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Quantitative lead determination in coating paint on children's outwear by LA-ICP-MS: A practical calibration strategy for solid samples

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ABSTRACT

Lead is a hazardous compound that affects the central nervous system in people, particularly children, and may cause some reversible and irreversible diseases. Legal regulations try to prevent the exposure from products especially produced for children such as coating paints, jewelry, toys, bed linen, textile, etc. The aim of this study was to determine the lead levels of coating paints on children's outwear selling in district bazaar by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and to specify the percent of non-complying samples. Here we described the solid matrix calibration method and confirmed the results with the microwave-assisted acid digestion method. Both comparative methods were validated by analysis of the certified reference materials (NIST SRM-612 glass matrix, NIST SRM-2582 powdered paint and ERM-EC681k) and bias% for accuracy and RSD% for precision were calculated lower than 6.8% and 7.3%, respectively. The recovery ranges of laser ablation and microwave-assisted acid digestion method for Pb were found to be between 88.2–98.1% and 95.3–101.3%, respectively. The limits of detection values were determined as 0.162 mg kg^{-1} for direct sampling in the ablation chamber and 0.002 ng mL^{-1} for aqueous solutions. Correlation result of 16 samples (r=0.99) examined in both methods was satisfactory. In coating paint samples, 14.65% of 198 (n=29) did not comply with the 90 mg kg^{-1} lead limit according to regulation. Validated quantitative laser ablation method may be preferred to quickly and reliably determine the Pb levels in other solid samples as well as coating paints.

1. Introduction

Lead (Pb) is known as a common environmental pollutant with long half life and its high levels accumulated in the body may cause intoxication in many organs and tissues. Chronic Pb exposure affects the central nervous system (CNS) and results in serious inhibition in learning and severe changes in behaviors, especially in children. Lead absorption may constitute a serious risk to public health, since it may cause slow cognitive development, impair intellectual performance in children and also increase blood pressure and cardiovascular diseases in adults [1–3]. Handling and mouthing of consumer products such as toys, clothing, and drawstring by children especially in 0–2 years old are the major ways of lead exposure via dermal contact and ingestion [4]. A study conducted showed a high proportion of recalls as well as a high number of deaths/injuries related to strangulation, lead paint or falls and these recalled products included hooded sweatshirts with drawstrings, baby cribs and children's jewelry [5].

Declared acute or chronic lead poisoning cases after oral or dermal exposure items like toys, batteries, fishing sinkers, jewelry, paints, etc. revealed the importance of prevention from lead exposure of children [6–9] and the regulatory limits of lead in consumer products are often lowered [10].

According to the Consumer Product Safety Improvement Act (CPSIA) by Consumer Safety Product Commission (CPSC) of the U.S. definition; "children's products that are designed or intended primarily for use by children 12 years of age or younger cannot contain greater than 100 mg kg^{-1} of total lead content in any accessible component part of the children's product as of the date of 2011 and the maximum limits of total lead that may be present in paint or any similar surface coatings produced for children as 90 mg kg^{-1}" since August 14, 2009. This limit applies to both paints and paint on toys and other articles intended for children and to certain household furniture items [11]. Also British standards about safety of toys (BS-EN71-3) determined similar limits for lead migration [12].

Regulations related to the use of hazardous chemicals in Turkey have recently been re-examined and adjusted to resolve some of the country's health and environmental issues to improve the quality of life and also for the adaptation to EU rules and regulations during the EU accession process. Over the last few years the public authorities

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have been trying to meet the world standards and have taken concrete steps in this regard in Turkey.

A number of analytical methods about textile products including hazardous compounds conducted by atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) techniques in aqueous samples have been reported [13,14]. Over the last few decades, solid samples are being preferred to study by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which is a developmental technique for in situ sampling. Although LA-ICP-MS is powerful for multi-element analysis and is easy to sample [15], in some cases, especially for specific matrices such as textile, coating surfaces, etc., studies are limited by the lack of standard reference materials (SRMs) in the case of a problem about elemental fractionation sources such as aerosol transport, vaporization, atomization, ionization, etc [16,17]. Several study results have been obtained by calibration curves generated from standard addition, direct liquid ablation or matrix-matched standard methods or in situ analysis without applying an internal standard by laser ablation in different sample types such as blood, rat brain tissue, anhydrous minerals and glasses [18–21]. Besides, numerous quantitatively validated reports and reviews have been published especially in geological and forensic fields explaining the technique in detail [22,23].

Researches on inorganic contents of textile products for both children and adults are limited while no published report is available about coating paints conducted either in Turkey or in other countries. A study determined the concentrations of some elements in textile samples such as Cu, Cd, Ni, Mn, etc. by flame and graphite furnace AAS after microwave digestion on textile products and they found concentrations of Cu and Cd in samples higher than the permitted values [24]. A study result of some elements with textile samples manufactured in Turkey was reported in another study conducted by AAS; the levels of Pb and Ni ions in textile material were found to be over the values for baby clothing according to Oeko-Tex [25]. Mataso and Cadore obtained validation results by an acid microwave closed vessel digestion method for textile products used as sports T-shirts and they found chromium in black fabrics as the major inorganic contaminant [14].

Children are exposed to Pb or other similar hazardous substances coming from environment or materials due to daily contact with clothes, bed linen, paints, toys, jewelry and similar products. In recent years, studies have investigated the presence of inorganic contamination in such kinds of consumables for children [26,27].

Guney and Zagury determined the total concentrations of As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, and Se in toys and jewelry ($n=72$) for children bought on the North American market and compared these results to regulatory limits. According to their results, metallic toys and children's jewelry ($n=24$) 20 items had total concentrations exceeding migratory concentration limits of the European Union. High Pb levels (65%) were also found in some samples [28].

Revealing the hazardous compounds over the restricted limits in products is important, especially in terms of safety for the environment and health of citizens, and safety for workers exposed during the production process as well as for end users [10].

The aim of this study was determination of the Pb levels in coating paints on textile products produced for children and sold in district bazaars in Istanbul and to emphasize their compliance with regulations in our country with a new calibration strategy for LA-ICP-MS.

2. Experimental

2.1. Instrumentation

Measurements were conducted by a Thermo Electron X Series II ICP-MS (Germany), coupled to Nd:YAG laser ablation (LA) unit operating at 213 nm wavelength (New Wave Research Laser Ablation System, Merchantek, USA). For treatment of the samples a microwave acid digestion (CEM, Mars5, Matthews, NC, USA) was used. Water used was deionized (Millipore Direct-Q3 System, 18.2 MΩ cm).

2.2. Reagents and standards

Argon gas with $>99.999\%$ purity was used for the ICP-MS system (Okser, Turkey). Also used were 65% (w/w) HNO_3 and 35% (w/w) H_2O_2 solutions, purchased from Merck with supra pure quality. Certificated calibration solution (10 $\mu g\ mL^{-1}$) used was purchased from High-Purity Standards, Charleston; Indium (In) and Gallium (Ga) (1000 $\mu g\ mL^{-1}$) were used as internal standards (IS) (Absolute Standards, Inc., Hamden, CT, USA). Standard Reference Materials (SRMs) used for Pb were as follows: (i) National Institute of Standards and Technology (NIST) SRM 612 glass matrix (Gaithersburg, MD); (ii) NIST-SRM 2582 Powdered Paint (Gaithersburg, MD); (iii) European Reference Material, ERM-EC681k, low density polyethylene (Geel, Belgium). NIST-SRM 610 (Gaithersburg, MD) was also used as the external calibration standard.

2.3. Optimization

Preliminary optimization of instrumental parameters was conducted using aqueous standards (10 ng mL^{-1}) for an initial quality control of the instrumental performance to conduct both liquid nebulization and laser ablation ICP-MS methods. Afterwards, a second optimization with glass standard (NIST-SRM 612) was accomplished for laser ablation system. All the double charges and oxide levels were checked out. As an external standard, NIST-SRM 610 was analyzed at the beginning and the end of the sequence of the sample to correct for drift and variation during the experiment and to evaluate the capability of a laser ablation technique for the analysis of coatings.

2.4. Sample selection

Child outwear (0–12 years) containing coating paints and manufactured in Turkey were collected from four different district bazaars of Istanbul, ten samples from each bazaar were bought inexpensively and at least three different stallholders were chosen to buy samples. Totally 198 different colored coatings were obtained from forty products (Fig. 1). All these 198 samples were analyzed for ^{208}Pb by LA-ICP-MS and the selected 17 samples were verified by microwave-assisted acid digestion followed by liquid-based ICP-MS analysis.

2.5. Sample treatment and validation

2.5.1. Laser ablation

Each coating paint in different colors was cut into parts with approximately 0.5×0.5 cm dimensions from child outwear as shown in Fig. 2 (left side) and adhered on laminas with the cyanoacrylate adhesive which was also used as blank. NIST-SRM 2582 powdered one was converted to pellet form as follows: a 0.5 g portion of the pre-dried powder material was pressed with a manual hand press tool into a disk-shaped pellet 1.3 cm diameter with a thickness of approximately 3 mm.

NIST-SRM 610 and 612 are universal standards used for any kind of laser ablation applications, but the analysis parameters such as laser energy, scan speed, frequency, etc. applied to the glass matrix are different from coating paint surfaces. For this reason and for the lack of coating paint reference material, a calibration study was conducted in three different matrices, glass, polyethylene and powder, which have decreasing rigidity and increasing lead