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INTERCOMPARISON AMONG THREE ACTIVATION ANALYSIS LABORATORIES IN SOUTH AMERICA

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ABSTRACT

Elemental concentrations were determined by INAA in Brick Clay and Ohio Red Clay (new bag) by three radioanalytical laboratories in Argentina, Brazil and Chile. Results were compared to unpublished data from the Conservation Analytical Laboratory, Smithsonian Institution. To better assess the analytical results obtained from laboratories the precision and accuracy of the method were evaluated by means of statistical methods. The results at a confidence level of 95% can be considered identical.

Key Words: Instrumental neutron activation analysis; Trace elements; Brick Clay; Ohio Red Clay.

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INTRODUCTION

It is already a generally accepted fact that chemical analysis of archaeological pottery yields very important information in provenance studies [1–4], and much of the information for judging pottery provenience lies in the trace elements [5–12]. The number of analytical data from investigations of different kinds of ceramics increases worldwide and this poses the serious question about comparison of results from different laboratories. The use of different analytical calibrations by different analytical laboratories makes data exchange problematic. As a result, exchanges of data and sources samples between laboratories are rare rather than routine [13]. Undoubtedly this is closely connected to the accuracy and precision of the analysis.

Precision reflects the reproducibility of measurements on sample of identical (or nearly identical) composition. When all measurements relevant to a provenance problem are made in the same laboratory and by the same techniques and are calibrated against the same standard material, high-precision measurements are often sufficient for an assignment of origin [14]. When measurements relevant to a problem are made in different laboratories or by different techniques, and are calibrated with different standard, systematic errors of measurement become important as well as uncertainties in the known abundances of the calibration standard. On the other hand, accuracy is an estimate of the closeness of a measurement to the true value.

The evaluation of analytical technique and individual laboratory performance is critical to maintaining a known quality of chemical data and to maintaining the confidence of the results. Of importance is wether a particular laboratory is producing results with the accuracy and by a generally acknowledged technique, or even with the accuracy and precision they claim for themselves.

Precision of measurement better than 5% has been demonstrated in individual laboratories from South America [15–17], however, the ability to reproduce results between different laboratories has not been demonstrated. This point is crucial since otherwise the results of researches performed at different laboratories cannot be related directly. Consequently, interlaboratory comparisons are imperative.

In this paper data from a study on intercomparability of INAA results obtained in three laboratories from South America are presented: Argentina, Brazil and Chile, named Lab A, Lab B and Lab C, respectively. INAA has been extensively used in these three countries for a long time; however, this is the first opportunity that analytical data are compared even though the three laboratories have participated in several intercomparison studies organized by IAEA. The characteristics of the gamma-ray spectrometers differed considerably, and consequently, important differences in the operating procedures are used, as well as in the data reduction. The three laboratories employed the same materials, Brick Clay NIST-SRM-679 and Ohio Red Clay (new bag), to perform the analysis.

Table 1. Analytical Conditions Adopted by Each Laboratory

Lab	Equipment	Standard	Decay Time	Isotope Measured
A	Ortec Ge (hyperpure) model GMX-25195-S. Active volume 177.4 cm^3	NIST-SRM-1633b	7 d	^{153}Sm (103.2);^{175} Yb (396.3); ^{140}La (1596.2)
			30 d	^{141}Ce (145.4); ^{60}Co (1173.2); ^{51}Cr (320); ^{134}Cs (795.9); ^{152}Eu (1408); ^{59}Fe (1099.2); ^{181}Hf (482.2); ^{46}Sc (889.3); ^{233}Pa (311.9)
B	Canberra-Ge (hyperpure) model, GX 2020 S100 MCA and Vispect 2 software. Active volume 124.4 cm^3	NIST-SRM-2704 ICHTJ-CTA-FFA-1	7 d	^{153}Sm (103.2); ^{175}Yb (393.3); ^{140}La (1596.2)
			15 d	^{141}Ce (145.4); ^{60}Co (1332); ^{51}Cr (320); ^{134}Cs (795.9); ^{152}Eu (1408); ^{59}Fe (1099.2); ^{181}Hf (482.2); ^{46}Sc (889.3); ^{233}Pa (311.9)
C	Canberra-Ge (hyperpure) detector model GR 1518, S100 MCA and SAMPO90 software Active volume 72 cm^3	NIST-SRM-1633b	6–7 d	^{153}Sm (103.2); ^{175}Yb (396.3); ^{140}La (1596.2)
			25–27 d	^{141}Ce (145.4); ^{60}Co (1332); ^{51}Cr (320); ^{134}Cs (795.9); ^{152}Eu (1408); ^{59}Fe (1099.2); ^{181}Hf (482.2); ^{46}Sc (889.3); ^{233}Pa (311.9)

EXPERIMENTAL

All samples and standards were dried in an oven at 105°C for 24 h before weighing. The dried samples were transferred to a desiccator in order to reach room temperature and aliquots of about 100 mg of each sample were weighed in quartz of high purity (Lab A) or into polyethylene bags and wrapped in aluminum foil in Labs B and C. Groups of 6 samples and one (Lab C) or two (Lab B) reference materials were packed in aluminum foil and irradiated at a thermal neutron flux of about 5×10^{12} n cm^{-2} s^{-1} for 8 h. In Lab A batches of ten samples and one reference material were irradiated at a thermal neutron flux of about 3×10^{13} n cm^{-2} s^{-1} for 5 h. Two measurement series were carried out. In Table 1 the analytical conditions adopted are summarized.

RESULTS AND DISCUSSION

To evaluate the analytical process of the three laboratories, the concentrations for Sc, Cr, Fe, Co, Cs, La, Ce, Sm, Eu, Yb, Hf and Th representing various groups in the Period Table were studied. The results for Brick Clay (NIST SRM-679) and Ohio Red Clay (new bag) obtained in the three countries were statistically compared with unpublished data obtained from Bishop for over a 17-year period (1982 to 1999) for Brick Clay and a period over 10 years (1989 to 1999) for Ohio Red Clay [18].

All possible interferences potentially occurring in gamma-ray spectrometry were considered and checked. A possible source of error in the determination of REE elements is the presence of significant amounts of fissible nuclides (^{235}U and ^{233}U). As it is well known, REE nuclides, especially among the light REE elements (La to Sm), are produced both by activation and by fission. In the present work no interferences were expected in the samples because of the very low uranium and thorium content. According to Glascock [4] the interference of uranium fission in the determination of La and Ce is negligible when the uranium concentration does not exceed 5 ppm.

All individual determinations in each set of data were tested for discordant result. Dixon's test at the significance level of $\alpha = 0.05$ [19] was applied for rejection of outliers. The data were treated as if only one outlier were present at a time. If the extreme (the highest or the lowest) result was declared discordant by the tests, it was rejected and the whole procedure repeated sequentially until no more discordant results could be identified. Correspondingly, the final data set (i.e. accepted laboratory averages after elimination of outliers) were used to calculate the standard deviation.

The arithmetic means of independent determinations of each element with standard deviations, outlier, relative standard deviation and relative error of the complete data set are shown in Tables 2 and 3 for Brick Clay and Ohio Red Clay, respectively. The reported error limits are the standard deviation of means which are generally greater than the uncertainties in counting statistics. The Dixon's criterion for outlier rejection resulted in rejection of extremely few of all the determinations.

As it can be seen in Tables 2 and 3 the results have been analyzed by comparing the data obtained by each laboratory with the overall mean obtained by Bishop data. For both materials the precision obtained for each laboratory was around 5% or less and agreed with the precision obtained by Bishop and it is comparable to those from the literature [20, 21].

For 50% of the elements studied (Sc, Cr, Fe, Co, Ce and Th) the relative error was less than 5%, and for the remaining elements it was around 10% showing that the agreement between laboratories is very good, and it is comparable to those from the literature [20, 21] confirming the high accuracy of the analytical procedure used. In archaeological studies data having moderate precision might be sufficient to identify the products of interrregional or long distances trade, especially if different ceramic resources areas are geologically diverse. However, greater precision is useful and often necessary- for the characterization and discrimination of production centers involving short distances or intraregional exchange [14].

Any disagreement between results must be attributed, among other parameters, to failure by the Lab to determine accurately the net counts in the respective γ-ray peak. The failure to determine the net counts in a peak accurately could be

Table 2. Results for Brick Clay Reference Material (NIST-SRM-679) in μg g^{-1}, Unless Indicated

					Bishop[b]		
Element	Lab	Outlier	Mean ± SD[a]	RSD, %	Value	RSD, %	RE, %
Cr	A	1	110 ± 7	6.4	109.7 ± 4.9	3.1	0.3
	B	0	104 ± 5	4.8			5.2
	C	0	109 ± 7	6.4			0.6
Fe, %	A	1	9.3 ± 0.4	4.3	9.03 ± 0.27	3.0	3.0
	B	2	9.0 ± 0.4	4.4			0.3
	C	0	9.2 ± 0.5	5.4			1.9
Co	A	0	28 ± 2	7.1	26.7 ± 0.5	2.0	4.9
	B	0	25.3 ± 0.8	3.2			5.2
	C	0	27 ± 1	3.7			1.1
Cs	A	0	11 ± 1	9.1	9.66 ± 0.30	3.1	13.9
	B	1	9.7 ± 0.4	4.1			0.4
	C	0	10.4 ± 0.5	4.8			7.7
Ce	A	2	106 ± 3	2.8	103 ± 2	2.4	2.9
	B	1	102 ± 4	3.9			1.0
	B	0	110 ± 7	6.4			6.8
Sm	A	2	10.3 ± 0.5	4.8	9.16 ± 0.23	2.5	12.4
	B	0	8.8 ± 0.9	10.2			3.9
	C	0	9.8 ± 0.4	4.1			7.0
Eu	A	0	2.0 ± 0.2	10.0	1.69 ± 0.05	3.0	18.3
	B	0	1.75 ± 0.09	5.1			3.6
	C	2	1.82 ± 0.06	3.3			7.7
Yb	A	1	4.0 ± 0.3	7.5	4.11 ± 0.22	5.3	2.7
	B	0	4.1 ± 0.6	14.6			0.2
	C	1	3.9 ± 0.1	2.6			5.1

[a] Lab A: n = 9, Lab B: n = 29, Lab C: n = 12.
[b] Bishop: n = 311.

due to multiple possible errors which are difficult to evaluate with high accuracy. These errors are likely to be systematic rather than random. One such source of error, and often the most important one, has to do with the method used to determine the background under each γ-ray peak. In order to find similarities among results and PCA brings out the correlation between different samples, the final data set were submitted to principal component analysis at a confidence level of 95%. To avoid the concentration of any element from having too much influence on the principal components, the data were auto-scaled to have zero mean and unit variance: $z_{nm} = x_{nm} - x_m/s_m$. Figs. 1 and 2 shows a bivariate plot of the first two principal components scores for Brick Clay and Ohio Red Clay. As it can be seen, the plots show that the samples form a very tight chemically homogeneous group providing a high degree of similarity between the results. The overall accuracy of the measurements for the elements studied are quite acceptable for routine INAA of archaeological or geological samples.

Table 3. Results for Ohio Red Clay, in μg g^{-1}, Unless Indicated

					Bishop[b]		
Element	Lab	Outlier	Mean ± SD[a]	RSD, %	Value	RSD, %	RE, %
Sc	A	0	19 ± 1	5.3	18.2±0.3	1.7	4.4
	B	0	18.5 ± 0.8	4.3			1.6
	C	0	18.4 ± 0.8	4.3			1.1
Cr	A	1	92 ± 5	5.4	91.8 ± 3.4	3.7	0.2
	B	0	90 ± 3	3.3			2.0
	C	0	90 ± 5	5.5			2.0
Fe, %	A	0	5.2 ± 0.3	5.7	5.09 ± 0.99	1.9	2.2
	B	0	5.2 ± 0.3	5.7			2.2
	C	0	5.2 ± 0.2	3.8			2.2
Co	A	0	24 ± 1	4.2	23.7 ± 0.8	3.3	1.3
	B	1	22.5 ± 0.8	3.6			5.1
	C	0	23 ± 1	4.3			3.0
Cs	A	0	10.9 ± 0.9	8.2	10.1 ± 0.4	3.9	7.9
	B	0	10.2 ± 0.4	3.9			1.0
	C	0	10.4 ± 0.6	5.8			3.0
La	A	2	56 ± 1	1.8	57.3 ± 1.1	1.9	2.3
	B	0	51 ± 4	7.8			11.0
	C	0	53 ± 3	5.7			7.5
Ce	A	0	116 ± 9	7.8	112 ± 3	2.7	3.6
	B	1	114 ± 3	2.6			1.8
	C	0	114 ± 8	7.0			1.8
Sm	A	2	10.2 ± 0.4	3.9	9.32 ± 0.40	4.3	9.4
	B	0	8.9 ± 0.9	10.1			4.5
	C	0	9.4 ± 0.5	5.3			0.9
Eu	A	1	1.8 ± 0.1	5.6	1.64 ± 0.05	2.8	9.7
	B	0	1.8 ± 0.1	5.6			9.7
	C	0	1.80 ± 0.05	2.8			9.7
Yb	A	2	4.4 ± 0.2	4.5	4.76 ± 0.28	5.8	7.6
	B	0	4.3 ± 0.5	11.6			9.7
	C	0	4.3 ± 0.2	4.6			9.7
Hf	A	2	7.1 ± 0.5	7.0	7.49 ± 0.25	3.4	5.2
	B	0	7.0 ± 0.2	2.8			6.5
	C	1	7.0 ± 0.2	2.8			6.5
Th	A	0	16 ± 1	6.2	15.6 ± 0.5	2.9	2.6
	B	0	15.4 ± 0.6	3.9			1.3
	C	0	15 ± 1	6.7			3.8

[a] Lab A: n = 22, Lab B: n = 30, Lab C: n = 14.

[b] Bishop: n = 124.

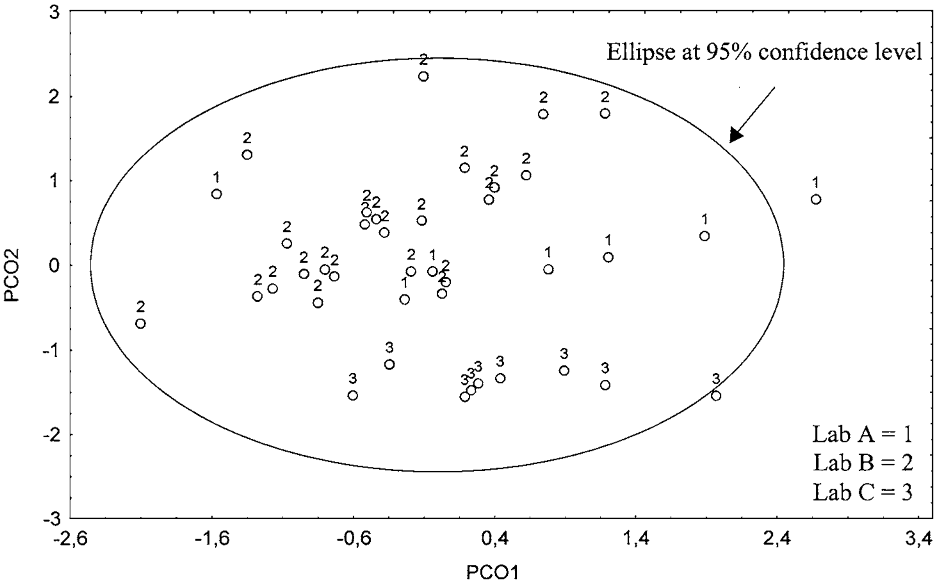

Figure 1. Plot of two principal components for brick clay.

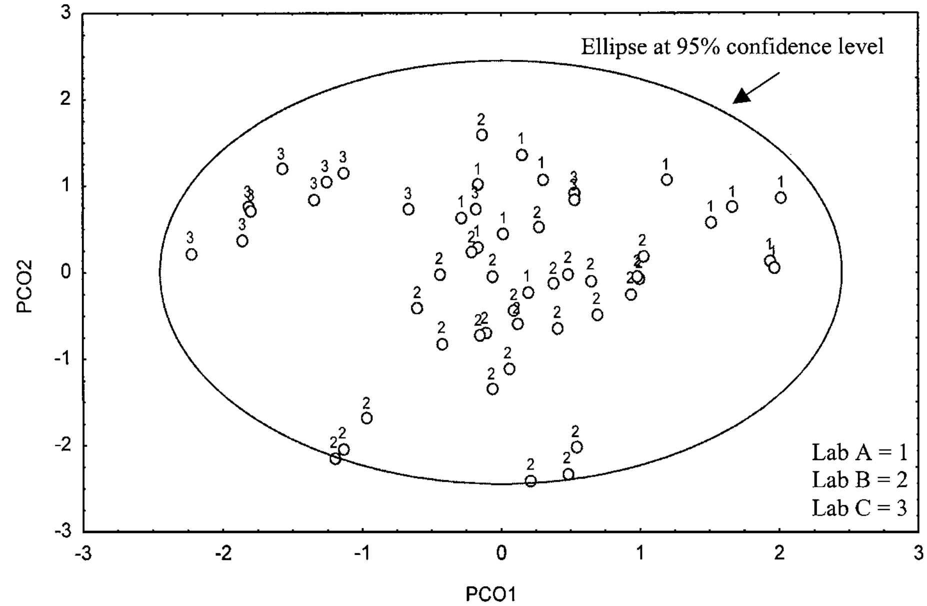

Figure 2. Plot of two principal components for Ohio red clay.

CONCLUSION

The results reported in this paper show unequivocally that elemental abundances measured by INAA at the three laboratories agree very well over a wide range of composition. This agreement means in the first instance that the laboratories can utilize each other data set with great confidence.

ABBREVIATIONS

INAA, instrumental neutron activation analysis; NIST, National Institute of Standard and Technology; SRM, standard reference material; REE, rare earth elements; PCA, principal component analysis, IAEA, International Atomic Energy Agency; RSD, relative standard deviation; RE, relative error.

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