Volume 88, issue 2, April 2008
ISSN 0026-265X

ELSEVIER

MICROCHEMICAL JOURNAL

Devoted to the Application
of Microtechniques
in All Branches of Chemistry

SPECIAL ISSUE

Selected Papers from the
1st International Symposium on
Multivariate Analysis and Chemometrics for
Cultural Heritage and Environment
Nemi, Italy, 2–4 October 2006

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Microchemical Journal 88 (2008) 136–141

MICROCHEMICAL JOURNAL

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On the importance of using scandium to normalize geochemical data preceding multivariate analyses applied to archaeometric pottery studies

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Received 1 August 2007; accepted 21 November 2007
Available online 31 December 2007

Abstract

This work enhances the importance on determining regional geochemical background by normalizing chemical data of archaeological ceramics, using one element as grain-size and mineralogical proxy, prior to any further statistical approach. It is well established that more relevant information can be derived from the concentration of any element when it is compared with some reference element. The main question is which element should be chosen to normalize concentration. A discussion on this issue is presented here.

A case study is presented, which includes the geochemical tracing of Roman kilns productions, differentiating between and within two sedimentary basins pottery assembly, belonging to several Roman ceramic production centres identified in the Tagus and Sado basins of Portugal. Due to the homogeneity of the used raw materials (estuarine sediments), the distinction and establishment of signatures for each production center become difficult.

A multivariate statistical approach after normalization of the chemical contents to a conservative element (Sc) is presented, well differentiating the three production centers and allowing the establishment of provenance for amphorae.

Keywords: Normalization procedures; Sc; Conservative element; Archaeometry; Geochemistry

1. Introduction

In ancient ceramic provenance studies regarding compositional characterization, one of the main approaches is to establish comparisons with reference groups, including materials of known origin (kilns) and/or with potential local/regional raw materials. The identification of raw materials used in making the pots is crucial, namely the clay and non clay components, as well as the identification of their source, that is if they belong to sedimentary deposits or residual deposits.

To compensate for grain-size and mineralogy effects on trace element concentrations, thus diminishing erroneous interpretation of ceramic provenance, a common approach used in determining regional geochemical background is to normalize geochemical data using one element as grain-size and mineralogical proxy, that is to express the ratio of the concentration of a given element to that of the normalizing factor.

This approach has been commonly used in environmental studies, especially in verifying whether the variation of elements in sediments is indeed the result of anthropogenic and/or natural activities [1–3].

Chemical approaches to archaeological materials characterization are mainly used to attend to questions posed by archaeologists that deal essentially with provenance, technology, and use. We present a case study of the application of geochemical tracing to Roman ceramic kilns production, differentiating between and within two sedimentary basins pottery assembly, discussing the importance of establishing a normalization factor in helping to accomplish the above-mentioned archaeological objectives. Hence normalization in this work is defined as a procedure to compensate for the influence of natural (geological and ceramic burial time) and anthropogenic (technology of production) processes on the measured variability of the concentration of elements. So, this methodological approach, emphasises the

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doi:10.1016/j.microc.2007.11.009

importance of a geochemical criterion (geochemical behaviour of the element chosen for normalization), instead a statistical criterion (like the element with minor standard deviation or the element with less variability amongst the case studies).

Production centres using clay materials of similar geological environments (estuarine sediments with a high degree of evolution), such as the Tagus and Sado basins, are not easily distinguishable, and mineralogical and textural approaches had not been useful for differentiating different production sites [4]. A preliminary chemical differentiation based on cluster and factorial analyses found difficult in distinguishing ceramics from Roman archaeological sites in the Tagus and Sado basins due to widespread compositional similarities within these regions, enhancing the importance in using geochemical fingerprints [5–7].

In this work the regional variability of some geochemical parameters in those two basins is considered in terms of their relationship to a chosen element (Sc) used as a normalization factor. The normalization procedure permits to obtain a new baseline, calculated from these relationships, better assessing the magnitude of possible natural anomalies, thus providing information on the natural variability, which is to obtain a natural geochemical background of each production center not influenced by pottery production technological actions, like the add of temper grains.

2. Materials and methods

Amphorae from three Roman ceramic production centres of the Tagus (Porto dos Cacos and Quinta do Rouxinol) and Sado (Herdade do Pinheiro) basins of Portugal are studied. In total, 300 ceramic samples were analyzed.

Chemical analysis was done by means of instrumental neutron activation analysis (INAA), using the Portuguese Research Reactor, at Sacavém, Portugal, obtaining the concentrations of Na, K, Fe, Sc, Cr, Co, Zn, As, Rb, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U.

Standard reference materials GSD-9 and GSS-1 were used to calibrate date. Aliquots of approximately 1 g each of powdered ceramics and reference materials were dried in an oven at 110 °C for 24 h and stored in a desiccator. Once dried, 200–300 mg of powder was measured into cleaned high-density polyethylene vials.

All samples were irradiated at RPI, Sacavém. Samples and standards were bundled together and irradiated at a thermal flux of 3.34×10^{12} n cm^{-2} s^{-1}; $\Phi_{epi}/\Phi_{th} = 1.4\%$; $\Phi_{th}/\Phi_{fast} = 12.1$ for 7 h. The bundles were rotated continuously during irradiation to ensure that all samples received the same neutron exposure. Iron (Fe) flux monitors were irradiated with the samples to allow corrections due to variation in neutron flux.

Multivariate statistical, namely clustering methods were employed by using the Statistica program [8], specifically the joining tree-clustering method, using the absolute concentration of the chemical elements and element/Sc ratios as variables. The amalgamation rule employed in the joining tree-clustering was the unweighted pair-group average, also referred as UPGMA (unweighted pair-group method using arithmetic averages). In this method the distance between the two clusters is calculated as the average distance between all pairs of objects in the two different clusters. The joining tree-clustering method uses the dissimilarities (similarities) or distances between objects when forming the clusters. These distances (similarities) can be based on a single dimension or multiple dimensions, with each dimension representing a rule or condition for grouping objects [8]. The most straightforward way of computing distances between objects in a multi-dimensional space is to compute

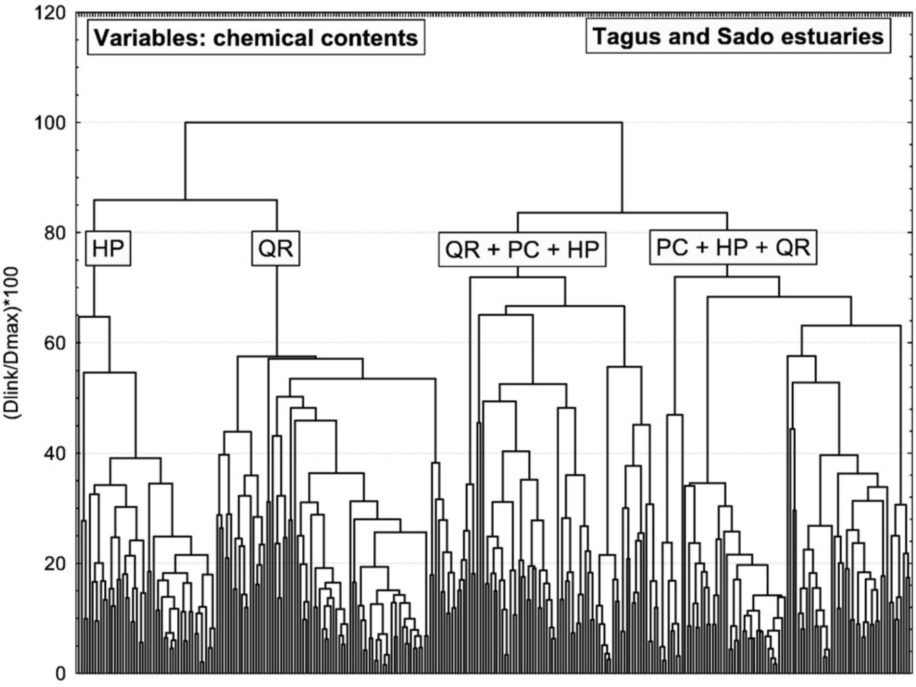

Fig. 1. Hierarchical tree (Unweighted pair-group average. 1 − Pearson *r*) – clustering of amphorae using chemical contents as variables.

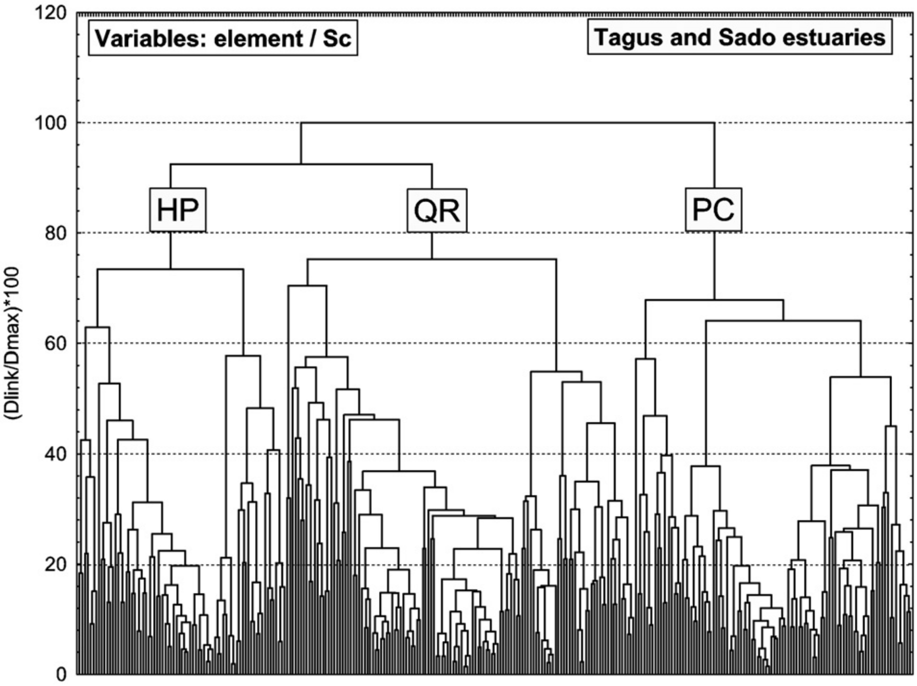

Fig. 2. Hierarchical tree (Unweighted pair-group average. 1 − Pearson *r*) – clustering of amphorae using element/Sc ratios as variables.

Euclidean distances. In the present case study the Euclidean mean was used as the similarity coefficient to identify outliers, being the measure of the actual geometric distance between objects in the space. The Pearson correlation coefficient was used to evaluate correlation between chemical parameters and samples. Highly similar samples give values of this measure close to 1, while unrelated ones give values close to 0. Their correlation value will be −1 if they are perfectly divergent. A Pearson correlation coefficient indicates the relationship between two ordered sets of numbers (in this case, absolute concentration of the chemical elements and element/Sc ratios expression data of ceramics from three roman production centers of two different basins). It indicates both how the two sets are related and the strength of that relationship.

3. Results

In the estuaries of the Tejo and Sado Rivers an intense occupation occurred in Roman times, with fish-salting facilities close to the river mouth and small peripheral units further away,

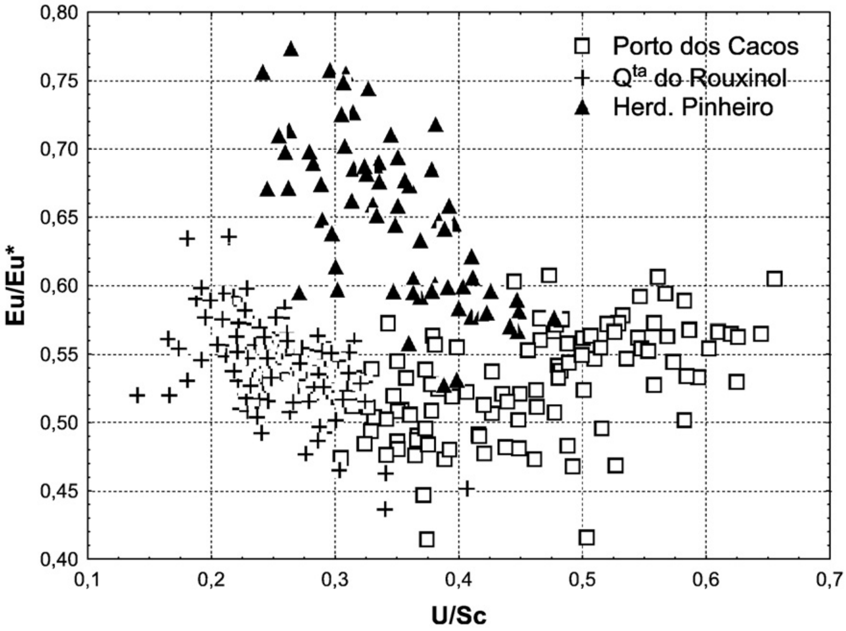

Fig. 3. Eu anomaly: U/Sc scatter plot of ceramics from Roman production centers of the Tagus (QR, PC) and Sado (HP) basins.

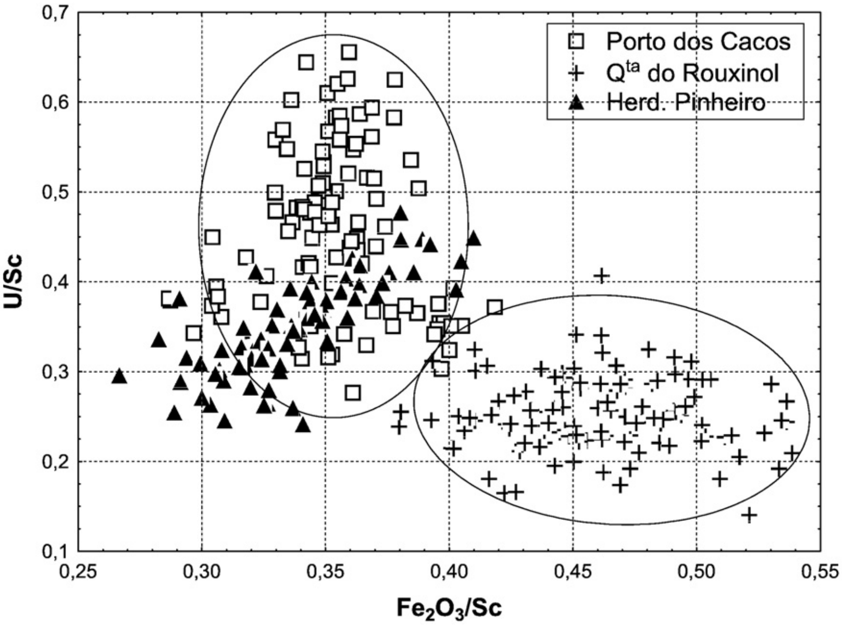

Fig. 4. U/Sc:Fe_2O_3/Sc scatter plot of ceramics from Roman production centers of the Tagus (QR, PC) and Sado (HP) basins.

and with pottery centres located upstream, upon the banks of the main river and its tributaries.

The three Roman production centers identified in the Tagus and Sado basins of Portugal, Quinta do Rouxinol (QR) and Porto dos Cacos (PC) in the Tagus basin, the Herdade do Pinheiro (HP) in Sado basin, comprise five hundred years of amphorae production of diverse typologies.

One of the main question/problem arises related with the establishment of each production center signature, contributing to the trade reconstruction (provenance: production centers vs reception centers). With this purpose the results obtained for the three Roman ceramic production centres were submitted to a statistical approach.

When trying to figure out chemical differences between and within the two basins, a first chemical differentiation based on cluster analysis using the absolute chemical elements contents as variables, enhanced the difficulty to distinguish productions within the same geological setting (Fig. 1). Due to the homogeneity of the used raw materials (estuarine sediments), also a previous compositional study [4] (mineralogical and chemical) enhances the difficulty in the distinction and establishment of signatures for each production center.

In this work, using normalized values relative to Sc as variables, the three production centers are clearly differentiated (Fig. 2).

Inter (Sado and Tagus) and intra-estuary (QR and PC) differentiation, particularly after normalization to Sc prior to any data management, support a better establishment of geochemical fingerprints of each production center. Eu anomaly together with U/Sc is the finest fingerprints to better differentiate the Tagus production centers from the Sado one (Fig. 3). On the other hand, U/Sc and Fe/Sc (Fig. 4) are the best fingerprints to better differentiate the two production centers from Tagus estuary (QR and PC).

4. Discussion

Normalizing geochemical data preceding any multivariate analyses applied to archaeometric pottery studies becomes a useful tool in this case study. In fact, this procedure enhances the differentiation of the three production centers, which present only fairly differences in the absolute concentration of chemical elements (trace elements). This similarity is due to the use of raw materials from the same or similar geological context, namely estuarine sediments with a high degree of evolution, even between the two basins (Tagus and Sado). Consequently, comparative studies of ceramics produced with similar raw materials, must pass by a first step of normalization procedure, in order to better establish chemical signatures of productions. The normalization is also very important when temper mainly composed of quartz was used, diluting chemical differences, being normalization a procedure to compensate for the influence of natural processes on the measured variability of the concentration of elements. Various granulometrical and geochemical approaches used for the normalization of trace elements data, namely in estuarine and coastal sediments, have been extensively reviewed by several authors [9–12].

Considering that it is well established that more relevant information can be derived from the concentration of any element when it is compared with some reference element, the question arises is which element should be chosen to normalize concentration. Among the elements studied, the selection of Sc as lithogenic and conservative element becomes more appropriate to normalize chemical data than other elements; the choice of this element is based on geochemical considerations and not statistical ones. Another important subject to be considered is that raw materials are related with a specific geological context which has also been considered.

Work developed by Sanei et al. [1] in sediment profiles from Pigeon lake, Canada, enhances the importance in determining the element's geochemical fraction to normalizing methods preference. They pointed out the normalization to organic matter, to carbonate fraction and to clastic mineral detritus fraction. Considering the two used normalization factors, textural and chemical, they have an important role in determining physical sorting and depositional pattern of abnormal elements concentrations. The use of grain-size fractions, such as sand, mud or clay, may be used as indicators of diluent, concentrator or accumulator of trace elements. On the other hand the use of Si, Al, Li, Sc, organic carbon, Fe, Mn and carbonates have also been reported as good normalization factors, according to their behaviour. The use of silicon reflects the amount and distribution of element content-poor quartz and it is a coarse-grained diluter of other elements. Aluminium is a chemical tracer of Al-silicates, used to account for granular variations of chemical elements in fine silt and clay size. An inert element such as aluminium, a major constituent of clay minerals, may be selected as an indicator of that fraction. It may be considered as a conservative major element, that is not affected significantly by, for instance, early diagenetic processes and strong redox effects observed in sediments however in the case of sediments derived from the glacial erosion of igneous rocks, it has been found that element/Al ratios are not suitable for normalizing granular variability [12–13]. Li and Sc are structurally combined in clay minerals and micas, being good indicators of clay minerals, particularly in sediments containing Al-silicates in all size fractions. Normalizing to organic content has also been widely used to correct for the strong affinity between some elements and organic content. Organic carbon indicates fine-grained organic matter and is a good tracer of organic contaminants. The use of Fe and Mn can correct data for the quantity of aluminosilicates, and also compensates for the effects of grain size. It indicates metal-rich silt and clay size Fe-bearing clay minerals, Fe-rich heavy minerals and hydrous Fe and Mn oxides, playing an important role as chemical tracer for Fe-rich clay fraction.

However, the use of the total concentration of Fe and Al for normalization of the sediments does not yield a satisfactory estimation of the quantity of aluminosilicates, since the oxy-hydroxide fraction of Fe and Al often interferes with the siliceous fraction [14]. Also the use of rare earth elements (REE) has been reported [1] to be used for normalizing as they also represent the quantity of aluminosilicates, the natural adsorption matrix for elements originating from the erosion of soils (clastic mineral detritus fraction). The authors mention the advantage of using REEs over Fe and Al as they are less influenced by other fractions such as the oxyhydroxides. Therefore, by normalizing the bulk concentration data to REEs, the group of clastic mineral detritus is eliminated. The use of carbonates (Ca and Sr represent the carbonate fraction) as normalization factor is valuable to eliminate the effect of carbonate fraction, indicating biogenic marine sediments, playing a role of diluter of contaminants, and sometimes also accumulates trace metals like Cd and Cu.

When dealing with ancient pottery production, whenever a possible anthropogenic input of a grain-size proxy is suspected, a preliminary investigation of the nature of the added temper is recommended before choosing the reference element; however, many times, that is not possible or recognisable, and also considering another variable, like the time burial, it is important, as it may induce element mobilisation/lixiviation. Therefore, the best option to take is to select a conservative element.

In ancient ceramic provenance studies, especially ceramics produced by raw materials derived from sediments, and with sight to its normalization, the Sc is a good element to be used as conservative element, being one of the ions most resistant and tends to remain in superficial environments. A detailed discussion of the geochemistry and reasons to prefer Sc over other lithogenic elements was reported earlier [10]. As advantages to the choice of Sc as reference element, we can underline the fact that Sc is neither enriched nor depleted comparing the Continental Crust with the primitive mantle and thus behaves more conservatively during weathering than Al, for example. Being Sc a conservative element, is most resistant and tends to remain in superficial environments during weathering, thus it will not be leached and carried away easily during ancient ceramic burial.

In the case study presented here we highlight the good choice among the elements with more residual behaviour, the selection of Sc (obtained with good precision and accuracy by INAA) to normalize data preceding any statistical treatment, allowing to clearly differentiate the three production centers.

In this work it is clearly shown that after normalizing element concentration relatively to Sc, the existing differences (even faintly) in trace elements concentration are enhanced with a clear differentiation between production centers (between and within Tagus and Sado estuaries) (Fig. 2). In consequence we were able to obtain reference groups, to be used in further studies of amphorae provenance, namely comparisons with other Roman consumption centers. After normalization of chemical data from the three Roman production centers to Sc, it should be noted that a clearer inter and intra-estuary differentiation occurs. This fact is well documented by the Eu anomaly, U/Sc and Fe/Sc variations, which are the best fingerprints to differentiate the Tagus production centers from the Sado one, and also the two production centers within Tagus estuary (QR and PC).

5. Conclusions

Comparative studies of ancient ceramics produced by similar raw materials, like estuarine sediments, must pass by a first step of normalization procedure, thus providing chemical signatures of productions. The normalization is also very important when temper mainly composed of quartz was used, diluting chemical differences. Normalization of elemental concentration to an immobile, conservative element provides deeper insights about other elements distribution than the consideration of the absolute concentration itself alone. The criteria used to choose the normalization factor must be supported by geochemical considerations/behaviour, and not only by statistical considerations.

Among the elements with more residual behaviour, Sc (obtained with good precision and accuracy by INAA) was selected to normalize data prior to any statistical treatment. In the case study presented here normalization to Sc clearly allows differentiating the three Roman production centers, with the establishment of good reference groups to be used in further studies of Roman pottery provenance.

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