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Enhancing the ICP-OES detection of lead by incorporating chemical additives

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ABSTRACT

ICP-OES emission spectrophotometry is an effective technique for the detection of metals in various samples. However the sensitivity of ICP-OES for lead requires improvement. Studies were done with usage of oxidizers and other additives to improve lead by hydride reaction but this present study found the influence of an oxidizing agent without any hydride reaction. In this attempt, three different oxidizers comprising hydrogen peroxide – nitric acid, vanadium pentoxide – nitric acid and potassium permanganate – nitric acid were compared. Then the influencing oxidizer and its reaction conditions were optimized. The proposed method was also applied for the detection of lead in various real samples like old paint scraps, plastic toys and food packaging material. The results revealed that the maximum amount of lead (23.84 mg/g) was present in old paint scraps among the analyzed samples.

KEYWORDS

Determination of lead by emission spectrometry;
Improved determination of lead by ICP-OES;
Oxidizers as additives for direct determination of lead by ICP-OES;
Determination of lead in paints;
Polymeric materials;
Additives enhanced atomic emission study.

INTRODUCTION

Lead pollution occurs widely and is reported from the atmosphere to foodstuffs which are harmful to human beings especially to children. Its presence in the body can lead to toxic effects for example, acute high lead exposures can cause serious physiological effects including death or long term damage to brain functions and organ systems. Effects of lead exposures vary according to exposure timings and levels[1]. According to the stipulation of the center for disease control (USA) and department of health (UK) typical levels of lead in blood for children are of the order of 100µg l^{-1}. The level of concentration of lead in plants is in the range 500-3000 µg l^{-1}[2]. The more important lead exposures occur in renovation of homes containing lead based paint; contact with interior lead paint dust; smoking and wine consumption, battery plants, chemical plants and disturbances of older structures containing lead based paints are now major contributors to total releases to the environment[3]. Therefore the determination of lead is very vital to take necessary precautions to avoid impact on health.

Atomic emission spectrometry is one of the most employed techniques for the determination of low concentration of toxic elements present in environmental samples due to its high selectivity and sensitivity for analyte determination[4,5]. But there is constant effort to improve the detection limit as there is no safe limit with regard to the toxicity of lead. In that pursuit, Thompson and Thomperson claimed to be the first to achieve the generation of plumbane for analytical purpose by using sodium borohydride but concluded that the efficiency of conversion of lead into its hydride was poorer compared to other elements[6]. Y. Madrid et al[7] studied several oxidant media for lead hydride generation from slurried food and vegetable sample and compared their accuracy, precision & selectivity in the determination of lead by hydride generation atomic absorption spectrometry and concluded that of the three oxidant media involving hydrogen peroxide- nitric acid, ammonium persulphate-nitric acid, potassium dichromate-lactic acid tested, potassium dichromate gave the best results for the determination of lead in slurry samples[7]. But dichromate is a suspected carcinogen and be discouraged.

In the present study, the investigation of the influence of some oxidizing agents on determination of lead without Hydride generation was done. To the best of our knowledge there was no such report on influence of these oxidizing agents on determination of lead by ICP-OES when analyzed as a direct sample without any hydride form. The study led to a reasonably good, simple procedure with promise to enhance the detectability of lead.

EXPERIMENTAL

Reagents and chemicals

All Analytical grade reagents including concentrated nitric acid, hydrogen peroxide (30 % by weight) were all procured from Merck (India), Mumbai, India. Certified standard of purity of Lead solution of 1000mg l^{-1} ("CertiPur"P/N1.070328.0100 traceable to NIST) was procured from Merck KGaA, Damstadt, Germany. Water purified using Milli-Q apparatus of Millipore, (Bedford, MA, USA) was used for all the analysis.

Apparatus

Lead determination was performed with Jobin-Yvon JY 24 model, a sequential ICP-OES spectrometer for multielement analysis, from JOBIN-YVON Emission Instruments S. A., Cedex, France. The model consisted of Meinhard nebulizer, Scottish spray chamber and J-YESS software.

Operation of JY24 ICP-OES

The ICP-OES system consisted of Scottish spray chamber and Meinhard nebulizer for the sample introduction. The argon gas used for plasma was set at 12 l min^{-1} and the same as auxiliary gas was set at 1.0 l min^{-1}. The sample prepared in a solution of nitric acid so as to constitute approx.5% by volume was aspirated through the nebulizer system. Initially the instrument was calibrated by selecting a carbon emission line and by verifying its characteristics response as recommended by the manufacturer (as argon gas of ordinary purity is recommended for this use, carbon from carbon dioxide available as impurity in argon is used in general; if not, a drop of methanol added to pure water is used for the same). After successful completion of the carbon search, the instrument could accept any new method[8].

Various concentrations of lead standard solutions like 0.2, 0.5. 1.0, 5.0 (mg l^{-1}) were prepared and 5 (mg l^{-1}) standard solution of lead was used to tune the instrument for lead analysis. The tuning was detailed as follows: Of some listed wavelengths for lead, a sensitive wavelength 216.979nm was chosen from the software. ICP-OES instrument was calibrated for the wavelength chosen by doing AUTOSEARCH repeatedly which was followed by AUTO ATTENUATION step for improving the detector sensitivity for that element [8].

After tuning the instrument as detailed above, the analysis began with collection of emission profiles so as to achieve the qualitative confirmation of lead. The collection of emission profiles was done by introducing initially the standard solutions of lead from lower to higher concentrations along with standard blank. Thorough rinsing of all the wetting lines with ultra pure water was followed. Then, similar profiles were attempted for each of the experimental solutions and its blank. By using the emission profiles collected for the standard solutions, background points were chosen as per the manufacturer's guidelines so as to get proper calibration plot with origin found through zero. Then samples were analyzed. Thorough rinsing of the entire sample route was ensured in between every run.

Sample preparation

Sample preparation involved the wet digestion using a mixture of nitric acid and hydrogen peroxide. Experimental blanks were prepared using all the reagents but the samples for each different set of experiments involving different reagents.

Sample preparation of old paint scraps

1 g of old paint scraps collected from old pubic structures was employed. Sample was digested with a mixture of 10 ml of nitric acid and 15 ml of hydrogen peroxide in a glass flask fitted with a condenser on a hot plate. Then the condenser was removed and digested sample transferred to the beaker. The contents in the beaker after expelling the excess of nitric acid and hydrogen peroxide by gentle heating (care was taken to avoid the beaker turning dry) was kept aside for cooling. The cooled sample is transferred to a 25 ml standard flask along with number of rinsings with water followed by the addition of 0.5ml of 50% hydrogen peroxide solution and 2.5 ml of nitric acid before completing the make up with water. The sample preparation is filtered before ICP-OES analysis.

Sample preparation of plastic box for food packaging or plastic toys

Samples of plastic boxes used for packing food or the plastic toy gathered locally were separately analyzed. Samples were cut into small pieces of approx.2-3mm and about 1g of sample was digested and prepared as detailed above.

Safety measures

Lead compounds are reported as highly toxic and health hazardous. Hence, wear and follow all the safety methods and avoid contact with skin or ingestion.

RESULTS AND DISCUSSION

Direct study of lead and its hydride formation in acid medium

Determination of metals by atomic spectrophotometry is normally facilitated only from acidic medium and so lead solution of 1 (mg l^{-1}) in nitric acid acidity of 5%v/v had been studied but the sensitivity of lead was not satisfactory by this direct approach. The next option was the hydride formation as that is normally helping to improve the sensitivity of elements but for lead, even this was not satisfactory in improving the sensitivity[6].

Influence of various oxidizers or additives

However the hydride formation of lead was im-

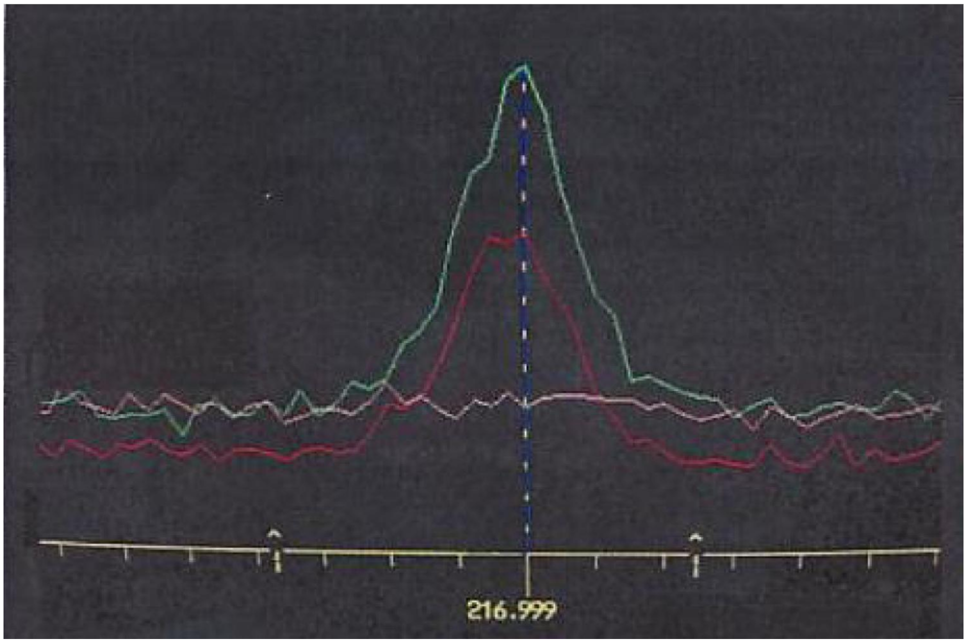

Figure 1 : The influence of H_2O_2 on Lead (Red line is normal signal and green line is enhanced signal for lead due to hydrogen peroxide and the base pale rose line is the blank for hydrogen peroxide solution)

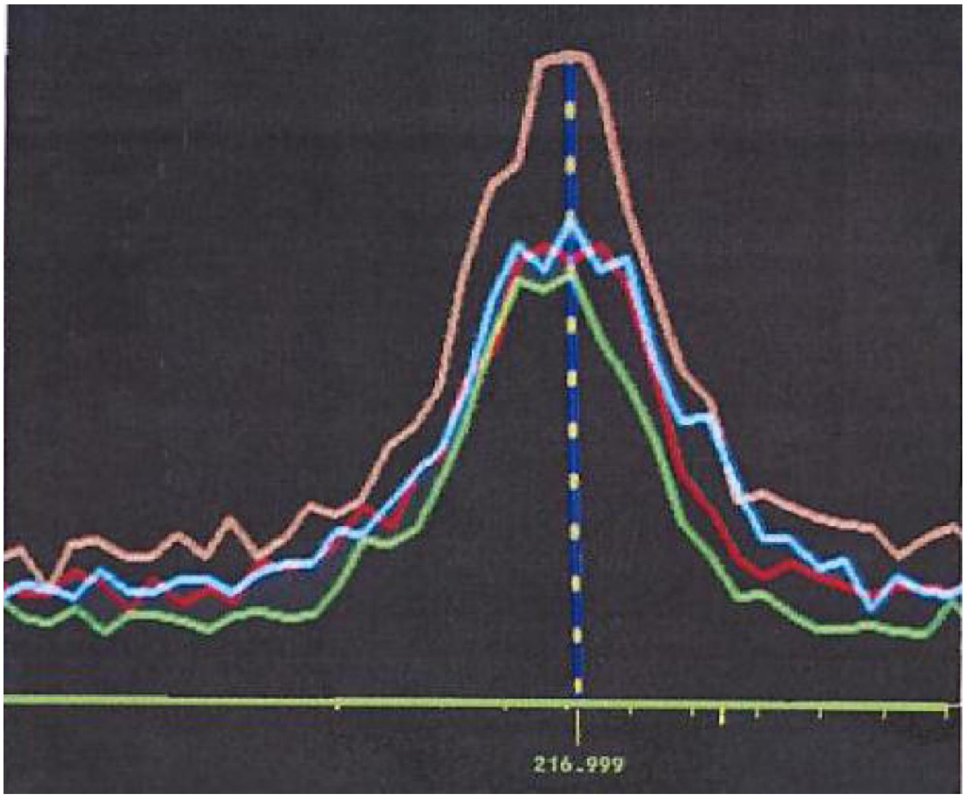

Figure 2 : Comparison of influence of various oxidizers on lead emission signal-green line is for lead in nitric acid as such (no other oxidizer); the other lines are caused when lead in nitric acid is additionally containing different oxidizers individually: peach coloured line is by hydrogen peroxide; red is by potassium permanganate; blue line is by vanadium pentoxide

proved with the usage of oxidizers and other additives so as to get improved sensitivity as reported[7,9-12]. In contrast, the present study made direct attempt (i. e. without any hydride formation) to find the influence of oxidizers on lead sensitivity. Hence, a couple of oxidizers in presence of acids were screened for probing their efficiency for improving the sensitivity of lead.

Hydrogen peroxide – nitric acid

To the standard solution of lead containing 1(mg l^{-1}), 2.5 ml of nitric acid and 0.5 ml of 50% aqueous solution of hydrogen peroxide(30% by wt) were added and the volume made up to 25 ml with Milli-Q water. The same procedure was followed for standard blank and hydrogen peroxide reagent blank. The influence of hydrogen peroxide is shown in Figure 1.

Potassium permanganate – nitric acid

To the 1 (mg l^{-1}) of lead standard solution, 2.5 ml of nitric acid and 1.0 ml of potassium permanganate of 0.1M were added and the volume made up to 25 ml with water. Potassium permanganate solution was further increased from 2 to 5 ml of 0.1M in different trials but produced no improvement in lead signal. The same procedure was followed for standard blank and potassium permanganate blank. The influence of potassium permanganate on lead signal was not significant‘igure 2 is shown to reveal this finding.

Vanadium pentoxide – nitric acid

To the 1(mg l^{-1}) of lead standard solution, 2.5 ml of nitric acid and 1.0 ml of vanadium pentoxide of 0.1M solution in water were added and the volume made up to 25 ml with pure water. Further increase of vanadium pentoxide was tried by adding from 2-5ml in different trials but led to no improvement in lead signal. The same procedure was followed for standard blank and vanadium pentoxide blank. The influence of vanadium pentoxide on lead signal was not found to be significant. Figure 2 is shown to prove this observation.

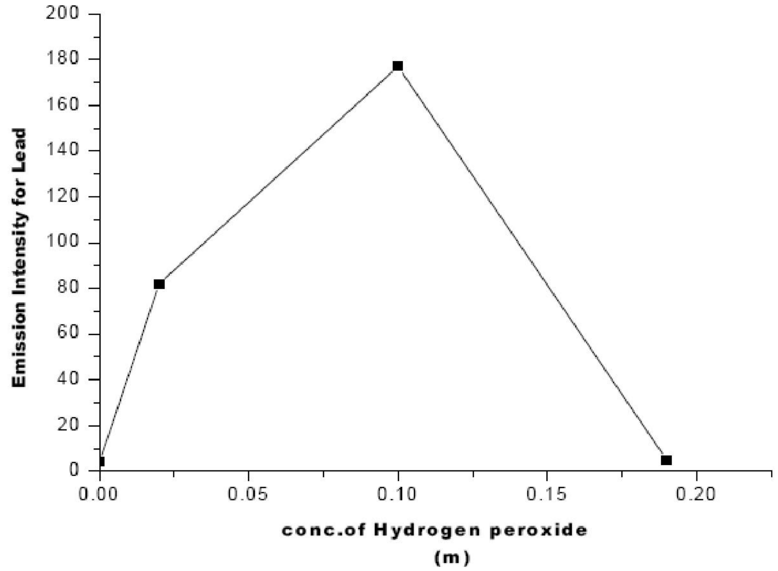

Figure 3 : The influence of hydrogen peroxide on lead detectability

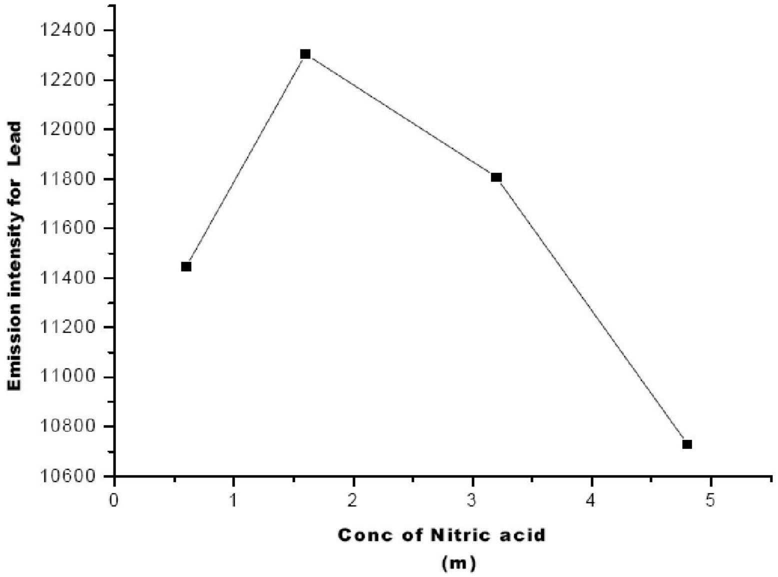

Figure 4 : The influence of nitric acid on lead sensitivity

These experimental results revealed that the peak profile for lead in the presence of hydrogen peroxide was stronger compared to the cases studied with other oxidizers or the one without any oxidizer. Baranguan et.al[12] reported that hydride generation of lead should take place through two stages as the first is the oxidization of lead (II) to lead (IV) and the next is lead (IV) to hydride form.

Optimizing the addition of hydrogen peroxide

Having judged that nitric acid–hydrogen peroxide combination worked efficiently for improving the lead spectral response, the next task emerged is to study their optimal concentrations to maximize their influence on spectral emission intensity of lead. Hence the following study was done.

To the 1(mg l^{-1}) of lead standard solution 2.5 ml of nitric acid and varying percentage of hydrogen peroxide and the volume made up to 25 ml with pure lab grade water.

From Figure 3, it can be seen that the sensitivity and selectivity of lead on the addition of hydrogen peroxides gives good results only at 0.1M. However that declined on further increase of hydrogen peroxide. Hence it is clear that hydrogen peroxide concentration is critical in this reaction.

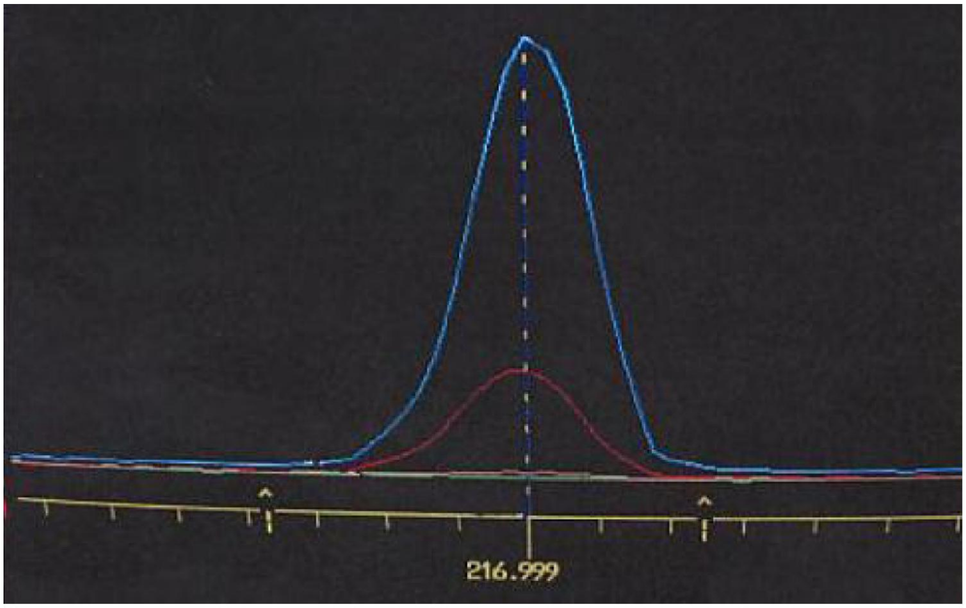

Figure 5 : Peak profile for lead in old Paint chip (blue line) and standard solution of lead is red line while their blanks are shown in green and peach colours as found close to the base line

Optimizing the addition of nitric acid

Then the intensity of lead was compared on varying the addition of nitric acid that is produced on Figure 4. The study involved 1 (mg l^{-1}) of lead solution, 0.5 ml of hydrogen peroxide of 50% aqueous solution of 30%w/v (representing 0.1M) and the addition of nitric acid was varied and diluted to 25 ml.

From Figure 4, it is noticeable that on increasing the level of nitric acid along with 0.1M of hydrogen peroxide, the intensity climbs to a maximum at 2.5 ml. Any further increase or decrease proved no beneficial to the sensitivity of lead. This 2.5 ml/ 25 ml corresponding to approximately 1.6M acidity. Hence it is clear that 1.6M acidity is crucial along with 0.1M of hydrogen peroxide for the detection of lead.

Is it chemiluminesence?

This present study is an unusual one hitherto unreported as influence of oxidizers on atomic emission of lead without hydride generation route for Atomic spectroscopy; however such reaction was reported as chemiluminesence that too stated in similar high temperature conditions but claimed to be facilitated through the formation of Pb-O. Besides, the chemiluminscence studies reported[13-14] were stated to be catalyzed by hydrogen peroxide in nitric acid. But one contradicting point to conclude this observation to be chemiluminescence is that at high temperature of plasma, Pb-O will dissociate to Pb. So, further studies to be done to conclude this.

Sample analysis

The experimental samples after filtration was used for analysis of lead by ICP-OES and the spectral responses for lead are shown in Figure 5. On analyzing the paint sample by the proposed method, it was found that 23.84 mg of lead present per gram of paint sample.

In the case of samples of toy and plastic box used for food packaging, lead was not detected.

CONCLUSIONS

This study reveals that only hydrogen peroxide – nitric acid combination enhances atomic emission signal and hence the detectability of lead among the three oxidant media hydrogen peroxide – nitric acid, vanadium pentoxide – nitric acid and potassium permanganate – nitric acid. The most noticeable observation of the additives on detectability of lead is only from the combination of hydrogen peroxide and nitric acid. Therefore the detection of lead with the proposed additives using ICP–OES is concluded to be an improvised and simple method. The analysis of lead in samples revealed that the maximum amount of lead (23.84mg) was present in paint (1g) among the analyzed samples.

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