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STANDARDISATION OF ELEMENTAL ANALYTICAL TECHNIQUES APPLIED TO PROVENANCE STUDIES OF ARCHAEOLOGICAL CERAMICS –
AN INTER LABORATORY CALIBRATION STUDY

A. Hein[a*], A. Tsolakidou[b✣], I. Iliopoulos[c], H. Mommsen[d], J. Buxeda i Garrigós[b], G. Montana[c], V. Kilikoglou[a]

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[*] Corresponding author. Tel. 0030-1-6503303; fax: 0030-1-6519430; e-mail: hein@ims.demokritos.gr

[✣] Present address: Laboratory of Archaeometry, N.C.S.R. "Demokritos", 15310 Agia Paraskevi, Greece

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G. Montana[c], V. Kilikoglou[a]

[a] *Laboratory of Archaeometry, N.C.S.R. "Demokritos", Agia Paraskevi, 15310 Attiki, Greece*
[b] *Equip de Recerca Arqueomètrica, Dept. de Prehistòria, Història Antiga i Arqueologia, University of Barcelona, C/ de Baldiri i Reixac, s/n, 08028 Barcelona, Catalonia, Spain*
[c] *Dipartimento di Chimica e Fisica della Terra ed Applicazioni alle Georisorse e ai Rischi Naturali, University of Palermo, Via Archirafi 36, 90123 Palermo Sicily, Italy*
[d] *Institut für Strahlen- und Kernphysik, University Bonn, Nußallee 14-16, 53115 Bonn, Germany*

Abstract

Chemical analysis is a well-established procedure for provenancing of archaeological ceramics. Various analytical techniques are routinely used and large amounts of data have been accumulated so far in data banks. However, in order to exchange results obtained by different laboratories the respective analytical procedures need to be tested in terms of their inter-comparability. In the present study

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[*] Corresponding author. Tel. 0030-1-6503303; fax: 0030-1-6519430; e-mail: hein@ims.demokritos.gr
[✣] Present address: Laboratory of Archaeometry, N.C.S.R. "Demokritos", 15310 Agia Paraskevi, Greece

the schemes of analysis used in four laboratories, which are involved in archaeological pottery analysis on a routine basis, are compared. The techniques under investigation are neutron activation analysis (NAA), X-ray fluorescence analysis (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). For this comparison series of measurements on different geological standard reference materials (SRM) were carried out and the results were statistically evaluated. An attempt is also made towards the establishment of calibration factors between pairs of analytical set-ups in order to smooth the systematic differences among the results.

Keywords: *inter-laboratory comparison, neutron activation analysis, X-ray fluorescence analysis, inductively coupled plasma spectrometry, standard reference materials, archaeological ceramics*

Introduction

A common approach to the determination of the provenance of ancient pottery is to analyse it chemically and then compare the chemical profiles with ones of known provenance. Provenancing of ancient pottery by chemical analysis is based on the "Provenience Postulate" which assumes that the chemical variability among natural sources of raw materials, exceed the variability within a given source [1]. In terms of pottery, it assumes that the within one population (group) variability should be smaller than the variability between two different populations [2]. This requires analytical techniques with high "discriminative power", high precision, in order to achieve necessary resolution between different but compositionally similar populations.

In general, the first step in provenance studies of pottery is the definition of the chemical composition (chemical fingerprint) of material of known origin, in order to form reference groups. These are chemically established groups of pottery of known or assumed provenance and are representative of pottery ware types of a certain production area. At a second stage, the chemical compositions of objects of unknown provenance are compared to those of the reference groups. As was already mentioned, the material of known origin is usually pottery of known provenance, judged by archaeological criteria [3], but occasionally clay deposits are used [4, 5]. However, pottery is preferred over clay because many factors (refining of the raw materials, mixing, tempering etc.) complicate the direct comparison between the composition of the raw material and that of pottery [6, 7, 8].

All the analytical techniques used for the characterisation of geological materials, have been also applied so far for the chemical analysis of pottery, in order to determine its provenance. The first analytical projects concerning the analysis of pottery were carried out with Optical Emission Spectrometry (OES) [9] and later with Neutron Activation Analysis (NAA) [10] and Atomic Absorption Spectrometry (AAS) [11]. Nowadays, the most widely employed technique in pottery provenance studies is NAA, followed by X-Ray Florescence Analysis (XRF) and in a lesser extent (and as an alternative to the analysis by OES and AAS) by Inductively Coupled Plasma Spectrometry (ICPS). However, several analytical traditions have been developed regarding the kind of pottery analysed and the chronological period it belonged to. As an example, in archaeometric studies performed around the Mediterranean, NAA has been mainly used for the analysis of prehistoric pottery though extensive data banks of XRF results exist for roman pottery. This situation is changing recently and data from both techniques, as well as ICP, are generated for several types of pottery.

For many years, the data produced by projects concerning the analysis of ancient pottery were of interest usually only to the laboratory that generated them. The different laboratories very rarely interacted in terms of exchanging results and comparing data. But with time, data banks as well as the number of reference groups for specific types of pottery increased considerably and it became evident that data should be exchanged among laboratories, in order to avoid duplications. In order for this to be achieved it was important to investigate the extent to which the data generated by different techniques and in different laboratories could be compared. Aiming at this, several studies were undertaken. Although most of the studies concerned comparisons between the results of different laboratories using the same technique [12, 13, 2], studies had been also carried out comparing the results obtained by different techniques [14, 15, 16, 17, 11, 18, 19].

The comparative studies that are mentioned above were all of a small range. The comparisons were performed either between two laboratories that were employing the same technique, or between two different techniques, and usually achieved by analysing a limited number of common samples (pottery samples or standard material).

In this paper we report the results of a wide range standardisation (intercalibration) study undertaken by four laboratories participating in a European Union project (GEOPRO). The standardisation was carried out among laboratories that use routinely the same or different techniques in the chemical analysis of pottery. Four geological reference materials and one pottery reference material were used for the study. The techniques employed were NAA, used routinely by two out of four laboratories, XRF, used routinely by two out of four laboratories, and ICP-OES and ICP-MS, used by one laboratory.

The laboratories that took part in the exercise and the techniques employed in each laboratory are listed below:

- Laboratory of Archaeometry, National Centre for Scientific Research "Demokritos", Greece (NAA)
- Equip de Recerca Arqueomètrica, University of Barcelona, Catalonia, Spain (XRF, ICP-OES, ICP-MS)
- Institut für Strahlen- und Kernphysik (ISKP), University of Bonn, Germany (NAA)
- Dipartimento di Chimica e Fisica della Terra ed Applicazioni alle Georisorse e ai Rischi Naturali, University of Palermo, Italy (XRF)

Measured materials

Five materials were chosen for the inter-calibration exercise. Four of them were geological reference materials showing different ranges of elemental concentrations and satisfying the homogeneity requirements [20, 21]. The fifth material is an in-house pottery standard used by one of the laboratories for calibration purposes. All the materials are of similar nature which is very close mineralogically and chemically to pottery and for this reason they are used as standards in ceramic analyses:

- **SOIL-7** (*soil-reference material with non-certified values for the minor and major elements*) provided by the *IAEA (International Atomic Energy Agency, Vienna, Austria)*

- **SL-1** (*lake sediment-reference material with recommended values for all the elements*) provided by the *IAEA*
- **SRM 679** (*brick clay-certified material*) provided by the *NIST (National Institute of Standards & Technology, USA)*
- **SRM 2711** (*Montana soil-certified material)* provided by the *NIST*
- **Bonn Standard** (*ceramic material*) in-house standard, basically based on the **Asaro-Perlman Standard** (Berkeley standard, [10]) but additionally doped with As, Br, Co, Ni and Zn.

In Table 1 the certified or recommended concentration values of the five materials are shown. Ten different replicates of each reference material were measured with each particular set-up (eleven replicates were measured for *SL-1* and *Bonn Standard* in the N.C.S.R. "Demokritos" and twelve replicates for *SRM 2711* in Bonn) in order to produce statistically relevant results and to estimate the analytical reproducibility. All standards were analysed by each laboratory, except for the *Bonn Standard* not measured in Bonn and SOIL-7 not measured at Demokritos, as both were used for the NAA calibration at the respective set-up. Furthermore the *Bonn Standard* was not analysed by XRF.

Definitions and terminology

In the following section the use of some terms regarding chemical analyses of pottery will be illustrated. Basically, the nomenclature suggested by the International Union of Pure and Applied Chemistry IUPAC [22] will be followed.

Precision, accuracy

The precision corresponds to the variation of independent results, obtained by applying on the same material the same experimental procedure under stipulated conditions [22]. Thus, a measure of the precision is the standard deviation of repeated measurements.

The term accuracy corresponds to the proximity of the analytical result to the true value. The true value is the ideal value that would have been measured if all causes of measurement errors had been eliminated.

Detection limits

When the suitability of different methods to measure concentrations of particular elements is evaluated, the detection limits should be considered as well. Every element, which is present in the sample, will give a signal consisting of a functional relation, which is given by the analytical procedure, and an error structure, which is commonly assumed to follow a normal distribution.

The first value to know, in order to define the detection limit, is the critical level. This corresponds to the minimum significant signal, which, in the case of a missing element and concurrent presence of all others, represents the largest expected statistically significant measured value for the missing element. It is also called lower limit of detection [23]. In case of a normally distributed background with a standard deviation σ_B a measured value of $3\ \sigma_B$ above the mean background signal ξ_B would for example give a 99.87 % probability that this signal corresponds to the presence of the measured element. The minimum detectable quantity is the minimum value that can be confidently detected and quantitatively evaluated. For this reason this value is also called limit of determination. Common values which are in use are $\xi_B + 3\ \sigma_B$ for the lower limit of detection and $\xi_B + 6\sigma_B$ for the limit of determination [23], which are the limits we adopted in the present work.

Analytical Methods

NAA in Bonn and at the N.C.S.R. "Demokritos"

Two NAA laboratories took part in this study, the one at the ISKP in Bonn and the other at the N.C.S.R. "Demokritos". Both have been working routinely on pottery analyses for many years [24, 25].

In Bonn about 80 mg of the powdered sample was mixed with about 40 mg of pure cellulose and pressed to a pill of 10mm diameter to provide reproducible measurement geometry. A batch of 43 pills, including one blank (pure cellulose pill), two $CaCO_3$ samples (because of the low Ca concentration in the Bonn Standard) and four samples of the Bonn Standard were irradiated for 90 min at the FRG research reactor in Geesthacht with a thermal neutron flux of about $5 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot s^{-1}$. Each sample was measured four times in the period between 4 and 25 days after its irradiation, with regard to different lifetimes of the radionuclides. Two different Ge γ-detectors were in use, which covered the energy ranges 40-400 keV and 100-1800 keV.

At the N.C.S.R. "Demokritos" about 130 mg of the powdered and dried sample were filled in a polyethylene vial, which was heat-sealed afterwards. The vials were irradiated for 45 min in the "Demokritos" swimming pool reactor, at a thermal neutron flux of about $3 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot s^{-1}$, in batches of 10, including two SOIL-7 standard samples. Each sample was measured twice, 7 and about 20 days after the irradiation. A Ge γ-detector covering the energy range of 80-1600 keV was used for the measurements.

In Table 2 the measured elements are listed with the estimated lower detection limits ($\xi_B + 3\sigma_B$). Except for Fe, Nd, Sb and U the same γ-lines were evaluated in both laboratories. In Bonn three more elements were evaluated: Ga and W, which were not measured at Demokritos because of rather small lifetimes, and Ti, which was evaluated in Bonn by using the ^{47}Sc line considering an (n,α)-reaction [26]. Since the Zr concentration of the Bonn standard is not known, it was determined with large error by a flux monitor.

Besides the mentioned lines, which are supposed to be the most suitable, routinely further lines of the same nuclides or the same lines in different measurements are evaluated in Bonn, in order to have additional control and to detect discrepancies between the measurements.[24, 27].

XRF Barcelona

The analysis by X-Ray Fluorescence was performed at the Scientific-Technical Services of the University of Barcelona. For the determination of the major and minor elements the sample was fused to a glassy pill (30mm diameter) by mixing 0.3g of dry sample with 5.7g of $LiBO_4$ (dilution 1/20) and firing it at a temperature of 1150^0 C using a high frequency induction furnace Perl'X-2. Every sample was prepared in duplicates and each pair of duplicates was treated as a single sample. For the determination of the trace elements the sample was prepared as a powder pellet by mixing 5g of dry sample with 2ml of a solution of a synthetic resin (Elvacite 2044, 20% in acetone). The mixture was homogenised until dryness, in an agate mortar. The powder pellets were made by adding the mixture in an aluminium capsule containing boric acid and by pressing the capsule in a Herzog press under a pressure of 200kN for 60s.

The fluorescence intensity was measured with a Philips PW 2400 wavelength dispersive spectrometer with a Rh excitation source and the quantitative analysis of the elements was performed with a calibration line made of 56 International Geological Reference Materials.

The lower limits of the concentration ranges of the elements that are determined by XRF according to the calibration done with the standards mentioned above are shown in Table 2.

XRF in Palermo

In Palermo, analytical measurements were obtained by the X-Ray Fluorescence facilities available in the Dipartimento di Chimica e Fisica della Terra of the University of Palermo. For both the major and trace elements determination a powder pellet was prepared mixing approximately 5 g of homogenized sample with 0.75 ml of a 4% solution Mowiol N50-98 (a polyvinyl-alcohol binder media, transparent in X-Rays). The mixture was subsequently compressed on a base of boric acid at about 20 tons/in^2 by a hydraulic press, obtaining a circular powder pellet of 4 cm in diameter.

The measurements were completed using a Philips PW 1400 wavelength dispersive X-Ray fluorescence spectrometer. A chromium (Cr) target was run at 50kV/50mA (2.5kw) for the major elements, while for the trace elements a Rh and a W anode tubes were alternatively used. Quantitative analysis was obtained through the construction of calibration lines made using 52 International Geological Reference Materials (USGS and NBS standards).

Also for the XRF in Palermo the lower limits of the concentration ranges of the elements that are determined are shown in Table 2.

Analysis by ICP-OES and ICP-MS

The dissolution of the samples for the determination of the elemental concentrations by both set-ups was done by acid attack in open beakers according to the following methodology: approximately 0.13g of exactly weighted dry sample were placed in a PTFE beaker. Then 5ml of HNO_3 (65%) and 5ml of de-ionised water were added and the beaker was heated in a sand bath for 1h with reflux. After cooling, 2ml of $HClO_4$ together with 10ml of HF were added and the solution was left covered for at least 12h at room temperature. The beaker was uncovered and the solution was evaporated almost to dryness. The addition of $HClO_4$ and HF and the evaporation steps were repeated until all SiO_2 was removed. After all SiO_2 had been removed, 5ml of $HClO_4$ were added and evaporated to dryness. At this final step the beaker was cooled, and 2.5ml of HNO_3 together with 2.5ml of de-ionised water were added and heated with a reflux in a sand bath until total salt dissolution. Finally the beaker was cooled and its content was diluted with de-ionised water in a volumetric flask up to 25 ml.

The measurements for ICP-OES were carried out with a Perkin Elmer Optima 3200 RL, Spectrometer, with a 40MHz RF-generator and working power between 750-1500W (simultaneous). The instrument was used for the measurement of all the elements except Na. The determinations were performed in a 1:10 dilution of the solution received after the dissolution procedure.

The calibration of the instrument was carried out using 1M HNO_3 as a blank solution and four multi-element standard solutions. The multi-element standard solutions contained all the elements determined by ICP-OES except from Na. The four standard multi-element solutions were prepared by diluting a concentrate multi-element standard solution that contained the elements: Al, Fe, Ca, Mg, K, Ti, Na, Mn, Ba, Ni, Sr, Sc, Co, Ce, La. For the preparation of the concentrate standard solution, mono-element CPI International standards were used.

The Na determination was performed by the Thermo Jarrell Ash spectrometer (simultaneous and sequential), with a 27.12 MHz RF-generator and working power between 750-1750 W. The calibration was done with four standard solutions with concentrations 0.5, 2.5, 5 and 10ppm Na.

The ICP-MS measurements were performed with a Perkin-Elmer model Elan-6000 spectrometer, with a cross flow nebulizer and a 40MHz RF-generator and a working power between 600-1600 W. Like in ICP-OES, prior the measurements the solutions were diluted in 1:10.

The instrument was calibrated with a 1M HNO_3 solution which was used as a blank and four multi-element standard solutions in a 1M HNO_3 matrix. that contained: Mn, Ti, Ba Cr, Rb, Sr, Zr, As, Ni, Sc, Th, Sb, Co, Nb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. For the preparation of the multi-element solution mono-element CPI International standard solutions were used.

In Table 2 the lower detection limit for the measurements by ICP-OES and ICP-MS is defined by the equation $C_L=3\sigma_B/S$ where σ_B is the standard deviation of the signal and S is the sensitivity, that is the slope of the calibration line that relates the intensity of the signal to the concentration ($S=I_C/C$) [28].

The analyses by ICP-OES and ICP-MS were performed at the Scientific-Technical Services of the University of Barcelona

Results and Discussion

Precision

In Table 3, the average coefficients of variation CV (standard deviation in percent) of the whole range of the determined element concentrations are presented. In the case of ICP-MS and ICP-OES the values correspond to the average of five data series (all five reference materials), in case of XRF (Bonn Standard was not measured) and NAA (Bonn Standard and SOIL-7 were not measured by NAA in Bonn and in the N.C.S.R "Demokritos" respectively) to the average of four data series respectively. In this context the average CVs of the measured element concentrations are an estimation of the measurement precision. However, it has to be considered that the CVs might not be homogeneous over a broad range of concentrations due to the fact that some concentrations may be close to the LDL or due to existing matrix effects. The average CVs presented here are valid for the concentration levels of the measured materials, which actually correspond to concentration levels in ceramics. The determined CVs were basically homogeneous with few exceptions, such as the NAA measurements of Ca values which were close to the LDL.

The measurements performed by XRF in both laboratories gave values with high precision for the majority of the elements determined. The exceptions were the high CVs for Sn and W measured in Barcelona but they were due to the fact that the measured concentrations for both elements were very close to the LDL of the setup and below the limit of determination. The same was valid for La and Y in Palermo.

A similarly high precision could be ascertained concerning the results obtained by NAA in the two respective laboratories. Apart from a few exceptions, such as Ba, Nd and Zr, the measured element concentrations showed average CVs clearly below 10%, most of them lower than 5 %. In the case of the mentioned elements the small intensities of the evaluated peaks, caused by the particular activation yield, resulted in poor counting statistics. Furthermore the measurement of these isotopes was affected by interferences that resulted from the ^{235}U fission decay induced by thermal neutrons. The inadequate counting statistics in the case of Ga, K and W was caused by the small lifetimes of the respective radioisotopes. The evaluation of ^{47}Ca was interfered by a strong ^{59}Fe peak, which was expressed in the rather high LDLs in Table 2. Especially the NAA in Bonn showed a high CV for Ca (almost 20%). In Bonn, besides of the use of an additional $CaCO_3$ standard, the alternatively used Ca evaluation with a ^{47}Sc peak, which was also produced by Ti, could cause uncertainties. Differences in the average standard deviations between the two laboratories, like in the case of Ni, could be explained with the different set of measured standards. Bonn Standard contains higher Ni amounts than SOIL-7. Furthermore Ni is determined by a nuclear reaction induced by the small part of the fast neutron flux, which was apparently lower in the research reactor Geesthacht compared to that of the reactor at Demokritos.

The precision for the analysis by ICP-OES is good for the majority of the elements determined with the exception of La and Ni. The measurement of all the elements (major, minor and traces) by ICP-OES, for time economy's sake, was carried out in a 1:250 dilution of the solid sample. This helped the more precise determination of the major elements but it created problems for the elements that were present in trace amounts in the sample. Thus the precision of La and Ni which are both present as traces in the materials measured was low but it was correlated to the relative amount of the element in the sample.

The data generated by ICP-MS gave high precision values for the majority of the elements. The exceptions were: Cr, Ni, Ta, Tm and U. The problems encountered in the determination of some of them were due to the procedure that was used during the preparation of the samples in a liquid form. As mentioned above, the samples were dissolved with an acid attack in open beakers with HF and $HClO_4$. Some of the elements in specific oxides are extremely resistant to the acid attack (Zr, Cr) and as a consequence the results of the analysis for these elements were neither accurate nor precise. Additionally, during the evaporation with HF of the samples, volatile fluorides of some elements (e.g Cr) were produced and the concentration of these elements in the resulting solution was lower than the expected one. This generation of the fluorides had a negative effect on the precision and the accuracy of the results.

Accuracy

Even though there are a few elements that were not determined with high precision, all individual values were considered at first after calculating the median and the mean values for the respective element concentrations. Median values were used along with mean values, in order to disregard analytical outliers when estimating the overall accuracy. The median value is the value midway the frequency distribution and it offers considerable resistance to the effects of isolated outliers [29, 22]. In Table 4 the resulting chemical compositions of all analysed materials are presented. Besides the median values (m_{total}), the lower and upper deciles are listed, which exclude the lowest and the highest 10 % of the measurement values respectively. Correspondingly the uncertainties of the mean values (M_{total}) are estimated by the standard deviations.

The listed mean values are in most cases in close agreement with the median values, showing absolute differences clearly below 5%. The exceptions are Ga, Ni, P, Ta, Th, W and Zr and for particular materials Ca, Co and Lu, which exhibit absolute differences of 10% and higher. These discrepancies and the coinciding high standard deviations indicate outlying measurement values by particular set-ups.

Most of the given values for the reference materials (certified or recommended) were close to the median and mean values of the presented measurements, taking in to account the uncertainties. The agreement, in most of the cases, between the measured and the reference values was remarkable, even if a few discrepancies were observed.

As far as the reference material SL-1 is concerned, the discrepancies referred to Al and Mg. However, for both elements the reference values for this material were given by IAEA for information purposes only.

For the SRM679 (Brick Clay) the only measured value that did not agree with the reference value was the one for Zn, which again was non-certified. For the SRM 2711 (Montana-Soil) discrepancies between measured and reference values were found for Cs, Hf and Zn. Whereas in the case of Cs and Hf the reference values were non-certified, the reference value for Zn was a certified one. For SOIL-7 deviations from the reference values were observed for P, which was non-certified, but for As, Ho, Nd, U and Zn, that had certified reference values, as well. The determined value for Cu was distant from the certified one that in any case was close to the LDL of the XRF in Barcelona.

The fifth material, Bonn Standard, which is an internal pottery standard, was a special case because it was not certified by any international organisation. Additionally, this material was only measured by NAA in one laboratory (NCSR Demokritos), and by ICP-OES and ICP-MS. The general trend in the results was that the measured values were slightly lower than the reference values. The majority of the measured values available come from ICP spectrometry and during the preparation procedure, problems were encountered for the dissolution of the material. Thus, it was necessary to submit the material to repeated evaporations and this might had resulted to a loss of volatile components. More specifically, the values for Ni, Rb, Sc and Th were lower than the given values.

Discussion

In order to examine the analytical results of the different set-ups in detail, a series of frequency distribution plots for all elements determined was produced and evaluated. As an example three series of these histograms are presented here, the histograms for Fe, K and La. These three elements were selected for the presentation because they were determined by most of the set-ups and because they represent both major and trace elements. Moreover, they reveal the inadequacies of the set-ups in the determination of specific elements.

In Figure 1 the respective histograms for Fe are shown. It can be observed that the values of the two XRF set-ups are in a close range each. They gave similar mean values as well, except in the case of SOIL-7 in which the XRF in Palermo gave a significantly higher value than the rest. Compared to the XRF set-ups the NAA set-ups show slightly larger spreads. The ranges of the values are overlapping and no significant differences are recognisable, in terms of clear gaps between the populations. The NAA values seem to be slightly lower than the XRF values. The values measured by ICP OES show the largest spreads and tend to be lower than the other values.

In Figure 2 the histograms for the K concentrations are presented. The values determined by the two XRF set-ups are very close for all the materials measured with a small deviation in the case of SOIL-7. The ICP-OES results agree with the results obtained by XRF but they show a slightly larger spread. The precision of the NAA measurements, especially in the case of the N.C.S.R. “Demokritos” as mentioned above, is low and it is reflected in the spread of the distributions.

In Figure 3 similar histograms regarding the La concentrations are shown. The concentrations measured by NAA and ICP-MS show all small spreads and give similar values, and only in the case of SL-1 the NAA values from Bonn are significantly lower. In Bonn several types of interferences are regarded, as for example ^{140}La by the production via the ^{235}U fission decay. With regard to the higher U concentration in SL-1 it is remarkable that for example the La concentration measured by NAA in Bonn is just for this reference material smaller than measured by NAA at the N.C.S.R. “Demokritos” or measured by ICP-MS. The XRF (only measured in Palermo) and ICP-OES values have larger spreads and whereas the XRF tend to give higher values the ICP- OES values are clearly lower.

The example graphs show that in some cases significant differences between concentrations measured with different set-ups can be expected. In order to explore these differences, the ratios of the mean values for elemental concentrations measured by the particular set-ups (M_{setup}) over the overall mean values (M_{total}) were determined. In the calculation that follows the M_{total} values were preferred to the reference materials’ values because a considerable number of the latter was either not certified or not given. Nevertheless, the ratios of the reference values over the M_{total} values were determined as well. Considering all analysed materials, the ratios were averaged and they are presented in Table 5, together with the respective standard deviations. In the case of the two NAA set-ups the reference materials Bonn Standard and SOIL-7 were not analysed in Bonn and Demokritos respectively. For this reason instead of M_{setup} the reference values were used, assuming that analysis of the calibration standard would have produced the respective reference values. The ratios represent the average deviations of the M_{setup} from the M_{total} . The presented average ratios illustrate primarily the systematic differences between the different set-ups. In this context the significance of the differences can be estimated with the standard deviations of the ratios. If the absolute difference is higher than two standard deviations then it is considered as significant. Additionally the average ratios of the x_{ref} and the M_{total} indicate in the cases of significant differences inaccurate measurements.

Whereas in some cases all ratios were close to one, like for Eu, Fe, K or Rb, in other cases there were obvious differences, like for As, Ce, Na, Nd, Sc, Ti, U and Zr. For these elements the concentrations measured with particular set-ups gave average ratios, which were significantly different to one. In these cases the absolute value of the difference between the ratio and one is at least equal to two standard deviations. The table also provides information on the deviation of each set-up from M_{total} and x_{ref}. For example, for elements, such as Ba, Co, Cs, La, Sb, Sm and Th, only one set-up gave an average ratio different to one, whereas the results from the other set-ups agreed to each other. In the case of Zn the ratios for the set-ups were close to one but the ratios for the reference values were significantly larger than one, which indicates that some set-ups gave lower values.

The average ratios for most of the elements were calculated with small standard deviations. However, for some elements like Ni, Ta, W and Yb the standard deviation was high. The Ni concentration was determined by all six set-ups but, apart from XRF, with relatively low precision. The W value was only measured by NAA in Bonn and XRF in Barcelona and the precision was rather low for both set-ups. In the case of Ta and Yb, which were measured each by the two NAA set-ups and by ICP-MS, the uncertainties of the ratios are mainly due to the ICP-MS values. A direct comparison between the values from the NAA at the N.C.S.R. “Demokritos” and the NAA in Bonn gave different average ratios with smaller spreads (Ta: 1.20 ± 0.02, Yb: 1.08 ± 0.03).

The next step was, to calculate average ratios between the results of pairs of set-ups. These ratios could be used in order to establish factors for adjusting the results between particular set-ups.

In practical terms the correction factors for the two NAA set-ups were tested by comparing chemical data of archaeological ceramics analysed at Demokritos, with the chemical ceramics databank of Bonn. More specifically, a group of 5 Bronze Age pottery sherds, coming from Macedonia - Northern Greece, which were analysed at Demokritos, in order to assign their provenance was compared with the large databank of over 3,000 profiles of greek Bronze ceramics, that have been analysed in Bonn. In a first attempt it seemed that the group of 5 sherds was close to a chemical pattern of pottery from Thebes (Central Greece), but some significant differences existed among particular elements. This can be observed in Figure 4(a) where the elemental differences of this group to the Theban pattern are expressed in units of average standard deviations. The most significant difference in this case is in Sc, which differs 5.5 standard deviations. After the application of the correction factors most of the differences were reduced to a level which allows to suggest that this group may have come from Thebes (Figure 4b). The elements that were influenced the most were Sc, Ta and U.

In general, it seemed that there existed a correlation between the spreads of the average ratios (Table 5) and the precision of the particular set-ups (Table 3). Since the listed average ratios referred to M_{total} values, inaccurate measurements by particular set-ups affected the rest of the ratios as well (e.g. the Ta $M_{ICP\text{-}MS}$). The question was raised if the results of particular set-ups had to be disregarded. Taking into account the values of Table 3 and Table 5, the element concentration values that should be eliminated are:

- NAA in Bonn: Ga, Ni, Zr
- NAA in Demokritos: Zr
- ICP-OES in Barcelona: Ni
- XRF in Barcelona: P and W
- ICP-MS in Barcelona: Ta

Apart from ICP-MS, the techniques that were used in the inter-calibration study presented here are commonly employed in the chemical characterisation of ancient pottery. Taking into account their requirements and potentials in the analysis of pottery, the analysts use them routinely for the determination of specific elements. As things have developed, regardless of the number and the kind of the elements that can be measured by each technique, there is a clear-cut use of their employment in the analysis of ceramics. Thus, NAA is mainly used for the determination of the trace and especially the rare earth elements. By XRF major, minor and trace elements are determined but some of the trace and mainly the rare earth elements are not taken into account in the further treatment of the results. Similarly, most of the trace elements determined by ICP-OES, are disregarded in the statistical evaluation of the results. Since ICP-MS has proved to have an enormous potential in the determination of trace elements it has started to being used as such in the analysis of pottery. Conclusively, the main focus in the evaluation of the results of the inter-calibration study is on the comparability of the results by techniques that are used for the determination of the same kind of elements. This means that the most positive result was that the measurements of the two NAA set-ups inter se, along with the measurements obtained by ICP-MS, as well as, the outcome of the two XRF set-ups inter se and compared to the outcome of the ICP-OES were in good agreement as it can be seen in Tables 5 & 6.

In order to assess the significance of the differences between the pairs of techniques, which are mentioned above, two-tailed t-tests were carried out on the raw as well as the corrected data of the measured materials. For the two NAA set-ups there were no statistically significant differences (5% level of significance) for Ba, Ca, Ce, Cs, Fe, K, La, Lu, Tb and Yb for the raw data of SRM 2711. After the application of the correction factors the elements As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, K, La, Lu, Nd, Rb, Sc, Sm, Ta, Tb, Th, U, Yb, Zn and Zr presented no statistically significant differences at the 5% level. For the elements Hf, Na and Sb the null hypothesis was accepted at the 1% level. For the comparison of the NAA in Bonn with the ICP-MS results no statistically significant differences were observed at the 5% level for the elements Ba, Ce, Lu, Th, Ti and U applying the t-test on the raw data of SRM 2711. On the corrected data and for the same level of significance there were no differences for the elements As, Ba, Ce, Co, Cr, Cs, Eu, La, Nd, Ni, Rb, Sb, Sc, Sm, Ta, Tb, Th, Ti and U. However, there were significant differences in the 1% level for Lu, Yb and Zr. From the above-mentioned results it is clear that there is a total agreement among the results of the three set-ups after the application of the correction factors.

The direct comparison of the raw data obtained for the SRM 2711 by the two XRF set-ups showed that there were no significant differences at the 5% level for Ba, Ce, Si, V, Y and Zr and for Sr at the 1% level. The application of the correction factors did not improve the agreement. Especially for the major elements unexpected statistically significant differences occurred. This can be explained by the fact that both set-ups produced results with very low CVs and in the t-test the mean values were considered as different, even though they were very close to each other. In fact the ratios of the mean values of the major elements were extremely close to one. The comparison of the XRF in Barcelona and ICP-OES results for the SRM 2711 after the application of the correction factors showed no statistically significant differences at the 5% level for Al, Fe, K, Mg, Na and Sr and for Ba and Ni at the 1% level.

An important point that has to be noted is that the majority of the setups under investigation in this study (XRF and NAA) were calibrated with different secondary standards. This means that the possible errors during the certification of the standards used for the calibration of each setup had been regenerated in their results. The agreement of the analytical results would be definitely improved, if the techniques were calibrated with the same standard. Thus, our next task, following the inter-laboratory calibration study, is the production of a new calibration standard for pottery analyses and the establishment of reference values. This project is in progress and the results will be published soon.

Conclusions

The results of the study indicated that, by using the presented analytical set-ups, the measured elemental concentrations widely agreed to each other. Even though some discrepancies emerged, these could be explained. As a result of the comparison, systematic differences between results of different set-ups could be smoothed with the use of the correction factors. These factors derived from average ratios between the median values, as measured by each particular set-up, and the overall median values. More distinctive factors could be found by comparing the particular set-ups directly.

The accuracy of the set-ups could be assessed by comparing the median values to the given reference values of the measured standard materials. In most of the cases the median values were in agreement with the reference values. In general terms, when a disagreement between the measured and the reference values was determined, the reference values were not certified.

However, even if some of the reference materials used in the study had non-certified values, this study will give the opportunity to the participants to calibrate other analytical set-ups by analysing the same materials.

In the present study four different techniques were compared. The comparison of set-ups, which were using the same techniques, was more straightforward and resulted in more distinct calibration factors. Nevertheless, it was possible to find calibration factors for set-ups, using different techniques, and these calibration factors decreased the differences between the particular results significantly. An important outcome of this inter-laboratory study was that there was a good agreement between the results obtained by different techniques that determined similar elements and that this agreement could be improved with the use of the correction factors. In this way results obtained in different laboratories can be used jointly.

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	SOIL 7			**SL-1**		**SRM 679**		**SRM 2711**		**Bonn Standard**	
	value	*confidence interval*		*value*	*error*	*value*	*error*	*value*	*error*	*value*	*error*
Al (%)	4.7	4.4	5.1	8.9		**11.01**	0.34	**6.53**	0.09		
As	**13.4**	12.5	14.2	**27.5**	2.9			**105**	8	38.2	2.7
Ba	159	131	196	**639.0**	53.0	**432.2**	9.8	**726**	38	674.3	30.0
Ca (%)	16.3	15.7	17.4	0.25		**0.1628**	0.0013	**2.88**	0.08	0.28	
Ce	**61**	50	63	**117.0**	17.0	105		69		86.72	4.20
Co	**8.9**	8.4	10.1	**19.8**	1.5	26		10		21.93	0.23
Cr	**60**	49	74	104	9	**109.7**	4.9	47		115.3	4.3
Cs	**5.4**	4.9	6.4	7.01	0.88	9.6		6.1		9.31	0.62
Cu	**11**	9	13	30.0	5.6			**114**	2	72.0	6.1
Dy	**3.9**	3.2	5.3	7.46	2.12			5.60			
Eu	**1.0**	0.9	1.3	1.6		1.9		1.1		1.37	0.36
Fe (%)	2.57	2.52	2.63	**6.74**	0.17	**9.05**	0.21	**2.89**	0.06	1.159	0.014
Ga	10	9	13	24				15		48.8	5.1
Gd				12						5.6	1.7
Hf	**5.1**	4.8	5.5	4.16	0.58	4.6		7.30		6.12	0.43
Ho	**1.1**	0.8	1.5	1.3				1			
K (%)	1.21	1.13	1.27	1.5		**2.433**	0.047	**2.45**	0.08	1.337	0.040
La	**28**	27	29	**52.6**	3.1			40		48.94	0.49
Lu	0.3	0.1	0.4	0.540						0.468	0.040
Mg (%)	1.13	1.10	1.18	2.9		**0.7552**	0.0088	**1.05**	0.03		
Mn (%)	**0.0631**	0.0604	0.0650	**0.346**	0.016	0.173		**0.0638**	0.0028		
Mo	2.5	0.9	5.1	1.3				1.6		6.39	
Na (%)	0.24	0.23	0.25	0.172	0.012	**0.1304**	0.0038	1.14	0.03	0.196	0.003
Nb	12	7	17	17							
Nd	**30**	22	34	43.8	2.8			31		35.6	
Ni	26	21	37	44.9	8.0			**20.6**	1.1	419	30
P (%)	0.0460	0.0460	0.0462	0.0831		0.075		**0.086**	0.007		
Pb	**60**	55	71	37.7	7.4			**1162**	31		
Rb	**51**	47	56	**113.0**	11.0	190		110		74.9	6.7
Sb	**1.7**	1.4	1.8	1.31	0.12			**19.4**	1.8	1.831	0.054
Sc	**8.3**	6.9	9.0	17.3	1.1	22.5		9		23.43	0.38
Si (%)	18.0	16.9	20.1			**24.34**	0.30	**30.44**	0.19		
Sm	**5.1**	4.8	5.5	9.25	0.51			5.9		6.13	0.13
Sn				4							
Sr	**108**	103	114	80		**73.4**	2.6	**245.3**	0.7		
Ta	**0.8**	0.6	1.0	1.6						1.67	0.05
Tb	**0.6**	0.5	0.9	1.4						0.78	
Th	**8.2**	6.5	8.7	**14**	1	14		14		15.64	0.44
Ti (%)	0.30	0.26	0.37	**0.517**	0.037	**0.577**	0.033	**0.306**	0.023	0.782	0.034
Tl								**2.47**	0.15		
Tm				0.660							
U	**2.6**	2.2	3.3	4.02	0.32			2.6		5.30	0.48
V	**66**	59	73	**170**	15			**81.6**	2.9		
W				6				3		5.08	
Y	**21**	15	27	85				25			
Yb	**2.4**	1.9	2.6	3.42	0.64			2.7		3.20	0.39
Zn	**104**	101	113	**223**	10	150		**350.4**	4.8	91.5	5.8
Zr	**185**	180	201	241				230			

Table 1

Reference values in ppm (µg/g) except indicated otherwise, for the five standard reference materials analysed. The confidence interval given for SOIL 7 and the uncertainties given for the other standard reference materials correspond to significance levels of 0.05. For a number of non-certified values no uncertainties are given. Certified values are printed in bold.

	XRF Bar	**XRF Pal**	**NAA Bonn**	**NAA Dem**	**ICP-MS**	**ICP-OES**
			LDL	*LDL*	*LDL*	*LDL*
Al	800	500				4
As			0.13	0.20	0.09	
Ba	100	100	40	30	0.010	0.3
Ca	300	200	4000	3000		0.6
Ce	13	36	1.0	0.5	0.006	
Co	5		0.10	0.08	0.020	
Cr		30	1.8	0.8	0.11	
Cs			0.2	0.2	0.016	
Cu	5					
Dy					0.06	
Er					0.022	
Eu			0.04	0.03	0.018	
Fe	490	350.000	90	60		0.5
Ga	5		1.3			
Gd					0.05	
Hf			0.13	0.10		
Ho					0.009	
K	400		200	600		20
La		20	0.05	0.04	0.005	0.13
Lu			0.03	0.01	0.016	
Mg	700	1400				5
Mn	80	150			0.023	0.16
Mo	3					
Na	700	400	2	5		2
Nb	6				0.007	
Nd			7	10	0.06	
Ni	5	15	30	10	0.03	2.4
P	40	90				
Pb	2					
Pr					0.005	
Rb	50	22	4	3	0.004	
Sb			0.15	0.03	0.04	
Sc			0.01	0.01	0.21	0.04
Si	5000	750				
Sm			0.03	0.01	0.05	
Sn	2					
Sr	20	32			0.007	0.013
Ta			0.06	0.08	0.016	
Tb			0.12	0.1	0.019	
Th	3		0.14	0.08	0.011	
Ti	60	20	1200		0.05	0.3
Tm					0.012	
U			0.2	0.2	0.010	
V	20	31				
W	5		0.3			
Y	7	13				
Yb			0.014	0.06	0.06	
Zn	20		2.3	6		
Zr	40	53	10	60	0.020	

Table 2

Comparison of the detection limits of the set-ups in the present study. Listed are the lower limits of the concentration ranges that can be measured by XRF and the estimated lower detection limits (LDL) for NAA, ICP-OES and ICP-MS. The LDLs were estimated with: $\xi_B + 3\sigma_B$. All values are given in ppm.

	XRF Bar	XRF Pal	NAA Bonn	NAA Dem	ICP-MS	ICP-OES
Al (%)	0.3	0.3				3.9
As			3.4	4.1	6.6	
Ba	4.3	3.0	**12.5**	**11.0**	3.4	4.3
Ca (%)	3.6	0.6	**19.2**	8.0		7.0
Ce	8.3	8.4	1.6	2.5	2.6	
Co	7.3		1.1	1.5	2.8	
Cr		2.1	3.3	2.5	**22.7**	
Cs			1.3	2.4	2.7	
Cu	5.6					
Dy					2.8	
Er					3.2	
Eu			2.1	2.9	2.8	
Fe (%)	0.4	0.8	1.1	1.1		3.7
Ga	3.1		**41.3**			
Gd					2.6	
Hf			2.2	2.4		
Ho					3.1	
K (%)	0.9	0.4	2.4	**10.0**		3.1
La		**10.1**	2.2	3.5	2.6	**16.3**
Lu			9.3	5.7	3.6	
Mg (%)	2.7	2.6				4.2
Mn (%)	1.6	3.8			3.6	4.8
Mo	7.1					
Na (%)	2.6	5.7	1.6	5.8		7.2
Nb	4.3				8.9	
Nd			**13.0**	**12.5**	2.7	
Ni	4.5	4.1	**22.1**	7.1	**12.4**	**31.4**
P (%)	**11.1**	2.2				
Pb	4.2					
Pr					2.7	
Rb	3.0	6.7	2.4	4.0	2.6	
Sb			5.2	4.9	7.6	
Sc			0.9	1.8	3.4	4.7
Si (%)	0.3	0.2				
Sm			6.6	5.8	2.8	
Sn	**59.6**					
Sr	2.1	4.6			2.8	4.9
Ta			3.4	4.9	**22.7**	
Tb			5.5	9.8	2.7	
Th	5.7		1.5	1.4	2.8	
Ti (%)	1.7	0.4	**25.7**		3.4	3.9
Tm					**21.0**	
U			6.6	7.9	9.9	
V	1.0	3.8				
W	**45.4**		**15.7**			
Y	2.9	9.4				
Yb			2.3	5.7	3.4	
Zn	1.4		8.8	**13.6**		
Zr	2.2	9.7	**10.4**	**18.6**	5.1	

Table 3

Average CVs (standard deviations in %) for the particular set-ups. In case of ICP- MS and ICP-OES the values correspond to the average of five data series and in case of XRF and NAA to the average of four data series respectively. CVs which range over 10% have been highlighted in bold face.

	Soil 7					**SL 1**					**brick**				
	median	*l. decile*	*u decile*	*mean*	*stddev*	*median*	*l. decile*	*u decile*	*mean*	*stddev*	*median*	*l. decile*	*u decile*	*mean*	*stddev*
Al (%)	4.80	4.32	5.10	4.75	0.33	11.0	10.0	11.1	10.8	0.4	10.9	10.3	11.3	10.89	0.40
As	15.8	14.8	16.6	15.8	1.0	30.8	29.1	31.3	31.5	2.4	9.3	8.0	10.4	9.3	1.0
Ba	160	131	175	156	19	640	581	691	633	56	436	373	482	433	44
Ca (%)	16.8	15.4	17.0	16.33	0.74	0.347	0.267	0.369	0.41	0.22	0.176	0.123	0.187	0.16	0.03
Ce	59.0	49.9	61.7	57.1	5.5	102.1	85.0	112.1	100.8	9.5	104.9	90.7	111.0	102.2	8.1
Co	8.7	8.3	11.1	9.5	1.5	20.1	19.6	22.0	20.3	1.2	26.0	25.0	26.7	25.9	0.6
Cr	53.9	50.4	66.0	57.2	6.3	105.0	99.5	115.6	105.1	11.8	96.0	59.6	103.9	91.7	17.4
Cs	5.85	5.43	6.32	5.87	0.41	6.90	6.76	7.71	7.05	0.45	9.84	9.61	11.12	10.20	0.64
Cu	5.00	4.00	5.10	4.90	0.57	25.0	24.0	25.2	24.80	0.92	28.0	27.0	30.0	28.40	1.07
Dy	3.67	3.62	3.73	3.67	0.08	6.43	6.18	6.60	6.42	0.20	6.64	6.41	6.74	6.59	0.18
Er	1.96	1.93	1.98	1.96	0.03	3.45	3.32	3.54	3.45	0.11	3.56	3.46	3.69	3.58	0.12
Eu	1.00	0.97	1.03	1.00	0.03	1.86	1.82	1.95	1.86	0.07	1.77	1.70	1.83	1.77	0.05
Fe (%)	2.55	2.41	2.72	2.56	0.13	6.96	6.51	7.29	6.93	0.30	9.04	8.79	9.35	9.05	0.24
Ga	10.0	5.1	10.1	8.4	2.3	23.0	22.0	23.1	22.8	5.4	27.0	15.6	29.6	25.5	5.1
Gd	4.98	4.86	5.05	4.96	0.09	8.58	8.31	8.91	8.61	0.28	8.69	8.47	8.84	8.67	0.21
Hf	5.09	4.91	5.37	5.11	0.18	4.70	4.64	5.01	4.72	0.22	4.53	4.35	4.65	4.51	0.13
Ho	0.67	0.66	0.68	0.67	0.01	1.18	1.13	1.22	1.18	0.04	1.21	1.18	1.25	1.21	0.04
K (%)	1.22	1.14	1.30	1.20	0.07	1.34	1.25	1.38	1.34	0.08	2.43	2.32	2.51	2.41	0.14
La	28.0	22.2	32.2	27.4	5.4	49.6	45.9	54.2	49.3	4.1	50.2	45.2	53.3	49.7	3.9
Lu	0.273	0.255	0.322	0.282	0.027	0.464	0.444	0.481	0.466	0.029	0.497	0.468	0.600	0.511	0.057
Mg(%)	1.16	0.99	1.22	1.13	0.09	0.67	0.59	0.70	0.66	0.05	0.80	0.71	0.86	0.80	0.06
Mn(%)	0.062	0.058	0.076	0.065	0.007	0.369	0.341	0.380	0.364	0.016	0.176	0.164	0.184	0.175	0.008
Na (%)	0.203	0.167	0.251	0.209	0.036	0.163	0.127	0.183	0.158	0.023	0.134	0.112	0.150	0.133	0.017
Nb	8.60	4.11	14.00	8.87	4.79	12.85	8.46	18.00	12.98	4.36	12.82	6.51	19.00	12.73	5.69
Nd	24.6	18.8	26.8	23.6	3.3	45.0	44.6	56.4	44.1	7.1	47.6	42.7	62.2	49.2	7.8
Ni	22.4	14.5	36.4	24.3	9.7	44.9	40.7	61.1	49.7	12.2	55.2	48.9	88.1	60.2	15.9
P (%)	0.061	0.053	0.075	0.062	0.009	0.116	0.102	0.175	0.132	0.033	0.070	0.051	0.123	0.081	0.032
Pb	56.5	54.9	59.1	56.7	1.9	37.5	36.9	39.2	38.0	1.5	25.0	22.9	26.1	24.7	1.5
Pr	6.81	6.64	6.93	6.79	0.14	11.84	11.45	12.17	11.87	0.37	12.42	12.13	12.76	12.45	0.33
Rb	53.2	50.2	57.0	53.4	3.0	110.9	100.5	119.1	109.8	7.7	187.0	158.0	199.1	182.5	16.8
Sb	1.84	1.72	2.02	1.85	0.14	1.33	1.30	1.46	1.34	0.10	0.81	0.68	0.88	0.80	0.08
Sc	8.00	6.56	9.16	7.96	1.06	16.40	13.20	17.01	15.81	1.76	21.75	17.22	24.08	21.18	2.55
Si (%)	17.2	16.9	17.6	17.2	0.3	24.5	24.2	24.7	24.53	0.11	24.2	24.0	24.4	24.3	0.1
Sm	4.50	3.79	5.17	4.49	0.62	8.77	8.59	9.20	8.44	0.83	8.87	8.05	9.15	8.7	0.7
Sn	3.00	1.90	5.00	3.10	1.37	3.00	1.00	4.80	2.89	2.32	3.50	0.80	5.10	3.20	1.99
Sr	105	95	115	104	8	77	70	91	78	8	74	68	82	74	5
Ta	0.78	0.66	1.26	0.90	0.30	1.23	1.19	3.59	1.83	1.10	1.27	1.06	2.58	1.51	0.57

Tb	0.670	0.618	0.711	0.665	0.033	1.097	0.992	1.245	1.10	0.10	1.162	1.019	1.204	1.141	0.078
Th	8.5	8.2	14.0	10.1	2.5	14.8	14.4	20.1	15.9	2.5	14.4	14.1	20.0	15.9	2.8
Ti (%)	0.309	0.253	0.354	0.318	0.114	0.461	0.437	0.546	0.467	0.062	0.543	0.492	0.626	0.55	0.06
Tm	0.240	0.237	0.276	0.267	0.081	0.443	0.405	0.454	0.42	0.07	0.469	0.441	0.475	0.459	0.025
U	2.21	1.88	2.32	2.14	0.18	3.94	3.90	4.58	4.0	0.5	2.68	2.50	3.17	2.776	0.313
V	62	61	65	63	2	217	185	259	221	35	195	166	235	198	32
W	2.38	1.50	4.10	2.70	1.26	2.00	1.00	2.00	1.8	0.5	2.00	1.00	2.74	1.8	0.9
Y	19.0	18.0	21.1	19.6	1.5	29.8	24.7	31.0	28.31	3.06	31.7	25.4	35.0	30.61	3.86
Yb	2.08	1.77	2.46	2.09	0.32	3.49	3.08	3.74	3.45	0.27	3.89	3.25	4.09	3.7	0.4
Zn	94	82	94	92	5	201	192	232	204	23	116	111	134	119.00	12.97
Zr	164	69	243	162	64	156	123	187	171	43	150	108	242	162	50

	montana					**Bonn**				
	median	*l. decile*	*u decile*	*mean*	*stddev*	*median*	*l. decile*	*u decile*	*mean*	*stddev*
Al (%)	6.50	6.03	6.60	6.42	0.24	16.3	15.9	17.0	16.3	0.5
As	101.7	93.1	110.5	100.9	8.8	35.3	31.7	38.1	34.8	2.8
Ba	651	603	734	663	57	690	604	734	679	53
Ca (%)	2.81	2.36	3.12	2.76	0.47	0.237	0.228	0.244	0.237	0.010
Ce	72.7	59.1	77.4	69.1	12.1	86.3	83.7	88.7	86.2	2.1
Co	10.0	9.6	11.0	10.3	1.1	22.5	21.7	23.3	22.5	0.7
Cr	42.7	37.8	45.5	42.4	3.9	82.7	25.2	107.0	78.3	30.3
Cs	6.75	6.53	7.46	6.90	0.41	9.33	8.82	10.07	9.44	0.51
Cu	100	95	104	99.60	3.50					
Dy	4.76	4.62	4.89	4.76	0.14	3.68	3.52	3.74	3.64	0.12
Er	2.70	2.62	2.83	2.72	0.09	1.88	1.77	1.92	1.86	0.08
Eu	1.09	1.04	1.14	1.08	0.06	1.33	1.27	1.37	1.33	0.05
Fe (%)	2.88	2.77	2.96	2.88	0.08	1.12	1.10	1.17	1.13	0.03
Ga	13.8	7.2	22.0	15.0	6.5					
Gd	5.89	5.72	6.12	5.93	0.20	5.51	5.29	5.54	5.45	0.12
Hf	8.20	8.03	8.50	8.22	0.30	5.97	5.86	6.09	5.98	0.12
Ho	0.90	0.87	0.94	0.90	0.03	0.64	0.61	0.65	0.63	0.02
K (%)	2.45	2.32	2.52	2.44	0.17	1.28	1.22	1.33	1.27	0.07
La	36.5	29.0	38.7	35.2	3.8	46.6	41.1	49.0	45.5	4.3
Lu	0.387	0.361	0.421	0.386	0.033	0.285	0.257	0.430	0.333	0.074
Mg(%)	1.07	0.94	1.22	1.08	0.11	0.30	0.29	0.31	0.30	0.01
Mn(%)	0.065	0.058	0.070	0.064	0.005	0.005	0.004	0.005	0.005	0.000
Na (%)	1.14	0.91	1.21	1.084	0.123	0.202	0.190	0.218	0.203	0.012
Nb	13.27	7.96	19.00	13.33	5.27	14.03	12.72	14.62	13.87	0.84

Nd	30.9	24.2	36.4	30.5	4.7	36.5	35.3	44.0	38.1	3.7
Ni	15.0	11.5	34.1	19.6	10.5	363	301	383	355	33
P (%)	0.087	0.084	0.105	0.091	0.009					
Pb	1090	1058	1115	1092	37					
Pr	8.46	8.17	8.65	8.45	0.26	10.03	9.69	10.18	9.96	0.25
Rb	116.0	99.1	123.8	114.5	10.7	69.7	64.3	71.6	68.4	2.9
Sb	19.76	18.22	21.72	19.71	1.90	1.90	1.73	2.07	1.91	0.18
Sc	9.00	6.80	9.80	8.49	1.17	20.06	15.60	21.32	18.98	2.52
Si (%)	30.3	30.2	30.4	30.4	0.1					
Sm	5.86	4.79	6.18	5.65	0.64	6.46	6.14	6.70	6.44	0.27
Sn										
Sr	229	213	255	233	16	116	109	121	115	5
Ta	1.43	1.18	2.60	1.65	0.74	4.63	1.88	5.83	3.99	1.98
Tb	0.789	0.706	0.844	0.781	0.064	0.711	0.680	0.793	0.727	0.051
Th	14.2	13.6	16.0	14.5	1.1	14.3	13.6	14.9	14.3	0.5
Ti (%)	0.289	0.247	0.330	0.30	0.07	0.833	0.789	0.897	0.835	0.045
Tm	0.357	0.351	0.380	0.370	0.039	0.236	0.221	0.249	0.236	0.012
U	2.84	2.48	3.38	2.940	0.501	5.37	4.90	5.98	5.40	0.49
V	79	78	83	80	2					
W	3.57	2.68	6.90	4.3	1.9					
Y	29.0	25.8	31.4	29.03	2.29					
Yb	3.08	2.55	3.28	3.0	0.3	1.87	1.70	3.16	2.37	0.68
Zn	302	251	340	297.05	31.82	93	75	99	89	11
Zr	262	82	339	244	91	116	101	243	167	68

Table 4

Median and mean values of the element concentrations as measured with the six analytical set-ups. Furthermore the lower and upper deciles and the standard deviations are listed, in order to estimate the ranges of measured concentrations. The values are given in ppm except indicated otherwise.

	XRF Bar		XRF Pal		NAA Bon		NAA Dem		ICP MS		ICP AES		ref. Values	
	factor	stddev	factor	stddev	factor	stddev	factor	stddev	factor	stddev	factor	stddev	factor	stddev
Al	1.01	0.01	1.04	0.02							0.96	0.03	0.96	0.09
As					1.07	0.05	0.92	0.04	1.00	0.05			0.92	0.10
Ba	0.94	0.03	1.01	0.05	0.98	0.04	1.01	0.04	1.04	0.03	1.01	0.06	1.03	0.04
Ca	0.95	0.21	0.97	0.22	1.28	0.50	1.04	0.12			0.85	0.20	0.88	0.27
Ce	0.88	0.01	0.96	0.05	1.02	0.01	1.07	0.04	1.06	0.04			1.06	0.08
Co	1.09	0.09			0.95	0.03	0.99	0.03	0.97	0.05			0.97	0.03
Cr			1.01	0.10	1.23	0.22	1.04	0.15	0.84	0.09			1.05	0.09
Cs					0.96	0.02	0.95	0.02	1.07	0.01			0.94	0.05
Eu					0.99	0.03	1.01	0.01	1.01	0.02			0.99	0.09
Fe	1.02	0.03	1.03	0.03	1.00	0.02	0.99	0.01			0.97	0.03	1.00	0.02
Ga	1.11	0.20			0.89	0.20							1.00	0.04
Hf					0.99	0.02	1.01	0.02					0.94	0.07
K	1.01	0.02	1.00	0.03	1.04	0.02	0.99	0.04			0.98	0.03	1.04	0.06
La			1.05	0.09	1.02	0.04	1.02	0.03	1.05	0.03	0.89	0.07	1.08	0.05
Lu					1.12	0.15	1.04	0.10	0.93	0.08			1.10	0.07
Mg	1.03	0.04	1.07	0.04							0.92	0.05	1.84	1.73
Mn	1.02	0.05	1.06	0.07					1.32	0.78	0.61	0.74	0.98	0.02
Na	0.88	0.07	0.86	0.03	1.04	0.08	1.07	0.07			1.12	0.06	1.07	0.07
Nb	1.40	0.06							0.68	0.19			1.40	0.13
Nd					0.86	0.04	1.17	0.06	1.00	0.07			1.06	0.17
Ni	0.84	0.06	1.21	0.17	1.40	0.18	0.92	0.09	0.86	0.18	0.82	0.22	1.04	0.12
P	1.19	0.12	0.81	0.12									0.81	0.15
Rb	0.96	0.09	0.96	0.10	1.06	0.04	1.01	0.05	1.01	0.03			1.00	0.05
Sb					0.96	0.03	0.95	0.04	1.06	0.03			0.96	0.03
Sc					1.16	0.04	1.06	0.02	0.83	0.01	1.01	0.06	1.07	0.02
Si	1.00	0.01	1.00	0.01									1.02	0.02
Sm					0.91	0.03	1.06	0.04	1.04	0.05			1.08	0.04
Sr	0.92	0.02	1.07	0.07					1.04	0.04	0.96	0.02	1.02	0.03

Ta					0.63	0.14	0.75	0.16	1.48	0.20			0.88	0.01
Tb					0.98	0.05	0.98	0.05	1.03	0.05			1.10	0.25
Th	1.25	0.10			0.93	0.10	0.93	0.08	0.92	0.05			0.88	0.06
Ti	1.09	0.08	1.13	0.03	0.99	0.18			0.93	0.05	0.96	0.09	1.05	0.08
U					0.93	0.04	1.09	0.04	1.00	0.05			1.02	0.15
V	0.92	0.08	1.08	0.08									0.95	0.16
W	1.03	0.38			0.97	0.38							2.16	2.09
Y	1.04	0.07	0.96	0.07									1.64	1.18
Yb					1.08	0.11	1.14	0.08	0.87	0.08			1.04	0.13
Zn	0.99	0.03			0.98	0.04	1.06	0.04					1.16	0.07
Zr	0.97	0.08	0.98	0.11	1.39	0.06	1.20	0.11	0.56	0.17			1.29	0.18

Table 5

Average ratios of the mean values M_{setup} as measured with the particular set-ups, over the overall mean values M_{total} of all set-ups. Furthermore, the standard deviations of the average ratios are listed. The last two columns show the average ratios and their standard deviations of the reference values of the measured materials (Bonn Standard was not considered).

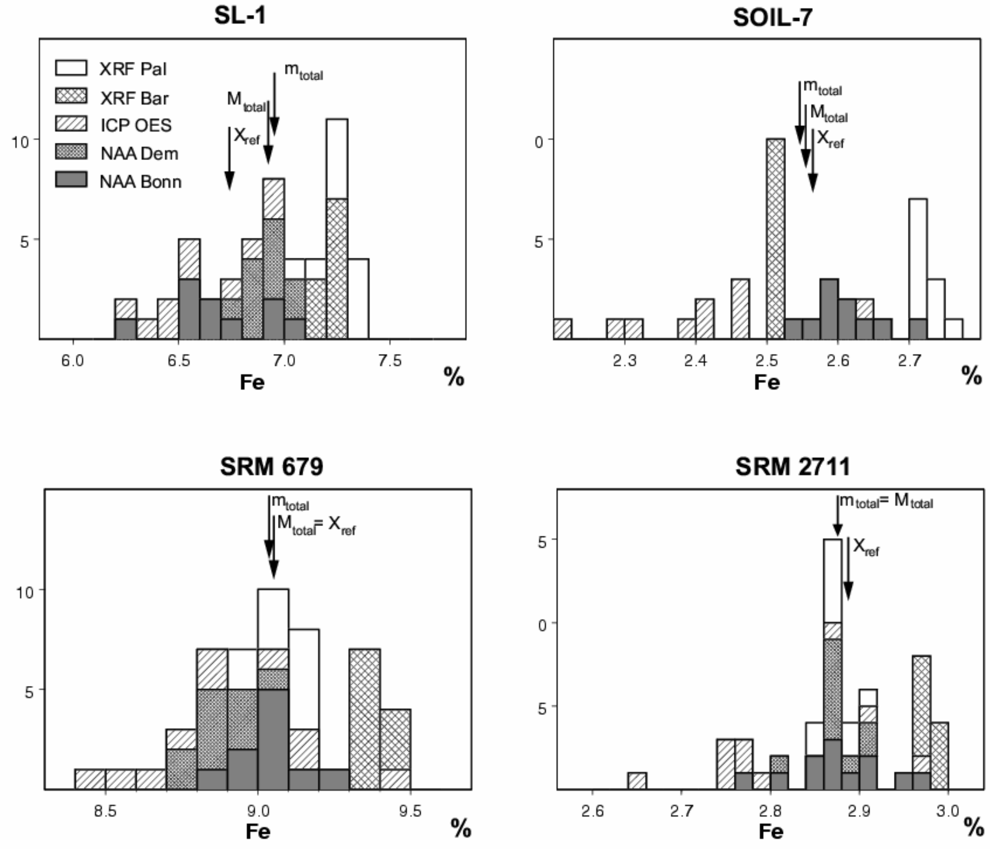

Figure 1

Frequency distribution diagrams of the Fe concentrations of the different standard reference materials, as they were measured with XRF, NAA and ICP-OES. The mean values M_{total}, the median values m_{total} and the reference values x_{ref} are indicated by arrows.

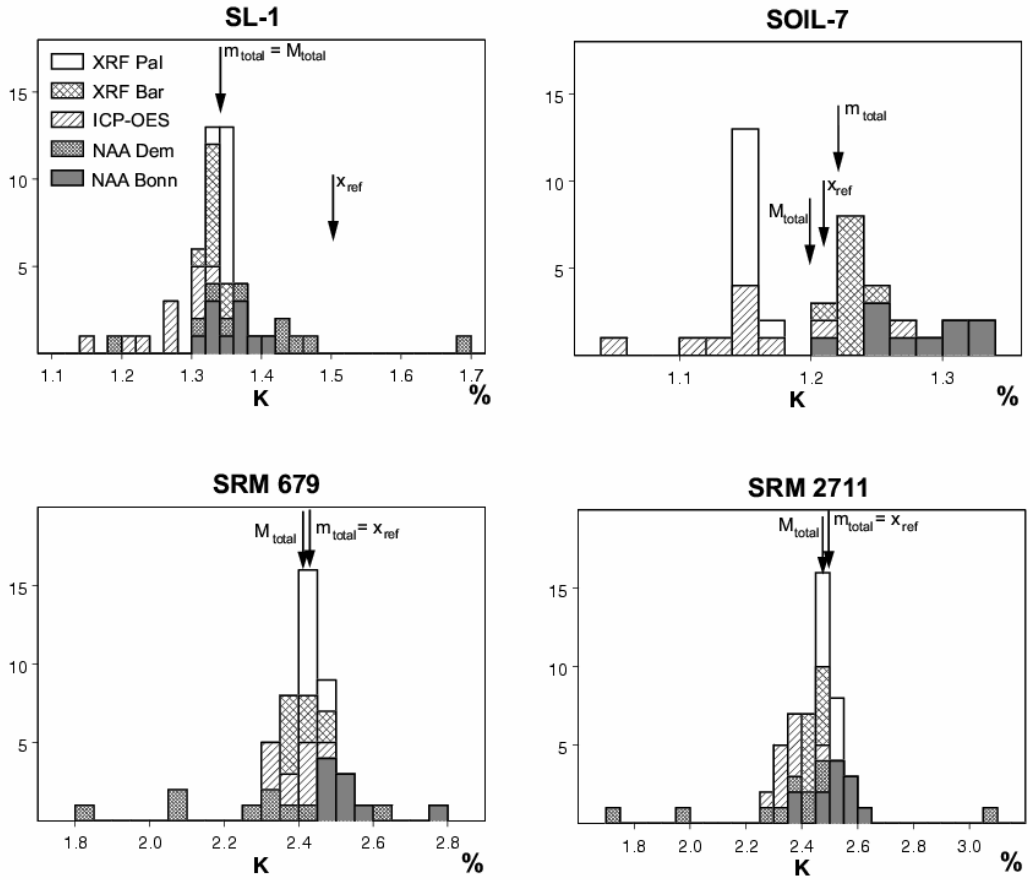

Figure 2

Frequency distribution diagrams of the K concentrations of the different standard reference materials, as they were measured with XRF, NAA and ICP-OES. The mean values M_{total}, the median values m_{total} and the reference values x_{ref} are indicated by arrows.

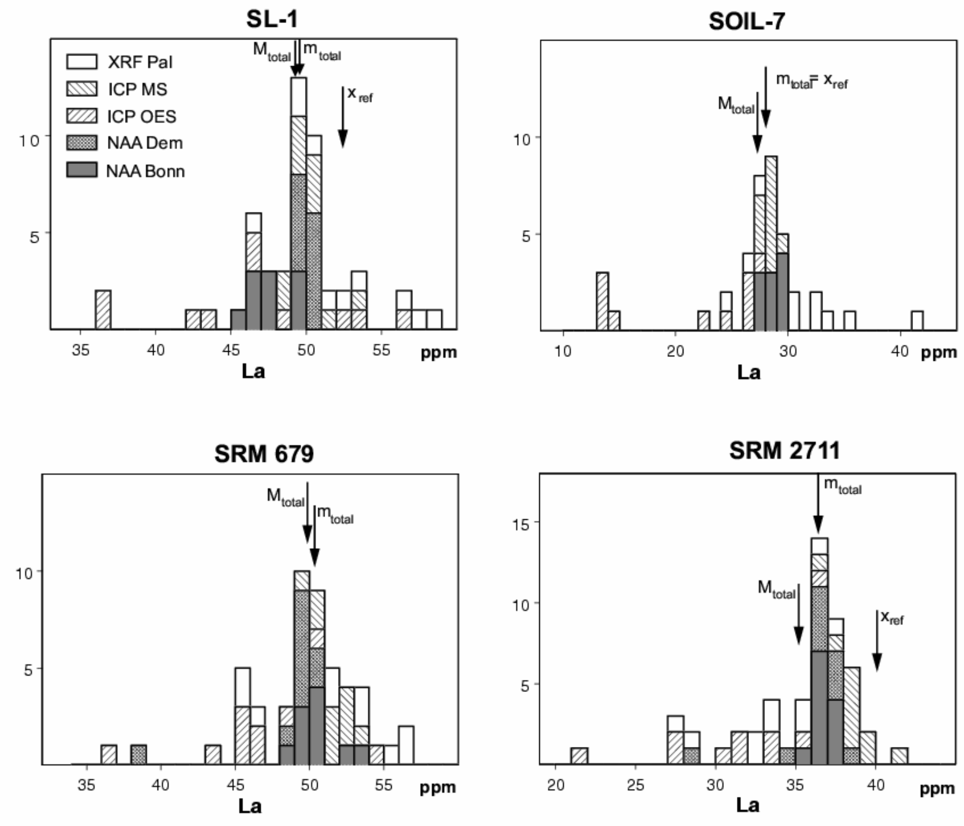

Figure 3

Frequency distribution diagrams of the La concentrations of the different standard reference materials, as they were measured with XRF in Palermo, NAA, ICP-MS and ICP-OES. The mean values M_{total}, the median values m_{total} and the reference values x_{ref} are indicated by arrows. In the case of SRM 679 no reference value is given.

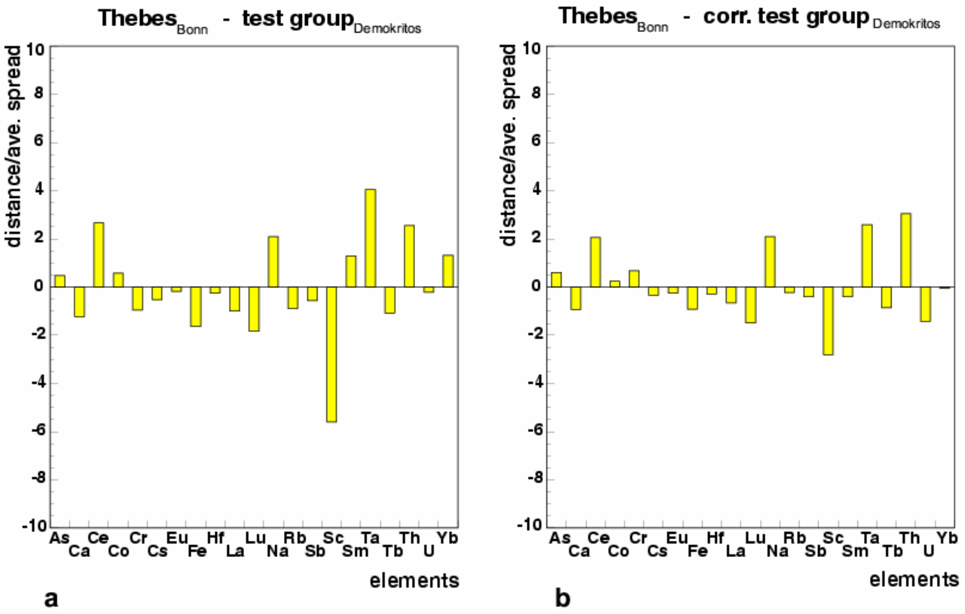

Figure 4

Comparison of a group of five Bronze Age pottery sherds analysed at Demokritos with the chemical profile of a group of Bronze Age ceramics from Thebes analysed in Bonn, before (a) and after (b) the application of the correction factors. The distances of the element concentrations are given in units of average standard deviations of both groups.