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THE ANALYSIS OF PORES CHARACTERISTICS FOR CUCUTENI CERAMICS

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Abstract: *With its slender shapes and decorative motifs, the Cucuteni ceramics represent the apogee of the European prehistoric pottery, being often compared with the creations of other historical ages. The ancient ceramic samples are studied using Scanning Electron Microscopy - SEM analysis for pores dimensions in randomly scattered positions on samples surface, in order to make a comprehensive classification of materials based on their own characteristics. The numerical statistical analysis of experimental recorded data includes the probability density function - histogram and the Gauss normal distribution, mean and standard deviation statistical values, for the surface pores dimensions of the studied ceramic materials.*
Keywords: *Scanning Electron Microscopy - SEM analysis, ancient Cucuteni ceramic, pores dimension, statistical analysis.*

1. INTRODUCTION

When humans first mastered the use of fire 10000 years ago, they learned how to make low temperature earthenware in open firing pits. That unsophisticated production was the start of ceramic development [3].
The ceramic is any class of inorganic, nonmetalic products, which are subjected to a temperature over 550 Celsius degrees during manufacture. They include metallic oxides, carbides, nitrides, borides, or any combination or compounds of these [3]. The art of pottery is one of the most ancient Romanian crafts, as proved by the beautiful ceramic objects dating from the Neolithic era, the period of a blooming civilization.

Figure 1: A map showing the main presence of the Cucuteni-Trypillian culture [12]

The Cucuteni-Trypillian culture, also known as Cucuteni culture (from Romanian), Trypillian culture (from Ukrainian) or Tripolie culture (from Russian), is a late Neolithic archaeological culture which flourished between ca. 5500 B.C. and 2750 B.C., from the Carpathian Mountains to the Dniester and Dnieper regions in modern-day Romania, Moldova, and Ukraine, encompassing an area of more than 35.000 km^2. Cucuteni is close to the city of Iasi; 55 km from Iasi, 8 km N.E. from Targu Frumos, 35 km from Pascani. One of the most special creation of the Cucuteni culture was the painted pottery. With its slender shapes and decorative motifs, the Cucuteni ceramics represents the apogee of the European prehistoric pottery, being often compared with the creations of other historical ages [12].
The Cucuteni Periodization was proposed by the German Archeologist Hubert Schmidt in 1932, the Tripolie periodization was proposed by T.S. Passek in 1949 [12].

Table 1: Periodization Cucuteni Trypillian culture (Mantu [9])

CUCUTENI	YEARS B.C.	TRYPILLIAN	YEARS B.C.
Precucuteni I-III	5100-4600	Trypillian A	4800-4500
Cucuteni A1-A4	4600-4050	Trypillian BI-BII	4500-4000
Cucuteni A/B	4100-3800	Trypillian BII	4000-3800
Cucuteni B	3800-3500	Trypillian CI-CII	3800-3500

Time dating of the ancient ceramic materials and the position into the geographic space, according to those materials structure, are the objectives and the applicability of this study.
The research is focused on the description of the physical-chemical characteristics of the ancient ceramics, based on the experimental characteristics obtained using non-destructive methods for solid materials and sorted into a sample database [11].
The ceramic materials are solid, with poly-crystalline structures, including welded grains, due to the physical-chemical processes occurred during the material burn [1]. The clay is a capillary – porous material, where the water is linked in different ways with the clay substance.
In order to characterize the ceramic materials, it is applied a new approach consisting in pores dimension measurement, based on SEM analysis and followed by an standard statistical analysis.

2. BASICS OF EXPERIMENTAL AND STATISTICAL METHOD

Based on the SEM-Scanning Electron Microscopy [2],[10], a randomly scatter pores dimensions experimental data are obtained for each ceramic surface sample. For practical purpose, the randomly pores dimension measurements have to be process using a statistical analysis.
The random variables for describing the samples are defined by a number of central grouping and variability parameters, and by the probability density function (histogram).
The central grouping tendencies parameters are: the mean value (mathematic average) and also other parameters rarely used in statistical analysis of chemical-analytical data, as the median and the module values [5],[6]. Those parameters are pointing out the central tendency, the symmetry and the homogeneity of the statistical series values.
The variability parameters are: the amplitude, the dispersion or the variance, the standard deviation or the quadratic average deviation. Those parameters are pointing out the variability, dispersion, the values scattering around the central tendencies [8].
The mean value (mathematic average) of $x_1, x_2,....x_i,....,x_n$ values is equal to their sum divided by the total n number:

$$\mu = \frac{x_1 + x_2 + x_3 + ... + x_i + ... + x_n}{n} = \frac{\sum x_i}{n} \quad \textbf{(1)}$$

The amplitude is the easiest form to characterize the scattering experimental data. It represents the difference between the highest value x_{max} and the smallest value x_{min} of a statistical data series:

$$\Delta x = x_{\max} - x_{\min} \quad \textbf{(2)}$$

The selection dispersion is the main parameter of the scattering experimental data. The dispersion or the variation of a statistical series (selection) is the mathematical average of the quadratic deviation of the selection values towards their mathematic average:

$$\sigma^2 = \frac{\sum (x_i - \mu)^2}{n} \quad \textbf{(3)}$$

The standard deviation or the selection quadratic average deviation σ is the square-root of the selection dispersion:

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{n}} \quad \textbf{(4)}$$

The probability function and the probability density function (histogram) of the random variable $X \in \{x_i, i = 1, n\}$ are defined as following:

$$F_X(x) = P[X \le x] \;\; ; \;\; f_X(x) = \frac{dF_X(x)}{dx} \;\; \Rightarrow \;\; f_X(x) \cdot \delta x = P[x < X \le x + \delta x] \quad \textbf{(5.a)}$$

having a Gauss normal distribution [10] with the following expression:

$$f_X(x) = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad \textbf{(5.b)}$$

where the distribution parameters are the mean value μ and the standard deviation σ from equations (1) and (4).

3. THE EXPERIMENTAL DATA

The macroscopic view of 28 samples, authentic ceramic, named as CP001, CP002, … , CP028, are shown in Figure 2a. Simultaneously, have been studied, using the same method, a number of 11 „false" samples (Figure 2b), nowadays-ceramic samples, named GF058, GF059, … , GF068.
The comparative study of the two sets „true" and „false" samples has as final objective the ceramic samples classification according to material, making possible to identify those two main ceramic classes.

Figure 2a: Authentic ancient ceramic samples

Figure 2b: Nowadays-ceramic samples

The ceramic samples structural analysis (surface pores dimension) has been made with the electronic microscope, based on the non-destructive scanning method SEM - Scanning Electron Microscopy, at University „Dunarea de Jos" Galati, Sciences Faculty, Physics Department.
The quest toward understanding the behaviour of condensed matter has relied on measuring structure, bonding, and properties at increasingly local levels. This has driven advances in techniques that probe both soft and hard materials directly as well as indirectly [2].
The SEM provides the investigator with a highly magnified image of the surface of a material that is very similar to what one would expect if one could actually "see" the surface visually. This tends to simplify image interpretations considerably, but reliance on intuitive reactions to SEM images can, on occasion, lead to erroneous results. The resolution of the SEM can approach a few nm and it can operate at magnifications that are easily adjusted from 10 to 300.000 times [4]. This method is an excellent tool and it has been found useful in many applications to analyse the archaeological potteries (Goldstein et al 2003, Tite et al 1992, Tite et al 1982) [10].

The files with the pictures obtained based on the SEM method (TIFF format) are imported into the AutoCAD program, for digital scaling and measurement of the pores dimensions. For the pores chemometrics analysis, at each sample have been made 50 digital measurements on a scattered randomly distribution in the sample picture field.

In Figures 3-4.a are presented the ceramic samples shiver pictures. In Figures 3-4.b are presented the ceramic samples SEM analysis pictures. In Figures 3-4.c are presented the pores dimension histograms for the ceramic samples. In Figures 3-4.d are presented the pores dimension Gauss normal distributions for ceramic samples.

Figure 3.a: Ceramic sample CP012 is discovered into an archaeological site from Iasi County

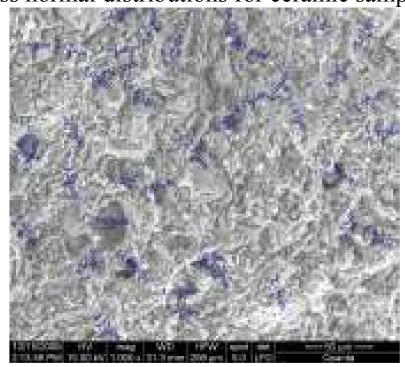

Figure 3.b: The SEM analysis– sample CP012

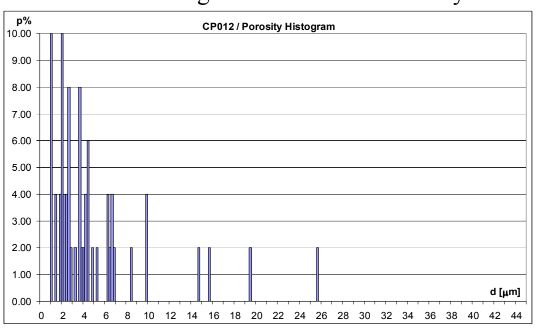

Figure 3.c: The pores dimension histogram for "true" ceramic sample CP012

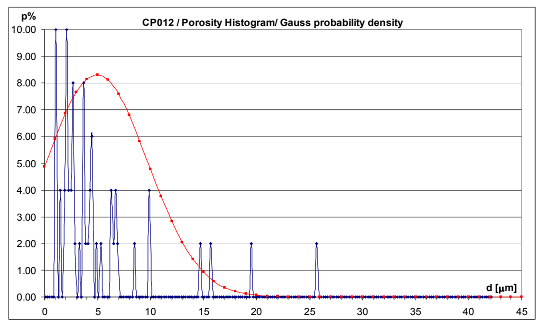

Figure 3.d: The pores dimension Gauss normal distribution for "true" ceramic sample CP012

For ceramic sample CP012 are obtained the following characteristics: the pores dimensions are in the following range 1.00 µm – 25.65 µm; the mean values of the pores dimension is 4.96 µm, for a SEM sampling resolution of 0.2 µm; the standard deviation of the pores dimension is 4.8 µm, for a SEM sampling resolution of 0.2 µm.

Figure 4.a: Ceramic sample GF063 is a nowadays-ceramic sample.

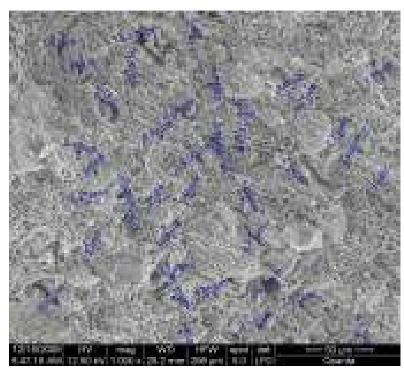

Figure 4.b: The SEM analysis– sample GF063

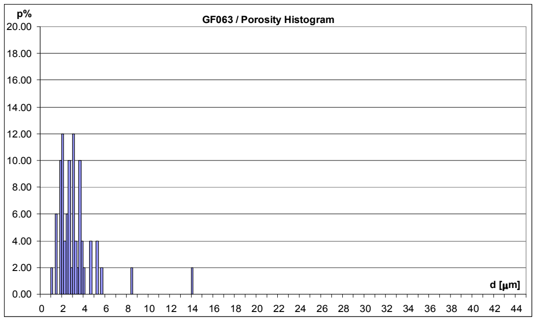

Figure 4.c: The pores dimension histogram for "false" ceramic sample GF063

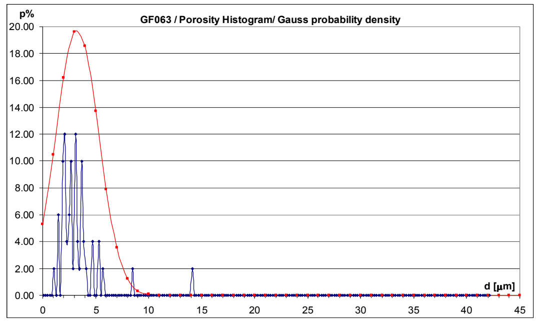

Figure 4.d: The pores dimension Gauss normal distribution for "false" ceramic sample GF063

For ceramic sample GF063 are obtained the following characteristics: the pores dimensions are in the following range 1.17 µm – 14.07 µm; the mean value of the pores dimension is 3.27 µm, for a SEM sampling resolution of 0.2 µm; the standard deviation of the pores dimension is 2.01 µm, for a SEM sampling resolution of 0.2 µm.

4. STATISTICAL RESULTS FOR SEM ANALYSIS EXPERIMENTAL DATA

In Tables 2.a,b are presented the statistical mean value and standard deviation for the pore dimensions, based on SEM analysis [2],[10], cumulated for all the „true" and „false" ceramic samples, as presented in Figures 2.a,b.
In Figures 5-6.a are presented the pores dimension histogram cumulated for all the „true" and „false" ceramic samples. In Figures 5-6.b are presented the pores dimension Gauss normal distributions cumulated for all the „true" and „false" ceramic samples.
In the case of „true" ceramic samples, the pores dimension distribution is extended on a wide significant values range 1 – 36.77 µm. In the case of „false" ceramic samples, the pores dimension distribution is grouped around a narrow significant values range 1 – 25.66 µm.

Table 2.a: The statistical mean value and standard deviation for the pore dimensions, based on SEM analysis for the 28 „true" ceramic samples (sampling resolution 0.2 µm)

Sample	CP001	CP002	CP003	CP004	CP005	CP006	CP007	CP008	CP009	CP010
Mean (µm)	4.17	3.98	6.14	4.28	5.44	4.41	4.15	4.60	5.82	3.76
Std.dev(µm)	4.33	2.19	4.94	3.28	3.09	2.40	2.42	3.80	5.61	1.25
Sample	CP011	CP012	CP013	CP014	CP015	CP016	CP017	CP018	CP019	CP020
Mean (µm)	4.74	4.96	5.20	4.22	3.89	4.89	4.01	4.94	5.40	3.28
Std.dev(µm)	5.30	4.80	5.19	3.12	3.18	4.34	2.87	2.46	2.75	1.33
Sample	CP021	CP022	CP023	CP024	CP025	CP026	CP027	CP028	CP	
Mean (µm)	5.38	5.20	4.44	4.32	6.62	4.61	4.68	4.30	4.71	
Std.dev(µm)	3.20	3.71	2.22	1.61	5.90	3.07	2.36	3.67	3.67	

Table 2.b: The statistical mean value and standard deviation for the pore dimensions, based on SEM analysis for the 11 „false" ceramic samples (sampling resolution 0.2 µm)

Sample	GF058	GF059	GF060	GF061	GF062	GF063
Mean (µm)	3.24	4.04	3.18	4.51	4.34	3.27
Std.dev(µm)	1.30	1.66	1.80	2.23	3.31	2.01
Sample	GF064	GF065	GF066	GF067	GF068	GF
Mean (µm)	3.46	3.09	5.14	3.27	2.44	3.64
Std.dev(µm)	1.22	0.94	3.93	1.30	0.85	2.21

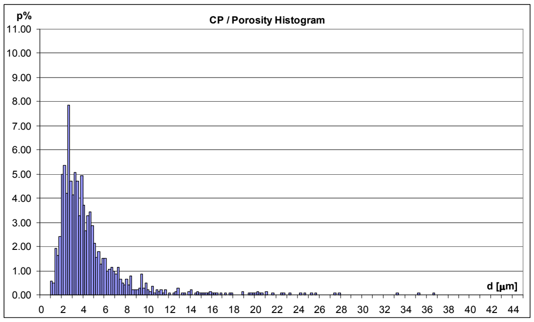

Figure 5.a: The pores dimension histogram cumulated for the 28 „true" ceramic samples

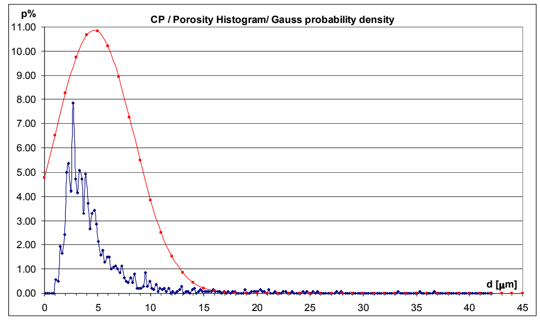

Figure 5.b: The pores dimension Gauss normal distribution cumulated for the 28 „true" samples

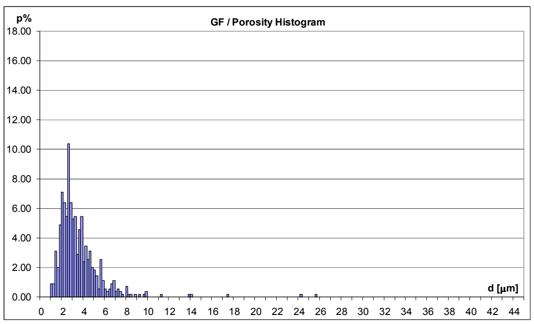

Figure 6.a: The pores dimension histogram cumulated for the 11 „false" ceramic samples

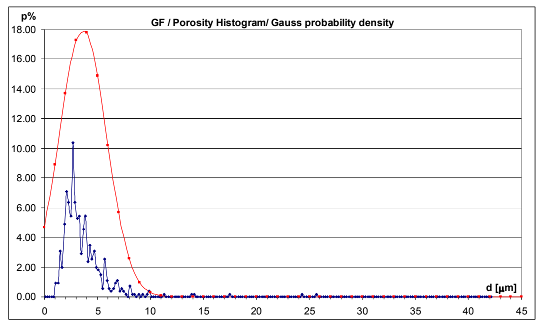

Figure 6.b: The pores dimension Gauss normal distribution cumulated for the 11 „false" samples

5. CONCLUSIONS

Based on the experimental data and the statistical chemometrics analysis of the ceramic samples (sections 3-4), it results the following conclusions of this study:

1. The measurements concerning the physical-chemical material sample series characteristics are linked to a significant property of the measured material. So, in this study the material property pores dimension, can be identified for an unknown sample, using less extended procedures as those initial measurements carried on for the reference samples [11].
2. The computer can be used both for image analysis and image processing using SEM method to study ceramic samples. The pores dimensions can be obtained very easily because the image information is collected via digital scanning and importing the image file into AutoCAD program for processing.
3. This study has included SEM pores dimensions analysis for 28 ancient Cucuteni ceramic samples and also 11 nowadays ceramic samples, making possible to obtain statistical criteria for ceramic identification.
4. From Tables 2.a,b and Figures 5-6, based on SEM analysis, in the case of „true" ancient ceramic samples of Cucuteni (mean 4.71 μm and standard deviation 3.67 μm values) the pores dimension have larger significant statistical values in compare to the nowadays ceramics (mean 3.64 μm and standard deviation 2.21 μm values).

In conclusion, based on experimental data for ancient and nowadays ceramic samples, using chemometrics results, as pores dimension statistical mean and standard deviation values, it can be recognized the pattern of the „true" ancient ceramic samples from a series that can include also „false" nowadays ceramic samples.

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