buffer concentration is important to ensure the rapid recovery of the pH in the column and to allow maximum efficiency in the extraction of metals. This study is presented in Fig. 5. As can be seen, the response (analytical signal/sample flow rate) reached its highest values at a buffer concentration of 0.004 mol L^{-1} .

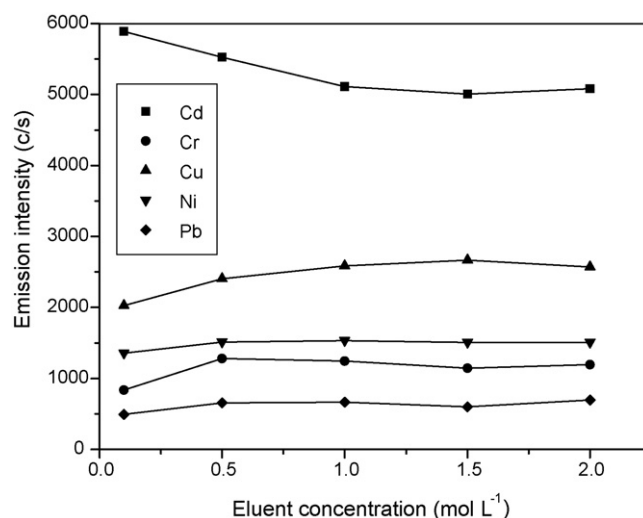


Fig. 4. Effect of eluent concentration on the retention of metals in the column. Conditions: pH 8.0, sample flow rate 8.0 mL min^{-1} , eluent flow rate 2.5 mL min^{-1} and buffer concentration 0.002 mol L^{-1} .

3.5. Performance of the system and analytical features

Table 2 presents some analytical performance and analytical characteristics of the developed procedure. The concentrations of the standards for construction of the analytical curves for the FI-ICP-OES procedure were in the $5.0\text{--}50.0 \mu\text{g L}^{-1}$ range ($N=6$). Without the preconcentration stage, the concentrations of the calibration standards were in the range from 0.1 to $5.0 \mu\text{g mL}^{-1}$ ($N=5$).

Parameters related with on-line preconcentration system also were accessed. Thus, the concentration efficiency (defined as the product of the enrichment factor and the sampling frequency per number of samples analyzed per minute) and the consumptive index (parameter that informs, how much amount of the sample volume is necessary to achieve a unit of enrichment factor) were calculated. The analytical frequency found in the optimized conditions was $20 \text{ samples h}^{-1}$.

Table 2
Analytical features of FI-ICP-OES procedure obtained using optimized conditions

Parameter	Cr	Cu	Ni	Pb	Cd
Analytical curves					
Without preconcentration ($\mu\text{g L}^{-1}$)					
a	7.4201	4.1972	3.3474	1.5262	22.799
b	33.307	7.5697	28.299	4.6718	221.69
After preconcentration ($\mu\text{g L}^{-1}$)					
a	120.08	300.99	303.87	80.572	2298.0
b	44.412	75.673	32.058	29.931	4.5283
LOD ($\mu\text{g L}^{-1}$)	0.58	0.23	0.059	0.54	0.020
LOQ ($\mu\text{g L}^{-1}$)	1.9	0.77	0.20	1.8	0.066
EF	16	72	91	53	100
%R.S.D. ($5 \mu\text{g L}^{-1}$)	4.13	3.38	5.34	3.15	5.06
%R.S.D. ($10 \mu\text{g L}^{-1}$)	3.76	3.01	1.6	3.06	4.01
Concentration efficiency (min^{-1})	5.3	23.8	30.0	17.5	33.3
Consumptive index (mL^{-1})	1.00	0.22	0.18	0.30	0.16

(a): Slope of analytical curve; (b): intercept; LOD: limit of detection; LOQ: limit of quantification; EF: enrichment factor and %R.S.D.: relative standard deviation (repeatability, $N=10$).

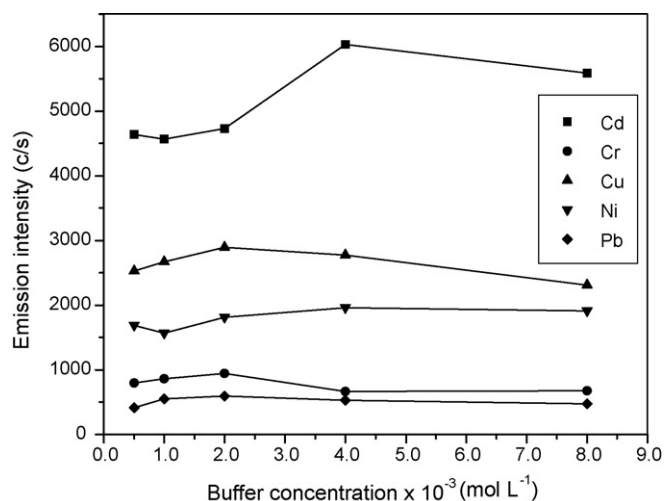


Fig. 5. Effect of buffer concentration on the retention of metals in the mini-column. Conditions: pH 8.0, sample flow rate 8.0 mL min⁻¹, eluent flow rate 2.5 mL min⁻¹ and HCl concentration 1 mol L⁻¹.

Table 3

Determination of Cu, Pb, Cd, Cr and Ni from a certified reference material (Orchard leaves, NIST 1571), cabbage and powdered guarana using the developed procedure

Sample	Metal	Content ($\mu\text{g g}^{-1}$)	
		Certified	Found
Orchard leaves (NIST 1571)	Cu	12 ± 1	12.6 ± 0.8
	Pb	45 ± 3	45.8 ± 0.3
	Cd	0.11 ± 0.01	0.11 ± 0.01
	Cr	2.6 ± 0.3	2.5 ± 0.1
	Ni	1.3 ± 0.12	1.4 ± 0.1
Cabbage	Cu	–	2.5 ± 0.2
	Pb	–	2.7 ± 0.4
	Cd	–	0.25 ± 0.05
	Cr	–	1.0 ± 0.1
	Ni	–	1.4 ± 0.3
Powdered guarana	Cu	–	1.8 ± 0.2
	Pb	–	3.3 ± 0.6
	Cd	–	0.10 ± 0.02
	Cr	–	1.7 ± 0.1
	Ni	–	1.6 ± 0.2

3.6. Application

The procedure was applied to determination of Cr, Cu, Ni, Pb and Cd in digested vegetable samples. The accuracy of the proposed method was checked by analysing one standard reference material, Orchard leaves NIST 1571. Table 3 presents results obtained for the determination of the five metals in SRM and real samples. The results revealed that values obtained in this study agree with the certified value reported for standard sample.

4. Conclusion

The proposed method was successfully applied to determination of metals in vegetable samples. This procedure combines

the advantages of an on-line system and determination of metals by Inductively Coupled Plasma Optical Emission Spectrometry. The on-line procedure developed is a precise and accurate alternative to conventional methods for determining cadmium, chromium, copper, lead and nickel. Besides, the method is very simple, sensitive and inexpensive. Due to good analytical characteristics, such as detection limit, enrichment factor and precision, the proposed procedure has been demonstrated to be very interesting for trace element analysis.

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