Determination of Trace Impurities In High Purity Aluminium Oxide Using INAA

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Summary: Instrumental neutron activation analysis (INAA) technique was used to investigate 24 trace impurities in high purity alumina. Na was found to be a major element with concentration 159 µg/g while Fe, Cr, Sr, K and Ba were in lower amounts having concentrations from 9 to 27 µg/g. The low amounts of impurities suggest that deleterious effects upon the properties of high purity Al_2O_3 should not occur. Remaining impurity elements were in trace amounts; i.e. concentrations from 0.003 to 1.50 µg/g.

Keywords: High purity; Aluminum oxide; Neutron activation analysis (INAA); Trace impurities.

Introduction

Increasing awareness of the deleterious effects of impurities at trace level on specific properties of high purity aluminum oxide used in various fields of modern technology has led to an urgent need for highly sensitive and accurate instrumental analytical techniques with low limits of detection (LODs). Moreover extensive use of alumina for different high technology applications such as electrical systems components, petroleum cracking catalyst, and thermoluminescence (TL) dosimetry crystal requires their precise characterization. High purity alumina is used in microelectronics as a substrate and package material in integrated circuits, as digital microelectronic circuitry and as insulators in electronic devices [1], in medicine as material for bi-ceramic endoprothesis, in the oil and in Petrochemical industries as effective catalyst for fuel cracking and in thermoluminescence (TL) dosimetry [2-6]. Chemical analysis of aluminum oxide powders can be performed by direct or solution-based methods. There are numerous problems in the direct analysis of high purity aluminum oxide, such as volatilization of aluminum oxide, non-availability of solid reference material for calibration, grain size limitations and high limits of detection (LODs). Electrothermal vaporization-inductively coupled plasma-atomic emission spectrometry (ETV-ICP-AES), electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS), electrothermal vaporization-inductively coupled plasma-optical emission spectrometry (ETV-ICP-OES) and electrothermal atomic absorption spectrometry (ETAAS) are widely used for the direct analysis of aluminum oxide powders. Aluminum oxide is thermally stable and often requires reagents to improve volatilization [1, 7-11]. Optimum sample pretreatment and vaporization temperatures and the most suitable thermo-chemical reagents are often analyte dependent. Moreover in case of multi-element determinations, compromising conditions have to be used.

Several approaches may be used for calibration in direct solids sampling analysis: i.e. calibration 1) with solid standard reference materials, 2) with analyte solutions or 3) by standard addition using aqueous multi-element solutions. In the direct analysis of solid samples calibration is usually a problem as the behaviour of the same element may be dependent on matrix composition. Generally calibration via standard addition is feasible but requires further sample preparation, especially in measurement of multiple elements [4-7].

In solution-based methods such as ICP-AES-MS and atomic emission spectrometry (AES) difficulties in Al_2O_3 digestion, pre-concentration and/or matrix separation steps are the major problems that result in higher detection limits and lower precision due to the dilution and contamination of the sample. Additionally due to the high melting-point, hardness and chemical inertness of aluminum oxide, dissolution is tedious and time-consuming [6-12].

As the concentrations of most of trace elements in high purity aluminum oxide are at parts per billion (ppb) or parts per million (ppm) levels,

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multi-element trace analysis by conventional chemical analysis is very difficult and problematic. Instrumental neutron activation analysis (INAA) followed by high resolution gamma-ray spectrometry is a well-established, sensitive, non-destructive, accurate, precise, specific, and universally applicable analytical technique, which can provide multi-elemental characterization of aluminum oxide with low limits of detection (LODs) and high accuracy [13-15]. The accuracy and the limit of detection of trace impurities using INAA is strongly dependent on the type of material analyzed and on the presence of any interfering elements, which may result in a high background masking the γ-peaks of trace impurities. The relative form of the NAA technique has been utilized extensively in our laboratory for the analyses of diverse matrices. We report the analysis of high purity aluminum oxide using INAA technique for the measurement of trace impurities.

Experimental

Sample Preparation

Sample of high purity aluminum oxide was purchased from Johnson Matthey, Materials Technology U.K, which contains low amounts of impurities. Sample contamination was avoided by taking care during sampling. Therefore all sample preparation procedures, up to the final sealing of the samples, were carried out at a clean bench facility. About 50-100 mg of the high purity aluminum oxide sample, in triplicate, were taken in 3 pre-cleaned labeled polyethylene capsules and heat-sealed. IAEA-SL-1 [16], lake sediment and IAEA-S7 [17], soil were employed as reference materials (RMs) for Quality Assurance (QA) purposes. The capsules containing samples and standards were finally packed and thermally sealed into polyethylene rabbits. The prepared targets along with the matrix appropriate standards were subjected to different irradiation protocols as discussed later.

Standard Preparation

Reference standards for the quantification of inorganic elements by INAA were prepared by taking ultrapure spectrographically standardized materials from Johnson, Matthey & Co., Limited, London. About 1 mg cm^{-3} of the materials was used to prepare stock solutions of the required elements. The solutions were diluted from 5 μg/g to a few ng/g to offer a wide range of standards for the elements to be determined. The solutions were dried on ash-less filter papers and sealed in polyethylene capsules for irradiation. Any undesired contribution of the filter paper was eliminated by simultaneous irradiation and counting of the blank filter paper and subtracting their contributions.

Neutron Irradiations

The samples and standards were irradiated for optimized protocols consisting of durations of 1 to 5 hours. Irradiations of samples were carried out at the Pakistan Atomic Research Reactor (PARR-2) pneumatic irradiation facility. PARR-2 is a 27 kW, Miniature Neutron Source Research Reactor (MNSR) with a thermal neutron flux of 1.0×10^{12} n/cm^2 sec. The optimized procedures for the determination of trace impurities in high purity aluminum oxide were developed using the nuclear data [15, 18] listed in Table-1a and 1b. To monitor the variations in the thermal neutron flux Au and Al foil flux monitors were placed between the samples. The thermal neutron flux was found to be the same for all samples with negligible fluctuations. Prior to counting the irradiated samples and standards were transferred to clean pre-weighed polyethylene vials. The capsules were re-weighed to assess the exact weight of the irradiated sample.

Gamma-ray Spectrometry

A high purity germanium detector (Canberra Model AL-30) was used to acquire γ-ray spectra. Gamma spectrometric system used comprised of a PC-based Intertechnique Multichannel Analyzer (MCA) (Intertechnique) and a sensitive spectroscopy amplifier (ORTEC model 2010) connected to the detector. The system has a resolution of 1.9 keV for the 1332.5 keV peak of ^{60}Co and a peak to Compton ratio of 40:1. For acquiring data GammaVision, Version 6.01 (Advanced Measurement Technology, Inc.)" software was used. The detector is energy calibrated daily using ^{152}Eu and ^{60}Co sources. As relative NAA is used the irradiation, cooling and counting times are identical for all samples and standards for each irradiation protocol. Moreover all samples/ standards are counted at the same distance from the detector. Results were obtained using validated in-house computer programs. All sources of errors were estimated to obtain the overall combined uncertainty in the calculations and background subtractions were also made for each irradiation [19].

Table-1: (a) Nuclear Data for Intermediate Irradiation Scheme [18].

Isotope used	Half life	γ-ray used (keV)	Irradiation time (h)	Cooling time (d)	Counting time (sec)
^{24}Na	14.96 h	1368.6	1	2	900
^{42}K	12.36 h	1524.7	1	2	900
^{140}La	1.7 d	1591.5	1	2	900
^{122}Sb	2.7 d	564.1	1	2	900
^{82}Br	35.4 h	554.3	1	2	900
^{153}Sm	1.9 d	103.2	1	2	900
^{175}Yb	4.2 d	396.3	1	2	900

where s=seconds, min=minutes, h=hours, d=days, w=weeks and y=years

Table-1: (b) Nuclear Data for Long Irradiation Scheme [18].

Isotope used	Half life	γ-ray used (keV)	Irradiation time (h)	Cooling time (w)	Counting time (h)
^{177}Lu	6.710 d	208.4	5	2	2
^{147}Nd	10.98 d	91.1, 531.0	5	2	2
^{131}Ba	11.80 d	469.3	5	2	2
^{117m}Sn	13.61 d	158.5	5	2	2
^{86}Rb	18.60 d	1078.8	5	2	2
^{233}Th	27.00 d	311.9	5	2	2
^{51}Cr	27.80 d	320.1	5	2	2
^{141}Ce	32.38 d	145.4	5	2	2
^{203}Hg	41.60 d	279	5	2	2
^{181}Hf	42.50 d	482.0	5	2	2
^{59}Fe	44.60 d	1099.3, 1291.6	5	2	2
^{46}Sc	83.90 d	889.3	5	2	2
^{85}Sr	64.84 d	514.0	5	2	2
^{75}Se	120.0 d	264.5	5	2	2
^{65}Zn	244.0 d	1115.5	5	2	2
^{134}Cs	2.060 y	795.8	5	2	2
^{60}Co	5.270 y	1173.2, 1332.5	5	2	2

where s=seconds, min=minutes, h=hours, d=days, w=weeks and y=years

Limit of Detection

The lowest concentration, which can be determined by any analytical technique, is its limit of detection. For the undetected elements, limit of detection (LOD) were calculated from the spectra using the following equation [19]:

$$LOD = \frac{3\sigma}{100} * X \qquad (1)$$

where, X is the mean value of concentration and σ is the standard deviation.

Like most techniques limit of detection for NAA depends on analyte, matrix, standard used for analysis and experimental conditions or system used for counting.

Results and Discussion

Two irradiation protocols were used for the quantification of elements using PARR-2 irradiation facilities. The devised optimum conditions employing 1 hour irradiation and 1-2 days cooling time were employed to quantify intermediate indicator radionuclides, i.e. ^{24}Na, ^{140}La, ^{153}Sm, ^{42}K, ^{122}Sb, ^{82}Br and ^{175}Yb, whereas 5 hours irradiation along with 2-3 weeks cooling time were used to determine isotopes with longer half-lives i.e. ^{177}Lu, ^{147}Nd, ^{86}Rb, ^{233}U, ^{51}Cr, ^{141}Ce, ^{181}Hf, ^{79}Hg, ^{60}Co, ^{59}Fe, ^{117m}Sn, ^{46}Sc, ^{75}Se, ^{134}Cs, ^{85}Sr, ^{131}Ba, ^{134}Cs and ^{65}Zn. Interferences by the matrix elements (Al and O) are eliminated using the above irradiation, cooling and counting protocols as aluminum is short-lived and decays during the cooling time whereas oxygen is not activated. Corrections for self-absorption due to penetration of gamma rays are not needed due to the small amount of samples (50-100 mg) used for analysis. The thermal to fast flux provided at the pneumatic irradiation facility of PARR-2 has a ratio of 5.2. This reduces the production of ^{24}Na via the ^{27}Al(n, α) reaction and also prevents the possibility of spectral interferences for most of the measured elements. Selection of γ-peak energies, their abundance and yield ratios provide interference free analysis of some trace elements. The interference free photo-peaks 1596.5 keV, 145.5 keV, 91.11 keV, 103 keV, 208.4 keV, 264.66 keV, 889.3 keV, 482.2 keV and 554.35 keV of ^{140}La, ^{141}Ce, ^{147}Nd, ^{153}Sm, ^{177}Lu, ^{75}Se, ^{46}Sc, ^{181}Hf and ^{82}Br respectively, were used for the measurement of these elements. The multiple γ-peaks of ^{59}Fe (1099.2 and 1291.6 keV), ^{60}Co (1173.2 and 1332.5 keV) and ^{134}Cs (604.7 and 795.8 keV), were used for the determining these elements. These multiple γ-peaks of radioactive nuclei allowed a cross-check of the accuracy. La and Yb are measured via the intermediate lived interference free γ-peaks of 1596.5 keV for ^{140}La and 396.3 keV for ^{175}Yb, respectively. ^{153}Sm and ^{124}Sb can be determined using both intermediate as well as long irradiation and counting schemes. For these elements the results corresponding to intermediate irradiation and counting schemes were taken because of the best quality assurance data. The observed interferences for ^{134}Cs in the presence of ^{124}Sb were overcome as mentioned earlier [16-20]. The γ-peaks of all the radionuclides were well resolved. Therefore the full energy peak area of 1115.5 keV of ^{65}Zn was well separated from the 1120.5 keV peak of ^{46}Sc [20-23].

Table-2: Analysis of IAEA Reference Materials (Concentration in µg/g) using INAA.

Element	**IAEA-S7 (Soil)[17]**		**IAEA-SL-1 (Lake Sediment)[16]**	
	Observed values	**Certified values**	**Observed values**	**Certified values**
Ba	**164.0 ± 28.8**	**(159)**	**658.0 ± 46.7**	**639.0 ± 53.0**
Br	**7.23 ± 1.80**	**7.00 ± 3.50**	**6.24 ± 1.23**	**6.82±1.73**
Ce	**63.7 ± 6.6**	**61.0 ± 6.5**	**105.0 ± 13.8**	**117.0 ± 17.0**
Co	**8.89 ± 0.98**	**8.90 ± 0.85**	**19.6 ± 0.4**	**19.8±1.5**
Cr	**64.5 ± 9.2**	**60.0 ± 12.5**	**101.0 ± 11.7**	**104.0 ± 9.0**
Cs	**5.25 ± 0.63**	**5.40 ± 0.75**	**6.96 ± 0.78**	**7.01 ± 0.88**
Fe	**25860 ± 600**	**(25700)**	**67420 ± 1400**	**67400 ± 1700**
Hf	**4.94 ± 0.32**	**5.10 ± 0.35**	**4.30 ± 0.50**	**4.16 ± 0.58**
Hg	**0.047 ± 0.050**	**(0.04)**	**0.16 ± 0.03**	**(0.13)**
K	**12340 ± 925**	**(12100)**	**14860 ± 865**	**(15000)**
La	**29.1 ± 2.4**	**28.0 ± 1.0**	**48.6 ± 4.5**	**52.6 ± 3.1**
Lu	**0.32 ± 0.15**	**(0.30)**	**0.52 ± 0.08**	**(0.54)**
Na	**2370 ± 86**	**(2400)**	**1769 ± 153**	**1720 ± 120**
Nd	**27.30 ± 3.18**	**30.00 ± 4.50**	**45.00 ± 4.02**	**43.80 ± 2.80**
Rb	**52.6 ± 4.4**	**51.0 ± 4.5**	**102.0 ± 9.4**	**113.0 ± 11.0**
Sb	**1.59 ± 0.19**	**1.70 ± 0.20**	**1.28 ± 0.11**	**1.31 ± 0.12**
Sc	**8.54 ± 0.94**	**8.30 ± 1.05**	**17.10 ± 1.28**	**17.30 ± 1.10**
Se	**0.37 ± 0.45**	**(0.40)**	**2.95 ± 0.45**	**(2.9)**
Sm	**5.05 ± 0.64**	**5.10 ± 0.45**	**9.30 ± 0.83**	**9.25 ± 0.51**
Sr	**102.0 ± 7.2**	**108.0 ± 5.5**	**85.70 ± 1.72**	**(80.0)**
Th	**8.14 ± 0.96**	**8.20 ± 1.10**	**14.30 ± 1.29**	**14.0 ± 1.0**
Yb	**2.24 ± 0.28**	**2.40 ± 0.35**	**3.30 ± 0.37**	**3.42 ± 0.64**
Zn	**108.0 ± 9.4**	**104.0 ± 10.5**	**218.0 ± 18.5**	**223.0 ± 10.0**

*Error quoted is the uncertainty at 95% confidence interval.
Values in parentheses are information values.

Method reliability was checked by analyzing the reference materials; IAEA-S7 (Soil) and IAEA-SL-1(Lake Sediment) employing the above mentioned optimized conditions and procedures. Table-2, in which the results for these standards are presented along with their certified data, shows that our values are in fairly good agreement with the certified/information values. Accuracy of the results maybe explained through plots of % difference between measured values and the certified values for each reference material as shown in Fig. 1a and 1b. In both these figures the % difference between our values and the certified values is >10 % for only Hg with most elements having this parameter < 5% or slightly above 5 %. For both RMs it can be seen that the concentration for Hg is given as an information value.

The results presented in Table-3 include elemental concentration in µg/g with uncertainties of twenty four elements determined in the Al_2O_3 sample. Concentration of each element was determined by relative method and reported on dry weight basis as an arithmetic mean of up to nine independent measurements obtained from three irradiation experiments. The overall uncertainty in concentration of impurity included uncertainty in standard deviation of mean values, uncertainty in weighing, uncertainty in counting, uncertainty in background, uncertainty in values of standard values etc. The overall or combined uncertainty in concentration of each element was calculated by error propagation formula [19].

$$Unc_{Total} = \sqrt{Unc^2_{Mean} + Unc^2_{BG} + Unc^2_{Count} + Unc^2_{Wt} + Unc^2_{CRM}} \quad (2)$$

where Unc_{Mean} is calculated by dividing the standard deviation by the mean value,

Unc_{BG} is uncertainty in background,

Unc_{Count} is uncertainty in counting,

Unc_{Wt} is uncertainty due to weighing,

and Unc_{CRM} is concentration uncertainty of an element in the reference material.

The combined uncertainty was calculated by multiplying Unc_{Total} by 2 to get a confidence interval of 95%. The detection limits for various elements were calculated by multiplying 3σ with the mean value where σ is the standard deviation associated with the peak area counts of the element whose concentration was being determined. Each element has different detection limit because of NAA sensitivity, which depends on isotope abundance, neutron cross section, half-life, and gamma ray abundance of the element measured. Na, Co, Sc, Cs, Cr and Th have very low detection limits whereas the remaining elements have reasonable range of LOD. The overall precision of the measurements were observed by %SD of counts under the peak for element determined against reference materials, which ranged from 2 to 10 % showing accuracy of our procedure and precision of our results. Most of the quantified elements were stable elements; however Th was detected though the $^{232}Th\ (n, \gamma,\beta)\ ^{233}Th \rightarrow\ ^{233}Pa \rightarrow ^{233}U$ reaction using the 311.9 keV peak.

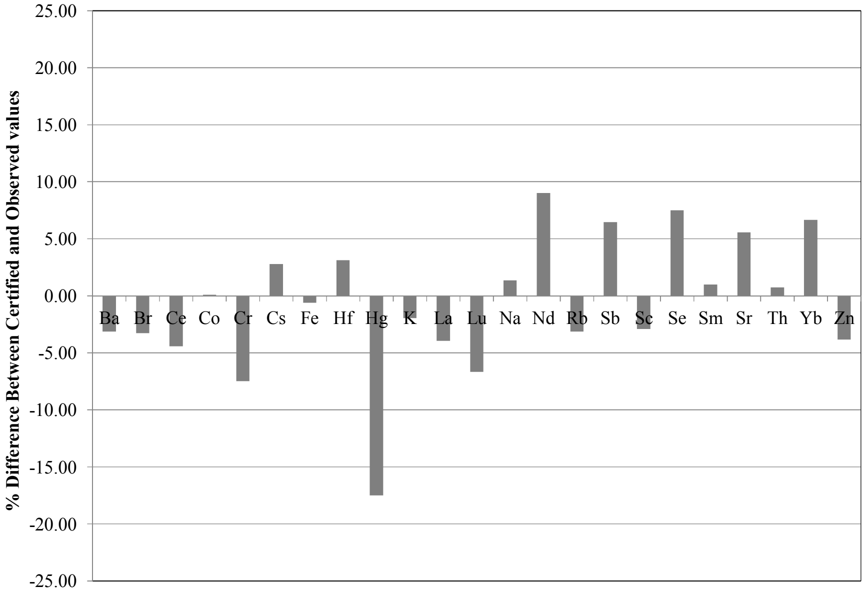

Fig. 1a: Quality Assurance Data for reference material IAEA-S7 (soil).

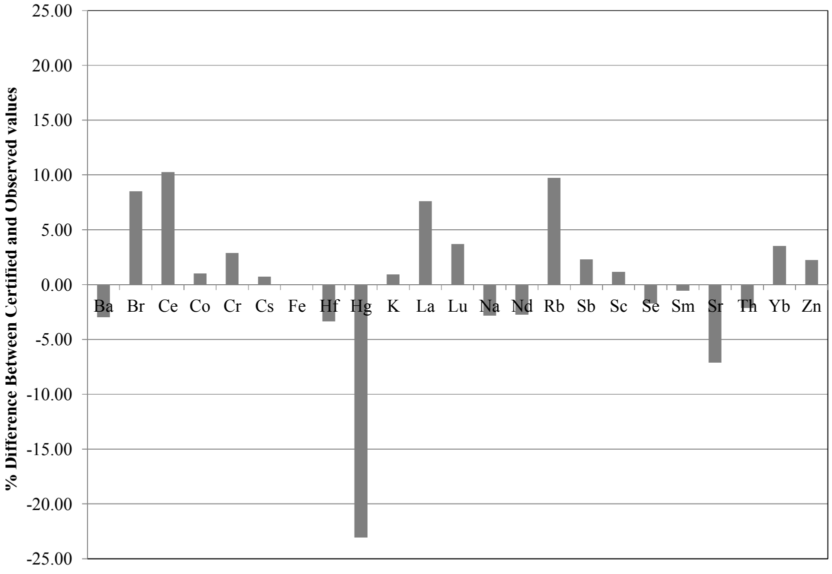

Fig. 1b: Quality Assurance Data for reference material IAEA-SL-1(lake sediment).

Table-3: Concentration of trace impurity elements in high purity aluminum oxide (All concentrations expressed in μg/g, at 95% confidence interval)

Element	Concentration	Uncertainty	Repeatability	LOD
Ba	**8.84**	**3.26 (36.88)**	**1.14 (12.90)**	**8.05**
Br	**0.30**	**0.18 (60.00)**	**0.03 (10.00)**	**0.25**
Ce	**0.50**	**0.13 (26.00)**	**0.07 (14.00)**	**0.79**
Co	**0.15**	**0.02 (13.33)**	**0.004 (2.67)**	**0.06**
Cr	**16.70**	**4.01 (24.01)**	**1.05 (6.29)**	**1.50**
Cs	**0.15**	**0.06 (40.00)**	**0.06 (40.00)**	**0.02**
Fe	**26.6**	**5.8 (21.88)**	**3.01 (11.32)**	**17.8**
Hf	**0.074**	**0.010 (13.51)**	**0.005 (6.76)**	**0.060**
Hg	**0.022**	**0.020 (90.91)**	**0.004 (18.18)**	**0.007**
K	**11.5**	**3.9 (34.00)**	**1.23 (10.70)**	**24.8**
La	**0.099**	**0.030 (30.30)**	**0.01 (10.10)**	**0.240**
Lu	**0.003**	**0.002 (66.67)**	**0.0004 (13.33)**	**0.003**
Na	**159**	**18 (11.19)**	**9.58 (6.03)**	**2.57**
Nd	**1.22**	**0.33 (27.05)**	**0.23 (18.85)**	**0.56**
Rb	**1.38**	**0.57 (41.30)**	**0.22 (15.94)**	**1.37**
Sb	**0.026**	**0.008 (30.77)**	**0.004 (15.38)**	**0.010**
Sc	**0.010**	**0.002 (20.00)**	**0.001 (10.00)**	**0.003**
Se	**0.048**	**0.040 (83.33)**	**0.009 (18.75)**	**0.030**
Sm	**0.006**	**0.001 (16.67)**	**0.0001 (1.67)**	**0.005**
Sn	**1.47**	**0.25 (17.01)**	**0.25 (17.01)**	**0.18**
Sr	**14.90**	**3.48 (23.36)**	**2.49 (16.71)**	**5.85**
Th	**0.48**	**0.08 (16.67)**	**0.03 (6.25)**	**0.08**
Yb	**0.058**	**0.010 (17.24)**	**0.005 (8.62)**	**0.060**
Zn	**0.05**	**0.02 (40.00)**	**0.008 (16.00)**	**0.02**

Data in parenthesis is in %

The results obtained for the Al_2O_3 sample during this study are given in Table 3. As can be seen from this table only 24 elements were determined. Na is the only major element with concentration 159 μg/g while Fe, Cr, Sr, K and Ba are all minor elements having concentrations from 9 to 27 μg/g. The remaining impurities are the trace elements having concentrations from 0.003 to 1.50 μg/g. Due to such low concentrations the measurement uncertainties of some elements (i.e. Br, Cs, Hg, Lu, Rb, Se and Zn) are quite high even though the % repeatability data is very reasonable, with only the data for Cs being >20%, indicating that the data for each element falls in a narrow range. Moreover the concentrations for some elements are near or below the detection limits (Ba, Br, Fe, Hf, Rb, Se and Sm and Ce, K, La, Lu and Yb respectively). Therefore, such low amounts should not impart any deleterious effects upon the properties of high purity Al_2O_3.

Conclusions

The INAA methodology presented in this work was effectively applied for the measurement of trace impurities in high purity Al_2O_3. Most of the interferences, particularly Compton background, were noticeably reduced using relative method and proper selection of γ-peak energies, their abundance and yield ratios. Generally detection limits were low for most of the measured elements. It can be inferred from the analysis that impurities levels of some elements were high (Ba, Cr, Fe, K, Na and Sr) and their adverse effects may be notable depending upon its applications.

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