HEAVY METALS IN GLASS BEADS USED IN PAVEMENT MARKINGS

A Thesis

by

KIRANMAYI PRAKASH MANGALGIRI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2012

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Bryan Boulanger
Committee Members,	Paul Carlson
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Head of Department,	John Neidzwecki

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ABSTRACT

Heavy Metals in Glass Beads Used in Pavement Markings. (May 2012)

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Pavement markings are vital for safely navigating roadways. The nighttime visibility of pavement markings is enhanced by addition of retroreflective glass beads, most of which are made from recycled glass. Concern has been raised over the presence of heavy metals in glass beads used in pavement markings and their effect on human and environmental health. Based upon the potential risk associated with the presence of arsenic and lead in the glass beads, two Bills are currently being considered before the 112th Congress of the United States of America seeking to set a maximum permissible limit for the amount of arsenic and lead in glass beads used within pavement marking systems on domestic roadways. This study was designed to support legislative decision making by providing data necessary for risk assessment.

The experiments carried out provide: an analysis of glass bead metal content and extractability; an evaluation of the relationship between arsenic content of the glass

beads and their retroreflective performance; an evaluation of analytical methods used to measure the total bead metal content; and an analysis of samples of glass bead and soil mixture from a glass bead storage site used to determine site-specific metal concentrations in the soil media.

Mean arsenic content, measured using the Pacific Northwest National Laboratory's KOH fusion digestion, in all the glass beads examined ranged from 11 ppm to 82 ppm, while mean lead content, measured using KOH fusion digestion, ranged from below quantification limit to 199 ppm. Total metal content measurements indicated a high amount of variability in the glass bead samples; most likely associated with the use of recycled glass feed during manufacturing. The relationship between the retroreflective performance and the arsenic content of the glass beads was analyzed and a weak but positive correlation was observed between the two factors. However, a more detailed study is required to evaluate the relationship between arsenic content and retroreflectivity. Different methods to evaluate the total metal content in glass beads were compared; it is recommended that any analytical method may be used, as long as the standard reference material is reproduced within the range of concentration expected in the glass beads. In the analysis of the field site samples of soil containing glass beads obtained from a glass bead storage and transfer facility, the mass content of beads in the soil varied from a mean of 19% to 78% depending on the location within the facility. However, a detailed analysis with larger number of samples must be performed to evaluate the effect of glass beads on the total arsenic content of the soil.

DEDICATION

To my parents

ACKNOWLEDGEMENTS

I would like to express my heartfelt gratitude to Dr. Bryan Boulanger, my advisor, for his guidance and support throughout my time at Texas A&M University. Without his direction and encouragement from the initial to final stages of this study, my education would be lacking. He is truly an inspiration and I thank him for his words of advice.

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I am grateful to my parents and my family for believing in me and supporting me in my endeavors. I am blessed to have wonderful friends at my research lab, in my department, from the university and back home. I thank them all for their encouragement and their support.

NOMENCLATURE

AASHTO	American Association of State Highway and Transportation Officials
ACS	Americal Chemical Society
AGBMA	American Glass Bead Manufacturers Association
BDL	Below Detection Limit
BQL	Below Quantification Limit
CFR	Code of Federal Regualations
CPG	Compliance Policy Guidance
CRT	Cathode-Ray Tube
DI	De-Ionized
DOT	Department of Transportation
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
FDOT	Florida Department of Transportation
FHWA	Federal Highway Administration
GFAA	Graphite Furnace Atomic Absorption
HF	Hydroflouric Acid
ICP-MS	Inductively Coupled Plasma - Mass Spectroscopy
KOH	Potassium Hydroxide
MCL	Maximum Contaminant Level

MDL   Method Detection Limit

N   Newton

NIST   National Institute of Standards and Technology

NJIT/RU   New Jersey Institute of Technology/Rowan University

PQL   Practical Quantitation Limit

SBRC   Solubility/Bioavailabilty Research Consortium

SRM   Standard Reference Material

SPLP   Synthetic Precipitation Leaching Procedure

TAMU   Texas A&M University

TCLP   Toxicity Characteristic Leaching Procedure

TxDOT   Texas Department of Transportation

USA   United States of America

UV   Ultraviolet

$mcd/m^2 \cdot lux$ millicandela per square meter per lux

mg/L   milligrams per liter

ppb   parts per billion (μg/L or μg/kg)

ppm   parts per million (mg/L or mg/kg)

rpm   rotations per minute

μg/L   micrograms per liter

μg/kg   micrograms per kilogram

μm   micrometers

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1. INTRODUCTION

Pavement markings are important for public safety because they convey important roadway information to drivers. Therefore, pavement markings need to be visible at all times; especially during low visibility conditions such as night time and wet weather. The visibility of pavement markings under poor visibility conditions is enhanced by the addition of glass beads that impart retroreflectivity to the marking. Retroreflectivity is the phenomenon by which glass beads reflect light in a particular direction. When used in pavement markings, the glass beads reflect the light from vehicle headlights back towards the driver. The glass beads used in pavement markings, generally made from recycled glass, contain heavy metals including lead and arsenic (Jahan et al., 2010; Boulanger et al., 2011). Due to factors such as physical and environmental stress, metals may leach out of the glass beads and enter the environment (Jahan et al., 2010; Boulanger et al., 2011).

Concern has been raised over the effect of this leaching on human and environmental health; particularly on the occupational safety of workers who are subject to exposure to glass beads during manufacturing, transport and application of glass beads to roadway surfaces. Currently, glass beads used in pavement marking systems are required to comply with specifications set by the American Association of State Highway and Transportation Officials (AASHTO). However, AASHTO M247 specifications do not

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This thesis follows the style of Journal of Environmental Quality.

currently address chemical composition of glass beads including metal content of the glass bead (AASHTO, 2008). Based upon the potential risk associated with the presence of arsenic and lead in the glass beads, two Bills are currently being considered before the 112th Congress of the United States of America (USA) seeking to set a maximum permissible limit for the amount of arsenic and lead present in glass beads used within pavement marking systems on domestic roadways. Additional legislation is also proposed within several states to limit the maximum amount of arsenic and lead in glass beads.

This study was designed to support legislative decision making by providing data necessary for risk assessment. The experiments carried out provide: an analysis of glass bead metal content and extractability, an evaluation of the relationship between arsenic content of the glass beads and their retroreflective performance, an evaluation of analytical methods used to measure the total bead metal content, and an analysis of samples of glass bead and soil mixture from a glass bead storage site used to determine site-specific metal concentrations in the soil media. The project has four aims used to provide the decision making support, including:

Aim 1. Evaluate total, extractable and bioaccessible metal content in the glass beads:
The metal content in the glass beads will be estimated as a function of three independent test methods – the total metal content measured using the Pacific Northwest National Laboratory's KOH fusion digestion, the extractable metal content measured through

EPA Method 3050B (EPA, 1996a), and the bioaccessible metal content of the glass

beads measured through the Oral Bioaccessibility Assay developed by the

Solubility/Bioavailability Research Consortium (SBRC) (Kelley et al., 2002).

Differentiating between total, extractable, and bioaccessible metal content is important

because the amount of metal potentially leaching from the glass beads into the

environment, and the amount that will be bioaccessible will be significantly different

from the total metal content of the bead. The result of this analysis will be used for

accurate risk characterization and impact assessment. Specifically, the results of this

experiment will allow for realistic exposure characterization to be included in the risk

assessment process, including occupational exposure and residential exposure due to

proximity.

Aim 2. Evaluate the relationship between total arsenic content in glass beads and the

retroreflective performance of the beads: The arsenic content in glass beads will be

statistically compared to the retroreflective performance of the glass beads to determine

if a relationship exists between the total arsenic content and the retroreflective

performance. Arsenic was used as a high temperature oxidant to remove impurities

during glass manufacturing process, and the research is interested to establish if

retroreflective performance is related to high arsenic content (Wright andUnited States

Army Ordnance Department, 1921). Any existing relationship between arsenic content

and retroreflectivity would have implication on the decision making process.

Aim 3. Compare different methods of estimating the total metal content in glass beads

used in pavement markings: Currently, there is no standard test that is prescribed for

measuring the total metal content in glass beads within the proposed legislation. EPA's

hydrofluoric acid (HF) digestion (EPA Method 3052) (EPA, 1996b) is considered the

standard test for measuring metal content in solids. However, this method is not widely

available in commercial laboratories and requires highly specialized equipment and

training to work safely with HF. Hence, several alternative methods of measuring total

metal content of glass beads used in pavement markings were performed. Results of this

exercise will help in adoption of standardized method of testing that will allow

comparison of metal content between different batches of glass beads. A standard test

method will also allow for better control and implementation of regulations regarding

metal content in glass beads.

Aim 4. Analyze metal content and composition of soils containing glass beads: Five soil

samples from a glass bead storage and transfer facility were collected to establish a

working maximum contamination level of soil by glass beads under normal storage and

transfer environments. The amount of glass beads in soil samples will be measured for

each sample and reported as percent mass. The result will inform the risk assessment

process as this data is currently missing, but is very necessary.

2. EXPANDED BACKGROUND

2.1 Pavement Markings

Pavement markings are vital for safe travelling on roadways. They mark roads boundaries and center lines which improves road safety. Cautionary information such as bends, curves, approaching railroads and intersections may also be provided to drivers though markings on the pavement, which helps in reducing accidents and saving lives. Pavement markings also provide traffic regulation information indicating special lanes, speed limits and other restrictions on usage.

A cost-benefit analysis of pavement markings shows that for every dollar spent on adding edge line pavement markings to roadways without pavement markings, a value of 60 dollars is gained (Miller et al., 1991). The demonstrated gains include savings of time, lives and loss of properties by reducing accident rates. The addition of a center line to a road itself has been reported to reduce accidents by 29% (Heydel, 2005). Because of their importance in roadway safety, making markings visible at all times is critical.

Visibility of pavement markings changes with lighting conditions and time. During the day, the contrast between the color of the pavement and that of the markings (usually white or yellow) enhances visibility. However, during low light conditions, such as night time or adverse weather conditions (such as cloudy weather, when visibility is low) visibility of pavement marking needs to be improved. Pavement marking visibility is

improved by addition of retroreflective elements along the pavement markings, most of which are recycled glass beads.

Mathematically, retroreflectivity is the ratio of reflected luminance to the source luminance (TxDOT, 2004). Hence, materials are said to be retroreflective or possess retroreflectivity if they are able to reflect back greater amounts of light in a particular direction than the amount that would be reflected in that direction due to scattering. Retroreflective elements in pavement markings retroreflect light back to the driver that is usually scattered away from the pavement surface, thus making the pavement markings more visible, as seen in Figure 1.
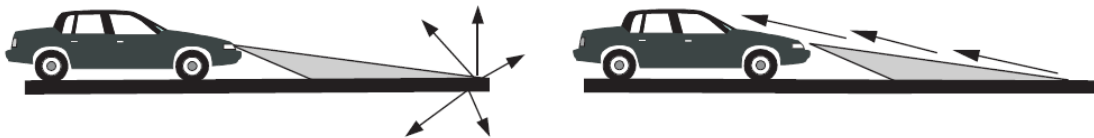
Figure 1: Retroreflective elements in pavement markings. The scattering of light from pavement without retroreflectors (left); Path of light on pavement with retroreflectors (right) (VDOT, 2011)

A pavement marking consists of three primary components – binders (thermoplastics, water based paints, preformed tapes, epoxy), reflectors (glass beads or raised pavement markers), and the pigment (color). The different application techniques and material specifications are described in specification or guidance documents prepared by state DOTs (Departments of Transportation).

Although ancient Romans used lighter colored stones to make road boundaries appear more visible (VDOT, 2011), use of retroreflective elements to enhance pavement visibility on modern roads was first reported in the 1920s (Lloyd, 2008). Initially, shiny brass cups were placed along the pavement marking to make them more visible. Other methods of improving visibility included using phosphorescent paint and addition of radioactive materials in the paint.

The use of glass beads to enhance visibility in pavement markings was first reported in the 1930s, but glass bead use was not popularized until World War II (VDOT, 2011). Glass bead addition was considered expensive, but turned out to be more cost effective in the long run, as they were durable (VDOT, 2011). With advances in technology, several other retroreflective elements, such as raised pavement markers with micro prismatic reflectors have been introduced successfully. However, glass beads remain the most cost effective and most popular method of improving retroreflectivity.

2.2 Glass Beads in Pavement Markings

Glass beads act as retroreflectors due to their ability to refract and reflect light back to the driver (or the source of the incident light) that would be otherwise scattered, thus making the pavement marking more visible. Figure 2 depicts this graphically. An incident light ray is refracted into the glass bead. The bottom surface of the glass bead, which is in contact with the paint acts as a mirror and reflects the light back. The

reflected light is refracted out of the glass bead at an angle directed towards the driver, thus making the returning beam of light stronger.
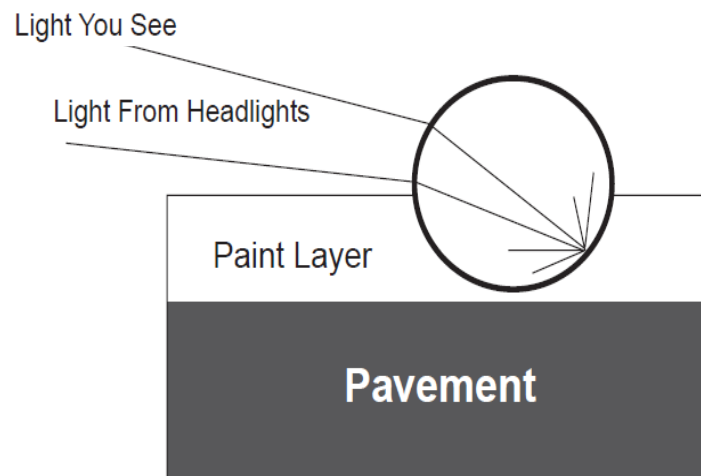
Figure 2: Retroreflection by glass beads (VDOT, 2011)

Factors that affect the visibility of pavement markings with glass beads include the number, density and the dispersion of glass beads in the marking (TxDOT, 2004). Because glass beads of standard gradation (particle size distribution) used in pavement markings are small in size, they may get submerged in paint or water if the pavement is wet, preventing the retroreflective action of glass beads. Hence, it is important to apply a combination of small and large beads on the markings. Larger beads do not submerge in paint and are not completely submerged in rain (Federal Specifications, 2007).

For the glass bead to retroreflect properly, glass beads must be round. They must also be only partially embedded in the paint (50 - 60 % is considered ideal (VDOT, 2011)) and

be manufactured in the prescribed size range. For good retroreflection, glass beads must have suitable refractive index and clarity. Because of the various properties that affect their functionality, all glass beads used in pavement markings must meet performance regulations set by AASHTO in specification M247. Additionally, glass beads used on traffic and airfield markings pavements must comply with federal specification TT-B-1325D.

Generally, glass beads used in pavement markings are made from recycled glass (reclaimed scrap glass and soda lime cullet as examples) (Federal Specifications, 2007). There are two methods of manufacturing glass beads (VDOT, 2011).

The direct method involves melting the reclaimed glass at a temperature above 1300°C. Due to the slow process of heating, most of the impurities from the glass are eliminated. The hot molten glass is sprayed through a fine nozzle in the reactor. As the glass droplets travel through air, they assume a spherical shape. When they cool down, they assume a solid state to form spherical glass beads. This method produces glass beads of higher refractive index (1.6 to 1.9).

The indirect method involves crushing recycled glass into a fine powder and passing the fine glass particles through a hot furnace (see Figure 3), which is several meters in height. As the crushed particles travel through the hot furnace, they melt partially and assume a spherical shape. This method is more economical and is more commonly used.

The indirect method produces glass beads of slightly lower refractive index (1.5). The
size and roundness of the beads produced in this upflow furnace method depends on
several other factors including grain size of the pulverized cullet, height of the furnace
and temperature of the furnace. The beads are produced continuously and bead samples
are tested in batches. Depending on the gradation and roundness of the samples,
temperature and other controls are adjusted to achieve a required gradation and
roundness criterion.
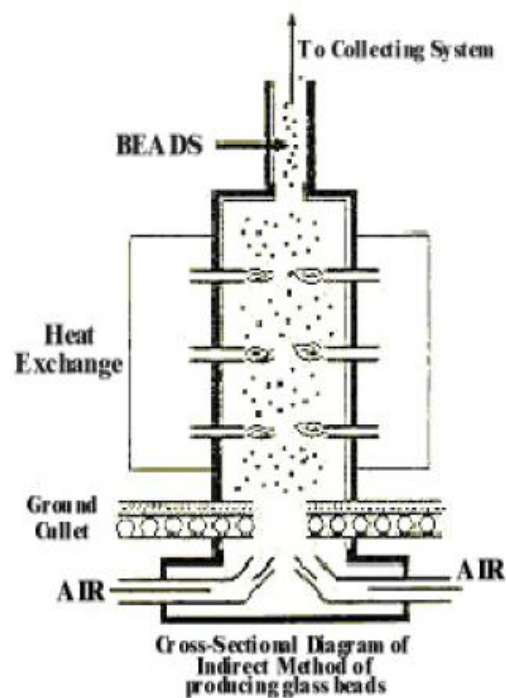
Figure 3: Indirect method of manufacturing glass beads (VDOT, 2011)

Glass beads used in pavement markings are normally coated with special coatings to enhance their performance. There are three primary types of coatings used to enhance different properties desired from the glass beads – adhesion, floatation and moisture resistance. Moisture causes glass beads to adhere to each other and not spread uniformly on the paint. A moisture resistance control coating reduces this tendency. Adhesion coatings allow glass beads to adhere with the paint or binder of the pavement marking and floatation allows the beads to float on the paint, as opposed to submerging in the paint. Coatings are applied singly or in combination as required by the user.

2.3 Environmental Concern over Use of Glass Beads in Pavement Markings

Examples of recycled glass used to make glass beads include broken glassware, household items such as light bulbs and other electronics, window glass and bottles. Soda lime glass is comparatively free of metals. Glassware used for storing food is also regulated for heavy metals such as lead and cadmium by the US FDA (CPG 7117.07 CPG7117.06, 21 CFR 109.16). However, glass from several other sources contains heavy metals. Glass from Cathode Ray Tubes (CRT) from old television sets contains metals such as lead, barium, strontium, arsenic, and mercury (Mear et al., 2006). Metal complexes such as cadmium sulfide, cobalt oxide, iron oxides, and nickel oxide are used to impart color to glass (Fettke, 1918). Sometimes, metals are also added to virgin glass to improve its clarity and refractive index, or as modifiers and stabilizers. Arsenic has been historically used as a high temperature oxidant to remove impurities during glass manufacturing to increase brightness and transparency (Wright et al., 1921).

Since glass beads used in pavement markings are made from recycled glass, their chemical composition varies with each batch of manufacturing, based upon the kind of glass found in the recycled glass feed. However, elevated concentrations of heavy metals in glass beads used on pavement markings have been reported by multiple studies (Jahan et al., 2010; Boulanger et al., 2011). Heavy metals such as lead and arsenic have a potential to leach from the glass beads and affect human health and environment. Since about 500 million pounds of glass beads are used on pavement markings on highways in USA every year (Jahan et al., 2010; Menendez, 2011), the potential of heavy metal leaching from glass beads is quite high. The leachate may have an impact on human and environmental health due to direct or indirect exposures. Particular concern is raised over the presence of arsenic and lead in the glass beads based upon the currently proposed regulations.

Arsenic is a naturally occurring metalloid that occurs in soil and bedrock. Although several regions in the world have arsenic outcrops in high concentrations, the introduction of arsenic in environment and its immobilization from its naturally occurring minerals are associated with anthropogenic activities such as mining, smelting, coal power production and geothermal energy production (Fowler, 1983). Arsenic has been used in pesticides, herbicides, glass manufacturing, semiconductors, paints and pigments, and medicine. It is a known toxic, carcinogen, and teratogen, and acts in a co-mutagenic fashion in the presence of UV light. Exposure to plants can lead to wilting, chlorosis, browning, and dehydration (EPA, 2011b). Most studies performed for arsenic

contamination of plants report an accumulation of arsenic in the roots and shoots of the plants. This is especially true for plants and plant products that are produced for consumption, including crops like rice (Rahman et al., 2007), vegetables (Pyles, 1982; Tlustos, 2002), and fruits and fruit juices (Reuters, 2011). Acute toxicity of arsenic in mammals results in a variety of dermal issues, including skin lesions, incurable ulcers on exposed skin, and accumulation of arsenic in the liver. Chronic exposure to arsenic leads to gastrointestinal problems, loss of strength, loss of appetite, fatigue, distress, and anemia. Arsenic also affects the central nervous system and causes seizures, behavioral problems, and muscular incoordination. Widespread occurrence and contamination has caused countries all over the world to regulate arsenic, which has been regulated in the environment and drinking water for several decades now. (Naidu et al., 2006; Henke, 2009). In the United States, the limit for arsenic in drinking water is set at 0.01 ppm (EPA, 2011a); although some states have lower limits.

Lead is a naturally occurring mineral. Lead enters the environment through various sources including automobile emissions, paints, batteries, ammunition and other industrial products and by products. In soil, lead can affect the microorganisms (Greene, 1993) which are important for nutrient cycling and maintaining soil ecosystems. Lead is known to accumulate in highly organic soils and is taken up by plants through their roots (Greene, 1993). Lead can also affect plants by the atmospheric deposition of lead on the leaves. Lead is toxic to aquatic organisms. It inhibits enzyme action in algae, preventing proper photosynthetic function (Bradl, 2005). Lead in aquatic systems is especially

harmful for fish as it affects their gills. It is also known to bioaccumulate in the bones

and liver of organisms (Bradl, 2005). In mammals lead affects the central nervous

system and hence causes headaches, muscle and joint pains, hearing problems, and

hyperactivity. It is known to behave similarly to calcium and this affects

neurotransmission (Bradl, 2005). Adults exposed to lead may develop increased blood

pressure, kidney problems, and reproductive problems (EPA, 2011c). Lead also causes

improper enzyme functioning leading to diseases such as anemia. Lead affects mental

and physical development in babies and children causing behavioral and developmental

issues. Lead is known to be teratogenic and can cause miscarriages and stillbirths. Due

to its toxic nature, lead is a regulated heavy metal and there is no safe level of lead in

drinking water. The maximum contaminant level (MCL) goal for lead is set to zero

(EPA, 2011c). If more than 10% of the tap water exceeds 15 ppb in a municipal system,

then a municipality is required to take active measure to reduce the lead level in water.

2.4 Relevant Laws and Regulations

The AASHTO M247 specification applies to all glass beads used in pavement markings

(AASHTO, 2008). The specification classifies glass beads into Type I and Type II,

based on their size and gradation (see Table 1). Details of the various physical properties

of the glass beads such as roundness (minimum of 70%), crushing resistance (retained

on 0.425 mm sieve, under a minimum force of 133 N), refractive index (1.5), moisture

resistance and floatation (90% floatation on xylene) are also provided. The specification

also describes sampling and testing methods for glass beads along with packing and

marking guidelines.

Table 1: Gradation of glass beads (AASHTO M247)

Sieve Size (mm)	US Sieve #	Type I	Type II
0.850	20	100	--
0.600	30	75-95	100
0.425	40	--	90-100
0.300	50	15-35	50-75
0.180	80	--	0-5
0.150	100	0-5	--

TT-B-1325D is a federal specification and is more detailed in description than AASHTO

M247. It is applicable to all beads used in traffic and airfield pavement markings and

classifies beads into four types. Type I and Type II beads are beads used in traffic

markings (similar to AASHTO M247). Type III and Type IV beads, with high refractive

indices, are used specifically on airfield markings. Like AASHTO M247, TT-B-1325D

specifies testing and sampling criteria, storing and packing guidelines, and physical

properties of beads such as the size, gradation, crushing resistance, floatation, and

refractive index of beads. The regulation also contains, in more detail, the other

specifications such as materials used for making glass beads (Type I glass beads must be

made from reclaimed glass), and other physical properties including specific gravity,

resistance to acid, resistance to lead, resistance to sulfide and resistance to chlorides. The

retroreflectivity criterion that various types of beads must satisfy is also provided. For

Type I glass beads, retroreflectivity readings should be 200-400 mcd/m^2·lux for white

pavement markings and 150-300 mcd/m^2·lux for yellow pavement markings.

Neither TT-B-1325D nor AASHTO M247 discuss the chemical composition or heavy

metal content of glass beads used in pavement markings.

2.5 Previous Studies Examining Heavy Metals in Glass Beads

2.5.1 NJIT/RU Study

A joint study conducted by New Jersey Institute of Technology and Rowan University

(NJIT/RU) was the first commenced study to investigate the amount and the effect of

heavy metals in glass bead samples used in pavement markings (Jahan et al., 2010).

Apart from a literature review on the current practices involved in use of glass beads and

the currently applicable legislations that are applicable to use of glass beads in pavement

markings, the NJIT/RU study examined various methods of investigating the total and

leachable metal content in glass beads. Tests were also conducted to study the leaching

of heavy metals from glass beads and the effect of environmental factors such as pH,

salinity, and time on metal leaching. Eighteen samples of glass beads obtained from

NJDOT were used for this study. Four handheld XRFs and HF digestion were used to

determine the total metal content in the sampled glass beads. Additionally, three tests

were conducted to evaluate heavy metal leaching from glass beads – a fractional factoral study, the toxicity characteristic leaching procedure (TCLP), and synthetic precipitation leaching procedure (SPLP). The study found that metals have a potential to leach out of the bead and into the environment based on environmental conditions. pH was determined to be the most relevant environmental parameter affecting leaching. No observation between initial metal concentration in the beads and metal concentration in leachate was observed.

2.5.2 TAMU-TTI Study

Texas Transportation Institute (TTI) conducted a study in association with Texas A&M University (TAMU) in 2010. The study was carried out to study the composition and leaching potential of metals within glass beads used in pavement markings. The total metal content of three bead samples supplied by the American Glass Bead Manufacturers Association (AGBMA) were determined following the Pacific Northwest National Laboratory's KOH fusion method (Brinkley, 1994). Column leaching studies were also conducted to determine the effect of environmental factors such as pH, temperature, and abrasion on leaching of heavy metals. The study observed that temperature and short term, high intensity UV exposure do not have an observable effect on metal leaching, although pH and abrasion do demonstrate a considerable effect.

3. OBJECTIVES

The broad objective of this study is to analyze the metal content in glass beads used in pavement markings. Based upon the objective, the following aims and tasks have been identified.

Aim 1: Evaluate total, extractable and bioaccessible metal content in the glass beads.

Task 1: Evaluate total metal content by KOH fusion method.

Task 2: Evaluate extractable metal by EPA 3050B.

Task 3: Evaluate bioaccessible metal content using the Oral Bioaccessibility Assay developed by the SBRC.

Task 4: Compare metal contents obtained in Tasks 1, 2, and 3.

Aim 2: Evaluate the relationship between total arsenic content in glass beads and the retroreflective performance of the beads.

Task 1: Measure the retroreflectivity of beads using a portable retroreflectometer.

Task 2: Compare results in Task 1 to arsenic content obtained by KOH fusion.

Aim 3: Compare different methods of estimating the total metal content of glass beads used in pavement markings.

Task 1: Evaluate total metal content of glass beads using HF digestion (performed by EPA).

Task 2: Evaluate total metal content of glass beads using field portable XRF measurements (performed by FDOT).

Task 3: Evaluate total metal content of glass beads using benchtop XRF measurements (performed by FHWA).

Task 4: Compare results from Tasks 1, 2 and 3 with that of the KOH fusion method in Task 1 of Aim 1.

Aim 4: Analyze metal content and composition of soils containing glass beads.

Task 1: Evaluate the mass of glass beads in soil samples collected from a glass bead storage and transfer facility that has been in operation for more than 20 years.

Task 2: Evaluate metal content of collected soil samples.

Task 3: Evaluate arsenic content in the respirable fraction of site soil samples (particles < 10 µm in size).

4. METHODS

4.1 Materials and Reagents

Fifteen samples of Type I AASHTO M247 glass beads were used for Aims 1, 2, and 3 of this study. The glass beads were supplied by DOT partners from various states. The bead samples were given a separate code upon receipt and blinded for the rest of the experiment to maintain anonymity of the source and make of the glass beads.

Soil samples collected from the vicinity of a glass bead storage and transfer facility were used for Aim 4 of this study. Five samples were taken from varying locations around the facility to obtain a representative sample. A control sample was collected from a site near the facility (approximately 400 m away) in order to evaluate soil metal concentrations.

De-ionized (DI) water was produced in the laboratory using a Barnstead® Nano pure DI water system. High purity ACS grade nitric acid (HNO_3), potassium hydroxide (KOH), and hydrochloric acid (HCl) were purchased from EMD®; high purity ACS grade potassium nitrate (KNO_3) was purchased from Sigma®; reagent ACS grade hydrogen peroxide (H_2O_2) was purchased from Sigma Aldrich®; high purity ACS grade oxalic acid was purchased from Fisher Scientific®; and regent grade glycine was purchased from JT Baker®. The standard reference materials (SRM612 and SRM2709a) were obtained from National Institute of Standards and Technology (NIST). All bead samples were

stored in food grade Ziploc® bags. Samples prepared for analysis were stored in 15 mL

polypropylene tubes and stored at 4°C until further analysis.

4.2 ICP-MS Analysis

ICP-MS analysis was conducted for all prepared samples. Detection limits and

quantitative limits calculated previously were used for Aims 1, 2, and 3 of this study. For

Aim 4, detection limits and quantitative limits were determined separately due to

installation of new ICP-MS towards the later stages of this study. Standards were

prepared for 100 ppb, 50 ppb, 10 ppb, and 1 ppb using standards from AlfaAesar®

Specpure® of 1000 µg/mL strength for each analyte.

An ELAN® DRC II ICP-MS and PerkinElmer® NexION 300 ICP-MS housed within

TAMU's Center for Chemical Characterization were used to quantify the concentration

of As, Cd, Cr, Cu, Pb, Hg, Ni, and Zn in solution samples produced by the experiments.

All samples were preserved in 1% (volume/volume) HNO_3 and stored at 4 °C. Samples

were allowed to come to room temperature before analysis. Analysis was carried out as

described in EPA Method 6020A (EPA, 1996c). Since arsenic and lead were the two

primary metals of concern, data processing and interpretation were only investigated for

these two analytes.

The Method Detection Limit (MDL) for arsenic and lead using ICP-MS was determined

according to 40 CFR Appendix B to Part 136 "Definition and Procedure for the

Determination of the Method Detection Limit". The MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The practical quantitation limit (PQL) was then set based upon the greater of the MDL or the lowest analyzed calibration standard. Samples where the analytes were present at concentrations above the highest calibration standard were diluted down to within the calibration range and reanalyzed.

4.3 Aim 1 Experiments

Three subsamples were extracted from each of the fifteen glass bead samples to determine the total, extractable, and bioaccessible fractions of arsenic and lead. The three experimental procedures are described below.

4.3.1 KOH Fusion Method for Total Arsenic and Lead

The total metal content in glass beads was assessed by the KOH fusion method developed by the Pacific Northwest National Laboratory (Brinkley, 1994). Samples were crushed using a porcelain mortar and pestle, and passed through US Sieve #230. 0.25 ± 0.075 g of crushed glass beads was heated in a carbon crucible with 1.8 ± 0.4 g of KOH and 0.2 ± 0.1 g KNO_3 on a Bunsen burner until the effervescence subsided and a complete melt was formed. The melt was cooled and then dissolved using DI water in a 1000 mL volumetric flask. The solution was acidified using 25 ± 5 mL of HNO_3 and 0.3 g of oxalic acid. HNO_3 was used in place of HCl to avoid chloride ion interferences in the metal analysis. The 1000 mL flask was filled up to the 1000 mL mark with

deionized water and 15 mL samples were taken and stored at 4°C for analysis by

ICP-MS.

Total metal content was calculated from the measured concentrations using the

following formula:

$$\text{Total Metal}\left(\frac{\mu g_{metal}}{g_{bead}}\right) = \frac{C \times \forall}{M}$$

where,   C – concentration of metal in fusion solution, μg/L

             $\forall$ – volume of solvent, L

             M – mass of beads, g

All samples were prepared in triplicates. DI blanks, method blanks and positive controls

(SRM612 obtained from NIST) were also performed.

4.3.2 EPA Method 3050B: Acid Digestion of Sediments, Sludges, and Soils for Extractable Arsenic and Lead

The extractable metal content of the glass beads was analyzed by EPA Method 3050B -

acid digestion of sediments, sludges, and soils (EPA, 1996a). Refluxing columns were

used as vapor recovery devices and water bath capable of heating up to 100°C was used

as heat source. A glass bead sample weighing 1.0 ± 0.01 g was placed in a circular

flask/ digestion vessel to which HNO_3, diluted with DI water (1:1 by volume), was

added. The sample was heated to 95°C in a water bath and then refluxed for 15 minutes.

After cooling an additional 5 mL of concentrated HNO_3 was added and the sample was heated to 95°C in the water bath and refluxed for 30 minutes. Because no fumes indicating ongoing oxidation were observed, additional HNO_3 addition and refluxing was not performed and the sample was heated for two hours without boiling at 95°C and then cooled. 2 mL of DI water and 3 mL of 30% H_2O_2 solution was added to the flask and this was heated to 95°C until effervescence was minimal. Upon cooling a 30% H_2O_2 solution was added in 1 mL aliquots and the above procedure repeated until no effervescence was observed. Less than 10 mL of H_2O_2 was added to an individual sample. Once the effervescence stopped, the sample was heated at 95°C without boiling for two hours. The sample was then cooled and filtered using Whatman® filter paper #41. The filtrate was diluted to 100 mL and 15 mL samples were taken and stored in polypropylene tubes at 4°C until analysis was conducted by ICP-MS.

Extractable metals content of glass beads was calculated from the measured concentrations using the following formula:

$$\text{Extractable Metal} \left(\frac{\mu g_{metal}}{g_{bead}} \right) = \frac{C \times \forall}{M}$$

where,   C – concentration of metal in extraction solution, μg/L

$\forall$ – volume of solvent, L

M – mass of beads, g

All glass bead samples were tested in triplicate. DI blanks and method blanks were conducted to serve as a check for accuracy.

4.3.3 Oral Bioaccessibility Assay for Bioaccessible Arsenic and Lead

Because *in vitro* testing is faster and eliminates the need for *in vivo* testing to determine

bioavailability of heavy metals in solids, the procedure developed at SBRC (Kelley et

al., 2002) was used to estimate oral bioaccessible metals. This method was found to

directly correlate results from *in vivo* bioavailability testing protocols for heavy metals

including lead and arsenic. A 0.4 M glycine solution with a pH adjusted to $1.5 \pm .05$ with

HCl was prepared. 1 g of glass bead sample was weighed and placed in a 125 mL bottle

reactor and 100 mL of glycine solution was added to it. The reactors were capped and

attached to a rotary shaker (Barnstead® Thermolyne LABQUAKE®) with zip ties. The

system was rotated at 8 rpm at a temperature of $37 \pm 5°C$ in an environment controlled

orbit shaker (Lab-Line Orbit® Environ-Shaker, Model #3948) for an hour and the shaker

was turned off. The supernatant of each reactor was extracted, transferred to a 15 mL

vials and stored at 4°C before ICP-MS analysis.

The bioaccessible metals content of glass beads was calculated from the measured

concentrations using the following formula:

$$\text{Bioaccessible Metal} \left(\frac{\mu g_{metal}}{g_{bead}} \right) = \frac{C \times \forall}{M}$$

where, C – concentration of metal in glycine solution, μg/L

$\forall$ – volume of solvent, L

M – mass of beads, g

All glass bead samples were tested in triplicate. DI blanks and method blanks were conducted to serve as a check for accuracy.

4.4 Aim 2 Experiments

The retroreflective performance measurements were conducted by creating pavement markings embedded with glass beads on metal sheets. The metal sheets were painted using a shoe to put down the paint. The shoe was dragged along the metal sheet to spread the paint marking with a uniform thickness over the entire length of the pavement marking to produce a paint strip of thickness equal to 15 mil (1mil = 0.001 inch).

Immediately following application of the paint, glass beads were applied on the surface using a bead dispenser for even but random and disperse application on the paint. Three replicate markings were used to assess the retroreflectivity of each glass bead sample. After curing the markings for 24 hours, a Delta[®] LTL-X retroreflectometer was used to measure the retroreflectivity of the pavement marking samples (reported as $mcd/m^2 \cdot lux$). The retroreflectivity was measured in two directions; in the direction of application of the paint and the opposite direction. The retroreflectometer was used to take five independent measurements from each direction, which were averaged to determine the final retroreflectivity value for each sample.

4.5 Aim 3 Experiments

Four methods were used to evaluate heavy metals in glass beads used in pavement

markings. These include 1) the KOH fusion method (as described in Section 4.3.1)

developed by Pacific Northwest National Laboratory, 2) EPA Method 3052 (microwave

assisted HF digestion) performed at EPA to evaluate metals in siliceous solids (Brinkley,

1994; EPA, 1996b), 3) benchtop X-Ray Fluorescence (XRF) analysis performed at

FHWA, and 4) Field-Portable XRF (FP-XRF) analysis performed at FDOT. Subsamples

from glass beads (with the exception of sample AA) received at TAMU were sent to

each agency for testing. SRM612 was also analyzed for total metals by EPA and TAMU.

4.6 Aim 4 Experiments

Five soil samples were collected from a glass bead storage and transfer facility of a

pavement marking company to study the contribution of glass beads to the total metal

content of soil. The pavement marking company has been storing beads on site for more

than 20 years. Beads were evident upon visual examination. The site samples serve as a

worst case exposure scenario.

4.6.1 Estimation of Content of Glass Beads in Site Soil Samples

Approximately 50 g of each site soil sample was subsampled and weighed. A particle

size distribution using a series of US Sieve #30, #40, #50, and #80 and was performed

and the fraction of soil retained on each sieve was weighed and kept separately. An

inclined plane made of a strip of Plexiglas® and light table was used to manually

separate out glass beads, based on roundness, color, and translucence, from a representative portion of each fraction of soil. The glass bead from each fraction were weighed and collected. The total glass beads mass in 50 g of soil sample was calculated as:

$$\text{Total Glass Beads} = \sum M \cdot r$$

where,   M – mass of fraction of soil retained on sieve, g

r – mass of glass beads in representative portion per mass of portion, g/g

The glass bead content in the site soil samples were calculated as:

$$\% \text{ Glass beads (by mass)} = \frac{\text{Mass of total glass beads}}{\text{Mass of soil sample } (\sim 50 \text{ g})}$$

4.6.2. Total Metal in Soil Samples

The total metals in site soil samples were evaluated using the KOH fusion method as described in Section 4.3.1.

4.6.3 Total Metals in Respirable Portion of Soil Sample

The respirable fraction (particles < 10 µm in size) of soil samples and blank samples was obtained by wet sieving process, which is a common procedure to extract dust from soil samples (Misra et al., 2001; Ljung et al., 2008; Ljung et al., 2011). Approximately 50 g of site soil sample was wet sieved using a US Sieve #10, #50, #230, and #800 using DI water. Water and soil particles passing through US Sieve #800 were collected and stored

in a glass beaker. Water from each sample was allowed to evaporate, leaving behind flakes of soil particles. The soil was scraped out with a spatula and stored in polypropylene tubes and analyzed for total arsenic using KOH fusion methods as described Section 4.3.1.

4.7 Quality Assurance/Quality Control (QA/QC)

QA/QC efforts focused on several areas including prevention of cross contamination, ensuring a representative subsampling from the initially provided samples, experimental controls and replicates, and QA/QC related to instrumental analysis.

Cross contamination prevention included controls on sample handling that involved marking the subsamples. Any materials coming into contact with the glass beads during the experiment were also pre-screened for their likelihood of cross contaminating the glass beads. The DI water used in all laboratory experiments, the 1% HNO_3 solution used for diluting samples, and the glycine solution used in the bioaccessible extraction were also evaluated for their background arsenic and lead content.

Experiments were carried out in triplicate to produce data between environmental factors that could be compared using statistical approaches. For every extraction procedure a method blank, which consisted of analysis without using any sample, was generated. DI blanks and method blanks were also generated for all experimental procedures. The total

content of arsenic and lead in the SRM612 (glass wafer) and SRM2709a (soil) was determined using the KOH fusion process.

Instrumental QA/QC followed the guidelines outlined in EPA Method 6020A (EPA, 1996c) and the method detection limit was determined as described in Section 4.2. Interferences were not observed for arsenic and lead and the instrument limit of detection and resulting method detection limits were able to observe quantifiable concentrations of metals within the experimentally derived samples.

5. RESULTS AND DISCUSSION

5.1 QA/QC

Table 2 reports the MDL in terms of the mass of arsenic and lead observed per mass of glass bead (ppm) for the methods used in Aims 1, 2, and 3, and Aim 4. The MDL for Aim 4 was determined separately due to installation of new ICP-MS towards the later stages of this study. Because the MDLs were lower than the lowest calibration standard (1 μg /L), the lowest calibration standard became the PQL. Analytes with a concentration between the PQL and the MDL are reported as below the quantitation limit (BQL). Analytes detected in the sample that were below the MDL but still had a measured value are reported as below the detection limit (BDL). Analytes with a no observable measured response are reported as non-detectable (ND). Interferences were not observed for arsenic and lead within the experimentally derived samples.

For the total metal extraction, 0.25 g of glass bead was used in the KOH fusion method and the final samples of extract were made up in 1 L of solution. For the extractable and bioaccessible extractions, 1 g of glass beads was used and the final extract volume was 100 mL. Therefore, the MDL for arsenic and lead in the glass beads for the extractable metal and bioaccessible metal extractions are different than the total metal extractions.

Table 2: MDL and PQL for arsenic and lead for total, extractable and bioaccessible tests

Aim	Metal	Calibration Standard	Total Metal (ppm)	Extractable Metal (ppm)	Bioaccessible Metal (ppm)
Aims 1, 2 and 3	Arsenic	MDL	3	0.07	0.07
		PQL	4	0.1	0.1
	Lead	MDL	0.16	0.004	0.004
		PQL	4	0.1	0.1
Aim 4	Arsenic	MDL	2.8	--	--
		PQL	4	--	--
	Lead	MDL	0.44	--	--
		PQL	4	--	--

5.2 Aim 1: Total, Extractable and Bioaccessible Metal Content in Glass Beads

5.2.1 Total Arsenic and Lead

The arsenic and lead content obtained through KOH fusion method for SRM are shown in Table 3. The total arsenic and lead in the glass beads measured using the KOH fusion method is presented in Table 4 and Figure 4. Mean arsenic content in all the glass beads examined ranged from 11 ppm to 82 ppm, while mean lead content ranged from below quantification limit to 199 ppm. The results for total metal analysis in glass beads show

large standard deviations for both arsenic and lead indicating a high degree of variability within the replicates of each bead sample. NIST suggests a nominal arsenic content of 50 ppm and a certified lead content of 38.57 ± 0.2 ppm in the SRM612 wafers. Unlike the variability observed within the samples of beads, the SRM demonstrated less than six percent variability between four SRM samples for both arsenic and lead. Since all QA/QC checks were met with the instrument, and acceptable results were obtained for the SRM, variability associated with instrument and methodology was ruled out.

The variability in glass beads could be associated with varying sources of glass and varying amount of heavy metals in the recycled glass and glass cullet used for manufacturing the glass beads. The inconsistency of the reclaimed product used to make the glass beads could result in very high concentration of heavy metals in some glass beads. This variability in different samples and subsamples of glass beads used in pavement markings has also been observed in previous study by NJIT/RU (Jahan et al., 2010) and TTI (Boulanger et al., 2011). More detailed studies spread over a larger size sample may provide a more realistic range of heavy metal concentration in glass beads used in pavement markings. Extraction tests may be modified to process a larger subsample, in order to reduce the chance of selecting a high metal content glass bead randomly.

Table 3: Total arsenic and lead content (ppm) in SRM

	Arsenic (ppm)		Lead (ppm)	
	Measured	Expected	Measured	Expected
SRM612	47 ± 5	$50^{\dagger}$	33 ± 6	$38.57 \pm 0.2^{\ddagger}$

†   Nominal arsenic concentration in glass matrix

‡   Certified lead concentration in glass matrix
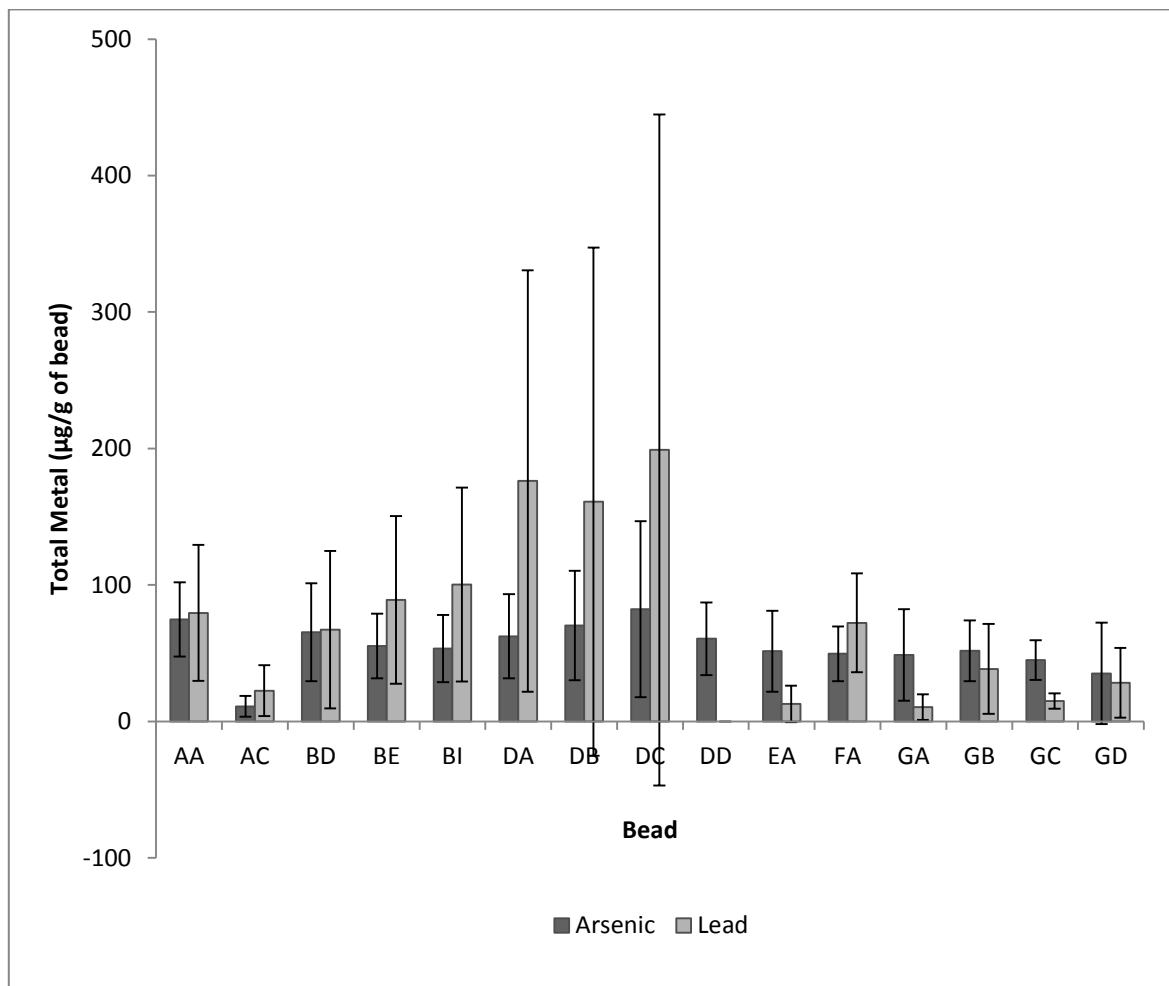
Figure 4: Total arsenic and lead (ppm) in the glass beads supplied by the DOT participants

Table 4: Total arsenic and lead content (ppm) in glass beads provided by DOT participants

Bead	Arsenic (ppm)	Lead (ppm)
AA	75 ± 27	79 ± 50
AC	11 ± 8	22 ± 19
BD	65 ± 36	67 ± 58
BE	55 ± 24	89 ± 62
BI	53 ± 25	100 ± 71
DA	62 ± 31	176 ± 154
DB	70 ± 40	161 ± 186
DC	82 ± 65	199 ± 246
DD	61 ± 27	BQL
EA	51 ± 30	13 ± 13
FH	50 ± 20	72 ± 36
GA	49 ± 34	10 ± 9
GB	52 ± 22	38 ± 33
GC	45 ± 15	15 ± 6
GD	35 ± 37	28 ± 26

†   only one viable data point

BQL   Below Quantification Limits (<4 μg/g for As and Pb)

BDL   Below Detection Limits (<3 μg/g for As , <0.16 μg/g for Pb)

Table 5: Extractable arsenic and lead content (ppm) in glass beads provided by DOT participants

Bead	Arsenic (ppm)	Lead (ppm)
AA	BDL	0.379 ± 0.091
AC	BDL	0.741 ± 0.450
BD	BDL	0.212 ± 0.062
BE	BDL	0.707 ± 0.293
BI	BDL	3.29 ± 1.00
DA	BDL	0.246 ± 0.002
DB	BDL	BDL
DC	BDL	BQL
DD	BDL	BDL
EA	BDL	BDL
FH	BDL	0.310 ± 0.037
GA	BDL	BDL
GB	BDL	BDL
GC	BDL	BDL
GD	BDL	BDL

†   only one viable data point

BQL   Below Quantification Limits (<0.1 μg/g for As and Pb)

BDL   Below Detection Limits (<0.07 μg/g for As, <0.004 μg/g for Pb)

5.2.2 Extractable Arsenic and Lead

The extractable arsenic and lead in the glass beads measured using EPA method 3050B

is presented in Table 5. The concentrations of arsenic were below the MDL (0.07 ppm)

for all the glass beads. For lead, several of the measured values fell between the MDL

(0.004 ppm) and PQL (0.1 ppm) and are hence reported as BQL. Using the lower limit

of calibration as PQL, lead was observed within the extractable metals extracts in seven

out of the fifteen samples at reportable concentrations. When observed, the levels of lead

ranged from 0.21 ± 0.002 up to 3.29 ± 1.00 µg extractable lead per gram of bead.

Therefore, when present, lead within the extractable metals extracts was up to 3.5% of

the total observed lead in the beads.

5.2.3 Bioaccessible Arsenic and Lead

The bioaccessible arsenic and lead content in the glass beads measured is presented in

Table 6. Bioaccessible arsenic concentrations were not in the reportable range for all the

glass beads as the observed value was below the MDL (0.07 ppm). For lead, several of

the measured values fell between the MDL (0.004 ppm) and PQL (0.1 ppm). Only three

bead samples reported lead above quantifiable concentrations, which lied in the range of

0.19- 3.59 ppm.

Table 6: Bioaccessible arsenic and lead content (ppm) in glass beads provided by DOT participants

Bead	Arsenic (ppm)	Lead (ppm)
AA	BDL	BQL
AC	BDL	3.59 ± 5.43
BD	BDL	BQL
BE	BDL	BQL
BI	BDL	1.74 ± 2.38
DA	BDL	BQL
DB	BDL	BDL
DC	BDL	BQL
DD	BDL	BDL
EA	BDL	BDL
FH	BDL	0.193 ± 0.019
GA	BDL	BDL
GB	BDL	BDL
GC	BDL	BDL
GD	BDL	BDL

†   only one viable data point

BQL   Below Quantification Limits (<0.1 μg/g for As and Pb)

BDL   Below Detection Limits (<0.07 μg/g for As, <0.004 μg/g for Pb)
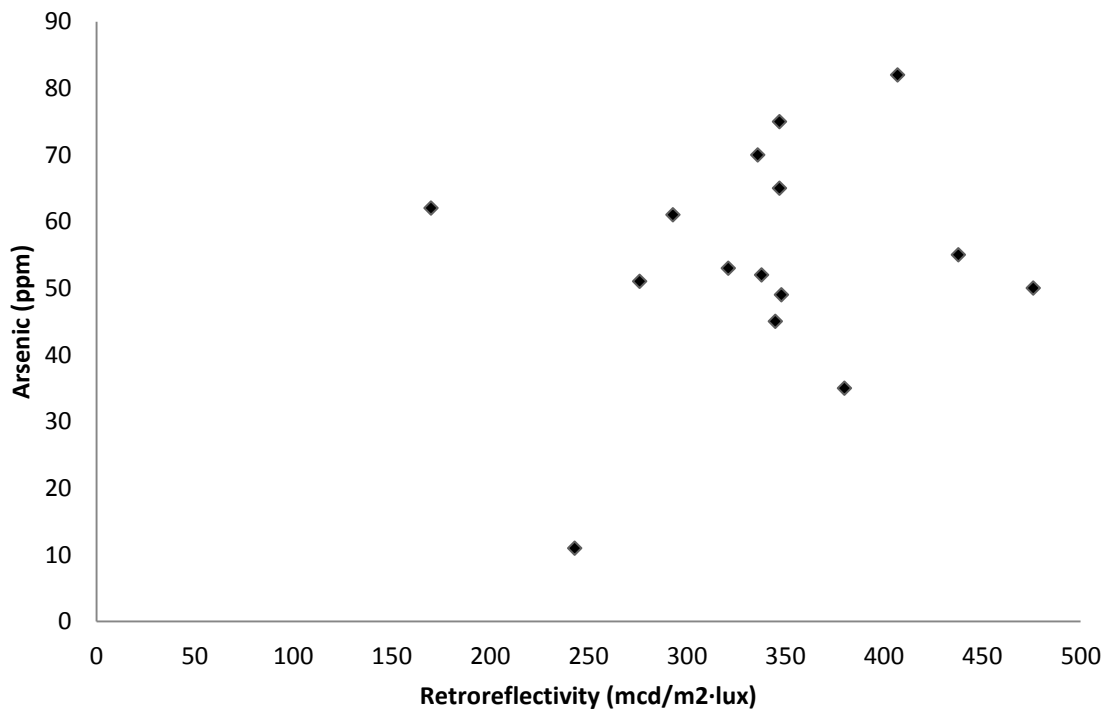
Figure 5: Relationship between arsenic content and mean retroreflectivity of glass beads

5.3 Aim 2: Evaluation of the Relationship between Retroreflectivity and Total Arsenic Content of Glass Beads

Table 7 and Figure 5 show the relationship between retroreflectivity and total mean arsenic content within the glass beads for all fifteen glass bead samples analyzed. The correlation was analyzed using the Pearson's product - moment correlation and the statistical correlation coefficient (Pearson's r) obtained was 0.19. The coefficient indicates a weak but positive correlation between the two factors, suggesting that a correlation may exist between the arsenic content and retroreflective performance of the glass beads. Since the range of average arsenic content in this study was very narrow and limited to below 100 ppm, additional study is required to demonstrate if a definite

relationship between the two parameters exists. The retroreflectivity data, however, also demonstrates that suitable retroreflectivity performance may be achieved at low levels of arsenic.

Table 7: Measurements of retroreflectivity and total arsenic content for glass beads

Sample ID	Retroreflectivity (mcd/m^2·lux)	Arsenic (ppm)
AA	347 ± 10	75 ± 27
AC	243± 8.7	11 ± 8
BD	347 ± 36	65 ± 36
BE	438 ± 52	55 ± 24
BI	321 ± 6.8	53 ± 25
DA	170 ± 39	62 ± 31
DB	336 ± 52	70 ± 40
DC	407 ± 65	82 ± 65
DD	293 ± 18	61 ± 27
EA	276 ± 14	51 ± 30
FH	476 ± 34	50 ± 20
GA	348 ± 19	49 ± 34
GB	338 ± 26	52 ± 22
GC	345 ± 11	45 ± 15
GD	380 ± 28	35 ± 37

5.4 Aim 3: Comparison of Total Metal Content in Glass Beads Evaluated from Different Methods

Initially KOH fusion digestion carried out at TAMU did not reproduce the SRM612 certified lead and nominal arsenic values provided by NIST. Incomplete digestion of glass beads during the fusion process was found to be the cause of the insufficient extraction. To ensure that the glass beads were completely digested and extraction was complete in the KOH fusion process, the crucible containing the KOH fusion melt was heated until the effervescence subsided (see description in Section 4.3.1) instead of only until a homogenous melt was obtained in the crucible as described in previous studies (Brinkley, 1994). After performing the initial digestions for the SRM for the second time and analyzing the extracts, the arsenic and lead content for the SRM were within the specified range of the values provided by NIST (see Table 3).

Comparing the metal contents obtained by KOH fusion and HF digestion performed by EPA, the concentrations obtained by KOH fusion were higher for arsenic and lead for the glass beads and the SRM. At first, this difference was associated with difference in preparation of glass bead sample and SRM prior to digestion. For KOH fusion, all glass beads and SRM were crushed and sieved, while for HF digestions the glass beads were not crushed or sieved and the SRM was only crushed. Due to differences in pretreatment of glass beads and SRM, EPA performed additional HF digestions on crushed beads. These crushed bead sample values were used for inter laboratory comparison. However, the EPA HF digested sample metal content were still much lower than KOH fusion,

which suggested a sample interference for KOH fusion digestions. Liquid extracts and crushed samples from TAMU were then sent to EPA to evaluate sources of error. When EPA analyzed the TAMU extracts and digested the TAMU crushed samples with HF digestions, EPA methods arrived at a similar metal contents to KOH fusion.

Based upon reanalysis, crushing of glass beads by pestle and mortar was speculated to be a potential source of contamination. It was also speculated that sieving of crushed glass beads could potentially introduce error (due to metal contamination from sieve or due to size selectivity of crushed glass beads). However, the SRM samples did not indicate an issue. Regardless, to further explore sources of contamination one glass bead (BI) and the SRM were analyzed to observe the effect of crushing and sieving on metal content in glass beads (see Table 8). Three replicates of the glass bead sample and SRM were prepared and analyzed by KOH fusion method as described in Section 4.3.1. The first replicate was neither crushed, nor sieved; the second was only crushed but not sieved; and the third was crushed and sieved. Each replicate was performed in triplicate. A method blank was also performed. Although differences in values were obtained for the glass bead, from the concentrations observed for the SRM it was concluded that crushing and sieving did not introduce significant error. Differences due to instrumental errors were voided by analyzing extracts from KOH fusion on both ICP-MS instruments at TAMU and Graphite Furnace Atomic Absorption (GFAA) at the EPA. After ruling out sources of method and instrumental error, the difference in data were placed upon the inter sample variability in metal content within the beads as noted in Section 5.2.1.

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Table 8: Total arsenic and lead (ppm) in BI and SRM612 to study the effect of crushing and sieving

Sample ID	Replicate ID	Crushing	Sieving	Arsenic (ppm)	Lead (ppm)
BI	Case 1	No	No	BDL	42.46
BI	Case 2	Yes	No	51.02	6.74
BI	Case 3	Yes	Yes	84.16	47.8
SRM	Case 4	Yes	No	46.4	7.75
SRM	Case 5	Yes	Yes	12.89	7.33
Blank	Case 6	-	-	BDL	BDL
SRM	Case 7	No	No	11.35	17.18

BDL   Below Detection Limits (<0.07 µg/g for As , <0.001 µg/g for Pb)

Due to the suspected variability of metal content in glass beads and the random distribution of high metal content glass beads in a sack of beads, either method appears to characterize the samples as long as SRM is evaluated and validates the extraction efficiency. However, since the heavy metal content in the SRM612 was known, some observations can be made on comparing results for the SRM. HF digestion coupled with ICP-MS reproduced the SRM content of arsenic and lead to within 85% and 90% of the target value for SRM analyzed (see Table 9 and Table 10). The ability for KOH fusion digestion coupled to ICP-MS analysis reproduced the SRM content of arsenic and lead to within 93.6% and 86.0% of the target value for an average all four samples of SRM612 analyzed in the study (see Table 3). In general, it was observed that

Table 9: Comparison of arsenic content (ppm) in glass beads from analytical round robin

Sample ID	FDOT (FP-XRF)	EPA (HF)	TAMU (KOH)	FHWA (XRF)
AC	ND	0.9	11.0	1.20
BD	ND	5.5	65.3	1.60
BE	ND	1.1	55.3	ND
BI	ND	1.0	53.3	ND
DA	7	1.0	62.4	ND
DB	ND	0.9	70.3	0.72
DC	ND	1.3	82.2	ND
DD	10	0.5	60.6	1.12
EA	ND	1.3	51.4	ND
FH	ND	2.6	49.5	1.00
GA	ND	0.3	48.6	ND
GB	ND	0.4	51.7	0.43
GC	ND	1.2	45.0	ND
GD	ND	0.5	35.1	ND
SRM	-	42.5	46.8	-

ND   Not Detected

-      Not Analyzed

Table 10: Comparison of lead content (ppm) in glass beads from analytical round robin

Sample ID	FDOT (FP-XRF)	EPA (HF)	TAMU (KOH)	FHWA (XRF)
AC	ND	4.1	22.5	12.2
BD	19	6.0	67.3	14.6
BE	ND	10.3	89.0	10.7
BI	15	8.6	100.4	22.4
DA	ND	2.2	176.2	ND
DB	ND	2.4	161.0	18.6
DC	ND	2.2	199.0	ND
DD	ND	3.8	3.1	9.2
EA	ND	2.7	12.8	ND
FH	12	5.6	72.2	17.9
GA	ND	32.8	10.5	ND
GB	ND	7.1	38.4	13.5
GC	ND	23.4	14.8	13.7
GD	ND	3.2	28.3	ND
SRM	-	42.0	33.4	-

ND   Not Detected

-    Not Analyzed

KOH fusion provides the closest result to the nominal arsenic content of the SRM for glass. It may be noted that several studies have reported better digestion of metals through alkali fusion methods compared to acid digestion (Uchida et al., 2005; Neo et al., 2009), however the metals considered in these studies were trace metals such as Re, Zr, Hf, Th, and U, but not analytes of interest this study.

The FP-XRF studies by FDOT did not detect arsenic and lead in 93% and 79% of the bead samples. The lack of detection could be associated with the fact the FP-XRF instruments usually have a detection limit in the ppm range (30 ppm or higher for lead (EPA, 2004)) and the possibility that the heavy metal content in the glass beads used for XRF studies may have very low concentration of arsenic and lead in them. This is associated with the variability in the metal content in the glass beads itself, as discussed in Section 5.2.1.

5.5 Aim 4: Analysis of Site Soil Samples Containing Glass Beads

5.5.1 Evaluation of Glass Beads Content in Site Soil Samples

The average glass bead content in site soil samples collected from a bead storage and transfer facility are listed in Table 11. The difference in the content of glass beads is due to different sampling locations in the vicinity of the facility including the storage zone and the loading zone. The glass beads content varied from 19% to a maximum of 78%. Since most of the workers at the glass beads manufacturing facility do not wear protective equipment other than a hard hat, they are likely exposed to a high volume of

glass beads through various routes of exposure including direct contact, accidental ingestion, and inhalation. A detailed study is needed to determine exact exposure paths and exposure patterns to residents and workers, working in the vicinity of the facility to estimate a more detailed and accurate risk exposure scenario.

5.5.2 Analysis of Total Metals in Site Soil Containing Glass Beads

The total metal content of site soil samples containing glass beads is presented in Table 11. The MDL for arsenic and lead is 2.8 ppm and 0.44 ppm in terms of per gram of sample, respectively. Total arsenic was not reportable in most cases (with the exception of samples 1 and 3). The lead concentration of SRM2709a (a SRM for metals in soil) was reported within 70.3% of the target value for an average of the three samples of SRM analyzed in triplicate (the certified value and reference value of lead and arsenic in SRM2709a is 17.28 ppm and 10.5 ppm). The mean concentration of lead in soil samples from the storage and transfer facility ranged between 11 ppm and 122 ppm with two samples above the control site's background levels. The elevated arsenic and lead content in the soil samples over the control may be associated with the presence of glass beads, which are made of recycled glass containing heavy metals. However, the glass bead content in field site soil sample does not correlate with the metal content in site soil samples. A detailed study with a greater number of samples from a variety of facilities is needed to assess the contribution of glass beads to the total metal content of the soil.

5.5.3 Analysis of Total Metals in Respirable Fraction of Soil Containing Glass Beads

The total arsenic content in the respirable portion (particles < 10 μm in size) is presented in Table 11. The concentrations of total arsenic were below the MDL (0.70 μg/L in aqueous phase) for all samples and are reported as BDL. These preliminary findings indicate that arsenic is not present in the respirable fraction. However, more studies involving larger sample sizes from multiple facilities are required to evaluate the contribution of glass beads to total arsenic content in the respirable fraction of the soil.

Table 11: Glass bead content (by mass), total arsenic and lead (ppm) in site soil samples and total arsenic (ppm) in respirable fraction of site soil samples

Sample ID	Glass bead content (w/w %)	Arsenic (ppm)	Lead content (ppm)	Arsenic in Respirable Fraction (ppm)
Sample 1	24.5%	2.9 ± --†	122 ± 164	BDL
Sample 2	19.8%	BDL	40.3 ± 18.9	BDL
Sample 3	48.0%	7.6 ± 0.5	34.5 ± 2.1	BDL
Sample 4	41.2%	BDL	14.1 ± 11.0	BDL
Sample 5	78.3%	BDL	11.9 ± 5.1	BDL
Control	0%	BDL	24.1 ± 11.5	BDL
SRM	-	BDL	22.4 ± 4.6	BDL

†   only one viable data point

-       Not Applicable

BDL   Below Detection Limits (<2.8 μg/g for As , <0.44 μg/g for Pb)

6. CONCLUDING SUMMARY

The heavy metal content of fifteen glass bead samples provided by state DOTs were evaluated. Mean arsenic content in all the glass beads examined ranged from 11 ppm to 82 ppm, while mean lead content ranged from below quantification limit to 199 ppm. Total metal content measurements indicated a high amount of variability in the glass bead sample metal contents; most likely associated with the use of recycled glass feed for manufacturing of glass beads. While extractable and bioaccessible arsenic and bioaccessible lead was not reportable in most cases, extractable lead was reported to lie in the range of from 0.21 ± 0.002 μg up to 3.29 ± 1.00 μg extractable lead per gram of bead for seven of the fifteen glass bead samples.

The relationship between the retroreflective performance and the arsenic content of the glass beads was analyzed and a positive, moderate correlation was observed between the two factors. A more detailed study is required to evaluate the relationship between arsenic content and retroreflectivity. However, all glass bead samples, including those with low of arsenic content, met the AASHTO retroreflective performance criteria.

In the absence of a standardized test to evaluate metal content in glass bead used in pavement markings, different methods to evaluate the total metal content in glass beads were compared. Both the KOH fusion and HF digestion perform similarly when the samples ground at TAMU were sent to EPA and analyzed. However, based on results

obtained for SRM612, KOH fusion performed slightly better than HF digestion method used by EPA. Furthermore, FP-XRF did not detect heavy metals in more than 85% of the beads, indicating that it may be unsuitable for detecting the low levels of heavy metals expected in glass beads used in pavement markings if used with factory installed calibration parameters. Due to the lack of correlation between data from different labs due to sample variability, it is recommended that any analytical method may be used to evaluate the total arsenic and lead content in glass bead samples as long as the SRM is reproduced within the range of concentration expected in the beads.

In the analysis of the contribution of glass bead to the total metal content in soil from a glass bead storage and transfer facility, the mass content of glass beads varied from an average of 19% to 78%. Low levels of arsenic and lead were observed in the field samples and no arsenic was observed in the respirable fraction. However, a detailed analysis with larger number of samples must be performed to evaluate the effect of glass beads on the arsenic content in the respirable fraction of soil.

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