Development and Validation of ICP-MS Method for Lead Determination at PPM Level in Molecular Sieves, Silica Gel and Silica Canister

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Abstract

A robust ICP-MS method was developed for determining the lead content in various packaging materials such as Molecular Sieves, Silica Gel and Silica Canister. The method was developed by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Sample preparation was done by acid digestion in microwave digestion vessel. The analytical method was validated by measuring several parameters Specificity, Limit of detection (LOD), Limit of quantification (LOQ), Linearity, Precision, and Accuracy. The method was applied satisfactorily for analyzing various molecular sieves, silica gel and silica canister samples.

Keywords: Inductively Couples plasma mass spectrometer; Microwave digestion; Molecular sieves; Silica gel; Silica canister

Introduction

Many Lead is a toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. Human exposure to lead is estimated to account for 143 000 deaths every year and 0.6% of the global burden of disease [1]. Lead is a cumulative toxicant that affects multiple body systems, including the neurological, haematological, gastrointestinal, cardiovascular and renal systems. Chronic exposure commonly causes haematological effects, such as anaemia, or neurological disturbances, including headache, irritability, lethargy, convulsions, muscle weakness, ataxia, tremors and paralysis [2]. Acute exposures may cause gastrointestinal disturbances (anorexia, nausea, vomiting, abdominal pain), hepatic and renal damage, hypertension and neurolog-ical effects (malaise, drowsiness, encephalopathy) that may lead to convulsions and death. Children are particularly vulnerable to the neurotoxic effects of lead, and even low levels of exposure can cause serious and, in some cases, irreversible neurological damage. Child-hood lead exposure is estimated to contribute to about 600 000 new cases of children with intellectual disabilities every year [3].

Very few methods are reported by Atomic absorption spectroscopy [4]. AAS, ICP-AES and ICP-MS are suitable techniques for these analysis, Out of these techniques ICP-MS is most suited for elemental analysis [5]. ICP-MS is highly sensitive and can detect the elements to very low levels (ppm, ppt, ppb) thus the technique is expensive. The mass spectra of elements are

simple and therefore can provide quick access for qualitative and quantitative analysis. AAS and ICP-AES techniques have a draw back for determination at very low level and less specific when compared to ICP-MS.

The present paper describes determination of Lead content in various packaging materials such as Molecular Sieves, Silica Gel and Silica Canister. These materials are used in various packaging materials such as tablets, packaged food, and leather items etc., the fact that lead is very toxic, these materials need to analyze for the content of Lead. To the best of my knowledge there are no specific methods for determination of Lead in these materials. Hence in the present paper, an excellent and sensitive analytical method was developed by ICP-MS for determination of toxic element Lead at ppm level [6].

Experimental

Samples details

Molecular sieves: Sodium aluminosilicate (Formula: $AlNaO_6Si_2$, M. Wt: 202.1 g/mol)
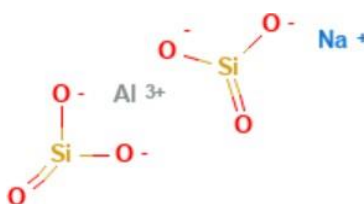
Structure

Details: A crystalline substance (especially a zeolite) with pores of molecular dimensions which permit the passage of molecules below a certain size. They contain tiny pores of a precise and uniform size and are mainly used as an adsorbent for gases and liquids. Molecular sieves are used to dry natural gas, along with performing desulfurization and decarbonation of the gas [7].

Silica gel and Silica canisters: Silicon Dioxide (Formula: $SiO2$, M.Wt: 60.08 g/mol)

Structure

Details: Little packets of silica gel are found in all sorts of products because silica gel is a desiccant it adsorbs and holds water vapour. In leather products and foods like pepperoni, the lack of moisture can limit the growth of mold and reduce spoilage [8].

TABLE 1 Chemical and Reagents

S.No	Reagents/Chemicals	Make	Grade	B. No. / Lot No	Valid up to
1	Nitric acid	J.T Baker	Ultrapure	168613	26-03-2020
2	Water	Fisher Chemical	LC/MS	183686	09-10-2019
3	HCl	Merck	Suprapur	Z0430318708	03-09-2019
4	Lead Nitrate	Merck	Emplura	DC6D660712	03-11-2020

Equipment

Instrument: Inductively Coupled Plasma Mass Spectrophotometer, Make: Agilent, Model: 7800 with Mass Hunter software. The method development and validation studies were done using Agilent Inductively Coupled Plasma Mass Spectrophotometer, Model 7800. The data were collected using Agilent Mass Hunter software [9].

Method Conditions

TABLE 2 Acquisition Parameters

Plasma Gas Flow	15.00 L /min
Mode	Helium
Helium gas flow	4.3 mL/min
Plasma voltage	1550 Watts
No. of sweeps	100
No. of replicates	3
Energy Discrimination	3 volts

Test Sample preparation

Transferred 10 g of sample into a 500 mL beaker, add 50 mL of 0.5 N Hydrochloric acid, covered with a watch glass, and slowly heated to boil gently for 15 min, cooled, and let the undissolved material settled in the beaker [10]. Decant the supernatant liquid through a Whatman No.3 filter paper into a 100 mL volumetric flask, retained as much as possible of the insoluble material in the beaker. Washed the slurry and beaker with hot water, decant each washing through the filter into the flask. Finally, washed the filter paper with hot water, cooled the filtrate to room temperature, diluted with water to volume and mix.

Reagent Blank Solution preparation

Added 50 mL of 0.5 N Hydrochloric acid into a 500 mL beaker, covered with a watch glass, and slowly heated to boil gently for 15 min, cooled, and let the undissolved material settled in the beaker. Decant the supernatant liquid through a Whatman No.3, filter paper into a 100 mL volumetric flask, retained as much as possible of the insoluble material in the beaker [11]. Washed the slurry and beaker with hot water, decant each washing through the filter into the flask. Finally, washed the filter paper with hot water, cooled the filtrate to room temperature, diluted with water to volume and mix.

Lead nitrate stock solution: Dissolved 159.8 mg of lead nitrate in 100 mL of water containing of 1000 mL volumetric flask added 0.1mL of Nitric acid then finally diluted to 1000 mL with water.

Intermediate stock solution (ISS): Transferred 0.8 mL of Lead nitrate stock solution into a 15 mL polypropylene tube added 0.1 mL of nitric acid finally diluted to 10 mL with water.

Preparation of Calibration Curve Standards

Preparation of Calibration blank (Zero Standard): Transferred 0.1 mL of nitric acid into a 15mL polypropylene tube then diluted this solution to 10 mL with water and mixed well.

Preparation of CC 1 Standard (LOQ): Transferred 0.12 mL of ISS -2 stock solution in to a 15 mL polypropylene tube, added 0.1 mL 0f nitric acid, and then diluted this solution to 10 mL with water and mixed well.

Preparation of CC 2 Standard (50 %): Transferred 0.2 mL of ISS -2 stock solution in to a 15 mL polypropylene tube, added 0.1 mL 0f nitric acid, and then diluted this solution to 10 mL with water and mixed well.

Preparation of CC 3 Standard (100 %): Transferred 0.4 mL of ISS -2 stock solution in to a 15 mL polypropylene tube, added 0.1 mL 0f nitric acid, and then diluted this solution to 10 mL with water and mixed well.

Preparation of CC 4 Standard (150 %): Transferred 0.6 mL of ISS -2 stock solution in to a 15 mL polypropylene tube, added 0.1 mL 0f nitric acid, and then diluted this solution to 10 mL with water and mixed well.

Preparation of CC 5 Standard (200 %): Transferred 0.8 mL of ISS -2 stock solution in to a 15 mL polypropylene tube, added 0.1 mL 0f nitric acid, and then diluted this solution to 10 mL with water and mixed well.

TABLE 3 Preparation of Calibration curve standards

Standard name	Nitric acid volume	ISS Standard volume	In volumetric flask and make up to volume	Concentration in ppb
Calibration blank	0.1 mL	0 mL	10 mL	0
CC1 standard (LOQ):	0.1 mL	0.120 mL	10 mL	153.8
CC2 standard (50%):	0.1 mL	0.200 mL	10 mL	256
CC3 standard (100%):	0.1 mL	0.400 mL	10 mL	512.6
CC4 standard (150%):	0.1 mL	0.600 mL	10 mL	769
CC5 standard (200%):	0.1 mL	0.800 mL	10 mL	1025

Calculation ppm w.r.t test preparation (µg/g)

Calculation ppm (µg/g) = $\dfrac{\text{(Instrument calc Conc. (ppb)-Blank Conc.) x Makeup Volume (mL)}}{\text{Sample weight in (mg)}}$

System suitability Criteria

- Correlation coefficient of linearity standard solution should not be less than 0.99.
- The Standard check accuracy should be in between 80% to 120%.

Method Validation

Linearity

Prepared the linearity solutions 1.5 ppm, 2, 5 ppm, 5 ppm, 7.5 ppm, 10 ppm (LOQ level 200% level of specification) as per the method and aspirated into the system [12]. The correlation coefficient was found 0.9999. Results are summarized in Table 1.

Limit of Detection (LOD) and Limit of Quantification (LOQ)

The LOD and LOQ were established based on visual evaluation as per ICH Q2 (R1) (10, 11) by aspirating a series of diluted solutions with known concentration. Prepared first level of linearity solution and aspirated into the system two times. LOD response was greater than blank response and LOQ response was greater than 3 times that of blank response. LOD is 0.75 ppm and LOQ is 1.5 ppm w.r.t. nominal analyte concentration. Results are summarized in Table 2.

Precision at LOQ level

Precision study was also carried at the LOQ level by aspirating six individual preparations and calculating the RSD percentage of the lead concentration. % RSD at LOQ level precision is 1.5%. Results are summarized in Table 3.

Accuracy

Prepared three test samples and six spiked test samples at specification limit. Aspirated these solutions into the system. Calculated % recovery of each spiked solution using linearity curve. The % recovery of all the spiked solutions is greater than 85%. Results are summarized in Table 2.

Specificity

Prepared calibration blank and LOQ standard as per the test method and aspirated into the system blank once and LOQ solution three times [12, 13]. Compared for the response of Lead in blank and LOQ solutions. The response in blank is less than 15 % that of mean response of Lead in LOQ solutions. In addition to the blank interference, successful demonstration of precision at LOQ level proved the specificity of the method. Results are summarized in Table 1.

Robustness

The robustness of the method was tested with different analyst and different days. Spiked sample solutions at specification level (5ppm) were tested. The mean recovery and %RSD are well within the acceptance criteria. The results show that the developed ICP-MS is highly robust. Application of the developed ICPMS method for Quality monitoring of Silica gel, Silica canister and Molecular sieves. Method verification has been performed for one batch of each sample Silica gel, Silica canister and Molecular sieves. Results are summarized in Table 3.

Conclusion

In this paper a specific, validated and well-defined ICP-MS method for the quantitative determination of Lead in Silica gel, Silica canister and Molecular sieves was demonstrated. Test procedure was found to be specific, precise and accurate. The batch analysis results show the developed ICP-MS was well suitable for the determination of Lead in different samples of Silica gel, Silica canister and Molecular sieves. The information presented here in could be very useful for Lead determination at ppm level and as well employed for Lead monitoring in Silica gel, Silica canister and Molecular sieves.

Acknowledgments

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