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Standard-less analysis of Zircaloy clad samples by an instrumental neutron activation method

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Abstract

A non-destructive method for analysis of irregular shape and size samples of Zircaloy has been developed using the recently standardized k_0-based internal mono standard instrumental neutron activation analysis (INAA). The samples of Zircaloy-2 and -4 tubes, used as fuel cladding in Indian boiling water reactors (BWR) and pressurized heavy water reactors (PHWR), respectively, have been analyzed. Samples weighing in the range of a few tens of grams were irradiated in the thermal column of Apsara reactor to minimize neutron flux perturbations and high radiation dose. The method utilizes in situ relative detection efficiency using the γ-rays of selected activation products in the sample for overcoming γ-ray self-attenuation. Since the major and minor constituents (Zr, Sn, Fe, Cr and/or Ni) in these samples were amenable to NAA, the absolute concentrations of all the elements were determined using mass balance instead of using the concentration of the internal mono standard. Concentrations were also determined in a smaller size Zircaloy-4 sample by irradiating in the core position of the reactor to validate the present methodology. The results were compared with literature specifications and were found to be satisfactory. Values of sensitivities and detection limits have been evaluated for the elements analyzed.
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1. Introduction

Zirconium and its alloys are important materials in nuclear industry [1]. Zirconium alloys are mostly used for fuel cladding and core components in water-cooled nuclear power reactors viz. boiling water reactors (BWR), pressurized light water reactors (PWR) and pressurized heavy water reactors (PHWR) [1]. Important alloys of zirconium have been developed to meet specific requirements in nuclear power reactor technology. For nuclear quality control, it is important to analyze these alloys to ensure their conformity to specifications/compositions [1]. Analytical methods, which

are non-destructive in nature and with negligible matrix effect and low detection limit, are preferred for the analysis of such materials. Non-destructive methods are preferred to avoid the time consuming and elaborate procedures of sample dissolution and chemical removal of major matrix elements or elements of interest as practised in techniques like flame-atomic absorption spectrometry (AAS), electrothermal atomization-AAS (ETA-AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) [1].

Instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) analysis are two commonly employed non-destructive methods for multielemental determination. The INAA approach is preferred due to high penetration power of neutrons and γ-rays in the sample [2]. However, INAA using conventional relative and k_0 methods demand definite shape and size of samples so that standards/comparators can be prepared in a similar geometry. Elemental concentration

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calculation using relative method is simple whereas in k_0-based INAA [3–6] the additional parameters such as thermal to epithermal neutron flux ratio ($\phi_{th}/\phi_e = f$), epithermal neutron flux shape factor (α) and relative or absolute full-energy peak detection efficiency (ε) of the detection system are required besides using nuclear constants such as Q_0 (ratio of resonance integral (I_0) to 2200 m s^{-1} (n, γ) cross-section (σ_0)) and k_0 [4,7]. The k_0-based INAA method for larger size and standard geometry/shape samples needs elaborate procedures for accounting the neutron self-absorption/flux perturbation during sample irradiation in a reactor and γ-ray self-attenuation for determining the efficiency of the detector [8,9].

Recently, we have proposed a k_0-based internal mono standard method of INAA for the analysis of large and non-standard geometry samples [10,11]. This method gives relative elemental concentration with respect to one of the elements present in the sample. The pre-knowledge of concentration of the mono standard or any one of the constituents is required to convert relative elemental concentrations to absolute values. The proposed method utilizes an in situ relative detection efficiency using γ-rays from the activation products of the elements present in the sample to overcome the problem of γ-ray self-attenuation in the sample. The method was validated by determining impurity concentrations in two large size synthetic samples [10] and relative elemental concentrations in two IAEA reference materials [11]. In special cases, where all the major and minor elements are amenable to NAA like in alloys and high purity metals, the absolute concentration can be found out by this method using mass balance. Since the mass of the mono standard is not required for arriving at the absolute concentration of the elements present in the sample, this method can be called as standard-less method. This method would be handy for the analysis of finished products of alloys and metals including high purity materials and archaeological samples, which are difficult to destroy or required to be preserved in the original shape.

The present paper reports the results of major, minor and trace element concentrations in finished product non-standard shape samples of Zircaloy clad tubes (Zircaloy-2 and -4) by the k_0-based internal mono standard INAA method. Zirconium (^{94}Zr) was used as the internal mono standard. Samples of different shapes and sizes were irradiated in the thermal column of the Apsara reactor, Bhabha Atomic Research Centre, Mumbai. One smaller size sample of Zircaloy-4 was irradiated in a higher neutron flux position (core position) of this reactor to obtain the elemental concentrations at a different condition of neutron spectrum and the results were compared with those obtained from larger size samples of the same material using thermal column.

2. Experimental

2.1. Samples and sample irradiation

In the present work, a sample of Zircaloy-2 clad welded to the end-plug and three samples of Zircaloy-4 clad were analyzed. The samples were of non-standard shape (geometry), and their masses varied between 344 mg and 24 g. The samples were sequentially cleaned with dil. HNO$_3$, water and acetone and sealed in polythene. Larger size samples were irradiated in the thermal column (duration of 4 h) and a small sample of Zircaloy-4 (mass = 344 mg) was irradiated in E8 position (duration of 1 h) of swimming pool type Apsara reactor. The thermal column of dimension 25×25 cm is situated at one end of the reactor pool with 2.5 m thick graphite. Samples were placed in an aluminum tray which was moved into the thermal column.

The f value of the thermal column is 5.6×10^3 [10], which corresponds to a thermal neutron component of about 99.98%. This value was obtained via cadmium ratio method using a thin indium foil (^{115}In) as a neutron flux monitor. The thermal equivalent neutron flux at the irradiation position was 2×10^{12} m^{-2} s^{-1}. Since the thermal column has a higher thermal component, α has no significance in concentration calculations and hence it was not determined. The f and α values of the E8 position of the Apsara reactor are 65.6 ± 1.8 and 0.013 ± 0.004, respectively [12] and these values were obtained by cadmium ratio method using dual flux monitors, ^{197}Au and ^{94}Zr [5]. The thermal equivalent neutron flux at E8 position is about 6×10^{15} m^{-2} s^{-1}.

2.2. Radioactive assay

After irradiation and appropriate cooling, samples were cleaned with acetone. They were assayed by high-resolution γ-ray spectrometry using a 40% HPGe detector coupled to a 4k-channel analyzer at random positions with respect to the detector. The resolution of the detector was 1.8 keV at 1332 keV of ^{60}Co. The sample-to-detector distance was 10–15 cm to minimize loss of counts due to coincidence effects, if any, and also for controlling the dead time below 5%. Peak areas under the full energy peaks were evaluated via peak fit method using the PHAST software, developed at our institute [13]. The software has features for energy calibration and determination of peak shape parameters. A second order polynomial in energy was used to calibrate the full width at half maximum (FWHM) of the individual peaks and is used for deconvolution of multiple peaks in the gamma ray spectrum.
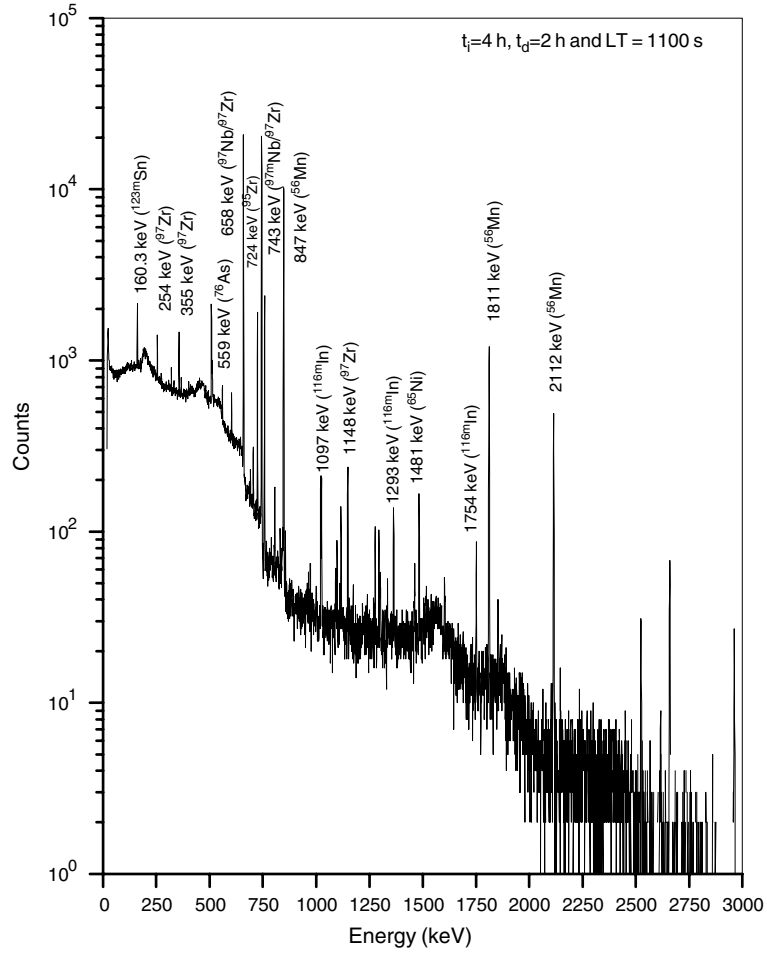
Fig. 1. Gamma ray spectrum of neutron activated Zircaloy-2 sample using thermal column of the reactor.

2.3. Calculations

When a sample is irradiated in a neutron flux, the ratio of mass (m) of an element (x) to mass of the internal comparator element (y) in the sample using the k_0-based internal mono standard method INAA is given by the following expression [11]:

$$\frac{m_x}{m_y} = \frac{((SDC) \times (f + Q_0(\alpha)))_y}{((SDC) \times (f + Q_0(\alpha)))_x} \times \frac{P_{A_x}}{P_{A_y}} \times \frac{(\varepsilon_\gamma)_y}{(\varepsilon_\gamma)_x} \times \frac{1}{k_{0,y}(x)},\tag{1}$$

where P_A is the net peak area under the gamma peak of interest, S is the saturation factor $(1 - e^{-\lambda t_i})$, D is the decay factor $(e^{-\lambda t_c})$, C is the term used for correcting the decay during counting period and is given by $(1 - e^{-\lambda LT})/\lambda$; t_i, t_c and LT are time durations for irradiation, cooling and counting of the sample, respectively, $Q_0(\alpha)$ is the α corrected Q_0 value [5] and ε_γ is the detection efficiency. The $k_{0,y}(x)$ is calculated from the

literature $k_{0,Au}$-factors [4,7] using the following expression:

$$k_{0,y}(x) = \frac{k_{0,Au}(x)}{k_{0,Au}(y)}.\tag{2}$$

Eq. (1) was used to calculate the elemental mass ratio in the case of core irradiation condition. When an irradiation position used has a high f value, as in the case of thermal column, the factor $[f + Q(\alpha)]_y/[f + Q(\alpha)]_x$ in Eq. (1) tends to unity and the calculation was done without this factor in Eq. (1). When all the major and minor elements present in the sample are amenable to NAA, the absolute concentrations can be determined by mass balance without resorting to the concentration of the internal mono standard as described in Ref. [10].

2.4. In situ detection efficiency calibration

Since the detection efficiencies (ε) appear as ratio ($\varepsilon_y/\varepsilon_x$) for the determination of relative elemental

concentrations (Eq. (1)), the relative efficiency determination is sufficient for the calculation of concentration ratios. Use of relative efficiency makes the method geometry independent. In the present work, in situ relative detection efficiency has been determined using the γ-rays of the activation products of elements present in the sample. The relative efficiency curves from individual radionuclide are expected to be parallel and differ by constant factors. Hence, when gamma rays from more than one radionuclide are required together to cover the requisite energy range, the expression for efficiency is

$$\ln \varepsilon_R(E_\gamma) = k_j + \sum_{i=0}^{m} a_i (\ln E_\gamma)^i, \qquad (3)$$

where $\varepsilon_R(E_\gamma)$ is the relative full energy peak detection efficiency of the γ-ray of energy E_γ, a_i's are the coefficients of the polynomial of order m and k_j is a constant characteristic of the jth nuclide. In our calculations, we have used a second order polynomial ($m = 2$). The details of in situ efficiency calibration are given in Ref. [11].

3. Results and discussion

The relevant nuclear data were taken from Refs. [4,7]. A gamma ray spectrum of the neutron-activated sample of Zircaloy-2 clad is given in Fig. 1, which shows the characteristic gamma lines of some of the radionuclides. The in situ relative efficiency plots for the thermal column irradiated Zircaloy-2 and the core position irradiated Zircaloy-4 samples are given in Fig. 2. The nuclides whose gamma lines are used for efficiency calibration are also indicated in the figure. The absolute concentrations were arrived at using the condition of mass balance. The results of analysis of Zircaloy-2 sample are given in Table 1. The results of Zircaloy-4 samples are given in Table 2. Results reported in Tables 1 and 2 are the weighted mean of concentrations obtained from independent measurements. The quoted weighted uncertainties were arrived at from the counting statistics of individual measurements. However, additional uncertainties from the parameters like $k_{0,Au}$-factor and efficiency (ε) are expected to be present with the determined values and are in the order of 1% and 2–5%,
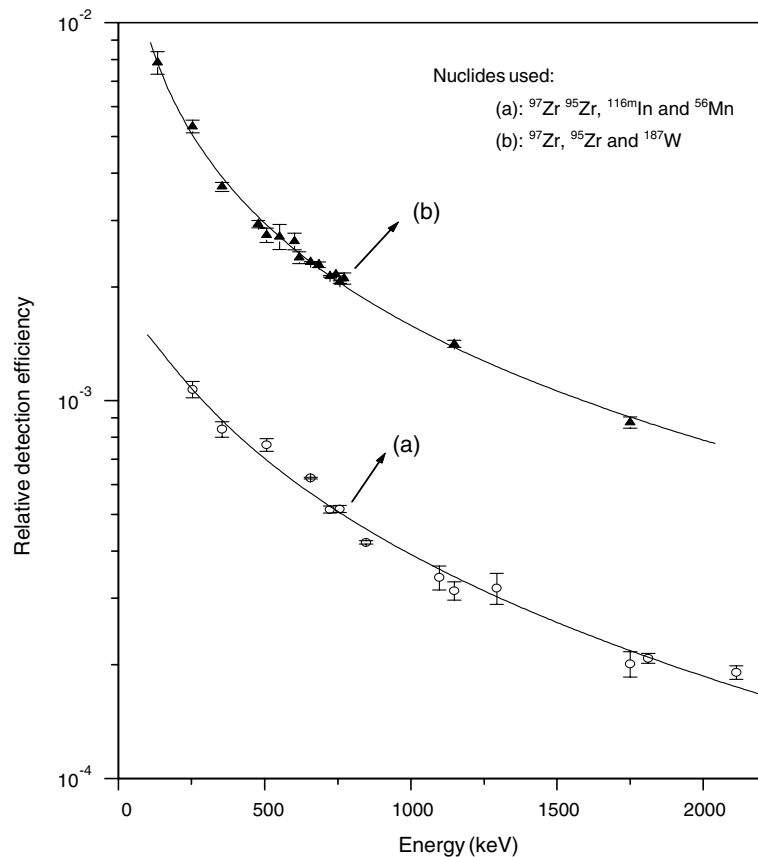

Fig. 2. In situ relative detection efficiency plots for (a) the Zircaloy-2 clad sample irradiated in thermal column of the reactor and (b) the Zircaloy-4 clad sample irradiated in core position of the reactor.

Table 1
Determined elemental concentrations (mg kg^{-1} unless % is indicated) of Zircaloy-2 clad welded to the end-plug

Element	Zircaloy-2 (24 g)	Literature composition Ref. [1]
As	4.5 ± 0.4	NA
Mn	10.7 ± 0.1	50
Hf	24.0 ± 0.7	100
Ta	16.3 ± 1.1	200
Co	6.8 ± 0.1	20
In	(1.0 ± 0.1) × 10^{-1}	NA
Ni%	(7.8 ± 0.4) × 10^{-2}	0.03–0.08
Cr%	(8.3 ± 0.1) × 10^{-2}	0.05–0.15
Fe%	(1.8 ± 0.2) × 10^{-1}	0.07–0.2
Sn%	(15.8 ± 0.3) × 10^{-1}	1.2–1.7
Zr%	98.2 ± 0.7	Balance

NA – not available.

respectively. Further uncertainties due to f, α and Q_0 parameters are also required to be considered when a core irradiation position is used in the k_0-based INAA [3]. The determined concentrations of the major and minor elements (Zr, Sn, Cr, Fe and/or Ni) in both the types of samples are in good agreement with the literature specifications (Tables 1 and 2) [1]. The elements like In, Mn, As, Co and Hf, though present in low level (mg kg^{-1}) could be determined in both the samples. Hafnium is present in all the samples in the range of 24–28 mg kg^{-1}. Nickel was not detected in Zircaloy-4 samples, since it is expected to be present in low concentration. Tungsten was detected only in Zircaloy-4(A) when the sample was analyzed using higher flux irradi-

ation position and tantalum was present only in Zircaloy-2. The results of trace impurities in Zircaloy-4(A) sample (Table 2), irradiated at the core position, were found to differ to some extent with the corresponding values obtained for bigger size sample (Zircaloy-4(B)) irradiated in the thermal column. The results suggest that the bigger size sample gives better analytical representativeness. Subsampling procedure at tens of mg level demands multiple measurements to account for possible heterogeneous distribution of impurities present at trace levels. The use of thermal column helps in overcoming the neutron flux perturbations in the samples and also yields negligible nuclidic interference reactions due to fast neutrons encountered in conventional INAA. The self-validation property of the INAA approach helps in confirming the analytical results where one element may have more than one isotope and one radioisotope/activation product has, in many cases, more than one gamma line. In the present study, all elements except chromium satisfy the self-validation property.

The experimental sensitivities (Counts s^{-1} mg^{-1}) and detection limits (L_D) were evaluated for both thermal column and core position irradiated samples. The results are shown in Table 3. It has been observed that the sensitivities of elements, as expected, are higher for the core position irradiated sample. The detection limits (L_D) of the elements were evaluated using the procedure prescribed by Currie [14]. The absolute detection limits (L_D, µg) of the elements obtained using the thermal column irradiations were poorer than using the core irradiations. On the other hand the relative detection limits ($L_{D,R}$ (µg g^{-1})) of elements in the case of thermal column irradiation sample were found to be comparable

Table 2
Determined elemental concentrations (mg kg^{-1} unless % is indicated) of Zircaloy-4 clad tubes

Element	Mass			Literature composition Ref. [1]
	344 mg Zircaloy-4(A)	15.6 g Zircaloy-4(B)	11.7 g Zircaloy-4(C)	
As	6.5 ± 0.3	5.9 ± 0.5	6.2 ± 0.2	NA
Mn	7.5 ± 0.1	6.7 ± 0.1	7.0 ± 0.2	50
Hf	28.0 ± 0.2	25.6 ± 1.0	27.6 ± 1.4	100
W	37.7 ± 0.6	ND	ND	100
Co	(11.0 ± 0.1) × 10^{-1}	(12.9 ± 0.2) × 10^{-1}	(13.1 ± 0.2) × 10^{-1}	20
In	(2.1 ± 0.1) × 10^{-1}	(1.2 ± 0.1) × 10^{-1}	(1.3 ± 0.1) × 10^{-1}	NA
Cr%	(8.4 ± 0.3) × 10^{-2}	(10.4 ± 0.3) × 10^{-2}	(9.4 ± 0.2) × 10^{-2}	0.07–0.13
Fe%	(19.6 ± 0.4) × 10^{-2}	(1.9 ± 0.2) × 10^{-1}	(1.8 ± 0.2) × 10^{-1}	0.18–0.24
Sn%	(16.3 ± 0.2) × 10^{-1}	(15.8 ± 0.8) × 10^{-1}	1.6 ± 0.1	1.2–1.7
Zr%	98.1 ± 0.4	98.4 ± 0.7	98.2 ± 0.6	Balance

NA – not available.

Notes: The samples A and B are taken from the same Zircaloy-4 clad tube. The sample A has been analyzed irradiating it in the core position (E8) whereas B and C with thermal column at Apsara reactor.

Table 3
Experimental sensitivities (S in Counts s^{-1} mg^{-1}) and detection limits (L_D in μg and $L_{D,R}$ in μg g^{-1}) for the samples irradiated in thermal column (TC) and core (E8) positions of Apsara reactor

Element	E_γ used (keV)	Zircaloy-2 (24 g), TC, $t_i = 4$ h, flux $\sim 2 \times 10^{12}$ n m^{-2} s^{-1}			Zircaloy-4 (344 mg), E8, $t_i = 1$ h, flux $\sim 6 \times 10^{15}$ n m^{-2} s^{-1}		
		S (C s^{-1} mg^{-1})	L_D (μg)	$L_{D,R}$ (μg g^{-1})	S (C s^{-1} mg^{-1})	L_D (μg)	$L_{D,R}$ (μg g^{-1})
As	559	5.0	31	1.31	659	0.1	0.29
In	1293	298.7	0.31	0.01	1.9×10^4	0.005	0.015
Mn	847	135.8	1.87	0.08	1.2×10^4	0.02	0.05
Hf	482	0.12	51.8	2.19	127.5	0.21	0.61
Ta	1221	2.1×10^{-2}	57.4	2.43	–	–	–
Co	1332	3.1×10^{-2}	86.6	3.67	34.0	0.11	0.31
W	686	–	–	–	1.1×10^3	0.20	0.57
Ni	1481	2.0×10^{-2}	4803	203	–	–	–
Fe	1099	1.0×10^{-4}	12 132	513	0.10	19.8	57.7
Cr	320	1.3×10^{-2}	505	21.4	13.0	1.9	5.5
Sn	160	3.0×10^{-2}	11 484	486	–	–	–
	158.5	–	–	–	0.59	48.4	141
Zr%	757	1.0×10^{-4}	18 696	791	0.16	19.4	56.6

'–' – element not detected.

or poorer by almost an order with that of core irradiation sample.

4. Conclusions

A non-destructive neutron activation analysis method for irregular shape of Zircaloy clad materials has been standardized. The method gives absolute concentrations of major, minor and trace elements without resorting to any chemical standards in favorable cases like alloys. Elements like As, In, Ta, W, Co and Hf, which were present in very low level, could be analyzed in the presence of major matrix elements of Zr, Sn, Fe and Cr. The present method shows the promise for its applicability to analyze high purity metals and alloys non-destructively without using any standard if all the major and/or minor elements are amenable to NAA.

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