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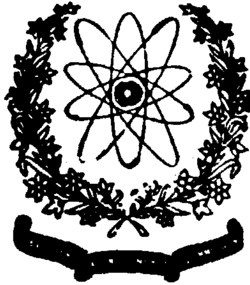

QUANTITATIVE MICROANALYSIS OF HAFNIUM – ZIRCONIUM SYSTEM BY X–RAY FLUORESCENCE

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CONTENTS

S/No	Description	Page
	ABSTRACT	
1.	INTRODUCTION	1
2.	EXPERIMENTAL	5
3.	RESULTS AND DISCUSSIONS	6
4.	CONCLUSIONS	8
5.	REFERENCES	9
6.	FIGURE CAPTIONS	10

ABSTRACT

In this publication, analysis of Hf in zirconium matrix using a wavelength dispersive X-ray fluorescence spectrometer, is reported. To liberate Hf fluoresence spectrum from the spectral interference of Zr-lines scattered in the second order, a novel approach has been used. The method is based on the principle of extinction properties of crystals. Crystals having these characteristics, donot scatter along certain orders of reflections, rather they act as additional strong absorbing media for the incident X-rays. Some of the crystals have very strong extinction coefficients; whereas some may do so only partially. For crystals having very strong extinction coefficients, the incident radiation is completely absorbed when at the exact angle for reflection. In the present investigations, to eliminate the second order spectrum of Zr, we replaced the analyzer crystal LiF (200) by Ge (111), as it was the only one readily available. Ge (111) and Si (111) crystals possess very strong extinction coefficients, i.e., these crystals have zero intensity for the reflections with the order of diffraction 'n' equal to 2 in the Brag equation, $2d \sin\theta = n\lambda$. In the present method, Hf was detected using HfLα, the most efficient line of the Hf L-series spectrum, like any other element in the periodic table, completely free from interference. Using Ge (111) crystal, Hf Lα peak occured at $2\theta = 27.95^{o}$. W X-ray tube presented a weak interference problem due to WLα_2 line occuring at $2\theta = 26.3^{o}$. However, with Si(111) crystal this interference is not likely to be present as now HfLα occurs at $2\theta = 29.1^{o}$. Also using Au X-ray tube efficiency of excitation for HfLα line was enhanced by, approximately, 75% and also the interference caused by WLα_2 line was not present as the Au Ll line occured at $2\theta = 25.82^{o}$. Ge(111) crystal was found to cause relatively large but constant level of background due to Ge Kα fluorescent radiations at $\lambda = 1.25$ Å. The lowest level of Hf concentration detected by the present method (within the criterion of 3σ) was 20 ± 5 ppm. Using Si(111) crystal, this limit can be improved further towards the lower side as the level of background expected in this case is much less compared with Ge(111). Si(111) emits a weak fluorescent radiation at $\lambda = 7.56$ Å, which is easily absorbed in air in the experimental chamber of the spectrometer.

1. INTERODUCTION

Zirconium is an important metal in the development of nuclear reactor technology. However, for nuclear reactor grade Zr, it is important, that the metal should be free from Hf impurities; the maximum permissible level of impurity being less than 100 ppm. The main source of Hf impurity in zirconium is the natural coexistence of Hf salts with zirconium deposits of zircon, for example, usually to the extent of about 1.5 at% of Hf in the form of hafnia (HfO_2) and/or hafnium silicate ($HfSiO_4$). In order to make zirconium metal free from hafnium impurity, several chemical methods like organic solvent extraction and fractional crystallization etc, are employed. In order to reduce the running cost of the plant, it is essential to monitor the hafnium concentration at various separation stages of the process. Detection of hafnium in zirconium matrix has always been a problem [7,8]. Several analytical techniques like standard chemical, spectrochemical and X-ray fluorescence etc, have been used. None of these methods seems to have succeeded sofar to detect Hf in Zr matrix, at least down to the limit of 100 ppm or less[1-8]. The atomic position of Hf and Zr is such that their spectral lines, both for the emission and X-ray fluorescence spectroscopy, overlap and make the detection of Hf difficult, especially when concentration are at the microgram level. Using the spectrochemical method, the lowest level of detection reported is about 10% of Hf (3). X-ray fluorescence methods seem to yield results down to 0.5% of Hf or so. Neutron activation analysis can detect Hf concentrations down to a few ppm level, but requires the availability of a nuclear reactor for the activation of a sample. Also results of analysis are not available for some days due to cooling etc, of hot (radioactive) samples. Chemical process plants, however, require the analysis results to be available as soon as possible. This can be done easily using an X-ray fluorescence method. This method can be used as an on-line technique; time required for analysis being only a few minutes.

X-ray fluorescence technique can be used in two different modes: the wavelength dispersion and the energy dispersion. In the wavelength dispersion method, fluorescent radiation emitted by the analyte is first dispersed (or diffracted) by a known plane of an

analyzing crystal and then detected by a suitable detector (NaI and/or a proportional counter). In the energy dispersion, the fluorescent radiation is detected as such without any dispersion, using a suitable solid state detector like Si(Li). For the detection of Hf, wavelength dispersive spectrometers were mainly used and efforts were continuously made to improve the detection efficiency of the system. Due to dispersion by the anlayzing crystal, resolution of a wavelength dispersive spectrometer is improved considerably. It is approximately 60 times that of the energy dispersive spectrometer (5). However, in the case of Hf - Zr system, the K-series spectrum of Zr diffracted in the second order by LiF(200) crystal, overlapes completely the L-series lines of Hf and thus complicates the analysis (7,8).

Under these circumstances, the energy dispersion method may appear to be a more attractive possibility for the analysis of Hf in Zr, as diffraction by a crystal in this case is not involved. But unfortunately, besides the poor resolution of an energy dispersive spectrometer, its sensitivity and limit of detection are also much inferior compared with a wavelength dispersive spectrometer. These parameters are governed by the count rate capacity of the instrument. In the energy dispersion method, the Si(Li) detector is count rate limited to 10,000 - 20,000 counts per second, but this must include all of the sample spectrum plus scattered primary radiation (5). As a matter of fact, the scattered primary radiation and background can comprise as much as 99% of the total (5). This leaves very little counts for the element of interest, especially the minor constituents. In the wavelength dispersion for NaI detector and gas filled proportional counters, count rate limitation is not a problem (5). Further it is often advocated that spectrum overlaping can be unfolded mathematically. But this can lead to large uncertainties and grossly incorrect results, particularly when the analyte line is weak and the interfering line is very strong, as is the case for Hf - Zr system (5). Energy dispersive spectrometers are useful for determining major constituents in completely unknown samples (5). Detection of Hf at the micrograme level demands resolution of the analyzing instrument to be high. Also the detectable limit of the instrument must be as low as possible. This is probably the reason that inspite of the problem of spectral

interference, wavelength dispersive X-ray fluorescence spectrometers were generally used to detect Hf in the Zr matrix; and efforts were continued to improve the efficiency and the lowest detectable limit of the instrument.

In the Hf - Zr system, Zr Kα line scattered in the second order of diffraction ($2\lambda = 1.58$ Å) overlaps completely the Hf Lα ($\lambda = 1.57$ Å) line. Similarly the Hf Lβ lines are interfered severly by the ZrKβ lines scattered in the second order. In order to eliminate or at least minimize the effect of this interference, several efforts have been reported in the literature (1-5, 8-9). Birks and Brooks (1) have carried out detailed investigations in this respect. Among these efforts included the use of HfLβ lines instead of HfLα line. The reason was that ZrKβ spectrum diffracted in the second order was relatively less intense and presumeable would have interfered HfLβ lines relatively less severely. The collimation of the spectrometer was improved. Also to eliminate continuous background and its spectral interference, W X-ray tube was replaced by more efficient X-ray tubes of Au and/or Mo. Then different excitation potentials for Hf (threshold potential for HfLα = 9.5 KV) and Zr (threshold potential for Zr Kα = 18 KV) were used so that only Hf lines were excited (1,4). To overcome the problem of spectral interference a different approach was also tried [1,7]. Integrated intensities of the unresolved HfLβ, first order and the ZrKβ, second order, peaks were corrected by comparison with the integrated intensities of the fully resolved Zr Kβ peaks.

All these atempts, undoubtedly made it possible to detect Hf concentrations in Zr, but the minimum detectable limit remained arround 0.5% or so.

Alternately, the X-ray tube potential was increased to excite K-series spectrum of Hf. These lines were free from spectral interference of Zr. The wavelength of HfKα line is rather small (0.22 Å). It would require excitation potential of the order of 80 KV (threshold voltage for HfKα = 67 KV). Further a wavelength of this order would require an analyzing crystal with a d_{hkl}-spacing of the order of 1 Å, such as one of the weaker planes in quartz crystal. These efforts would thus produce an highly expensive spectrometer with extremely poor efficiency.

Despujols and Lumbros (3), using a curved crystal of Al in a wavelength dispersive spectrometer, have reported detection of Hf to the limit of 0.016%. In these studies Hf$L\beta_2$ line was used. Ricci (9) has reported determination of Hf to the level of 1.2 ppm in samples of Zr from a chemical separation plant, using an energy dispersive X-ray fluorescence spectrometer. For the determination of Hf content, Ricci (9) used Hf $L\beta_1$ line. Also Ricci (9) assumed that the Zr $K\beta_1$ line was absent at voltages used in the reported analysis. The analysis was reported to be performed at the x-ray tube voltage of 40 KV and 14mA filament current. For the excitation of Hf fluorescene spectrum, an x-ray tube of Ag was employed. Also the spectrum was unfolded mathematically. It may, however, be pointed out that 40 KV is not a low excitation voltage. We have noted in this laboratory the emission of Zr $K\beta_1$ line at various excitation voltages. Zr $K\beta_1$ line was always found to be excited to appreciable extent even at voltages as low as 20 KV and 5 mA filament current. Further for the excitation of Hf spectrum, Ag ($L\alpha$, 4.054 Å ; $L\beta_1$, 3.934 Å) is not an efficient target. X-ray tube of Ag is generally recommended for the analysis of light elements like Cl (Z = 17, Kabs 4.397 Å) and S (Z = 16, Kabs 5.018 Å) etc. (4). Moreover, as pointed out earlier and also discussed in detail by Birks (5), the energy dispersion method is suitable only for the determination of major constituents and mathematical unfolding of the spectrum is likely to lead to large uncertainties, if the analyte line is weak and the interfering line is strong.

In this paper, we present our investigations on the analysis of Hf in the matrix of zirconium (ZrO_2 and/or Zr-alloys etc.) using a different approach to eliminate the spectral interference of Zr on the fluorescence spectrum of Hf. The results of these investigations are the first of their kind and to the author's knowledge no such measurements are reported in the literature. Our method to liberate the Hf spectrum from the spectral interference of Zr is based on the principle of extinction characteristics of crystals. Crystals having extinction properties for certain orders of reflections, act as very strong absorbing media when at the exact angle for diffrction, for such orders (10). Some crystals, e.g., Ge(111) and Si(111), possess very strong extinction

coefficients for the second order of reflections. In these crystals, (222) reflections are absent. Thus if the generally used LiF (200) crystal in a wave-length dispersive spectrometer is replaced by Ge(111) and/or Si(111), the Zr Kα as well as Zr Kβ, lines scattered in the second order will not be present. So we can detect Hf, directly like any other element in the periodic table, free from any interference, using HfLα line, which is the most intense line of its L-series of spectrum. Also elimination of the interfering Zr-lines was total; and no contribution from the Zr Kα (second order) etc. was noted. This was checked by using a sample of pure ZrO_2 having purity of 5N (99.999%). Also this method of eliminating the spectral interference was general and could be used for the analysis of any other system where second order reflections caused interference, e.g., Nb - Ta system. Using Ge(111) and/or Si(111) Hf concentration levels as low as 20 ppm or so could be easily determined in zirconium metal or its alloys, approximately, with an accuracy of ± 10%. Compared with Ge(111), Si(111) would be relatively, a better crystal as its background level is expected to be small. Si emits a weak fluorescent radiation at λ = 7.56 Å , which is absorbed in air in the spectrometer chamber. Ge(111) emits a strong fluorescent radiation at λ = 1.25 Å and required pulse height descrimination for its elimination.

2. EXPERIMENTAL

Experimental set-up used in the present studies was a wavelength dispersive X-ray fluorescence spectrometer Model 3064 of M/s Rigaku Corporation, Japan. Samples for analysis were prepared by mixing oxides of Hf and Zr all having a purity of 5N (99.999%). These were obtained from M/s Hohnsons and Mathew (U.K.). ZrO_2 and HfO_2 were mixed in known proportions from 1.95 at % of Hf metal in the form of HfO_2, in ZrO_2 down to 50 ppm of Hf. The mixture was ground in a mortar and pestal of agar to a particle size, less than 50 microns, in isopropyl alcohol. To ensure, thorough mixing of the contents, the process was repeated at least 4 times for each sample. Every time when alcohol dried off, it was added again and grinding continued. Further for the next charge, to avoid any contamination from the previous sample, the mortar and pestal were thoroughly washed first in running water and then in alcohol. Also

first samples with low concentration of Hf were ground and analyzed. The fine powder thus obtained was placed in an aluminium ring and pressed to a pressure of 20 tons under an hydraulic press to form round disc shaped samples. Thickness of these samples was about 3 mm. These samples were mounted on the spectrometer powder specimen mount. Area of the sample surface exposed to X-rays was 11.1 cm. The present machine permitted analysis of samples both in the vacuum and in air. In the present studies determination of Hf, was carried out using the most intense line of its spectrum, (Hf $L\alpha$) and using Ge(111) analyzing crystal. Hf fluoresence lines were excited using both the W and AU x-ray tubes. Heterogeneity of samples was examined by analyzing them on their both sides. Matrix corrections were applied according to the standard procedures described by Bertin (4) and others (10). Peak intensity was obtained by subtrcting the average background intensity from the maximum peak intensity. Background was noted on both sides of the peak and average taken. Also background was counted for the same time as the peak intensity. For this analysis, fixed time counting was used and care was taken that the number of counts was large enough so that statistical error due to counting was less than 1%. The minimum detectable limit was determined using the criterion of 3σ, described by Bertin (4) and Birks (5), σ being the standard deviation. For analysis only those samples were used which had smooth and plain surfaces. The present investigations were carried out at 50 KV x-ray tube voltage and 50 mA filament current.

3. RESULTS AND DISCUSSIONS

Results of these investigations are shown in figures 1 to 4. Figs. 1a and 1b illustrate the chart recorder traces of x-ray fluorescence spectra for a pure ZrO_2 sample (purity, 99.999%; Zr = 74.03% and Hf $\leq$ 20 ppm) and the one containing 1.95% of Hf. These spectra were recorded with W X-ray tube. The diffraction angle range covered was from 24° to 33°. As is obvious from Fig. 1a, there was only one peak in the spectrum at $2\theta = 26.3^{o}$. This is due to the W $L\alpha_2$ line and is contributed from the X-ray target. In the observed range of the spectrum no line due to Zr was noted. Any contribution from Zr $K\alpha$ line, scattered in the second order, would have appeared arround $2\theta = 28^{o}$. But the spectrum clearly indicates the absence of this peak.

In the spectrum shown in Fig. 1b, peak due to $WL\alpha_2$ is present. Also there are two additional peaks one strong at $2\theta \approx 27.95^o$ the other relatively weak $2\theta \approx 31.75^o$. The strong peak is due to Hf $L\alpha$ line, and the weak peak is the contribution from Hf Ll line. It is, obvious from the spectrum the HfL_α peak is completely free from any spectral interference except that $WL\alpha_2$ line, is overlapping slightly at its rising tail side. Also the background level can be easily marked. This is important for accurate determination of the peak intensity and hence the concentration of the analyte. Interference due to W-line can be removed using a different x-ray target. This is shown in Fig. 2 which illustrates the X-ray fluorescence spectra obtained on the same samples as in Fig. 1, but using the x-ray tube of Au. Experimental conditions were also the same. It is obvious from Fig. 2a that the peak due to $WL\alpha_2$ line is no longer present, and instead a new peak due to $AuL\gamma_3$ line has emerged at $2\theta \approx 25^o$. This peak is contributed from the Au X-ray tube. In Fig. 2b, peaks due to $HfL\alpha$ and $HfL\alpha$ lines occur at the same position as in Fig. 1b. The only difference is that now intensity of the $HfL\alpha$ peak, has increased substentially (75%), and the spectral interference observed in Fig. 1b due to $WL\alpha_2$ peak is also not present. The background level on both sides of $HfL\alpha$ peak can be accurately marked. These features suggest that Au is more efficient and useful target for the excitation of Hf spectrum.

In Fig. 3, traces of $HfL\alpha$ line for different concentrations of Hf (from 1.95% to 50 ppm) are plotted. Fig. 4a shows the calibration curve for these concentration of Hf. A straight line passing through the origin, indicates clearly the linearity and accuracy of detection of the present method over the entire range of Hf concentrations. In Fig. 4b, the lower part of the calibration curve shown in Fig. 4a is plotted again for lower concentrations of Hf (1200 ppm to 30 ppm). Using Ge(111) crystal, the lowest level of hafnium concentration detected in the present studies was 20 ppm with an accuracy of $\pm$ 10%. These results were also cross-checked using the neutron activation analysis method.

4. CONCLUSION

Results of the present investigations show clearly that the problem of spectral interference in the analysis of Hf, caused by the second order reflections of Zr, can be easily overcome by using Ge(111) and/or Si(111) analyzing crystals. In these crystals second order reflections are absent, because of their strong extinction coefficients for second order reflection. X-ray tube of Au was the most efficient and useful x-ray target for the excitation of Hf - spectrum. It yields spectral-interference-free peak for HfL_{α} line. Due to weak fluorescent radiation, Si(111) crystal has certain advantage over Ge(111) crystal. The strong background observed in case of Ge(111) crystal can be eliminated using Si(111) crystal. The method proposed is simple and straight forward. It does not involve any mathematical unfolding of the spectrum. Also no special sample preparation methods are required. Ge(111) and Si(111) crystals are relatively less expensive and are easily available from various supplier. Also these crystal can be easily mounted on a wavelength dispersive spectrometer. Analysis time required is also small; being only a few minutes.

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FIGURE CAPTIONS

Fig. 1: X-ray fluorescence spectrum of ZrO_2 samples using a W-target:

a) Ultrapure ZrO_2 (99.999%).

b) ZrO_2 containing 1.95% of Hf.

Fig. 2: X-ray fluorescence spectrum of ZrO_2 samples using a Au - target:

a) Uptrapure ZrO_2 (99.999%).

b) ZrO_2 containing 1.95% of Hf.

Fig. 3: Traces of hafnium $L\alpha$ peaks at different concentration levels reaging from 1.9514% to 84 ppm. These traces were recorded using manual counting method.

Fig. 4: Calibration curve for Hf in the concentration range from 1.9514% to 84 ppm.

Fig. 5: Calibration curve for Hf in the concentration range from 1200 ppm to 30 ppm.

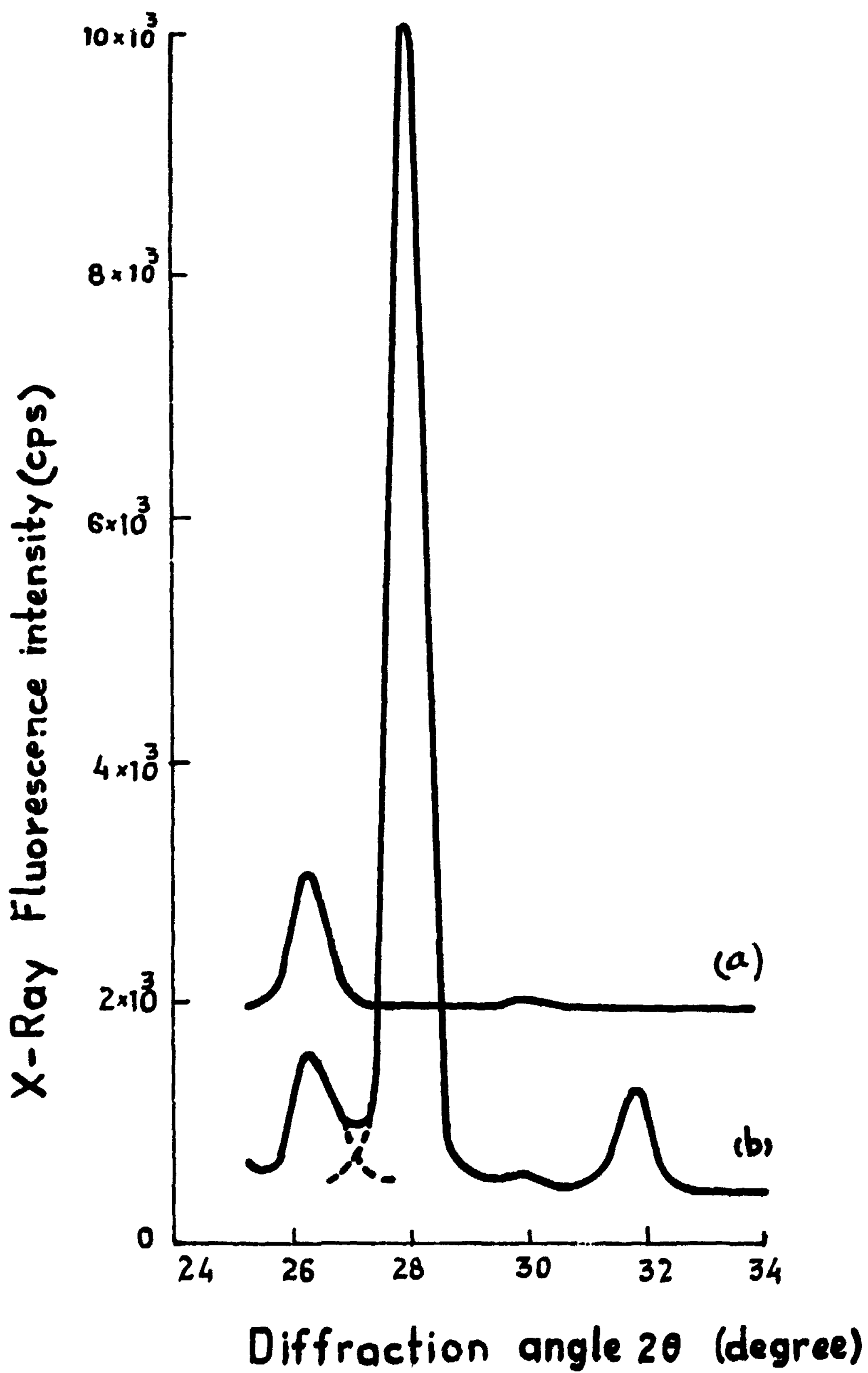

Fig. 1

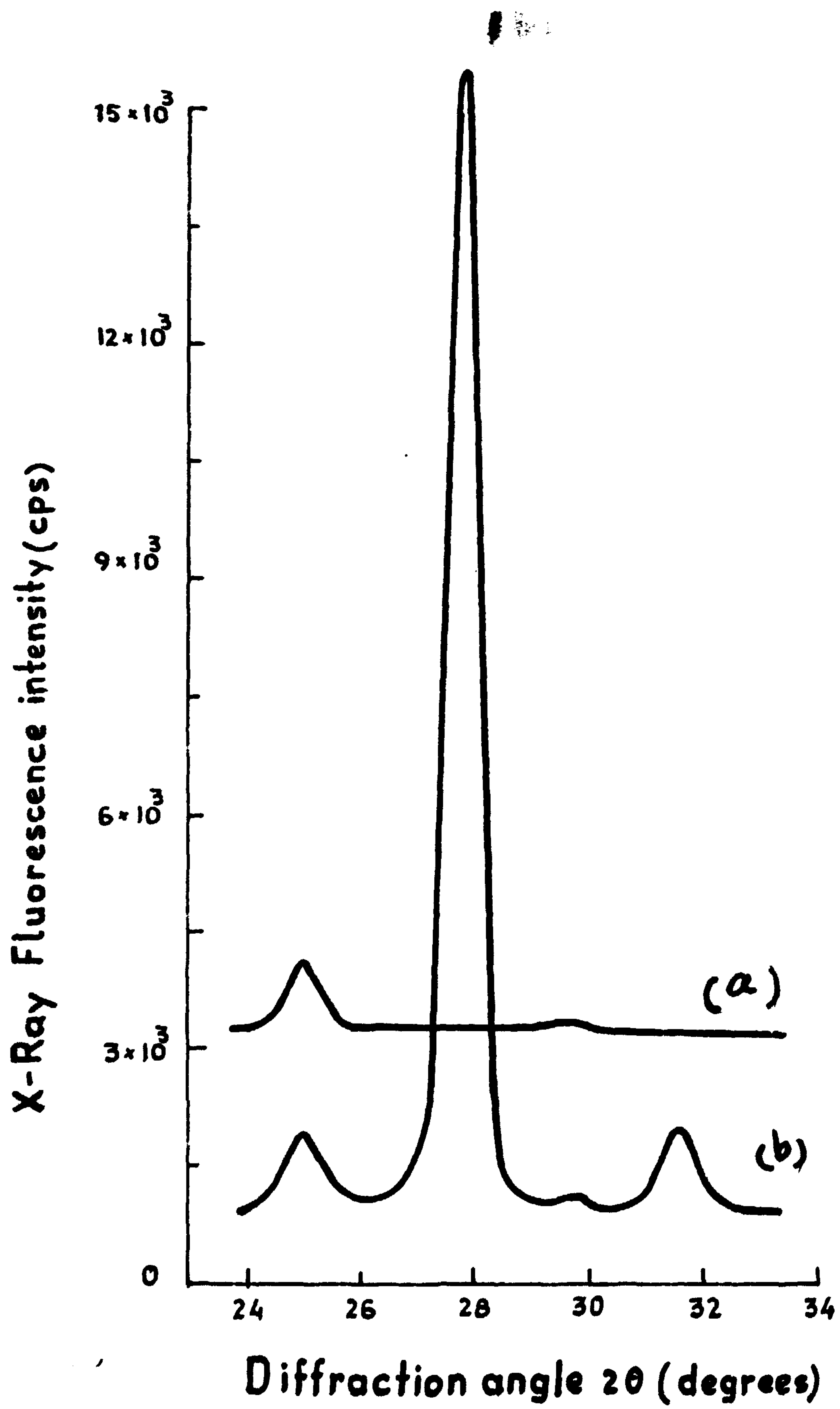

Fig. 2.

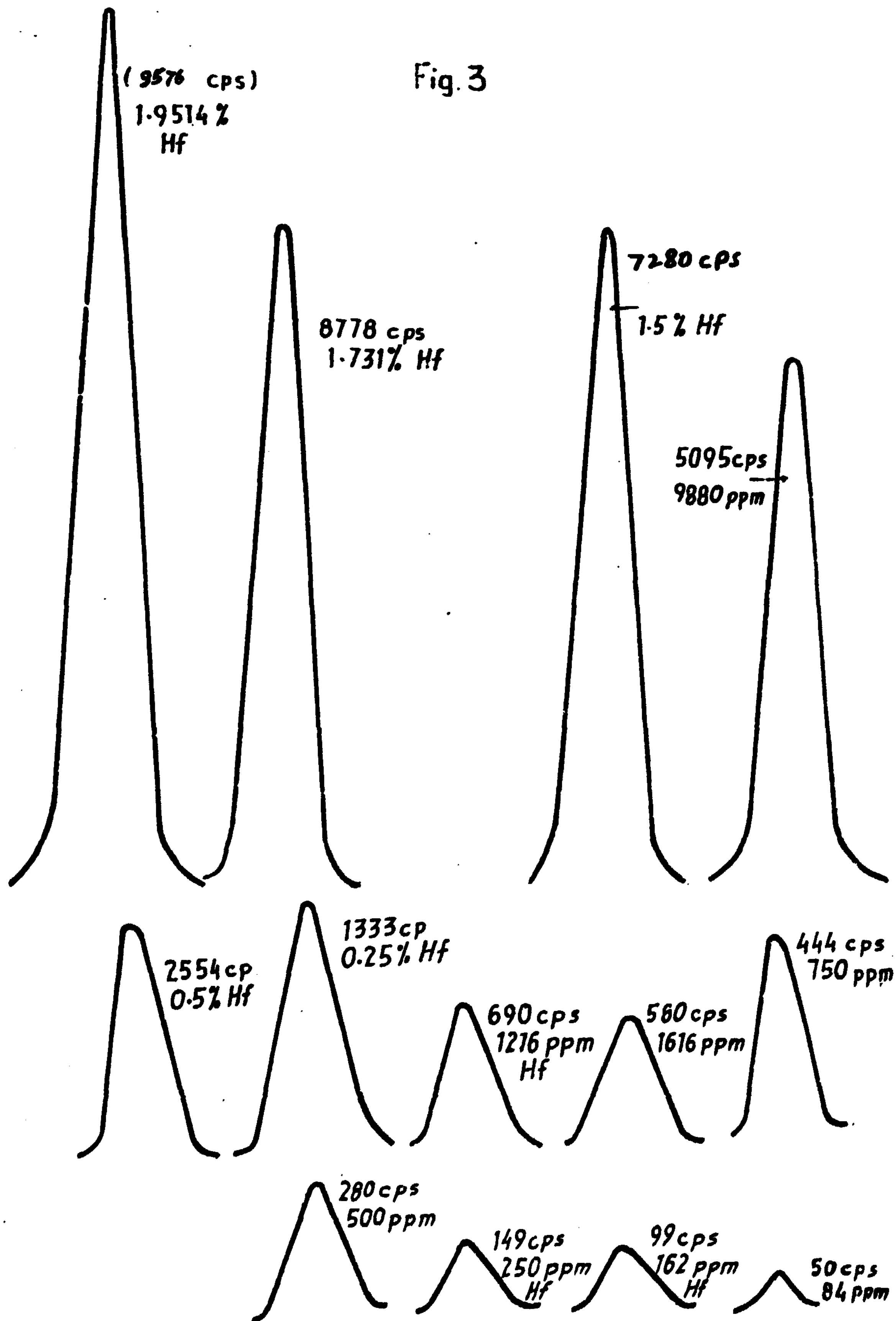

Fig. 3

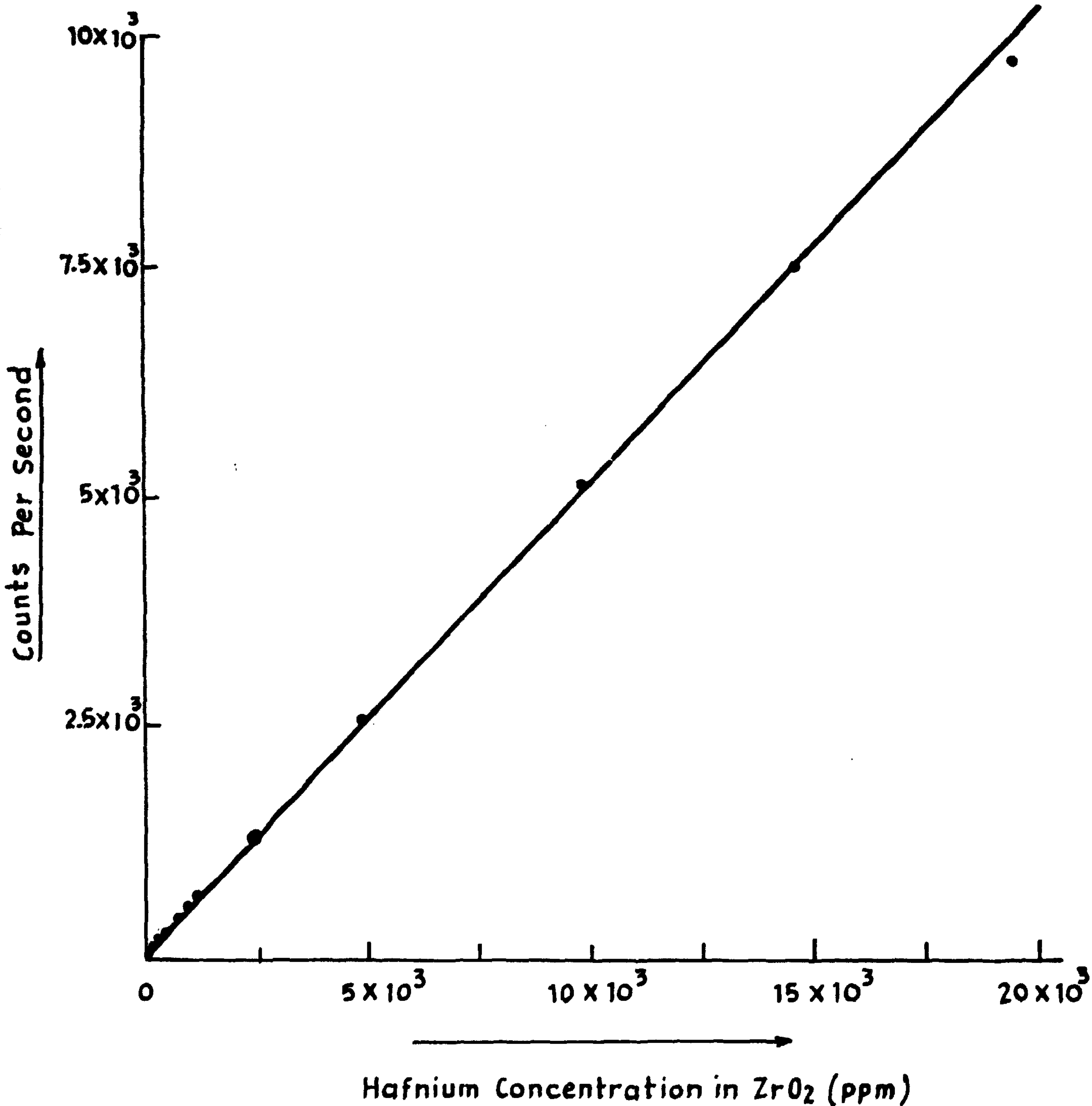

Fig. 4: Test cases
Estimation of Hf in Alpha
ZrO_2 (old lot) = 8778 cps
= 1.7313 ± 0.017%

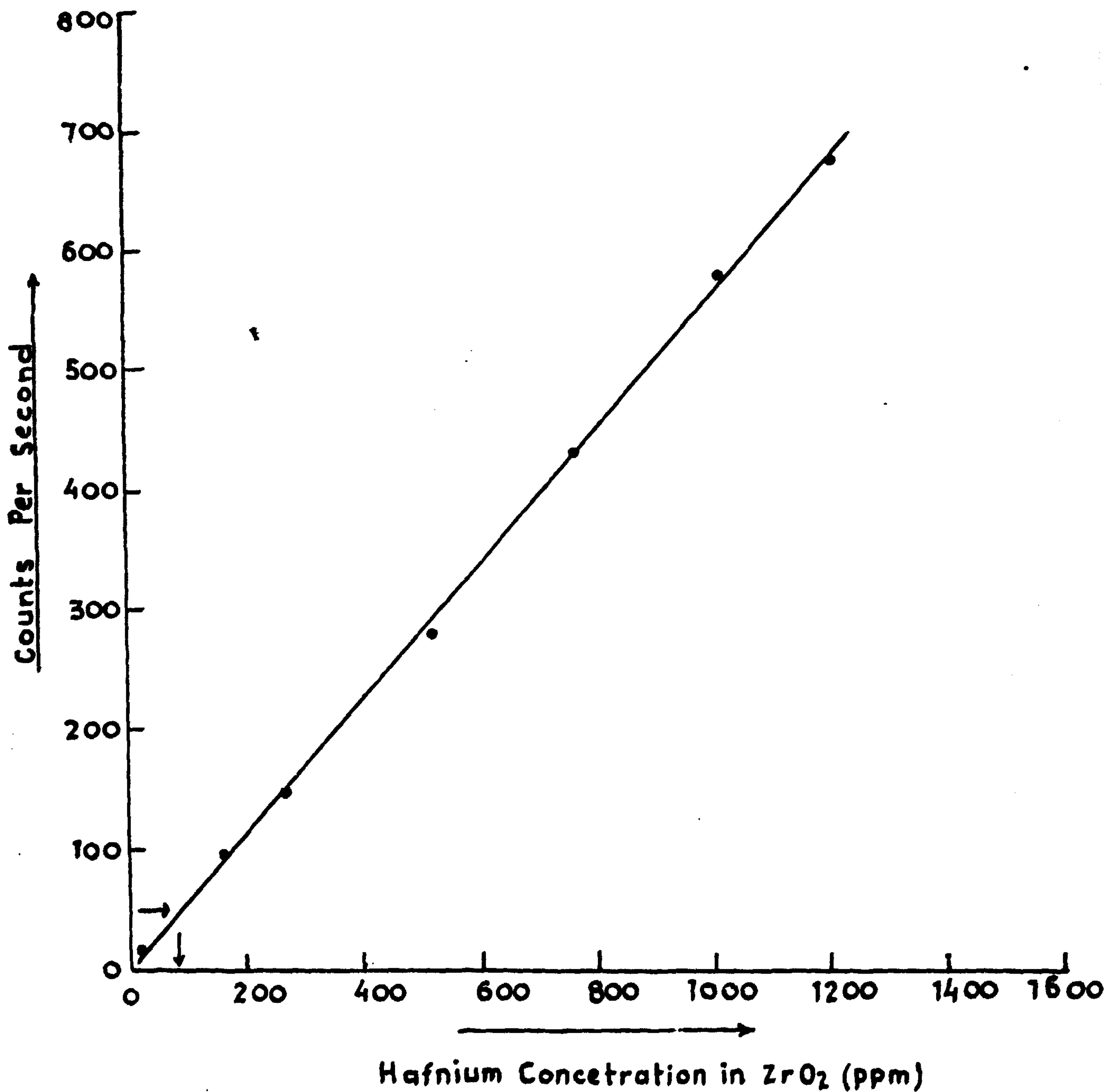

Fig.5: Test case : Zircalloy-4
Estimated concentration of Hf - 84 ± 12 ppm(2σ)