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DISPERSIVE X-RAY FLUORESCENCE (WDXRF) TECHNIQUE

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ABSTRACT :

A wavelength dispersive x-ray fluorescence(WDXRF) method is described for the estimation of niobium in ZrO₂ matrix in the concentration range of 0.5 to 35%. Analysis of Nb is desired during the reclamation of zirconium from Zr-2.5% Nb scrap. Zr- 2.5% Nb is used in water cooled nuclear power reactors on account of high creep resistance and strength. For the reclamation of these metals from the scrap, chlorination is done to produce mixed chloride. The mixed chloride is treated to obtain individual chloride for eventually converting to respective metal. Analysis is required to ascertain purity of these metals reclaimed from the scrap. Primary x-rays from gold target x-ray tube were used to excite the K lines of Nb. A linear relation has been found between the intensity of Nb-K $\alpha_{1,2}$ line and concentration in the above range and the detection limit was 0.03% for 10 seconds counting time.

Key words : High Purity Zirconium-Niobium Alloy, Wavelength Dispersive X-ray Fluorescence (WDXRF) Technique.

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I. INTRODUCTION:

Zircaloy-2, Zircaloy-4 and Zr-2.5 Nb alloys are the main materials used in the core of nuclear power plants. Among these alloys, Zr-2.5 Nb has become standard material for pressure tubings, on account of better neutron economy, strength, higher corrosion and in creep resistance for our nuclear power plants. The alloy permits the use of a thinner wall material and helps to reduce the loss of neutrons by parasitic absorption.

Zr-2.5 alloy, when used in for manufacture of reactor components, a certain amount of scrap is generated. The scrap is very low in hafnium and has costly niobium metal. Thus utilisation of this scrap would be beneficial. The scrap, low in interstitial, is recycled by either direct melting or after appropriate blending with the fresh alloy. The scrap, with a large degree of contamination with interstitials, requires chemical processing as the interstitials are difficult to remove because they form stable components.

Since, Kroll process(magnesio thermic reduction of ZrCl₄) remains the main industrial process for the production of Zirconium, any process which produces Zirconium and Niobium chloride would be ideally suited for the utilisation of the scrap. Chlorination offers this possibility and generates mixed chlorides of Zirconium and Niobium . The mixed chloride can be reduced to Zr-Nb sponge but Zr-Nb sponge has been found to be extremely hard to be readily chipped out from the Kroll vessel. Thus the separation of mixed chlorides to individual chloride is required for the

production of these metals. Therefore, a rapid, accurate and sensitive method is required for the estimation of Niobium in Zirconium at the various stages of reclamation process.

A Wavelength Dispersive X-ray Fluorescence(WDXRF) technique is ideally suited for rapid and accurate analysis of Niobium in Zirconium matrix. Therefore a WDXRF method has been developed to estimate Nb in ZrO_2 matrix. Such a method has not been reported in the literature. Although we find some reports of using ICP-AES(1), flame atomic absorption spectrometry(2) and EDXRF(3) for the estimation of impurities (including Niobium) in different matrices like ceramics and Zircon, but all these methods suffer from the disadvantage of dissolution of sample which is a time consuming process. The method developed by us, in addition to rapidity, has another advantage of capability of analysing wide range of concentrations i.e. from 0.03% to 35%.

II. EXPERIMENTAL:

II.1. OPERATING CONDITIONS:

Choice of x-ray tube operating condition is important for determining best signal to noise ratio for a particular analyte. Choice of x-ray tube current(mA) is less a problem than the choice of x-ray tube voltage(kV) because current affects both line and background intensity linearly and therefore does not affect the line to background ratio. However the voltage affects both the intensities very differently(4). Generally it is preferable to select effective voltage for an analyte line. Effective potential(voltage)(4) is defined as approximately three times the excitation potential of the analyte line, since at this potential continuum hump falls on the shorter wavelength side of the analyte absorption edge of the element. For Nb K-lines the excitation potential is 18.984 keV. But since in our case the range of analysis varies from 0.5% to 35% of Nb, we observed that the secondary x-rays coming out of the sample is too high to be counted by the detector if the x-ray tube is operated at effective potential(60kV). Therefore, instead of operating the tube at 60kV it was

decided to operate it at 35kV which gives enough counts for 10 seconds counting time. Operating at lower potential also gives improved signal to noise ratio.

Other instrumental parameters are summarised in Table-1.

Table-1: Instrumental Conditions.

X-ray Spectrometer	Philips PW 1220 semiautomatic X-ray Spectrometer
X-ray generator	Philips PW 1140 ultrastabilised Generator, Voltage and current regulated to 0.01%
X-ray tube	Philips 3kW Gold target tube operated at 35kV, 10mA
Analysing crystal	LiF(200), first order
Collimator	Fine(160mm)
Detector	Scintillation counter ; Voltage:950V.
Pulse Height selection	Baseline: 150 div. Window: 300x1 div
Counting time	10 seconds.

II.2. STANDARD PREPARATION:

A set of standards containing Nb in the concentration range of 0.5 to 35% in ZrO₂ matrix was prepared by dry mixing procedure. 200 mg of ZrO₂ standard/sample was mixed with 200 mg of boric acid as a binder. The mixture is pressed as a double layer over a primary boric acid pellet at a pressure of 10 tons. The ratio 1:1 of ZrO₂ and boric acid gives a stable pellet of infinite layer thickness and the amount is sufficient to spread the sample uniformly over a 30 mm diameter pellet. A set of nine standards in concentrations of 0.0%(blank), 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 15%, 25% and 35% are prepared, in the form of double layer pellets as described above.

II.3. ANALYTICAL PROCEDURE:

In the Philips PW 1220 x-ray spectrometer there is a provision to load four samples at a time. A blank, standards and samples are loaded in these positions. These are sequentially exposed to primary x-rays from the x-ray tube. X-ray intensities at experimentally determined 2θ angle are counted. The net peak counts for the analyte line is obtained by subtracting blank counts (N_b) from total peak counts (N_p). A plot of net peak counts vs concentration is used as working curve to determine analyte concentration in unknown sample.

III. RESULTS AND DISCUSSION:

III.1. PRINCIPLE OF THE METHOD:

Nb K-series line ($K\alpha_{1,2}$) are chosen for analysis purpose as this is the most intense line. Nb K-series lines require excitation potential greater than 18.984keV for their excitation. Zirconium has its K absorption edge at 17.996keV. So at the operating condition of 35kV both Niobium and Zirconium K-lines will be excited. Since Niobium $K\alpha_{1,2}$ (16.581keV) energy is lower than Zirconium K edge (17.996keV) energy there can not be any matrix absorption effect due to Zirconium. At the same time Zr $K\alpha_{1,2}$ (15.744keV) or Zr $K\beta_2$ (17.967keV) line are having energy lower than Nb K-edge so there can not be any matrix enhancement effect to the $K\alpha_{1,2}$ analyte line of Nb. Also Zr and Nb being adjacent elements their mass absorption coefficients are practically same for Nb $K\alpha_{1,2}$ line hence wide variation in composition will have little effect on the intensity of Nb $K\alpha_{1,2}$ line. This is the reason as to why the calibration curve, inspite of wide variations in the concentration of Nb (0.5% to 35%) in ZrO_2 matrix, shows the wide linearity. To reconfirm the wide linearity in the above concentration range, we plotted two different calibration curves, one for 0.5% to 2.5% range and other for 0.5% to 35% range. Both of these calibration graphs were used to obtain the analyte concentration. It was found that the analytical results so obtained were identical for the same sample from both the calibration graphs. Calibration plot for Nb in the concentration range

0.5% to 35% is shown in figure 1. The errorbars shown in the plot are due to statistical variations in the countings at those concentrations.

III.2. SENSITIVITY AND DETECTION LIMIT:

The theoretical minimum detection limit(TMDL) is taken as the concentration for which signal above background is equal to three times the standard deviation of the background counts (N_b) for a given counting time. This is also known as 3σ limit where σ denotes the standard deviation of the background counts N_b . It is calculated as

$$TMDL = 3 \frac{\sqrt{N_b}}{N_p - N_b} \times \text{Concentration}$$

The calculated lower limit of detection for the present method is 0.03%.

III.3. PRECISION:

The precision of the method is determined by recording fifteen values in three sets of five each for the analyte line in each standard. The present standard deviation is calculated by

$$\%SD = \frac{\sqrt{\sigma_p^2 + \sigma_b^2}}{N_p - N_b} \times 100$$

where

σ_p = Standard deviation in peak counts

σ_B = Standard deviation in background counts

N_p = Peak count

N_B = Background count

The average percent relative standard deviation for the analyte is 1.3%.

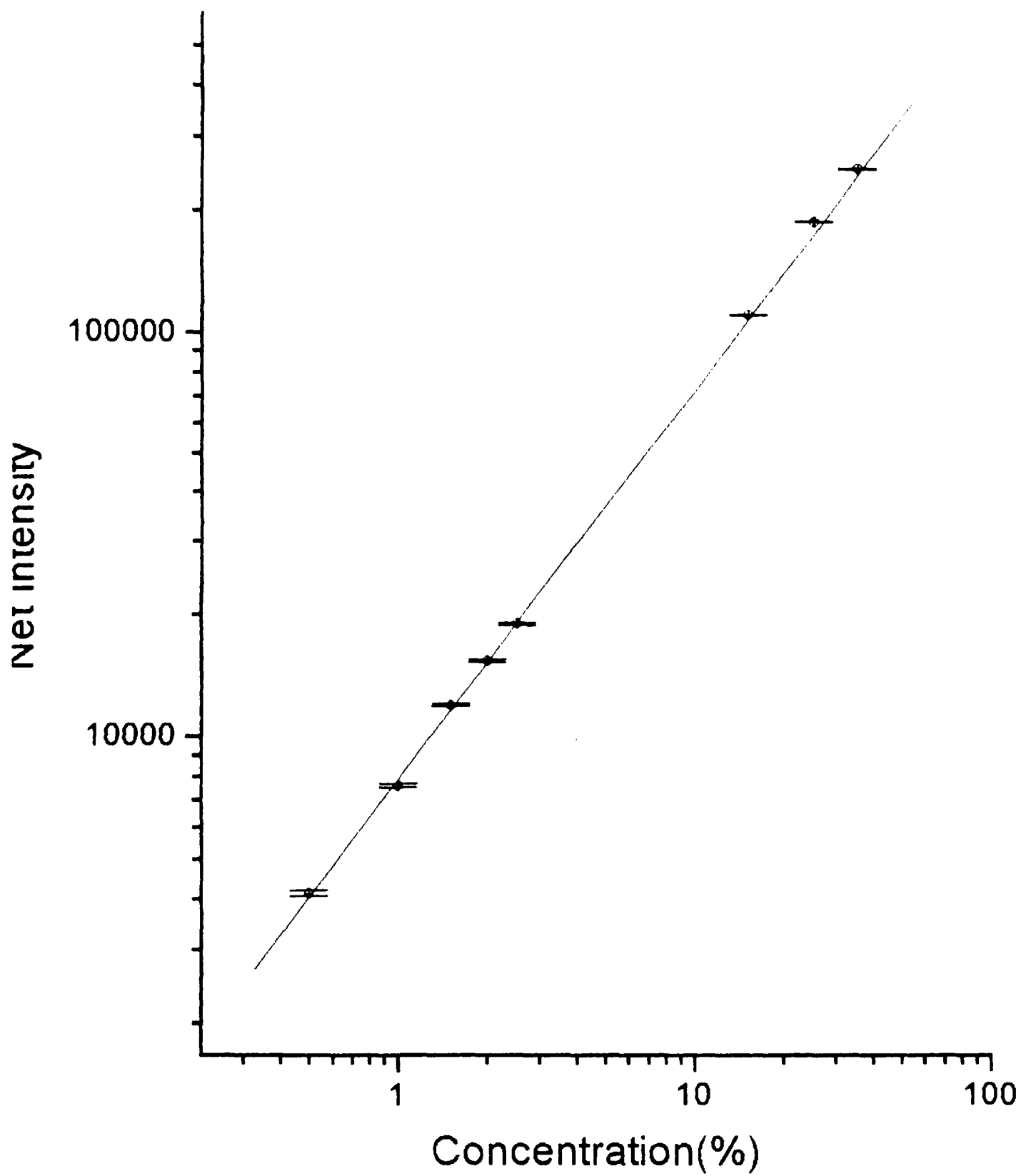
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REFERENCES:

1. Zhang Yongsheng, Yankuang Ceshi, (Chinese), 13, 121(1994).
2. Pan, Bochun; Yu, Yingho, Guangpu Shiyanshi(Chinese), 12, 10(1995).
3. C.T. Yap, Z. Nat. Forsch(W. Germany), 42a, 1253(1987).
4. Bertin P. Eugene, Principles and Practice of X-ray Spectrometric Analysis, Secnd. Edition, Plenum Press, pn. 124.(1975).

Fig.1. Calibration Plot for Nb in ZrO₂ Matrix



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