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# PRELIMINARY RESULTS OF MAGNETIC AND XRF METHODS OF HELLENISTIC AMPHORAE: CASE STUDY

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## ABSTRACT

A set of fragments of 5 different archaeological vessels (Hellenistic period amphorae handles found in the same context) has been examined and compared with the modern sample (made from clay taken from the same stratigraphy). The research aims and tasks have been the following: a) a search for a criterion of similarity or difference in archaeological ceramics from the point of view of chemical composition or physical properties; b) a trying of development of a technique for less- or non-destructive rapid analysis of archaeological ceramics. During the analysis of the obtained results data, we did not find any unambiguous signs could separate the set on groups. The obtained data analysis has shown that all the amphorae fragments set and tempered clay are from the same clay source. During the experiment the research task was changed to confirmation of the homogeneity of material and production technology for the set. The combination of the four (4) methods was used: kappametry, magnetic hysteresis measurement, XRF and MAS-NMR.

**KEYWORDS:** archaeological pottery, XRF, x-ray fluorescence, MAS-NMR, nuclear magnetic resonance, kappametry, hysteresis, magnetic properties, ceramics.

## INTRODUCTION

Pottery is the most abundant and widespread of all archaeological materials. Often it is the pottery that gives the basic dating information about the archaeological site under study. Unfortunately, most of the mass pottery material does not contain any individual information in the form of stamps or unique features and is sent to backfill. Nevertheless, the use of physical and chemical methods for the study of such materials has been widely known for a long time. These methods have been proved to be working really well on the following tasks: determination of the firing temperature, determination of the type of clay, detection of minerals, dating (Bordeepong et al., 2012). Each time a physicochemical investigation of this type of object is performed, a very specific problem is solved. Until recently there have not been any established methods: each experimental work is innovative in its own way and proves the applicability of the technique used. In this regard, from the rank-and-file archaeologists perspective, natural scientific methods of investigation are somewhat complicated and inaccessible. This experimental paper and subsequent experimental work is designed to show that the available physicochemical methods are useful even for routine archaeological work with a tiny weight of samples and take very little time.

Physico-chemical methods make it possible to obtain very useful and indispensable information. The study of the magnetic properties of soils and clays is widely used to explore the anthropogenic processes and processes of soil formation (Fassbinder, 2015). The magnetic susceptibility of the ceramic can be used to determine the clay burning temperature (Rasmussen et al., 2012).

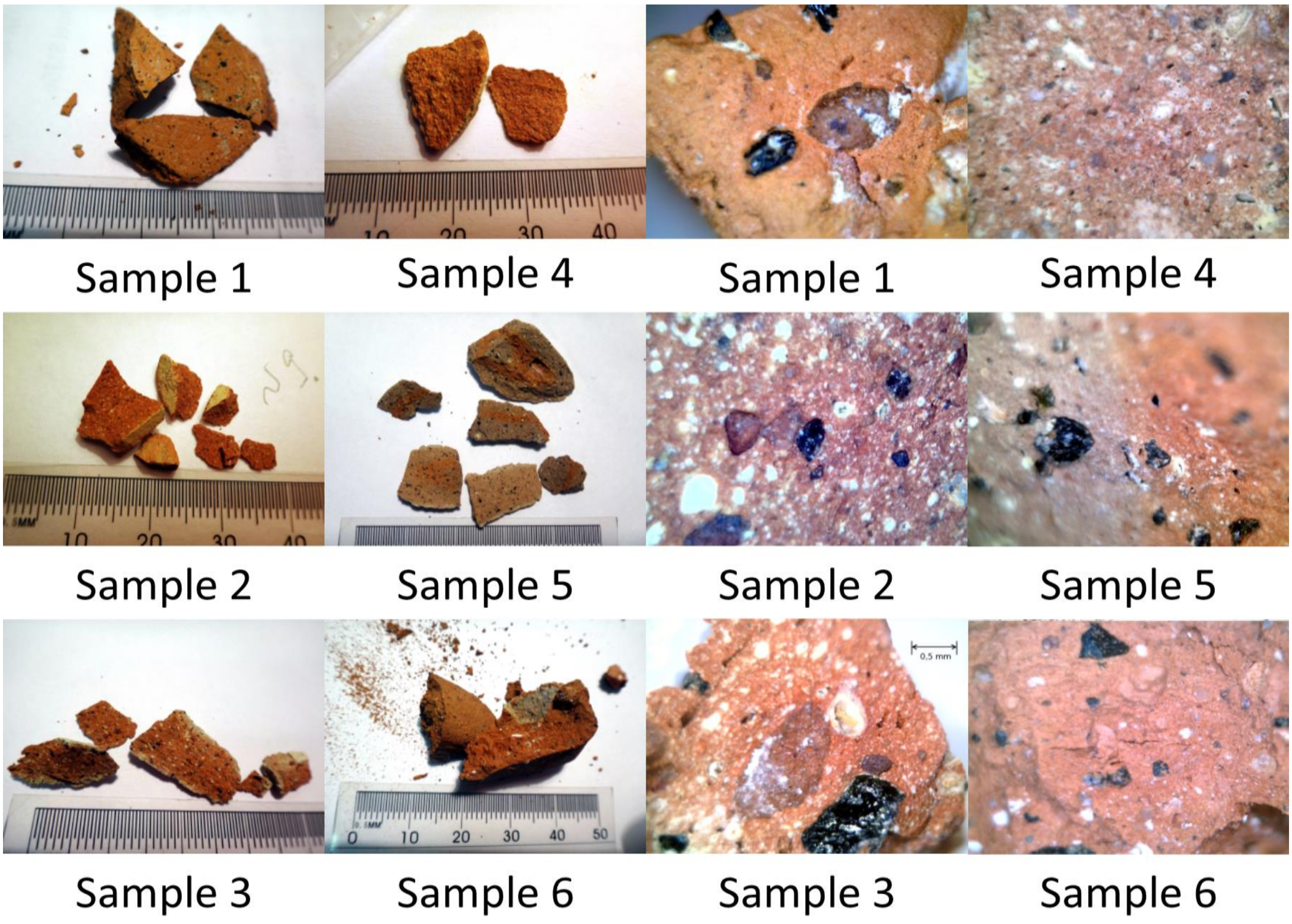



*Figure 1. Sample photos (left) and magnified photos (right).*

The X-Ray Fluorescence (XRF) method is well known and is applied not only to study ceramics, but also many other archaeological artifact materials (Shackley, 2012). An impressive comparative analysis of XRF, Total reflection XRF (TXRF), portable XRF (pXRF) is given in the case study of archaeological bricks (Bonizzoni et al. 2013). An example of a statistical and mineralogical approach to the analysis of XRF data of antique pottery is discussed in detail in the paper (Papachristodoulou et al., 2006). Good examples of the pottery origin study is shown in the work (Pillay et al. 2000; Javanshah, 2017). The number of portable XRF (pXRF) applications is increasing from year to year (see; Pappalardo et al., 2003; Mantzourani and Liritzis 2006; Papadopoulou et al. 2006; Papageorgiou and Liritzis, 2007; Liritzis et al. 2002, 2007; Liritzis 2005; Liritzis & Zacharias, 2010).

Any method of the Magnetic Resonance methods group (NMR, ESR, etc.) is commonly used only in combination with other different methods for archaeological artifacts research purposes because of the complexity of the solid-state magnetic resonance data analysis. The application of Magic Angle Spinning NMR (MAS-NMR) for pottery, as that kind of material, often helps with interpretation. Successful results were shown in several papers (Capitani et al. 2012, Mangone et al. 2009, Presciutti et al. 2005, Sheriff et al. 1995).

One of the main questions that the study tries to answer is: what could be the criterion for the similarity and differences in archaeological pottery from the point of view of chemical composition or physical properties and how can it be measured.

In this work a set of uninformative fragments from 5 different archaeological vessels of Hellenistic age (307-273 BC.) (Fig.1) has been studied. The set is compared with the modern sample provided by the archaeological museum upon request (see similar approach in Liritzis et al., 2018). Initially, the work was based on the factor of unknown details of the samples' origin. During the obtained data analysis there were no unambiguous signs characterizing the sample as an isolated or grouping the set into parts. It is known that all the samples came from the same site. Thus, the research focus was moved to confirming the uniformity of raw materials and production technology for the set.

## MATERIALS

A part of the Hellenistic production complex was excavated and studied on the Chora (agricultural area) of Tauric Chersonese (land plot № 82) in 2014-2015 years. The complex can be interpreted as a part of a pottery workshop. There were found several structures and pits, cut in the bedrock, clearly having manufacturing function. Of special interest is the Structure № 2, which obviously was used as a clay-preparing basin. Two layers of clay were found on the bottom: one can be interpreted as an untempered clay stock, the second is clay tempered with the bonding agents and ready for the pottery production. The filling of Structure № 2, as well as the lying on the rock bottom layer and the top layer (above the structures), were rich of pottery fragments. Most of them were the fragments of transport-, table- and building ware of Chersonesian production. A lot of pottery fragments found there has the production spoilage.

Among others, more than 30 fragments of Chersonesian amphorae stamped handles were found. Many of them carried the same Magistrate's name. Therefore, it was suggested that all these handles belonged to amphorae made on site, in this workshop. To verify this assumption, it was decided to compare the found amphorae handles pottery material with the ready-made ceramic paste from the bottom of Structure № 2.

A set of the 5 amphorae handles and a clay sample found in situ was studied (see Pic.1). All of them are chipped from stamps on the Hellenistic Chersonesian amphorae:

- Sample 1 – The handle of the Chersonesian amphora with the stamp of astynomos Heroksenos (307-297 BC. (Kats 2007, p. 326, 442)).
- Sample 2 – The handle of the Chersonesian amphora with the stamp of astynomos Athanadoros, the son of Nikeas (286-273 BC. (Kats 2007, p. 326, 442)).
- Sample 3 – The handle of the Chersonesian amphora with the stamp of astynomos Herakleios (307-297 BC. (Kats 2007, p. 326, 442)).
- Sample 4 – The handle of the Chersonesian amphora with the stamp of astynomos Herakleios (307-297 BC. (Kats 2007, p. 326, 442)).
- Sample 5 – The handle of the Chersonesian amphora with the stamp of astynomos Heroksenos (307-297 BC. (Kats 2007, p. 326, 442)).
- Sample 6 – Modern-made experimental sample.

The special-made sample of clay with bonding agents, named "Sample 6" (found on the bottom of the pool for the preparation of clay, which was part of the workshop) was included in the study set for comparison with the rest of samples in order to test the same-site-manufacturing assumption. During the experiment, the clay collected from the bottom and walls of the pool was diluted with water. The objects of various forms were made from it (handles, weights, etc.). The firing was carried out in a laboratory common coal oven. The firing temperature range was approx. 350-800°C.

The emphasis was placed on the non-destructive techniques or minor (grams) sampling. The archaeological ceramics is regarded as meta-material: it is not natural, it was made artificially to perform certain functions and must have a set of specific physical properties. In this case, the professional practice of pottery making and especially the manufacture of building brick ware (roof tiles, etc.) can be safely called the modern term Hi-Tech. For example, it is known (by archaeological sources, see Bobrinsky 1978) that the burning temperature was maintained at more than 1000°C during a day (or even more) in a case of roof tiles or some big vessels with a volume of more than 1 $m^3$. Hence, we have used the metamaterial research tools on a first approach; that is, measurement of magnetic susceptibility (both portable and lab design available), magnetic hysteresis measurement, XRF (portable also available as pXRF) and (magic angle spinning) MAS-NMR.

## METHODS

Photos with magnification are made by a hand-held USB microscope with a x500 increase. Magnetic susceptibility was measured on the MFK1-FA Multi-function Kappabridge. The measurements were made at 976 Hz in the field F1 = 200 A/m (Bratitsi et al., 2018).

The samples were rubbed manually in an agate mortar and crushed all down to the fraction of 1mm. Fragments of mineral wipers sometimes remained unmilled and those large stones did not participate in the study. The samples were not dried especially, only kept in the room conditions, so they contained atmosphere water absorbed.

The magnetic hysteresis was measured on a LakeShore GMW vibratory magnetometer.

XRF was conducted on the energy dispersive X-Ray spectrometer Shimadzu EDX-800HS. Polypropylene film was used. The sample was investigated in powder form. The collimator was 10mm. The shooting was conducted in an air atmosphere, so we do not fix elements from Hydrogen to Sodium because of the absorption by air Oxygen. The X-ray tube is Rhodium. Therefore, due to Compton scattering, we have Rhodium signals in all the XRF data.

NMR measurements were carried out on a Bruker Avance III NMR spectrometer WB 400 MHz at room temperature. The sample was rotated at 10 kHz frequency. The measurements conditions were repeated from the paper by Abo-Mosallam et al., (2010).

## RESULTS IN BRIEF

*1. Macro photos.* The samples are fragments of chips (Fig.1). The differences in color and additives are visible both macroscopically (see left part of Fig.1) and with magnification (see right side of Fig.1). The small number of samples does not allow them to be grouped according to this feature, unfortunately. Moreover, all the fragments are different.

*2. Magnetic susceptibility (MS).* The mass magnetic susceptibility was investigated. Each value was obtained by averaging of 3 independent measurements.

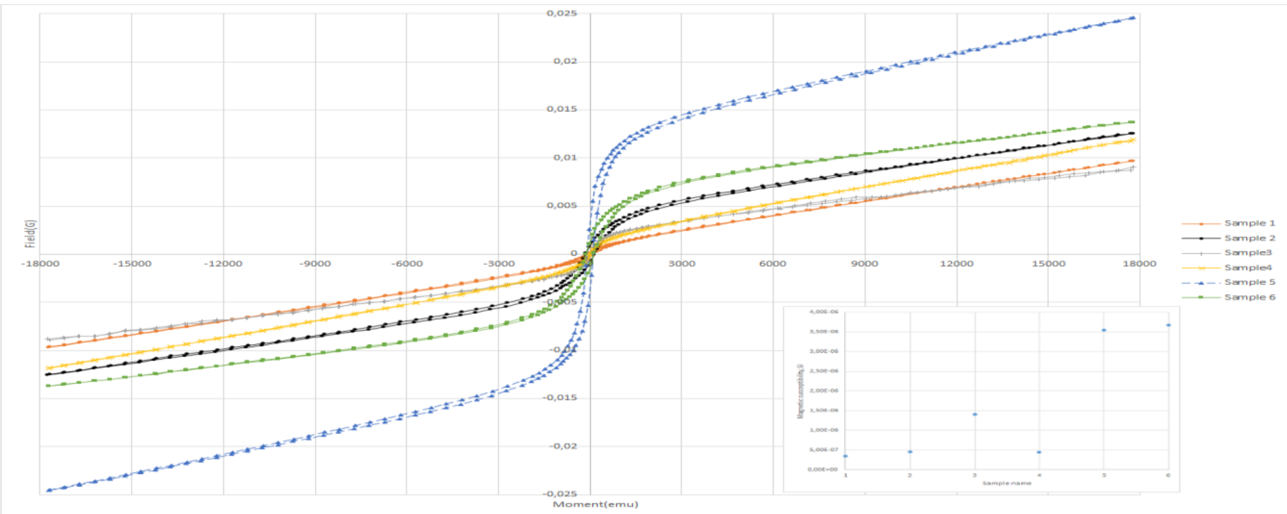


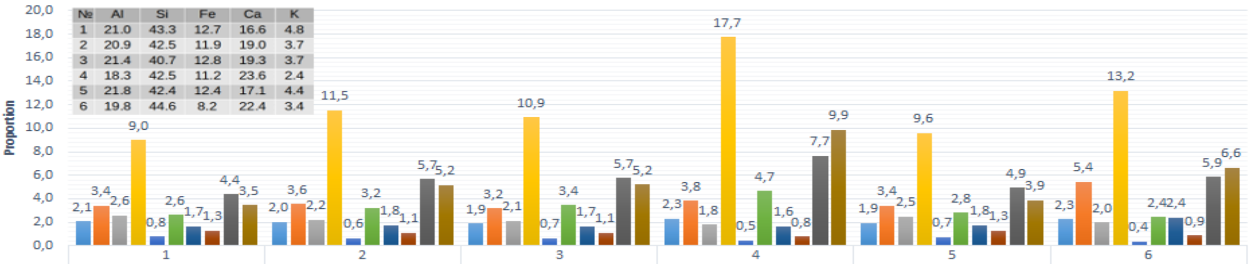

***Figure 2. The magnetic hysteresis graph and magnetic susceptibility data (added on right lower side).***

Similar results were obtained for the Samples 1, 2, 4. They can be called the lower limit: (3.5-4.5)*$10^{-7}$ (see Fig.2.A). For the Sample 3, the $\chi$ value is 1.5 times higher: 14.1*$10^{-7}$. The Sample 5 and Sample 6 have similar values, which refer to the upper limit of the measured values: (35.5-36.8)*$10^{-7}$. In total, the magnetic susceptibility of the studied set of the samples showed a spread in values of 10 times. This shows the potential possibility of using the method for a fast analysis of archaeological ceramics. The investigated set can be divided into 2 groups: The samples 1, 2, 3, 4 with smaller values of MS (kappa) and the Samples 5,6 with maximum values. It can also be said that the entire set exhibits paramagnetic properties. In this case, the Sample 5 and Sample 6 are at the upper boundary of the range of the magnetic susceptibility of paramagnets.

*3. Magnetic hysteresis.* The changes are very small (see Fig.2.B) and do not allow to single out groups. The graph shows the presence of a weak coercive force in the Sample 5 and Sample 6, which this indicates the presence of a magnetic domain structure in the composition of the material and the manifestation of weak ferromagnetic properties by the Sample 5 and Sample 6.

4. *XRF*. Only some indicative chemical elements were measured on a qualitative manner (see the experimental technique section) - therefore we can observe only relative ones, see Fig.3. Not all the possible relative combinations are shown. There are the most variative values only shown on the graph. The greatest difference is in the Si/Fe ratio of the Sample 6, the ratio is 1.5 times higher than in the rest, see Fig.4. The ratio Si/K growth for the Sample 4. For the ratio Ca/K we observe the largest spread of values, but the quantity K is small and difficult to accurately assess. Therefore, the Ca/K ratio is ambiguous and requires further investigations.

| № | Al | Si | Fe | Ca | K |
|---|---|---|---|---|---|
| 1 | 21.0 | 43.3 | 12.7 | 16.6 | 4.8 |
| 2 | 20.9 | 42.5 | 11.9 | 19.0 | 3.7 |
| 3 | 21.4 | 40.7 | 12.8 | 19.3 | 3.7 |
| 4 | 18.3 | 42.5 | 11.2 | 23.6 | 2.4 |
| 5 | 21.8 | 42.4 | 12.4 | 17.1 | 4.4 |
| 6 | 19.8 | 44.6 | 8.2 | 22.4 | 3.4 |




| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Si/Al | 2,1 | 2,0 | 1,9 | 2,3 | 1,9 | 2,3 |
| Si/Fe | 3,4 | 3,6 | 3,2 | 3,8 | 3,4 | 5,4 |
| Si/Ca | 2,6 | 2,2 | 2,1 | 1,8 | 2,5 | 2,0 |
| Si/K | 9,0 | 11,5 | 10,9 | 17,7 | 9,6 | 13,2 |
| Fe/Ca | 0,8 | 0,6 | 0,7 | 0,5 | 0,7 | 0,4 |
| Fe/K | 2,6 | 3,2 | 3,4 | 4,7 | 2,8 | 2,4 |
| Al/Fe | 1,7 | 1,8 | 1,7 | 1,6 | 1,8 | 2,4 |
| Al/Ca | 1,3 | 1,1 | 1,1 | 0,8 | 1,3 | 0,9 |
| Al/K | 4,4 | 5,7 | 5,7 | 7,7 | 4,9 | 5,9 |
| Ca/K | 3,5 | 5,2 | 5,2 | 9,9 | 3,9 | 6,6 |

Sample name

*Figure 3. XRF data graph. The proportions of element amounts are shown. The absolute values are added on top left area.*

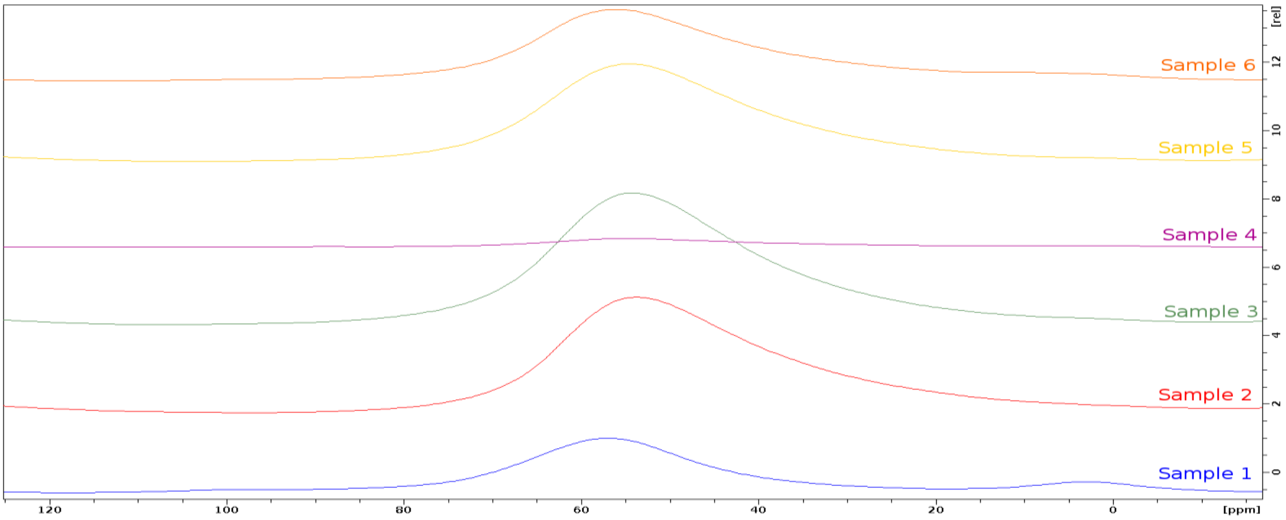



*Figure 4. The MAS-NMR 27Al spectras. Sample 4 spectra is exceptional – no peaks detected.*

5. *MAS-NMR*. This is not a fast method. It is used to obtain additional information about the chemical structure of the material. This could help with other methods data analysis. Since ceramics are a porous aluminosilicate that absorbs water, magnetic resonance methods can be used to study this material by water-environment relationships at least.

The Si spectrum (see Fig.6) is taken without the accumulation for this step, therefore it contains a data noise. There is not a lot of detected signals in the spectral information, one central line only can be seen. This does not change from sample to sample.

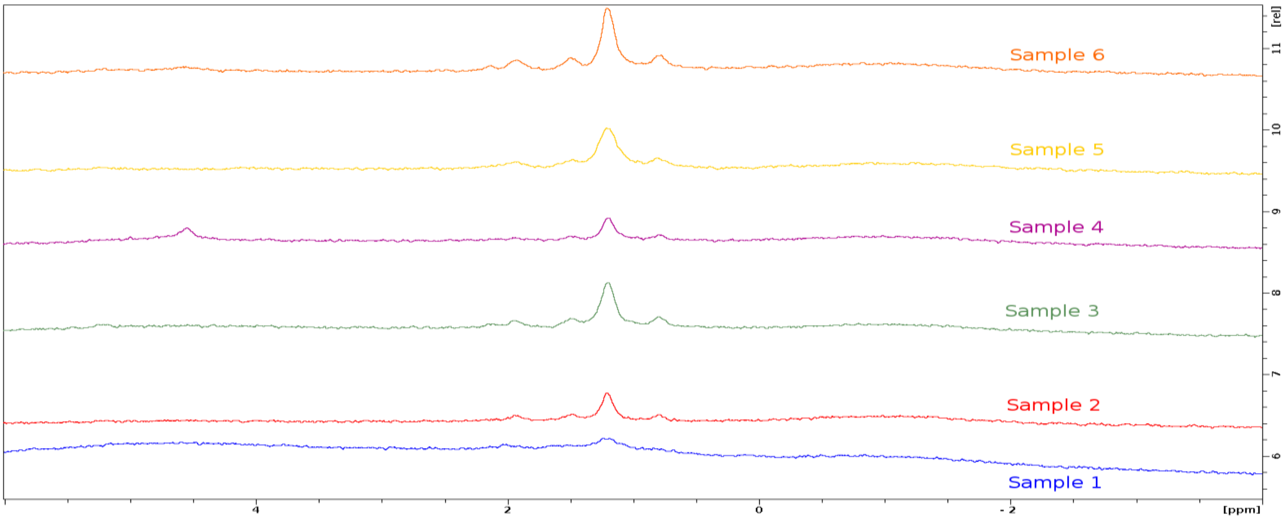



***Figure 5. The MAS-NMR 1H spectras. All the spectras varies.***

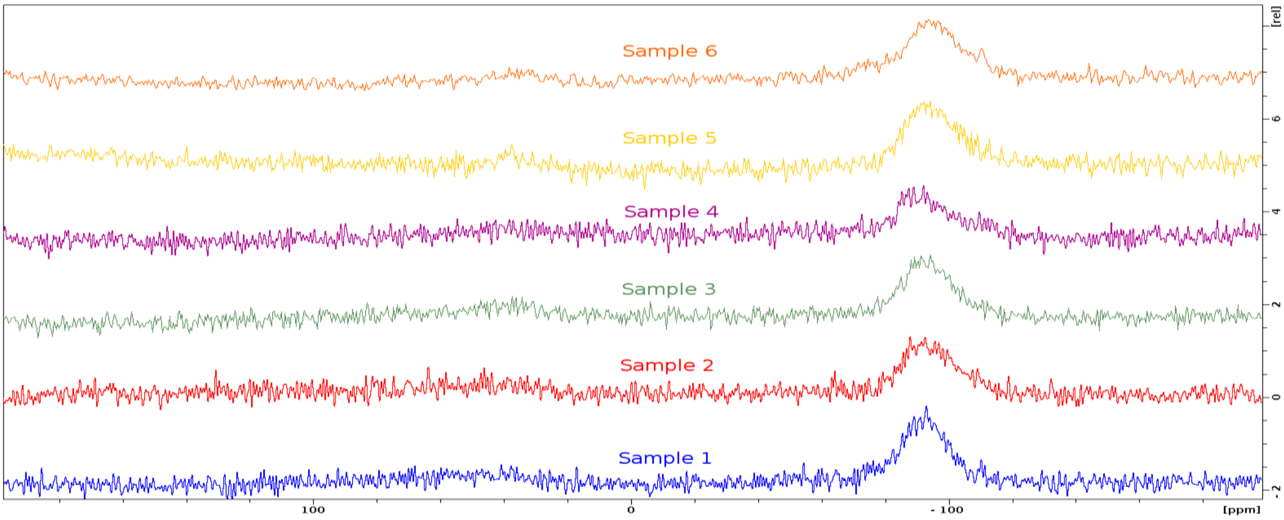



***Figure 6. The MAS-NMR 29Si spectra. Peaks are weak. The noise prevents to characterize their difference.***

The Al spectras are more informative and diverse (see Fig.4). The Sample 4 spectra is distinguished by a small integral intensity and lines amplitude. Samples 1,2,3,5,6 spectra are quite similar in the amount and shape of lines. The only exceptions are the presence of a line near “0 Hz” position for the Sample 1 and different line amplitudes for all the samples. In our samples it can be signals from $AlO_4$ or $AlO_6$. Since the experimental conditions remained the same for each sample, we can assume the relative content of the element from the Integral Intensity Ratio. These values are in relative units: "Sample 1" ~ 27.3; "Sample 2" ~ 38.9; "Sample 3" ~ 46.7; "Sample 4" ~ 8.8; "Sample 5" ~ 44.2; "6" ~ 33.4. For the Sample 4 the minimum of MAS-NMR signal Integrated Intensity correlates well with the small Al ratio by the XRF data.

## DISCUSSION

A Magistrate was a local official who controlled the observance of amphora standards (his name was stamped on the amphora handles). Product parameters controlled were only the volume and appearance of the amphora. The pottery paste composition was on the manufacturer responsibility and could vary. But the composition still depends on the available clay and bonding agents. An attempt to divide the samples archaeologically by magistrates and according to dates – has not worked. The dispersion according to archaeological dates is small: just 10-15 years. So, the possible results from the Magistrate-analysis do not match with this natural analysis results.

By the present approach and without a detailed analysis of the structure of the solid-state MAS-NMR spectra, we can isolate the Sample 4. Magnetic hysteresis secures the Sample 5 and Sample 6. Magnetic susceptibility also indicates the difference between the Sample 5 and Sample 6. XRF indicates some differences between the Samples 4 and Sample 6. Thus, among the results of the methods used it is proved a uniformity of the studied samples.

## 6. CONCLUSION

Selective handles of Hellenistic amphorae have been analysed for characterization and provenance purposes. The use of the described methods (kappametry, measurement of magnetic hysteresis, X-ray fluorescence and MAS-NMR) has shown the absence of simple characteristic that could allow the grouping of the studied samples. This allows us to conclude that the examined samples belongs technologically to a single group: they created with one type of raw material using with insignificant changes in additives. However, the main part of the test of ceramics of the investigated set is uniform.

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