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Enhancing trends of intensity signal of trace level Hf in zirconium oxide using AES sequential addition method

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A sensitive, rapid and simple method to detect Hf at trace level in Zr has been described. It is based on the sequential addition of sample after each pre excitation period, in presence of graphite as buffer. The improvement with respect to the other published procedures lies in the use of solid powdered sample, omitting the step of wet chemistry or use of any optical filter. The enhancing trends of intensity curves were also studied for various stages. The coefficient of variation was found to be within the range 6 - 12% for different batches of samples. The detection limit was found to be $30 \mu\text{g g}^{-1}$. The improved sensitivity, accuracy and rapidity make it suitable for routine evaluation of Hf using emission spectroscopy.

Key words: Hafnium, zirconium, intensity, AES

INTRODUCTION

The fabrication of nuclear fuel cladding poses some stringent specified conditions, so it has to pass through certain rigorous quality tests to meet these specifications. Generally different analytical, spectroscopic techniques are employed for the accurate estimation of impurities in refractory matrices or the characterization of nuclear fuel but each technique has its own inherited limitations (Rehana, 1990; Shenkay, 1990; Waring, 1964). Zirconium is generally used for cladding purposes as it is corrosion resistant in acid medium as well as in other corrosive salts. Moreover, it has the added quality of high melting point, and high strength. It has low neutron absorption cross-section, (0.8 barns) as well. These qualities render it highly suitable for cladding of uranium pellets. However, Hf is always, inevitably associated with Zr, in natural resources. But Hf is pet aversion for use in nuclear reactor cladding fuel because of its very high neutron absorption cross section of 105 barns. The quality assurance concerning Hf level in Zr is of prime significance and poses a high challenge to analytical chemists. Although many analytical techniques have been quoted in literature to determine Hf at ultra trace level, but each

technique has its inherited limitations in its accurate estimation. The NAA is reactor dependent and needs the availability of a nuclear reactor. Atomic Absorption Spectrophotometry, Inductively Coupled Plasma Emission Spectrometry, and Mass Spectrometry, or ICP-M. Spectrometry may be successfully applied to determine Hf but they involve the wet chemistry, co-precipitation and dissolution of zirconium, itself is a rigorous and time consuming process (Baluch et al, 1990; White, 1982; Korte and Donovan, 1983; Sataynarayana, 2000).

XRF has been successfully used for Hf measurement in zirconium (Hasney, 1990; Kirby et al, 2002; Waring, 1964). This could also be one of the reasons for the apparent lack of published data on the use of other spectroscopic techniques. Nevertheless, XRF need a comparatively large amount of Zirconium which some-times may not be easily available with many laboratories. Hence it was important to develop an emission spectro-graphic techniques obviating all the cumbersome dissolution or irradiation processes. The volatilization of Hf and Zr is very difficult due to their refractory nature especially when one is present in significantly high concentration. Moreover both of them possess quite similar properties which makes it rather difficult to estimate Hf accurately. Their oxides are even more refractory as they are reduced to carbides at the graphite electrode surface. The carbides

Table 1. Equipment and operating conditions

Arc focused on the grating	
Slit width, μ	20
Slit height, mm	2
Grating angle	986
Grating, G/mm	1180
Dispersion (2 nd order), A/mm	2.5
Preburn period, s	15
Exposure period, s	110
Power source	dc-arc
Current, A	25
Exhaust	Closed
Electrode gap, mm	3
Electrode: Anode	RW0006
Cathode	RW0067
Anode charge (total),mg	300
Wave length region, nm	225.6-340.6
Atmosphere	air

on reaction with air atmosphere may change into nitrides which are stable and are a source of highly undesirable cyanogens bands. Hence some spectroscopic techniques using controlled atmosphere have been used for the estimation of Hf. In Emission Spectroscopy, some workers have used the ordinary or tape method to measure high range of Hf (Naunde, 1963; Rossi, 1960).

In the present study, a method has been developed for the measurement of Hf at very low level without involving the creation of inert atmosphere or any filter and only making use of sequential addition. This methodology can be useful where only Atomic Emission Spectroscopy (AES) is available or for comparative studies with other techniques. The study was also aimed to study the evolution behavior of Hf from a refractory matrix such as zirconium. The possible interferences, masking or partial overlapping of the neighboring analytical lines of impurities, especially Zr and Fe have been thoroughly investigated. Atomic Emission spectroscopy was used as its resolution was 0.007 nm in 2nd order which is the best available in other analytical spectroscopic techniques. This facility helped us to measure Hf down to a very low level of concentration without interference of any Zr line. Different spectral lines have been used for high and low ranges separately.

MATERIALS AND METHOD

Chemical reagents

The chemicals used were spec-pure (Johnson Matthey) for the preparation of calibration samples. Ringsdorff graphite powder was utilized during the course of studies.

Apparatus

A 3.4 Jarrel Ash type, Mark IV spectrograph was used with a plane

grating of 1180 grooves/mm. A Jarrel Ash non-recording densitometer, photoprocessor, Model No.34-301. Plate calibration, ASTM Designation, E-1167-70a.

Procedure

A mixture of sample weighing 100 mg with 10% graphite powder was loaded into the electrode after thorough mixing in a clean agate mortar. A plastic tamping rod of appropriate diameter with a small protruding structure of conical shape was used to press the powdered sample inside the crater which also created a small hole in the center in the compact sample as per ASTM recommendations E402-70a (ASTM, 1971). This action not only helped in uniform compaction and packing of the finely ground powdered sample but also played a crucial role in smoothly releasing the sample from the crater into the arc stream above the electrode rim eliminating the sudden jumps of the sample. Any particles falling on the rim of the anode were slightly and carefully brushed off so that these particles do not drag along the rest of the material into the gap between electrodes on the initiation of the exposure. This action helped to eliminate the darkening of the spectra caused by sudden eruption of powder. Operating equipment and experimental conditions are given in Table 1. The whole operation was undertaken following the instructions, in commensuration with the CITAC, Ed.1.0,1995 and ISO 17025.

After the loading of the electrodes, the exposure started with a preburn period of 15 s during which the shutters were closed to avoid the recording of the spectrum. Then 50 mg of sample was again loaded and subjected to another preburn of 15s which was subsequently followed by another preburn of 15 s along with an exposure period of 125s. The exposures were taken in triplicate at a current value of 25A; following the recommended practice of ASTM designated E-115 and photometric processing and calibrations under the instructions of ASTM, E-115-71 and E-116-70a. A computer program KAPGAM was used to convert percentage into intensity.

RESULTS AND DISCUSSION

The main hindrance in the determination of Hf in Zr while both are in solid powdered form, lies in the similarities of their physical and chemical properties. Both are refractory as depicted in Tables 2 and 3. The heat of vaporization of Hf 155 k-cal/g atom is higher than that of Zr, 120 k-cal/g atoms. Although both are very high, anyhow the study is undertaken making use of these properties along with other behaviors. The main objective of the study was not only to reduce background of Zr to a minimum level to get rid of its adjacent spectral lines to Hf but also to force Hf to appear into the plasma at appropriate time. Another goal of the proposed methodology was to enhance the pouring in of a sufficient amount of Hf excited atoms in the plasma so as to make it detectable. For this purpose either carrier distillation techniques or other pre-separation methods have been used in the past, where carrier action or solvent action could have been operative contributing to the line intensity (Rautscheka, 1978; Schroll et al, 1963; Rehana and Shahid, 1999).

Relationship between intensity and current

After that, it is desired that the residence time of Hf atoms

Table 2. Specifications of Zr. for nuclear reactor.

S. No	Specifications	Values
1	Melting Point, °C	1855
2	Boiling Point, °C	3580
3	Density, g/ (cm) ³	6.506
4	Thermal conductivity cal /g .	0.0505
5	Heat of vaporization, k- cal /g. mole	120
6	Atomic volume, W/D	14.1
7	First Ionization Energy, K – cal / g – mole	160
8	Vickers Hardness	110
9	Linear coefficient of expansion, K ⁻¹	5.7 x 10 ⁻⁶
10	Electrical Resistivity, μΩ . cm ⁻¹	41.4
11	Compressibility, cm ² kg ⁻¹	11.77 x 10 ⁻⁶
12	Modulus of Elasticity, psi	11. 2 x 10 ⁶
13	Heat of fusion, k- cal /g. atom.	3. 74
14	Specific heat @ 25 °C, cal /g	0. 0 0 6

and ions in plasma zone is increased to such a level so as to make them capable of producing easily detectable image. Therefore a high current value was required to achieve these goals. Nevertheless a very high current value in pre burn period might possibly burn the sample superfluously and increase the stray lines resulting in high background. This action may also drag a fairly handsome fraction of Hf into plasma unnecessarily at this stage. Thus the preburn current plays a decisive role in determining the amounts of Hf and Zr being vaporized into plasma stream. After variation of preburn current from 5 to 20 amperes, it was observed that 10A rendered the maximum intensity (Figure 1). A further increase in current at this stage decreased the Hf concentration, hence 10 A was selected. In order to study the influence of current on the ultimate exposure period, the variations were made from 15 to 30A (Figure 2) which depicted that 25A rendered the maximum intensity of Hf. An extended current value resulted in high background only.

Interactive forces and Plasma

It may also be envisaged from this figure that at 25A, comparatively weak interactive forces and low potential exist between matrix and the analyte. This reinforces the speculation that at this stage not very strong forces are operative between the Hf and the rest of the matrix due to high temperature which could possibly throw an appreciable portion of the excited atoms into the plasma stream. Apart from these forces in action, it can also be inferred from a good Regression value of 0.9932 that this process is occurring slowly and smoothly at a constant pace from low to high current but only up to 25A after which it deteriorated.

Table 3. Specifications of Hf w. r. t nuclear reactor.

Specifications of Hf.	
Melting Point	2227 °c
Boiling Point	4 6 0 3 °c
Density	13.31 g /cm ³
Thermal conductivity @ 50°c	0.0533 cal / (s. cm °c)
Heat of vaporization	1 5 5 k- cal / g – atom.
Atomic volume	1 3. 6 W/ D
First Ionization Energy	1 2 7 K – cal / g- mole
Linear coefficient of expansion	5. 9 x 1 0 ⁻⁶ K ⁻¹
Electrical Resistivity	3 5.1 μΩ cm ⁻¹
Modulus of Elasticity @ 20 c	\1 9. 8 x 1 0 ⁶ psi
Thermal Neutron Cross Section	105 barns / atom
Heat of fusion	32.4 cal/g

Role of buffer in the excitation of Hf

In our studies Ringsdorff graphite was used as buffer, chosen on the basis of optimum behavior. This played an important role in controlling the conditions in the arc so that the spectral emission of the analyte remains unaffected during the fluctuations caused during the heavy emission of zirconium. Thus improving the physical characteristics of the arc helping in smooth vaporization. It also minimizes the probability of the particles sticking to the inner walls of the cavity (Rehana and Shahid, 1999). Some times the presence of some impurities may even suppress the intensity of the analyte. Therefore it is desirable to use impurity free zirconium.

The influence of amount of buffer with respect to the net intensity signal produced is demonstrated in Figure 3. The concentration of Hf in Sample-Buffer mixture increases with increasing proportion of Buffer up to 10% reaching a maxima resulting in the enhancement of intensity. This limit was curtailed due to the limitation of the size of the crater of the electrode which is slowly diminishing due to the burning of the walls. Nevertheless, we selected the 10% buffer concentration on the basis of the minimum background and maximum signal to noise ratio. In the arc column, the ionization of the principle constituent of the vapor has the effect of controlling the arc temperature and since the emission intensity is related exponentially to the source temperature, the effect of buffer on the arc temperature is very crucial. The buffer also provides a substantial proportion of the energetic particles in the arc collisions which gives rise to excitation. The collision properties including possible metastable states of the buffer should be considered carefully. Background emission both, continuous and line, produced by buffer might also play a role in decreasing the quality of spectra. The buffer should not only maintain constant volatilization rate but also help in reducing the arc wandering of the anode spot. It is mentioned elsewhere that a wandering arc leads to low intensity where-

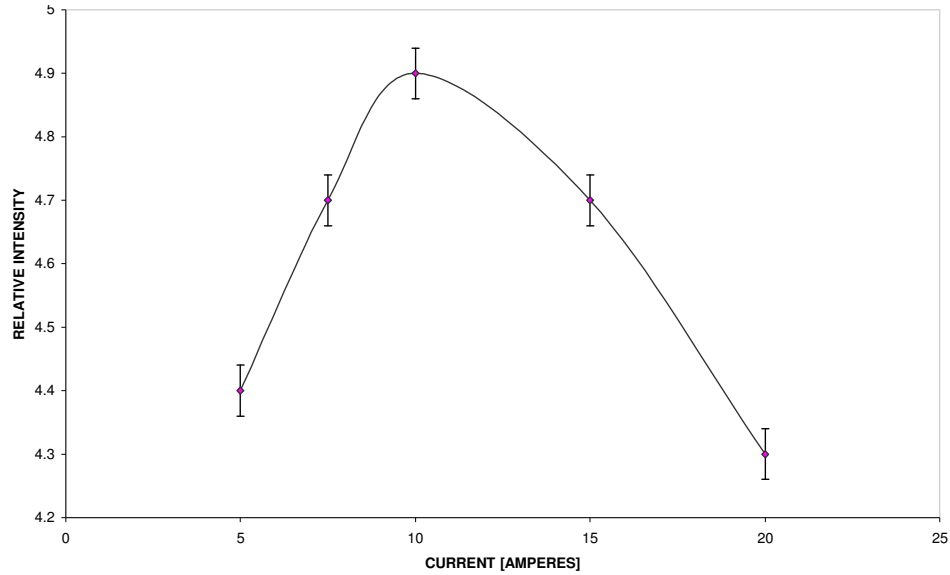


Figure 1. Influence of pre-burn current on intensity.

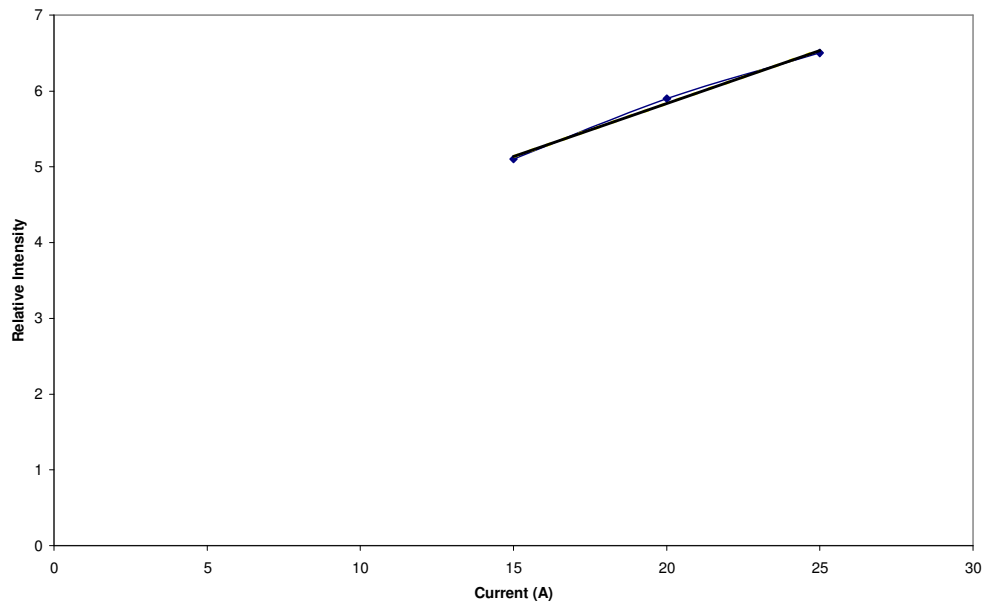


Figure 2. Influence of current on intensity.

whereas a smooth and steady arc results in higher intensity (Harrison, 1969). The results of Intensity dependence on Buffer addition are then analyzed by the following equation:

$$I = A + b C_{\text{add}}$$

Where A and b are the characteristics constants for the excitation system in the plot of Intensity dependence on Buffer concentration as shown in Figure 3.

A straight line is obtained in the concentration range of

2.5 - 10 (mass percentage of buffer with respect to the total mass of the sample). The line has a correlation coefficient of 0.968 (linear regression) and a slope less than unity. However, a negative slope for higher concentration of mass percentage of additive depicts a reduction in intensity. This could be attributed to the pertinent decrease of Hf concentration in the total charge in anode. The buffer is of low density and hence occupies more space leaving less room for sample powder. Various parameters calculated for these plots are given in Table 4. The small value of b signifies that a slow but smooth

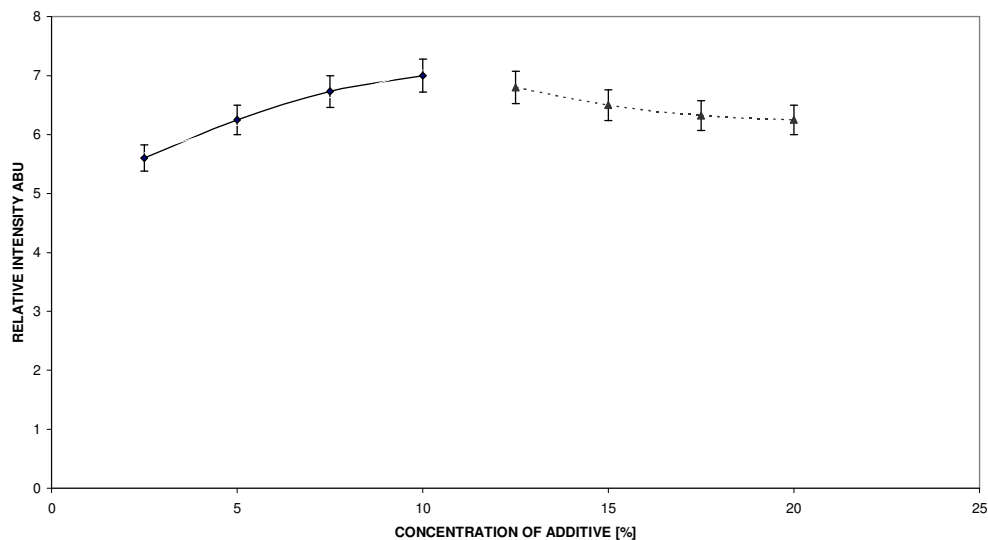


Figure 3. Variation of intensity with different graphite percentage.

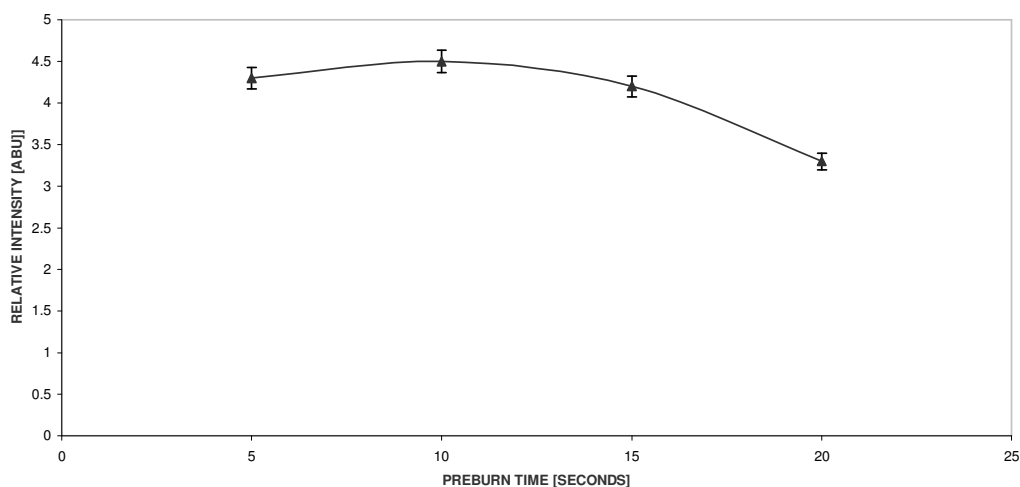


Figure 4. Influence of pre-burn duration on intensity.

excitation was taking place. However, the reactive forces are operative to make volatile compounds of analyte. A high value of "A" depicts that after reaching a threshold value excitation energy corresponding to the excitation energy, E , the volatilization of Hf occurs. It is in conformity with the refractive nature of the Hf. However if the percentage of graphite exceeded 10%, then a slight decrease in intensity was observed as mentioned earlier. The total amount of sample was varied from 100 to 300 mg. During the first experimental series, the combination of sequential addition was 100-50-50 mg, then 200-50-50 mg was used. In the third stage, the whole experimental study was undertaken using the combination 150-75-75 mg. It was found that total amount of 300 mg produced the maximum intensity keeping all the other conditions constant if the third option was used.

Duration of preburn

The duration of preburn was crucial as it indicated whether Hf was able to escape into plasma or not. If so, then to what extent, its amount was vaporized into the plasma or how much of its proportion was able to rush into the plasma. If during preburn, an appreciable amount escaped into plasma zone then it was a big loss in the total amount of the Hf in the sample during final exposure hence we had to select such a time span, during which either zero (in ideal cases) or very negligible concentration of Hf vaporized into the plasma sector during preburn as it would escape detection. The preburn time (henceforth marked as PBT) was varied from 5 to 20 s. It may be envisaged from Figure 4 that 10 s PBT, rendered the optimum intensity. was observed that 15 to 20 s ren-

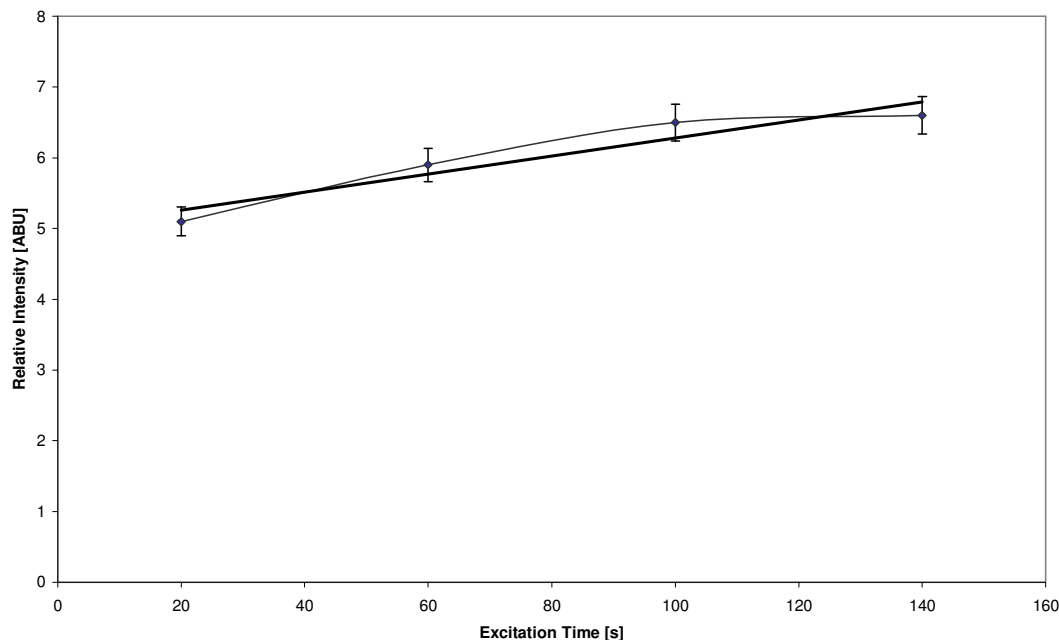


Figure 5. Dependence of intensity on the excitation period.

Table 4. Behavior of different parameters with respect to the evolution of Hf

Behavior of different parameters with respect to the Hf evolution					
S. No.	Parameters of excitation System	Range	b^I	A^{II}	$R^2^{(III)}$
1	Mass percentage of Buffer	2.5-10 (set A) ^{IV}	0.1872	5.225	0.968
2	" (%)	12.5-20 (set B)	-0.0732	7.657	0.9268
3	Ultimate exposure current(Amperes)	15-25 (for 140 s)	0.14	3.0333	0.9932
4	Ultimate exposure period [s]	80-140	0.0128	5.005	0.911

b^I =slope

A^{II} =intercept

$R^2^{(III)}$ = Linear regression

IV = Three replicates for each set were taken

dered the optimum intensity. However 15 s was selected as further time selection was merely wastage of time. The preburn time interval was also varied for first, second and third stage. We found that resultant intensity did not give much any pronounced difference, except increasing confusion, so it was abandoned.

Influence of exposure time

The ultimate exposure time was changed from 80 to 140 s. (Figure 5). The pictorial representation indicates that excitation up to 140s rendered the maximum intensity. The smooth and steady emergence of Hf is depicted in this plot. Although the intensity appeared to be increasing with prolonging time span but it was accompanied with higher background which caused a great hindrance in measuring Hf spectral lines accurately and reproducibly. Therefore we selected the 140 s for excitation including

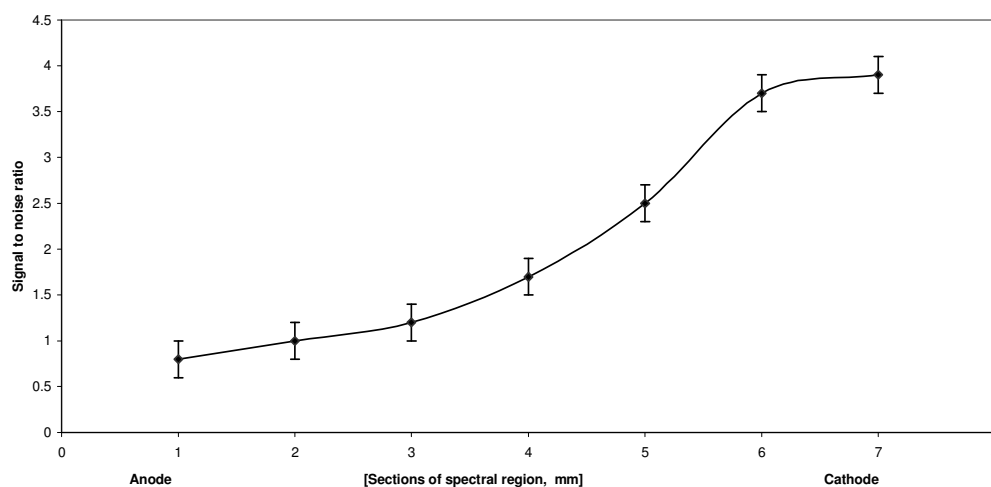
the preburn time. The behavior of Hf with and without sequential addition method may be inferred from these graphs that an enhancing effect is pertinent in the evolution of Hf when sequential addition is undertaken but with comparatively poor R^2 value. Nevertheless, it was significantly overcome by the addition of Ringsdorf graphite, as shown in the Table 5.

Variation of signal to noise ratio in cathode region

When the spectral line of hafnium was measured by distributing it into seven segments, it was found that the section near cathode region was more intense, hence rendering a better signal to noise ratio. The concentration measured in this section was much improved than in the cathode region. The behavior is depicted in Figure 6 for these segments which are arbitrarily chosen.

Table 5. Behavior of Hf with and without sequential addition

Behavior of Hf evolution with and without sequential addition				
S. No.	Conditions and status of the sample	R ²	b	A
1	Without Sequential Addition	0.9902	0.0138	1.325
2	With Sequential Addition	0.9268	0.0228	1.655
3	With Sequential Addition and Buffer	0.9924	0.0278	1.655

**Figure 6.** Variation of signal to noise ratio between anode and cathode region.

RESULTS

Selection of hafnium spectral lines

The selection of Hf lines was a cumbersome task as majority of Hf lines were masked by Zr or Fe lines, partially or fully. In order to avoid the effects of full or partial shielding and interferences of spectral lines of the matrix and free of background, a great deal of scrutinization was done. Hf line 253.1193 nm with an assigned value of intensity was selected. Its corrected version, given in the MIT Tables^[21] was 253.1196 nm with its designated intensity as 200 which is sufficient enough to trace its concentration down to even $10 \mu\text{g g}^{-1}$. It was found to be free of any interference from Zr or Fe lines, the main interfering elements. Special caution was taken to observe these partial or full shielding or overlapping since many workers quoted spectral lines which had the interference of Fe or Zr. It is also imperative to use Hf free zirconium. It is difficult to get it in pure form hence an in house developed method enabled us to get Hf free Zr or Johnson Matthey Specpure Calibration Kit could be used. Reverting back to Hf spectral lines, another line 251.2689 nm with assigned intensity of 25 with a rectified value of 251.2702 nm associated with an intensity of 200 was found to be very useful in detecting it down to $10 \mu\text{g g}^{-1}$ or even lower provided the Hf free Zr is made available. The uncorrected locations were found to have some

probability of Fe, Zr or other interferences. These lines enabled us to detect Hf down to $10 \mu\text{g g}^{-1}$. The detection limit was based on the last easily measurable signal in triplicate and also on 3σ . Other spectral lines with possible overlapping are given in Table 6. The reproducibility of the procedure was calculated by variation coefficient by the following equation:

$$v = 100/C [\sqrt{\sum d^2 / (n-1)}]$$

Where

N = No. of replicates

C = Average concentration

For 9 replica of a sample, the coefficient of variation was found to range between 4.3 to 12 %.

Trueness of Results

In absence of a primary standard, a secondary standard was used to check the trueness of the results obtained from the proposed method, the results are given in Table 7.

Conclusion

In the proposed method, the estimation of Hf demonstrated that it was possible to detect the Hf in solid pow-

Table 6. Selection of Hf spectral lines and possible interferences

S. No.	Analytical lines of Hf (nm)	Internal Standard line of Zr (nm)	Intensity	Atomic /ionic status	Partial or full shielding/ interferences by neighboring lines
1	286.6373	286.9811	50	-	Possible interference by Si 286.628 if present in high concentration. Mo 282.2863 Fe line 310.907 may interfere.
2	282.2677	286.9811	30	II	Mo 310.1345 may partially overlap if present
3	310.9117	309.9230	50	II	Weak interference by very weak Fe 253.1084 line.
4	310.1397	309.9230	60	II	No significant interference, can be used for high concentration of Hf.
5	356.1664	309.9230	20	II	No overlapping or partial shielding was observed. Good for high concentration of Hf.
6	253.1196	286.9811	200	II	Free of any interference by commonly present impurities, may be used for trace level estimation.
7	251.2702	286.9811	200	II	Interference doubted if Ta is present in high concentration otherwise feasible for measurement of the low concentration of Hf.

Table 7. The comparison with a CRM.

The comparison with a CRM.				
S. No	Sample name ¹ .	Our experimental value ² .	Certified value	Percentage variation coefficient
1.	YCT-2N	40.6	45.3	7.8

The exposures were taken on different days¹.
Nine replicates were executed²

dered form at trace level using a small quantity of sample provided highly pure and Hf –free Zirconium oxide is used for the preparation of the reference materials. The proposed method has increased the detection manifold with the easiness of sample handling, without imposing any stringent conditions of using a filter.

Thus allowing several samples to be tested /analysed in the same run without involving the intricacies of dissolution, extraction, pre separation and/or co-precipitation. The developed method enabled for the first time, the detection of Hf down to 10 µg/g with emission spectrography in the shortest time and with very small sample

consumption. The intensity curves depict an enhancing trend with the use of sequential addition.

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