AN ARCHAEOMETRİC STUDY ON ANCİENT IZNİK CERAMİCS

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Abstract
The present paper reports the results of chemical, physical, mineralogical and petrographical methods used for the elemental and technological characterization of a group ancient Iznik ceramics (sherds and kiln wasters) obtained from the sites of Iznik kiln excavation. In the Results, the bulk chemical composition of body, slip and glaze pastes of which provides the recipes regarding the raw material of body, slip and glaze and glaze formula as well, and technological properties such as the porous, glassy and mineral phases, texture and the orientation of grains and aggregates and firing limitation were given.

Key Words: SEM in-situEDAX, polarizing microscope, thin section analysis, porosity ancient Iznik ceramics

1. Introduction
The combination analytical instrumental techniques have provided large number of experimental data to investigate the elemental and technological characteristics of archaeological materials. The results obtained from such studies have contributed to evaluate the technological skill and cultural and economical aspects of past societies. It has been increasingly very important to establish data bank from analyses carried out by different techniques, and exchanging information with inter-laboratory work in order to obtain the significant results that bring about the solution for archaeologist' hypotheses. The present study is Archaeometric analysis focused on reconstructing the technology and organisation of production for village crafts that would make a good deal of employment in Iznik.
Iznik(ancient Nicea) is the town on the main routes linking Middle-East to Balkans through Anatolia since the 4^{th} century BC and it has lived the periods of the Helenistic, Roman, Byzantine and Seljuk civilization. During the Ottoman era Iznik emerged as the principal center for production of tiles and ceramic wares between the years of 1335 and 1600.Towards the end of sixteenth century ceramic production declined in techniques and village craftsman were not successful to re-produce the production standards of the past and, thus Iznik lost inhabitants due to the un-employment.
Thousand of ceramic finds such as fragments, sherds, stilt, fired and misfired pieces obtained from the Iznik Kiln sites [1] contributed a great deal to the scientific investigation of Iznik ceramics after a long typology and assemblage studies on ceramic fragments [2].

2.Experimental
Materials: 20 samples representing the different type of Iznik ceramics obtained from the Iznik Kiln Excavation were analyzed in respect of bulk chemical and mineralogical composition and thin section characteristics. Appearances of ceramics are shown in Table1.
Methods and Instruments: In this work, SEM (scanning electron microscope, Jeol, JMS 330 attached to energy dispersive x-ray spectrometer), MIC 1080 Euromex binocular polarizing microscope (RTI) with Olympus camera and stereo microscope as well were used. Porosity measurements were carried out by Autoscan 33 mercury porosimeter.
The polished section of ceramics coated with carbon was examined through glaze into body in the SEM with back scattered electron detector. Petrographic analysis carried out by polarizing and stereo microscope in 30µm of thickness of sherds .The chemical composition of body, slip, glaze and colorants were determined by SEM in-situ EDAX (energy dispersive x-ray

analysis) method which provides quantitative data together with high quality imaging facilities.

3.Results and Discussion

Regarding the mineralogical composition red and white bodied ceramics were consisted mainly of quartz, calcium-aluminum silicate and its hydrated form, and a few accessory mineral such as mica (biotite), rutil, epidote(originated from the iron rich calcareous clay) in some ceramic body paste. XRD result were given elsewhere [3] previously. Differences in chemical composition, Table 2, of red and white-bodied ceramics with respect to silica, aluminum, potassium and lead oxides were quite distinctive. The intensity of red color suggested that firing of red-bodied ceramics were carried under oxidation atmosphere, otherwise in the reducing atmosphere a gray and dark brown color might be obtained. White-bodied ceramics contained lead-alkali fritt, which provided a strong glaze and body interaction. Furthermore, Imaging facilities of SEM method and petrography, Figures 1-15, made the red and white-bodied ceramics possible to differentiate as to the textural characteristics such as grain and aggregate sizes, distribution of quartz, glassy opaque minerals and interstitial matrix. In white-bodied ceramics, angular shaped quartz aggregates are bounded to glassy phase effectively. The ratio of quartz aggregates to glassy phase of white-bodied ceramics was higher than the red–bodied ceramics.

The slip layers of ceramics were quartz fritt-type. In general slip contained finer quartz aggregate, less glassy phase and iron-bearing mineral than body, and to some extent, chemical composition of slip, Table 3, was different in comparison with body. The result of chemical composition of dye oxide applied on the slip given in the Table 4 is difficult to relate any particular oxides.

Chemical composition of glaze and colorant shown in Table 5 can be classified into groups with respect of the percent amount of lead, tin (if exist) alkali and earth alkali, aluminum and silicon oxides which are the main components of glaze formula. Scientific results, generally, agreed in the data of style and typology given by archaeologist and art historians, nevertheless dating of ceramics has been needed because of the almost all ceramics contained P_2O_5 which has been known to be used as bone ash in the seventeenth century to obtain white ground under glaze, probably, instead of slip layer.

Porosity data, Table 6 and Figures 16-23, showed that Distribution of pore sizes varied within a large range, and Porosity originated mostly from the voids that lay between the grains. Shifting to larger pore sizes might be due to imperfect shrinking and sintering. It is supposed that most of the pores in the body-paste might be comparable in the dimensions to the grains of raw material though, grains adhere to form aggregates or large secondary particles, and thus varies pore sizes might occur after firing process. The smaller bulk density indicated relatively high firing temperature. The approximate glaze formula of red-bodied ceramics implied that the firing temperature varied between 950-1100^{o}C whereas the firing temperature of white-bodied ceramics revealed consistency between 950-1050^{o}C. The firing temperature of white-bodied particular ceramics was possible to be higher than 1100^{o}C after the discovery of kiln types which have circular stacking chambers and domed area.

4.References

[1] **O. Aslanapa, S. Yetkin, A. Altun,** *Iznik Kiln Excavation. The Second Round 1981-1988,* T.T.T. Foundation, Istanbul, 1989.

[2] **A. Altun, H. Arlı, Y.Demiriz, B. Arlı, G. Öney, Z. Sönmez,** *The Story of Ottoman Tiles and Ceramics,* Creative publisher, Istanbul,1997.

[3 **T. Tulun. E. Uzgil, A. Güleç, A. Tekin, A. Batur, Y. Kahya, G. Köksal, G. Sağlamer, A.Altun, B. Arlı, H. Arlı, V. Çobanoğlu, C. Esen,** *A Multidisciplinary study on Ancient*

Iznik Ceramics, 31st International Symposium on Archaeometry, 27 April-1 May 1998, Budapest, Hungary Proceedings(in press).

FIGURE CAPTIONS

Fig.1 Thin sec. photo of Samp. 12, slip containing small Q grains in glaze and slip, relatively large Q aggregates and iron minerals in slip, red paste,slip type
Fig.2 Thin sec. photo of Samp. 22, glaze with dense Q grains, slip containing Q grains and biotite, and iron minerals, white paste, damascus
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Fig.17 Sample 6 XII. century Seljuk, Red paste
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Fig.20 Sample 14 Red paste, Miletus
Fig.21 Sample 20 White paste, Blue and White
Fig.22 Sample 23 White paste, Rhodes
Fig.23 Sample 24 White paste, Rhodes

Table 1 Describtion of ceramics

Sample No	Excavation code	Century	Description
1	IZN/96ALP IV	-	fired red paste, kiln piece (stilt)
2	IZN/96BDH C7	-	red paste, ware-body piece, without slip and glaze
3	IZN/96BHD C7	-	red paste, ware-body piece, with slip and without glaze
4	IZN/96BHD C7	-	red paste, ware-side piece with slip and without glaze
5	IZN/96ALP IV	XII, Seljuk	red paste, ware-body piece, print technique
6	IZN/96ALP IV	XII, Seljuk	red paste, ware-side piece, print technique
7	IZN/96ALP IV	-	fired red paste, brick piece with glaze
8	IZN/96BHD F9	-	red paste, ware-side piece, monochrome glaze
9	IZN/96BHD F9	-	red paste, jug-handle piece, monochrome glaze
10	IZN/96BHD C7	XIII-XIV	red paste, ware-body piece, sgrafitto without glaze
11	IZN/96ALP IV	XIII-XIV	red paste, ware-body piece, sgrafitto with glaze
12	IZN/96BHD C7	XIV	red paste, ware-body piece, slip without glaze
13	IZN/96BHD C7	XIV	red paste, ware-body piece, slip with glaze
14	IZN/96BHD C7	XIV	red paste, ware-body piece, Miletus without glaze, sgrafitto technique
15	IZN/96ALP IV	XV	red paste, ware-body piece, Miletus with glaze
16	IZN/96BHD F9	XV	red paste, ware-body piece, Miletus with glaze
17	IZN/96BHD F9	XV-XVI	white paste, ware-bottom piece, without slip and glaze
18	IZN/96BHD F9	XV-XVI	white paste, ware-body piece, monochrome glaze
19	IZN/96BHD F9	XV-XVI	white paste, ware-body piece, monochrome glaze
20	IZN/96BHD F9	XV-XVI	white paste, ware-side piece, Blue and white
21	IZN/96BHD F9	XVI, 1.half	white paste, ware-body piece, Golden Horn
22	IZN/96BHD D7	XVI, 1.half	white paste, ware-body piece, Damascus
23	IZN/96BHD F9	XVI, 2.half	white paste, ware-bottom piece, Rhodes
24	IZN/96BHD D7	XVI, 2.half	white paste, ware-body piece, Rhodes

Table 2 Body Composition Data

Sample No	Na_2O	MgO	Al_2O3	SiO_2	K_2O	CaO	TiO_2	FeO
1	0.27±0.02	1.62±0.04	11.36±0.37	38.23±1.92	3.65±0.13	13.93±0.73	1.79±0.17	25.42±0.69
2	0.51±0.05	0.58±0.04	16.49±1.54	44.72±0.28	5.85±0.21	2.03±0.17	2.31±0.19	26.86±1.27
3	1.75±0.07	3.14±0.19	21.17±0.38	54.04±1.60	2.68±0.23	8.41±0.82	1.17±0.08	7.25±0.52
4	0.80±0.08	6.82±0.66	18.09±0.01	52.92±1.67	2.32±0.06	9.64±0.67	0.99±0.10	9.25±0.34
5	1.41±0.02	4.41±0.43	19.66±1.41	52.74±2.69	3.20±0.08	10.26±0.45	0.82±0.04	9.45±0.50
6	1.09±0.11	4.73±0.49	20.01±1.10	53.95±3.00	2.85±0.20	8.41±0.40	0.85±0.03	9.10±0.19
7	0.80±0.07	3.39±0.16	19.20±1.21	55.23±0.44	3.49±0.18	8.55±0.20	1.00±0.10	8.41±0.85
8	4.62±0.13	3.27±0.01	20.45±0.97	52.66±0.45	1.60±0.16	8.80±0.57	0.72±0.06	7.34±0.60
9	1.33±0.11	4.16±0.43	19.32±0.15	52.57±1.34	2.11±0.08	10.80±0.52	0.72±0.04	9.21±0.93
10	1.12±0.09	3.32±0.01	20.85±0.21	54.31±0.65	2.92±0.10	7.11±0.01	1.06±0.08	8.38±0.04
11	1.58±0.16	3.63±0.39	18.42±1.97	58.95±5.96	2.50±0.28	7.60±0.83	1.26±0.06	0.55±0.05
12	1.57±0.16	3.88±0.38	20.37±0.70	54.95±0.31	2.86±0.51	6.53±0.04	1.03±0.11	8.30±0.23
13	1.19±0.11	3.29±0.07	20.68±0.64	54.45±1.42	3.80±0.35	8.69±0.95	0.72±0.06	7.49±0.33
14	1.19±0.13	3.91±0.00	20.57±0.24	54.87±0.37	2.95±0.01	7.49±0.27	0.86±0.09	7.84±0.46
15	1.28±0.12	4.30±0.35	20.20±0.07	52.29±2.38	2.51±0.06	8.38±0.49	0.79±0.11	10.34±1.03
16	1.91±0.18	4.22±0.40	19.19±0.75	52.67±0.52	2.35±0.20	9.94±0.50	1.04±0.11	7.92±0.31
17	3.00±0.28	2.30±0.14	4.69±0.40	80.17±1.12	1.36±0.15	3.29±0.17	0.67±0.06	1.23±0.11
18	2.07±0.13	0.86±0.06	1.95±0.02	86.72±0.43	0.86±0.08	2.85±0.23	0.31±0.01	2.28±0.22
19	1.91±0.14	1.09±0.04	6.67±0.72	71.39±1.95	1.89±0.06	7.54±0.53	0.50±0.05	3.82±0.16
20	2.65±0.16	1.19±.09	3.33±0.01	85.24±2.15	0.66±0.06	2.76±0.02	0.50±0.04	1.52±0.15
21	2.23±0.18	1.95±0.16	3.81±0.10	81.70±2.71	1.03±0.09	3.32±0.28	0.34±0.03	2.79±0.25
22	1.19±0.10	1.02±0.11	2.33±0.24	82.78±1.02	1.20±0.11	4.12±0.36	0.34±0.03	6.40±0.59
23	1.10±0.11	0.78±0.07	2.76±0.25	83.37±1.26	0.87±0.05	5.38±0.32	1.28±0.10	3.51±0.33
24	2.39±0.14	0.93±0.08	2.32±0.07	80.55±5.11	0.59±0.01	3.89±0.20	0.48±0.01	4.81±0.18

Table 3 Slip Composition Data

Sample No	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
3	75.63	13.61	2.03	0.38	1.00	0.70	0.65	3.78
4	55.70	21.92	7.65	2.76	7.57	2.50	1.26	3.46
8	59.33	15.46	3.47	0.52	12.45	2.79	2.51	1.83
11	52.92	24.46	1.22	0.48	5.20	1.47	1.22	3.31
12	65.55	18.86	2.34	0.65	6.04	1.86	0.54	2.17
13	67.91	16.73	3.15	1.21	5.27	1.49	0.77	2.42
13[a]	50.69	19.60	9.63	1.11	9.21	3.33	2.05	2.96
13[b]	53.02	14.71	12.89	1.45	10.56	1.80	1.14	3.22
16	51.10	16.80	12.21	1.05	8.31	3.98	1.63	2.55
22	85.68	3.28	0.95	0.55	2.90	1.11	1.68	1.04

Table 4 Glaze + Colourant

Sample No	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	PbO	Mn
7	28.98	1.66	1.43	0.21	4.60	0.74	1.03	2.54	47.46	-
8	64.58	11.35	3.07	0.56	5.45	2.48	9.23	1.18	-	0.4
9	53.56	18.12	5.16	1.19	5.14	2.79	1.07	2.64	-	-
13[a]	71.06	11.28	2.03	0.44	5.65	0.90	0.56	2.05	3.95	-
13[b]	30.00	4.00	1.13	-	2.85	1.20	1.71	0.47	58.98	-
19	50.66	2.06	5.47	-	2.33	0.85	8.17	1.59	21.68	-

a Brown glaze, b green glaze

Table 5 Slip + Colourant

Sample No	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	PbO	P_2O_5	SnO_2
15[a]	56.62	22.90	1.90	0.57	7.65	1.06	3.46	1.87	2.03	1.03	-
16	66.88	8.76	1.20	0.24	2.45	1.14	6.16	1.95	4.31	1.61	-
18	82.00	2.77	1.28	0.14	2.49	1.01	3.88	0.78	-	1.26	-
20	80.65	0.77	1.23	-	1.61	0.21	3.13	0.60	7.97	1.19	0.42
21	74.44	3.07	0.61	0.72	1.89	0.79	2.98	0.73	11.91	0.58	-
22	79.59	2.53	1.24	0.17	4.07	1.16	1.99	0.85	5.14	0.28	-
23	65.87	1.61	1.51	0.29	2.17	0.19	4.25	0.67	20.81	1.13	-

a Slip+Blue dye

Table 6 Porosity data

Sample No	Bulk density g/cc	Apparent density g/cc	Pore diameter A°	Total pore volume, %
1	1.7203	2.9115	7.09E+03	55.38
2	1.8910	2.7116	1.17E+04	52.04
3	1.4317	2.1903	5.94E+03	35.64
4	3.5497	37.2417	5.53E+03	90.49
5	2.6063	6.0986	5.51E+03	59.02
6	1.7511	3.2679	5.99E+02	-
7	11.4660	-	1.52E+03	-
8	1.6161	4.4297	1.47E+05	-
9	-	-	5.08E+04	23.36
10	2.041	4.8375	6.46E+03	61.31
11	0.9827	1.4601	5.47E+04	32.69
12	4.1173	16.900	5.08E+04	81.26
13	1.8980	3.5583	7.16E+03	52.0
14	1.5261	3.0538	6.46E+04	56.56
15	2.6139	4.8541	6.46E+04	46.16
16	3.9878	43.4727	7.11E+04	-
17	1.4954	3.0491	5.93E+04	51
18	2.7503	3.9985	7.11E+04	40
19	1.6613	3.0846	3.00E+04	46
20	1.6384	-	8.89E+04	-
21	1.7446	4.8039	5.08E+04	65
22	1.6522	2.9083	6.46E+04	48
23	1.5544	3.0869	7.11E+04	51
24	2.2903	3.5983	8.20E+04	38

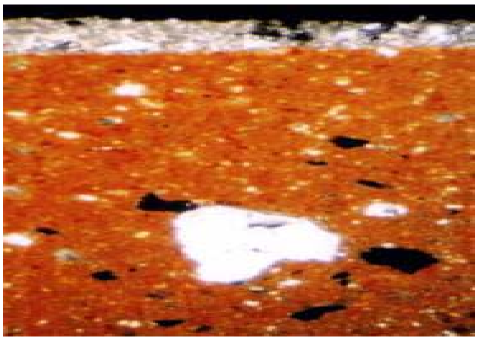

Fig.1 Thin sec. photo of Samp. 12, slip containing small Q grains in glaze and slip, relatively large Q aggregates and iron minerals in slip, red paste, slip type

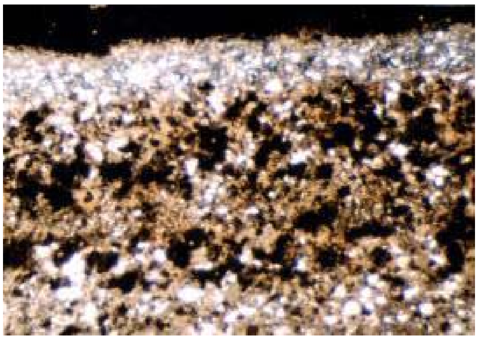

Fig.2 Thin sec. photo of Samp. 22, glaze with dense Q grains, slip containing Q grains and biotite, and iron minerals, white paste, damascus

Fig.3 Thin sec. photo of texture, glaze+slip with dye and body ,and poros are also seen

Fig.4 SEM mic.grph.,Samp.7 Coloured glaze brick piece

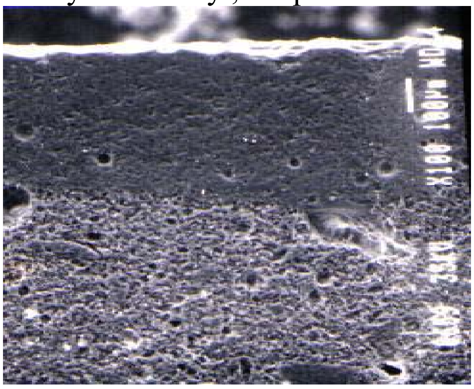

Fig.5 SEM mic.grph., Samp.8 Monochrome glaze

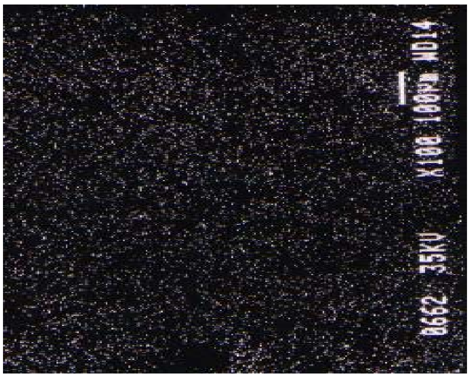

Fig.6 X-ray map of Samp. 9 Aluminum

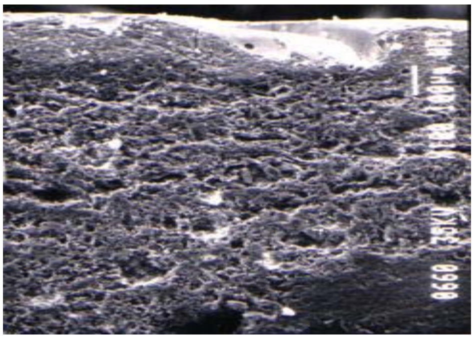

Fig.7 SEM mic.grph., Samp. 9
Coloured dye+ quartz particles interstitial glass

Fig.8 X-ray map of Samp. 9 Calcium

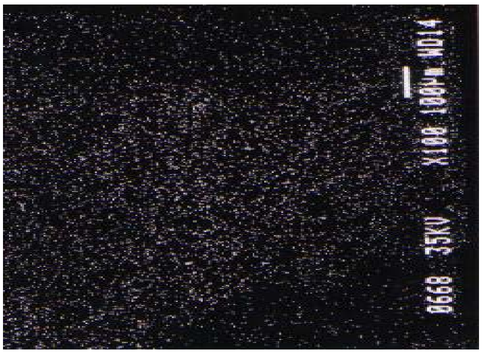

Fig.9 X-ray map of Samp. 9 Ironpaste, fine

Fig.10 X-ray map of Samp. 9 Potassium

Fig.11 X-ray map of Samp. 9 Magnesium

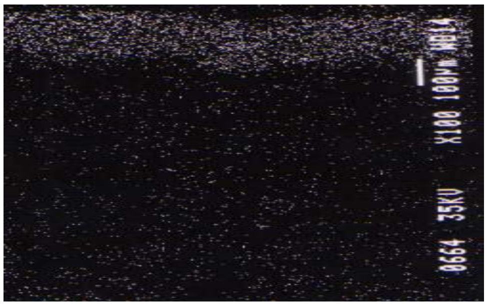

Fig.12 X-ray map of Samp. 9 Lead, glaze+ slip+paste

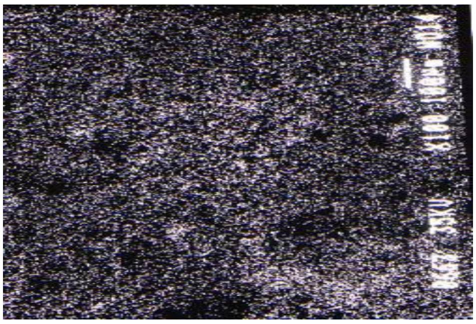

Fig.13 X-ray map of Samp. 9 Silicon

Fig.14 SEM mic.grph., Samp. 11, glaze+slip+body, finer quartz particles with interstitial glass

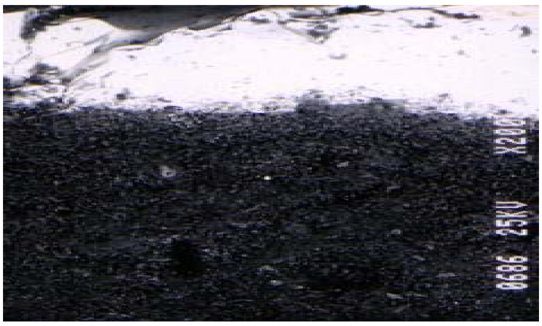

Fig.15 SEM mic.grph., Samp.13, Brown glaze, slip type, glaze+slip, glassy phase+small Q aggregates

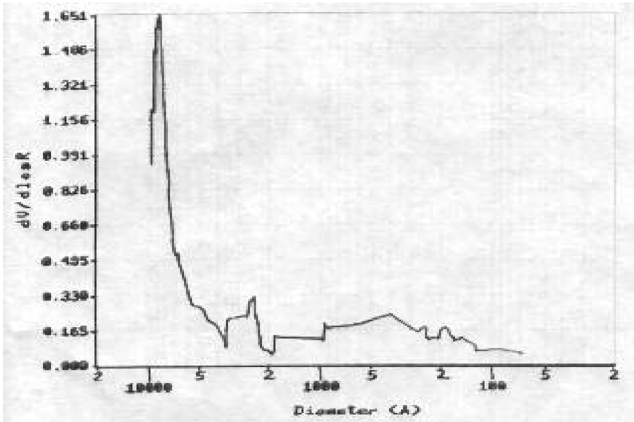

Fig.16 Sample 5 XII. century Seljuk, Red paste

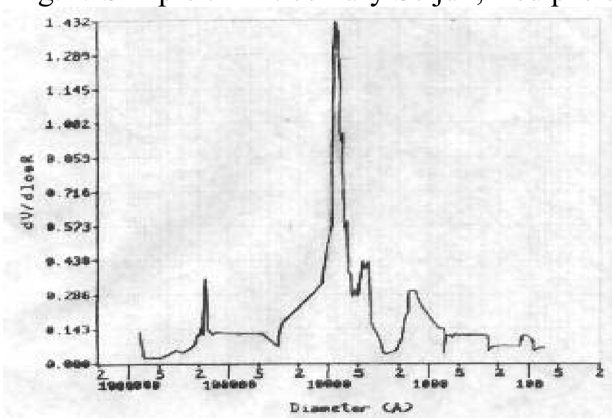

Fig.17 Sample 6 XII. century Seljuk, Red paste

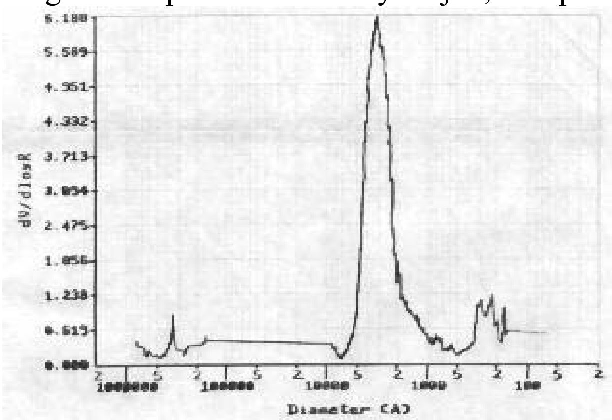

Fig.18 Sample 11 Red paste, Sgrafitto

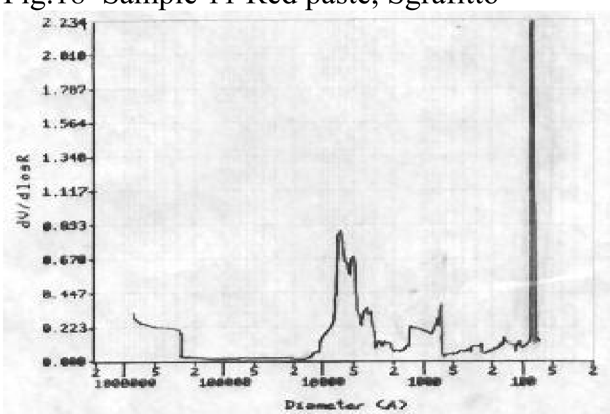

Fig.19 Sample 12 Red paste, Slip type

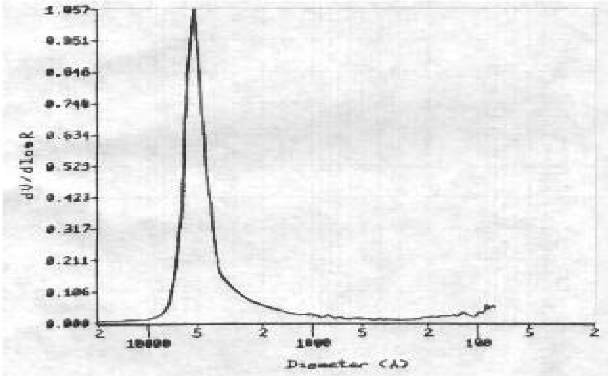

Fig.20 Sample 14 Red paste, Miletus

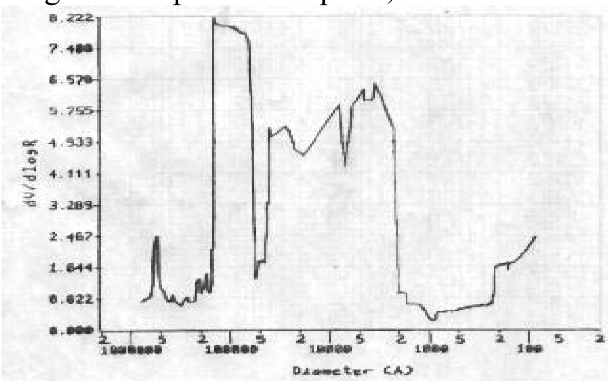

Fig.21 Sample 20 White paste, Blue and White

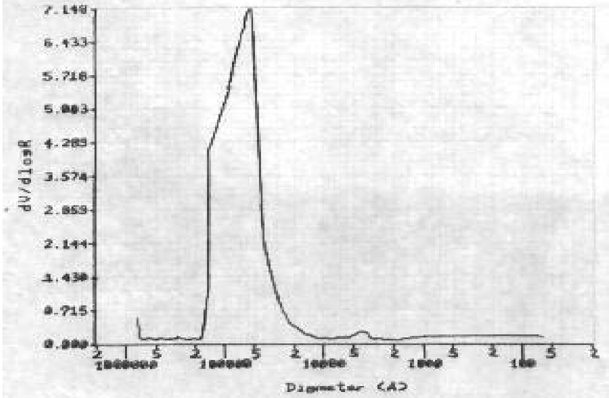

Fig.22 Sample 23 White paste, Rhodes

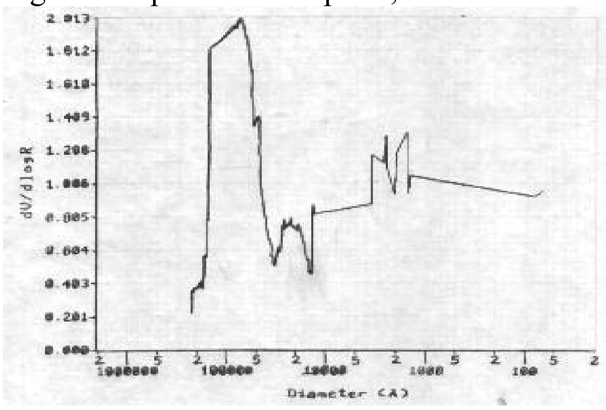

Fig.23 Sample 24 White paste, Rhodes