A novel analytical method for sensitive determination of lead: Hydrogen assisted T-shape slotted quartz tube-atom trap-flame atomic absorption spectrometry

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ABSTRACT

Lead is a toxic metal which affects human health badly due to its high toxicity. The wide application range of lead causes environmental contamination of air, water and soil. Flame atomic absorption spectrometry is one of the simple and economical instrument used for the determination of heavy metals, but it has low sensitivity due to low sample introduction efficiency. In this study, a sensitive analytical method was developed by using T-shaped slotted quartz tube as an atom trap unit to get lower detection limit for lead. The trapped atoms were released using hydrogen gas which supplies reducing environment in T-SQT-AT-FAAS system. Factors such as trapping period, sample and fuel flow rates were optimized to obtain high sensitivity. Under the optimum conditions, limits of detection and quantitation were found to be 0.6 and 2.1 $\mu g\ L^{-1}$, respectively. Accuracy of the developed method was checked and results found under the optimum conditions agreed with the certified value of coal fly ash standard reference material. The developed method was applied to water samples to figure out its suitability.

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1. Introduction

The human body requires several elements in their right proportions in order to sustain various biochemical and metabolic processes. Other metals including cadmium, arsenic, nickel and copper have tendency to cause harm to the human body even at very low concentrations [1]. Lead is one of the heavy metals that poses health concerns to humans and other living organisms. This element is commonly used in commercial products such as ceramics, alloys, paints, lead acid batteries, gasoline and pipes [2,3]. This wide application and usage make human activities (anthropogenic) the main source of lead based environmental contamination. It has many health effects; exposure to toxic levels of lead could result in complications of the reproductive, nervous and hematological systems, as well as the kidneys [4]. The maximum allowable level of lead in drinking water is set at 10 $\mu g\ L^{-1}$ and 15 $\mu g\ L^{-1}$ by the World Health Organization and US Environmental Protection Agency [5]. Low levels of lead in environmental samples require very sensitive analytical method to perform accurate and precise determination.

Inductively coupled plasma techniques with optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) offer multi-elemental determinations [6,7]. Atomic absorption spectrometric methods such as hydride generation (HGAAS) and graphite furnace (GFAAS)/Electrothermal Atomic Absorption Spectroscopy (ETAAS) also provide very sensitive determinations for metals, but these instruments could not perform simultaneous determinations [8–11]. Flame atomic absorption spectrometry (FAAS) is one of the earliest instrumental techniques for the determination of variety of elements, and still a preferred technique due to its robustness, accuracy and precision [12]. It is also ideal for routine laboratory studies due to its easy operation and cost effectivity. However, the low efficiency of the sample introduction unit limits the sensitivity of FAAS for most metals [13]. In place of getting the rather sensitive but expensive instruments, preconcentration methods could be used to improve the sensitivity of FAAS for several metals.

Different extraction/preconcentration methods have been used for both separation and preconcentration of organic/inorganic analytes from the matrices and the more recent microextraction techniques produce high outputs and analyte recovery while using sorbents or very low amounts of toxic solvents [14,15]. The amount of analyte reaching the flame after preconcentration can be significantly increased despite the low nebulization efficiency, but they need longer analysis time. Another analytical method used to enhance the its sensitivity is the coupling of slotted quartz tube (SQT) to the flame burner unit. SQTs work on two principles; increasing the dwell time of atoms in the light path and trapping analyte atoms on the inner surface of the quartz tube

[16]. In the first principle, atoms enter the slotted tube housing the flame and do not immediately exit due to the confined space and relatively narrow exit slot. This delay results in increased interaction of atoms with light source and a subsequent increase in absorbance signal [17]. The second working principle of SQT can either be achieved on a coated or uncoated tube surface. Metals including Pd, Ta and W having very high melting points are used to coat the inner surface of the tube to enhance trapping efficiency [18]. The amount of atoms trapped on the tube surface increase with increasing trap period and volume of sample aspirated into the flame. Trapping is achieved using lean flame, after which 10.0–50.0 μL of organic solvents such as ketones and ethers, are applied to produce high temperatures for the revolatilization of trapped analyte atoms [19]. In addition, Delves Cup method some other strategies where quartz is located on the flame have been used in literature to improve the sensitivity for different elements. For example, in Delves Cup system, a metal crucible or boat (usually made from nickel or tantalum) is positioned over the flame. Low volume of sample is introduced into the cup and the heated sample vapor passed into a quartz tube also heated by the flame. In this method, atoms remain in the optical path for a longer period of time, and so sensitivity is improved and very low detection limits can be obtained (sub ng/mL levels) [20,21].

The main purpose of this study was to develop a novel analytical method to improve the sensitivity of the conventional FAAS for the determination of lead at ultra trace levels. T-SQT and application of hydrogen was firstly used in literature to improve the analytical sensitivity of lead. Hydrogen causing reducing environment was applied for the revolatilization of trapped analyte atoms.

2. Materials and methods

2.1. Instrumentation

An ATI UNICAM 929 AA model atomic absorption spectrometer equipped with a deuterium background correction system was employed in the measurements. An air/acetylene mixture was used to generate the flame. Analytik Jena AG brand Pb hollow cathode lamp operated at the wavelength of 283.3 nm with 0.50 nm spectral bandpass and 15.0 mA of lamp current. A lab made 16.0 cm long T-shaped slotted quartz tube (T-SQT) with two slots positioned 180° with respect to each other was used in trapping studies. Upper and lower slot length were 3.2 cm and 5.5 cm; inner and outer diameter of the tube was 1.5 cm and 1.8 cm, respectively. The light emitted from the Pb hollow cathode lamp passed through the center of the quartz tube for more interaction with lead atoms. An air knife positioned each side of the quartz tube was used to protect electronic components from the flame that occurs after hydrogen burning.

2.2. Reagents

All standard solutions were prepared by diluting 1000.0 mg L^{-1} stock solution of lead purchased from High-Purity Standards. Standard and working solutions were prepared daily using deionized water obtained from A Milli-Q® Reference System. Tap water was filtered through a 0.45 μm membrane filter to remove particles before recovery studies. All glasswares were washed using detergent, rinsed with deionized water and soaked into a nitric acid bath overnight prior to use.

Standard Reference Material (Trace Elements in Coal Fly Ash, 1633c) was supplied from National Institute of Standards & Technology. About 0.20 g coal fly ash was taken into a Teflon vessel. 4.0 mL of each concentrated nitric acid and hydrogen peroxide solutions were added and microwave digestion was applied to the mixture. The heating program of microwave oven used for sample digestion is given in Table 1. After the digestion step, the final solution was diluted with deionized water to 50.0 mL.

Table 1
Temperature program for coal ash digestion.

Step	1	2	3
Temperature (°C)	100	150	180
Ramp time (min)	5	5	5
Hold time (min)	5	5	10

2.3. Procedure

Standard or sample solutions including lead were introduced to the T-SQT-FAAS system by nebulizer with a optimum flow rate for a certain period. Air/acetylene mix was kept at a minimum value to generate lean flame to trap lead atoms on the inner surface of quartz tube. After collection of lead atoms, hydrogen gas was supplied through a channel perpendicular to the quartz tube to produce reducing environment instantly for the purpose of releasing atoms at once to obtain a sharp signal. A schematic presentation of T-SQT-AT-FAAS system is given in Fig. 1.

2.4. Safety precautions

There is a risk of explosion as hydrogen gas is used as part of this system. Thus, some security measures have been taken to prevent this risk and to protect the individuals in the working area. As stated in the experimental procedure, hydrogen gas was used to release the atom. A one-way valve was placed on the gas line. After the trapping period the valve was kept open for 1 s to provide hydrogen flow and was closed afterwards. The outlet pressure for the hydrogen regulator was set to 5.0 bar for the supply of hydrogen to the system at a higher flow rate.

A cover with a reinforced glass was placed in front of the burner and slotted quartz tube to ensure the safety of the individuals in case of an uncontrolled explosion. In addition, safety glasses were used throughout the entire study.

3. Results and discussion

Optimization of the parameters including sample flow rate, flame type, trapping period, SQT height and hydrogen flow rate was conducted to increase sensitivity of the system. 20.0 μg L^{-1} standard lead solution was used during entire optimization studies.

3.1. Sample flow rate

Sample solution was introduced to the system through the nebulizer. To provide fine droplets of aerosol formation, solution including analye was sprayed to the system. The fine structure of these droplets ensures homogeneous combustion in the flame. The sample flow rate affects the efficiency of nebulization and hence the amount of trapped analyte per unit time. According to the optimization studies, an increase in the absorbance values was observed with increased sample flow rate to a point. Different flow rates were tried and 5.3 mL min^{-1} was assigned as optimum flow rate value. The sample volume was kept constant during this optimizastion.

3.2. Flame type

The sample solution is transferred to the burner after aerosolized by nebulizer and then analyte atoms are trapped on the inner surface of the quartz tube placed on the burner. The amount of trapped atoms are immersely proportional to temperature, so trapping studies should be carried out at the lowest flame temperature at which the atomization can develop. In this study, lean, stoichiometric and reach flames were tried. Sharp absorbance signals were obtained in the lean flame while