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# Simultaneous determination of cadmium and lead in medicinal plants by anodic stripping voltammetry

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**Abstract**

A simple method for the simultaneous determination of Cd and Pb in medicinal plants by differential pulse anodic stripping voltammetry, using a hanging mercury drop electrode, was developed. The pre-concentration of the metals was performed in 0.8 mol $L^{-1}$ HCl at −0.73 V for 180 s. The sample preparation was carried out by dry-ashing 1.0 g of finely pulverized plant samples for 2.5 h at 500 °C. The determination limit of the method was 0.12 and 0.010 mg $kg^{-1}$ for Pb and Cd, respectively. The method was applied to the quantification of cadmium and lead in samples of *Hypericum perforatum*, *Mikania guaco*, *Mikania glomerata* and *Peamus boldus*. The voltammetric method was shown to be useful for the control of contaminants in medicinal plants.


*Keywords:* Cadmium; Lead; Heavy metals; Medicinal plants; Stripping voltammetry

## 1. Introduction

Medicinal plants are consumed worldwide for the treatment of several diseases and are important raw materials for the pharmaceutical industry for the production of phytopharmaceuticals. In recent decades the use of phytopharmaceuticals and herbal medicines has increased worldwide, for several reasons, among them, that side-effects are often lower than those presented when synthetic drugs are employed, as well as due to the higher costs of many conventional pharmaceutical formulations [1].

As with other vegetation, medicinal plants are composed of many constituents and present great variability due to different growth, harvest, drying and storage conditions. Furthermore, they can be contaminated, as are other agricultural products, by pesticides, heavy metals and microorganisms [2]. Environment conditions in developing countries, pollution from irrigation water, the atmosphere and soil, sterilization methods and inadequate storage conditions [3] all play an important role in contamination of medicinal plants by heavy metals.

Ingestion of heavy metals through medicines and foods can cause accumulation in organisms, producing serious health hazards such as injury to the kidneys, symptoms of chronic toxicity, renal failure and liver damage [4,5]. Metals are probably the oldest toxins known to man.

The World Health Organization (WHO) has established standards for the quality control of medicinal plants including the classification, botanical identification, determination of active principles and identification of contaminants [6]. The WHO recommends qualitative and quantitative assays of heavy metals in phytotherapeutics, especially in raw materials of doubtful origin and plants produced by intensive agricultural means [7].

Several analytical methods have been reported for the quantitative determination of Pb and Cd in food,

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environmental and pharmaceutical matrices, including spectroscopic and electroanalytical methods. These methods comprise atomic absorption spectrometry [8–11], inductively coupled plasma optical emission spectroscopy [12], anodic stripping voltammetry [13], cathodic stripping voltammetry [14] and adsorptive voltammetry [15]. The electroanalytical methods present high selectivity and excellent detectability for the quantification of trace metals in complex matrices.

This paper describes the development of a simple method using anodic stripping voltammetry for the simultaneous determination of Cd and Pb in medicinal plants. The proposed method was applied to the determination of Cd and Pb in samples of *Hypericum perforatum*, *Mikania guaco*, *Mikania glomerata* and *Peamus boldus*, plants widely used in Brazil.

## 2. Experimental

### 2.1. Solutions and reagents

The reference samples R1 (sample 100, Grass GR94—*poaceae*) and R2 (sample 119, Rosa Plant, *Rose L.*) were furnished by the Agronomic Institute of Campinas (IAC) and were from the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL), Plant Sample Exchange Programme (PSEP) January–March, 2001.

All chemicals used were of analytical-reagent grade. All solutions were prepared with water obtained from a Milli-Q purification system. Heavy metal standard stock solutions (1000 mg $L^{-1}$) of cadmium and lead were provided by TECLAB (São Paulo, Brazil).

### 2.2. Sample preparation

#### 2.2.1. Sample preparation by dry-ashing

Samples of *H. perforatum*, *M. guaco*, *M. glomerata* and *P. boldus* were purchased from Homeopathic Pharmacies located in São Paulo, Brazil.

About 1.0 g of powdered vegetal material was placed in a porcelain crucible and mineralized in a muffle furnace for 2.5 h at 500 °C. After cooling, the ashes were humidified with water, dissolved with 2 mL of 6 mol $L^{-1}$ HCl and the suspension was heated until complete evaporation of the liquids. The residue was dissolved in 5 mL of 2.0 mol $L^{-1}$ HCl, heated and filtered. The filtered residue was washed with 5 mL of 2.0 mol $L^{-1}$ HCl. The combined filtrates were diluted with water to 25 mL.

#### 2.2.2. Wet digestion with $HNO_3/H_2O_2$

This treatment of the sample was based on the papers of Mingorance et al. [16] and Rodushkin et al. [17], with some modifications. Finely powdered leaf samples (1.0 g) were digested in concentrated $HNO_3$ (10 mL) and 30% (v/v) $H_2O_2$ (1 mL) for 2 h at 120 °C. The solution was evaporated to reduce the volume and then was cooled. The digested material was filtered and diluted to 25 mL.

### 2.3. Voltammetric determination of Cd and Pb in samples

A volume of 10 mL of the sample solution from the sample preparation was transferred to the voltammetric cell. After deaeration, Cd and Pb were determined by differential pulse anodic stripping voltammetry (DPASV), through the standard addition method. The voltammetric parameters comprise: deposition potential, −0.73 V; deposition time, 180 s; stirring speed, 300 rpm; scan rate, 5 mV $s^{-1}$; pulse amplitude, 50 mV and pulse duration, 40 ms. The current–potential curves were registered in the potential intervals of −0.54 to −0.29 V and −0.73 to −0.54 V, for Pb and Cd, respectively.

### 2.4. Instrumentation

All voltammetric measurements were performed using a Radiometer Copenhagen Polarograph, model POL 150, connected to a Radiometer Copenhagen stand, model MDE 150. A hanging mercury drop electrode (HMDE) and a platinum wire were used as working and counter electrodes, respectively. All potentials were recorded against an Ag/AgCl, $KCl_{sat}$ reference electrode. Pure $N_2$ was bubbled through the sample solutions for 400 s before the measurements. The voltammetric cell was decontaminated in 6 mol $L^{-1}$ $HNO_3$.

## 3. Results and discussion

Hydrochloric acid and ammonium citrate have been widely recommended for the determination of several heavy metals by anodic stripping voltammetry [18–20]. It was verified that in both supporting electrolytes, 0.10 mol $L^{-1}$ HCl and 0.10 mol $L^{-1}$ (pH 3) ammonium citrate, the corresponding peaks for Pb and Cd were well defined. However, the current peak intensities for Pb and Cd were greater in the HCl supporting electrolyte than with the citrate buffer, even after changing the pH of the ammonium citrate from 3 to 5. In addition to the better detectability obtained with the HCl medium, this supporting electrolyte would be particularly convenient considering that, in sample preparation, this acid is employed to redissolve the residues obtained after the digestion procedure. Changes in the HCl concentration over the range of 0.010–1.0 mol $L^{-1}$ did not affect the current intensity and the peak potentials of either peak. The current intensities increase with the deposition time between 60 and 240 s and, for a solution containing 20 ng $mL^{-1}$ of Cd and Pb, no deviation from linearity was observed. A time of 180 s was chosen, considering detectability and analytical frequency.

After establishing the optimized conditions for the quantification of cadmium and lead, the influence of the vegetal sample matrix on the voltammetric determination was