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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.

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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

flask. Afterward, this mixture was sonicated at room temperature for 20 min and subsequently brought up to the final volume with milli-Q water. Then, a 3.0 mL aliquot of the slurry was transferred to the reaction flask of the hydride generator. A total of 1.3 mL 6 mol L^{-1} hydrochloric acid and 300 μL isoamyl alcohol were added and deionized water was added to a final volume of 10 mL. The sodium tetrahydroborate solution was added to the reaction flask over a period of 6 s, and the cold vapor that was generated was carried into the quartz *T* tube, which was coupled to the AAS spectrometer.

The samples of standard reference material were prepared using the same conditions.

2.4. Sample preparation using a microwave oven

The digestion was performed using 0.2 g fertilizer sample, followed by the addition of 2.0 mL concentrated nitric acid, 3.0 mL hydrogen peroxide and 3.0 mL ultra-pure water. The program of the microwave oven was established in seven steps at a pressure of 35 bar as shown in Table 2. In the seventh step, the system was cooled for 30 min using forced ventilation. After digestion, the samples and the blank solutions were transferred to plastic flasks, and deionized water was added to achieve a total volume of 25 ml. This procedure was performed in triplicate for each sample that was analyzed.

2.5. Optimization of the experimental conditions – factorial design

The experimental conditions established for the preparation of the slurries were performed using a two-level full factorial design involving the following factors that affected the absorbance of mercury, which was used as the chemometric response: thiourea and lanthanum chloride concentration and the duration of sonication. The order of all experiments was randomized. The experimental conditions for these factors are presented in Table 3. All the chemometric data were processed using the statistical program Statistica 6.0.

The curvature test in the factorial design allows the evaluation of the chemometric response around the central point of the experiments [21,22]. For this test, the curvature was calculated using the following equation: Curvature $= R_{FD} - R_{CP}$, where R_{ED} is the average of the responses obtained from experiments specified by the factorial design, and R_{CP} is the average of the responses obtained for the central point. Positive curvature results indicate a condition of minimal chemometric response that is close to the central point. Negative results indicate a condition of maximum chemometric response around the central point [21].

Table 2
Microwave heating program for sample digestion of phosphate fertilizer.

Step	Time ($_{min}$)	Power (W)	*T* (°C)
1	5	800	80
2	2	800	80
3	4	1000	120
4	2	1000	120
5	10	1000	180
6	10	1000	180
Ventilation	30	–	–

Table 3
Optimization of the preparation of the slurry for Hg determination by CV AAS.

Experiment	[Thiourea] (w/v)	[$LaCl_3$] (w/v)	Sonication time ($_{min}$)	Analytical signal
1	−1 (0.00%)	−1 (0.0%)	−1 (10)	0.00320
2	1 (0.30%)	−1 (0.0%)	−1 (10)	0.04629
3	−1 (0.00%)	1 (10.0%)	−1 (10)	0.01900
4	1 (0.30%)	1 (10.0%)	−1 (10)	0.05442
5	−1 (0.00%)	−1 (0.0%)	1 (30)	0.00602
6	1 (0.30%)	−1 (0.0%)	1 (30)	0.04718
7	−1 (0.00%)	1 (10.0%)	1 (30)	0.02371
8	1 (0.30%)	1 (10.0%)	1 (30)	0.06255
9 (CP)	0 (0.15%)	0 (5.0%)	0 (20)	0.05885
10 (CP)	0 (0.15%)	0 (5.0%)	0 (20)	0.05706
11(CP)	0 (0.15%)	0 (5.0%)	0 (20)	0.05385

Sample mass = 0.2 g; slurry volume = 10.0 mL.

3. Results and discussions

3.1. Conditions for the determination of mercury using CV HR CS AAS

The quantification of mercury was performed using the HF-50 module coupled to the HR CS AAS spectrometer. The experimental conditions that were related to the concentration of the hydrochloric acid solution and the volume and concentration of the sodium tetrahydroborate solution were optimized in our laboratory during the development of a previous work.

$[HCl] = 6\ mol\ L^{-1}$, $[NaBH4] = 1.0\%$ and $V_{NaBH4} = 4.0\ mL$

3.2. Experimental conditions for the preparation of the fertilizer slurries

A full two-level factorial design was performed to determine the experimental conditions for the preparation of the fertilizer slurries. The factors involved were thiourea and lanthanum chloride concentrations and the duration of sonication. The experimental conditions, the coded levels of these factors and the obtained chemometric response (analytical signal) are shown in Table 3.

The results obtained by factorial design were evaluated, and the effects of the factors and their interactions were calculated. The values of the main effects expressed as interval confidence were

$$Effect_{[Thiourea]} = +0.03963 \pm 0.00771$$

$$Effect_{[Lanthanumchloride]} = +0.01425 \pm 0.00771$$

$$Effect_{Sonicationtime} = +0.00413 \pm 0.00771$$

Thus, for the experimental conditions of thiourea concentration (0.00–0.30%), lanthanum chloride concentration (0.0–10.0%) and duration of sonication (10–30 min), the obtained effect values can be interpreted as follows:

The thiourea concentration has a positive effect. Consequently, the increase of this factor increases the analytical signal. The chemical explanation for this observation is that this reagent improves the mercury extraction from the solid sample to the liquid phase of the slurry.

The lanthanum chloride concentration also has a positive effect, and as predicted, the increase of this reagent increases the analytical signal. In this case, the explanation is that lanthanum chloride acts as release agent due to the strong reactions between the mercury(II) ion and phosphate ion from the matrix.

The thiourea concentration affects the process of cold vapor generation three times (0.03963/0.01425) more than the lanthanum chloride concentration.

As shown in Table 3, the analytical signals are very low for the minimum concentrations of thiourea and lanthanum chloride (experiments 1 and 5).
The duration of sonication has no significant effect on the generation of cold vapor. Thus, experiments performed in the range of 10–30 min did not affect the analytical signal.
All possible interactions between the factors are not significant.
The experimental errors were calculated by results from triplicate measurements of the central point.

The curvature test was also applied using the data shown in Table 3. A negative curvature was observed, which indicates that near the region of the central point there is an experimental condition of maximum analytical signal.

3.3. Evaluation of lanthanum chloride as a release agent

Additional experiments were performed to evaluate the performance of lanthanum as a release agent during the determination of mercury by HG AAS. Slurries were prepared following the general procedure that was proposed in Section 2.3. The lanthanum chloride mass varied from 0.00 to 1.00 g. Other tests were also developed using a mercury solution with a concentration of 0.30 $\mu g\,L^{-1}$ without phosphate. The data obtained for mercury solutions and slurries are shown in Table 4.

The results that are shown in Table 4 demonstrate that for the range studied (0.0–10.0%), lanthanum chloride does not affect the reaction or the formation of metallic mercury, and it also proves to be an efficient release agent for the elimination of interference from the matrix. Lanthanum chloride with a concentration of 4% (w/w) is sufficient for the determination of mercury in fertilizer slurries.

Thus, considering the interpretation of the obtained results, the experimental conditions that were established for the preparation of the slurries were thiourea concentration of 0.30%, lanthanum chloride concentration of 4.0% and duration of sonication of 20 min.

3.4. Method validation studies

The proposed method allows the determination of mercury in phosphate fertilizer samples by CV AAS with analytical curves in the range of 0.16–25.00 $\mu g\,L^{-1}$ and limits of detection and quantification [23] (calculated as 3 δ/s and 10 δ/s, where δ is the standard deviation of the blank solution and s is the slope of the analytical curve employed) of 0.05 and 0.16 $\mu g\,L^{-1}$, respectively. The calibration technique of the method was evaluated by comparison of the slopes of the curves obtained with aqueous standards and with analyte addition in a phosphate fertilizer sample. The regression equations with aqueous standards and analyte addition were $A_{Hg}=0.0767C+0.0086$ ($R^2=0.9991$) and $A_{Hg}=0.0773C+0.0293$ ($R^2=0.9957$), respectively where A is the integrated absorbance and C is the concentration of Hg in $\mu g\,L^{-1}$. Considering the high similarity among the slopes of the curves, this method allows the quantification of mercury using external calibration with aqueous standards. The precision, expressed as relative standard deviation, was 6.36 and 5.81% for two fertilizer samples with mercury concentrations of 0.24 and 0.57 $mg\,kg^{-1}$, respectively. The limits of detection and quantification that were calculated for sample masses of 0.20 g were 2.4 and 8.2 $\mu g\,kg^{-1}$, respectively. The accuracy of the method was confirmed by analysis of the standard reference material of 695 NIST phosphate fertilizer that was furnished by the National Institute of Standards and Technology. The mercury concentration that was determined using the proposed method (1.962 ± 0.046 $mg\,kg^{-1}$) agrees with the certified value (1.955 ± 0.036 $mg\,kg^{-1}$).

Table 4
Evaluation of lanthanum chloride as release agent.

Experiment	[$LaCl_3$] (%)	Analytical signal for Hg solutions[a]	Analytical signal for slurries
1	0	0.03081	0.00183
2	2	0.03168	0.02197
3	4	0.03144	0.02498
4	6	0.03170	0.02479
5	8	0.03134	0.02495
6	10	0.03256	0.02523

[a] [Hg]=0.30 $\mu g\,L^{-1}$ without phosphate.

3.5. Application – mercury determination in fertilizer samples

The proposed method was applied to the determination of mercury in six different phosphate fertilizers. The samples were acquired in Salvador City, Brazil in March – April 2011. The results obtained, as confidence intervals (95% level), and the types of fertilizer are shown in Table 5. The mercury content found in the samples varied from 0.24 to 0.57 $mg\,kg^{-1}$.

These six samples were also analyzed by ICP-MS after complete digestion employing microwave radiation. The concentrations of mercury that were detected by this method are presented in Table 5. The results obtained by CV AAS were compared with the results achieved by ICP-MS using the linear regression method. The obtained equation was as follows:

$$[\text{CV AAS}] = 1.03 \pm 0.15\,[\text{ICP–MS}] - 0.04 \pm 0.06$$

The evaluation of this equation demonstrates that there is no evidence for a systematic difference between the two methods that were employed for the determination of mercury in the fertilizer samples, considering that the obtained slope and intercept do not differ significantly from the "ideal" values of 1 and 0, respectively.

The amount of fertilizer required for phosphor control in soil depends on the P_2O_5 content present in the fertilizer. Moreover, the maximum limit of mercury content in phosphate fertilizer that is regulated by the Brazilian Government also depends on the P_2O_5 content, which is represented by the following expression [24]:

$$\text{Maximum limit of mercury } (mg\,kg^{-1}) = 0.05 \times P_2O_5 \text{ content (expressed as \%)}$$

Thus, the maximum allowable limits for mercury for the six analyzed fertilizers were calculated and are shown in Table 5. The

Table 5
Determination of mercury in phosphate fertilizer samples[a].

Sample	Type of fertilizer	P_2O_5 (%)	Hg found ($mg\,Kg^{-1}$)		Maximum limit[b] of Hg ($mg\,Kg^{-1}$)
			CV AAS	ICP-MS	
1	Simple superphosphate	18	0.32 ± 0.06	0.28 ± 0.01	0.90
2	Triple superphosphate	42	0.36 ± 0.05	0.32 ± 0.03	2.10
3	Mono-ammonium phosphate	52	0.37 ± 0.07	0.35 ± 0.01	2.60
4	Natural phosphate 1	30	0.24 ± 0.05	0.21 ± 0.02	1.50
5	Natural phosphate 2	33	0.32 ± 0.03	0.31 ± 0.01	1.65
6	Organic phosphate	14	0.57 ± 0.03	0.55 ± 0.01	0.70

[a] Results as interval confidence at 95% level.
[b] Maximum limit stipulated by Brazilian Government.

results demonstrated that the concentrations of mercury found in the six analyzed samples are lower than the maximum limit stipulated by the Brazilian Government [24].

4. Conclusions

The full two-level factorial design demonstrated that the experimental conditions that were established for thiourea concentration and lanthanum chloride concentration are statistically significant for the generation of cold vapor of metallic mercury.

The matrix interference due to the complexation reaction between mercury(II) ion and the large amount of phosphate ion from the sample was eliminated by the addition of lanthanum chloride, which acted as a release agent.

The phase transfer of mercury from the solid sample to the slurry was improved using thiourea as an auxiliary complexing agent.

The proposed method has a limit of quantification, precision and accuracy that is necessary for the analysis of phosphate fertilizer samples.

The detected concentrations of mercury in the analyzed phosphate fertilizer samples are lower than the maximum limit that is allowed by the Brazilian Government.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.11.001.

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