



# Multivariate optimization of a digestion procedure for bismuth determination in urine using continuous flow hydride generation and atomic fluorescence spectrometry



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## ABSTRACT

A sensitive method has been developed for the determination of bismuth in urine using continuous flow hydride generation and atomic fluorescence spectrometry (HG AFS). The conditions for bismuth hydride generation as well as some instrumental parameters were optimized using univariate methodology. Experimental conditions for sample digestion using nitric acid, hydrogen peroxide and a reflux system by “cold finger” were optimized employing a two-level full factorial design and a Box-Behnken design. Nitric acid used during sample preparation showed a negative effect on Bi determination by HG AFS, and a drying step was required after digestion. The established conditions for sample digestion allowed a low residual carbon content. Thus, the proposed method, using 5 mL urine, allowed bismuth determination with limits of detection and quantification of 0.02 and 0.08  $\mu\text{g L}^{-1}$ , respectively. Accuracy was assessed by the spike/recovery test using urine samples and the recoveries obtained varied from 91 and 97%. Precision expressed as relative standard deviation (RSD) was lower than 10%. This method was satisfactorily applied for the determination of bismuth in five urine samples. The bismuth contents found ranged from 0.30 to 0.66  $\mu\text{g L}^{-1}$ .

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## 1. Introduction

Bismuth and its compounds are widely used in the preparation of cosmetics, in chemical and metallurgic industries and in medicine. In medicine, it has been used for years in the production of drugs for treating gastrointestinal disorders [1]. Its use in antacids, peptic ulcer treatments and some kinds of gastritis treatments is due to the fact that bismuth has the ability to protect the gastric mucosa against various lesions [2]. The use of bismuth-based pharmaceuticals, as well as the use of this element in various industries, has contributed to its greater distribution in the environment, and also to the increased human exposure. Bismuth is considered a non-essential element for organisms. According to Breward [3], the normal daily intake is 5  $\mu\text{g}$  bismuth and may cause reversible toxicological clinical state when in excess. Among the disorders related to bismuth intoxication, it is possible to mention: hepatorenal impairment, neurologic dysfunction (encephalopathy), myoclonus and confusion [4,5].

Bismuth is poorly absorbed by the body, and excreted primarily in urine. In relation to the concentration of this metal, urine analysis is

an important way for the evaluation and differential diagnosis of diseases that present clinical characteristics similar to bismuth intoxication symptoms, such as Creutzfeldt-Jakob Disease and Hashimoto's encephalopathy [6,7]. Reynolds et al. [6] report, in a case study, a patient who was using bismuth salicylate to help control diarrhea and presented clinical symptoms of intoxication by bismuth, like progressive neurological decline. Bismuth levels in the patient's blood were far above the testing laboratory's threshold for bismuth toxicity, which is 200.0  $\text{ng mL}^{-1}$ . In urine, bismuth levels were 292.5  $\text{ng mL}^{-1}$ , where a normal value is usually lower than 1.0  $\text{ng mL}^{-1}$ . Teepker et al. [8], report the development of the typical clinical course of Bi encephalopathy in a 49 year-old woman with chronic gastric ulcers after Bi medication abuse for 5 years. Such cases show the severe consequences resulting from the availability of medication containing Bi for treating gastrointestinal disorders.

In analytical methods usually developed for bismuth determination, the sample passes through the digestion process, more specifically by acid digestion, using heating on a hot plate and beaker [9–13]. Samples are not often digested when ET AAS is used as a detection technique. In such cases, the sample is only diluted with acid medium. A good and simple alternative for sample digestion is the use of ceramic heating plates and Erlenmeyers, which can be easily coupled to “cold finger” reflux systems. The use of Erlenmeyers favors procedures that require a

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drying step, compared to digestion tubes, and the “cold finger” allows that acids used for digestion condense by reflux, decreasing the need for the addition of reagents during digestion, which are normally required in conventional open system procedures. This consequently reduces reagent consumption and the risk of contamination [14]. Digestion procedures can be optimized using multivariate design. It allows the simultaneous assessment of the effects of the variables and their interactions on the digestion procedure, as well as the simultaneous determination of the best condition. Advantages like reduction in the number of experiments and evaluation of the interactions between the studied variables (factors) are achieved. Thus, the consumption of reagents is lower and the laboratory works too [15,16]. This type of optimization stands out in relation to univariate optimization, which involves the optimization of one variable at a time, while the others are set at a value. Since it does not evaluate the effect of interactions between variables, it can generate inefficient optimizations, since it can provide critical conditions, not considering interactions when they are significant to the system.

Several methods have been developed for determination of bismuth in urine. They include spectrophotometry [9], Electrothermal Atomic Absorption Spectrometry (ETAAS) [12,17], Hydride Generation Atomic Fluorescence Spectrometry (HG AFS) [11], Hydride Generation Atomic Absorption Spectrometry (HG AAS) [10], Hydride Generation Inductively Coupled Plasma Optical Emission Spectrometry (HG ICP OES) [18] and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [19]. Hydride generation combined with atomic spectrometry is a well-established technique for the determination of elements that form stable volatile hydrides such as Se, Bi, As and Sb. The elimination of the nebulization step, increase in analyte transport efficiency and elimination of some atomization interferences are several advantages provided when using vapor generation methods. Under these conditions, better limits of detection are obtained [20–22]. The use of atomic fluorescence spectrometry associated with the hydride generation has been highlighted for elemental analysis due to the high sensitivity and to its relatively low cost [23]. This coupling has been successfully applied to the determination of hydride forming elements in several types of samples [11,24–27].

Thus, in this study, multivariate design was used to evaluate and optimize the experimental conditions for urine digestion using ceramic heating plates and “cold finger” reflux system to determine bismuth in urine by continuous flow hydride generation and atomic fluorescence spectrometry (CF HG AFS). Two-level full factorial and Box-Behnken designs were used to achieve this objective.

## 2. Experimental

### 2.1. Instrumentation

An atomic fluorescent spectrometer (Aurora Lumina 3300, Vancouver, Canada) was used as a detector. This spectrometer is coupled with a continuous flow hydride generation and fitted with a quartz tube atomizer with diffusion flame and automatic ignition, as well as a source of bismuth hollow cathode lamp (HCL) of high intensity. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as a carrier gas for bismuth hydride and as an shield gas. The experimental conditions and operating parameters are summarized in Table 1.

Digestion of urine samples was carried out using an Erlenmeyer flask with reflux system “cold finger” and ceramic heating plate (IKA C-MAG HS 10, Staufen, Germany). The analysis of digestion products for the determination of residual carbon were performed using an inductively coupled plasma optical emission spectrometer (ICP OES) (Varian Vista PRO, Mulgrave, Australia). Table 2 shows the operational conditions used during the determination of carbon by ICP OES.

Bismuth quantifications were also performed using ET AAS to compare the proposed method with another analytical method. For this was used a high-resolution continuum source graphite furnace atomic

**Table 1**

Settings and operating conditions of the HG AFS for Bi determination.

Parameters	Conditions
Bi-HCL, wavelength (nm)	223
Lamp current (mA)	100
PMT (V)	260
Flame composition	H <sub>2</sub> /air
Argon flow rate (carrier gas) (mL min <sup>-1</sup> )	500
Argon flow rate (shield gas) (mL min <sup>-1</sup> )	700
NaBH <sub>4</sub> flow rate (reducing solution) (mL min <sup>-1</sup> )	2.5
Acidified sample flow rate (mL min <sup>-1</sup> )	2.5
Signal integration time (s)	6

absorption spectrometer (HR-CS GF AAS) model ContrAA 700 from Analytik Jena AG (Jena, Germany). The graphite furnace temperature program used for bismuth determination is shown in Table 3.

### 2.2. Reagents and solutions

Analytical grade reagents were used in the development of this study and all solutions were prepared using high-purity water obtained from a Milli-Q water purification system (Millipore, Bedford, USA). In the digestion step, concentrated nitric acid (Merck, Germany) and hydrogen peroxide (30% v/v, Merck, Germany) were used. Standard bismuth solutions used in the experiments were prepared by diluting a 1000 mg L<sup>-1</sup> Bi stock solution (Merck, Germany) with hydrochloric acid. A 1.5% (w/v) sodium tetrahydroborate (Merck, Germany) solution prepared in a 0.5% (w/v) sodium hydroxide (Merck, Germany) solution were prepared daily for hydride generation.

### 2.3. Urine sample preparation - digestion procedure

Urine digestion was performed in 125-mL Erlenmeyer flasks. An aliquot of 5 mL sample and 5 mL concentrated HNO<sub>3</sub> were added to Erlenmeyers. Each flask was attached to a “cold finger” reflux system. Digestion was conducted at a temperature of 120 °C and under reflux by 25 min. During this period, 4 mL H<sub>2</sub>O<sub>2</sub> were gradually added. After 25 min, the reflux system was removed and samples were taken to dryness. After dried, the residue was dissolved in 2 mol L<sup>-1</sup> hydrochloric acid and transferred to 10-mL volumetric flasks.

### 2.4. Bismuth determination by HG AFS

For bismuth determination, digestion residues dissolved in 2 mol L<sup>-1</sup> HCl and 1.5% (w/v) NaBH<sub>4</sub> were transported separately with the aid of a peristaltic pump to the hydride generation cell, which works as a first gas–liquid separator. Both solutions were transported at a flow rate of 2.5 mL min<sup>-1</sup>, to the hydride generator, simultaneously, where the formation reaction of the hydride occurs. Volatile bismuth hydride (BiH<sub>3</sub>) and hydrogen were transported to a second gas–liquid separator and to the quartz cell with the aid of a carrier gas (argon). After the decomposition of hydride in H<sub>2</sub>/air flame, Bi is detected by AFS.

**Table 2**

Instrumental conditions for residual carbon determination by ICP OES.

Parameters	Value
RF generator (MHz)	40
RF incident power (kW)	1.0
Plasma gas flow rate (L min <sup>-1</sup> )	15.0
Auxiliary gas flow rate (L min <sup>-1</sup> )	1.5
Nebulizer argon gas flow rate (L min <sup>-1</sup> )	0.4
Carbon spectral line (nm)	247.856
Spray chamber	PTFE Sturman-Masters
Nebulizer	V-Groover

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