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Review

Improvement of sensitivity of electrolyte cathode discharge atomic emission spectrometry (ELCAD-AES) for mercury using acetic acid medium

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ABSTRACT

A method has been developed to improve the sensitivity of the electrolyte cathode discharge atomic emission spectrometry (ELCAD-AES) for mercury determination. Effects of various low molecular weight organic solvents at different volume percentages as well as at different acid molarities on the mercury signal were investigated using ELCAD-AES. The addition of few percent of organic solvent, acetic acid produced significant enhancement in mercury signal. Acetic acid of 5% (v/v) with the 0.2 M acidity has been found to give 500% enhancement for mercury signal in flow injection mode. Under the optimized parameters the repeatability, expressed as the percentage relative standard deviation of spectral peak area for mercury with 5% acetic acid was found to be 10% for acid blank solution and 5% for 20 ng/mL mercury standard based on multiple measurements with a multiple sample loading in flow injection mode. Limit of detection of this method was determined to be 2 ng/mL for inorganic mercury. The proposed method has been validated by determining mercury in certified reference materials, Tuna fish (IAEA-350) and Aquatic plant (BCR-060). Accuracy of the method for the mercury determination in the reference materials has been found to be between 3.5% and 5.9%. This study enhances the utility of ELCAD-AES for various types of biological and environmental materials to quantify total mercury at very low levels.

Contents

1. Introduction

Electrolyte cathode discharge atomic emission spectrometry (ELCAD-AES) possesses attractive analytical features and is an upcoming analytical technique. It has got advantages such as low detection limits for many metals (10 s of ppb) [1–3], low power consumption (<75 W), lower construction and operating costs and does not demand for vacuum as it operates in atmospheric air pressure and detection is accomplished through a emission spectrometer. Gubkin [4] first demonstrated the possibility of the electrolysis of aqueous solution of metallic salts using glow discharge in 1887 and since then efforts have been made for further developments and further investigations on fundamental characteristics of ELCAD by a number of authors [1,5–9].

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Determination of mercury in environmental and biological samples at low levels is very much demanding nowadays. Many methods are available to determine mercury at low levels such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [10], cold vapour atomic absorption spectrometry (CV-AAS) [11–15], atomic fluorescence spectrometry [16–18] and inductively coupled plasma mass spectrometry (ICP-MS) [19]. ELCAD-AES technique provides better detection limits for mercury compared to that of ICP-AES [20–22]. So ELCAD-AES is preferred as this technique has got comparable sensitivity for mercury with the above techniques and because of its earlier mentioned advantages. The ELCAD-AES technique was earlier successfully tested for elemental analysis of aqueous solutions in continuous as well as flow injection mode [7,22–24]. However there is a still need for improvement of sensitivity for the determination of mercury at very low levels in environmental and biological samples with or without matrix presence. The direct determination of analyte in the presence of sample matrix (without matrix separation) involves more dilutions to eliminate matrix related problems which further bring down the analyte concentration to further low levels. Hence sensitivity of the analytical technique often becomes a criterion for the determination of mercury. Therefore improvement in the sensitivity of the technique is very much needed to carry out such analyses and also enhances the utility of the technique for various materials.

It was reported in the literature [25–28] for cold vapour generation method of atomic absorption and atomic emission spectrometry that the sensitivity for vapour generation can be enhanced by the presence of organic substances. The effect of low molecular weight organic substances such as ethanol, formic acid, and acetic acid on the mercury vapour generation efficiency was investigated using solution cathode glow discharge (SCGD) coupled to ICP-AES for the detection [25]. This study indicated that SCGD can utilize the low molecular weight organic substances for enhancement of sensitivity of mercury. However, there are no reports on the usability of these organic solvents with ELCAD-AES technique.

This paper reports on the improvement of sensitivity of ELCAD-AES for mercury determination using organic solvents. Different organic solvents were examined for their ability to improve the mercury sensitivity. A method has been developed for the significant enhancement in mercury signal in aqueous solutions using acetic acid. The proposed method was validated by applying it to reference materials, Tuna fish (IAEA-350) and Aquatic plant (BCR-060). Analytical figures of merit for the determination have been presented.

2. Experimental

2.1. Instrumentation

A high-voltage D.C. power supply (H1003, Aplab, India) with a variable output of 50–1000 V, 0–300 mA was used in constant voltage mode. To limit the discharge current, a ballast resistor, 2.5 KΩ was introduced in series with the anode. A peristaltic pump (Miniplus, M312, Gilson, France) was used to pump the sample solution at a constant flow rate 1.0 mL/min. The atomic emission spectrometer which earlier formed a part of a Jobin-Yvon (Moden: JY-38, France) inductively coupled plasma atomic emission spectrometer (ICP-AES) with a 1.0 m Czerny–Turner grating (3600 lines/mm) monochromator was used. The emitted light was detected with a photomultiplier tube (Model R928, Hamamatsu, Japan). Monochromator control and data acquisition were performed with the MS-DOS based software integral to the JY-38. Spectral resolution of the monochromator was 0.013 nm. The atomic emission line at 253.652 nm of mercury was selected. A closed microwave digestion system (Model: MARS-5, M/s. CEM, USA) was used for sample digestion. Samples were digested in 100 mL XP-1500 PTFE digestion vessels.

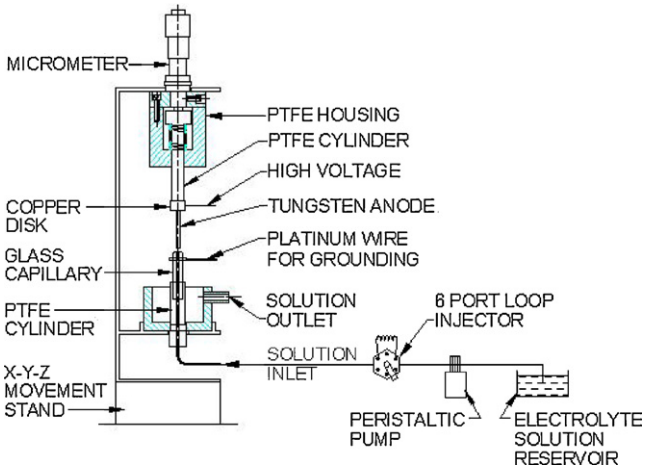

Fig. 1. Schematic diagram of ELCAD-AES source.

2.2. ELCAD cell

The cell, described in detail in earlier paper [22], mainly consisted of two parts, a tungsten pin anode 20 mm long and with a 1 mm diameter maintained at a potential between 700 and 1000 V housed in the upper part with a micrometer to precisely adjust the gap between the electrodes; the sample solution was pumped through the glass capillary in the bottom half, inserted into a PTFE cylinder which in turn was fixed to a PTFE reservoir for the overflowing solution that was continuously drained by gravity when it crossed certain level. A platinum 'O' ring was placed over the glass capillary, about 3 mm below the top and connected to the ground of the power supply. The draining sample solution flows along the 'V' groove cut across the face and down one side of the capillary and is thus continuously in contact with the cathode, and in turn acted as the cathode, maintained at ground potential. The anode could be precisely moved up or down to accurately vary the inter electrode distance. The cell is mounted on a platform built using 3 micropositioners (three independent micrometer screw gauges) so that it can be moved precisely in *x*, *y* and *z* directions to accurately position the plasma to obtain the maximum signal output by the spectrometer. This arrangement has been shown in Fig. 1. The gap between tungsten anode and liquid cathode was reduced to near touching to ignite the discharge initially. The emission from the discharge plasma was collected on to the inbuilt-lens of the spectrometer by adjusting the position of plasma. Subsequent to many experiments, the optimized conditions chosen for the maximum emission signal with a stable plasma were, an inter-electrode gap of 1-mm, a solution flow rate of 1 mL/min, and a constant potential of 0.76 kV which produced an average discharge current of 55 mA. The bias voltage of photomultiplier tube was set at 950 V. With an integration time of 0.5 s per point, 11 points were taken for scanning each peak. Emission line of mercury, 253.652 nm was used for the measurement of mercury signal.

2.3. Test solutions and samples

Ultra-pure water (>18 MΩ cm: resistivity) obtained by a combination reverse-osmosis (RO) – mixed bed ion-exchanger – Milli-Q (Millipore, Bangalore, India) water purification system was used for the analysis. Sub-boiled nitric acid was prepared in-house using quartz sub-boiling units in our laboratory. Stock standard of mercury of 1 mg/mL was prepared and the working standards were

Table 1
Digestion program of microwave system.

S. no.	Max power (Watts)	% Power applied	Ramp time (min)	Pressure limits (psi)	Temperature limit (°C)	Hold time (min)
1	600	50	2	500	100	2
2	600	70	3	500	150	2
3	600	80	2	500	180	2
4	600	100	2	500	200	5

prepared daily by sequential dilutions. Ethanol, formic acid and acetic acid of analytical reagent grade were used. The certified reference materials, Tuna fish (IAEA-350) and Aquatic plant (BCR-060) were used for the application of the proposed method.

2.4. Digestion of reference materials and preparation of its acetic acid medium

Accurately 0.25 g of Tuna fish (IAEA-350) was weighed into microwave digestion vessel, 3 mL of concentrated nitric acid was added and left for pre-digestion at ambient temperature for 30 min. The process blank was prepared in an identical manner, but without addition of the sample. All the vessels were then tightly capped and placed in the microwave oven and subjected to program given in Table 1. The vessels were then allowed to cool to ambient temperature, opened and then 2 mL of hydrogen peroxide was added, capped and subjected to the same program given in Table 1 and cooled. The sample solutions were evaporated to near dryness by an infrared lamp and then diluted to 10 mL with 0.2 M nitric acid solution. Four aliquots of 0.4 mL each were taken out from the sample solution and mixed with 0.1 mL of acetic acid. Of these, three aliquots were spiked with known amounts (25 ng, 50 ng, 100 ng absolute) of analyte (Hg) and then all the solutions were made up to 2 mL with high pure water and maintained its acidity to 0.2 M using nitric acid. For standard addition calibration method, the process blank, unspiked and spiked samples (spiked mercury concentrations: 12.5 ng/mL, 25 ng/mL, 50 ng/mL) were passed through the ELCAD-AES by injecting a 100 μL aliquot of each solution into the corresponding blank solution flow channel flowing at a rate of 1.0 mL/min into the ELCAD plasma in the order of increasing concentration of analyte to minimize any memory effect. For Aquatic plant CRM (BCR-060, 500 mg), mercury was leached into the solution by applying the same microwave program (Table 1). The leached solutions of Aquatic plant CRM were treated similarly as the Tuna fish CRM solutions and analyzed by ELCAD-AES.

3. Results and discussion

3.1. Studies using organic solvents

The effects of low molecular weight organic substances such as ethanol, formic acid, and acetic acid on the mercury signal were investigated using ELCAD-AES. The usability of these organic solvents with ELCAD-AES technique for the mercury determination at low levels was examined.

Initially a set of mercury (500 ng/mL) solutions as well as their corresponding blank solutions (without mercury) containing 10% (volume ratio) ethanol and of different acidities (0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.4 M) were prepared using nitric acid. Similarly mercury solutions of 10% formic acid as well as 10% acetic acid of same acidities along with corresponding blanks were also prepared. Emission signals of mercury were recorded for all these solutions using ELCAD-AES. It was observed that the plasma was unstable at the acid molarities, 0.3 M and 0.4 M. Among three acid molarities (0.05 M, 0.1 M, 0.2 M) that produced the stable plasma, the 0.2 M solution

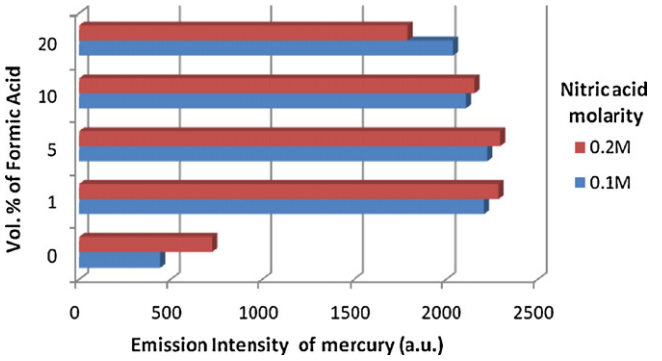

Fig. 2. Variation of mercury signal at different volume ratios of formic acid and different molarities of nitric acid.

yielded maximum signal for mercury. Hence acid molarity of the solution was optimized at 0.2 M for further studies using organic solvents.

Solutions of mercury (500 ng/mL) containing 0%, 5%, 10%, 25%, 50%, 75%, 100% (v/v) of ethanol, formic acid and acetic acid were separately prepared in 0.2 M acidity using nitric acid. Corresponding blank solutions (without mercury) were also prepared. Emission signals of mercury were measured for all these solutions using ELCAD-AES. It was found that the discharge plasma was unstable at 25%, 50%, 75% and 100% volume ratios of all the three organic solvents (ethanol, formic acid, acetic acid). Maximum enhancement of mercury signal was found to be around 40% with the stable plasma of ethanol. In case of formic acid, the increase in the mercury signal was about 300% where as for acetic acid the signal enhancement was observed to be around 400%. Among the three organic solvents studied, the signal enhancement for mercury was least with ethanol, where as the other solvents, formic acid and acetic acid resulted in higher signal enhancement.

A set of mercury solutions (500 ng/mL) of acid molarities, 0.1 M and 0.2 M with different volume percentages (1%, 5%, 10%, 20%) of formic acid and their corresponding process blanks were prepared and passed into the ELCAD plasma. As the discharge plasma was unstable at the acid strengths higher than 0.2 M the studies were restricted to 0.2 M. The emission intensities of mercury were recorded for all the solutions and plotted in Fig. 2 against the acidity as well as volume ratio of formic acid. Similarly the mercury solutions of acetic acid of same volume rations and acidities were treated. The measured emission intensities of the acetic acid solutions were plotted as a function of acidity and volume percentage of acetic acid in Fig. 3.

The 3D bar graphs in Fig. 2 indicated that maximum signal intensity was observed at 1% volume ratio of formic acid and then gradually decreased at higher volume ratios of formic acid. Same trend was observed for both acid molarities, 0.1 M and 0.2 M.

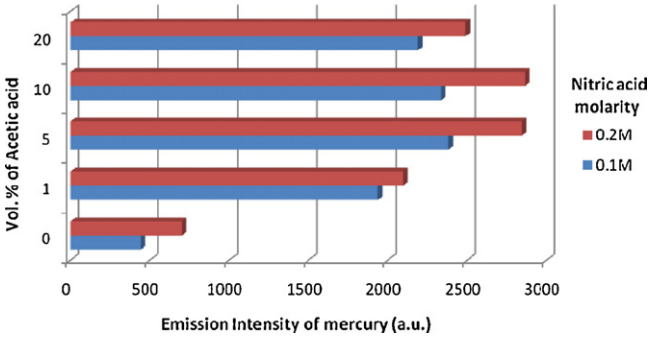

Fig. 3. Variation of mercury signal at different volume ratios of acetic acid and different molarities of nitric acid.

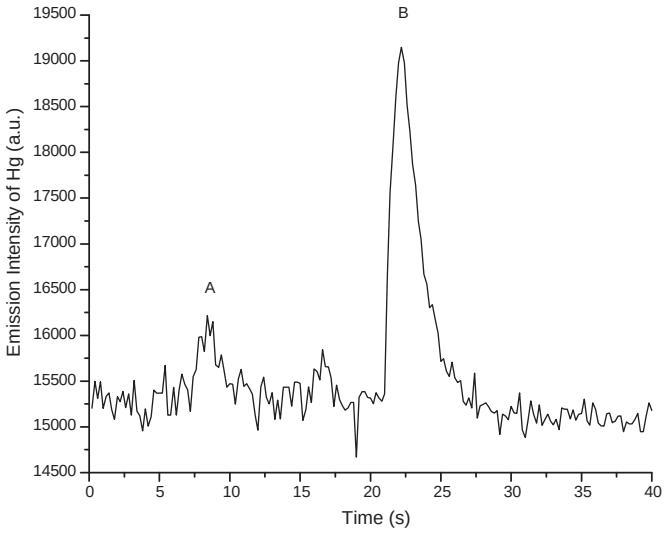

Fig. 4. Effect of 5% acetic acid on mercury signal in flow injection mode of ELCAD-AES. (A) 100 ng/mL Hg solution without acetic acid. (B) 100 ng/mL Hg solution with 5% acetic acid.

However maximum signal was produced with 0.2 M acidity compared to 0.1 M solutions. The net signal enhancement with formic acid at 1% volume ratio was found to be 300% compared to that of the solutions without formic acid. Similar observations were reported in the literature [25] for the range of volume ratios of 0–1% of formic acid. In case of acetic acid, Fig. 3 illustrated that enhancement was high at both the volume ratios, 5% and 10% of acetic acids and the signal was then started decreasing at higher volume ratios of acetic acid. The same trend was seen for both the acid molarities, 0.1 M and 0.2 M. However the highest signal was produced with 0.2 M acidity compared to that of 0.1 M. The net signal enhancement with the acetic acid at 5% as well as at 10% volume ratios was calculated as 400% against that of the solution without acetic acid. For the volume ratio range 0–1% of acetic acid, similar trend was reported in the literature [25]. On comparison with formic acid, the enhancement of the signal with acetic acid was higher. Although both 5% and 10% volume ratios of acetic acid were producing equal enhancement for mercury, the lower volume ratio, 5%, was selected for further studies to minimize the use of organic solvents.

3.2. Flow injection studies

The flow injection mode is generally useful for the low volume samples and is preferred for solutions having high dissolved solid content as these may lead to the blockage of the sample capillary over a period of time. Therefore the study on the effect of the acetic acid on the mercury signal was performed in flow injection mode too.

Two different mercury standard solutions along with corresponding blank solutions (without mercury) of 0.2 M acidity were prepared; one was containing mercury of 100 ng/mL concentration but no acetic acid. Other one was containing mercury of 100 ng/mL and 5% acetic acid. A 100 μL aliquot of each mercury solution was injected in the order mentioned above into the corresponding blank solutions flow channel flowing at a rate of 1.0 mL/min into the ELCAD plasma. The emission signal of Hg was continuously monitored as a function of time and shown in Fig. 4. The peak A in Fig. 4 represents the 100 ng/mL Hg solution containing no acetic acid, peak B is for the 100 ng/mL Hg solution containing 5% acetic acid. These two peaks, A and B, were recorded against their corresponding blanks. Fig. 4 indicates that upon addition of 5% (v/v) acetic acid to the mercury solution, there is a significant improvement for mercury (peak B compared to peak A). As the emission peaks obtained in the flow injection mode are not generally symmetric in shape the areas under these peaks are considered to compute the total signal intensity instead of their peak heights. So areas under the peaks A and B in Fig. 4 were calculated and the magnitude of the signal enhancement was determined. The enhancement for mercury was found to be 500% with the addition of 5% (v/v) acetic acid in flow injection mode. The reason for the signal enhancement of mercury may be because of change in the boiling point or surface tension of the mercury solution by acetic acid and thereby changes in its vaporization rate.

The analytical performance of ELCAD-AES for the determination of mercury using 5% acetic acid was evaluated. Under the optimized parameters the repeatability, expressed as the percentage relative standard deviation (%RSD) of background signal for mercury was found to be 10% (based on spectral peak area, $n = 6$) for acid blank solution containing 5% acetic acid. The %RSD for mercury standard of 20 ng/mL concentration containing 5% acetic acid was determined to be 5% ($n = 6$) based on the peak area after the average blank peak area had been subtracted, on multiple measurements with a multiple sample loading in flow injection mode. Limit of detection was determined based on the formula, $3\sigma/m$ (σ is the standard deviation corresponding to six blank measurements and m is the slope of the calibration graph of mercury) and found to be 2 ng/mL in flow injection mode for inorganic mercury. Comparison of this detection limit with the detection limit of mercury (10 ng/mL) obtained without the acetic acid (reported in our earlier paper [22] in flow injection mode) indicates that the use of acetic acid results in 5 times improvement in the detection limit of ELCAD-AES technique for mercury and thereby increase in its sensitivity for mercury.

3.3. Quantification of mercury in biological certified reference materials

With the improved sensitivity of the ELCAD-AES technique for mercury, the technique was applied for the direct determination of mercury in certified reference materials without separation of mercury from its matrix. The quantification of mercury in the reference materials was investigated with acetic acid medium. Two biological certified reference materials: Tuna fish (IAEA-350) and Aquatic plant (BCR-060) were taken for the application of the proposed method. The materials were digested by microwave system as described above. The methyl mercury present in Tuna fish material was converted into inorganic mercury during the digestion process. Hence all the mercury in the sample solution was present in only inorganic form. The mercury present in the Aquatic plant was leached into the solution by the microwave system. The completely digested sample solution of Tuna fish material (250 mg) was evaporated to near dryness using infrared lamp and then diluted to 10 mL using high pure water and maintained in 0.2 M acidity with nitric acid. As the sensitivity for mercury was improved significantly with the addition of 5% acetic acid (peak B of Fig. 4), the diluted CRM solution was further 5 times diluted with 0.2 M acidity water to contain approximately 20 ng/mL mercury (certified value of mercury is $4.68 \pm 0.44\ \mu g\ g^{-1}$). That is, the typical dilution factor was 50 for mercury for a 250 mg of Tuna fish reference material, IAEA-350. Similarly mercury (leached from Aquatic plant CRM, 500 mg) solution was evaporated to near dryness by infrared lamp and diluted to 8 mL using 0.2 M acidity water to contain approximately 20 ng/mL.

Since very low ionic emission was observed in the ELCAD-AES spectra [1], less chance of spectral interferences was expected. However matrix interferences do exist to some extent in the ELCAD method because of much lower energy of the ELCAD plasma compared to the inductively coupled plasma discharge. Hence,

Table 2
Comparison of mercury concentrations determined by ELCAD-AES in the biological certified reference materials with the corresponding certified values.

Sample	Certified value ($\mu g\,g^{-1}$)	ELCAD-AES value ($\mu g\,g^{-1}$)	Accuracy
Tuna fish (IAEA-350)	4.68 ± 0.44	4.84 ± 0.19	3.5%
Aquatic plant (BCR-060)	0.34 ± 0.04	0.36 ± 0.02	5.9%

the standard addition method was used for the direct measurement of the analyte in the presence of matrix. Four standard addition solutions for each certified reference material were prepared after adding known amounts of mercury as described in Section 2.

The conditions used in ELCAD-AES measurements for the evaluation of the quantification were: inter-electrode gap of 1 mm, a solution flow rate of 1 mL/min, and an applied constant potential of 760 V with an average discharge current of 55 mA. The bias voltage of photomultiplier tube was set to 950 V. Emission intensities of mercury were recorded in the flow injection mode for the analyte in spiked and un-spiked samples using the ELCAD spectrometer. After taking areas under the measured peaks of the unspiked and spiked samples a standard addition calibration was built. Concentration of the mercury in these reference materials were determined from the standard addition calibration plot and listed in Table 2. Comparison of these values with their corresponding certified values indicates an agreement between the values obtained by ELCAD-AES and corresponding certified values for mercury. The results may be seen to show an accuracy of 3.5% and 5.9% with an analytical precision of 3.9% and 5.5% for Tuna fish and Aquatic plant materials respectively based on the multiple measurements on multiple sample loadings ($n = 5$). The agreement indicates that the proposed method of using acetic acid and followed by the determination by ELCAD-AES has the potential to be applied for the sensitive determination of mercury in biological materials after digestion with very low amounts of the sample.

3.4. Matrix effects

As per the Jobin Yvon, France, spectrometer software, the emission line of mercury, 253.652 nm is having the possibility of spectral interference from the emission lines of Fe, Mn, Ti in ICP source. The effects of these elements as matrix, in ELCAD source on the determination of mercury at low levels were investigated by passing the solutions containing Fe, Mn, Ti, in the concentration range 10–1000 μg/mL into the ELCAD-AES. It was observed that there were no spectral interferences from Mn and Ti in the range, 10–1000 μg/mL and from Fe in the range 10–100 μg/mL. Beyond 100 μg/mL levels of iron, spectral interference of right hand side tail of iron peak was observed on the mercury peak. The interfering line of iron may be attributed to the line, 253.560 nm (atomic line of iron). The iron present in the Tuna fish CRM as well as in the Aquatic plant CRM did not affect the determination of mercury as the diluted CRM solutions passed into the ELCAD-AES contained iron less than 100 μg/mL.

4. Conclusions

The proposed method of using low molecular weight organic solvents has been found to be useful to enhance the sensitivity of the ELCAD-AES for mercury determination. The organic solvent, acetic acid resulted in better enhancement for the mercury signal compared to other solvents such as ethanol and formic acid. Acetic acid of 5% (v/v) with 0.2 M acidity has been found to give maximum enhancement for mercury. Enhancement of 500% has been observed in the flow injection mode of ELCAD-AES. The detection limit for mercury obtained in the proposed method has been computed to be 2 ng/mL. The proposed method has been validated by applying it to the determination of mercury in certified reference materials, Tuna fish (IAEA-350) and Aquatic plant (BCR-060). With the improved sensitivity the ELCAD-AES can be effectively used to quantify the mercury at very low levels in variety of materials such as biological and environmental samples.

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