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Characterization of the Alphabet Reform Painting

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Abstract: The Alphabet Reform painting which shows Ataturk teaching the new alphabet is important for the history of the Republic of Turkey. This painting was made by Nazmi Ziya GÜRAN in 1933. The painting is now maintained by the Ministry of Interior. In this work, the Alphabet Reform painting was analyzed for characterization and restoration purposes. The fabric of the canvas, pigments (organic-inorganic) and the binder of paint were characterized by Fourier Transform infrared spectroscopy-attenuated total reflectance (ATR-FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and high-performance liquid chromatography-coupled with diode array detection (HPLC-DAD) analysis methods. The CIEL*a*b* color parameters of the paint were determined by color measurement spectrophotometer. According to the results, the canvas was found to be of fibers of vegetable origin and the binders were determined to be linseed oil and dammar varnish. Red alizarin (madder lake organic pigment) and dark blue ultramarine pigments were detected as the organic pigments while CdS (yellow), Pb red (flesh color), $PbCO_3$ (white), ZnO (white), $BaSO_4$ (white), FeO (brown) and Cr_2O_3 (green color) were detected as the inorganic ones.

Keywords: Oil paintings, FTIR-ATR, SEM, HPLC, restoration.

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INTRODUCTION

There are a limited number of art pieces that survived to this day. It is inevitable that eventually there have been deteriorations or flaking on these pieces of art. Conservator-restorers are trying to restore these alterations developed over time. Restoration practices may be different for each art specimen. The successful restoration of artworks requires an in-depth analysis of the pieces. For instance, with the analysis of old paintings so much information can be attained such as the pigments used in the piece of art and changes that may occur in these pigments over time (1-6), organic and inorganic substances (7-11), the binders (12-13), the areas with retouches or patches on these pieces, the areas with varnish, structural deteriorations (such as cracking, flaking, peeling, and tearing) (14-15), painting technique of the artist (16) and the types of the varnish (17-19) or the canvas that were used (such as silk, linen, hemp, cotton, jute) (20) which are of great importance for the restoration of these paintings. One can even have an idea about the palette of the artist given that he or she has the chance to analyze several pieces of art that belonged to that artist (21).

Today, many different methods are used in the analysis for restoration and preservation of artworks that are a part of cultural heritage in many countries around the world.

Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy, and energy dispersive x-ray spectroscopy (SEM-EDX) have proven themselves to be efficient methods for analysis in scientific examination of works of art over a long period of time (11).

Identification of pigments in artefacts can be a source of valuable information in concern with conversation and art history of the object. Numerous studies on the identification of pigments by FTIR analysis can be found in literature (2-5, 21-26). Regardless of the fact that many inorganic pigments such as ultramarine blue, lead white, malachite and Prussian blue fall into mid-IR region with their characteristic absorption bands, there are many that either do not absorb in that region at all or have absorptions that are at the low wave number end of the region and are not characteristic enough. However, through an extensive attenuated total reflectance – fourier transform infrared (ATR-FTIR) study, it was found that historically most widespread inorganic white, yellow, blue, green, brown and black pigments could be differentiated by examining their vibration bands in the region of 550-230 cm^{-1} (22).

High Performance Liquid Chromatography (HPLC) is also another useful technique for the used for the characterization of artworks. Many objects within a cultural heritage site may contain organic or inorganic materials. Many researchers have used HPLC analysis method to separate into components and to determine the dyestuff in the artwork (8-10, 27, 28).

These techniques along with others were used extensively in many studies for the characterization of old paintings. For instance, Jana Zelinska et al., investigated the main altar of the St. James Church in Slovakia (7). 25 inorganic pigments, substrate and organic binder samples which were taken from the wood panel were identified using FTIR, SEM-EDS and optical microscopy. FTIR findings led them to conclude that linseed oil was used as a binder whereas SEM-EDX results revealed the presence of azurite, chalk, and lead white (7).

Thiago G. Costa and his friends have examined Louis-Auguste's five paintings. They used UV-induced visible luminescence, SEM-EDX and FTIR spectroscopic techniques. As a result of FTIR analysis, they found carbonates, sulfates, alumina silicates, iron oxides, and Prussian blue as pigments and they found that an oil-based binder was used. According to EDX results, Pb element was found in all samples (15).

Milene Gil et al., studied Jose de Escovar's panel and mural painting by FTIR, SEM-EDX and technical photography (ultraviolet fluorescence–visible-Infrared) methods. They found Fe, lead white, red lead oxide, red mercury sulfide, calcium hydroxide, titanium, copper, zinc, and sulfur. They have identified the presence of an oil binder by the bands at 2926 cm^{-1}, 2854 cm^{-1} and 1703 cm^{-1} as a result of FTIR analysis and they have attained information about the artist's painting techniques (16).

In another research, Thiago G. Costa and his friends investigated the painting called "Primeira Missa no Brasil" which was originally made by Victor Meirelles in 1860 and its replica by Sebastiao Vieira Fernandes in 1929. This painting was also analyzed with FTIR, EDX and UV-induced visible luminescence methods. They identified the presence of prussian blue, lithopone, lead white, chrome yellow, cobalt blue pigments in the paintings. FTIR and EDS analyses showed a correlation between the elemental composition of pigments used by Meirelles and Fernandes, especially for lead (29).

In this work, we aimed to characterize the pigments and the binder of the Alphabet Reform painting. The painting was introduced to the Mimar Sinan Fine Arts University from the Ministry of Interior of Republic of Turkey to be restored. This painting was made by Nazmi Ziya GURAN who was influenced by the impressionist movement in Paris and who liked to reflect the opposite colors side by side, in 1933. This painting is of great importance for the history of Turkey for it shows Ataturk introducing the new alphabet reform to public. FTIR-ATR, SEM-EDX, and HPLC methods were used to characterize this painting.

MATERIALS AND METHODS

Materials

Purpurin and alizarin reference samples, and dimethylformamide were purchased from Sigma Aldrich. Acetonitrile, trifluoroacetic acid, hydrogen chloride, and methanol were purchased from Merck. The painting was obtained from the Ministry of Interior of Republic of Turkey.

Sample Collection

Samples were taken with a scalpel from paintings (11 samples) and also from the canvas. Samples (S1, S2, S3, S4, S5, S6, S7, S8, S9, S10 and S11) taken from the parts of the painting marked in Figure 1 (S1-S11) were examined.

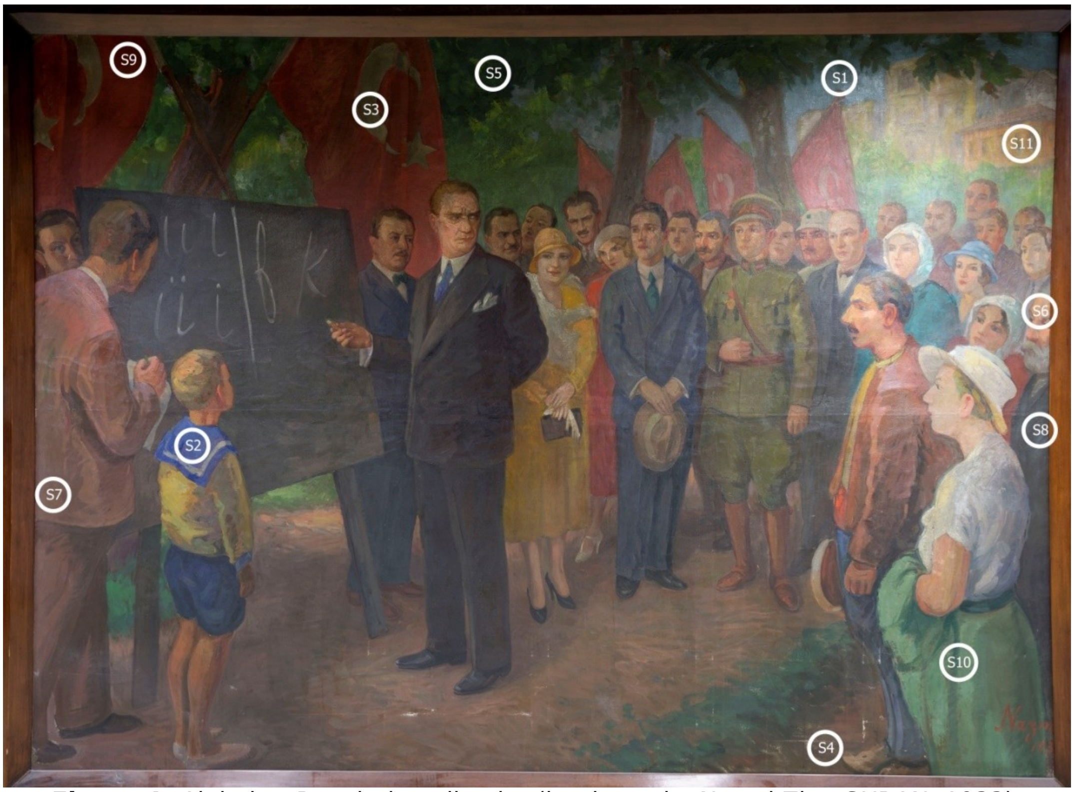


Figure 1. Alphabet Revolution oil paint (by the artist Nazmi Ziya GURAN, 1933).

Infrared-UV Imaging of the Painting

Infrared and UV authentications were as described in earlier reports (13-16, 30-31). Ambient light photograph of the oil painting was taken using a Canon 5D Mark III camera. Infrared and ultraviolet images were acquired with an OptoLab camera for the documentation process. The images are shown in Figure 2a and 2b, respectively.

Figure 2. a) IR image (left) and b) UV image (right) of Alphabet Revolution oil paint.

Color Measurements

The color measurements were as described in earlier reports (32-35). The L*, a* and b* values for the paintings were measured with a Konica Minolta CM 700d spectrophotometer.

HPLC

The HPLC analysis of the pigments was performed as described in earlier reports (36-39). Acetonitrile-water and water-trifuluoroacetic acid were used as the mobile phase. Purpurin and alizarin were used as references.

SEM-EDX

SEM-EDX analysis was performed according to an earlier work (34). A Tescan Vega 3 Easy probe SEM with a Bruker 410-M EDX detector and Esprit 1.9 software was used to characterize the morphology of the canvas and other components. SEM–EDX instrumental conditions were a working distance of 8.05-16 mm and energies of 5-20 kV at a magnification of 100 to 800. Back scatter detectors were used for secondary electrons with a 30s collection time.

FTIR-ATR

The FTIR-ATR analysis was conducted as described in earlier reports (40-42). For the analyses of pigments and binders, the ATR-FTIR technique was applied. The analyses were performed with UATR Accessory for Spectrum Two, Diamond (1 Reflection) FTIR spectrometer (Perkin Elmer Diamond /ZnSe). A total of 60 scans were collected in the 4000 - 400 cm^{-1} spectral range, while the resolution employed was 4 cm^{-1}.

RESULTS AND DISCUSSION

Color Analysis

The color measurement results supply an important information of the color palette of the artist and it is vital for restorative purposes. During the restoration process, the color palette can be prepared according to the L*, a* and b* values of the painting. Here L* expresses white or black color (0-100); a* expresses red (a˃0) or green (a˂0) color and b* expresses yellow (b˃0) or blue (b˂0) color. The color measurement results of the painting samples with the CIE L*a*b* are shown in Table 1. When restorers and conservators need to restore artworks, these values can be used (18, 43, 44).

SEM-EDX Analysis

In order to determine the elemental components of cultural heritage artifacts, SEM-EDX technique is used. SEM images were obtained for the samples taken from the predetermined areas of the painting shown in Figure 1. Also SEM-EDX measurements were carried out. SEM image that belongs to the canvas of the painting is shown in Figure 3. It is seen that the canvas has fibers from plant origin either from flax or hemp (45). FTIR analysis was also carried out on the same canvas and standard flaxseed fibers as shown in Figure 4. As a result of comparison between the canvas and standard flax fibers, it was seen that the band are in compliance with each other and it was decided that canvas was made of flax. According to the results of element analysis for the oil painting samples shown in Table 2, the main elements were found in these samples are Pb, Cd, Ba, Zn, Fe and Al metals.

Table 1. Color measurement results of all samples.

Sample	L*	a*	b*
S1	60.68	-8.03	-2.65
S2	40.95	1.51	-25.51
S3	43.11	3.53	11.07
S4	34.80	2.87	7.00
S5	38.42	-12.26	12.50
S6	56.81	16.90	27.41
S7	40.20	6.01	8.30
S8	31.29	-1.82	1.64
S9	32.91	14.44	7.99
S10	41.41	-10.25	12.39
S11	59.28	7.87	20.12

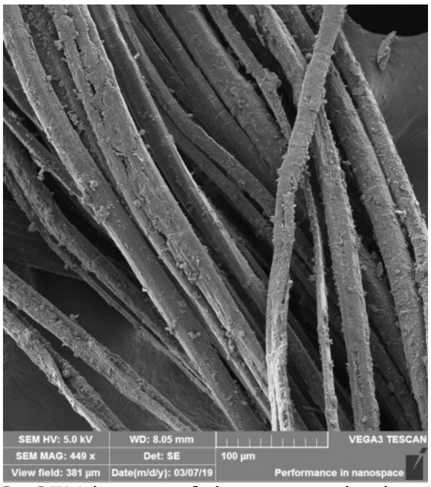


Figure 3. SEM image of the canvas in the Alphabet Revolution oil paint.

FTIR-ATR Analysis

FTIR was used to characterize the molecular composition of the selected paint samples and gain some information on the degree of hydrolysis of the paint. IR spectra of all samples are presented in Figure 5. The main bands detected in the FTIR-ATR spectra of the samples are summarized in Table 3. It can be seen from the FTIR spectra of the samples that the samples have organic and inorganic components which mean that the samples contain pigments and binder. Based on the FTIR data the binder of the painting was identified as linseed oil while it is thought that dammar resin was used as a varnish. The FTIR spectrum of reference linseed oil is presented in Figure 6. When Table 3 and the FTIR spectrum of the reference linseed oil in this figure are examined, the presence of common bands (2900-2800 cm^{-1}, 1700-1750 cm^{-1}, 1450-1550 cm^{-1}, 1000-1200 cm^{-1}) indicated that the binder in the samples is linseed oil. According to IR results of all samples -except canvas; the surface the painting layer is thought that covered by dammar varnish, as it is indicated by main absorption bands at 1700-1750, 1450-1550, 1350- 1400 cm^{-1} (13,17-18).

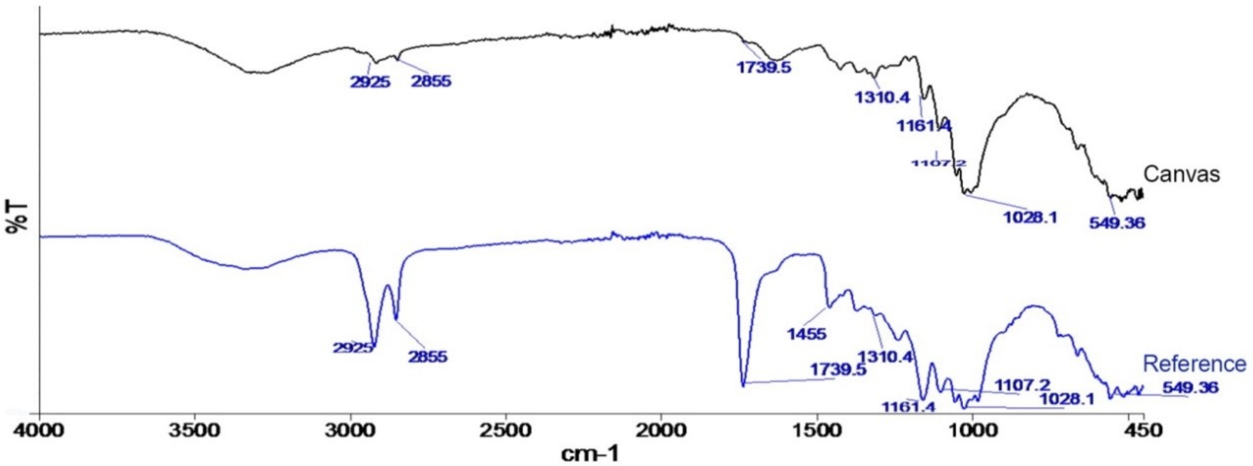
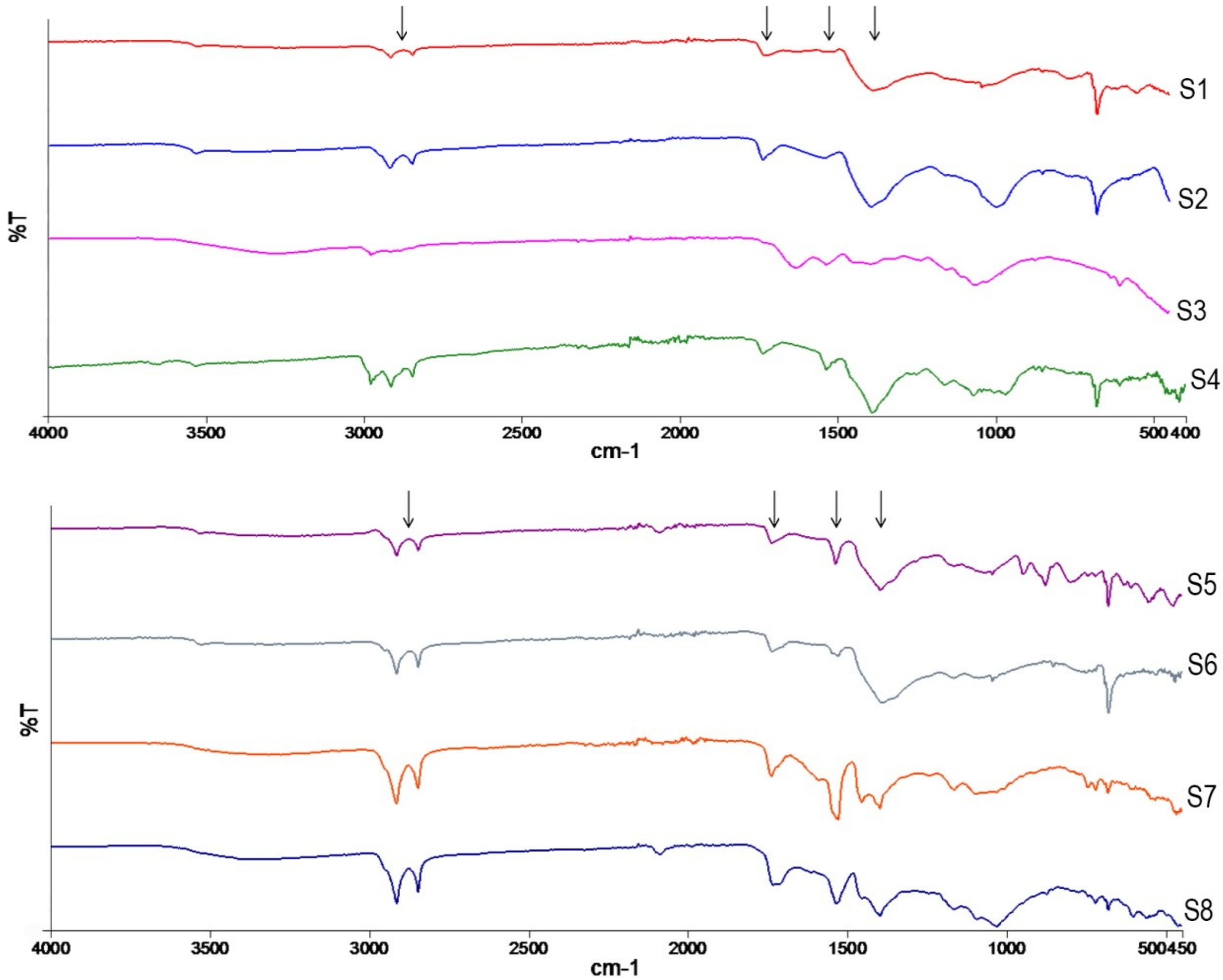


Figure 4. FTIR-ATR spectra of the canvas with paint on it in the Alphabet Revolution oil painting and the reference sample which was prepared by applying linseed oil on the linen canvas.



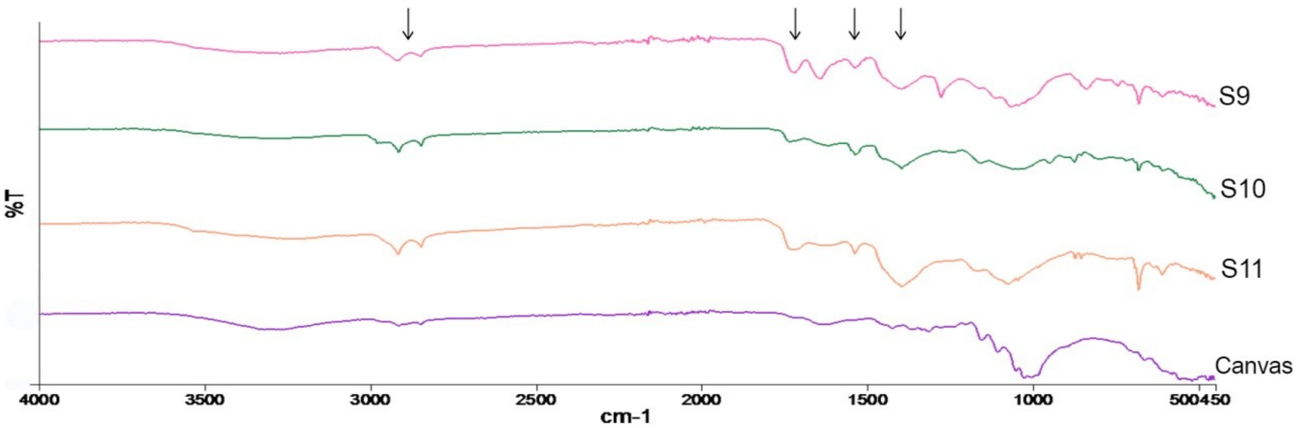


Figure 5. ATR-FTIR comparisons of all the samples in the Alphabet Revolution oil paint.

Table 3. FTIR analyses results: Characteristic bands in all samples in the 400-4000 region.

Sample	Bond type						
	O-H (cm^{-1})	C=O ester bond (cm^{-1})	C-H (cm^{-1})	C-O (cm^{-1})	CO_3^{-2} Carbonate (cm^{-1})	COOH Carboxylic acid (cm^{-1})	COO- carboxylate Fatty acid (cm^{-1})
S1	-	1729	2845-2917	1043	1389	-	-
S2	-	1734	-	997	1395	2500-3500	1535
S3	3537	1733	2848-2913	-	1393	-	1514
S4	-	1737	2848-2913	-	1391	-	1531
S5	-	1739	2848-2917	-	1395	-	1536
S6	3534	1738	2849-2917	-	1390	-	1530
S7	-	1736	2851-2917	-	1397	-	1529
S8	3300	1734	2849-2916	-	1397		1535
S9	3355	1734	2850-2923	1044	1402	-	1531
S10	-	1732	2851-2920	1040	1395	-	1542
S11	-	1727	2849-2918	-	1394	-	1539
Canvas	3265-3320	**-**	2851-2920	1025	1312 1424	-	-

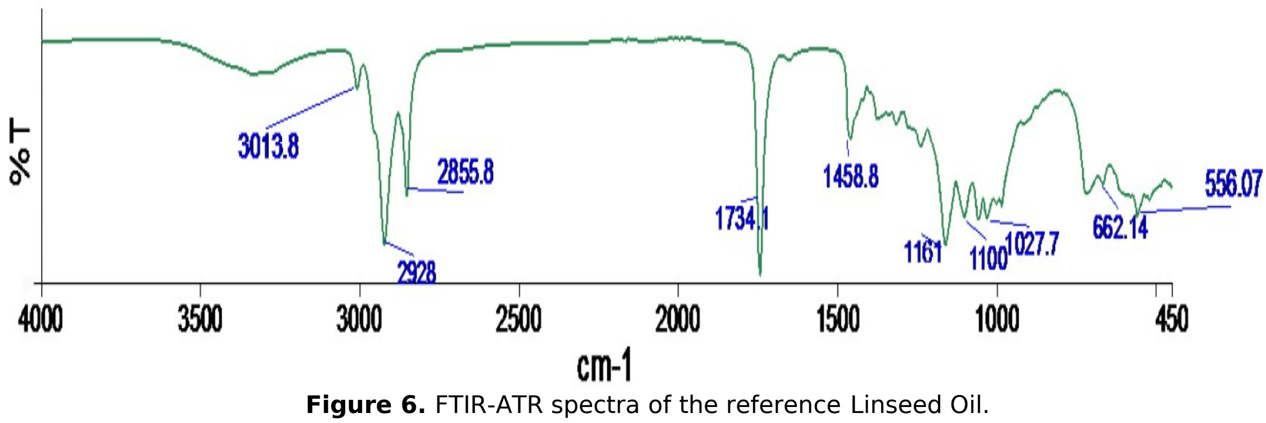


Figure 6. FTIR-ATR spectra of the reference Linseed Oil.

Table 2. SEM-EDX analysis results of all samples in the Alphabet Revolution oil paint.

Sample	Color	Elements and Percentages (%)																
		C	O	Na	Mg	Al	Si	P	S	K	Ca	Cr	Fe	Co	Zn	Cd	Ba	Pb
S1	**Blue**	21.95	20.08	0.51	-	0.32	-	-	-	-	-	0.91	-	-	1.33	-	-	54.91
S2	**Blue**	36.41	30.46	1.90	0.56	2.43	2.27	-	2.55	-	0.04	-	-	-	0.81	-	-	22.56
S3	**White**	37.56	26.76	-	-	0.23	0.10	-	2.97	0.03	0.29	--	-	-	26.97	-	4.97	0.72
S4	**Brown**	34.51	30.84	1.72	0.71	2.39	4.25	0.14	3.93	1.06	6.29	-	2.13	-	1.73	-	1.73	8.57
S5	**Green**	20.92	18.21	0.81	-	0.43	-	-	0.86	1.42	0.38	6.12	0.55	-	8.13	-	1.18	41.00
S6	**Flesh color**	9.99	11.63	0.33	-	0.86	-	-	1.25	0.02	0.31	-	-	-	1.29	1.17	0.04	72.80
S7	**Brown**	42.46	16.69	0.87	-	0.98	0.65	-	0.61	-	0.58	-	2.61	-	1.13	0.16	-	33.27
S8	**Black**	52.18	24.76	0.75	-	0.67	0.38	0.14	0.67	-	1.02	0.67	0.89	-	1.60	1.26	0.46	14.12
S9	**Red**	39.69	25.20	0.36	0.18	0.58	0.41	-	2.11	0.25	1.85	-	0.35	-	2.15	0.59	0.09	26.19
S10	**Green**	34.79	24.26	0.63	-	0.19	0.07	-	0.34	0.80	1.47	4.93	0.28	0.31	8.49	-	0.04	23.39
S11	**Yellow**	21.59	14.57	0.19	-	0.51	-	-	2.67	0.08	1.63	-	0.07	-	4.65	6.74	1.28	46.04

HPLC analysis

Samples 1, 2, and 9 were subjected to HPLC analysis. We could not be able to detect any organic dyes for samples 1 and 2. However, for sample 9 we successfully determined the presence of alizarine and purpurin pigments. The full HPLC chromatogram of sample 9 is given in Figure 7 and the overlay spectra of alizarine and purpurin references with the corresponding spectra at 27.57 and 28.83 minutes in the HPLC chromatogram of sample 9 are presented in Figure 8 and 9, respectively.

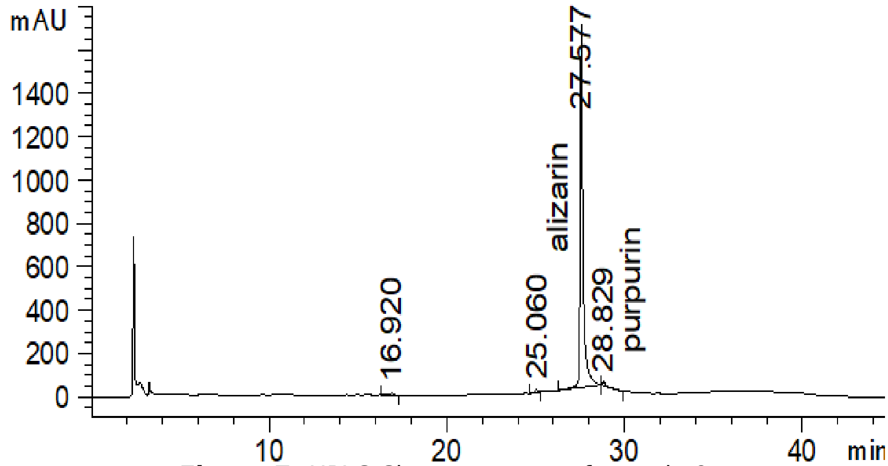


Figure 7. HPLC Chromatogram of sample 9.

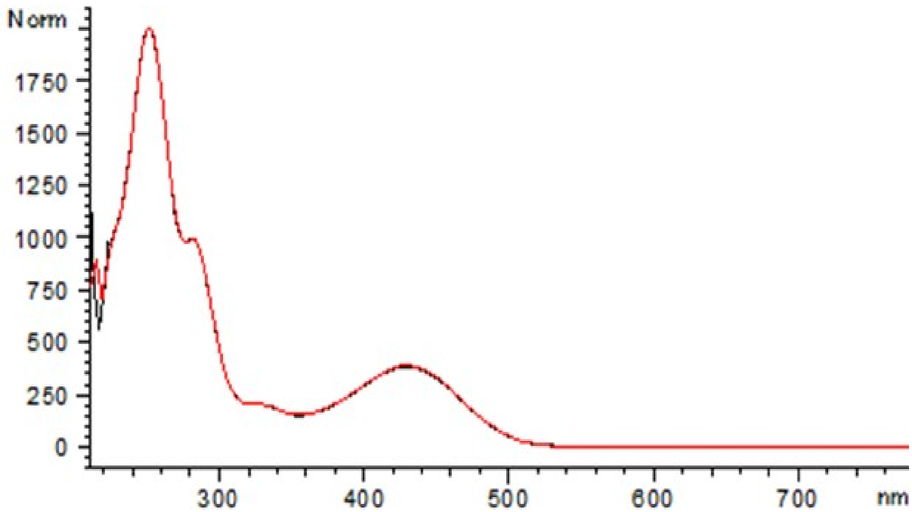


Figure 8. Comparison of the spectrum of alizarin dyestuff with the spectrum obtained at retention time at 27.57 minutes for sample 9. (**red line**: reference alizarin; **black line**: sample 9.)

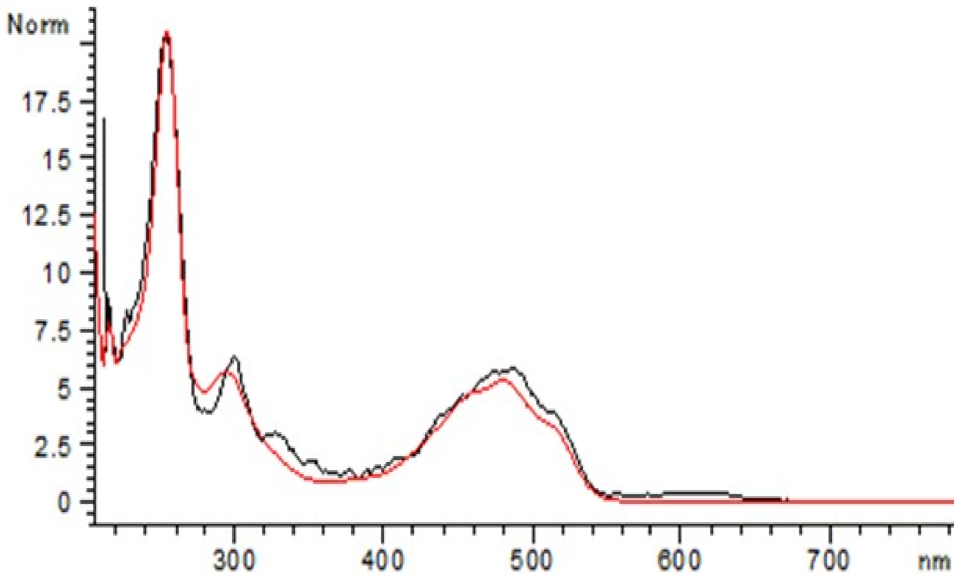


Figure 9. Comparison of the spectrum of purpurin dyestuff with the spectrum obtained at retention time at 28.83 minutes for sample 9. (**red line**: reference purpurin; **black line**: sample 9.)

General Evaluation of the Results

Based on the FTIR-ATR, HPLC analyses and the SEM-EDX results the main components of the samples were determined as follows:

Part S1: SEM-EDX results showed the presence of Pb, Zn, and Cr. Based on FTIR spectrum the presence of CO_3^{2-} vibrations at 1389 cm^{-1} and the green color of this section, the pigments in this region can be $PbCO_3$, ZnO and Cr_2O_3. The band at 678 cm^{-1} is also a characteristic peak for $PbCO_3$ (7). Moreover, band at 2917 and 2845 cm^{-1} which are attributed to stretching of C-H groups of the binder and a band at 1729 cm^{-1} which is due to characteristic ester carbonyl were detected in this sample. These findings show that an oil based binder could be used in the painting.

Part S2: In the FTIR spectrum of this sample, a broad band between 3500 and 2500 cm^{-1} indicates the presence of carboxylic acid groups which can be attributed the hydrolysis of the oil based binder (46) due to aging. Other important bands in this spectrum can be listed as follows: Ester (RCOOR) band at 1734 cm^{-1}, CO_3^{2-} band at 1395 cm^{-1} ($PbCO_3$), C-O at 997 cm^{-1}, which is a characteristic peak for ultramarine blue (21) and the band at 679 cm^{-1}($PbCO_3$). According to the SEM-EDX result of sample 2; Na, Ca, Al, Si, S, O elements were found and no organic dyes were found according to HPLC analysis. The FTIR result of sample 2 is considered to be consistent with the FTIR results of reference ultramarine blue (21, 47) and the sample is thought to be synthetic ultramarine blue ($Na_{6-10}Al_6Si_6O_{24}S_{2-4}$) (24)**.**

Part S3: The important bands in the FTIR spectrum for this sample were determined as follows: -OH band at 3537 cm^{-1}, C-H stretching vibrations at 2918 and 2848 cm^{-1}, ester (RCOOR) band at 1733 cm^{-1}, carboxylate COO- band at 1514 cm^{-1} (which may suggest palmitate oil), 1393 cm^{-1} and 679 cm^{-1} for $PbCO_3$, and Zn-O at 767 cm^{-1} (48). EDX revealed the existence of Pb, Zn, Ba elements in this sample. The white color and these findings suggest the presence of Zinc White (ZnO), Barium White ($BaSO_4$) and Lead White ($PbCO_3$) pigments.

Part S4: This sample produced a similar FTIR spectrum to samples above. It was found to contain Ca, Fe, Pb, Zn and Ba according to EDX results**.** The brown color of this region indicates the presence of Fe_2O_3 (hematite) (49) pigment in addition to others such as Zinc White (ZnO), Barium White ($BaSO_4$) and Lead White ($PbCO_3$). The presence of Ca could be attributed to presence of Gypsum ($CaSO_4.2H_2O$).

Part S5: Different than other spectra Cr-O band 476 cm^{-1} was detected in this sample (22), and the presence of Cr was also confirmed by EDX measurements.

Part S6: In addition to organic groups the presence of lead was proved by FTIR analysis for this sample. Similar band were found for this sample as detailed above. EDX revealed the presence of S, Pb, Cd and Zn for this sample. Based on these findings we suggest that a blend of CdS yellow and Zn-Pb white were used to obtain flesh color.

Part S7: The FTIR and EDX results suggest that Fe_2O_3, CdS yellow and white pigments were mixed to obtain the brown color on this region.

Part S8: The EDX results for this sample gave the highest carbon percentage among other samples. Therefore, the black color of this region is attributed to the presence of carbon black.

Part S9: HPLC result for this sample showed the presence of organic pigments. Madder lacquer dye (Rubia tinctorum L.) and a mixture of CdS yellow, Fe_2O_3 and Pb-Zn white inorganic pigments were found.

Part S10: The main pigment for this green colored region was found as Chromium oxide green. Other spectral evidence show that it is mixed with white pigments and gypsum as well as oil based binder.

Part S11: In addition to similar FTIR bands in all samples a band at 601 cm^{-1} was detected in the fingerprint region of the FTIR spectrum of this sample. This band is consistent with the reference band of CdS (3)**.** Based on this FTIR result and EDX findings for this sample, it can be said that CdS yellow pigment and white pigments were used for the yellow color of this region.

Canvas: The following bands were detected in the FTIR spectrum of the canvas: at 3265-3320 cm^{-1} (-OH band), 2851 cm^{-1}, 2920 cm^{-1}, 1621 cm^{-1} (-C=O band), 1424-1321 cm^{-1} (CO_3^{2-}) and 1025 cm^{-1} (C-O). As can be seen from Figure 4, this FTIR spectrum is very similar to the reference spectrum (linen).

Based on all these findings and evaluations the pigments found in the selected sections of the painting are listed in Table 4.

Table 4. Identified pigments in the Alphabet reform painting.

Sample	Color	Detected Pigments
S1	GREEN	Lead White ($PbCO_3$) Zinc White (ZnO) Chromium oxide green (Cr_2O_3)
S2	BLUE	Lead White ($PbCO_3$) Zinc White (ZnO) Ultramarine blue ($Na_{6-10}Al_6Si_6O_{24}S_{2-4}$)
S3	WHITE	Zinc White (ZnO) Barium White ($BaSO_4$) Lead White ($PbCO_3$)
S4	BROWN	Zinc White (ZnO) Barium White ($BaSO_4$) Lead White ($PbCO_3$) Gypsum ($CaSO_4.2H_2O$) Iron oxide (Fe_2O_3)
S5	GREEN	Lead White ($PbCO_3$) Zinc White (ZnO) Barium White ($BaSO_4$) Chromium oxide green (Cr_2O_3)
S6	FLESH COLOR	Lead Red ($PbO_2.2PbO$) Lead White ($PbCO_3$) Zinc White (ZnO) Cadmium yellow (CdS)
S7	BROWN	Lead White ($PbCO_3$) Zinc White (ZnO) Iron oxide (Fe_2O_3) Cadmium yellow (CdS)
S8	BLACK	Lead White ($PbCO_3$) Zinc White (ZnO) Barium White ($BaSO_4$) Gypsum ($CaSO_4.2H_2O$) Chromium oxide green (Cr_2O_3) Cadmium yellow (CdS) Iron oxide (Fe_2O_3)
S9	RED	Madder (*Rubia tinctorum* L.) lake Lead White ($PbCO_3$) Zinc White (ZnO) Gypsum ($CaSO_4.2H_2O$) Cadmium yellow (CdS) Iron oxide (Fe_2O_3)
S10	GREEN	Lead White ($PbCO_3$) Zinc White (ZnO) Gypsum ($CaSO_4.2H_2O$) Chromium oxide green (Cr_2O_3) Iron oxide (Fe_2O_3)
S11	YELLOW	Lead White ($PbCO_3$) Zinc White (ZnO) Barium White ($BaSO_4$) Gypsum ($CaSO_4.2H_2O$) Cadmium yellow (CdS)

CONCLUSION

In this work, the Alphabet Reform painting was analyzed by ATR-FTIR, SEM-EDX and HPLC-DAD analysis methods. The CIE L*a*b* values were also identified. Both organic and inorganic structures, pigments, binders (linseed oil), auxiliary driers (Ca and K elements) and the type of the canvas (linen) used were identified. Red alizarin (madder lake organic pigment) and dark blue ultramarine pigments were detected as the organic pigments while CdS (yellow), Pb red (flesh color), $PbCO_3$ (white), ZnO (white), $BaSO_4$ (white), FeO (brown) and Cr_2O_3 (green color) were detected as the inorganic ones.

These results will provide some guidelines for restorers and conservators during restoration and conservation processes. Restorers can apply patching according to the type of canvas. Retouch applications can be easily applied since dyes and pigments are identified. According to the chemical properties of organic and inorganic substances detected on the surface, this study also provides a guidance in the selection of suitable surfactants and solvents for cleaning.

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CONFLICT OF INTEREST : The authors declare no competing interests.

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