



# Development of a method for the sequential determination of cadmium and chromium from the same sample aliquot of yerba mate using high-resolution continuum source graphite furnace atomic absorption spectrometry



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## ABSTRACT

A simple, fast and sensitive method for the sequential determination of cadmium and chromium from the same sample aliquot of yerba mate and leaves of yerba mate is proposed using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sample analysis. The measures were made using the analytical line at 228.802 nm for cadmium and 357.869 nm for chromium, and three pixels each for evaluation. The reference material NCS ZC73014 (trace elements in tea) has been analyzed and the results were in agreement with the certified values. A characteristic mass of 0.37 pg and 2.4 pg was obtained for cadmium and chromium, respectively. The limits of detection were 0.25 ng for cadmium and 0.72 ng for chromium, and the precision, expressed as relative standard deviation, was around 10%. Thirteen commercial samples and five leave samples were analyzed and the concentration of cadmium varied between 0.28 and 2.06  $\mu\text{g g}^{-1}$  and that of chromium between 0.27 and 2.37  $\mu\text{g g}^{-1}$ . The process of infusion preparation resulted in a leaching of around 25% for cadmium and 60% for chromium.

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## 1. Introduction

Yerba mate (*Ilex paraguariensis*) is a tree originating from South America that grows in a limited zone within Argentina, Brazil and Paraguay and its processed leaves are consumed as infusion by the local population [1,2]. Infusion of the yerba mate is made with water at 60–70 °C and the beverage is classified as *chimarrão* [3,4]. The preparation may also be done with cold water, being referred to as *tererê* [2].

Studies with yerba mate related high quantities of the purine alkaloids (methylxanthines such as caffeine and theophylline), polyphenols (chlorogenic acids and its derivatives), saponins and flavonoids [1]. Research on the *Ilex paraguariensis* confirmed positive effects on health as antioxidant, anti-inflammatory, antimutagenic, lipid-lowering activities, diuretic activities, hepatoprotective and hypocholesterolemic effects, inhibition of low density lipoprotein, central nervous system stimulation and also a beneficial effect on the cardiovascular system have been reported [1,2,5].

Although the literature reports various benefits in the consumption of yerba mate, no study indicates the presence of potentially toxic metals, such as cadmium and chromium. These elements are present in vegetables, fruits, fertilizer and soil [6–9] and might also be present in the yerba mate and consequently be ingested.

During the last century cadmium was used widely in industries. It can enter the environment from natural sources and anthropogenic activities and stays intact for long periods of time. Food is the major source of cadmium exposure in the general population. Chronic exposure to cadmium may cause several adverse health effects, including renal and bone damage [10]. Several occupational studies have reported an excess risk of lung cancer in humans from exposure to inhaled cadmium [11].

Chromium occurs in the environment primarily in two valence states, trivalent and hexavalent. Chromium (III) is an essential element for humans. Chronic inhalation exposure to chromium (VI) was reported to result in effects on the respiratory tract, with perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, asthma, nasal itching and soreness [12].

For the determination of cadmium or chromium the literature reports the use of voltammetry [13–15]; inductively coupled plasma-

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optical emission spectrometry (ICP OES) [16–18]; flame atomic absorption spectrometry (FAAS) [19]; high performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC-ICP-MS), [19]; inductively coupled plasma mass spectrometry (ICP-MS) [17,20]. The use of graphite furnace atomic absorption spectrometry (GF AAS) was reported by many authors. Borges et al. [7] determined cadmium in fertilizer samples using Pd/Mg as chemical modifier. Chromium was investigated in the same samples applying Mg as chemical modifier [8]. Dessuy et al. [21] investigated the presence of cadmium in pewter cups using Pd/Mg as chemical modifier.

With the use of high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS), equipped with a charge-coupled device (CCD) array detector, several limitations of classical line source AAS could be overcome, particularly those associated with spectral interferences [22]. Moreover, using HR-CS AAS, it is possible under certain conditions to determine two or more elements simultaneously or sequentially from the same sample aliquot. The sequential determination of cadmium and chromium is recent and only a few studies have been published reporting this application [23,24]. In this case, the absorption lines are well separated in different areas of the spectrum, and two different atomization temperatures are applied in the sequential determination, since the analytes have different volatilities. It is only important to make sure that the less volatile analyte is not lost during atomization of the more volatile one [24].

Besides enabling the sequential determination of elements from the same sample aliquot, the technique allows the introduction of solid samples directly into the atomizer. This essentially eliminates any sample preparation, which is time-consuming, often requires the use of hazardous acids and results in a significant dilution of the samples, and hence a decrease in the analyte concentration [25].

The goal of this work is the development of an analytical method for sequential determination of cadmium and chromium in yerba mate and leaves of yerba mate using HR-CS GF AAS with direct solid sample analysis. In order to investigate the amount of the metal that is leaching out to the hot water, the preparation of *chimarrão* was simulated and the results were compared.

## 2. Experimental part

### 2.1. Instrumentation

The samples were lyophilized using a freeze dryer Model ModulyonD (Thermo Electron Corporation, USA); a micro-mill A-11 Basic (IKA-Werke, Germany) was used for grinding the dry leaves.

All measurements were carried out using a Model contraAA 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany), equipped with a flame and a transversely heated graphite tube atomizer in two separate sample compartments. The spectrometer consists of a high-intensity xenon short-arc lamp operating in a hot-spot mode, a high resolution double monochromator and a CCD array detector with 588 pixels, 200 of which are used for analytical purposes. The analytical lines at 228.802 nm for cadmium and 357.869 nm for chromium were used, applying the center pixel (CP) and one adjacent pixel at each side (CP ± 1).

Transversely heated and pyrolytically coated solid sampling (SS) graphite tubes without a dosing orifice (Analytik Jena, Part no. 407-A81.303) and SS graphite platforms (Analytik Jena, Part no. 407-152.023) were used for all measurements, inclusive for the infusions. An M2P microbalance (Sartorius, Göttingen, Germany) was used for weighing the samples directly onto the SS platforms. A pre-adjusted pair of tweezers, which is part of the SSA 6 manual solid sampling accessory (Analytik Jena), was used to transfer the SS platforms to the atomizer. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the purge gas with a flow rate of 2.0 L min<sup>-1</sup> during all stages, except during atomization, where the internal flow was stopped.

### 2.2. Reagents

The nitric acid (Merck, Germany) used to prepare the aqueous calibration standards, was further purified by sub-boiling distillation in a quartz apparatus (Kürner Analysentechnik Rosenheim, Germany). Distilled (in a quartz apparatus) and deionized water (DDW) with a specific resistivity of 18.2 MΩ cm from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout. All containers and glassware were soaked in 1.4 mol L<sup>-1</sup> HNO<sub>3</sub> for at least 24 h and rinsed three times with DDW before use. The cadmium and chromium stock standard solutions (1000 mg L<sup>-1</sup> in 0.014 mol L<sup>-1</sup> nitric acid) were prepared from Titrisol concentrates (Merck, Germany). The working standards were prepared by serial dilution of the stock solution with 0.014 mol L<sup>-1</sup> nitric acid.

### 2.3. Sample preparation and reference material

The yerba mate samples used for this study were of two types: thirteen commercial samples and five leave samples. The leave samples were lyophilized for a period of 7 h. After this procedure, the samples were ground and the particle size was controlled using a 250 μm polyester sieve. The commercial samples passed for the same procedure, except for the lyophilization stage. The certified reference material used to check the accuracy of the methods was the NCS ZC 73014 - trace elements in tea - from the China National Analysis Center for Iron and Steel, Beijing, China. The optimized graphite furnace temperature program used for all the determinations is shown in Table 1.

### 2.4. Infusion preparation

In order to investigate the leaching of cadmium and chromium to the water an infusion was prepared, simulating the preparation of *chimarrão*. A mass of approximately 250 mg of the sample (yerba mate or leaves) was weighed into a beaker; 20 mL of DDW was added and covered with a watch glass. The infusion was heated to 60–70 °C for different time periods: 10, 30, 60 and 120 min. This experiment was realized in triplicate for each time period.

## 3. Results and discussion

### 3.1. Use of the modifier

It has been reported in the literature that chemical modifiers are not necessary for the determination sequential of cadmium and chromium. Zmozinski et al. [23] in the study of the tannin noted that using the NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> or Mg(NO<sub>3</sub>)<sub>2</sub> as chemical modifier, the absorbance signal did not change significantly for cadmium and chromium standard solutions and decreased significantly for the pine tannin samples. Duarte et al. [24], noted that the effect of a Pd/Mg modifier was not pronounced in the determination of cadmium in biomass samples. Thus, the use of chemical modifier was not considered in the present study.

**Table 1**  
Graphite furnace temperature program for the determination of cadmium and chromium in yerba mate samples.

Stage	Temp./°C	Ramp/°C s <sup>-1</sup>	Hold/s
Drying	90	5	20
Drying	110	5	10
Pyrolysis	450	100	20
Atomization	1500	3000	5
Change of wavelength			
Pyrolysis	1500	1000	1
Atomization	2500	3000	5
Cleaning	2550	1000	7

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