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Development of an ICP-AES method for analysis of lead in iron ore sinter

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Abstract

Globally, the toxic effects of lead, cadmium, mercury and hexavalent chromium are an area of growing concern in different industrial sectors such as automobiles, steel making, home appliances and the chemical industry. To tackle this problem, different legislations are in force in different countries for the various industries having the possibility of contamination of these toxic elements. Due to these legislations, there is a pressure on the manufacturers to ensure that the processes involved must be free of these toxic elements or they should ensure that they are not contributing more than the prescribed permissible limits to the environment. In this context, it is important to know how much toxicity is arising from a particular industrial sector.

The present work is related to the presence of lead in the sintering process in an integrated steel plant. There is a possibility of lead contamination during the sintering process as it involves utilization of waste from the steel plant such as EAF dust, flue dust and other sludge type materials which are generally by-products of the steelmaking process. As mentioned above, it is essential to know the content of lead in sinter before taking the appropriate course of mitigatory action. In the present work, the authors have discussed a method for analysis of lead in iron ore sinter by using the Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) technique.

The aim of the present work was to present and discuss the analytical findings during the course of method development for analysis of lead. In this study, the authors have analyzed an iron ore sinter sample sent by the Bureau of Analyzed Standards (BAS, UK) for the purpose of certification. The major emphasis of this study was the choice of the analytical emission wavelength used for detection of lead in the sample and it was observed that the best results were obtained at 220.353 nm. The method for sample preparation has been discussed in the present work and has been adapted from IS: 1493 (Part 7)-1993. The validation of the method was carried out by a certified reference material, viz., BCS-877/1 (Furnace dust). Analysis of the sample revealed that the average value of the quadruplicate analysis was 0.138% Pb which was closer to the approximate value of 0.15%, as provided by BAS, UK. Thus, the method was found to be suitable and satisfactory for analysis of lead in iron ore sinter samples.

Keywords: lead, determination, iron ore sinter, BAS, ICP-AES, validation

Introduction

The process of sintering is one of the important processes in the integrated steel plant. In this process, fine particles of iron ore, secondary iron oxide wastes such as mill scale, collected dusts, coke breeze, water treatment plant sludge and fluxes are agglomerated by combustion. This agglomeration is essential to enable the passage of hot gases during operation of blast furnace.[1] Sintering involves the heating of iron ore, fluxes, coal and coke leading to a semi-molten mass which solidifies into porous pieces of sinter with the size and strength that is appropriate for use in the blast furnace. Sintering plant thus help in reduction of the solid waste of the steel plant by combusting the waste products and capturing the trace iron present in the mixture.[2] However, during this process, there can be a possibility that the sinter may get contaminated with some traces of lead, zinc and cadmium which are toxic in nature. One of the major sources of lead, zinc and cadmium is the dust from electric arc furnace (EAF) processes in steelmaking plants. The dust is identified as a potential hazardous waste by USEPA if it contains lead or cadmium or zinc.[3]

There is a rising concern regarding the toxic effects of lead in different finished products such as home appliances and automobiles and the issue has raised severe environmental concerns in different parts of the world especially the developed countries such as the US, Europe and Japan. This has resulted in establishing different legislations for taking care of various environmental concerns regarding presence of toxic materials such as lead, cadmium, mercury and hexavalent chromium in different products. For instance, producers of home appliances have been prohibited from using four heavy metals (mercury, lead, cadmium, and hexavalent chromium) and two bromine based fire retardants in their products as per the regulations of WEEE (Waste Electrical and Electronic Equipment) directive and RoHS (Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment) (Dec. 2002). In India, the Environment (Protection) Act, 1986, is the umbrella legislation which authorizes the Central Government to protect and improve environmental quality, control and reduce pollution from all sources, and prohibit or restrict the setting and /or operation of any industrial facility on environmental grounds. Thus, the analysis and determination of lead in iron ore, sinter and other related materials used in the steel industry is necessary.

In the above context, the Japanese Industrial Standard (JIS) has specified different methods for the analysis of environmentally

harmful elements such as lead in steel and materials used in the steel making process. These methods include spectrophotometric determination of lead after diphenylcarbazone extraction.[4] and atomic absorption spectrometric determination after iodide extraction.[5] The JFE Technical report describes the determination of lead by ICP-MS technique.[6] In the present work, the authors have described a method for analysis of lead in iron ore sinter by ICP-AES technique wherein the test sample preparation has been done as per the method described in IS: 1493 (Part 7)-1993.[7] which is similar to the method described in ISO 8753: 1987.[8] These details have been described in the subsequent sections of the paper.

Experimental

Reagents required

Concentrated hydrochloric acid (HCl), concentrated nitric acid (HNO$_3$), 40% hydrofluoric acid (HF) were procured from M/s. Rankem, India. Whatman filter paper no.41 was procured from M/s. Whatman and lead standard solution (1000ppm) was procured from M/s. Accu Standard, USA. Sodium carbonate (99.9%) purity was procured from E-Merck, India. Iron powder (purity: 99.999%) was procured from M/s. Alfa Aesar. Double distilled water[9] confirming to Type II of ASTM D 1193-06 was used in the preparation of the reagent solutions.

Apparatus required

Polytetrafluoroethylene (PTFE) beaker (250ml) with a PTFE cover was used for sample preparation. Spectro make CIROS ICP-AES instrument was used for the analysis of the samples.

Preparation of test sample solution

The sample taken for the study was an iron ore sinter sample sent by the Bureau of Analyzed Standards (BAS, UK) for the purpose of certification. The sample required no pre-treatment and was homogenized by BAS itself. As advised by BAS, the sample was only pre-dried at 105°C and used for the analysis. The sample preparation was then done as per the method discussed in IS 1493 (Part 7)-1993. 1gm of sample was accurately weighed in a precision balance and transferred to the PTFE beaker. The sample was moistened with a few drops of water and 40ml of HCl was added to the beaker. This was supplemented by 10 ml of HF and then the beaker was covered with the lid. The contents of the beaker were then heated at about 100°C for 20mts followed by heating at about 200°C till complete dryness was achieved. At this stage, 5ml of HNO$_3$ was added to the beaker and the content was re-heated to evaporation to just about 1ml. The obtained salts were dissolved using 10ml HCl and again the content was evaporated to dryness. The obtained salts were again dissolved in 10ml HCl and 10ml of water was added and the entire contents were filtered through the Whatman 41 filter paper into a 250ml beaker. The residue was washed with 10% HCl and finally with warm water for 3 times to obtain the filtrate A.

Subsequently, the residue was charred along with the filter paper in a platinum crucible at 550°C till a constant weight was obtained. Then, 0.5gm of sodium carbonate was added and the contents of the crucible were fused in medium heat of a Bunsen burner. The fused melt was then extracted using 20% HCl solution and the extract was combined with the filtrate A and taken up in a 250ml volumetric flask, and the volume was made up to mark with water. In this manner, the test sample solution was prepared. In addition to the sample, an experimental blank solution was also prepared in a similar fashion by not taking any type of sample.

Preparation of calibration solutions

Calibration solutions were prepared by suitable dilution of the stock solution (1000ppm) in 100ml volumetric flasks. 0, 10, 20, 50 and 100ppm calibration solutions were prepared for analysis of lead and named as Cal-1, 2, 3, 4 and 5 respectively. To maintain the matrix of these calibration solutions with that of the test sample solutions, 0.5g of sodium carbonate, 5ml of concentrated nitric acid and 10ml of concentrated hydrochloric acid was added to each of these calibration solutions respectively. Also, 0.55g of pure iron (99.999% purity) was added to each of these standards for maintaining the matrix effect as the sinter sample was having about 55% iron.

Results & discussion

Choice of wavelength

IS: 1493 (Part 7)-1993 describes the determination of lead using the Flame Atomic Absorption Spectrometric method (FAAS) at an absorption wavelength of 283.3nm by using a lead hollow cathode lamp as the light source.

In FAAS technique, the possibility of spectral interference is relatively less due to the use of the specific cathode lamp as the light source for the element of interest. For the case of lead, two absorption lines viz., 283.3nm and 217.0nm can be used for analysis in the FAAS technique. However, the 283.3nm line is preferred over the 217.0nm line due to the increased noise levels at 217.0nm for FAAS.[10] In case of the ICP-AES technique, emission wavelengths are used for analysis. Four emission wavelengths were available for lead in the ICP instrument, viz., 220.353nm, 405.778nm, 283.305nm and 261.418nm. All the four lines were selected during calibration to observe and judge as to which wavelength can be taken as the final line for analysis. The calibration solutions were run in the instrument and the spectral scan for each wavelength was recorded for comparison. It was observed from the regression analysis that all the four wavelengths were having an excellent correlation for the calibration standards.

Then, the lower limits of detection (LOD) and background equivalent concentration (BEC) for each wavelength were compared for further decision making for fixing the correct wavelength. This comparison is presented in Table 1 and these parameters have been computed as per the instrument software.

Table 1 Comparison of regression analysis for calibration solutions of lead for different wavelengths

Wavelength (nm)	LOD (ppm)	Co-relation coefficient	BEC (ppm)
220.353	0.245	0.99998	6.88
405.778	0.489	0.99997	25.7
283.305	0.211	0.99999	23.5
261.418	0.423	0.99996	18.7

It can be observed that of the four wavelengths selected, the wavelength 283.305nm is having the highest co-relation coefficient and is also having the lowest LOD. However, this line is not suitable in the present case as it is beset with the problem of interference from iron, which is the major constituent of the sinter sample. A similar argument can be put forward for wavelength 261.418nm as iron is

the major interference to this line also. If the spectral scan of these two lines is observed (Figure 1), adjacent peaks for iron can be observed in the close vicinity for these lines, viz., Fe 283.309nm and Fe 261.382nm, which lead to spectral interference causing anomalous results. Therefore, these two lines cannot be considered for analysis in the present case.
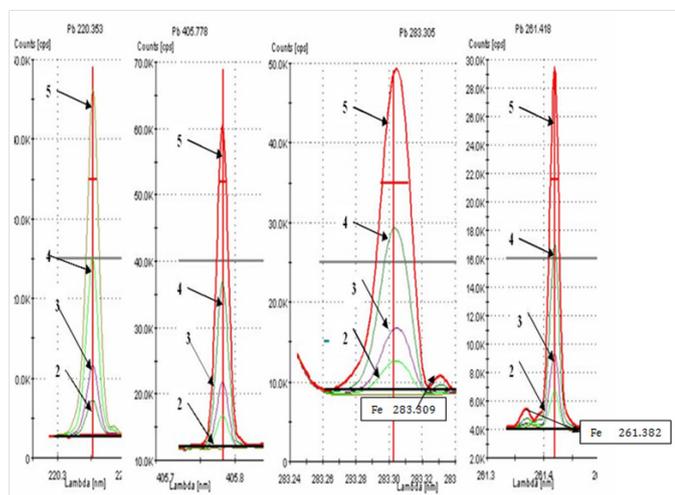

Figure 1 Spectral scan of lead calibration solutions for different wavelengths.

Referring back to Table 1, it can be observed that the line 405.778nm is again having an excellent co-relation coefficient, but the BEC value is significantly high and the LOD is also nearly two times higher as compared to that of line 220.353. The BEC can be defined as that concentration of the solution that results in an analyte emission signal which is equivalent in intensity to that of the background emission signal for a particular wavelength. The BEC can be therefore useful as an indicator of relative sensitivity for an emission line. It can be said that an unusually high BEC is indicative of any problems associated with the efficiency of the sample introduction system. Reference can also be made to a general agreement among different researchers that the best emission wavelength for analysis of lead is the 220.35nm line.[10,11] Hence, the line 220.353 nm was selected as the wavelength of choice.

Validation of method

The method was validated by analyzing a certified reference material (CRM), BCS-877/1 (Furnace dust) prepared in a similar fashion and the CRM was analyzed at 220.353nm. The analysis was carried out in duplicate and it was observed that the result was in agreement with that of the certified value. The result is presented in Table 2.

Table 2 of analysis method for lead in iron ore sinter by analyzing CRM BCS -877/1

S.N.	Observed value	Certified value for BCS -877/1
	Pb (%)	Pb (%)
1	1.001	0.9989±0.0307
2	0.996	0.9989±0.0307

Also, 20ppm and 50ppm solutions of lead were prepared and tested as unknown samples in the method. The results are presented in Table 3 and suggest excellent agreement.

Table 3 of standard lead solutions at wavelength 220.353nm

S.N.	Sample id	Observed value
		Pb (ppm)
1	Pb-20 ppm	20.289
2	Pb-50 ppm	50.038

Sample analysis

The experimental sinter sample was prepared and analyzed in quadruplicate and the results are presented in Table 4. The samples solutions were denoted as Pb-1, 2, 3 and 4 respectively.

Table 4 Comparison of sinter sample analysis for lead at different wavelengths

Sample identity	% Pb	% Pb	% Pb	% Pb
	220.353nm	405.778nm	283.305nm	261.418nm
Pb-1	0.142	0.111	0.305	4.94
Pb-2	0.137	0.095	0.3	5.022
Pb-3	0.138	0.103	0.314	4.949
Pb-4	0.136	0.103	0.303	4.846

It can be observed from Table 4, that the value for lead in the experimental sample was best for wavelength 220.353nm, as this line was having the lowest BEC among all the other lines (as observed from Table 1) taken for the analysis. Also, the obtained value was closer to the approximate value of 0.15%, which was provided by BAS, UK. From Table 1, it can be also observed that the 283.305nm line was having the lowest LOD, but the BEC was very high. Also, due to major interference from iron (which is present in the sinter sample), the analysis result of the experimental sinter sample is anomalous in case of wavelength 283.305nm. In a similar manner, the results for the other lines can be discussed and thus, it can be again concluded that wavelength 220.353nm is the best analytical wavelength for analyzing lead in iron ore sinter.

Conclusion

A method for analysis of lead in iron ore sinter has been developed using ICP-AES technique. The sample preparation procedure in this method was adopted from IS 1493 (Part 7)-1993. During the course of method development it was found and concluded that emission wavelength 220.353 nm was much more appropriate for analysis in the ICP-AES technique as compared to other emission wavelengths viz., 283.305nm, 261.418nm and 405.778nm. The method was validated by using CRM 877/1 (furnace dust) and also by analysis of 20ppm and 50ppm solutions of lead.

Acknowledgements

Conflict of interest

Author declares that there is no conflict of interest.

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