DATA ANALYSIS OF THE RESULTS SUBMITTED IN THE PROFICIENCY TEST OF IAEA-CU-2006-06 (ANCIENT CHINESE CERAMIC) – MORE DATA INPUT USING K_0-INAA

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In the first part of this paper, the data submitted in the proficiency test (PT) conducted under the IAEA co-ordinated research project has been statistically evaluated. The data contains elemental concentrations determined in the IAEA-CU-2006-06 (ancient Chinese ceramic) powder by different laboratories using various analytical techniques. The analysis has been performed by using relative deviation and relative standard deviation. The use of rescaled sum of z-score, sum of square of z-score and principal component analysis has been suggested to determine the overall laboratory performance. The second part of the paper provides elemental concentrations of four elements (Eu, Lu, Sr and Zr) determined by our laboratory by k_0-INAA. Finally, principal component analysis has been applied to get inter-laboratories patterns on the scores plot. The overall analysis reveals that INAA produces results with high accuracy and precision and with good sensitivity for a large number of elements.

Keywords: Ancient Chinese ceramic, IAEA-CU-2006-06, NAA, k_0-INAA, Principal component analysis1.

1. Introduction

The elemental analysis of ancient pottery and ceramics is not only important in its characterisation but it also provides data for provenance studies. The basic assumption in provenance studies is that the artefacts produced in a particular area bear its geochemical fingerprints. Although, many techniques are available for elemental analysis in archaeological samples but the most suitable technique must be accurate and sensitive for a large number of trace elements and it must require small amount of the sample. Non-destructive techniques are preferably used in archaeology, these include: instrumental neutron activation analysis (INAA) [1], proton induced gamma-ray emission (PIGE) [2], proton induced x-ray emission (PIXE) [2,3] and x-ray fluorescence spectrometry (XRF) [3]. Other techniques which require sample preparation such as ashing, digestion, dilution, separation and extraction include: atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectroscopy [4], inductively coupled plasma spectrometry (ICP) coupled with different detection devices such as optical emission spectroscopy (ICP-OES) [2], atomic emission spectrometry (ICP-AES) [4] and mass spectrometry (ICP-MS) [3] and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) [5]. Recently, a new standardization approach has been introduced in NAA, known as k_0-standardization [6,7]. The k_0 concept was introduced during 1970s and today it has become a reliable analytical tool and has been adopted by many laboratories. The k_0-standardization requires an accurate characterization of irradiation and counting facilities and the use of composite nuclear constants known as k_0-factors. The k_0-factors are independent of reactor spectrum and of detector characteristics and are measured experimentally. Our laboratory at PINSTECH has also implemented this approach for the 30 kW Pakistan Research Reactor (PARR-2) [8] and for the 10 MW tank in pool type reactor (PARR-1) [9].

For the last few decades the International Atomic Energy Agency (IAEA) has been supporting laboratories in its Member States. This support is usually provided by launching new projects and by arranging intercomparison exercises or proficiency tests (PT) for the analysis of various types of analytes in complex matrices [10]. Participation in

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the proficiency tests [11] is an important step in quality assurance and laboratory accreditation procedures. In 2006, the Chemistry Unit of the IAEA's Laboratories, Seibersdorf, organised a proficiency test entitled "Application of nuclear analytical techniques to investigate the authenticity of art objects". The main aim of this PT was to assess and provide a chance to the participating laboratories to improve their analytical capability by analysing major, minor and trace elements in ancient Chinese ceramic (IAEA-CU-2006-06) [12]. IAEA distributed ancient Chinese ceramic sample as powder to different laboratories registered for this PT. The results submitted by the participating laboratories were compiled by the IAEA in the form of a report [12]. Although our laboratory did not participate in the PT but analysed the ceramic sample employing k_0-INAA [13] using PARR-2 irradiation facility. Results of 31 elements were reported, with 23 elements within ±10% of the target values, in our previous publication [13].

The main aim of the present study is to analyse the data submitted by the participating laboratories to the IAEA with more emphasis on the INAA results regarding their accuracy and precision. We have suggested the use of rescaled sum of z-score, sum of square of z-score and principal component analysis as single score of merit for a laboratory. This paper also reports the results of four elements not reported in our previous work [13] determined in IAEA-CU-2006-06. These elements have been determined by k_0-INAA using the 10 MW PARR-1 reactor.

2. Experimental

2.1. Experimental setup

The thermal to epithermal neutron flux ratio (f) and epithermal neutron flux shape factor (α) were determined by Al-0.1%Au wire (0.11 mm, IRMM-530RC, EU, Geel) and ZrO_2 powder (99.99%, Aldrich). The ceramic sample weighing ~100 mg was packed inside a polyethylene rabbit for neutron irradiation along with flux monitors. All irradiations were carried out at PARR-1, a 10MW material testing reactors (MTR). The reactor uses 19.99% enriched uranium core (U_3Si_2-Al), light water as moderator and graphite as reflector. The flux characterization of the PARR-1 can be found in reference [9].

After irradiation the samples were transferred to pre-weighed polyethylene capsules and γ-ray

spectra were acquired using a p-type coaxial high purity germanium (HPGe) detector (Eurisys Mesures) with 60% relative efficiency and 1.95 FWHM at 1332 keV γ-ray of ^{60}Co. The detector is connected to an Ortec-570 amplifier and Trump PCI 8k ADC/MCA card with GammaVision-32 ver. 6 software. Full peak efficiency calibration of the detector was performed at various heights using ^{241}Am, ^{133}Ba, ^{137}Cs, ^{60}Co and ^{152}Eu point calibration sources, which covered the energy range 59-1408 keV [8].

2.2. Data analysis and performance evaluation

The performance evaluation criteria, as set by the PT organizers, take into account accuracy and precision of the reported values. More details can be found in the IAEA report [12]. In this paper data analysis has been performed by using relative deviation and relative standard deviation. Although these indicators for each individual result furnishes useful information, however, a single figure of merit that summarises the overall performance of a laboratory will also be helpful for the assessment of a laboratory's long-term performance. To assign a number to the overall performance of a laboratory, we suggest the combined use of "rescaled sum of z-score" [11] and "sum of square of z-score" [11]. Moreover, principal component analysis, an exploratory method, provides a useful tool to visualise the overall standing of a laboratory.

All calculations in this study have been performed in Microsoft EXCEL. In the application of k_0-INAA the f and α were obtained by Solver add-in, which is part of Microsoft EXCEL. The $k_{0,Au}$ and Q_0 factors have been taken from a compilation by De Corte *et al.* [14].

2.3. Relative deviation and relative standard deviation

The accuracy in the reported concentration is calculated by the relative deviation (RD), which for element i is defined as:

$$RD_i = \frac{\overline{x}_{rep,i} - x_{ref,i}}{x_{ref,i}} \tag{1}$$

where $\overline{x}_{rep,i}$ is the average of the reported values and $x_{ref,i}$ is the target or certified reference value.

The scatter in the data is determined by relative standard deviation (RSD), which for element *i* is defined as:

$$RSD_i = \frac{\sigma_{rep,i}}{\overline{x}_{rep,i}} \qquad (2)$$

where $\sigma_{rep,i}$ is the standard deviation of the reported values.

Sum of rescaled z-score (RSZ)

The rescaled sum of *z*-score is defined as:

$$RSZ = SZ / \sqrt{I} \qquad (3)$$

$$SZ = \sum_i z_i = \sum_i \frac{x_{rep,i} - x_{ref,i}}{\sigma_{ref,i}} \qquad (4)$$

where *I* is the number of elements reported by a laboratory. RSZ is zero-centred with variance *I*, it is interpreted as standard normal deviates. RSZ value of 3 or more indicates a significant event, which means a consistent positive or negative bias.

Sum of square of z-score (SSZ)

The sum of square of z-score is defined as:

$$SSZ = \sum_i z_i^2 \qquad (5)$$

This score has a chi-squared $\left(\chi^2\right)$ distribution with *I* degrees of freedom. If SSZ is higher than the critical value of chi-squared, it indicates the presence of values with big discrepancies.

Principal component analysis (PCA)

PCA [15] is a mathematical approach which decomposes multivariate data into a set of eigenvectors and associated eigenvalues. When PCA is applied on a data matrix **X**, having dimension (*M* × *N*), where *M* represents the laboratories and *N* the elements, for a suitable number of components *K*, the **X** matrix decomposes into scores matrix, a loadings matrix and an error matrix of dimensions (*M* × *K*), (*K* × *N*) and (*M* × *N*) respectively. When one scores vector is plotted against another, provided suitable number of principal components have been chosen, the information regarding patterns of the objects (laboratories in our case) can be obtained.

Similarly, when loadings vectors are plotted, the relationship of the variables (elements in our case) can be visualised from the plots. The **X** matrix in this study contains elemental concentration data taken from the IAEA report [12] with laboratories as rows and elements as columns.

3. Results and Discussion

The participants of the PT submitted results for 37 elements, while target values for 44 elements were provided by the originator of this PT (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti, Ba, Be, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Hf, La, Li, Lu, Nb, Nd, Ni, Pb, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, U, V, W, Y, Yb, Zn and Zr) as certified and 6 elements (As, Bi, Gd, Ho, Pr and Tm) as information values. Originally, the material was characterised by eight laboratories from China. They used NAA, XRF, ICP-MS, ICP-AES, ICP-OES, atomic fluorescence spectrometry (AFS) and flame atomic absorption spectroscopy (FAAS). The techniques applied by the participants of this PT were AAS (1 laboratory), ICP (3 laboratories), INAA (12 laboratories), PIXE (3 laboratories), PIGE (2 laboratories), prompt gamma activation analysis (PGAA) (1 laboratory) and XRF (7 laboratories). Out of the 24 participating laboratories 4 laboratories used combination of more than one technique for the analysis.

The maximum number of results submitted by a single laboratory was 32 elements using PIXE-INAA-XRF techniques, while the minimum number of elements reported by single laboratory was 9 elements using ICP-OES and AAS. On the average 18 elements were reported per laboratory. The analysis of the reported elements reveals that Fe was quantified by maximum number of laboratories (22), Li was determined by least number of laboratories (2 laboratories: ICP-MS and ICP-OES); on average each element was reported by 12 laboratories.

3.1. Results by all analytical techniques

3.1.1. All results

The analysis of accuracy in the results has been performed by relative deviation (RD) and the scatter of the data has been measured by relative standard deviation (RSD). The results of RD and RSD are presented in Fig. 1, which shows that Mg produced maximum RD (125 %) followed by Sm (54 %) and V (48 %), the RSD was also very high,

more than 100 %, for these elements. There are 14 elements (Al, Cs, Dy, Ga, La, Li, Lu, Nb, Rb, Sc, Si, Tb, Th and W) which produced acceptable results by all laboratories.
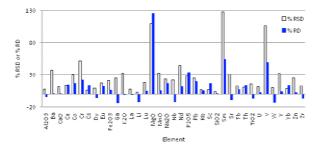

Figure 1. Relative deviation and relative standard deviation of all the reported data.

Table 1. Results of RSZ and SSZ with critical chi-square values for SSZ.

Technique-Lab code	RSZ	SSZ	Chi-Square (critical value)
PGAA-1	4.2	55	21
INAA-5	3.5	**17**	28
INAA-6	10.0	457	30
INAA-7	**1.0**	**5**	26
PIXE-INAA-XRF-10	9.3	1430	46
INAA-11	**0.0**	190	38
ICP-MS-11A	-3.1	117	17
INAA-12	**2.4**	**27**	35
INAA-13	-3.8	54	36
INAA-16	6.3	370	30
XRF-17	**-0.3**	**37**	39
INAA-18	4.6	40	34
ICP-OES-18A	**2.9**	143	28
INAA-20	**-0.6**	**17**	35
XRF-22	-6.5	121	20
INAA-24	16.5	1420	38
INAA-25	**-0.1**	78	33
ED-XRF-26	**1.6**	**16**	26
PIXE-27	8.1	292	18
XRF-PIGE-29	**2.9**	157	30
ICP-OES-AAS-30	**-2.7**	56	17
PIXE-PIGE-32	-5.3	115	29
XRF-34	23.9	8927	21
XRF-36	31.2	6253	20

An analysis made by RSZ and SSZ for all the participating laboratories is presented in Table 1. There are 10 laboratories which produced RSZ < 3

and 6 laboratories with SSZ $< \chi^2_{crit}$. The laboratories which qualified both tests are Lab-7 (INAA), Lab-12 (INAA), Lab-17 (XRF), Lab-20 (INAA) and Lab-26 (XRF); all of these laboratories produced accurate results. There are laboratories with acceptable values of RSZ but did not qualify the SSZ test having one or more discrepant values. Similarly, the laboratories qualified the SSZ test but failed the RSZ test indicate good individual results but with the presence of either positive or negative bias in the results. All other laboratories, which failed both tests, indicate inaccurate results with the presence of biased values.

3.1.2. Accepted results

The maximum number of accepted results for 28 elements was produced by a laboratory which used a combination of analytical techniques (PIXE-INAA-XRF), the next technique in the list is XRF with 25 accepted results, and then INAA occupies the next 7 places with highest number of accepted results. However, on the basis of % acceptable results (see Fig. 2), there are 7 laboratories with 100% acceptable results. One laboratory out of these 7 used XRF and the rest INAA. An analysis made by using RD and RSD is presented in Fig. 3,
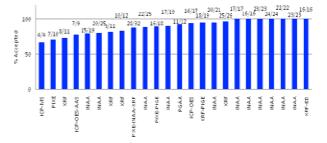

Figure 2. Percentage of the accepted results submitted by different laboratories with labels indicating number of accepted results to total results submitted.
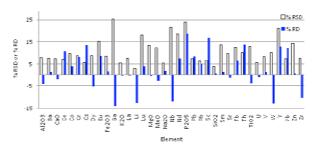

Figure 3. Relative deviation and relative standard deviation of all the accepted data by all techniques,
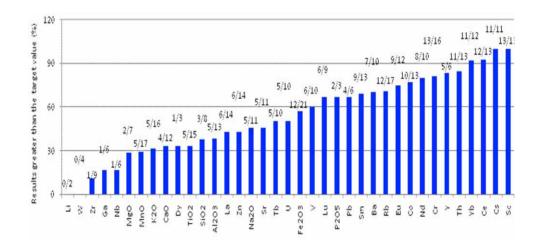
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Figure 4.   Percentage of the results showing higher than the target value for different elements by all techniques.

which shows K, La, Mg, Si and Zn produced less than 1% RD and 14 elements (Al, Ba, Ca, Co, Dy, Fe, Lu, Mn, Na, Sm, Sr, Ti, U and V) were reported with less than 5% RD. The maximum RD of 18 % was found in results for P. Similarly maximum RSD of 25% was found in results for Ga, followed by P, Nb and Y.

There are certain elements, which show noticeable trend as seen in Fig. 4. The elements reported by a large number of participating laboratories with relatively higher RD includes Sc by 13 labs: 16.7 % RD, Th by 13 labs: 13.8% RD, Cs by 11 labs: 13.6% RD, Yb by 12 labs: 12.2 % RD and Ce by 13 labs: 10.7% RD. All reported results of these elements show positive bias indicating either systematic error made by all laboratories or inaccurate target values.

Since a large number of the participating laboratories used INAA, therefore in the next sections the results obtained by INAA analysis are discussed.

3.2.   Results using INAA

The analysis includes the data from only those laboratories, which exclusively used INAA and not a combination of INAA with other techniques.

3.2.1. All results

There are 11 laboratories, which used INAA exclusively. The maximum number of elements reported is 25, minimum is 16 and average is 21. The average number of element reported by INAA is higher than the average number of elements (18) reported by all techniques. The elements reported by all INAA laboratories include Ce, Cr, Eu, La, Rb, Sc, Th and Yb, and the element Nb is reported by only 1 laboratory. On the average each element was reported by 7 laboratories. The elements not reported by INAA laboratories includes Li, P, Pb, Si and Y. Either these elements cannot be determined by INAA (Li, P and Pb) or have high detection limits (Si and Y). Si can be measured [13] by the $^{29}Si(n,p)^{29}Al$ reaction if the concentration of Si and other experimental conditions are favourable. The measurement of Y by INAA is difficult especially in geological matrices. The results given in Section 3.1.1 of this paper show 14 elements analysed correctly or within acceptable criteria of IAEA by all techniques, the results by INAA adds 9 more elements (Ca, Co, Cr, Eu, Mn, Nd, Sm, Sr and V) to the list as acceptable by all INAA laboratories. In total 21 elements (Al, Ca, Co, Cr, Cs, Dy, Eu, Ga, La, Lu, Mn, Nb, Nd, Rb, Sc, Sm, Sr, Tb, Th, V and W) have been reported by INAA which are acceptable.

RD of individual elements shows highest value for Mg followed by Ga, Na and Nb with more than 20% RD. An analysis of RSD shows that Mg has maximum RSD (> 50%) followed by Ba, Fe, Ga, K, Na Nd, Ti, Zn and Zr each having more than 20% RSD.

3.2.2. Accepted results

The maximum number of results rejected were for Mg followed by Na, Zr, K, Ti, Ba, Zn and others. In the case of Mg; 2 results out of 3 are rejected, the most probable reason for this appears to be:

1. Deconvolution of the 843 keV peak of Mg with the large peak of Mn at 846 keV.

2. Presence of nuclear interference caused by the ^{27}Al$(n,p)^{27}$Mg reaction because Al is always present in geological samples.

The results for Na have been reported by 9 labs, out of which 3 are rejected, which is mostly due to the presence of nuclear interference caused by ^{27}Al$(n,\alpha)^{24}$Na and ^{24}Mg$(n,p)^{24}$Na reactions, depending upon the reactor flux because at low flux these interferences are not significant. Zr is reported by 3 labs, 1 rejected and 1 accepted with warning. Zr is mostly quantified at 756.7 keV because at 724.2 keV other spectral interferences are present. Ti is reported by 5 labs, 1 is rejected and 2 accepted with warnings. The incorrect concentration of Ti is most probably due to the small cross section of ^{50}Ti$(n,\gamma)^{51}$Ti reaction, which generates small peak with large peak fitting error, and the short half-life of ^{51}Ti, which requires a proper live time correction. Zn has been reported by 6 laboratories, among them 1 is rejected. The correct concentration of Zn requires the correct deconvolution of 1115.5 keV peak of ^{65}Zn, which is usually accompanied by peaks of ^{160}Tb at 1115.1 keV and ^{46}Sc at 1120 keV.

The results by INAA show that 20 elements (Al, Ba, Ca, Co, Dy, Fe, K, La, Lu, Mg, Mn, Na, Nd, Rb, Sm, Tb, Ti, U, V and Zn) were measured with less than 10% RD, 10 elements (Ce, Cr, Cs, Eu, Sc, Sr, Th, W, Yb and Zr) have below 20% RD and only two elements (Ga and Nb) were quantified with more than 20% RD. The RSD for 21 elements (Al, Ba, Ca, Ce, Co, Cr, Cs, Dy, Eu, Fe, K, La, Na, Rb, Sc, Sr, Th, U, V, Yb and Zr) is less than 10%, 7 elements (Lu, Mn, Sm, Tb, Ti, W and Zn) is below 20% and for 2 elements (Ga and Nb) it is more than 20%. If accuracy and precision are considered together then 11 elements (Al, Ba, Ca, Co, Dy, Fe, La, Na, Rb, U and V) have been quantified with less than 10% RD and RSD. Only Ga and Nb have more than 20% RD and RSD.

3.3. Our results by k_0-INAA

We have already reported results of 31 elements by k_0-INAA and Si by (n, p) reaction [13]. As described in Section 3.1.2 Ce, Cs, Sc, Th and Yb have been reported by participants of PT with positive bias. Similar trend is shown by our results. The accuracy and precision of our data is very similar to the results presented in the Section 3.2.2. However, we reported Ga with 13% RD and 10% RSD, which shows better accuracy and precision of our results.

In this study we report four more elements (Eu, Lu, Sr and Zr) determined by k_0-INAA. The results are presented in Table 2 with experimental conditions. Sr and Zr were measured using Høgdahl convention [9,16]. Since Eu and Lu are non 1/v nuclides, therefore Westcott's convention [17] is used in their quantification. In Westcott's convention, Westcott's g-factor is determined, which is a measure of the deviation from the 1/v cross section behaviour in thermal energy region. The detail about the determination of f, α and Westcott's g-factor for PARR-1 can be found in our previous work [9]. The results for Lu, Sr and Zr produced less than 1 z-score, while Eu produced 1.6 z-score thus indicating acceptable accuracy for these elements. Sr and Zr generated less than 10% RSD, while Eu and Lu were quantified with less than 15% RSD.

Table 2. Additional results of IAEA-CU-2006-06 (Chinese ceramic) with experimental conditions.

Element	Irradiation Time	Decay Time	Measurement Time	Radionuclide	Energy (keV)	Concentration (µg g^{-1})	
						Determined	Reference
Eu	1 h	1 week	2 h	^{152}Eu	344.4	1.7±0.2	1.4±0.2
Lu	1 h	1 week	2 h	^{177m}Lu	208.4	0.69±0.10	0.61±0.12
Sr	10 min	1 h	1 h	^{87m}Sr	388.5	116±8	103±16
Zr	1 h	1 week	2 h	^{95}Zr	756.7	374±20	337±42

3.4. *Application of principal component analysis on the acceptable results*

Since the reported data contains missing values, therefore only those elements were selected where missing data was not more than three. Similarly, only those laboratories were selected where missing data for elements was also not more than three. The missing data was filled by the average of the elements of accepted results. In this way the data matrix **X** was formed with dimension (14×17) i.e., data of 14 laboratories including the IAEA target values and our results (k_0 laboratory) and 17 elements (Ce, Co, Cr, Cs, Eu, Fe, K, La, Lu, Na, Rb, Sc, Sm, Tb, Th, U and Yb). Since the concentration values for different elements were at different scale therefore all the columns were first mean centred and then divided by the corresponding standard deviation of the column, the process is called standardisation [15].

After applying PCA, a comparison of the results is made by plotting the scores of the third principal component (PC3) against the second principal component (PC2). The distance between the target values and individual laboratory is an indicator for the overall performance of that laboratory. The greater the distance, the more number of rejected results associated with a laboratory are expected. The plot is presented in Fig. 5, which shows two distinct laboratories having lab code 11 and 24. The labs 11 and 24 both reported 3 elements with either higher or lower than the IAEA target values. These elements were also rejected by the IAEA result evaluation criteria. In this way, PCA supports the result evaluation criteria of IAEA. Similarly, loadings plot of PC3 against PC2 is presented in Fig. 6, on comparing scores plot with loadings plot it reveals that lab 11 reported higher values for Ce and U and lower values for K. Similar interpretation can be made about laboratory 24 having higher values for Fe, K and Na. Fig. 5 shows the IAEA results somewhere in the middle of the plot, where it is close to Lab 13 (all acceptable), 20 (all acceptable), 7 (all acceptable) and 16 (one rejected). Our results by k_0 are also not far from the IAEA results. The results of Lab 10, which used a combination of three techniques (PIXE-INAA-XRF) indicated by P-I-X, is also shown on the same figure. The analysis shows that PCA is a useful data exploratory technique and can be applied for exploratory data analysis.
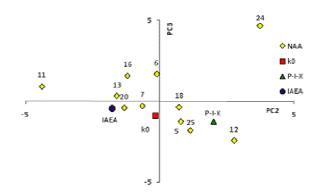

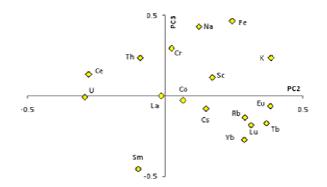Figure 5. Scores plot of PC3 vs PC2 for IAEA, NAA, PIXE-INAA-XRF (Lab 10) and k_0-NAA results.

Figure 6. Loadings plot of PC3 vs PC2 for IAEA, NAA, PIXE-INAA-XRF (Lab 10) and k_0-NAA results.

4. Conclusions

The statistical data analysis performed in this study shows that the average reported concentrations of Mg, Sm and V produced highest RD. The elements K, La, Mg, Si and Zn were quantified with less than 1% RD by all accepted results, whereas, Ce, Cs, Sc, Th and Yb determined by all or most of the laboratories have higher than the certified reference values indicating a serious discrepancy. However, for the analysis performed by INAA only, all laboratories have acceptable results for 21 elements (Al, Ca, Co, Cr, Cs, Dy, Eu, Ga, La, Lu, Mn, Nb, Nd, Rb, Sc, Sm, Sr, Tb, Th, V and W). Among all the reported data, the results by INAA show 20 elements (Al, Ba, Ca, Co, Dy, Fe, K, La, Lu, Mg, Mn, Na, Nd, Rb, Sm, Tb, Ti, U, V and Zn) with less than 10% RD, which indicates that INAA is a highly accurate and sensitive technique for most of the elements in ceramic material. The application of RSZ and SSZ scores reveal the overall performance of individual laboratory, whereas, PCA provides a tool to visualise the laboratories with similar results. This

paper also concludes that with the use of k_0-INAA and (*n,p*) reaction, 35 elements in the ceramic material can be quantified.

5.   Recommendations

Some suggestions/recommendations have been provided for PT organisers.

1. The final report on the results of PT should contain more analysis detail such as in the case of INAA, the method of calibration whether it was relative, k_0 or any other. The analysis scheme such as irradiation, decay and counting times should be mentioned. The significant interferences should be reported.

2. Some laboratories applied a combination of techniques such as laboratory No. 10 used PIXE, INAA and XRF. We think it would be useful for the scientific community to know which technique was used for which element.

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