



Determination of toxic elements in glass beads used for pavement marking by ICP OES

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ABSTRACT

A simple and rapid method for the simultaneous determination of As, Sb and Pb in glass beads used for pavement markings on highway surfaces by axial view inductively coupled plasma optical emission spectrometry is presented. Three sample preparation approaches using a 3:1 mixture of HNO₃ and HF were evaluated: (01) an open beaker approach; (02) a microwave-assisted digestion system, based on EPA method 3052 and (03) an ultrasound-assisted digestion. To react with the excess of residual fluoride, H₃BO₃ and ZrOCl₂ were investigated. Spectral interference was evident when ZrOCl₂ was used for determination of As. Ultrasound-assisted digestion using 3 mL of HNO₃ and 1 mL of HF for 1 h at 40 kHz followed by addition of H₃BO₃ was chosen for in-depth study. Quantification limits (10 s, n = 10) based on a 0.1 g subsample diluted to 50 mL were: 30 mg kg⁻¹ for As (193.696 nm), 10 mg kg⁻¹ for Sb (206.834 nm) and 5 mg kg⁻¹ for Pb (220.353 nm). Analysis of spiked samples provided recoveries in the range of 87 to 104% for all analytes. Of nineteen Brazilian and imported samples analyzed, As was present above the quantification limit in five, Sb in one and Pb in almost all. Some samples, all imported, showed values above the limit allowed by the Brazilian legislation, i.e., 200 mg kg⁻¹ for As, Sb and Pb. Solubility tests showed high levels of As leaching for all imported samples, above the specification limit. Leachability tests showed that the glass beads cannot be classified as toxic materials; however, the release of potentially toxic elements could cause some environmental risks.

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1. Introduction

Highway markings, consisting mainly of vertical signs as well as horizontal markings and traffic signals, serve to regulate, warn and guide users of a road, so it can be easily understood and perceived. Thus, glass beads are embedded on highway pavement markings to provide retroreflectivity, which is an optical phenomenon that plays a crucial role in maintaining the guiding function of the highway striping to ensure safe driving. The phenomenon of retroreflection occurs when the incident light is reflected from the material in the same direction as the emitting source. In the case of glass beads embedded in the marking material, the light emitted by a vehicle's headlight reaches the glass beads and is redirected to the vehicle, allowing improved night vision. These beads are incorporated in two ways – either by being spread onto the top surface of the road during painting (“drop-on beads”) or by being blended into the paint material during manufacture (“intermix beads”). Integrating glass beads of good optical quality is essential to ensure clear visibility at night [1–4].

Glass beads are manufactured by melting and reforming waste glass, i.e., mainly from recycled glass. Several organizations debate the merits of

such material, since many companies specializing in highway markings use inexpensive grades of imported glass beads in order to reduce the cost of the process. Historically, glass manufacturers used toxic elements – arsenic, antimony and lead – as clearing, discoloring and refining agents. Eventually, the glass beads degrade and end up in drains, potentially affecting ground water. The same potential impact on groundwater and the surrounding areas occurs when road markings are removed as part of normal routine road maintenance [1–4]. The American Association of State Highway Transportation Officials (AASHTO) has recommended that toxic elements in glass beads used for highway markings must meet a maximum allowable limit of 200 ppm for arsenic, 200 ppm for lead, and 200 ppm for antimony [5]. These limits were also adopted by the Brazilian Association of Technical Standards (ABNT) [6]. To provide tools for legislative compliance of these standards, it is essential to develop reliable analytical methods for the determination of these analytes in glass matrices. The glass used for manufacturing highway markings is the soda–lime silica glass, typically composed primarily of 71–75% (m/m) silica (SiO₂) derived mainly from sand, 12–16% (m/m) sodium oxide (NaO) produced from soda ash (Na₂CO₃), and 10–15% (m/m) calcium oxide (also known as lime from limestone – CaCO₃). A number of other minerals of lower concentrations are needed to impart specific properties to the glass, including lead oxides (PbO and Pb₃O₄) for increased refractive index, antimony oxide (Sb₂O₃) and arsenic oxide (As₂O₃) as fining agents and decolorizers [4].

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Traditionally, the use of an atomic spectrometry technique of adequate sensitivity for determination of trace metals and constituents in siliceous matrices requires total dissolution of the sample, usually accomplished by a combination of acids, involving HF [7], HF/HNO₃/HClO₄ [8,9], HF/HCl [10], HF/HNO₃ [11], and HF/HNO₃/HCl [8,12–14]. Frequently, sample digestion is conducted in a closed system under pressure with microwave heating [9,11–14]. Specifically for glass beads intended for highway marking, Jahan et al. [4] evaluated total digestion on a hot plate with HNO₃/HF followed by determination of As, Sb and Pb using ICP-MS (inductively coupled plasma mass spectrometry) and the non-destructive technique of XRF (X-ray fluorescence spectrometry). Results revealed that the XRF correlated well with digestion and ICP-MS analysis. They also studied more environmentally relevant conditions by application of leaching tests from the US Environmental Protection Agency – EPA 1311 (TCLP: toxicity characteristic leaching procedure) and EPA 1312 (SPLP: synthetic precipitation leaching procedure). The most important factors affecting leaching were pH and time. Boulanger et al. [15] also studied leaching of recycled glass, with total analyses by XRF and by ICP-MS following potassium hydroxide fusion for determination of As, Cd, Cr, Cu, Pb, Hg, Ni and Zn. Cadmium, Cr, Cu, Hg and Ni were not observed in glass bead samples by XRF for any samples. The presence of titanium did not allow for qualitative confirmation of Pb and Zn. Arsenic was qualitatively identified. The quantitative determination of As, Cd, Cr, Cu, Pb and Ni was made by ICP-MS following potassium hydroxide fusion, but the possibility of loss of elements by volatilization, such as arsenic, which can affect the accuracy of the analysis, was not evaluated. Significant interferences were observed for Hg and Zn, so these analytes were removed from the list included in the study. Boulanger et al. [15] also investigated the leaching potential of toxic elements from the provided recycled glass bead samples under laboratory conditions: using a peristaltic pump, de-ionized water was passed through the columns filled with glass bead samples. The column effluents were collected and the analytes were determined by ICP-MS. The pH, ultraviolet light exposure, temperature and abrasion effects were evaluated.

The Brazilian Association of Technical Standards (ABNT) prescribes the EPA's total digestion method (EPA 3052), that employed HNO₃ and HF through microwave-assisted digestion [11] following determination of the analytes by ICP OES (inductively coupled plasma optical emission spectrometry) and/or X-ray fluorescence (XRF EPA 6200) [16] for the total amount of toxic elements present in glass beads. The objective of this study was to develop an alternative ICP OES-based methodology for analysis of arsenic, lead and antimony in samples of glass beads used for road markings. The more environmentally relevant processes of element release from glass beads were investigated with leaching and solubility tests using the Brazilian or the EPA norms.

2. Experimental

2.1. Instrumentation

Measurements were conducted using a simultaneous axial view ICP OES spectrometer, model VISTA PRO (Varian, Mulgrave, Australia). Peak height emission intensities were measured for all analytes. Experimental parameters are summarized in Table 1. In order to avoid attack by residual HF on the torch and other quartz components, an inert system was used, consisting of a V-groove nebulizer (made of Teflon®), Sturmman Master spray chamber (made of Teflon®) and an alumina injector tube. This system is also adequate for solutions with considerable dissolved salt content, and proved to be very stable in all experiments. >Argon of 99.996% purity was supplied by White Martins (São Paulo, Brazil). A microwave oven, model MDS 2100 (CEM Co., Matthews, NC, USA), was employed for dissolution of the samples in acid. A model USC 1400 (40 kHz) ultrasonic bath from Unique Group (São Paulo, Brazil) was used to aid the dissolution of the samples and a model SM 002 mill

Table 1
ICP OES instrumental parameters.

Radiofrequency	40 MHz
Forward power	1.5 kW
Plasma gas flow rate	15.0 L min ⁻¹
Auxiliary gas flow rate	1.5 L min ⁻¹
Nebulizer pressure	160 kPa and 180 kPa ^a
Nebulizer type	V-groove and concentric glass K ^a
Spray chamber	Sturman Master and cyclonic ^a
Replicate read time	3 s
Replicates	5
Torch type	Demountable torch with a 1.8 mm I.D. alumina injector tube
Analytical lines	193.696 nm (As); 206.834 nm (Sb) and 220.353 nm (Pb)

^a Conditions for the leachability and solubility tests.

from Equilab (Minas Gerais, Brazil) was used to grind the samples. The samples were examined by SEM (scanning electron microscope, model Quanta 200-FEI Company, Oregon, USA) both before and after the solubility tests.

2.2. Reagents and samples

All chemicals were of analytical grade. High purity water (resistivity of 18.2 MΩ cm) was obtained by deionization (DIW) in a Milli-Q system (Bedford, MA, USA). The following reagents were used: 65% v/v HNO₃ (Merck, Darmstadt, Germany, no. 1.00456); 37% v/v HCl (Merck, no. 1.00317); 40% v/v HF (Merck, no. 1.0034); CH₃COOH (Merck, no. 21606); NaOH (Merck, no. 1.06498); and a 4.4% m/v solution of H₃BO₃ (Merck, no. 1.00165). A 0.56 mol L⁻¹ solution of ZrOCl₂·8H₂O (Vetec, Rio de Janeiro, RJ no. 574) was prepared by dissolving 91 g of ZrOCl₂·8H₂O in 300 mL of DIW followed by addition of 65 mL HCl and dilution to 500 mL with DIW in a volumetric flask. Millipore 0.45 μm cellulose ester filters (no. HAWP04700, Billerica, MA, USA) were used in conjunction with a 47 mm Millipore Sterifil (no. XX11.047.00) vacuum filtration system. Standard solutions containing 1000 μg mL⁻¹ of As (AccuStandard no. ICP-03N-1), Sb (AccuStandard no. ICP-02N-1) and Pb (AccuStandard no. ICP-29N-1) were used to prepare the multi-element standard solutions used for calibration. A concentration range from 0.1 to 2 mg L⁻¹ of the analytes and for spiking the samples was used. Nineteen samples of glass beads were provided by various manufacturers: fourteen from Brazil and five imported from the same country.

2.3. Analytical procedures

2.3.1. Total dissolution

Samples were ground in a mill and passed through a 150 μm sieve. Three different procedures were investigated; samples numbered 13 and 15 were used for this purpose.

2.3.1.1. Procedure 01 (digestion in an open system). An approximately 0.1 ± 0.0500 g subsample was weighed into a 50 mL Teflon beaker and 3 mL of HNO₃ and 1 mL of HF were added. The acids were slowly evaporated under heating at approximately 250 ± 5 °C, to small volume (almost to dryness) [17]. After cooling, 10 mL of 4.4% (m/v) H₃BO₃ was added and the solution was filtrated and made up to 50 mL with DIW in a volumetric flask.

2.3.1.2. Procedure 02 (microwave system). An approximately 0.1 ± 0.0500 g subsample was weighed into an appropriate vessel and 3 mL of HNO₃ and 1 mL of HF were added. The vessel was closed with a cap and heated in the microwave system using the following program: ramp the temperature to 180 ± 5 °C over approximately 5 min and hold at this temperature for 10 min [11]. After cooling to room temperature, 10 mL of 4.4% (m/v) H₃BO₃ was added and the solution was then diluted to 50 mL with DIW in a volumetric flask.

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