

Analytical Methods

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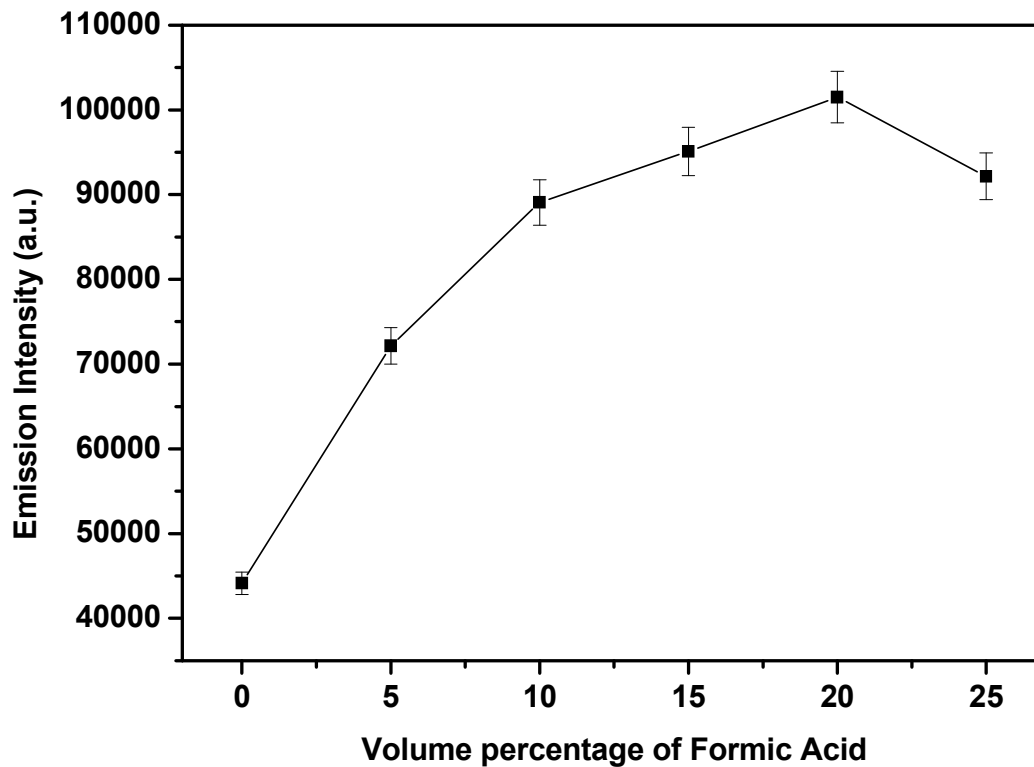
Graphical abstract

Fig. 1: Variation of the emission signal of Cd with different volume ratios of formic acid.

Error values (n = 4) are standard deviation values.

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Determination of cadmium in Zircalloys by electrolyte cathode discharge atomic emission spectrometry (ELCAD-AES)

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ABSTRACT

28 An electrolyte cathode discharge atomic emission spectrometric (ELCAD-AES)
29 method has been reported for the determination of cadmium in Zircalloys. Formic and acetic
30 acids are examined to improve the sensitivity of ELCAD-AES for cadmium determination.
31 The sensitivity of ELCAD-AES is improved 2-fold with 20% (v/v) formic acid. With 20%
32 (v/v) formic acid, the improved detection limit of ELCAD-AES for cadmium is found to be 2
33 ng mL⁻¹. Earlier reported matrix separation procedure using ammonium pyrrolidine
34 dithiocarbamate (APDC) and methylisobutylketone (MIBK) for the extraction of Cd from
35 Zirconium matrix has been optimised for ELCAD-AES analysis of cadmium. This procedure
36 is found to be useful for the quantitative determination of cadmium in Zircalloys by ELCAD-
37 AES. The precision expressed as percentage relative standard deviation of the signals of
38 multiple analyses (N=5) of ELCAD-AES method using above matrix separation procedure
39 has been found to be 10-15% for trace Cd. This ELCAD-AES method is validated with the
40 certified values of Zircaloy CRM and the glow discharge quadrupole mass spectrometry
41 (GD-QMS) values of Zircaloy sample.
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Keywords: ELCAD-AES, GD-QMS, Zircaloy, Cadmium.

1. Introduction

Zirconium-based alloys such as Zircaloy-2 and Zircaloy-4 are widely used in nuclear industry as cladding materials for boiling water reactors (BWR) fuels, pressurized water reactors (PWR) fuels and CANDU reactor fuels. These materials exhibit a very good combination of properties such as low neutron absorption, high creep resistance, stress-corrosion cracking resistance, reduced hydrogen uptake, corrosion and/or oxidation resistance, especially in the case of Zircaloy-4.¹⁻⁴ Since cadmium has high neutron absorption cross section and also causes stress corrosion cracking in these alloys, maximum allowed limit of cadmium in these alloys is restricted to $0.5 \mu\text{g g}^{-1}$ for nuclear applications.⁵⁻⁶ Therefore, accurate determination of cadmium in these alloys is very essential which require sensitive analytical techniques to determine Cd at these levels.

Various analytical methods have been developed for determination of Cd at low levels in zirconium based materials by using various instrumental techniques such as graphite furnace atomic absorption spectrometry,^{7,8} inductively coupled plasma atomic emission spectrometry,⁹⁻¹¹ inductively coupled plasma mass spectrometry,¹² and glow discharge mass spectrometry.^{13,14}

However, low power direct current atmospheric pressure glow discharges (dc-APGD) are nowadays considered one of the most promising and alternative excitation sources against traditional plasmas such as inductively coupled plasma and microwave induced plasma. These glow discharges are generated between metallic anodes and cathodes that are electrolyte solutions overflowing from inlet tubes or capillaries (electrolyte cathode discharge, ELCAD) or sprayed at the exit of capillaries toward counter electrodes (liquid sampling atmospheric glow discharge). They are used in optical emission spectrometry and mass spectrometry for the determination of different metals in water samples and other environmentally relevant liquid matrices.¹⁵⁻¹⁸

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Electrolyte cathode discharge atomic emission spectrometry (ELCAD-AES) has many desirable advantages over conventional plasma sources. Advantages of this technique over atomic spectroscopy and atomic mass spectrometry techniques are: 1) ELCAD source does not require discharge gas (i.e. argon) as in ICP-OES or the flame gases (acetylene etc.) as in flame AAS, 2) ELCAD-AES does not need vacuum as in mass spectrometry, 3) the capital cost of the ELCAD-AES is low, 4) it consumes little power (<75 W), however still offers low detection limits (10s of ppb)¹⁹⁻²² for specific set of elements. Gubkin²³ 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 discharges of aqueous solutions by a number of authors.^{19,24-28} ELCAD-AES technique was earlier successfully tested for a set of elements present in aqueous solutions.^{21,22,24,29-34} This reveals that several papers have dealt with quantifying analytes in actual samples by ELCAD and ELCAD like instruments. Earlier the ELCAD-AES was applied for the determination of major to trace level elements other than cadmium in Zircalloys.²² The authors²² reported that elements Ni, Co, Fe, Mn, Mg, Cu, Cr, Pb, and Ca were determined in Zircalloys by ELCAD-AES without separating the matrix. To our knowledge there are no reports in the literature about the determination of cadmium in zirconium based materials by using ELCAD-AES.

This paper reports the determination of cadmium in Zircalloys by using ELCAD-AES. Formic and acetic acids are examined to improve the sensitivity of ELCAD-AES technique for cadmium. Direct analysis of cadmium in Zircalloy by ELCAD-AES using 20%(v/v) HCOOH has been presented. A method for the quantitative determination of cadmium in Zircalloys is reported using a matrix separation procedure of APDC and MIBK. Analytical figures of merit of the proposed method are evaluated and presented. ELCAD-AES concentrations of cadmium determined by this method in a Zircaloy certified reference

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3 material and also in a Zircaloy sample are compared with the corresponding certified values
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5 of CRM and GD-QMS values respectively.
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10 11 **2. Experimental**

12 13 14 15 **2.1. Instrumentation**

16 17 18 **2.1.1. ELCAD - AES**

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21 The ELCAD source described in detail in an earlier paper,³¹ mainly consists of two
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23 parts. First part is a tungsten pin anode (20 mm long and 1 mm diameter) housed in the upper
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25 part with a micrometer to precisely adjust the gap between the electrodes and maintained at a
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27 potential between 700 and 1000 V. The second is a solution cathode in the lower part which
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29 consists of a glass capillary inserted into a PTFE (polytetrafluoroethylene) cylinder which in
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31 turn is fixed to a PTFE reservoir for the overflowing solution that is continuously drained by
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33 gravity when it crosses certain level. A platinum 'O' ring is placed over the glass capillary,
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35 about 3 mm below the top and connected to the ground of the power supply. The draining
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37 sample solution flows along the 'V' groove cut across the face and down one side of the
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39 capillary and is thus continuously in contact with the grounded electrode, and in turn acts as
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41 the cathode of the source. The anode can be precisely moved up or down to accurately vary
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43 the inter electrode distance. The source is mounted on a platform built using 3
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45 micropositioners (three independent micrometer screw gauges) so that it can be moved
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47 precisely in x, y and z directions to accurately position the plasma to obtain the maximum
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49 emission signal output by the spectrometer. This schematic diagram of this arrangement was
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51 given in an earlier paper³¹. The gap between tungsten anode and liquid cathode is reduced to
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53 near touching to ignite the discharge initially.
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The emission signal from the discharge plasma is collected on to the inbuilt- lens of the spectrometer by adjusting the position of discharge. Mezei et al³⁵ reported that the intensity of H β line was maximum near cathode. Similarly the intensities of the various analytes studied by these authors were also found to be maximum near the cathode reason only. Hence the H β line was used to optimize the discharge position for this work. The position of the discharge was optimized such a way that the emission signal of hydrogen (H β line) at 486.133 nm was maximised by moving the source up and down (along the line joining cathode and anode, i.e. vertical direction) using the micrometer. The bias voltage of photomultiplier tube was set at its maximum voltage of 990 V.

Discharge parameters were optimized with 1.0 $\mu\text{g mL}^{-1}$ cadmium solution having 0.2 M acidity to obtain a stable discharge and maximum emission signal for cadmium at 228.8 nm. The average discharge current was found to be 45 mA (for discharge voltage of 700 V), 49 mA (720 V), 53 mA (740 V), 55 mA (760 V), 61 mA (780 V), 64 mA (800 V). The variation of Cd emission signal is plotted in Fig.1 as a function of discharge voltage. The Fig.1 shows that Cd signal is gradually increasing with the discharge voltage. However, the signal fluctuation is also found to be increasing with the voltage. The relative standard deviation (n=4) of the Cd signal was observed to be 2 % at the discharge voltage of 700 V, 2 % at 720 V, 3 % at 740 V, 3 % at 760 V, 5 % at 780 V and 10 % at 800 V. The tungsten (anode) pin was observed to be red hot at the discharge voltages of 780 V and 800 V. Therefore the discharge parameters were optimised at 760 V (discharge voltage) and 55 mA (discharge current). The optimized discharge conditions are listed in Table 1. The number of points (11) taken for scanning each peak (Table 1) indicates the points for a spectral line only. As the spectrometer software scans the reference wavelength (H-beta line) at 486.1 nm every time before scanning analyte line, total approximate scanning time and consumed volume of the solution for an emission line are found to be 30 seconds and 1 mL respectively.

Hence on the average it takes 1 mL per element. The time required for the stabilization of the discharge is 1 minute.

Atomic emission spectrometer (Model: JY-38, Jobin-Yvon, France) which was earlier a part of a inductively coupled plasma atomic emission spectrometer (ICP-AES) with a 1.0 m Czerny – Turner grating (3600 lines mm⁻¹) monochromator was used. 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 K Ω 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 of 1.0 mL min⁻¹. 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 emission line of hydrogen (H β line), 486.133 nm was used as the reference wavelength³¹ for the spectrometer.

2.1.2. GD-QMS

A glow discharge quadrupole mass spectrometry (Model GQ-230, VG Elemental, UK), was used for the analysis of Zircalloys. The operating parameters were 1.0 kV (average) discharge voltage, 3.0 mA discharge current, 30 mL min⁻¹ discharge gas (argon gas) flow rate. The dual detector system (Model No. 4870V, Galileo Electro-Optics Corp., Sturbridge, MA, USA) which utilizes an electron multiplier for ion counting for trace elements (ion currents < 3 x 10⁻¹³ amp) and a Faraday cup for the measurement of major and minor elements (ion currents > 3 x 10⁻¹³ amp) was used. The Faraday cup and Electron Multiplier detectors were cross-calibrated by measuring the signal intensity at mass 76 (⁴⁰Ar³⁶Ar⁺). Detector calibration factor was adjusted to be 2550 \pm 200 by adjusting the HT voltage to the electron multiplier before the scanning.

2.1.2.1. Sample preparation for GD-QMS

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Being a surface technique, surfaces of the Zircaloy certified reference material (Zircaloy-X868-13D, M/s. Teledyne Wahchang, Albany, USA) and sample pins of typically size 20 mm x 3 mm were cleaned with methanol, dried under infrared lamp and mounted on pin sample holder. The Zircaloy-X868-13D was used as a standard to generate relative sensitivity factors for the GD-QMS analysis. Each sample was loaded into the GD system and evacuated to a vacuum of around 1×10^{-3} mBar (around 0.1 Pa) prior to striking the discharge to remove surface atmospheric contaminants. Plasma cleaning of the surface was also carried out for 50 minutes to remove the embedded gaseous contaminants on the surface. Then analytical measurements were carried out at a mass step of 0.01 amu with 140 points. A single scan for Faraday cup (for zirconium isotope) and 20 scans for electron multiplier (for Cd) were used for each measurement. Four repetitive measurements were recorded for each sample.

2.2. Test solutions, Samples and Standards

Ultra-pure water (>18 M Ω cm: resistivity) obtained by a combination of reverse-osmosis (RO), mixed bed ion-exchanger Milli-Q (Millipore, Bangalore, India) water purification system was used for the analysis. High purity nitric and hydrochloric acids were prepared in-house using quartz sub-boiling units in our laboratory. Reagent grade hydrofluoric acid was used. Stock standards of analytes were of 1 mg mL^{-1} concentrations provided by Merck. Working standards in the concentration range of $\mu\text{g-ng mL}^{-1}$ were prepared daily by sequential dilution. Ammonium pyrrolidine dithiocarbamate (APDC), Methylisobutylketone (MIBK), formic acid, acetic acid were of reagent grade. The Zircaloy certified reference materials (Zircaloy-4 NIST-360b, Zircaloy-X868-13D, M/s. Teledyne Wahchang, Albany, USA) and Zircaloy samples were used for this study. The composition of these Zircaloy reference materials is given in Table 2.

2.3. Sample Digestion and Matrix separation procedure for cadmium

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3 About 500 mg of Zircaloy certified reference material (Zircaloy-4 NIST-360b) was
4 dissolved in the mixed solution of nitric acid (7 mL) and hydrofluoric acid (7mL). The
5 solution was evaporated to near dryness by IR lamp and diluted to a total volume of 10 mL
6 with water and maintained in 0.1 M acidity using nitric acid. The process blank and other
7 Zircaloy samples were treated identically.
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16 All the digested sample solution (i.e. 10 mL) was mixed with 1 mL of 3% APDC and
17 2 mL of MIBK in a separating funnel and was continuously shaken for 2 minutes to extract
18 cadmium into MIBK layer. After separating organic layer, the aqueous layer was mixed with
19 2 mL of fresh MIBK and again shaken for 2 minutes to extract residual cadmium into MIBK
20 layer. Then aqueous layer was drained out. The extracted (two) fractions of organic layers
21 were mixed together and the mixed solution was added with 1 mL of 2M nitric acid and then
22 shaken for two minutes for back-extraction of cadmium into aqueous layer. The later step
23 was repeated with fresh 1 mL of 2M nitric acid. The total (2M) aqueous solution containing
24 extracted cadmium was mixed with formic acid and water in such a way that the final
25 solution contained 20(v/v) formic acid and acid molarity of 0.2 M. Identically the process
26 blank was treated. The standard addition solution of samples along with process blank
27 solution were analysed by ELCAD-AES for cadmium.
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45 **3. Results and Discussion**

46 **3.1. Studies on the determination of Cd in Zircaloy CRM without separating matrix**

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52 Stability of the electrolyte cathode discharge depends on both conductivity and matrix
53 content of the solution being passed into the source. Instability of the discharge increases
54 with the increase in concentration of matrix content in the solution. Our earlier studies²²
55 showed that maximum Zr matrix concentration that was allowed to the ELCAD-AES
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3 discharge was 5 mg mL^{-1} . Hence same matrix concentration (5 mg mL^{-1}) was used for further
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5 studies on cadmium and its quantification.
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9 The matrix interferences such as enhancement or suppression of analyte signal are
10 expected to be higher in the ELCAD technique¹⁹ compared to inductively coupled plasma but
11 less than by flame emission as the temperature¹⁹ of the ELCAD plasma is about 5000 K
12 (excitation temperature of iron) which lies somewhere between commonly used acetylene-
13 nitrous oxide flames (2800 K) and inductively coupled plasma (8000 K). The iron excitation
14 temperature is one of the parameters to consider the matrix effects. Normal temperature of
15 the flame in Flame-AAS, discharge plasma in ELCAD and inductively coupled plasma in
16 ICP source reported in the literature were 2800 K, 5000 K and 8000 K respectively. As the
17 temperature of the flame or plasma is the main factor for the matrix effects, hence this factor
18 was compared between F-AAS and ELCAD plasma. Therefore, standard addition method
19 was used for the direct measurement of the cadmium in the presence of Zr matrix by
20 ELCAD-AES to eliminate these matrix effects. A set of standard addition solutions each
21 containing 5 mg mL^{-1} concentration of digested Zircaloy matrix (Zircaloy-4 NIST-360b) was
22 prepared in 0.2 M acidity using nitric acid. The corresponding process blank solution was
23 also prepared identically. These sample and blank solutions were analysed by ELCAD-AES
24 directly without separating matrix for cadmium. The emission signals of Cd were recorded at
25 its emission wavelength of 228.802 nm. The concentrations so obtained are listed in the third
26 column of Table 3 for cadmium in the Zircaloy SRM and a Zircaloy sample.
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52 The recorded ELCAD-AES signals for Cd in Zircaloy SRM and Zircaloy samples
53 were found to be close to the respective process blanks. Hence the concentration of Cd was
54 determined using the process blank value of above Zircaloy materials and listed in Table 3 as
55 limit values. Using the certified value of Cd in Zircaloy SRM (Zircaloy-4 NIST-360b), the
56 level of Cd in its final SRM solution containing 5 mg mL^{-1} matrix concentration was
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3 computed to be $< 5 \text{ ng mL}^{-1}$. This value was found to be very close to its ELCAD-AES
4 detection limit (5 ng mL^{-1}). Due to the dilutions (total dilution factor was 200 for cadmium)
5 required to minimise the matrix effects and the inadequate sensitivity of ELCAD-AES for
6 cadmium, it could not be quantified in Zircalloys directly by ELCAD-AES. In order to
7 quantify cadmium in Zircalloys either sensitivity of the ELCAD-AES needs to be improved or
8 a matrix separation method has to be adopted.
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18 **3.2. Studies on the enhancement of sensitivity of ELCAD-AES for the analytes**

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21 Initially, efforts were made to improve the sensitivity of the ELCAD-AES for Cd
22 determination. Since the low boiling organic solvents were earlier found to improve the
23 emission signals of specific elements,^{22,36-39} two low boiling point organic solvents, acetic
24 acid and formic acid, were examined with their different volume ratios for Cd signal
25 enhancement.
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34 The effects of formic and acetic acids were investigated separately in the range of 0-
35 25% (v/v) on the signal enhancement of element Cd by ELCAD-AES with each solution
36 containing Cd of 500 ng mL^{-1} concentration and their corresponding process blank solutions.
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38 It was earlier reported that ELCAD plasma was unstable beyond 25% (v/v) of these organic
39 solvents³⁹. Compared to acetic acid medium, formic acid produced more enhancement for
40 Cd. Enhancement of Cd signal with acetic acid was found to be only 1.2 times (maximum)
41 higher than that of 0% acetic acid. Whereas enhancement of Cd signal with formic acid was
42 observed to be 2.3 times (maximum) compared to that of 0% formic acid. This reveals that
43 effect of formic acid on Cd signal was more compared to that of acetic acid. Hence further
44 studies were performed only with formic acid.
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58 The signal enhancement by these organic solvents is attributed to the reduction in the
59 surface tension of aqueous solution as it can promote the generation of small droplets during
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3 the aspiration processes.⁴⁰ Schwartz et al.,⁴¹ presented a evidence that the desolvation
4 mechanism in ELCAD sources is electrospray-based. As the organic solvent lowers surface
5 tension, this could result in an increased amount of electrospray, and a higher transfer (higher
6 through put) of analyte to the discharge and correspondingly improved analyte signal. Our
7 observation also supports the earlier noted observations.⁴¹ Xiao et al.,⁴² observed a slightly
8 increase in the emission intensities of OH and N₂ in the presence of formic acid, which
9 indicated that the discharge intensity of plasma was enhanced to some extent with the
10 addition of formic acid. That is the signal enhancement may be caused by the change of
11 discharge characteristics (e.g., excitation temperature, ion density) in the presence of organic
12 substances. Therefore the magnitude of signal enhancement could vary with type of organic
13 solvent (i.e. acetic acid or formic acid). Hence the acetic acid could not enhance the signal as
14 high as formic acid for cadmium.

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33 Emission signals of Cd obtained with different volume ratios of formic acid are
34 shown in Fig. 2 after subtracting corresponding blank signals. Fig. 2 shows 20% (v/v) formic
35 acid produces maximum enhancement for Cd. Signal enhancement factor for Cd was
36 determined to be 2.3 with 20% (v/v) formic acid compared to that of 0% HCOOH and is
37 indicating the improvement is about 2-fold for Cd. In the previous studies²² with formic acid
38 on other elements, the improvement was 2-fold for Ni, Co, Fe, Mn, Mg, Cu, Ca and 5-fold for
39 Pb in Zircalloys by ELCAD-AES.

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The repeatability, expressed as the percentage relative standard deviation of
background signal for cadmium was found to be 10% for acid blank solutions containing
20% (v/v) HCOOH on multiple measurements (N = 5) with a multiple sample loadings (N =
4). The %RSD of Cd signal with 1000 ng mL⁻¹ Cd solution containing 20% HCOOH was
determined to be 5% after average blank peak signal was subtracted, on multiple
measurements (N = 4) with a multiple sample loadings (N = 4).

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Detection limit of Cd depend on sensitivity as well as fluctuation of the background signal. The use of formic acid resulted in improvement in sensitivity for cadmium with the same background fluctuation. That is, background emission spectral characteristics in presence of formic acid were similar to that of without formic acid and hence the improvement in the detection limit was found. Detection limit was computed based on the $3\sigma/m$ formula (σ is the standard deviation corresponding to ten blank measurements and m is the slope of the calibration graph of each element). With 20% (v/v) HCOOH the detection limit was computed to be 2 ng mL^{-1} . Comparison of detection limits obtained with (2 ng mL^{-1}) and without HCOOH (5 ng mL^{-1}) indicates that formic acid improved the detection limit about two times.

Concentration level of Cd in Zircaloy SRM (NIST-360b, Cd: $< 1 \text{ } \mu\text{g g}^{-1}$) solution containing matrix of 5 mg mL^{-1} is around 5 ng mL^{-1} . As the maximum allowed limit for Cd in Zircaloys is $0.5 \text{ } \mu\text{g g}^{-1}$ for nuclear applications, the Zircaloy samples prepared for nuclear industry in general will contain Cd less than $0.5 \text{ } \mu\text{g g}^{-1}$. Hence the improved detection limit of 2 ng mL^{-1} with formic acid is still not sufficient for the quantification of Cd by ELCAD-AES. Hence the concentrations of Cd determined in Zircaloy CRM and Zircaloy sample using formic acid (20%v/v) are listed as limit values (i.e. based on the process blank signals) in fourth column of Table 3. Therefore, quantitation demands for a matrix separation procedure for accurate determination of Cd at these levels by ELCAD-AES.

3.3. Matrix separation for cadmium determination

A solvent extraction procedure with APDC reagent and MIBK solvent is widely used method for the separation of cadmium from zirconium matrices.⁹ In this procedure, cadmium was separated from Zr matrix and extracted into MIBK solvent and then back extraction of Cd from MIBK was done by using 4M nitric acid medium. Therefore this solvent extraction

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3 procedure has been adopted to separate Cd from Zircaloy and to determine Cd by ELCAD-
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5 AES.
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9 However, the solvent extraction procedure cannot be used directly (i.e. as it is) for
10 ELCAD-AES studies as the 4M nitric acid solution used in that procedure to extract Cd from
11 MIBK solvent will not be tolerated in ELCAD source. This solution needs to be diluted to
12 bring it to 0.2 M nitric acid medium as the solutions of higher molarities (>0.2M) can
13 produce instability in the ELCAD discharge.³¹ But, this dilution step lowers the cadmium
14 content in the final solution. Hence a separate study was carried out to check whether lower
15 molarities (< 4 M) of nitric acid can be useful for back extraction of Cd from MIBK
16 quantitatively. Various standard aqueous solutions containing cadmium of 1000 ng absolute
17 were mixed with freshly prepared 0.5 mL of 5% APDC and extracted into MIBK solvent by
18 shaking the solution in separating funnel for two minutes. Back extractions (N=4) were
19 performed with different acid molarities 1M, 2M, 4M of nitric acid. The average percentage
20 recoveries of back extraction of cadmium were found to be 72%, 98%, 103% for the acid
21 molarities 1M, 2M, 4M respectively. Besides 4M nitric acid medium, 2M nitric acid medium
22 was also found to back extract Cd quantitatively from MIBK medium. So, 2M nitric acid
23 medium is preferable over 4M nitric acid medium for back extraction of Cd as it reduces the
24 dilution factor two times for analysis by ELCAD-AES. The effect of major elements Sn, Fe,
25 Cr, Ni of Zircaloy (Table 2) on the recovery of cadmium was also studied using 2M nitric
26 acid medium by taking equivalent amounts of these matrix elements (present in 500 mg of
27 Zircaloy sample) into a 0.2M solution containing cadmium of 1000 ng absolute amount. The
28 levels of the matrix elements Cr, Fe, Ni, Sn in Zircalloys are given in Table 2. The levels of
29 these elements (equivalent amounts) present in around 500 mg of Zircaloy-4 NIST-360b
30 material were computed from Table 2 and added to the solution containing 1000 ng absolute
31 amount. The solvent extraction was performed after adding 0.5 mL of 5% APDC to this
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3 solution and extracted cadmium into MIBK and then back extracted into aqueous layer with
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5 2M nitric acid solution. It was found that recovery of Cd was 98% in presence of these
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7 elements. Hence for all subsequent solvent extraction studies 2M nitric acid medium was
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9 used to back extract cadmium from MIBK solvent.
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14 Therefore using this solvent extraction procedure cadmium was separated from
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16 Zircaloy matrices such as Zircaloy CRM and Zircaloy sample and quantified by ELCAD-
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18 AES with standard addition calibration method and listed in fifth column of Table 3.
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21 22 **3.4. Validation of the results** 23 24

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26 ELCAD-AES concentrations obtained through matrix separation method of APDC
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28 and MIBK were validated with certified values of Zircaloy CRM (Zircaloy-4 NIST-360b)
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30 and with GD-QMS values of Zircaloy sample. ELCAD-AES values of these alloys obtained
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32 by three ways: first one without separating matrix and without formic acid, second one
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34 without separating matrix and with formic acid and third one with matrix separation and with
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36 formic acid are listed in Table 3 and compared with the corresponding certified values of
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38 Zircaloy CRM and GD-QMS values of Zircaloy sample.
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43 The precision expressed as percentage relative standard deviation of Cd signals of
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45 multiple analyses (N=5) of this ELCAD-AES method using matrix separation procedure was
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47 found to be between 10-15%. The detection limit of cadmium in Zircaloys with the final
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49 procedure (i.e. ELCAD-AES with matrix separation) was determined based on the $3\sigma/m$
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51 formula (σ is the standard deviation corresponding to ten process blank measurements and m
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53 is the slope of the calibration graph of cadmium) using the process blank solution obtained
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55 after matrix separation. It was found to be 2.0 ng mL^{-1} and the detection limit was found to be
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57 72 ng g^{-1} in solid Zircaloy. The detection limit 72 ng g^{-1} was computed for the solid sample
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59 by multiplying the total dilution factor to the solution detection limit 2.0 ng mL^{-1} as was used
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3 for the quantification. Detection limits attained using GD-QMS are dependent on factors such
4 as integration time, the number of points and the number of repeated scans. The detection
5 limit was defined as three times the noise on the background signal.⁴³ The detection limit for
6 cadmium in Zircalloys was computed to be 25 ng g⁻¹ under optimized conditions (for 20 ms
7 integration time and 140 points and the number of repetitive scans was 10) by GD-QMS. It is
8 low enough to be useful in the context of nuclear materials as the maximum allowable
9 concentration is 500 ng g⁻¹.

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20 The limit values listed in 3rd and 4th column of Table 3 are obtained based on the
21 process blank signals. On comparison, these limit values are found to be close to both the
22 certified values and GD-QMS values. The accurate values (i.e. not limit values) listed in 5th
23 column of Table 3 obtained with the matrix separation procedure are found to be technically
24 in agreement with the corresponding certified values and GD-QMS values. As all the
25 certified values for Cd are only less than values, statistical comparison could not be done.
26 Here both certified and the GD-QMS values are “less than” values where as ELCAD-AES
27 values of matrix separation procedure are accurate values (i.e. non limit values) for Cd in
28 Zircalloys. This reveals ELCAD-AES values can be useful to assess the Zircalloys for Cd
29 level. For GD-QMS analysis, the availability of Zircaloy standard certified for Cd accurately
30 (i.e. not limit value) is a big problem. As the maximum allowed concentration of Cd in
31 Zircalloys for nuclear industry is 0.5 µg g⁻¹, ELCAD-AES with the matrix separation
32 procedure can be an alternative analytical tool to assess the levels of Cd in Zircalloys. Thus
33 this ELCAD-AES method is useful for the quantification of cadmium present at trace levels
34 in Zircalloys.

3. Conclusion

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ELCAD-AES method using matrix separation procedure has been found to be useful for
the determination of trace cadmium in Zircalloys. After the separation of Cd from Zirconium

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3 matrix using 5% APDC and MIBK, 2M nitric acid has been found to back extract cadmium
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5 quantitatively from MIBK. A 20% (v/v) HCOOH is enhancing the sensitivity of ELCAD-
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7 AES for Cd and improves its detection limits by two folds. Matrix separation method of
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9 APDC and MIBK enhances the usability of ELCAD-AES technique for the determination of
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11 trace Cd in Zircalloys. The accurate ELCAD-AES results (i.e. not limit values) obtained by
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13 the ELCAD-AES method are found to be in technically agreement with the corresponding
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15 certified values of CRM and GD-QMS values. The studies reveal that ELCAD-AES
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17 technique can be utilised for Zircalloys and Zirconium based materials for low level Cd
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19 determination.
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Table 1 Operating parameters of ELCAD-AES.

Operating parameters	Set Value
Discharge voltage	760 V
Average discharge current	55 mA
Inter-electrode gap	2 mm
Solution flow rate	1 mL min ⁻¹
Integration time	0.5 s per point
Number of points taken for scanning each peak.	11 points

Table 2 Certified values of reference materials used in ELCAD-AES and GD-QMS analyses

Element	Certified values	
	Zircaloy-4 NIST-360b	Zircaloy-X868-13D*
	($\mu\text{g g}^{-1}$)	($\mu\text{g g}^{-1}$)
Si	(60) ^a	179±4
P	(10) ^a	35±3
Ti	20±10	122±16
V	<(30) ^a	93±5
Cr	1000±100	580±26
Mn	10±5	56±2
Fe	2100±100	2787±66
Ni	25±10	134±6
Co	<10	42±1
Cu	20±10	83±2
Nb	<50	570±12
Mo	<10	128±2
Hf	80±10	178±6
Ta	<100	716±4
W	<50	112±13
Pb	<(5) ^a	101±11
Na	---	<10
Mg	<(1) ^a	<5
Ca	---	<10

	Cd	<1	<0.2
		%	%
	Sn	1.55±0.03	1.23±0.03
	Zr	98.091	98.709

a: Bracketed values are approximate values. *: Zircaloy-X868-13D, M/s. Teledyne Wahchang, USA..

Table 3 Comparison of ELCAD-AES concentrations of Cd in Zircalloys with certified and GD-QMS values.

Zircaloy	Concentration of cadmium			
	Certified value ^a $\mu\text{g g}^{-1}$	ELCAD-AES ^b (without HCOOH) $\mu\text{g g}^{-1}$	ELCAD-AES ^b (with HCOOH) $\mu\text{g g}^{-1}$	ELCAD-AES (with matrix separation) ^c $\mu\text{g g}^{-1}$
Zircaloy-4	< 1	< 1	< 0.5	0.46 ± 0.05
NIST-360b				
Zircaloy sample	< 0.4 *	< 1	< 0.5	0.33 ± 0.03

* : GD-QMS value.

^a : Uncertainty is the combined uncertainty value. ^b & ^c : Uncertainty is the standard deviation value. N=4 for both ELCAD-AES and GD-QMS values.

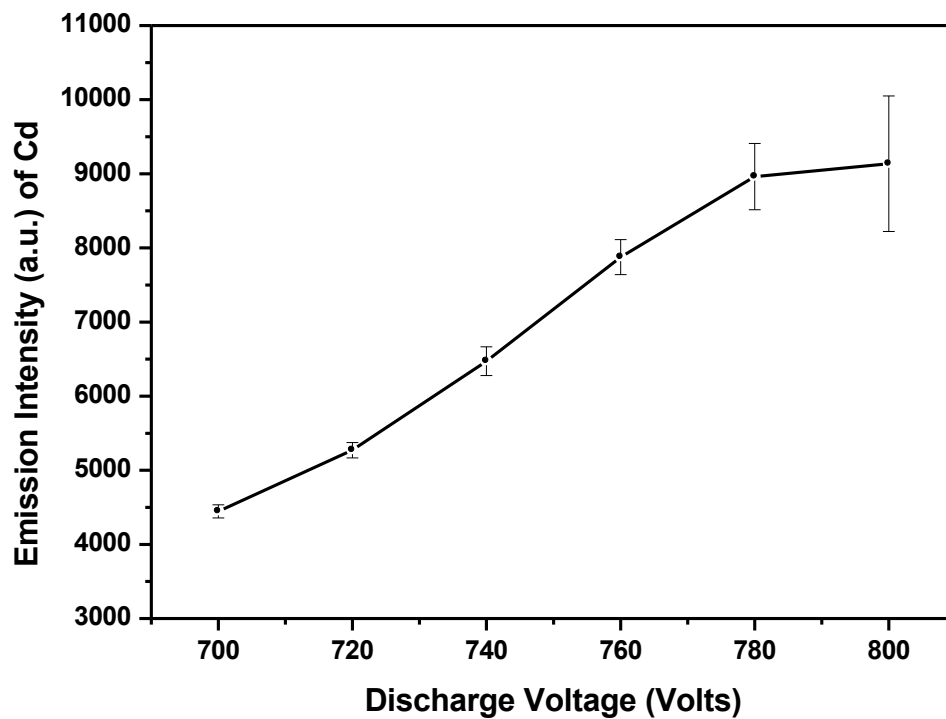


Fig. 1: Variation of emission signal of Cd with discharge voltage. Error values ($n = 4$) are standard deviation values.

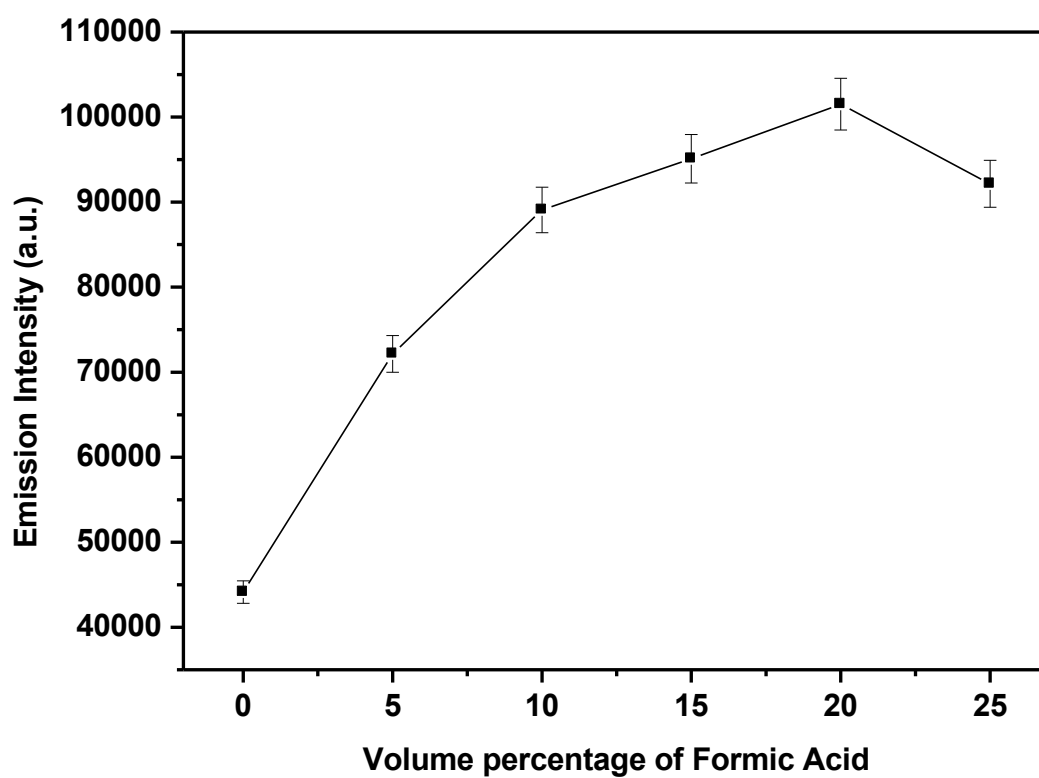


Fig. 2: Variation of the emission signal of Cd with different volume ratios of formic acid. Error values ($n = 4$) are standard deviation values.

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8 **Fig. 1: Variation of emission signal of Cd with discharge voltage. Error values (n = 4)**
9 **are standard deviation values.**
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14 **Fig. 2: Variation of the emission signal of Cd with different volume ratios of formic**
15 **acid. Error values (n = 4) are standard deviation values.**
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