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Determination of mercury in phosphate fertilizers by cold vapor atomic absorption spectrometry

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ABSTRACT

In this paper, a method for the determination of mercury in phosphate fertilizers using slurry sampling and cold vapor atomic absorption spectrometry (CV QT AAS) is proposed. Because mercury (II) ions form strong complexes with phosphor compounds, the formation of metallic mercury vapor requires the presence of lanthanum chloride as a release agent. Thiourea increases the amount of mercury that is extracted from the solid sample to the liquid phase of the slurry. The method is established using two steps. First, the slurry is prepared using the sample, lanthanum chloride, hydrochloric acid solution and thiourea solution and is sonicated for 20 min. Afterward, mercury vapor is generated using an aliquot of the slurry in the presence of the hydrochloric acid solution and isoamylic alcohol with sodium tetrahydroborate solution as the reducing agent. The experimental conditions for slurry preparation were optimized using two-level full factorial design involving the factors: thiourea and lanthanum chloride concentrations and the duration of sonication.

The method allows the determination of mercury by external calibration using aqueous standards with limits of detection and quantification of 2.4 and 8.2 μg kg^{-1}, respectively, and precision, expressed as relative standard deviation, of 6.36 and 5.81% for two phosphate fertilizer samples with mercury concentrations of 0.24 and 0.57 mg kg^{-1}, respectively. The accuracy was confirmed by the analysis of a certified reference material of phosphate fertilizer that was provided by the National Institute of Standards & Technology (NIST). The method was applied to determine mercury in six commercial samples of phosphate fertilizers. The mercury content varied from 33.97 to 209.28 μg kg^{-1}. These samples were also analyzed employing inductively coupled plasma mass spectrometry (ICP-MS). The ICP-MS results were consistent with the results from our proposed method.

1. Introduction

Phosphor is an essential nutrient for agriculture. In this context, there is a global concern about contamination from phosphate fertilizers because they contain appreciable amounts of toxic elements such as arsenic, cadmium, chromium, lead and mercury [1–3]. Thus, there have been many published studies that address this subject. A study [4] evaluated the mercury contamination in a geographical area that was influenced by the emissions of phosphate fertilizer industries in Rio Grande, Brazil. The results demonstrated that the concentrations of mercury in soil collected close to the fertilizer factory reached levels of 800 μg kg^{-1}. Mirlean and Roisenberg [5] investigated the concentrations of cadmium and arsenic emissions during the production of phosphate fertilizer. The maximal concentration of cadmium was 9.3 mg kg^{-1} as a location that was close to the factory. The average concentration of cadmium was 3.5 mg kg^{-1}, which is approximately one hundred times higher than the established background concentration (0.03 mg kg^{-1}). The arsenic concentrations varied from 7.5 to 27.5 mg kg^{-1}. Ferreira [6] proposed a procedure for determining total arsenic and arsenic(III) in phosphate fertilizers and phosphate rocks employing slurry sampling and atomic absorption spectrometry. Two phosphate fertilizer samples were analyzed, and the total concentration of arsenic was in the range of 12.6–19.5 mg kg^{-1}. A method for determining cadmium in fertilizers has been proposed using slurry sampling and high-resolution continuum source

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graphite furnace atomic absorption spectrometry [7]. The cadmium content in the analyzed samples using this method varied from 0.07 to 5.5 $\mu g\, g^{-1}$. Mar and Okazaki [8] analyzed several phosphate rocks that were used for the production of fertilizers. The cadmium concentrations ranged from 0.15 to 507 $mg\, kg^{-1}$. Kane and Hall [9] proposed a procedure employing inductively coupled plasma optical emission spectrometry for the determination of arsenic, cadmium, cobalt, chromium, lead, molybdenum, nickel and selenium in fertilizers. The sample preparation was performed using microwave digestion.

Mercury has been traditionally determined using vapor generation coupled to analytical techniques such as atomic absorption spectrometry (CV AAS), fluorescence spectrometry (CV AFS), inductively coupled plasma optical emission spectrometry (CV ICP OES) and inductively coupled plasma mass spectrometry (CV ICP-MS) [10,11]. In general, these methods are simple and free of interferences. However, the quantification of mercury in phosphate matrices using these techniques is complicated because mercury(II) ions form strong complexes with phosphor compounds, thus hindering the reduction of mercury ions for the cold vapor formation of metallic mercury.

Slurry sampling constitutes a good alternative for the determination of mercury in phosphate fertilizers. This technique allows sample preparation without heating, which could cause mercury loss. Additionally, it does not require complete dissolution of the sample, which is a great advantage considering the low solubility of phosphate matrices [11,12]. Several authors have recommended the use of thiourea during the preparation of the slurry for the determination of mercury. Thiourea increases the efficiency of the extraction of mercury from the solid sample to the liquid phase of the slurry [13,14].

The chemometric tools of experimental design have been frequently used during the development of analytical methods [15–17]. These techniques allow method optimization with greater efficiency, lower reagent consumption and less manual work. Factorial design permits the identification of the effects of experimental factors on the studied processes [18,19].

This work proposes a method for the determination of mercury in phosphate fertilizer using slurry sampling and CV AAS. Because of the high concentration of phosphate in the matrices, lanthanum chloride is used as a release [20] agent.

2. Experimental

2.1. Instrumental

The determinations of mercury were performed manually employing an HS50 hydride generator system (Analytik Jena, GLE, Berlin, Germany) coupled to a CONTRAA 700 spectrometer (Analytik Jena, GLE, Berlin, Germany). This equipment consists of a high-intensity xenon short-arc lamp operating in the hot-spot mode, a high-resolution double monochromator and a CCD array detector. It was operated at a wavelength of 253.6519 nm and a current of 13 A; the mercury concentration was determined by the peak height.

The preparation of the slurries was carried out using a Model USC - 1850 ultrasonic bath UNIQUE (Indaiatuba, S.P., Brazil) with a temperature controller. The frequency was 25 kHz, and the power was 154 W.

The high-purity water used for the preparation of the solutions and slurries was obtained from a Milli-Q Plus water purification system from Millipore (Bedford, MA, USA). This system produces water with a resistance of 18.2 mΩ cm.

Table 1
Instrumental conditions for determination of mercury by ICP-MS.

Incident power 1400 W
Extraction −184 V
Plasma gas flow 13 $L\, min^{-1}$
Nebulizer flow 0.92 $L\, min^{-1}$
Dwell time 10 ms (peak jump)
Sweeps/reading 100
Measurements 3–30 scans
Conditions $^{140}Ce^{16}O^{+}/^{140}Ce^{+} < 2\%$ and $^{137}Ba^{++}/^{137}Ba^{+} < 3\%$
Differential aperture (DA) −40.8 V
Standard mode
Isotope ^{202}Hg
Hexapole bias −4.0 V
Pole bias −3.7 V
DA −40.8 V
Signal ^{115}In (1 $mg\, L^{-1}$) > 40 kcps

A quartz distillation system from Milestone (Bedford, MA, USA) was used for the distillation of analytical-grade nitric acid that was employed in all work.

The sample preparation for the determination of mercury using ICP-MS was carried out using a Start *D* model microwave digestion system (Millestone, Sorisole, Italy) equipped with 10 TFM® 100 mL vessels and a ceramic vessel jacket.

The analysis of the fertilizers by ICP-MS was performed using a quadrupole XSeries II inductively coupled plasma mass spectrometer (Thermo Scientific, Germany) fitted with a standard concentric nebulizer, Peltier-cooled spray chamber option and Xs interface. Ion extraction was conducted in the Xs+ mode, and the instrument was operated under standard conditions without use of the collision cell. Argon (99.997%, White Martins, Salvador, Brazil) was used as the carrier gas.

Table 1 shows the operational conditions employed during the determination of mercury by ICP-MS. The monitored isotope was 202.

2.2. Reagents

The calibration curves for the determination of mercury by CV AAS were prepared daily in the range of 0.16–25.00 $\mu g\, L^{-1}$ by the serial dilution of a stock solution (1000 $mg\, L^{-1}$) from Merck (Germany) with a 0.05% (v/v) nitric acid solution. A 1% (w/v) sodium tetrahydroborate solution that was stabilized with 0.05% (w/v) sodium hydroxide was the reducing reagent. This reagent was also prepared daily using analytical grade reagents from Merck and filtered through a 0.45-μm filtration membrane. The 1.0% (w/v) thiourea solution was prepared by dilution of the reagent from Merck with high-purity water. The lanthanum chloride used was obtained from Merck. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the carrier gas for the mercury vapor.

The accuracy was confirmed using the standard reference material SRM 695 Trace Elements in Multi-Nutrient Fertilizer, which was provided by the National Institute of Standards and Technology (Gaithersburg, MD, USA).

The analytical curves used for the determination of mercury by ICP-MS were prepared with concentrations in the range of 0–25 $\mu g\, L^{-1}$ in 2% ultrapure nitric acid. Internal standardization was applied with solutions of 50 $\mu g\, L^{-1}$ concentrations of ^{45}Sc, ^{72}Ge, ^{103}Rh and ^{205}Tl.

2.3. Slurry preparation and the determination of mercury by CV AAS

A total of 0.2 g fertilizer sample, 0.4 g lanthanum chloride, 4.0 mL 6 $mol\, L^{-1}$ hydrochloric acid, 3 mL 1% (w/v) thiourea and 50 μL hydrogen peroxide were added to a 10.0 mL volumetric