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CHEMOMETRIC METHOD FOR THE AUTOMATED IDENTIFICATION OF CUCUTENI CERAMICS BASED ON ATR-FTIR SPECTRA

Mirela Praisler[1*], Daniela Domnisoru[1] and Leonard Domnisoru[2]

[1] *'Dunarea de Jos' University of Galati, Faculty of Sciences and Environment, Department of Chemistry, Physics and Environment, Domneasca Street 47, RO 800008, Galati, Romania*
[2] *'Dunarea de Jos' University of Galati, Faculty of Naval Architecture, Domneasca Street 47, RO 800008, Galati, Romania*

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Abstract

A chemometric software application was developed in order to obtain an automatic identification of original *Cucuteni* ceramic artifacts and distinguish them from fake ceramic samples similar to those found on the black market. The software application is based on Principal Component Analysis (PCA), a method of artificial intelligence that allowed us to build multivariate models that can be used for the efficient spectral discrimination of genuine *Cucuteni* ceramic samples. The spectra obtained by Fourier Transform Infrared Spectroscopy with ATR-Attenuated Total Reflection (FTIR-ATR) for a set of *Cucuteni* ceramic samples discovered in archaeological sites from Moldova - Romania were used as input database for the detection system.

Keywords: Cucuteni ceramics, FTIR-ATR technique, Principal Components Analysis

1. Introduction

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 regions. Ancient ceramic objects are usually considered the most specific indicators of each civilization because they are very resistant and thus maintain their aesthetic characteristics for long periods of time. In the case of the *Cucuteni* culture, the ceramic samples are the most important archaeological artefacts, as this culture became famous particularly due to the surprisingly beautiful pottery its people produced. On the other hand, the genuine and well-developed aesthetic sense of artistry used in decorating the clayware makes the *Cucuteni* ceramic artefacts so wanted on the black market of archaeological objects. In addition, due tot the

* E-mail: Mirela.Praisler@ugal.ro

high interest and demand for *Cucuteni* ceramic artefacts, fake ceramic samples imitating genuine *Cucuteni* ceramic artefacts are often encountered (Figure 1).

The aim of this study was to determine objective criteria to be used for the characterization and identification of *Cucuteni* ceramic artefacts for forensic and security reasons. The research is focused on the description and selection of physico-chemical characteristics of *Cucuteni* ancient ceramics that can be used in order to classify ceramics objects in 'authentic' and 'fake' samples [1]. The positive identification of such ceramic samples was performed based on a non-destructive, sensitive, selective and fast analytical technique, i.e. Fourier Transform Infrared Spectroscopy with Attenuated Total Reflection [2], [Bruker, *Bruker Optics FTIR Spectrometer System Tensor 27 IR, ATR Golden Gate, Opus Software*, 2009, available from: http://www.brukeroptics.com]. The spectral data was organized in a FTIR database that was then processed by using a flexible artificial intelligence technique, i.e. Principal Component Analysis (PCA) [3, 4]. Modern archaeometry includes the use of artificial intelligence methods, which allow us to process simultaneously databases including a very large number of physico-chemical or spectral variables and derive conclusions that are otherwise so time consuming to obtain [5].

2. Experimental procedure

FTIR spectroscopy is an important tool for the analysis of ceramic materials. The absorptions are associated with the vibrations of atom molecules excited by irradiation with infrared light. Each molecule or chemical group absorbs infrared light at specific wavenumbers, the spectrum being a fingerprint of the absorbing molecular structure [2].

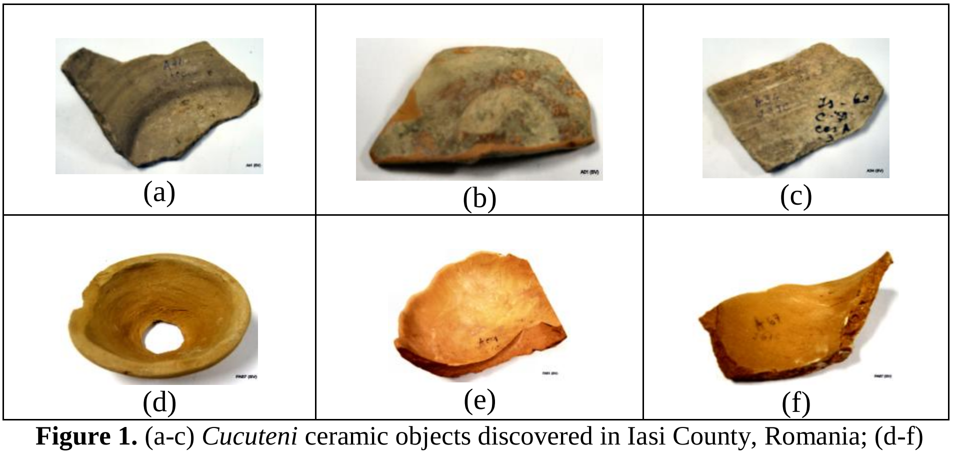

Figure 1. (a-c) *Cucuteni* ceramic objects discovered in Iasi County, Romania; (d-f) imitations of *Cucuteni* ceramics.

The spectra of 70 ceramic samples were recorded with a Bruker TENSOR 27 IR FTIR-ATR Spectrometer. A number of 50 samples are authentic *Cucuteni* ceramic artefacts and 20 samples are imitations obtained by experimental archaeology in the laboratory. In order to record a FTIR spectrum, a small amount of powder (1-3 grams) was collected from the surface of the ceramic sample, and then the powder was placed on to the diamond radiation area of the ATR Golden Gate device. The spectrometer collects the spectral data and turns the interferogram in numeric format, then it performs the Fourier Transformation (FT) of the analytical signal and yields the FTIR spectrum file [Bruker, *Bruker Optics FTIR Spectrometer System Tensor 27 IR, ATR Golden Gate, Opus Software,* 2009, available from: http://www.brukeroptics.com]. The procedure is very fast, lasting 1-2 seconds, with fully automatic spectrum recording. Each spectrum was recorded twice, once on each side of the ceramic samples. A number of 24 scans were recorded for each sample in the 4000 to 550 cm^{-1} spectral range, using the reflection mode with a resolution of 4 cm^{-1}.

3. Results and discussion

Representative FTIR-ATR spectra of authentic and fake ceramic samples are presented in Figure 2, in absorbance vs. wavenumber (550÷4000 cm^{-1}) format. We can see that the selectivity of the FTIR-ATR spectroscopy is extremely helpful in discriminating authentic *Cucuteni* ceramic samples from their imitations, based on the intensity of the main peaks. The authentic samples are characterized by a strong (partially overlapped) pair of peaks found around 2400 cm^{-1}, characterized by an absorbance of 0.15, while the same pair of peaks have an absorbance of only 0.10-0.08 in the spectra of the imitating ceramic samples. On the other hand, the large peaks showing around 950 cm^{-1} have a medium to low intensity (0.08 – 0.04) in the spectra of *Cucuteni* ceramic objects, and a very strong intensity (0.14 – 0.22) in the spectra of the fake ceramic samples. In other words, the high selectivity of the FTIR-ATR technique recommends it as a powerful tool that can be used to distinguish between *Cucuteni* ceramic objects and imitations without any further spectra processing.

However, the exquisite sensitivity of the FTIR-ATR spectrum shape to very small variations in the structure and composition of the sample becomes in this case a disadvantage. The variation in peak intensity encountered in the spectra of authentic *Cucuteni* samples becomes a challenge in recognizing a *Cucuteni* sample as a true one, i.e. in classifying a *Cucuteni* sample as such, based on its FTIR-ATR spectrum. These intensity variations appear due to the fact that the manufacturing process used at the time of the *Cucuteni* culture (5500 - 2750 BC) was rudimentary. As a result, variations in manufacturing parameters, such as temperature, yielded variations in the structure and composition of the pottery [6]. The same variations are observed in the spectra of the ceramic samples obtained by experimental archaeology (see Figure 2 c, d), in which the clayware manufacturing techniques are kept as close to the most probable original ones as possible. In conclusion, the sensitivity of the FTIR-ATR technique becomes in our application a challenge for the capacity of FTIR-ATR spectra to recognize a true *Cucuteni* sample as such (true positive), or a fake sample imitating *Cucuteni* ceramics (true negative).

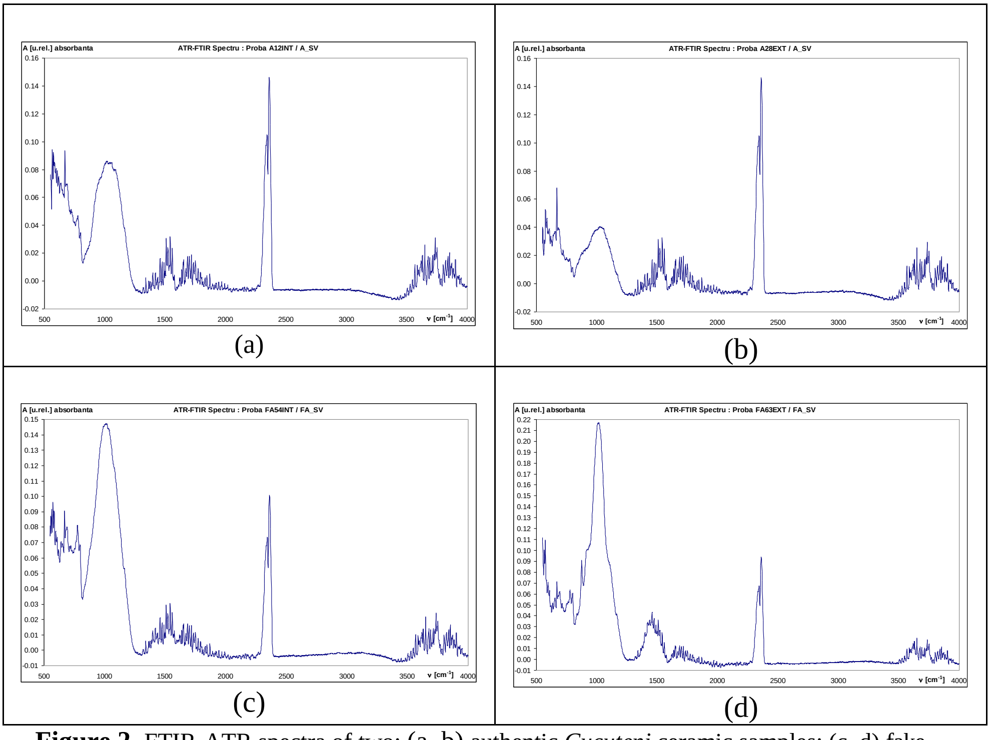

Figure 2. FTIR-ATR spectra of two: (a, b) authentic *Cucuteni* ceramic samples; (c, d) fake ceramic samples.

In order to diminish as much as possible the rate of classifying *Cucuteni* artefacts as false negatives or of classifying imitating ceramic objects as false positives, artificial intelligence was used to process the data obtained by ATR-FTIR spectroscopy. A successful multivariate method that has been applied for the identification of ceramics belonging to various cultures or ages is Principal Component Analysis (PCA). This data processing method is based on the eigen values and vectors of the multivariable covariance matrix. It allows the extraction of the relevant information present in large experimental databases, through the decomposition on principal components (PC) resulting eigen vectors, according to the significance of the eigen values (principal components variability) [7, 8].

In order to characterize the authentic ceramic samples with PCA, we have build a spectral database consisting of 102 ATR-FTIR spectra, representing 1789 variables, i.e. the absorptions measured in the range 550–4000 cm^{-1} at 1.93 cm^{-1} apart. PCA has been carried out with the *XLSTAT* software [*XLSTAT Addinsoft Program User Guide (educational licence)*, 2009, available from http://www.xlstat.com, accessed: 21/04/2011], developed as a Visual Basic application under Microsoft-Excel environment. A number of 99 eigenvalues were used for the decomposition on significant principal components in the case of the authentic ceramic samples and 42 eigenvalues for the fake ceramic samples.

Table 1. Eigenvalues of the covariance matrix for the first principal components in the case of the *Cucuteni* ceramic samples.

PCA	PC1	PC2	PC3	PC4	PC5
Eigenvalue	922.736	580.803	132.358	61.299	49.468
Variability (%)	51.578	32.465	7.398	3.426	2.765
Cumulative %	51.578	84.044	91.442	94.868	97.634
PCA	**PC6**	**PC7**	**PC8**	**PC9**	**PC10**
Eigenvalue	10.075	8.589	4.980	3.652	2.655
Variability (%)	0.563	0.480	0.278	0.204	0.148
Cumulative %	98.197	98.677	98.955	99.159	99.308

Table 1 presents the first ten eigenvalues of the covariance matrix, PCs and the corresponding variability, for true ceramic samples. The diagram of first five PCs obtained for the 102 spectra characterizing the *Cucuteni* ceramic samples is presented in Figure 5. We can see that the cumulated explained variance increases significantly up to the 3rd PC (PC1 51.6%, PC2 32.4%, PC3 7.4%), for higher order PCs the explained variance of all individual PCs dropping down under 4%, practically fading out in significance for PCA data decomposition. In conclusion, only PC1, PC2 and PC3, which are cumulating 91.442% of the information, were kept for further investigation. Figures 3b, c and d present the projections of the spectra of the *Cucuteni* ceramic sample onto the main three PCs.

In order to characterize the fake ceramic samples PCA, we have build up a database formed with 42 ATR-FTIR spectra by using the same variable distribution, i.e. 1789 spectral variables (absorptions measured at wavenumbers in the range 550–4000 cm^{-1}, 1.93 cm^{-1} apart). Table 2 presents the first ten eigenvalues of the covariance matrix and the corresponding variability for each PC in the case of fake ceramic samples. Figure 4a presents the amount of spectral information imbedded in the first five principal components (PC). In the case of fake ceramic samples, the first three PCs are also explaining most of the information contained by the FTIR-ATR spectra (PC1 40.4%, PC2 37.7%, PC3 9.0%), the rest of the PCs bringing little valuable information to the system. Still we should notice that the variability in the spectra of fake samples is larger than in the case of true *Cucuteni* samples. The first three PCs account for a cumulative explained variance of only 87.104% in the case of fake samples, i.e. less than in the case of *Cucuteni* ceramic samples.

The projections of spectra of fake ceramic sample onto the main three principal components are presented in Figures 4b, c, d. Comparing Figures 3b and 4b we can notice that the scores of the *Cucuteni* ceramic artifacts are grouped around PC1, in the up-left and down-right quadrants, while the scores of the fake ceramic samples are scattered in all PC1-PC2 projection area.

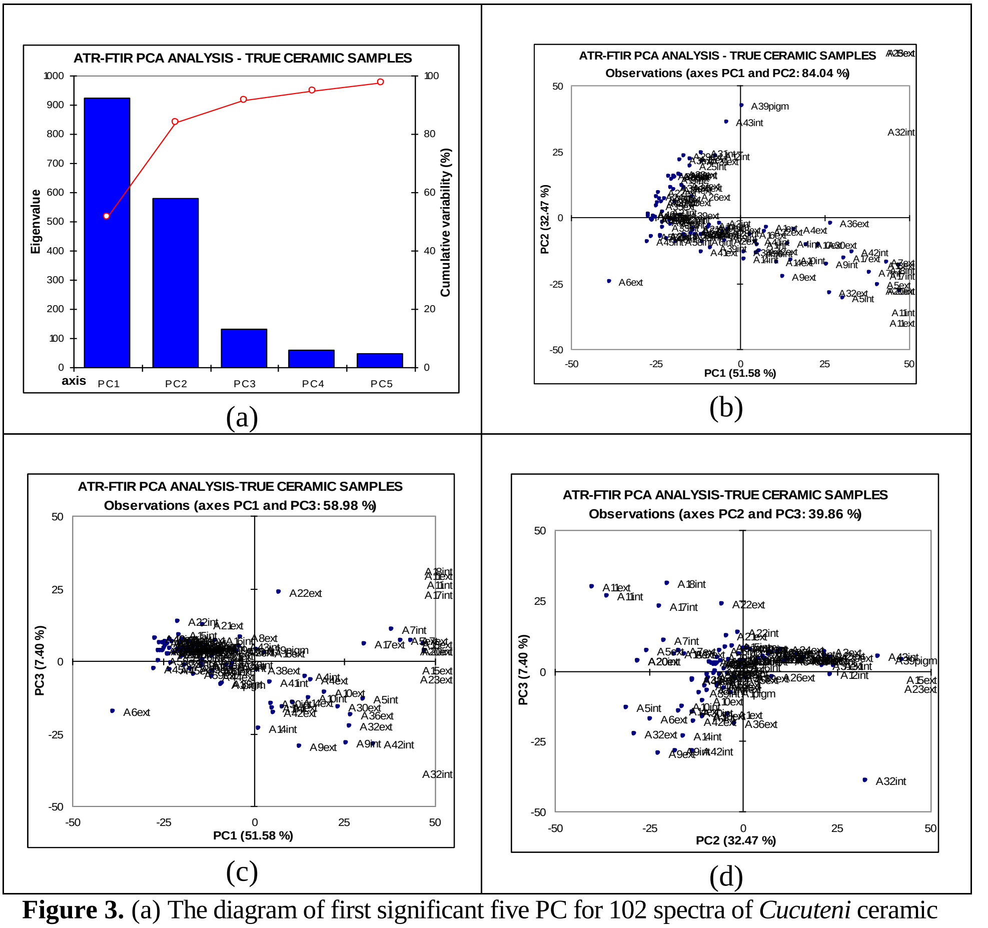

Figure 3. (a) The diagram of first significant five PC for 102 spectra of *Cucuteni* ceramic samples; (b) Score plot PC2 vs. PC1 characterizing the spectra of *Cucuteni* ceramic samples; (c) Score plot PC3 vs. PC1 characterizing the spectra of *Cucuteni* ceramic samples; (d) Score plot PC3 vs. PC2 characterizing the spectra of *Cucuteni* ceramic samples.

Table 2. Eigenvalues of the covariance matrix for the first principal components in the case of the fake ceramic samples.

PCA	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**
Eigenvalue	723.022	673.761	161.503	127.904	42.253
Variability (%)	40.415	37.661	9.028	7.149	2.362
Cumulative %	40.415	78.076	87.104	94.253	96.615
PCA	**PC6**	**PC7**	**PC8**	**PC9**	**PC10**
Eigenvalue	15.844	9.435	4.570	3.715	2.450
Variability (%)	0.886	0.527	0.255	0.208	0.137
Cumulative %	97.501	98.028	98.284	98.491	98.628

On the other hand, by comparing Figures 3c and 4c, we can observe that the scores of the *Cucuteni* ceramic artefacts are grouped around PC1 in centre of the PC1-PC3 projection area and in the down-right quadrant, while the scores of the fake ceramics are grouped in the up-right and down-left quadrants. Figures 3d and 4d indicate that the scores of the *Cucuteni* ceramic artefacts are grouped around PC1, in the central and down-left quadrant, while the scores of the fake ceramic samples are scattered in the whole PC2-PC3 projection area.

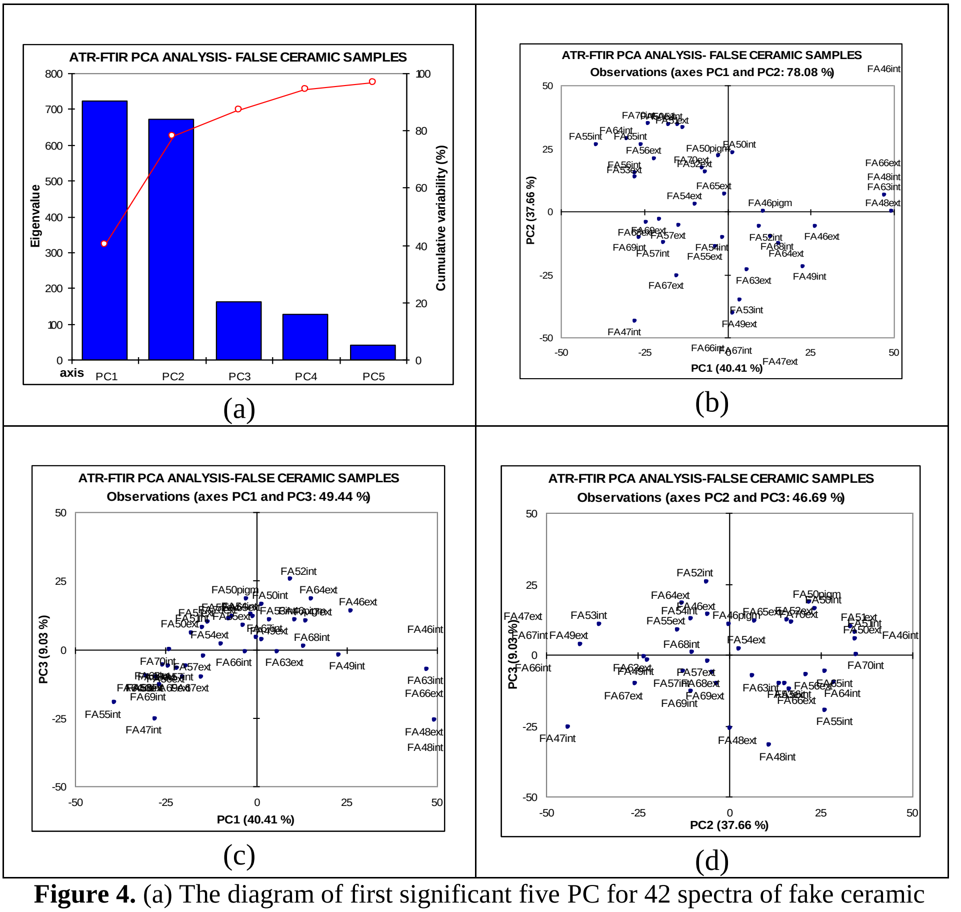

Figure 4. (a) The diagram of first significant five PC for 42 spectra of fake ceramic samples; (b) Score plot PC2 vs. PC1 characterizing the spectra of fake ceramic samples; (c) Score plot PC3 vs. PC1 characterizing the spectra of fake ceramic samples; (d) Score plot PC3 vs. PC2 characterizing the spectra of fake ceramic samples.

4. Conclusions

FTIR-ATR spectroscopy is a powerful technique for the characterization of the origin of ceramic samples. The analytical differences between *Cucuteni* ancient ceramic samples (positives) and fake ceramic samples (negatives) obtained by FTIR-ATR spectroscopy allow an efficient discrimination of the two classes of objects by visual inspection. However, in the particular case of ancient ceramic artefacts, significant differences in peak intensity appear due to instabilities in the manufacturing process (e.g. temperature control). This study has demonstrated that the problem can be successfully overcame. Further processing the FTIR-ATR spectral information can decrease the rate of false positives (fake ceramic samples identified as *Cucuteni* ancient ceramics) or false negatives (*Cucuteni* ancient ceramics identified as fake ceramic samples) significantly. Performing a PCA analysis is the key to obtain archaeological criteria to positively identify an unknown sample and assign its class identity.

The criterion of sensitivity will certainly be improved by enlarging the sample collection and associated spectral database with ceramic artefacts of different cultures, ages, geographical origin, manufacturing technique or structure. We should also notice that the proposed combination of methods can be successfully applied for the evaluation of the origin or the quality of industrially present-day manufactured ceramics. Reliable identification criteria based on FTIR-ATR spectroscopy coupled with artificial intelligence techniques such as PCA can be very useful for consumer protection or forensic tests.

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