CHEMICAL CHARACTERIZATION AND PROVENANCE STUDIES OF ARCHEOLOGICAL SAMPLES

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By
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September 2003

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality , as thesis of degree of Master of Science

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ABSTRACT

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Data that is collected by chemical analyses of the archeological samples can be used to find out the the raw materials used and the techniques practiced in the ancient pottery production. In addition, provenance studies of archeological samples that are commercially important may give an idea on the commercial relationships between the past civilizations.

This study was conducted to investigate the chemical compositions and provenance of the amphora samples that are found around Sinop and Heraclea Pontica (Black Sea Coast) in Turkey, Ibn-Hani (Eastern Mediterranean Coast) in Syria, Tanais and Gorgippia on Northern Black Sea region of Russia. Some amphorae, which are morphologically similar to those of Colchian amphorae, but having apparently distinctive clay properties, are called Pseudo-Colchian, and they were also analyzed during the studies. The mineral compositions of the samples were found out by powder X-Ray Diffraction analyses, and the elemental compositions were sought by X-Ray Fluorescence spectroscopy. Principal component analysis and cluster analysis are applied to the data collected from XRF measurements for the provenance classification of the samples. The results obtained from both statistical methods complemented each others and were in good agreement.

According to the results of this study, the pink clay, red clay and white clay amphorae from Sinop are all found to be composed of the minerals quartz, feldspars, pyroxenes, calcite and hematite, but varying in amounts with respect to type and color. Considering the mineralogical compositions, it is proposed that the average baking temperature of the red clay amphorae is around 800 – 850 ^{o}C whereas it is around 950 ^{o}C for the white clay ones. The red color observed for the red clay Sinopean amphorae was attributed to the presence of hematite minerals. On the other hand white color was attributed to the formation of mineral phases such as pyroxenes, throughout the chemical reactions that take place in the clay matrix at higher baking tempertures and low oxidation environments for the white clay Sinopean amphorae.

In provenance classification of the samples, it was found that the separations between the samples occur mainly due to variations in the concentration of elements Ca, Fe, Ti, Ni, Rb and Sr. White clay amphorae from Antioch and Ibn Hani, and the red clay carrot type amphora from Tanais are found to be the Sinopean production. On the other hand, the white clay amphorae from Tanais was found to be more similar to the ones from Heraclea Pontica and different from those of Sinop. The colchian amphorae from Gorgippia and Pseudo-Colchian amphorae were found to represent typical differences from all other samples, but also from each others.

Keywords:

Sinop, Heraclea Pontica, Ibn Hani, Tanais, Gorgippia, Colchis, Colchian, Pseudo-Colchian, Amphora, Tile, Tubulure, Workshop, Chemical Composition, Provenance, Powder X-Ray Diffraction, X-Ray Fluorescence Spectroscopy, Principal Component Analysis, Cluster Analysis.

ÖZET

ARKEOLOJİK ESERLERİN KİMYASAL ANALİZLERİ VE KÖKEN TAYİNİ

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Kimya Bölümü Yüksek Lisans
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Eylül 2003

Arkeolojik eserlerin kimyasal analizi sonucu elde edilen veriler, bu eserlerin üretiminde kullanılan hammaddeler ve eserlerin üretim teknikleri hakkında bilgi edinmemizi sağlar. Bunun yanında ticari değeri olan örneklerin köken tayinleri tarih öncesi ticari ilişkilerin anlaşılmasına yardım eder.

Bu çalışmada Türkiye'nin Karadeniz Bölgesinden Sinop ve Ereğli, Suriye'nin Doğu Akdeniz kıyısından Ibn Hani, ve Rusya'nın Kuzey Karadeniz kesimlerinden Tanais ve Gorgippia'dan gelen amfora örneklerinin, kimyasal analizleri ve köken tayinleri yapılmıştır. Analizler sırasında mineral kompozisyonları X-ışını kırınımı yöntemiyle, elementel kompozisyonlar ise X-ışını floresans spektroskopisi ile bulunmuştur. Örneklerin kökenlerinin bulunmasında, elementel kompozisyonlar, temel bileşenlerine ayırma ve kümeleme metotları ile istatistiksel olarak yorumlanmıştır. Her iki istatistiksel yöntemden elde edilen sonuçların birbirini tamamlayıcı ve birbirleriyle uyum içinde oldukarı gözlenmiştir.

Çalışmalar sonucunda Demirci-Sinop yöresinden gelen pembe, kırmızı ve beyaz hamurlu amforaların hepsinin kuvartz, feldispar, piroksen, kalsit ve hematit minerallerinden oluştuğu; ancak bu minerallerin miktarlarinin amfora tipi ve rengine göre değiştiği görülmüştür. Mineral komposizyonlari ve miktarları göz önüne alınarak pişirme sıcaklığı, kırmızı hamurlu amforalar için 800-850 ^{o}C, beyaz hamurlu amforalar içinse 900-950^{o}C olarak belirlenmiştir. Diğer yandan kırmızı hamurlu amforalardaki rengi hematit minerallerinin verdiği kanısına varılmıştır. Kırmızı hamurlu amforalardan daha yüksek sıcaklıklarda pişen beyaz hamurlu amforalarda ise yüksek pişirme sıcaklığında özellikle piroksen minerallerinin oluşması beyaz renge sebebiyet vermiştir.

Örneklerin köken tayinlerinde Ca, Fe, Ti, Ni, Rb ve Sr elementlerinin örnekler içindeki miktarları belirleyici olmuştur. Temel bileşenlerine ayırma ve kümeleme yöntemleri göstermiştir ki Ibn Hani ve Antakya'dan gelen beyaz hamurlu anforalar ile Tanais'ten gelen "havuç" tipli kırmızı hamurlu amfora Sinop kökenlidir. Diğer yandan Tanais ve Ereğli'den gelen beyaz hamurlu amforaların birbirine benzediği fakat Sinop'takilerden farklı olduğu görülmüştür.

Gorgippia'dan gelen "Colchian" amforalarının ve morfolojik olarak "Colchian" amforalarına benzeyen fakat kendilerine özgü hamur bileşimleri nedeniyle "Pseudo-Colchian" olarak anılan amforaların diğer örneklere göre farklılıklar içerdiği görülmüştür. Aynı zamanda bu amforaların birbirleri içerisinde de bazı farklılıklar taşıdıkları gözlenmiştir.

Örneklerin mineral yapılarının karşılaştırılması da istatiksel yöntemlerle yapılan köken tayini sonuçlarını destekleyen sonuçlar ortaya koymuştur.

Anahtar Kelimeler:

Sinop, Ereğli, Ibn Hani, Tanais, Gorgippia, Colchian, Pseudo Colchian, Amfora, Kiremit, Tübülür, Atölye, Kimyasal Analiz, Köken Tayini, Toz X-Işını Kırınımı, X-Işını Floresans Spektroskopisi, Temel Bileşenlerine Ayırma Yöntemi, Kümeleme Yöntemi.

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1. INTRODUCTION

In archeometric research, it is essential to acquire information on the compositional characteristics of archeological samples. By this way, the researcher can have an idea about the raw materials used in making the samples, the production techniques employed, the burial conditions and even the provenance of the samples. This whole information then can be used in reconstruction of the environmental context, which resembles the ancient conditions that the potters were working.

Today many chemical-analysis techniques are applicable to samples of archeological interest to gather both qualitative and quantitative information on their chemical compositions. X-ray fluorescence spectroscopy (XRF) [1-6], atomic absorbtion and emission spectroscopy (AAS-AES) [3, 7], instrumental neutron activation analysis (INAA) [8-10], particle induced X-ray emission spectroscopy (PIXE) [4,11,12] and inductively coupled plasma-mass spectrometry (ICP-MS) are the most widely used techniques to obtain information on the elemental composition of the archeological samples. Among these techniques XRF spectroscopy is a very practical one, which can collect simultaneous data on a large group of elements, where low detection limits in the range of ppm levels can easily be reached. In addition the analyses are done without sample consumption, therefore the samples can be reused in other experiments. On the other hand powder X-ray diffraction (PXRD) patterns can be used to obtain information on the minerological compositions [2, 5, 13, 14], again without consumption of the sample. Other tecniques such as Mössbauer spectroscopy [2, 15, 16], X-ray photoelectron spectroscopy [17], infrared spectroscopy (IR) and thermal-analysis[7,18] can be used to investigate the stuctural properties.

Table 1.1 summarizes the techniques for chemical analysis that are applicable to archeological studies. A researcher may choose one or more of the techniques that are sufficient enough to meet the considerations given in the frame of a work. Whichever techniques are used, the main purpose of analysing the chemical compositions of archeological samples is to find relations between the physically observed properties of

Table 1.1: Comparison of some common methods of physicochemical analyses in the chemical characterization of pottery.[1]

	X-Ray Diffraction	X-Ray Fluorescence Spectroscopy	Atomic Absorption Spectroscopy	Optical Emission Spectroscopy
Sample size and preparation	2 – 20 mg, powdered	100 mg -3 g powdered, pressed into a pellet	10 mg – 1g powdered	5 – 100 mg powdered
Destructiveness	Sample reusable	Sample reusable	Sample destroyed	Sample destroyed
Target of analysis	Bulk composition	Bulk composition	Bulk composition	Bulk composition
Components analyzed	Crystalline minerals	80 elements, Z > 12	50 elements, not rare earths and nonmetals	30 – 40 metallic elements
Concentration range	Major, minor (>1%)	Major, minor, trace 10 ppm – 100 %	Major, minor, trace 10 ppm -10 %	Major, minor, trace to 100 ppm
Accuracy and precision	Semi quantitative	High (2 % - 5%) Problems with sample matrix	High (2%)	Low to moderate (10%)
Data Interpretation	Photographic recording or computerized intensity vs. diffraction angle recording.	Rapid calibrations and multielement analyses.	Manual, automatic recording, slow multielement analysis	Photographic recording, rapid multielement analysis
Typical Uses and Applications	Clay minerals, inclusions, high temperature minerals in glazes	Ceramic body, surface coatings (slip, glaze, paint)	Ceramic body, surface coatings	Ceramic body surface coatings

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[1] See also Rice 1987, p. 374: [19]

Table 1.1 continued.

	Neutron Activation Analysis	Particle Induced X-Ray emission Spectroscopy	X-Ray Photoelectron Spectroscopy	Mössbauer Spectroscopy
Sample size and preparation	50 – 100 mg powdered , pressed into a pellet or whole	Few mg, cut section or powdered pellet	ca. 1 mg, cut section or powder	Whole or powdered
Destructiveness	Sample destroyed	Slight	Slight	None
Target of analysis	Bulk composition	Point analysis or bulk composition	Bulk composition	Bulk composition
Components analyzed	75 elements	Elements with $Z > 13$	Elements with $Z > 10$	Elements with Mössbauer effect (Fe, Ni, Al, Zn, Eu)
Concentration range	Major, minor, trace, ultra trace ppb – 100%	Major, minor, trace	Major, minor	-
Accuracy and precision	1% - 5%	5 %	Semi quantitative	Qualitative
Data Interpretation	Rapid multielement analysis	Multielement analysis	Rapid multielement analysis	Slow detection
Typical Uses and Applications	Ceramic body, raw materials, slip, glaze	Ceramic body (focused beam point analysis), inclusions, slip, paint	Bulk composition, can detect carbon	Generally limited to iron (e.g. , the Fe_2O_3 / FeO ratio)

samples and their production techniques, which are not available through sole archeological examinations of the profiles of the ceramic material.

Besides chemical analyses, petrographic studies can provide valuable information on the mineralogical compositions and textures of samples. Based on the images of thin-sections observed down a polarising optical microscope (POM) or a scanning electron microscope (SEM), qualitative information on the material composition of the samples could be obtained. The results are used to figure out the formation of 'ceramic fabrics', such as the association of rock types and minerals, grain sizes, and the differences in ceramic technology [13, 14, 20].

The quantitative information coming from chemical analyses are usually interpreted statistically to determine the provenance of ancient pottery [1, 3-5, 8-14, 16, 21]. Such methods include principal component analysis (PCA), cluster analysis and discriminant analysis. In addition the time period that the sample of interest belongs can be searched upon comparing the chemical data with those of well known reference samples [3].

In studying with archeological samples, analyzing the chemical contents by chemical analyses, gathering information on the nature of clasts, the clast grain size distribution and relative amount of clasts in ceramic matrixes by petrological examination, and finally comparing them with the geographical information and the fabrics of trusted reference samples from possible production centres; may be the most effective way of attributing the provenances.

Within many types of ceramic vessels, amphorae are of particular interest due to economic implications of this kind of pottery. In ancient Greece and Roman Empire they were designed specifically for transportation purposes, and were bought and traded for its content. The transported goods were usually oil, wine, vinegar, olives, and 'salted products' such as fish and capers. [14, 20]

Different shapes and colors observed for the amphorae could be related to their use for different types of storage. However, the color and shapes of the vessels were found to change mainly through successive periods of production, also. This observation is common among the amphorae, which were found in Aegean, Mediterranean and Asian territories[5, 14, 20, 22]. The tendency to change in shape could be due to the improvement of jars in stacking or handling [20]. On the other hand the color depends on the clay, where the clay quality might be associated with the property of the transported good.

Due to their commercial significance, examination of amphora samples that were found at different excavation sites can lead to an understanding of commercial relations between early states. For such an examination, archeological and scientific evidences must be combined to find out the production centres of transported and imported amphorae. In most cases the archeological evidences come from the examination of typologies and collecting the stamp informations on handles of the jars if present. Besides, evidence for the shipping of amphorae may come from the ruins and shipwrecks that are found in underwater excavations[23].

Although publications related to chemical characterization and provenance determination of pottery from diverse regions in Mediterranean, Aegean and East Asian territories with archeological significance are widely increasing parallel to advances in chemical analysis techniques, there is little amount of work cited for the chemical characterization of Sinopean pottery [5, 24, 25]. This may be due to the late exploration of the excavation sites located around Sinop.One of those excavation sites was found in 1993, near Demirci region located at 15 kilometres south of Sinop. As a result of the excavation of Demirci workshops a typology of the amphorae, which were produced there could be established [26-29].

The main scope of this work was to characterise the chemical composition of pottery, which were found in the workshops of Demirci Bay. Besides, the diversity of the colour of the clay among the different types of Sinopean amphorae was attempted to be explained. To figure out the techniques employed in Sinopean pottery production, the scientific approach aimed to find out the raw materials used, the temper added, the highest firing temperature reached and the firing atmosphere achieved in the kiln during the pottery production. Therefore, the chemical compositions of the Sinopean pottery were compared with those of the clay samples and possible temper materials obtained from the Demirci region. The analyses for these purposes consisted of mineralogical examination of pottery and raw material by PXRD patterns, and collection of elemental data through XRF spectroscopy.

Another aspect of scientific analyses was to confirm the circulation of amphorae produced in the Black Sea and Eastern Mediterranean Sea regions. Figure 1.1 shows the map of these regions. Besides Sinop, these sites are Heraclea Pontica (today Ereğli) and Antioche (today

Antakya) from Turkey, Ibn Hani from Syria, Tanais and Gorgippia from northern Black Sea regions of Russia, and finally Colchis. Furthermore, the so-called "Pseudo-Colchian" amphorae were discovered in some of the regions given above [30]. These amphorae have morphological elements that are typical of Colchian amphorae, but with different clay appearance.

Regarding the exportation of amphorae, partly traced commercial roads up to now pointed to two main axes: one in the direction of the all Black Sea region, the other one in the direction of the Eastern Mediterranean Sea [5]. It is believed by the archeological expertise that the Sinopean amphorae were being exported all in these directions. Particularly Antioche and Ibn Hani in the Eastern Mediterranean coast were foresighted to import Sinopean amphorae.

In order to explore the commercial net in these directions, provenance studies of the collected amphorae samples were done. For the attribution of the samples to likely production centres, the elemental data collected by XRF spectroscopy are used in multivariate statistics such as PCA and cluster analysis.

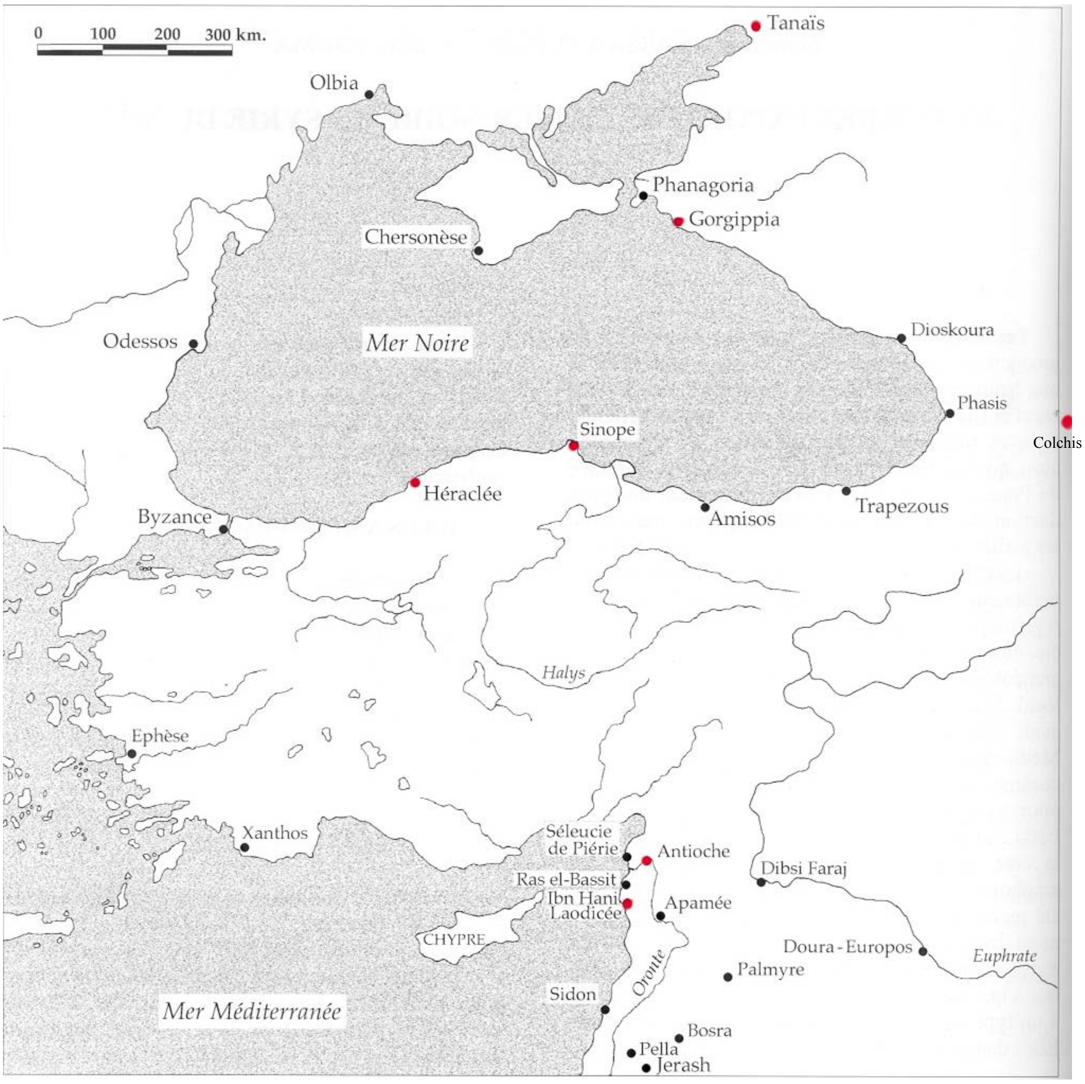


Figure 1.1: The map showing the Black Sea area and Eastern Mediterranean region.

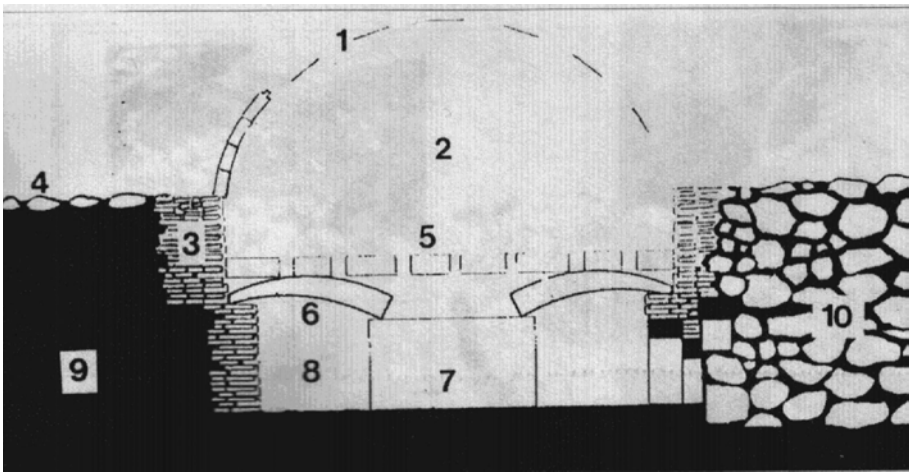
1.1 The Sinopean Pottery in Detail

The workshop in Demirci Bay was found first in 1994 excavations, following the survey in 1993. Since then a total of nine kilns have been found in the region, and various types of pottery were detected to spread in a wide area around the kilns.

Among the pottery found in Demirci Bay are tiles and tubulures used in the walls and external covers of the kilns; the common wares such as cooking pots and vases, fine ceramics known as “terra-sigillata”, and amphora samples of various shapes and colors. Some overfired samples of amphora were found in the remains near the kilns. Besides, raw clay samples and possible temper materials were obtained in the region near the workshop.

Figure 1.2 shows the structure of the kilns found in Demirci workshop in a general scheme. In addition the aerial views of a kiln from the excavation site is shown in the figure. The kiln is composed of two separated parts: The heating room buried under the ground and the baking room that lies on the heating room. The roof of the baking room is made of the tubulures, which were attached to each other by some sort of supporting material such as clay-mud. Surprisingly, the tubulures were found to have two sides with red and white colors in the same vessel while the white sides of the tubulures are most probably facing inside the kiln. These kilns are mostly used in the production of amphorae and tiles.

The amphorae and the tiles found in Sinop show diversity of colours and shapes. The colours observed for the amphorae relate to different periods, which succeed each other, and correspond to specific shapes [5].



a.Central structure of the Demirci-Sinop kilns.

1: External covering which is built up from the tubulures.
2: Baking room.
3: Wall built from broken tiles.
4: Stone layer at the ground.
5: Grill separating the baking and heating rooms.
6: Supporting chords.
7: Arterial columns.
8: Heating room.
9: Earth filling.
10: Entrance

b. Aerial view of a kiln showing the arterial columns.

Figure 1.2: Central structure of the Demirci-Sinop kilns. [1]

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[1] See also Kassab Tezgör & Tatlıcan 1999, p. 319 [23].