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DETERMINATION OF ZIRCONIUM AND HAFNIUM IN SOLUTION BY X-RAY FLUORESCENCE SPECTROMETRY

A PRACTICAL APPROACH

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The samples were introduced into the XRF spectrometer in ordinary flat bottom polyethylene bottles for the estimation of Zr or Hf in presence of one another in solution. By using high voltage (50 kV) and high current (50 mA) least limits of detection obtained were an order of magnitude better than other conventional analytical techniques. Relations of intensity to concentration in various concentration ranges have been determined and the results are compared with those of other analytical techniques.

Introduction

Zirconium and hafnium are suitable metals for nuclear, space, metallurgical and marine technology because of their excellent properties like thermal stability, mechanical strength and corrosive resistance to acids, alkalis and saline water. Zirconium metal occurs in meteorites, sediments, terrestrial materials, igneous and volcanic rocks[1] and is a major component of various precious stones and gems.[2] Hafnium is invariably found in nature along with zirconium. Generally, commercial grade zirconium contains 1–5% hafnium. Further purification of this metal is done by solvent extraction, ion exchange or fractional crystallization techniques.[3-5]

Complete separation of these metals is very difficult due to their congeneric chemical properties. Lanthanide contraction in hafnium makes the atomic radii (Zr = 1.45 Å and Hf = 1.44 Å) and ionic radii (Zr^{4+} = 0.74 Å and Hf^{4+} = 0.75 Å) identical.[6] Analysis of such chemically similar elements by conventional analytical techniques in presence of one another is lengthy and destructive.[7,8]

Hafnium was discovered and confirmed[9] by X-ray fluorescence (XRF) which has been considered to be one of the most suitable techniques for determination of zirconium in hafnium or hafnium in zirconium.[10] Brooks and Townshend have reviewed various methods of estimation of these metals in the presence of one

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another by various techniques using the difference in their physical, chemical, electronic, and nuclear properties.[11] Concentrations of these metals in aqueous solutions have also been studied earlier by energy dispersive X-ray fluorescense (EDXRF) spectrometer using radioisotopes as excitation sources. The samples were presented directly to the spectrometer in a special type of thin film sampling cups. The lower limits of detection (LLD) observed in these studies were high.[11]

Wavelength dispersive X-ray fluoresence (WDXRF) spectrometric technique has been used by us to determine zirconium and hafnium concentrations from aqueous solutions. The method is particularly useful for the measurement of low concentrations of one element in the presence of other elements.[12],[13] K_α line of zirconium and L_{β_1} line of hafnium have been used as analyte lines. It is known that second order zirconium lines interfere with the first order hafnium lines. The interference was minimized earlier by applying low voltages to the tube where LiF (100) crystal was used, or by applying high voltage to the tube and using Ge(III) or Al(III) crystal, or by using longer collimators to resolve interfering lines.[11] In our case these interelemental influences have been studied empirically by regression analysis, using the intensity to concentration data obtained for both elements.

In these studies the sample solutions were introduced into the spectrometer in ordinary flat bottom polyethylene bottles (Fig. 1) directly. This is unlike the earlier sampling techniques such as palletization, bead formation, deposition and precipitation on a substrate which potentially enhances the analyst's personal errors signifi-

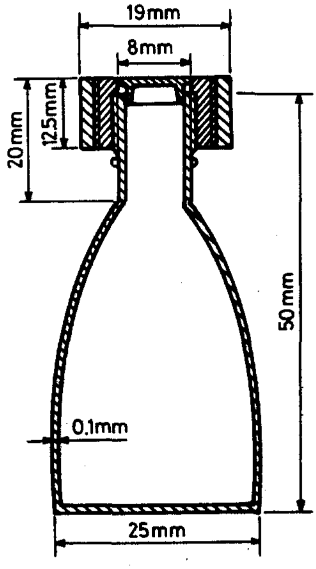


Fig. 1: Polyethylene sampling bottle for counting

cantly. We used high voltage (50 kV) and high current (50 mA), and observed significantly lower LLDs. As against the earlier authors we have not used the chemical separation or preconcentration before presenting the solutions to the spectrometer.[10]

Experimental

A Siemens wavelength dispersive X-ray fluorescence spectrometer SRS 200 was used with the following attachments: Chromium X-ray tube; Soller slit with angular divergence of 0.15°; LiF (100) crystal; NaI(Tl) scintillation counter and linked through an universal interface LC-200 to a PDP-11/04 computer.

In the preliminary studies chlorides of zirconium (Fluka item Nos. 96600 and 96609) and oxide of hafnium (Fluka item No. 51310) were used. For trace calibrations and determinations certified high purity ZrO_2 powder and Hf lumps from Johnson Matthey (JMC item Nos. 596001 and 598009), England, were digested with 1:1 mixture of sulfuric and hydrofluoric acid. The solutions were digested and heated to near dryness three times before dissolving the residue in 3M nitric acid to the required volume. All other chemicals used were either AnalaR or their equivalent grades.

Table 1
X-ray lines and absorption edges of zirconium and hafnium
crystal = LiF 100 (2d = 4.027 Å)

Zirconium				Hafnium			
Line*/edge**	Order	Lines		Line/edge	Order	Lines	
		$2\theta°$	keV			$2\theta°$	keV
K edge	–	19.67	18.00	L edge	–	31.66	11.26
$K_{\beta2}$	1	19.73	17.89	$L_{\gamma2}$	1	33.02	10.78
$K_{\beta1}$	1	20.07	17.59	$L_{\gamma3}$	1	32.84	10.84
$K_{\alpha1}$	1	22.51	15.70	$L_{\gamma1}$	1	34.05	10.47
K_{α}	1	22.55	15.67	L edge	–	33.27	10.73
$K_{\alpha2}$	1	22.63	15.62	L edge	–	37.52	10.55
$K_{\beta2}$	2	40.08	17.89	$L_{\beta2}$	1	38.46	9.30
$K_{\beta1}$	2	40.80	17.59	$L_{\beta3}$	1	39.27	9.12
$K_{\alpha1}$	2	45.95	15.70	$L_{\beta1}$	1	39.91	8.98
K_{α}	2	46.04	15.67	$L_{\alpha1}$	1	45.88	7.86
$K_{\alpha2}$	2	46.21	15.62	$L_{\alpha2}$	1	46.22	7.81

*X-ray wavelength and 2θ table, N. V. Philips Gloeilampenfabrieken – Holland. X-ray Application Laboratories.

**Converted to keV from R. THEISEN and D. VOLLATH. Tables of X-ray Mass Attenuation Coefficients, Verlag Stahleisen, Düsseldorf, 1967.

To record spectra, 3.0 ml of the blank solution and solutions having 0.5% m/v zirconium or hafnium concentrations were presented to the spectrometer. Using the literature values (Table 1), K lines for Zr and L lines for Hf were identified (Fig. 2). ZrK_α and $HfL_{\beta 1}$ lines were selected for the present studies and have been analyzed for the low background, peak and the high background after counting in steps of 0.025 2θ values. This peak analysis is shown graphically in Fig. 3. To calculate net intensities from gross intensities, all measurements at the backgrounds and peaks were done in triplicate. Net intensities have been calculated after subtracting weighted averages of background counts from the peak counts.

Lower limit of detections (LLD) were observed as a function of counting time for four solutions, two of them contained 100 mg $\cdot$ l^{-1} of the others (Fig. 4). Each sample was counted for ten to four hundred seconds. The equation used to calculate LLD is given below:

$$LLD = 3C/N(2N_b/T)^{-0.5} \qquad (1)$$

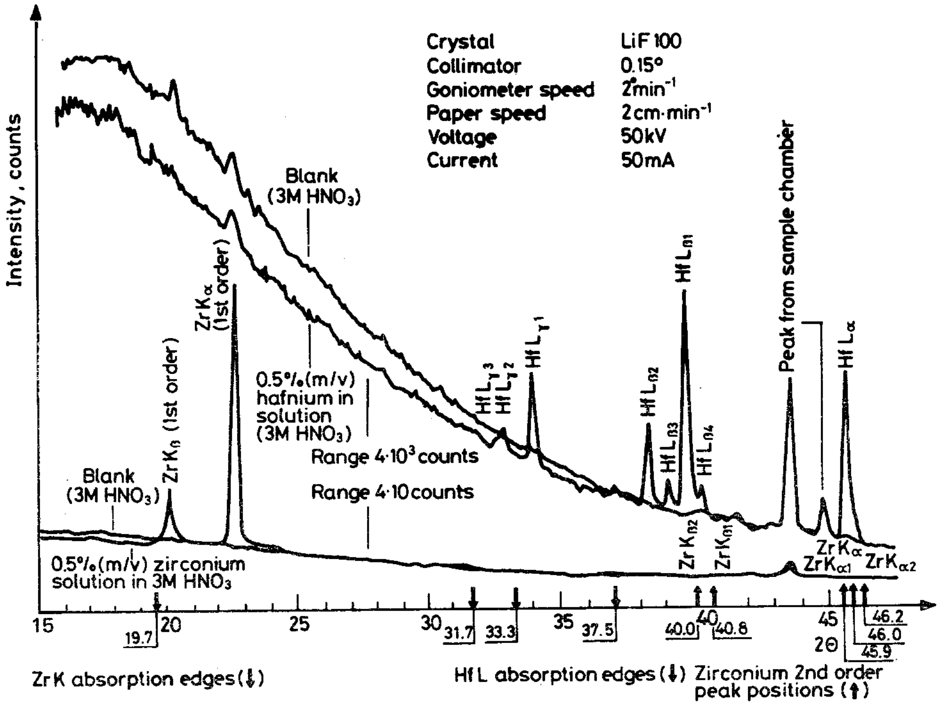
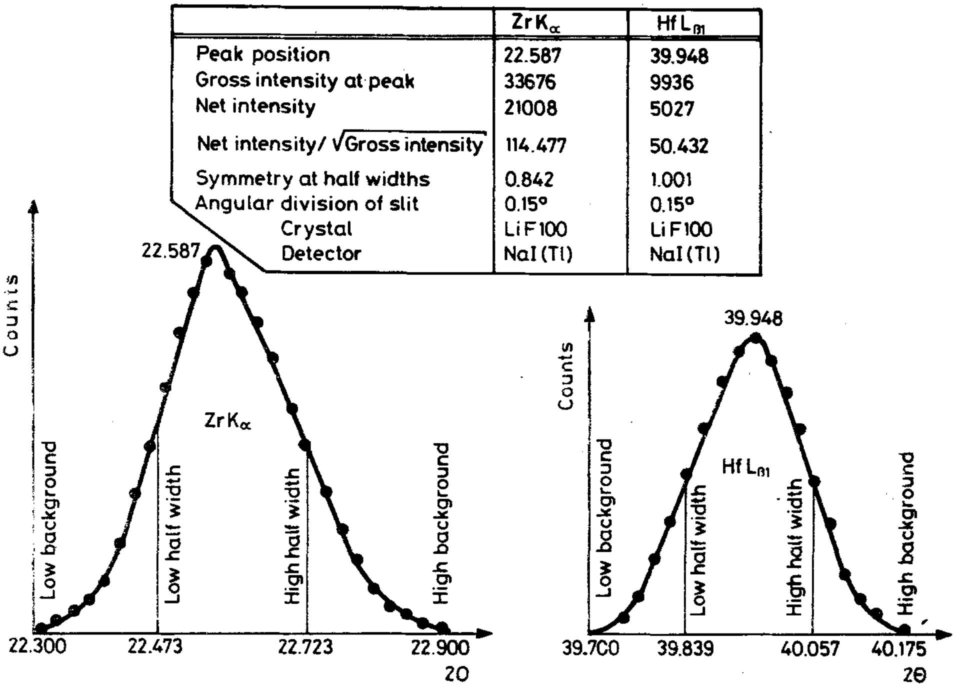


Fig. 2. XRF spectra of zirconium and hafnium



	ZrKα	HfLβ1
Peak position	22.587	39.948
Gross intensity at peak	33676	9936
Net intensity	21008	5027
Net intensity/ √Gross intensity	114.477	50.432
Symmetry at half widths	0.842	1.001
Angular division of slit	0.15°	0.15°
Crystal	LiF100	LiF100
Detector	NaI(Tl)	NaI(Tl)

Fig. 3. Peak analysis of ZrK_{α} and $HfL_{\beta 1}$

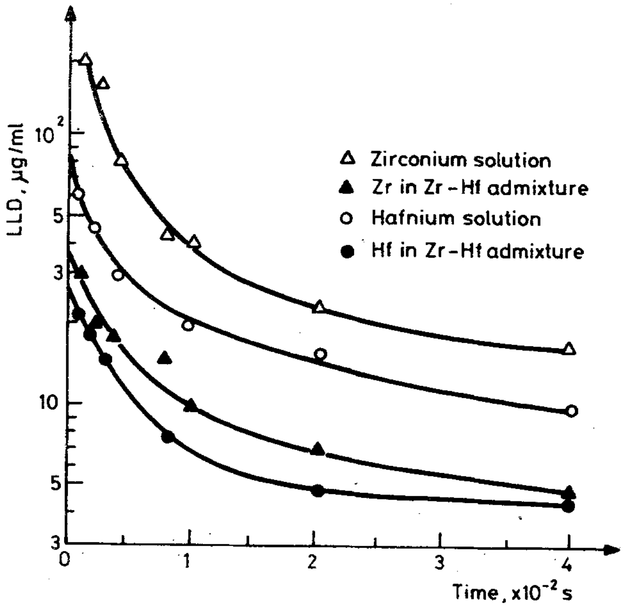


Fig. 4. Lower limit of detections (LLDs) of zirconium and hafnium as a function of counting time

where C – concentration of analyte in solution (mg · l^{-1}),
N – peak counts,
N_b – higher background counts,
T – time of counting.

The equation bears a confidence level above 99% specified by 3 in it.[14] The counting time selected for the present work was 20 seconds for ZrK_α and 100 seconds for $HfL_{\beta 1}$.

Standard calibration curves showing relative intensity as a function of pure zirconium or hafnium concentrations are shown in Fig. 5. Relative intensities have been calculated from net intensities by dividing the latter by the lowest net intensity values.

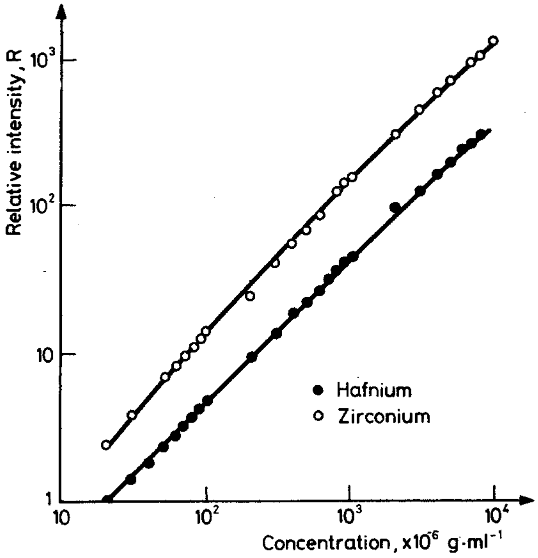


Fig. 5. Relative intensity of ZrK_α and $HfL_{\beta 1}$ lines as a function of Zr and Hf concentrations in aqueous solution

Similar continuous variation (Fig. 5) curves for zirconium and hafnium in their admixtures have been plotted for three different concentration ranges shown below.

Set A

C_{Zr} = Zr concentration = 10 20 30 40 50 60 70 80 90

C_{Hf} = Hf concentration = 90 80 70 60 50 40 30 20 10

Set B

C_{Zr} = 100 200 300 400 500 600 700 800 900

C_{Hf} = 900 800 700 600 500 400 300 200 100

Set C

C_{Zr} = 1000 2000 3000 4000 5000 6000 7000 8000 9000

C_{Hf} = 9000 8000 7000 6000 5000 4000 3000 2000 1000

In addition to the above, a comprehensive study for traces of hafnium in zirconium solution was undertaken where their concentrations were varied in 3M HNO_3 medium in the range of 1–50 $g \cdot l^{-1}$ for zirconium and 0.02–1 $g \cdot l^{-1}$ for hafnium. These samples were counted for calculating the net intensities. The calibrations studies were done by using Siemens software program OLD–TV80. The program works with the equations:[15]

$$C_i = a_{i0} + a_{i1} N_{i2} N_i^2 + N_j \Sigma m_{ij} N_i + \Sigma b_{ij} N_j$$

where C_i – concentration of element to be analyzed,
N_i – No. of counts (net intensity) of the element to be analyzed,
N_j – No. of counts (net intensity) of the matrix elements,
a, m, b – calibration coefficients.

The results are shown in Table 2. These relationships were then applied to simulated and blind samples and some of the representative results are shown in Tables 3 and 4. Our results are compared with other analytical techniques.

Results and discussion

The equations of Table 2 were applied to simulated and blind samples containing other impurities as well. In general the results obtained by us were in conformity with the known results as shown in Table 3 as representative. Some of the results shown in Table 4 were either on the lower side (IIIa and IIIb) or significantly on the higher side (ZH–V). On examining the samples, it was observed that the ionic species formed in the solutions were either in the hydrolyzed or in polymeric[7,27] form. Ions such as $Zr(OH)^{3+}$, $[Zr(OH)_2(NO_3)_4]^{2-}$ were responsible for the lower

Table 2
Best fitting calibration equations in various ranges and compositions

Sr. No.	Equation	Zirconium concentration range, mg · l^{-1}		Hafnium concentration range, mg · l^{-1}	
		from	to	from	to
1	$C_{Zr} = 3.16 \cdot 10^{-3} N_{Zr}$	10	100	–	–
2	$C_{Zr} = 20 + 3.16 \cdot 10^{-3} N_{Zr}$	100	1 000	–	–
3	$C_{Zr} = 1200 + 1.5 \cdot 10^{-3} N_{Zr} + 10^{-9} N_{Zr}^2$	1 000	10 000	–	–
4	$C_{Hf} = 0.021 N_{Hf} + 62.45 \cdot 10^{-8} N_{Hf}^2$	–	–	10	100
5	$C_{Hf} = 40 + 0.024 N_{Hf} - 6.94 \cdot 10^{-8} N_{Hf}^2$	–	–	100	1 000
6	$C_{Hf} = -203 + 0.026 N_{Hf} + 0.37 \cdot 10^{-8} N_{Hf}^2$	–	–	1 000	10 000
7	$C_{Zr} = 27 + 2.217 \cdot 10^{-3} N_{Zr} - 3.194 \cdot 10^{-3} N_{Hf}$	10	100	100	10
8	$C_{Zr} = 320 + 2.09 \cdot 10^{-3} N_{Zr} - 2.056 \cdot 10^{-2} N_{Hf}$	100	1 000	1 000	100
9	$C_{Zr} = 7542 + 2.346 \cdot 10^{-3} N_{Zr} - 9.213 \cdot 10^{-2} N_{Hf}$	000	10 000	10 000	1 000
10	$C_{Hf} = -150 + 7 \cdot 10^{-2} N_{Hf} - 4.63 \cdot 10^{-6} N_{Hf}^2 + 5.88 \cdot 10^{-3} N_{Zr} - 1.51 \cdot 10^{-6} N_{Zr} N_{Hf}$	10	100	100	10
11	$C_{Hf} = 680 + 2.06 \cdot 10^{-2} N_{Hf} - 2.09 \cdot 10^{-3} N_{Zr}$	100	1 000	1 000	100
12	$C_{Hf} = 3800 + 7.231 \cdot 10^{-2} N_{Hf} - 4.039 \cdot 10^{-3} N_{Zr} + 2.348 \cdot 10^{-8} N_{Zr} N_{Hf}$	1 000	10 000	10 000	10 000
13	$C_{Zr} = 4005 - 8.091 \cdot 10^{-4} N_{Zr} + 6.043 \cdot 10^{-9} N_{Zr}^2 - 9.463 \cdot 10^{-2} N_{Zr} + 1.046 \cdot 10^{-7} N_{Zr} N_{Hf}$	1 000	50 000	20	1 000
14	$C_{Hf} = -35 - 1.854 \cdot 10^{-4} N_{Zr} - 2.046 \cdot 10^{-9} N_{Zr} N_{Hf} + 3.108 \cdot 10^{-2} N_{Hf} - 1.935 \cdot 10^{-7} N_{Hf}^2$	1 000	50 000	20	1 000

Table 3
Determined concentrations of zirconium and hafnium in simulated blind sample solutions in 3M HNO_3

Known, mg · l^{-3}		Determined, mg · l^{-1}	
C_{Zr}	C_{Hf}	C_{Zr}	C_{Hf}
2 250	360	2 268	354
5 000	60	4 947	54
5 000	100	4 878	102
5 000	150	5 029	158
5 000	200	4 898	202
7 500	60	7 441	61
10 000	100	9 961	106
20 000	60	20 577	64
40 000	40	40 364	36
49 000	20	49 835	24

Table 4
Reported Zr–Hf contents in interlaboratories comparison

Sample	Other significant impurities in matrix	Element	Reported results, % m/m					
			I	II	III	IV	V	VI
ZH–I	Al, Ca, Fe, Ni, Si	Zr	67.8	69.8	67.8	68.3	67.8	67.9
		Hf	1.75	1.74	1.77	2.02	1.75	1.70
ZH–III (a)	Al, Ca, Fe, Mg, Ni, Si, Zn	Zr	70.7	73.1	68.6	73.2	72.7	69.1
		Hf	0.18	0.19	0.16	0.17	0.14	0.15
ZH–III (b)	Al, Ca, Cr, Cu, Fe Mg, Ni, Si, Zn, Na	Zr	70.1	69.7	64.6	70.3	69.8	68.1
		Hf	0.14	0.18	0.12	0.14	0.12	0.14
ZH–V	Ca, Mg, Mn	Zr	68.6	68.7	80.1	70.5	70.1	68.8
		Hf	1.5	1.5	1.9	1.9	1.6	1.7

Results reported by various techniques like (I) INAA, (II) EDXRF, (III) WDXRF using solutions, (IV&V) WDXRF using powders, (VI) electrochemical and emission spectrometry.

values and $[Zr_2O_3]^{2-}$ and $[Zr_3O_4]^{4-}$ for the higher values as compared to those in the calibration standards. The same behaviour was observed for hafnium also. Such modification in the ionic forms are possible as these ions take a longer time to gain equilibrium.[7,10] Attempts to avoid these effects earlier have been made by using one normal sulfuric acid.[12]

On observing the four spectra of Fig. 2, the strong background is quite prominent in the low 2θ region. Generally, the radiations responsible for the background in a spectrum are due to the inelastic collisions of the primary X-ray photons with the elements in the sample, their container and the environments.[16] The prominent first-order line spectra can be seen in Fig. 2 and zirconium and hafnium intensities can be compared. The position of the second order lines, though not visible, have been indicated. These second order lines significantly interfere when traces of hafnium are present in solutions having large quantity of zirconium. All other lines can be used as analyte lines for the respective element. During these studies ZrK_α and $HfL_{\beta 1}$ lines have been chosen as analyte lines on the basis of their prominence, expected absorption or enhancement, and a less interference from the second order zirconium lines on hafnium lines.[11] The influence has been minimized by using net intensities rather than the gross intensities at the peak only. The exact position of the peaks and backgrounds thus have to be searched and the peaks analyzed as shown in the Fig. 3. LLDs as a function of counting time are shown in Fig. 4, which helped to assess the minimum counting time at the peaks and backgrounds.

The conversion of these intensities to the chemical concentrations need calibration curve of Fig. 5 for the pure solutions and Fig. 6 for admixtures. The deviation from

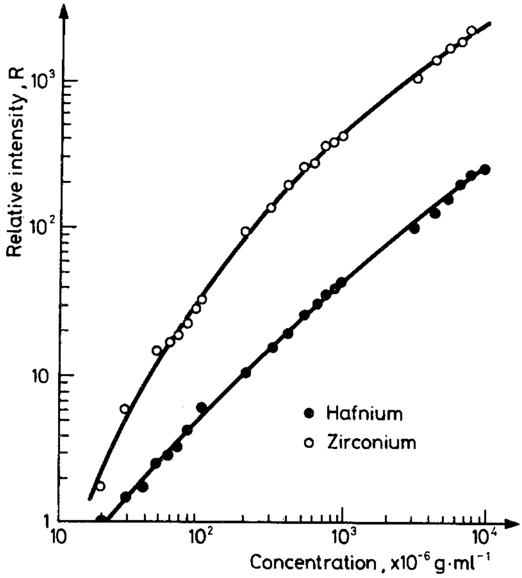


Fig. 6. Relative intensity of ZrK_{α} and $HfL_{\beta 1}$ lines as a function of Zr and Hf concentration in their admixtures in nitric acid

linearity in different ranges is not very prominent in these figures but is quite significant when best fitting equations are to be seen in Table 2. It will be quite interesting for theoreticians to correlate these empirical coefficients with those of fundamental parameters for development of various correction algorithms.[18-26] During our studies, a Siemens software correction program[17] has been used which is claimed to have universality for its capability of correcting all interelemental effects such as absorption, enhancement, background correction, dead-time correction, flexibility, accuracy and economy.[15,17] The approach has been initiated by SHERMAN,[18,19] reviewed and improved by authors like RASBERRY, HEINRICH, SPARKS, VREBOS, HELSEN, KUCZUMOW, LI-XING and WERFEL.[20-26]

Conclusion

In this work hafnium and zirconium concentrations in solutions have been determined without preliminary ion separations or ion preconcentrations as has been done by earlier authors. Here more rugged polyethylene bottles have been used instead of fragile thin film presentation technique. However, the LLDs obtained under these conditions are comparable with the earlier authors. Furthermore, the method is non-destructive, requires less time for analysis and can be reported with confidence.

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