



## Original Article

# Analysis of Zirconium and Nickel Based Alloys and Zirconium Oxides by Relative and Internal Monostandard Neutron Activation Analysis Methods



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## ABSTRACT

**Background:** The chemical characterization of metallic alloys and oxides is conventionally carried out by wet chemical analytical methods and/or instrumental methods. Instrumental neutron activation analysis (INAA) is capable of analyzing samples nondestructively. As a part of a chemical quality control exercise, Zircalloys 2 and 4, nimonic alloy, and zirconium oxide samples were analyzed by two INAA methods. The samples of alloys and oxides were also analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and direct current Arc OES methods, respectively, for quality assurance purposes. The samples are important in various fields including nuclear technology.

**Methods:** Samples were neutron irradiated using nuclear reactors, and the radioactive assay was carried out using high-resolution gamma-ray spectrometry. Major to trace mass fractions were determined using both relative and internal monostandard (IM) NAA methods as well as OES methods.

**Results:** In the case of alloys, compositional analyses as well as concentrations of some trace elements were determined, whereas in the case of zirconium oxides, six trace elements were determined. For method validation, British Chemical Standard (BCS)-certified reference material 310/1 (a nimonic alloy) was analyzed using both relative INAA and IM-NAA methods.

**Conclusion:** The results showed that IM-NAA and relative INAA methods can be used for nondestructive chemical quality control of alloys and oxide samples.

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## 1. Introduction

The chemical characterization of materials is an important step in chemical quality control (CQC) exercises. It involves the determination of major, minor, and trace concentrations of elements with good accuracy and precision. CQC helps in ensuring the quality of the material as per the required specifications. In the case of nuclear reactor materials, the finished products should meet the stringent chemical specifications for major to trace constituents for better performance of a nuclear reactor during its operation. The materials of interest are mainly nuclear reactor structural materials of alloy and oxide matrices. It is important to use suitable analytical techniques to analyze these complex matrix samples to obtain good quality results. The routinely used analytical methods are mostly wet chemical and spectroscopic techniques, such as atomic absorption spectroscopy, inductively coupled plasma optical emission spectroscopy (ICP-OES), and ICP-mass spectrometry (ICP-MS), as well as chromatographic techniques. Although these techniques give high quality results, they are destructive methods and are associated with a cumbersome dissolution process that uses various acids. In some cases, radioanalytical techniques such as X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA), prompt gamma-ray NAA (PGNAA), and ion beam analysis are used. Nuclear analytical techniques, such as INAA and PGNAA, have several advantages. They are able to perform simultaneous multielement determination, are nondestructive in nature, have a negligible matrix effect, are highly sensitive and selective, and have achievable high precision and accuracy.

Routine work using conventional INAA is mainly carried out using the relative method, in which *a priori* knowledge of the constituents in a sample needs to be known. By contrast,  $k_0$ -based NAA uses a single comparator such as gold ( $^{197}\text{Au}$ ) or any other suitable element that is coirradiated with the same neutron flux along with the sample [1–3]. As the single comparator is different to the element of interest, this method requires neutron spectrum parameters, namely, the epithermal neutron flux shape factor ( $\alpha$ ) and the subcadmium to epithermal neutron flux ratio ( $f$ ), absolute detection efficiency, and the  $k_0$  factor [4, 5] for concentration calculations. In the case of  $k_0$ -based internal monostandard NAA (IM-NAA), an element present in the sample, which is expected to be reasonably homogeneous, is used as the monostandard [6–8]. IM-NAA using *in situ* relative detection efficiency [7, 8] is useful for the analysis of small- as well as large-size (g–kg scale) and nonstandard geometry samples. The  $k_0$ -NAA method was adapted in 1995 in our laboratory. Later, in 2003, the IM-NAA in conjunction with *in situ* relative efficiency method was developed. The irradiation positions of APSARA [9] and KAMINI [10] reactors were characterized for  $f$  and  $\alpha$  values by the cadmium ratio method using multflux monitors. As IM-NAA gives mass fraction ratios with respect to the internal monostandard, knowledge of the concentration of internal monostandard is required to obtain absolute concentrations of the elements in the sample. When all the major and/or minor elements present in a sample are amenable to NAA, e.g., in zircalloys and stainless steels, IM-NAA is useful for calculating the absolute concentrations by a standard-less approach using the mass balance procedure.

The IM-NAA method was successfully applied for the standard-less analysis of nuclear reactor structural materials such as zircalloys [7, 11] and stainless steels [7, 8, 12]. For validation of the IM-NAA method, British Chemical Standards (BCS) certified reference materials (CRMs) 225/1 (low alloy steel) and 466 (austenitic stainless steel) [8, 12, 13] were analyzed. Various analytical techniques have been used for the analysis of alloys and oxides including NAA [14], prompt gamma-ray NAA [15, 16], XRF [17], spectroscopic methods such as ICP-OES [18–21], atomic absorption spectroscopy [22–26], and ICP-MS [27–29].

This research paper deals with the chemical characterization of zirconium and nickel based alloys by IM-NAA and compares results with conventional INAA and ICP-OES. Samples in triplicate analyzed by INAA, IM-NAA, and ICP-OES are nimonic alloys, Zircaloy 2, and Zircaloy 4. Zirconium oxide samples (four replicates) were analyzed by INAA and direct current Arc OES (DC Arc OES). This sample (zirconium oxide) could not be analyzed by IM-NAA as the neutron flux parameters ( $f$  and  $\alpha$ ) of irradiation position at Dhruva reactor are not available. In addition to the comparison of results with relative INAA and ICP-OES, a nimonic alloy CRM—BCS CRM 310/1—was analyzed using IM-NAA as well as relative INAA methods.

## 2. Materials and methods

### 2.1. About the samples

Different alloys are important in almost all fields of modern science and technology. The elements Fe, Ni, Cr, Zr, Pb, and Ti are the base materials for most of the alloys. High nickel alloys are used in the chemical, petrochemical, turbine, and aerospace industries. High Ni alloys (having 50–80% Ni), such as nimonic alloys, are used in the pressure lining of steam generators and are also preferred over stainless steels as structural materials in fast nuclear reactors. Swelling under the prevailing irradiation conditions of high temperature is low for these alloys, and they are less prone to stress corrosion cracking.

Zirconium occurs in nature, mostly in the form of a silicate mineral known as zircon, which is extensively used in the glass and ceramic industries. Zirconium oxide ( $\text{ZrO}_2$ , zirconia), prepared from zircon, is used as traditional and advanced ceramics and as a refractory material. It is used as a material for machinery wear parts, insulations and coatings, and solid electrolytes for fuel cells. It is also used as a raw material for the preparation of various zirconium-based alloys. Zirconium forms alloys with a variety of metals, such as Nb, Ni, Fe, Sn, and Cr. These elements are added to zirconium to improve the mechanical properties and to decrease corrosion by water at high temperatures. Tin, as an alloying element, is most effective in imparting corrosion resistance without seriously affecting neutron economy in nuclear reactors [30]. Zirconium alloys are mostly used for fuel cladding and core components in water-cooled nuclear power reactors, viz. boiling water reactors, pressurized light water reactors, and pressurized heavy water reactors. Zirconium-based alloys are the major structural components for nuclear (thermal) reactors, namely,

Zircaloy 2 (as fuel clad in boiling water reactors) and Zircaloy 4 (as fuel clad in pressurized heavy water reactors). Zirconium has been chosen for nuclear reactor components on the basis of a lower neutron absorption cross section (0.18 barn) for thermal neutrons, as well as its good corrosive resistance and mechanical properties. Zircaloys 2 and 4 and  $ZrO_2$  samples were collected from the quality control laboratory of our department, and nimonon alloy samples and reference material were collected from Material Science Division, Bhabha Atomic Research Centre (BARC; Mumbai, India). Along with other applications, these materials are useful in nuclear reactor technology programs. The properties of the above-mentioned materials depend on their composition as well as on minor and trace mass fractions. Therefore, it is important to analyze the materials of interest for the determination of major to trace level mass fractions as a part of a CQC exercise. In the present work, INAA methods along with ICP-OES and DC Arc OES techniques have been used for compositional characterization of different alloys and trace elements in oxides.

## 2.2. Reagents and standard solutions

### 2.2.1. ICP-OES

Acids, HF,  $HNO_3$ , HCl, and  $H_2SO_4$  of suprapure grade (Merck Ltd., India) were used in this work. The standard solutions of 1 mg/mL (Merck Ltd., India) (all elements of interest except chlorine) were used to obtain the calibration curves in ICP-OES determinations. High purity water was obtained from a MilliQ water system and used throughout the experiments for preparation of all sample and standard solutions [31, 32].

### 2.2.2. DC Arc OES.

In the case of zirconium oxide analysis by DC Arc OES, Specpure grade oxides of individual elements, AgCl,  $SrF_2$ , supplied by SPEX Industries, Los Angeles, USA and high purity pre-analyzed  $ZrO_2$  were used for the preparation of standards [33].

## 2.3. Analytical methods

### 2.3.1. Spectroscopic methods (ICP-OES and DC Arc OES)

The samples of nimonon alloys were dissolved using  $HNO_3$ , HF, and HCl in a polytetrafluoroethylene (PTFE) vessel [31, 32]. The samples of zircaloys were dissolved using HF and  $HNO_3$  in a PTFE vessel. The resulting solutions were diluted to appropriate volumes using Millipore Water. Reagent blanks were also prepared for blank correction. These solutions were analyzed with ICP-OES.

The samples of zirconium oxide were analyzed directly. The powdered samples were pressed into pellet forms. A set of standards spiked with trace amounts of analyte in a high purity zirconium matrix and 5% AgCl +  $SrF_2$  carrier with 0.003% Pd as an internal standard were prepared using specpure compounds [33]. A blank standard was also prepared in a similar manner without the addition of analyte. The sample pellets were analyzed by DC Arc OES.

### 2.3.2. INAA

Samples with a mass of about 100 mg were heat sealed in polyethylene pouches. The standards were prepared using

appropriate amounts of Merck standard solution (1,000 mg/L). Required amounts of standard solution were transferred onto the filter paper, then dried and heat sealed in polythene. The samples were irradiated for 1 minute in the pneumatic carrier facility (PCF) of the Dhruva reactor, BARC. The longer duration of irradiation (6 hours) of samples was carried out by the pneumatic fast transfer system (PFTS), KAMINI reactor of IGCAR (Indira Gandhi Centre for Atomic Research), Kalpakam, India. The Dhruva reactor operates at 50 MW power, and the thermal equivalent flux was  $5 \times 10^{13}$  n  $cm^2/s$ . The KAMINI reactor operates at 20 kW power, and the thermal equivalent flux was  $6 \times 10^{11}$  n  $cm^2/s$ . The PCF in the Dhruva reactor provides only short duration (1 minute) irradiation. As longer duration irradiation was not available in the Dhruva reactor, the PFTS of KAMINI reactor in the IGCAR was used. The radioactive assay was carried out using a 40% HPGe (high-purity germanium) detector coupled to an 8k channel analyzer in the BARC. Peak areas were evaluated using peak-fit software PHAST, which was developed at our institute [34]. A 25% HPGe detector coupled to MCA of Eurysis Measures was used for radioactive assay at the Fuel Chemistry Division, IGCAR.

Both relative INAA and IM-NAA methods were used to determine the concentration of various elements. The PCF of the Dhruva reactor was used for short- and medium-lived nuclides by the relative NAA method, and the KAMINI reactor was used for short- to long-lived nuclides by the IM-NAA method as well as for long-lived nuclides by the relative method of NAA.

In IM-NAA [8], the ratio of mass ( $m$ ) of an element ( $x$ ) to the mass of the comparator element ( $y$ ) in the sample is given by Eq. (1)

$$\frac{m_x}{m_y} = \frac{((SDC)(f + Q_0(\alpha)))_y P_{Ax} (\epsilon_\gamma)_y k_{0,Au}(y)}{((SDC)(f + Q_0(\alpha)))_x P_{Ay} (\epsilon_\gamma)_x k_{0,Au}(x)}, \quad (1)$$

where  $P_A$  is the net peak area under the gamma ray 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 the counting period and is given by  $((1 - e^{-\lambda LT})/\lambda LT)$  (where  $t_i$ ,  $t_c$ , and  $LT$  are time durations of irradiation, cooling, and counting, respectively);  $f$  is the subcadmium to epithermal neutron flux ratio;  $Q_0(\alpha)$  is the ratio of the resonance integral ( $I_0$ ) to thermal neutron cross section ( $\sigma_0$ ) corrected for  $\alpha$ ;  $\epsilon$  is the absolute detection efficiency;  $k_{0,Au}$  is the literature-recommended  $k_0$  factor [5]; and  $x$  and  $y$  stand for the element of interest and the internal monostandard, respectively. The  $f$  and  $\alpha$  values of the PFTS position of the KAMINI reactor are  $25.1 \pm 0.4$  and  $0.0406 \pm 0.0025$ , respectively [10]. The *in situ* relative efficiency was obtained using the following expression [7,8]:

$$\ln \epsilon_\gamma = k_j + \sum_{i=0}^m a_i (\ln E_\gamma)^i \quad (2)$$

where  $a_i$  is the coefficient of the polynomial of order  $m$  and  $k_j$  is a constant characteristic of the  $j$ th nuclide. In the calculations, a second-order polynomial ( $m = 2$ ) was used. *In situ* relative detection efficiency was obtained using gamma lines of activation products of different elements in these samples. Details of *in situ* relative detection efficiency can be found in the

**Table 1 – Relevant nuclear data of elements of interest.**

Element	Activation product	Half-life	Gamma ray energy (keV)
Al	<sup>28</sup> Al	2.24 min	1,778.9
Cl	<sup>38</sup> Cl	37.24 min	1,642.7, 2,167.4
Ti	<sup>51</sup> Ti	5.76 min	320.1
V	<sup>52</sup> V	3.75 min	1,434.0
Cr	<sup>51</sup> Cr	27.70 d	320.1
Mn	<sup>56</sup> Mn	2.579 h	846.8, 1,810.7, 2,113.1
Fe	<sup>59</sup> Fe	44.50 d	1,099.3, 1,291.6
Ni	<sup>65</sup> Ni	2.517 h	366.3, 1,115.5, 1,481.8
In	<sup>116m</sup> In	54.4 min	138.3, 416.9, 818.7, 1,097.3, 1,293.5, 1,507
Zr	<sup>97</sup> Zr	16.74 h	254.2, 355.4, 703.8, 1,148.0
	<sup>95</sup> Zr	64.02 d	724.2, 756.7
Sn	<sup>123m</sup> Sn	40.06 min	160.3
Hf	<sup>181</sup> Hf	42.39 d	133.0, 136.3, 345.9, 482.2
Ta	<sup>182</sup> Ta	114.4 d	67.8, 100.1, 152.4, 222.1, 1,121.3, 1,189.1, 1,221.4, 1,231

Note. From “Recommended nuclear data for use in the  $k_0$  standardization of neutron activation analysis,” by F. De Corte, A. Simonits, 2003, *At. Data Nucl. Data Tables*, 85, p. 47–67. Copyright 2003, Elsevier B.V. With permission.

literature [6–8]. The gamma rays, along with relevant nuclear data of the activation products, are given in Table 1 [4]. Other relevant data for IM-NAA, not given in the table, were taken from the work of De Corte and Simonits [4, 5].

The relative detection limit ( $L_D$ ; in mg/kg) [35] was calculated using the following equation:

$$L_D = \frac{2.71 + 3.29 \sigma_B}{LT \times S \times W_{sam}}, \quad (3)$$

where  $\sigma_B$  is the square root of background counts ( $C_B$ ) of the sample under the photo peak of interest,  $LT$  is the live time of counting in seconds,  $S$  is the sensitivity in counts per second (cps) per microgram of the analyte, and  $W_{sam}$  is the mass of the sample of interest in grams.

### 3. Results and Discussion

The samples of Zircalloys 2 and 4, and nimonic alloys were analyzed by IM-NAA, relative INAA, and ICP-OES. The samples of zirconium oxide were analyzed by relative INAA and DC Arc OES. Results of INAA and OES were obtained with the relative method using elemental standards. In the case of IM-NAA, Ni was used as the internal monostandard in the nimonic alloy sample and reference material, and the concentration of Ni was obtained from the relative method. In the case of IM-NAA of Zircalloys, Zr was used as the internal monostandard, and the concentrations were obtained using the standard-less approach because all major and minor elements are amenable to NAA [11]. The uncertainties quoted in the results are standard deviations at  $\pm 1s$  confidence limit from triplicate sample analyses.

For method validation, BCS CRM 310/1(nimonic alloy) was analyzed by both IM-NAA and relative NAA methods, and the results are given in Table 2. The elements determined in this

**Table 2 – Determined mass fractions (wt%) in BCS CRM 310/1 (a nimonic alloy) by INAA methods.**

Element	IM-NAA	INAA	Certified value
Al	1.04 ± 0.02	1.05 ± 0.03	1.06
Ti	2.48 ± 0.05	2.44 ± 0.09	2.43
Cr	19.4 ± 0.6	19.5 ± 0.7	19.43
Mn	0.38 ± 0.03	0.32 ± 0.02	0.35
Fe	0.23 ± 0.02	0.25 ± 0.01	0.25
Ni	59.1 ± 1.5	58.5 ± 1.04	58.6

Detection limit for V by INAA is 10 µg/kg.

BCS, British Chemical Standard; CRM, certified reference material; IM-NAA, internal monostandard neutron activation analysis; INAA, instrumental neutron activation analysis.

CRM were Ni, Ti, Al, Mn, Fe, and Cr, and the % deviations of the determined values are in the range of  $\pm 0.2$ –8% with respect to the certified values. Uncertainty values were in the range of  $\pm 2$ –9%. Certified values reported by BCS are nominal concentrations without any uncertainties. The results obtained for two nimonic alloys are given in Table 3. Concentrations of seven elements, comprising the main constituents (Ni, Cr, Fe, Mn, and Ti) and two trace elements (Al and V), were determined by IM-NAA and relative INAA methods. The main constituents were also determined by ICP-OES. The values of INAA methods as well as ICP-OES are in good agreement and within the specification limits [36]. The uncertainties are in the range of 1–10% for relative NAA and IM-NAA methods, and 1–9% for ICP-OES. Specified composition (range or single maximum value) is assigned by a fabricator for a particular sample for its use, which will give its best performance. Because the total concentration is 100%, concentrations on all minor and trace elements are added and then subtracted from 100 wt.% to obtain the concentration of the major matrix element, and this is termed as balance.

The results obtained for Zircalloys 2 and 4 along with their specifications are given in Tables 4 and 5, respectively. The  $3\sigma$  detection limits obtained by relative INAA for the Zircaloy 2 sample, calculated using Eq. (3) [35], are given in Table 3, and they are in the range of 0.03–302 mg/kg. The uncertainties with the results of the three methods were in the range of  $\pm 1$ –10%. The % deviations between IM-NAA and relative INAA methods, in general, are within  $\pm 10\%$  (except for indium in Zircaloy 4), whereas the % deviations between IM-NAA and ICP-OES are within  $\pm 7\%$ . The results of IM-NAA were obtained using the standard-less approach as described earlier. Trace concentrations of Hf, Mn, In, and Cl were determined in zircalloys, and they were within the specification limits [37]. The results of the IM-NAA method were in good agreement with those obtained using the relative INAA and ICP-OES methods, and were also in good agreement with the specified composition [37]. The result for chlorine is not reported by ICP-OES, because it is difficult to be determined in air atmosphere. It requires an argon atmosphere because its intense emission lines are absorbed in the air (thus it is not a sensitive method for chlorine).

The results of the two samples of zirconium oxide are given in Table 6. Concentrations of six elements—Al, Ti, V, Cl, Mn, and Ni (activation products with half-lives in the range of 2.2

**Table 3 – Determined mass fractions (in mg/kg, unless % is specified) in two nimonic alloy samples by INAA and ICP-OES methods.**

(Element)	Nimonic Alloy-1			Nimonic Alloy-2			Specifications [36]
	INAA	IM-NAA	ICP-OES	INAA	IM-NAA	ICP-OES	
Al	56 ± 2	55 ± 2	53 ± 3	84 ± 5	86 ± 3	90 ± 2	NA
Ti (%)	0.25 ± 0.01	0.24 ± 0.01	0.24 ± 0.01	0.34 ± 0.02	0.33 ± 0.01	0.33 ± 0.01	0.2/0.6
V	248 ± 10	251 ± 8	256 ± 10	147 ± 8	151 ± 6	148 ± 7	NA
Cr (%)	19.3 ± 0.4	19.6 ± 0.6	19.1 ± 0.6	19.3 ± 0.4	19.4 ± 0.4	19.0 ± 0.4	18.9–21
Mn (%)	0.98 ± 0.02	0.97 ± 0.01	0.95 ± 0.02	0.56 ± 0.01	0.55 ± 0.01	0.57 ± 0.02	1.0 max
Fe (%)	0.11 ± 0.01	0.13 ± 0.01	0.11 ± 0.01	0.12 ± 0.01	0.14 ± 0.01	0.12 ± 0.01	5.0 max
Ni (%)	79.3 ± 1.3	79.3 ± 1.3	79.6 ± 2.0	79.6 ± 1.5	79.6 ± 1.5	80.0 ± 1.2	Balance

ICP-OES, inductively coupled plasma optical emission spectroscopy; IM-NAA, internal monostandard neutron activation analysis; INAA, instrumental neutron activation analysis; NA, not available; ND, not detected.

**Table 4 – Determined mass fractions (in mg/kg, unless % is indicated) in Zircaloy 2 by relative INAA, IM-NAA, and ICP-OES methods.**

Element	IM-NAA	INAA	ICP-OES	Specifications	L <sub>D</sub> (mg/kg)
Cl	10.8 ± 0.6	11.4 ± 0.8	ND	20	0.5
Cr (%)	0.10 ± 0.01	0.080 ± 0.007	0.09 ± 0.01	0.05–0.15	50
Mn	3.65 ± 0.10	3.91 ± 0.11	4.03 ± 0.15	50	0.05
Fe (%)	0.15 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	0.07–0.2	114
Ni (%)	0.056 ± 0.005	0.051 ± 0.005	0.052 ± 0.002	0.03–0.08	75
Zr (%)	98.1 ± 1.0	98.0 ± 0.8	98.01 ± 0.88	Balance	140
In	0.158 ± 0.014	0.162 ± 0.011	0.160 ± 0.012	NA	0.03
Sn (%)	1.61 ± 0.05	1.54 ± 0.04	1.58 ± 0.03	1.2–1.7	302
Hf	62 ± 3	65 ± 2	60 ± 2	100	1.6
Ta	22.7 ± 1.1	21.3 ± 1.3	22.1 ± 0.9	200	1.0

ICP-OES, inductively coupled plasma optical emission spectroscopy; IM-NAA, internal monostandard neutron activation analysis; INAA, instrumental neutron activation analysis; NA, not available; ND, not detected; L<sub>D</sub>, detection limit.

**Table 5 – Determined mass fractions (in mg/kg, unless % is indicated) in Zircaloy 4 by relative INAA, IM-NAA, and ICP-OES methods.**

Element	IM-NAA	INAA	ICP-OES	Specifications
Cl	14.1 ± 0.5	14.8 ± 0.6	ND	20
Cr (%)	0.087 ± 0.003	0.089 ± 0.004	0.090 ± 0.003	0.07–0.13
Mn	3.28 ± 0.16	3.24 ± 0.18	4.05 ± 0.20	50
Fe (%)	0.193 ± 0.008	0.19 ± 0.01	0.191 ± 0.006	0.18–0.24
Zr (%)	98.2 ± 1.0	98.4 ± 1.0	98.3 ± 1.0	Balance
In	0.118 ± 0.012	0.105 ± 0.010	0.112 ± 0.010	NA
Sn (%)	1.49 ± 0.06	1.50 ± 0.08	1.45 ± 0.05	1.2–1.7
Hf	23.3 ± 2.0	22.2 ± 1.5	21.8 ± 1.5	100

ICP-OES, inductively coupled plasma optical emission spectroscopy; IM-NAA, internal monostandard neutron activation analysis; INAA, instrumental neutron activation analysis; NA, not available; ND, not detected.

**Table 6 – Mass fractions of impurities determined (in mg/kg) in zirconium oxide samples by INAA and DC Arc OES methods.**

Element	ZrO <sub>2</sub> sample 1		ZrO <sub>2</sub> sample 2		Specification (mg/kg)	Detection limit, L <sub>D</sub> (µg/kg)
	INAA	DC Arc OES	INAA	DC Arc OES		
Al	28.2 ± 0.9	27.1 ± 1.2	35.8 ± 1.4	36.1 ± 1.8	50	40
Cl	115 ± 4	ND	108 ± 3	ND	NA	300
Ti	14.1 ± 0.4	15.3 ± 0.5	8.1 ± 0.2	7.8 ± 0.3	150	20
V	36.1 ± 1.2	39.1 ± 1.5	21.3 ± 0.6	21.1 ± 0.8	NA	50
Mn	2.02 ± 0.12	1.95 ± 0.08	1.92 ± 0.11	2.05 ± 0.12	25	56
Ni	11.3 ± 0.6	12.1 ± 0.4	18.1 ± 0.8	17.9 ± 0.9	25	430

ICP-OES, inductively coupled plasma optical emission spectroscopy; DC, direct current; IM-NAA, internal monostandard neutron activation analysis; INAA, instrumental neutron activation analysis; NA, not available; ND, not detected.

minutes–2.6 hours)—were determined using PCF of the Dhruva reactor using 1 minute irradiation, and the values are in the range of 2–115 mg/kg. The uncertainties from four replicate analyses are in the range of  $\pm 2$ –6%. For comparison, samples were also analyzed by DC Arc OES. The determined concentrations of Al, V, Mn, and Ni are in good agreement (within  $\pm 1$ –4%, except for V in ZrO<sub>2</sub>-1) with the INAA results. Results are also found to be within specification limits [37]. In samples of zircalloys and ZrO<sub>2</sub>, the result for chlorine is not reported because it is difficult to be determined in air atmosphere by ICP-OES. It requires argon atmosphere because its intense emission lines are absorbed in the air, and thus this is not a sensitive method for chlorine.

The INAA method, to some extent, is matrix-independent owing to the high penetration powers of neutron and gamma rays. It does not matter if similar samples from other manufactures are analyzed and the results as well as uncertainties on results will be similar. It has been demonstrated that INAA (relative and internal monostandard) methods are capable of determining many elements without “destroying” the samples. For samples such as alloys and oxides, the INAA method is preferred over conventional wet chemical techniques because of its nondestructive nature and the simultaneous determination of major, minor, and trace element concentrations.

ED-XRF is another nondestructive technique like INAA. It is a multielement determination technique, and the samples can be analyzed without any destruction. However, samples need to be pelletized, the sample mass requirement is higher compared with INAA, and, most importantly, because XRF is a matrix-dependent method, without matrix matching composition standard(s), the results will be erroneous. The detection limits as well as method precision (% Relative Standard Deviation (% RSD)) achieved by INAA are better than those achieved by ED-XRF for many elements. By contrast, total reflection XRF is a sensitive multielement technique with lower detection limits than ED-XRF and INAA; however, samples need to be converted into solution form.

When a research reactor is in operation, the samples can be irradiated and analyzed by INAA without incurring any cost within the department. However, for samples from outside users, if they are not under any collaborative project, nominal payments have to be made. It should be noted that NAA utilizing research reactors are not available to all users in our country as they are located in nuclear research centers, and only a limited number of users can gain access either through collaboration or via services on request through proper channels. The turnaround time for analysis by INAA is longer (1–2 weeks) than that of ICP-OES because of the varying half-lives of activation products. While discussing turnaround time and cost, one should not forget about the good quality results provided by INAA (with good precision and accuracy), and it is considered an alternative technique to conventional techniques such as ICP-OES and DC Arc OES.

#### 4. Conclusions

Both IM-NAA and relative INAA methods were optimized to determine major, minor, and trace concentrations of elements in different alloy samples. Results obtained by both NAA

approaches are found to be in a good agreement. In the case of zirconium oxides, six trace elements, using their short- and medium-lived activation products, were determined by relative INAA methods. The PCF of the Dhruva research reactor was advantageously used for the quick determination of mass fractions belonging to short- and medium-lived nuclides. The uncertainties of the determined elements were within  $\pm 10$ %. The results of BCS CRM 310/1 (a nimonic alloy) obtained by relative INAA and IM-NAA methods were found to be in good agreement with the certified values. INAA results were also found to be in good agreement with those obtained by ICP-OES for alloys, and by DC Arc OES for zirconium oxides. The present work demonstrates that if INAA methods are available, samples of metallic alloys or oxides can easily be analyzed without any destruction. The results indicated that INAA methods are useful for CQC work concerning alloys and oxides.

#### Conflicts of interest

All authors have no conflicts of interest to declare.

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#### REFERENCES

- [1] F. De Corte, A. Simonits, A. De Wispelare, J. Hoste, Accuracy and applicability of the  $k_0$ -standardization method, *J. Radioanal. Nucl. Chem.* 113 (1987) 145–161.
- [2] R.N. Acharya, A.G.C. Nair, A.V.R. Reddy, S.B. Manohar, Validation of a neutron activation analysis method using  $k_0$ -standardization, *Appl. Radiat. Isot.* 57 (2002) 391–398.
- [3] R. Acharya, A.G.C. Nair, K. Sudarshan, A. Goswami, A.V.R. Reddy, Development and applications of  $k_0$  based NAA and prompt gamma-ray NAA methods at BARC, *J. Radioanal. Nucl. Chem.* 278 (2008) 617–620.
- [4] F. De Corte, A. Simonits,  $k_0$ -Measurements and related nuclear data compilation for (n,  $\gamma$ ) reactor neutron activation analysis: IIIb. Tabulation, *J. Radioanal. Nucl. Chem.* 133 (1989) 43–130.
- [5] F. De Corte, A. Simonits, Recommended nuclear data for use in the  $k_0$  standardization of neutron activation analysis, *At. Data Nucl. Data Tables* 85 (2003) 47–67.
- [6] K. Sudarshan, A.G.C. Nair, A. Goswami, A proposed  $k_0$  based methodology for neutron activation analysis of samples of non-standard geometry, *J. Radioanal. Nucl. Chem.* 256 (2003) 93–98.
- [7] A.G.C. Nair, R. Acharya, K. Sudarshan, S. Gangotra, A.V.R. Reddy, S.B. Manohar, A. Goswami, Development of an internal monostandard instrumental neutron activation analysis method based on in situ detection efficiency for

- analysis of large and nonstandard geometry samples, *Anal. Chem.* 75 (2003) 4868–4874.
- [8] R. Acharya, A.G.C. Nair, K. Sudarshan, A.V.R. Reddy, A. Goswami, Development and applications of the  $k_0$ -based internal mono standard INAA method, *Appl. Radiat. Isot.* 65 (2007) 164–169.
- [9] R. Acharya, K.B. Dasari, J.S. Brahmaji Rao, C.R. Venkata Subramani, A.V.R. Reddy, Characterization of irradiation sites of APSARA reactor for  $k_0$ -based IM-NAA and its validation and application, *IEEE Trans. Nucl. Sci.* 60 (2013) 3051–3056.
- [10] J.S. Brahmaji Rao, E. Senthilvadivu, N.P. Seshadreesan, R. Acharya, C.R. Venkatasubramani, A.V.R. Reddy, Characterization of pneumatic fast transfer system irradiation position of KAMINI reactor for  $k_0$ -based NAA, *J. Radioanal. Nucl. Chem.* 294 (2012) 137–141.
- [11] R. Acharya, A.G.C. Nair, A.V.R. Reddy, A. Goswami, Standard-less analysis of Zircaloy clad samples by an instrumental neutron activation method, *J. Nucl. Mater.* 326 (2004) 80–85.
- [12] R. Acharya, A.G.C. Nair, A.V.R. Reddy, A. Goswami, Application of  $k_0$ -based internal mono standard instrumental neutron activation analysis method for composition analysis of stainless steel clad sample, *Anal. Chim. Acta* 522 (2004) 127–132.
- [13] R. Acharya, K.K. Swain, A.V.R. Reddy, Analysis of SMELTS and reference materials for validation of the  $k_0$ -based internal monostandard NAA method using in-situ detection efficiency, *Nucl. Instrum. Methods A* 622 (2010) 411–414.
- [14] M. Franek, V. Krivan, Multi-element analysis of aluminum-based ceramic powders by instrumental and radiochemical neutron activation analysis, *Anal. Chim. Acta* 282 (1993) 199–207.
- [15] A.G.C. Nair, K. Sudarshan, N. Raje, A.V.R. Reddy, S.B. Manohar, A. Goswami, Analysis of alloys by prompt gamma-ray neutron activation, *Nucl. Instrum. Methods A* 516 (2004) 143–148.
- [16] A.G.C. Nair, R. Acharya, K. Sudarshan, R. Tripathi, A.V.R. Reddy, A. Goswami, Determination and validation of prompt  $k_0$ -factors with a monochromatic neutron beam at the Dhruva reactor, *Nucl. Instrum. Methods A* 564 (2006) 662–668.
- [17] G. Radha Krishna, H.R. Ravindra, B. Gopalan, S. Syamsunder, Determination of iron in nuclear grade zirconium oxide by x-ray fluorescence spectrometry using an internal intensity reference, *Anal. Chim. Acta* 309 (1995) 333–338.
- [18] X. Ma, Y. Li, Determination of trace impurities in high-purity zirconium dioxide by inductively coupled plasma atomic emission spectrometry using microwave-assisted digestion and wavelet transform-based correction procedure, *Anal. Chim. Acta* 579 (2006) 47–52.
- [19] D. Merten, J.A.C. Broekaert, R. Brandt, N. Jakubowski, Analysis of  $ZrO_2$  powders by microwave assisted digestion at high pressure and ICP atomic spectrometry, *J. Anal. At. Spectrom.* 14 (1999) 1093–1098.
- [20] M.T. Larrea, I. Gomex-Pinilla, J.C. Farinas, Microwave-assisted acid dissolution of sintered advanced ceramics for inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 12 (1997) 1323–1332.
- [21] B.B. de Lima, R.A. Conte, C.A. Nunes, Analysis of nickel–niobium alloys by inductively coupled plasma optical emission spectrometry, *Talanta* 59 (2003) 89–93.
- [22] H.M. Liu, S.Y. Chen, P.H. Chang, S.J. Tsai, Determination of bismuth, selenium and tellurium in nickel-based alloys and pure copper by flow-injection hydride generation atomic absorption spectrometry with ascorbic acid prereduction and cupferron chelation–extraction, *Anal. Chim. Acta* 459 (2002) 161–168.
- [23] S.Y. Chen, M.S. Wu, S.J. Tsai, Determination of silicon in nickel-based alloys using electrothermal atomic absorption spectrometry with longitudinal Zeeman-effect background correction and zinc oxide pretreatment, *Anal. Chim. Acta* 435 (2001) 357–366.
- [24] T. Ashino, K. Takada, Determination of trace amounts of selenium and tellurium in nickel-based heat-resisting superalloys, steels and several metals by electrothermal atomic absorption spectrometry after reductive coprecipitation with palladium using ascorbic acid, *Anal. Chim. Acta* 312 (1995) 157–163.
- [25] B. Gong, Y. Liu, Z. Li, T. Lin, Determination of selenium and tellurium in nickel and nickel/iron-based alloys by graphite furnace atomic absorption spectrometry with a nickel/palladium matrix modifier, *Anal. Chim. Acta* 304 (1995) 115–120.
- [26] K. Dash, S. Thangavel, S.M. Dhavile, S.V. Rao, S.C. Chaurasia, J. Arunachalam, Vapor phase matrix extraction of high purity di-boron trioxide and trace analysis using electrothermal AAS, *Anal. Chim. Acta* 546 (2005) 229–235.
- [27] D. Pollmann, F. Leis, G. Tolg, P. Tschopel, J.A.C. Broekaert, Multielement trace determinations in  $Al_2O_3$  ceramic powders by inductively coupled plasma mass spectrometry with special reference to on-line trace preconcentration, *Spectrochim. Acta, Part B* 49 (1994) 1251–1258.
- [28] K. Kakane, Y. Uwamino, H. Morikawa, A. Tsuge, T. Ishizuka, Determination of trace impurities in high-purity aluminium oxide by high resolution inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 369 (1998) 79–85.
- [29] T. Kagawa, M. Ohno, T. Seki, K. Chikama, Online determination of copper in aluminum alloy by microchip solvent extraction using isotope dilution ICP-MS method, *Talanta* 79 (2009) 1001–1005.
- [30] R. Krishnan, M.K. Asundi, Zirconium alloys in nuclear technology, *Proc. Indian. Acad. Sci.* 4 (1981) 41–56.
- [31] A. Sengupta, V.C. Adya, Determination of common analytes at trace levels in Zr matrix by ICP-AES without chemical/physical separation, *At. Spectrosc.* 34 (2013) 207–215.
- [32] V.C. Adya, A. Sengupta, S.V. Godbole, Study of the spectral interferences of zirconium on other analytes in the analysis of nuclear materials by CCD based ICP-AES, *At. Spectrosc.* 35 (2014) 25–32.
- [33] N. Pathak, V.C. Adya, S.K. Thulasidas, A. Sengupta, S.V. Godbole, Direct determination of trace elements in  $ZrO_2$  by D.C. Arc-carrier distillation technique using CCD-based spectrometer, *At. Spectrosc.* 35 (2014) 17–24.
- [34] P.K. Mukhopadhyay, in: *Proceedings of the Symposium on Intelligent Nuclear Instrumentation (INIT-2001)*, Bhabha Atomic Research Centre, Mumbai, India, 2001, pp. 307–310.
- [35] L.A. Currie, Limits for qualitative detection and quantitative determination. Application to radiochemistry, *Anal. Chem.* 40 (1968) 586–593.
- [36] Nimonic Alloy 80A, SPECIAL METALS [Internet]. Copyright© Special Metals Corporation, 2004 [cited in 2013]. Available from: <http://www.specialmetals.com>.
- [37] C. Ganguly, Advances in zirconium technology for nuclear reactor application, in: P.K. De (Ed.), *Proceedings of the Symposium Zirconium—2002 (ZIRC-2002)* September 11–13, BARC, Mumbai, 2002, pp. 1–27.