

Determination of Mercury in Fly Ash by Flameless Cold Vapour Atomic Absorption Spectrometry Using Hydride Generator

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An accurate, reliable and sensitive method has been developed for the determination of mercury in fly ash. Hydrofluoric acid reacts with fly ash and releases mercury, which is converted into non-volatile form by reacting with nitric acid and perchloric acid. The elemental mercury formed after reduction with sodium borohydride (NaBH_4) is determined by flameless atomic absorption spectrometry using hydride generator. The fly ash sample analyzed was received from National Council for Cement and Building Materials (NCCBM), which will be used as reference material in future. The validity of the method has been established by comparing the results obtained from NIST certified reference material 1633(b). The standard deviation has been calculated by analyzing ten replicates of both fly ash samples.

Key Words: Flameless atomic absorption spectrometry, Hydride generator, Fly ash.

INTRODUCTION

Fly ash causes environmental pollution and mercury is recognized as an environmental contaminant and its organic compounds, especially methylmercury, are known to be capable of damaging the central nervous system, and so it is important to determine the level of mercury in this material. Mercury shows poor sensitivity when determined by conventional flame atomic absorption spectrometry. Because of this, specific methods of atomization have been developed and employed by several workers, which helped in increasing the sensitivity of mercury by atomic absorption spectrometry. In the earlier method of Hatch and Ott¹, inorganic mercury is reduced with stannous chloride in an aeration flask, and metallic mercury which gets volatilized is passed through an absorption cell using nitrogen or argon as carrier gas. Carron and Agemian² used various preserving agents for keeping mercury in aqueous solution. Feldman³ used nitric acid and potassium dichromate for preserving mercury in dilute solution, but it is essential to store the solution of mercury in a glass container⁴, since mercury has been found to diffuse through polyethylene. Koirtyohann and Khalis⁵ determined mercury by AAS (cold vapour) in the presence of different variables. URE⁶ published a review concerned with analytical aspects of non-flame atomic absorption and fluorescence method for the determination of mercury. Wimberley⁷ determined mercury in soil, ores and in organic materials

by heating samples at 1000°C in an induction furnace, sweeping the liberated mercury through a trap, and then amalgamating with gold. Elrick and Horowitz⁸ determined mercury in rocks and sediments by digesting a sample with aqua regia followed by potassium dichromate. Mniszek⁹ and Annon¹⁰ have used 10% nitric acid with few crystals of potassium permanganate after oxygen combustion of coal sample. Recently a new oxidation method for conversion of organomercurials into inorganic mercury using sodium tetrahydroborate(III) has been developed by Capelo and Lavilla¹¹. Ma and Xu¹² determined mercury in geochemical standard reference material. Biestor, Gosar and Covelli¹³ determined mercury in river sediment collected from mining residue using aqua regia. In another method Huggett and Steevens¹⁴ determined mercury by weighing the sample in a BOD bottle and digesting the sample in presence of aqua regia. In the present investigation an analytical method has been developed for the direct determination of mercury in fly ash. The sample is digested in a PTFE beaker with a mixture of hydrofluoric acid, nitric acid, perchloric acid and hydrogen peroxide. Hydrofluoric acid breaks silica and releases mercury, which on reacting with nitric acid and perchloric acid is converted into a non-volatile form. The final solution is made in hydrochloric acid. The metallic mercury obtained after reducing with NaBH_4 in volatile form was passed into a quartz window cell using argon as the carrier gas and mercury is determined by flameless AAS (cold vapour) at a wavelength of 253.7 nm. The method is reproducible and the uncertainty of measurements in the determination of mercury in ten replicates is found to be < 2.5%.

EXPERIMENTAL

An atomic absorption spectrometer (Varian SpectrAA-10) with a vapour generation accessory VGA-77 was used. Details of instrumental parameters are mentioned in Table-1. Autocalibrated transferpette of 0.5–5 mL volume range of E. Merck (Germany) was used and pipettes of other range and volumetric flasks of Borosil Glass Works Ltd., India were used. All the acid digestion and dilution work was carried out in a cleaned laminar flow bench equipped with proper exhaust system of Atlantis make.

Nitric acid (69%) and hydrochloric acid (35%) of GR grade (purified by sub-boiling point distillation in a quartz glass device), perchloric acid GR grade (70%), all from E. Merck (India), hydrofluoric acid (49%) of semiconductor grade (Fluka) and hydrogen peroxide (35%) of Fluka make were used. De-ionized water (18 mega ohm resistivity) prepared from Millipore milli-Q water purification system, USA was used. The standard stock solution of 1000 ppm of mercury was prepared from high purity metal by dissolving 1 g of mercury metal in 5 M sub-boiled nitric acid and final volume was made to 1000 mL by de-ionized water. Subsequent dilutions were done from stock solution to get the desired range. These solutions were used for standard addition and calibration of the instrument.

Procedure

Ten weighings of each preserved undried 2.0 g of fly ash and NIST CRM 1633(b) were taken in different cleaned PTFE vessels. Another ten weighings of

each sample 0.1 ppm (2.5 mL of 1 ppm in 25 mL flask) of standard solution of mercury were added. To the vessels containing the sample, 15 mL of 1 : 1 nitric acid, 5 mL perchloric acid, 8 mL hydrofluoric acid and 8 mL 30% hydrogen peroxide were added. The PTFE vessel was kept for at least 1 h, and then heated on a hot plate slowly at 70°C for 1 h after opening the vessel. Then heated to fuming till syrupy condition, cooled up to room temperature and the fuming process repeated once again by adding HF, nitric acid and perchloric acid to syrupy solution. The whole content of PTFE vessel after cooling to room temperature was boiled with 15 mL hydrochloric acid and final volume in each case was made up 25 mL by de-ionized water. The dilution of these solutions (without addition) was made by taking 12.5 mL aliquot of each sample and CRM 1633 (b) and made up to 25 mL by 1 : 1 hydrochloric acid. In the case of standard added solution, 5 mL of stock solution was taken and final volume was made up to 25 mL by 1 : 1 hydrochloric acid. The absorbance of each sample was measured to optimum conditions given in Table-1. Reagent blank was also prepared and correction was applied wherever required for ten replicates of each sample. Mean absorbance value of each solution from ten replicates of each sample and CRM was taken into consideration for calculation of concentration of mercury. The results were further verified by standard addition in which known quantity of mercury solution was added in the beginning and the sample was processed as above.

Calibration

The calibration of the instrument was carried out with the help of standard solution of mercury prepared from high purity metal in sub-boiled nitric acid. Standard solutions of desired concentration of the major elements present in NIST CRM were added in standard solution of mercury to match the sample solution and to avoid interference.

RESULTS AND DISCUSSION

To determine traces of mercury in fly ash containing 60% silica, converting it into nonvolatile form, use of a mixture of hydrofluoric acid, nitric acid and perchloric acid is found suitable. The use of PTFE vessel has an advantage because on addition of acids mercury cannot escape as this can be closed tightly and the vapours after condensation react with other acids, and this converts mercury into nonvolatile form. Once converted into nonvolatile form the vessel is heated further for fuming at controlled temperature after opening it. 16 mL hydrofluoric acid is sufficient to volatilize silica; if it is found to be insufficient, 4–5 mL of HF is added further and heated so that the colour of the residue changes from gray to white. The solutions in some cases are found to be turbid which become clear after keeping for 30 min. KI has serious interference in the determination of mercury; as a precaution the tubes of hydride generator can be changed to avoid interference and all the glassware can be preheated before using. Hydrofluoric acid should be completely removed after fuming and there should be no free perchloric acid because its presence in hydride generator reduces the

signal intensity. The results obtained by flameless AAS-HG method for mercury in fly ash and NIST CRM 1633 (b) have been given in Table-2. The results obtained are in good agreement with NIST¹⁵ certified value with RSD less than 2.5%. The results obtained by standard addition have been given in Table-3. The results obtained are in good agreement with the expected results. The reproducibility is better in the proposed method and can be seen from the standard deviation value. The uncertainties have been reported as standard deviation by determining mercury in ten replicates of each sample. Blank value levels are found to be low and all the data reported have been corrected for the blank values.

TABLE-1
DETAILS OF INSTRUMENT AND STANDARD SETTING FOR FLAMELESS AAS-HG

Equipment		Varian spectra AA-10 atomic absorption spectrometer (flameless) with cold vapour generation accessory, VGA-77 of same make					
Element	Lamp make	Wavelength (nm)	Slit (nm)	Reductant	Nitrogen (mL min ⁻¹)	Flow rate (mL min ⁻¹)	
Mercury	Varian	253.7	0.20	NaBH ₄ 0.4% NaOH 0.5% HCl 5 M	100	NaBH ₄ +NaOH	1.0
						HCl	1.0
						Sample	7.0

TABLE-2
COMPARATIVE RESULTS OF ANALYSIS OF MERCURY IN TEN WEIGHING OF EACH SAMPLE BY AAS-HG (COLD VAPOUR) (mg/kg) (WITHOUT ADDITION OF STANDARD MERCURY SOLUTION)

Element	NIST fly Ash CRM 1633 (b)		Fly Ash NCCBM
	Certified value (±)*	Result obtained by proposed method (±)*	Results obtained by proposed method (±)*
Mercury	0.141 ± 0.019	0.146 ± 0.02	0.230 ± 0.02

(±)* Indicates uncertainty of measurements as mentioned in NIST certificate

(±)* Precision expressed as standard deviation of ten identical replicates.

TABLE-3
COMPARATIVE RESULTS OF ANALYSIS OF MERCURY IN TEN WEIGHINGS OF EACH SAMPLE BY AAS-HG (COLD VAPOUR) (mg/kg) (WITH THE ADDITION OF STANDARD MERCURY SOLUTION)

Element	NIST fly ash CRM 1633 (b)		Fly ash NCCBM	
	Expected value	Observed value	Expected value (±)*	Observed value (±)*
Mercury	1.39	1.25 ± 0.10	1.48	1.36 ± 0.11

(±)* Precision expressed as standard deviation of ten identical replicates.

Conclusion

Using the proposed method it is possible to determine mercury in fly ash with good precision and accuracy with a standard deviation less than 2.5%.

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