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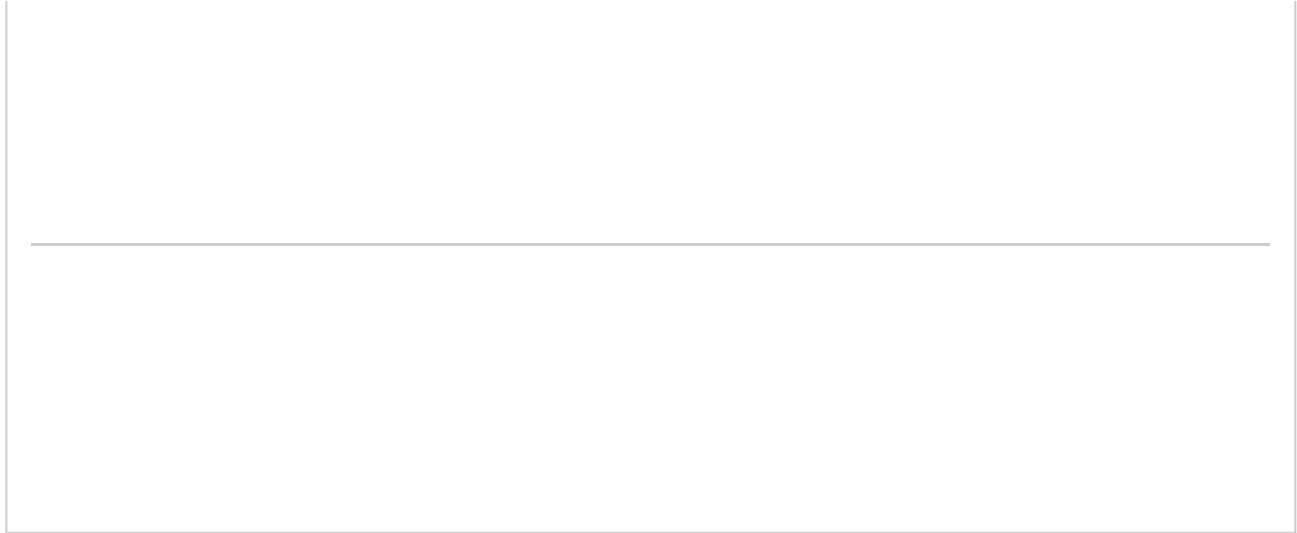
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Neutron resonance capture analysis and chemometric tools: an integrated approach

M Nardini^{1,2}, C Andreani^{1,3,5,6}, R Senesi^{1,3,5,6}, A Scherillo⁷, F D'Agostino⁸, L Romano⁸, C Scatigno^{1,4}, and G Festa^{1,3,5}

¹ Università degli Studi di Roma "Tor Vergata", Centro NAST, Via della Ricerca Scientifica 1, Rome, 00133 Italy

² Physics Institute, Fondazione Policlinico Universitario A. Gemelli, Catholic University of the Sacred Heart, Largo Francesco Vito 1, Rome, 00168 Italy

³ Università degli Studi di Roma "Tor Vergata", Dipartimento di Fisica, Via della Ricerca Scientifica 1, Rome, 00133 Italy

⁴ Università degli Studi di Roma "Tor Vergata", Dipartimento di Scienze e Tecnologie Chimiche, Via della Ricerca Scientifica 1, Rome, 00133 Italy

⁵ Centro Fermi - Museo Storico della Fisica, Centro Studi e Ricerche "Enrico Fermi", Piazza del Viminale 1, Rome, 00184 Italy

⁶ CNR-IPCF Sezione di Messina, Viale Ferdinando Stagno d'Alcontres 37, Messina, 98158 Italy

⁷ ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK

⁸ Sapienza - University of Rome, Italian Institute of Oriental Studies, Rome, Italy

E-mail: roberto.senesi@uniroma2.it

Abstract. A joint approach based on the Neutron Resonance Capture Analysis (NRCA) integrated by chemometric tools namely Principal Component Analysis (PCA) is used to determine the semi-quantitative isotopic composition of a large set of Sumerian pottery. Here, we present NRCA results from the experimental campaign carried out on the INES beamline at the ISIS pulsed neutron and muon source (Rutherford Appleton Laboratory, UK). The potteries come from the archaeological site still under excavation of Abu Tbeirah, a 3rd millennium BCE site located in Southern Iraq, in the S-E periphery of the city of Nasiriyah. NRCA allows to determine the presence and the relative isotopic amounts, while the Principal Component Analysis distinguishes the elements/isotopes linked to the raw materials from the decay products due to contaminants that affect the potteries under investigation.

1. Introduction

Neutron Resonance Capture Analysis (NRCA) is an experimental technique whereby a neutron with energies in excess of few eV and up to hundreds of keV is resonantly absorbed by a nucleus, and a prompt-gamma cascade is emitted. The energy of the resonance is characteristic of the element and isotope that produce the gamma, and can be used to identify the chemical composition of the investigated sample by the comparison with (n,γ) cross section libraries [1]. Moreover, the intensity of the resonance is proportional to the number of absorbing centres via the (n,γ) cross section. NRCA was developed at the GELINA facility in Belgium, a pulsed neutron source with a linear electron accelerator [2], and at the ISIS pulsed neutron and muon source in the UK [3, 4], where the intense flux at electron-volt (epithermal) [5] neutron energies



is available. Experiments have been performed on the Italian Neutron Experimental Station (INES) [6] over the last decades [7, 8, 9], and more recently on the VESUVIO spectrometer at ISIS [10], whose NRCA capabilities have been discussed in a separate contribution to this volume as an application to materials-science investigations [11]. Here, we present a joint semi-quantitative approach that integrates NRCA measurements with statistical tools via a multivariate analysis namely Principal Component Analysis (PCA) to reveal possible correlations between the isotopes for the investigated samples, bringing to the fore the main properties of the pottery data set. From a chemometric point of view, the primary aim of this analysis is determining the most significant reference basis representing the experimental data and minimizing the noise. The output of the statistical approach is described through the Principal Components (PCs) that allow to define the parameters' variance due to the different correlations among the dataset. These techniques allow to identify member of clusters and to study the variance and correlations along the data [12].

2. Experimental set-up

The entire set of 36 pottery samples found at the site of Abu Tbeirah [13] was investigated through the NRCA technique at the Italian Neutron Experimental Station (INES), ISIS pulsed neutron and muon source in the UK. Artefacts were placed within the instrument tank, with the primary flight path between the sample and the TS1 water moderator $L_1 = 22.804$ m. Prompt-gamma radiation was detected using an Yttrium Aluminium Perovskite crystal YAIO_3 coupled with a photomultiplier and positioned above the tank at a distance $L_2 \simeq 1.0$ m from the sample position. As the gamma radiation travels at the speed of light, the time needed for a photon to travel from the sample to the detector can be neglected compared to the time a neutron takes to move from the moderator to the sample position. Therefore, time-of-flight (ToF) measurements were performed, and the energies of incident neutrons are directly related to ToF values via the *a priori* knowledge of L_1 , using the relation:

$$E = \frac{1}{2} m_n \frac{L_1^2}{\text{ToF}^2} \quad (1)$$

with E the energy of the incident neutron, and m_n its mass. Measured spectra show the sharp resonances, and an environmental background of photons from the moderator, generated within the blockhouse, and within the neutron beam stop. The simpler analysis of NRCA spectra is based on the indexing of the observed resonances by comparing the centre of each measured peak to tabulated libraries [1], up to hundreds of keV. Some examples of (n, γ) cross sections for chlorine, iron, sodium, and manganese are shown in Figure 1.

3. Results and discussion

NRCA spectra and pictures of two potteries are shown in figure 2. The indexing of the observed resonances results in the recognition of potassium, chlorine, iron, manganese and sodium as the principal signals in the NRCA spectra.

It could be noted that sample 22 is characterized by an high signal from the ^{35}Cl respect to sample 23, both sample show a small peak for ^{39}K and sharp and close peaks of ^{23}Na and ^{56}Fe . A broad peak from ^{55}Mn is present in both spectra, this broad shape depends on ^{55}Mn (n, γ) cross section, see figure 1 (e). A semi-quantitative determination of the relative amounts of these isotopes/elements are then attempted based on the normalisation procedure:

$$\rho_i = \sum_j \frac{I_{r_j,i}}{d \cdot \sigma_i(t_{r_j,i})} \quad (2)$$

where $I_{r_j,i}$ is the peak amplitude, from the detector output, of the j -th resonance of i -th element, $\sigma_i(t_{r_j,i})$ is the value of (n, γ) cross section calculated at time $t_{r_j,i}$ where one can find the

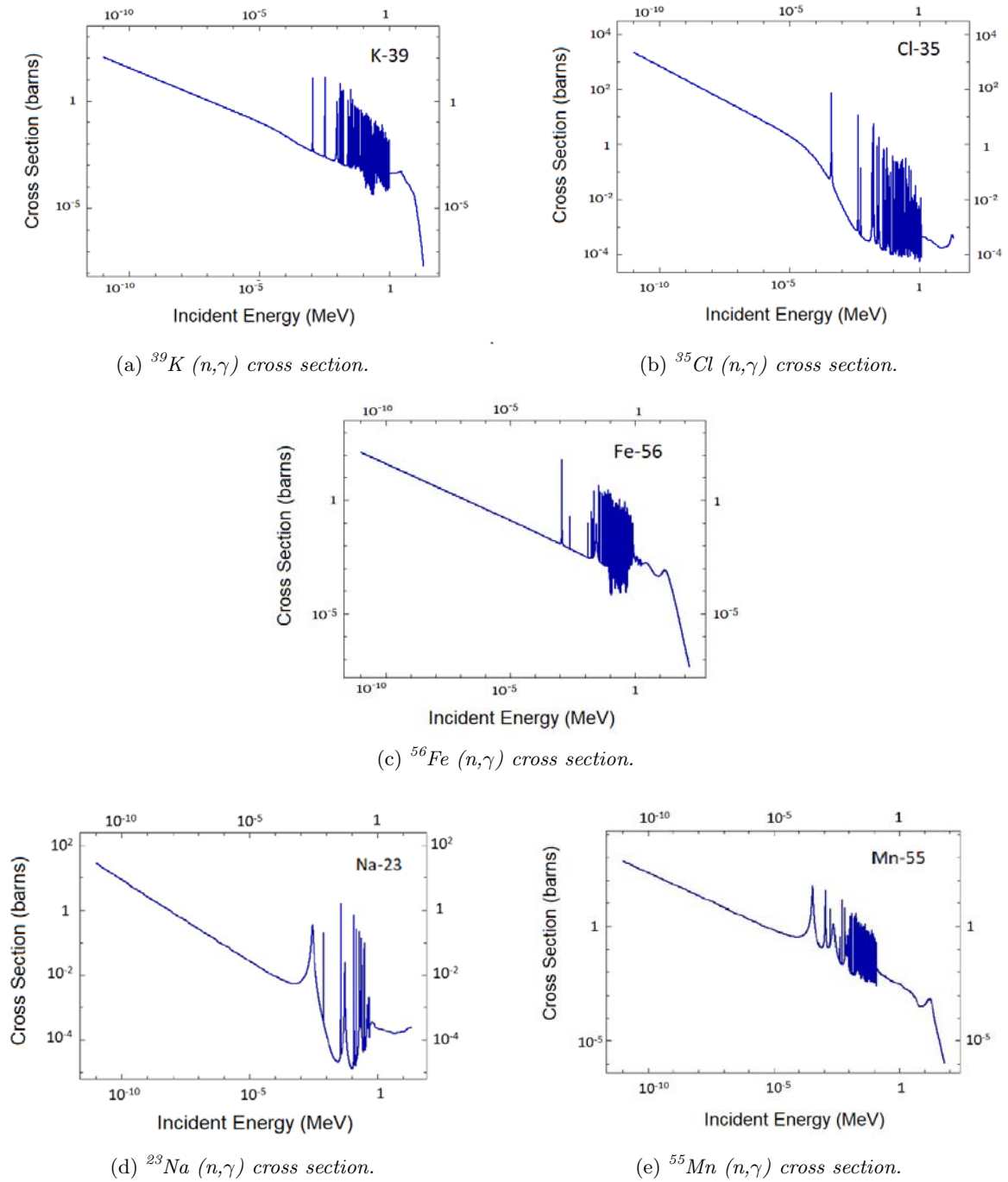


Figure 1: Cross sections for the (n,γ) process of ^{35}Cl , ^{56}Fe , ^{23}Na , and ^{55}Mn elements.

maximum of the resonance peak r_j for the i -th element, and d is the value of sample thickness. The resulting values for the relative concentrations ρ_i (in arbitrary units) of the most abundant isotopes are listed in Table 1. These values are obtained through a normalization process to be able to compare results obtained from the same set of samples. Errors in table are calculated using error propagation theory from equation 2.

Data are treated through a chemometric tool namely PCA. The dataset is organized by a

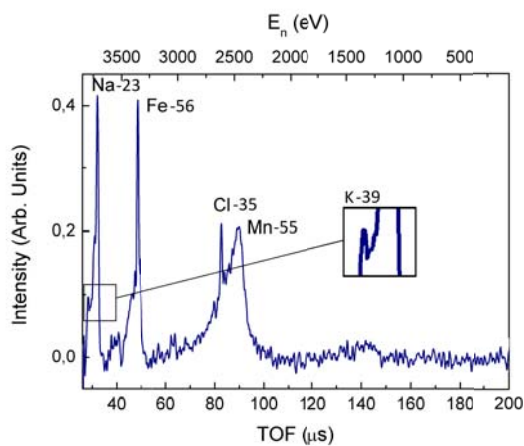
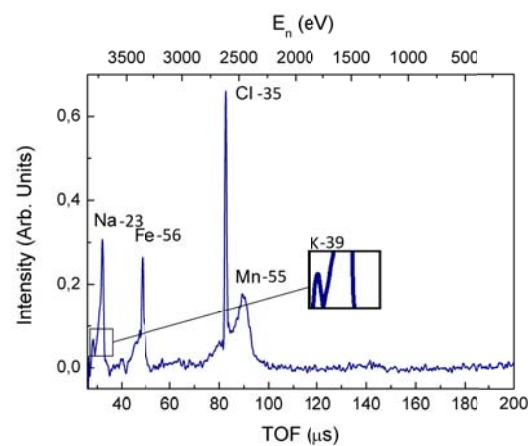
(a) *Sample 22.*(b) *Sample 23.*(c) *NRCA spectrum of sample 22.*(d) *NRCA spectrum of sample 23.*

Figure 2: Pictures and Neutron Resonance Capture Analysis spectra with isotopes assignment of pottery samples.

matrix with 36×10 entries, samples and variable respectively. The algorithm used is the singular value decomposition (SVD), with the cross-validation method, and mean centre data as a model input. The software used is the Unscrambler package - version 10 (chemometric software package — Camo, Woodbridge, NJ, USA) [14]. PCs Loading plot of the relative amount of the isotopic composition on the entire set of samples is showed in figure 3; it shows the correlation among the detected isotopes/elements.

Two principal components (PCs) are extracted, representing 97% of the total variance (PC1: 89% and PC2: 8%). The first Loadings plot (Fig. 4a) shows two groups: ^{35}Cl and ^{23}Na , characterized by a positive value of PC1 and PC2 (that means that are markers of the whole set of data) and ^{56}Fe , ^{39}K and ^{55}Mn grouped in the center of PCs with a small variability, indicating an homogeneity of the element distributions on the analyzed data. ^{35}Cl and ^{23}Na are clearly linked to the decaying products such as sodium chloride contamination, while the second group is linked to the primary minerals (present in the raw material) and secondary minerals (products of thermally induced reactions), as well as the firing minerals (formed after the production, during their use and mainly their burial, as a result of either transformation of metastable firing minerals or infiltration of any solution) [15]. Actually, ^{56}Fe could be related

Table 1: Normalized peak intensities of the whole set of 36 samples resulting from the Neutron resonance capture analysis spectra.

Sample	ρ_{K-39}	ρ_{Na-23}	ρ_{Fe-56}	ρ_{Cl-35}	ρ_{Mn-55}
1	0.025 ± 0.006	1.8 ± 0.4	0.009 ± 0.002	1.1 ± 0.2	0.0030 ± 0.0008
2	0.013 ± 0.004	1.3 ± 0.3	0.007 ± 0.001	0.33 ± 0.07	0.0028 ± 0.0007
3	0.016 ± 0.003	1.1 ± 0.2	0.006 ± 0.001	0.44 ± 0.07	0.0026 ± 0.0005
4	0.012 ± 0.001	0.7 ± 0.1	0.006 ± 0.000	0.38 ± 0.03	0.0019 ± 0.0002
5	0.023 ± 0.005	1.3 ± 0.3	0.007 ± 0.001	0.33 ± 0.07	0.0031 ± 0.0007
6	–	1.0 ± 0.2	0.005 ± 0.001	0.6 ± 0.1	0.0030 ± 0.0008
7	0.020 ± 0.004	1.2 ± 0.2	0.007 ± 0.001	0.7 ± 0.1	0.0032 ± 0.0006
8 B	0.031 ± 0.007	1.9 ± 0.4	0.010 ± 0.002	0.26 ± 0.07	0.0036 ± 0.0009
8 W	0.018 ± 0.004	1.2 ± 0.2	0.010 ± 0.002	0.5 ± 0.1	0.0044 ± 0.0009
9	0.027 ± 0.006	1.3 ± 0.3	0.007 ± 0.001	0.5 ± 0.1	0.0031 ± 0.0007
10	0.014 ± 0.002	0.7 ± 0.1	0.005 ± 0.001	0.63 ± 0.07	0.0017 ± 0.0003
11	0.019 ± 0.003	1.3 ± 0.2	0.008 ± 0.001	0.66 ± 0.09	0.0029 ± 0.0005
12	–	1.9 ± 0.5	0.012 ± 0.003	1.3 ± 0.3	0.004 ± 0.001
13	0.017 ± 0.004	1.0 ± 0.2	0.005 ± 0.001	0.9 ± 0.1	0.0020 ± 0.0005
14	0.033 ± 0.009	1.9 ± 0.5	0.010 ± 0.002	1.1 ± 0.3	0.004 ± 0.001
15	0.021 ± 0.007	1.3 ± 0.4	0.007 ± 0.002	0.3 ± 0.1	0.004 ± 0.001
17	0.020 ± 0.005	1.5 ± 0.3	0.007 ± 0.001	1.2 ± 0.2	0.0023 ± 0.0006
18 L	0.016 ± 0.003	1.3 ± 0.2	0.007 ± 0.001	0.27 ± 0.06	0.0041 ± 0.0007
18 S	0.022 ± 0.005	1.1 ± 0.2	0.006 ± 0.001	0.27 ± 0.06	0.0031 ± 0.0007
19 L	0.010 ± 0.004	0.7 ± 0.2	0.005 ± 0.001	0.19 ± 0.06	0.0021 ± 0.0007
19 S	0.012 ± 0.004	0.6 ± 0.2	0.004 ± 0.001	0.19 ± 0.06	0.0018 ± 0.0006
20	–	1.2 ± 0.2	0.007 ± 0.001	0.24 ± 0.06	0.0034 ± 0.0007
21 L	0.013 ± 0.004	1.0 ± 0.2	0.005 ± 0.001	0.39 ± 0.08	0.005 ± 0.001
21 S	–	1.0 ± 0.2	0.005 ± 0.001	0.27 ± 0.06	0.0028 ± 0.0007
22	0.007 ± 0.001	0.8 ± 0.1	0.006 ± 0.000	0.21 ± 0.02	0.0023 ± 0.0002
23	0.009 ± 0.002	1.1 ± 0.2	0.006 ± 0.001	0.27 ± 0.05	0.0034 ± 0.0005
24	0.013 ± 0.004	1.3 ± 0.3	0.008 ± 0.001	0.33 ± 0.07	0.0028 ± 0.0007
25	–	0.9 ± 0.2	0.004 ± 0.001	0.12 ± 0.04	0.0023 ± 0.0006
26 L	0.005 ± 0.002	1.1 ± 0.2	0.007 ± 0.001	0.27 ± 0.06	0.0023 ± 0.0006
26 S	–	0.9 ± 0.3	0.006 ± 0.002	0.14 ± 0.06	0.0029 ± 0.0009
27	–	1.0 ± 0.2	0.006 ± 0.001	0.21 ± 0.06	0.0027 ± 0.0008
28	–	1.0 ± 0.2	0.008 ± 0.002	–	0.0036 ± 0.0009
29	–	0.6 ± 0.1	0.005 ± 0.000	0.32 ± 0.02	0.0020 ± 0.0002
30	–	0.5 ± 0.1	0.003 ± 0.000	0.21 ± 0.02	0.0010 ± 0.0002
31	–	0.9 ± 0.2	0.006 ± 0.001	0.59 ± 0.09	0.0028 ± 0.0005
32 L	–	0.6 ± 0.1	0.006 ± 0.001	0.18 ± 0.03	0.0023 ± 0.0004
32 S	–	0.6 ± 0.1	0.005 ± 0.001	0.13 ± 0.04	0.0018 ± 0.0005
33	–	0.8 ± 0.2	0.005 ± 0.001	0.55 ± 0.09	0.0025 ± 0.0005
34	–	1.0 ± 0.2	0.006 ± 0.001	0.9 ± 0.2	0.0026 ± 0.0006
35	–	0.8 ± 0.2	0.004 ± 0.001	0.50 ± 0.09	0.0023 ± 0.0005
36	–	0.9 ± 0.2	0.004 ± 0.001	0.6 ± 0.1	0.0020 ± 0.0005
37	0.008 ± 0.002	0.5 ± 0.1	0.006 ± 0.001	0.13 ± 0.03	0.0025 ± 0.0004

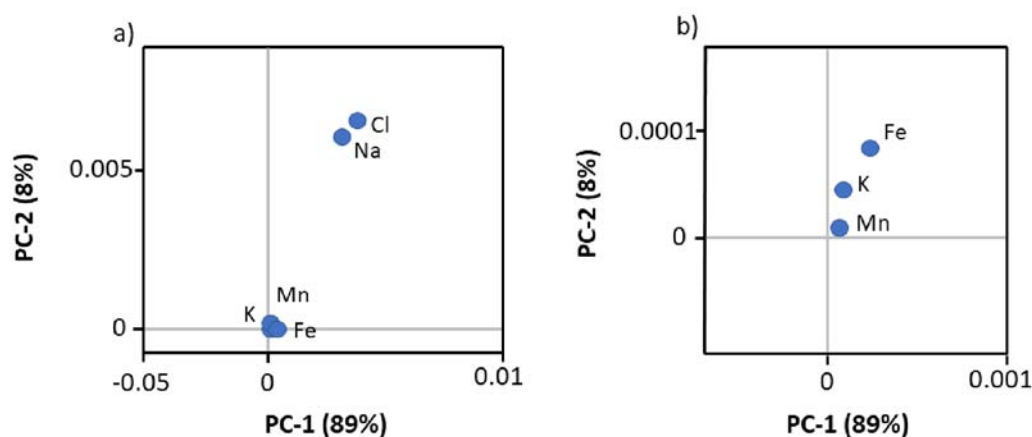


Figure 3: Principal Component Analysis (PCA) of the NRCA measurements on the ceramics performing in the entire ceramic set (36 samples). a) PCA Loading plot of the relative amount of the isotopic composition on the entire set of samples; b) Zoom of the PCA Loading plot in the origin region.

to the hematite or inorganic impurities (aluminoferrites and ferrites) responsible of the reddish hue of potteries [16].

4. Outlook and conclusions

A new integrated approach based on Neutron Resonance Capture Analysis (NRCA) and chemometric tools namely Principal Component Analysis (PCA) is used to determine the semi-quantitative elemental/isotopic composition of a large set of Sumerian potteries from the Abu Tbeirah archaeological site. The NRCA technique shows that the main isotopes present in the entire set of samples are ^{39}K , ^{56}Fe , ^{55}Mn , ^{23}Na and ^{35}Cl . The PCA technique allows the determination of isotope correlations, pointing out the main primary or firing minerals (such as ^{39}K , ^{56}Fe , ^{55}Mn) and the decay products such as sodium chloride (^{23}Na and ^{35}Cl) as pollutant, into two separate groups. The closed group around the center of the PCs belonging to raw materials, give us clues about the homogeneity of the pottery set and on the similar manufacturing processes. Actually, a groundwater aquifer, affected by probable saline intrusion results into characteristic fingerprints of the geo-hydrological surrounding.

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