Determination of Cd in soybean and wheat seeds using TS-FF-AAS and preconcentration with cloud point extraction (CPE)

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Abstract

Cadmium is a toxic element associated with the environment. Seeds can accumulate it, so it is important to determine the concentration of this element.

Thermospray Flame Furnace (TS-FF) coupled to a flow-injection preconcentration system can be used to enhance detectability in flame atomic absorption spectrometry (FAAS) providing an alternative to the use of ET-AAS or ICP-MS.

The method is based on the adsorption of a complex of Cd and methyl green, potassium iodide and Triton X-114 in a minicolumn filled with cotton. The elution was carried out with HNO_3. The system consists of a peristaltic pump, an injection valve and a nickel tube 10 cm long with 7 holes. The analytical determinations were carried out by FAAS at 228.8 nm.

The seeds were milled, and 1.8 g of the obtained flour was digested by means of an acidic treatment with a mixture of HNO_3/H_2O_2. The resultant solution was neutralized with solid NaOH.

The figures of merit were: LD (3s) and LQ (10s): 0.6 and 2.1 µg L^{-1} respectively, linearity: up to 10 µgL^{-1} (r^2 = 0.999), precision: s_r(%) = 2.8 (n = 5), sampling frequency: 30 h^{-1} with a preconcentration factor of 30 compared with FAAS.

Accuracy was evaluated with the CRM Wheat Flour 1567a (NIST), the recoveries were between 98% and 105 % (n = 10). There was no evidence of the influence of potential interferences.

This method can be implemented for the control of Cd levels in soybean and wheat seeds.

Keywords: cadmium, thermospray, soybean, wheat

Introduction

Cadmium is one of the most toxic elements associated with environmental and industrial pollution, either as a secondary product of metallurgic industry, where it reaches the soil by aerial deposition, or through the use of phosphate fertilizers and the use of compost. Soybean and wheat seeds can accumulate this element from the environment, and then it is very important to determine the concentration of Cd in the seeds because wheat is the raw material of many foods [1].

Analytical determinations of Cd can be performed using different detection systems. Once the pretreatment of the sample is performed (digestion, extraction, preconcentration), this element can be quantified by flame atomic absorption spectrometry (FAAS), by atomic absorption spectrometry with electrothermal atomization (ET-AAS) or by atomic emission inductively coupled plasma (ICP-OES, ICP-MS), among others [2].

Thermospray Flame Furnace (TS-FF) coupled to a flow-injection preconcentration system can be used to enhance detectability and sensitivity in flame atomic absorption spectrometry (AAS) of some volatile elements providing an alternative to the use of ET-AAS or ICP-MS [3].

To further improve detectability of trace elements, strategies of on-line preconcentration can be used. Cloud point extraction (CPE) is a separation/preconcentration procedure which has proved to be very efficient for determination of trace elements in varied matrices and also in good agreement with the principles of Green Chemistry [4-7].

CPE is based on the principle that a surfactant containing aqueous solution becomes cloudy and separates into two phases, if certain conditions are adjusted appropriately as temperature, pressure or if an adequate substance is added. When the surfactant solution becomes cloudy it has reached the "cloud point". At this point, the original layer of surfactant phase is separated into a small volume of solution which will be rich in the analyte of interest (linked to organic or inorganic species by having high affinity), trapped by micellar type structures [4].

Flow injection systems with micelle mediated preconcentracion are made up with minicolumns filled with cotton, this material is commonly used for the retention of micellar aggregates [5].

In Uruguay the local regulation establishes that the maximum concentration of cadmium admitted in solid foods is 0.2 mg kg^{-1} [8]. Thus analytical methods used for the determination of this element in foods should provide high sensitivity.

The aim of this work is to propose an automated method for routinely Cd determination in soybean and wheat seeds using a flow injection system (FI) with on-line CPE preconcentraton coupled to Thermospray Furnace (TS-FF) and detection by flame atomic absorption spectrometry (FAAS).

Materials and Methods

All reagents were of analytical reagent grade. Purified water (ASTM Type I) was obtained from a Millipore (São Paulo, Brazil) Simplicity 185 purifier fed with glass-distilled water.

All glassware was soaked overnight in 10% (v/v) nitric acid and then rinsed exhaustively with distilled water. For calibration, adequate dilutions in purified water were prepared from a standard stock solution of Cd 1000 mg L^{-1} in HNO_3 4% (v/v) (SCP SCIENCE traceable to NIST).

The proposed method is based on micelle formation by the reaction between the reagent methyl green, and potassium iodide (KI) using Triton X-114 surfactant. These micelles are retained in a Teflon PFA minicolumn (60 x 2.5) mm packed with 40 mg of cotton. Elution is carried out with HNO_3 1 mol L^{-1}.

The system consists of a peristaltic pump (Rainin Dynamax) fitted with Tygon tubing, a 6-ports injection valve (Valco Cheminert), connections coils were made from 0.8 mm internal diameter Teflon PFA tubing. The detection system used consisted of an atomic absorption spectrometer Perkin Elmer AAnalyst 200, equipped with a thermospray flame furnace system (TS-FF-AAS). A nickel tube of 10 cm long by 10 mm of diameter with 7 holes was used above an adapted burner with ceramic supports. The measurements were carried out at a wavelength of 228.8 nm using a deuterium lamp for background correction.

During the preconcentration step, the reaction occurs between the Cd present in the sample, KI 0.5 mol L^{-1}, methyl green 0.005 mol L^{-1} and Triton X-114 0.5% (v/v), to form micelles that are retained on the cotton minicolumn. After

one minute of preconcentration (charge position), micelles are dissolved in HNO_3 1 mol L^{-1} in the elution step (elution position).

Figure 1 ilustrates the system.

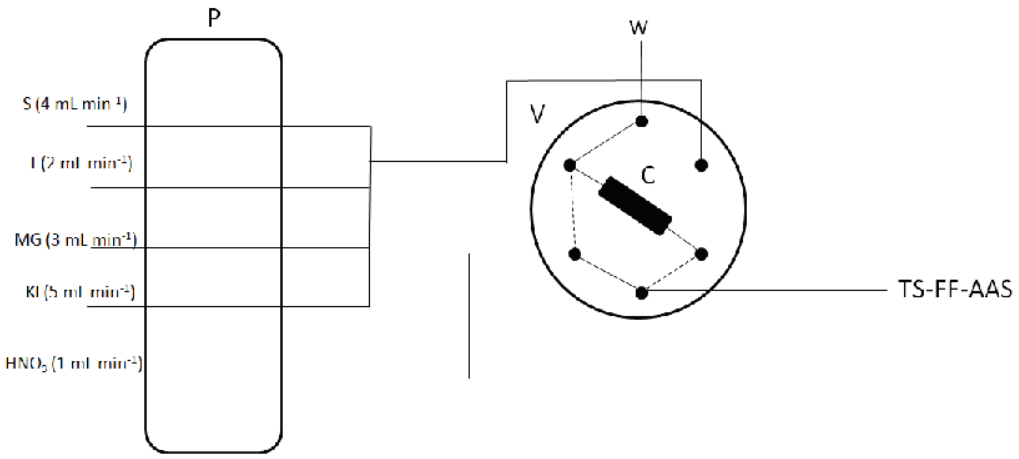

Figure 1. Flow injection system used for the preconcentration of Cd. P: peristaltic pump; V: 6-port injection valve; C: Column, W: waste, S: sample, T: Triton X-114, MG: methyl green, KI: potassium iodide, HNO_3: nitric acid. Solid lines represent the valve position during the preconcentration step, dotted lines represents the valve position during the elution step.

The soybean and wheat seeds were obtained from a local distributor (Agropecuaria Valdense S.R.L). The seeds were milled, and 1.8 g of the obtained flour was digested by means of an acidic treatment with a mixture of 30 mL of HNO_3 and 4 mL of H_2O_2 (30% (v/v) heated in a hot plate for 30 minutes in a vessel with reflux and afterwards the evaporated volume was completed to 25 mL with purified water. The resultant solution was neutralized with solid NaOH.

Certificate reference material of wheat flour purchased from NIST (1567a) was also prepared as described above. Reagent blanks were also run.

Results and discussion

The optimum concentrations of the reagents were obtained by means of a three-level central composite design [9].

It was decided to work with 1 minute as preconcentration time, because it is a reasonable time in agreement with good results in terms of the best net signal. The operative parameters of the system were optimized using multivariate experiments, where the net signal of a standard solution was monitored.

Once the operative conditions were optimized, the figures of merit were evaluated to complete the validation of the method. The results obtained are show in Table 1.

Accuracy was evaluated by means of trueness and precision. Trueness was studied using a reference material of wheat flour (NIST-1567a) by means of the recoveries of Cd. The precision of the method was evaluated taking into account the intermediate precision (relative standard deviation between 3 days).

Table 1. Figures of merit

Parameter	Result
Limit of detection (3s)	0.6 µg L^{-1}
Limit of Quantification (10s)	2.1 µg L^{-1}
Linearity	up to 10 µg L^{-1}
Precision (sr, n=5)	2.8 %
Accuracy (n=10)	98% - 105%
Sampling frequency	30 h^{-1}
Enrichment factor	30 respect to FAAS
Preconcentration factor	6 respect to TS-FF-AAS
Sample consumption (mL)	4

The validated method was applied to analyze 24 samples of wheat and 14 of soybean seeds, the obtained values were in the range of 0.03 and 0.10 mg kg^{-1} and 0.02 and 0.11 mg kg^{-1} of Cd respectively.

Conclusions

All the analyzed samples met the requirements of the regulations and can be used as raw material for food.

The proposed method was successful for the application and can be implemented for the control of Cd levels in wheat and soy seeds.

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