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On-site Raman analysis of Kütahya potteries (17-18th centuries) at The Musée national de Céramique, Sèvres, shows different glaze compositions. Because of the *nakkashame* regulation Iznik wares do not fluctuate in composition/nanostructure, whereas the variation in this respect for Kûtahya wares is large. The spinel-type materials, used to draw the black lines, appear to be at the origin of the sharpness of the depicted figures.

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On site Raman analysis of Kütahya fritwares

On-site Raman analysis of Kütahya fritwares

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Abstract
On site Raman analyses were performed at the Musée national de Céramique, Sèvres, France, on Kütahya pottery. A comparison is made with Iznik and Safavid productions. Two Raman signatures of silicate glazes (with an index of polymerisation ~ 0.6-1 indicating a lead silicate composition, with characteristic Si-O stretching doublet at ~985 and 1050 cm^{-1}) are recognized and associated with the colour. Considering the peak position and the ratios of Q_n (n = 1, 2 and 3) components allow for the classification of the different productions. Differentiation between Kütahya and Iznik Ottoman pottery is straightforward from the centres of gravity. The procedure is also efficient to discriminate between early and late Iznik production. The white colour arises from a α-quartz slip. Although Iznik production does not fluctuate, as a consequence of the *nakkashame* regulation, composition/nanostructure dispersion of Kûtahya wares is large and different families can be recognized. The non-stoichiometric character of the spinel-type materials used to draw the black lines appears to be at the origin of the sharpness of the depicted figures.

Keywords : pottery, glaze, Kütahya, Ottoman, archaeometry, pigment

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INTRODUCTION

Leading experts generally base their certification of ancient artefacts on stylistic analysis and on personal sensory perceptions. However, greater objectivity is mandatory for identification and dating purposes. We have previously demonstrated the potential of Raman spectroscopy as a non-destructive on-site technique for the characterization of ceramics and glasses [1-4]. Different manufacturing technologies often result in products of very similar external appearance (from the visual and sensory points of view), but which differ completely in their micro/nanostructure. A lot of information about the production process remains written in the sample and non-destructive Raman analysis of the micro-structure (for ceramics) and nano-structure (for glasses and enamels) offers a way to retrieve the information, which assists in the identification and sometimes dating of ancient artefacts. Salient features can be extracted from bodies, glazes and pigments from different productions [5, 6].

Kütahya wares and the history of their production remain a source of debate among scholars, especially for the period following the town's conquest by the Ottomans in 1428 [7]. Some of the earlier fritwares are generally assigned to Iznik productions (blue and white wares sometimes classified as Touran, Roumi or Abraham of Kütahya style), but their production by Kütahya kilns was questioned. The real development of the production of Kütahya wares dates back to the end of the 17th century, following the emancipation of Byzantine and Armenian Christian communities [7]. Eighteenth century production received considerable attention but dated artefacts are rare and the oldest are from 1716 [8]. Among famous Kütahya wares is the series of 165 illustrated tiles made for the Saint-Sepulchre Church at Jerusalem, ordered in 1718 by Abraham Vardapet and attributed to the painter T'oros. In fact, these tiles were placed in the Armenian Saint-James Cathedral and then removed. Around fifty of them are conserved, including two in the Musée national de la Céramique, Sèvres (Plate 1). Many other churches, mosques and monasteries in Istanbul, Kütahya, Ankara, Konya, Efkere, Kayseri, Sivas, Nicosia, Jaffa, etc. have Kütahya tiles in their collections. Carswell collected a variety of marks, more or less sibylline [8]. Many pieces commonly classified as Kütahya ware have a hand-made Turkish mark "Sivas" and some scholars concluded that similar productions were made elsewhere, including of course in the town Sivas. Furthermore, copies or fakes were made since the 19th century in different places. Neutral, scientific-based analyses of the objects would therefore be highly useful to improve the classification and understanding of these productions.

On-site analysis of Medici pottery demonstrated that the Raman signature of glazes and their pigments is a powerful tool to identify and classify rare ancient ceramics [5]. Preliminary analysis has shown that we are able to differentiate between Kütahya and Iznik ware [9]. The exact origin of many "Kütahya " wares is still an open question, which is not well documented from the material science point of view. A non-destructive analysis, performed in the secure area of museum collection rooms, appears to be the only way of making progress with the identification and classification of these precious artefacts.

We report a preliminary on-site Raman analysis of a selection of "Kütahya" wares, including tiles (from the Saint-James Cathedral), a flask, a bowl and a small dish from the Musée national de Céramique, Sèvres (France). A comparison will be made with the Raman signatures of Iznik and Safavid wares.

EXPERIMENTAL

Samples

The objects analysed are shown in Plate 1. They belong to the collection of the Musée national de Céramique, Sèvres (France). Among the samples studied are the famous "Saint-Sepulchre" tiles (MNC 7460[1] and 7460[2]), a flask (MNC 16469), a bowl (MNC4630[3]) and a dish (MNC6876). A Safavid dish (MNC 21840) was also analysed for comparison purposes. Note that its décor and chocolate bottom could indicate that this pottery is a copy of Vietnamese/Chinese productions [10].

Technique

On-site micro-Raman spectrometry was performed using a portable HE532 Jobin Yvon Raman system (Longjumeau, France). The analyser is optimised to work with a 532 nm laser excitation. The spectra were recorded in the 160-3000 cm^{-1} range, using Olympus MSPLAN™ Ultra Long Working Distance objectives (x80 and x50, total magnification x800 and x500). A portable XYZ plate (weight ~3 kg) supports the SuperHead™ allowing micrometer scale displacements (see Plate 1) to select a "good" location for spectral recording. In addition the object itself is put on a stage, which can be moved in different directions. Typically, the power of illumination at the sample was 10-20 mW. A filter, which drastically decreases the laser intensity, enables one to choose the area to be analyzed and to focus the laser spot. This is attained by moving the SuperHead™ using the XYZ micrometer. LabSpec® (Jobin-Yvon) software was used to control the HE system and the data acquisition. Details are given in ref [9].

Peak fitting and data processing

In undertaking a curve fit of the Raman spectra, a linear baseline was first subtracted using LabSpec® software. The same spectral windows were used for the extraction of the components, using the Origin® software peak-fitting module (Microcal Software, Inc.) [1, 9]. The integral area, the bandwidth and the peak position were calculated for each component. A Gaussian shape was chosen for all Raman lines assigned to glassy silicates, because of the amorphous state of the examined material, whilst a Lorentzian shape was used for crystalline phase components: pigments, crystalline precipitates or un-reacted pristine α-quartz.

Raman spectra make it possible to:

- i) identify crystalline phases within the body. This is easily accomplished by comparison with the spectra in existing spectral databases ([1, 2, 11-14] and refs therein) and
- ii) gain information about the structure and composition of glassy silicates.

Silicate structures consist of more or less connected (polymerized) SiO_4 tetrahedra. Because the SiO_4 tetrahedron is a very well defined vibrational and structural entity, its different configurations have specific vibrational fingerprints. The different spectral components give information on the connectivity of the SiO_4 polymeric units and thus on the glass composition, nanostructure and processing temperature. A clear differentiation is possible through the relative intensities of the components of the Si-O stretching and bending modes at ca. 1000 and 500 cm^{-1} respectively. From the literature (e.g. [1, 4] and refs therein) the different spectral components of the stretching envelope were assigned to specific silica vibrations. The following assumptions were made: i) for the Si-O stretching range extending from 700 to 1300 cm^{-1} (see previous work), we postulated 5 components namely Q_0, Q_1, Q_2, Q_3 and Q_4 according to the number of oxygen atoms bonded per tetrahedron, ii) we postulated rather similar bandwidths for Si-O bending components, the number of bands also being 5; iii) one or two narrow bands were added, if necessary, to take crystalline phases (α–quartz, peak at 464 cm^{-1}) and pigment signatures (cassiterite, spinels, …) into account.

RESULTS AND DISCUSSION

As observed for Iznik fritwares, many Raman spectra show the clear signature of α-quartz (narrow 464 cm^{-1} peak, see Figs 1-2), originating from a white slip This signature is very strong for spectra recorded at the interface between the glaze and the body and for the colourless glaze.

Raman signature of the glassy silicate constituting the glaze.

Glasses are silicate networks in which the SiO_4 tetrahedra are joined together by the oxygen atoms located at the vertices. These SiO_4 tetrahedral connections are modified by the incorporation of aluminium, magnesium, iron… alkali/earth and alkaline metallic ions (fluxing oxides) into the silicate network, which changes the physical properties of the glass such as melting temperature, viscosity, thermal expansion, colour, chemical resistance, etc. In the Raman spectra these modifications of the SiO_4 tetrahedral vibrational unit (a strong covalent-bonded moiety) can be detected mostly through changes in the intensity, line-width and spectral position of the associated bands [14]. By comparing Raman spectra of glassy or crystalline pure silicates and aluminates, it becomes clear that the Raman cross-section of Si-O bending and stretching modes is orders of magnitude stronger than that of their Al-O (Mg-O) bond counterparts. This arises from the more covalent character of the Si-O bond. Indeed, when compared to the strong covalent character of a Si-O bond the Raman cross-section of a very ionic Al-O bond can be neglected and as a first approximation, we can consider that SiO_4 is the only vibrational unit.

The glass (nano)structure is actually a function of two key factors, namely the bulk composition and temperature of the melt equilibrium. Glass and glaze can be matured at temperatures ranging from *ca.* 600°C (for instance for pottery lustre) to ~1450°C (high temperature fired porcelain glaze). Obviously, the preparation techniques employed are dependent on the kiln/furnace temperatures that can be achieved, which in turn justify the use of a specific bulk composition. We have thus deduced a correlation between the processing temperature and the raw materials, which is inherent to the preparation technique and should be reflected in the Raman spectra as a combination of the effect of temperature and composition [4]. The Raman intensity of the Si-O bending and stretching envelopes vary with composition and their different components inform on the connectivity of the SiO_4 polymeric units and, thus, on the glass composition, nanostructure and processing temperature ([1, 4] and references therein). From the literature (e.g. [1, 7] and refs therein) the different spectral components of the stretching envelope were assigned to the tetrahedron vibrations with zero (Q_0 or isolated SiO_4), one (Q_1 or dumbbell $-SiO_3$), two (Q_2 or $=SiO_2$), and three (Q_3 or $\equiv SiO$) bridging oxygen atoms per tetrahedral group. Q_4 corresponds to fully polymerised tetrahedra, as in pure amorphous silica. Decomposition of the bending and stretching massifs is illustrated with the examples given in Figs 1 and 2.

The plot of the calculated area of each component as a function of their peak position (Figs 3 and 4), gives a graphic representation of the intrinsic homogeneity of a specific ceramic production process and can be used to identify artefacts made with different processes. Examination of Iznik fritwares ([9] and Fig. 5) shows that the Raman signature of the silicate glaze (i.e. its composition and nanostructure) does not change very much from the beginning (late 15th century) to the apogee (mid to late 16th century) of this production. A small compositional shift is however associated with the decline of the production (17th century [15]). In contrast, a rather large variety of signatures was observed for the 5 samples of this work, all assigned to Kütahya production. The main difference consists in the wavenumber position of the stretching massif summit, ranging from ~980 to 1080 cm^{-1} (see Figs 1 and 2).

Extraction of the Q_n components shows that the peak position and the relative intensity of the Q_2 and Q_3 components change (Table 1). The Q_0 characteristic remains almost unchanged, as commonly observed for glassy silicates (Q_0 the Si-O stretching mode of isolated SiO_4 tetrahedra is not affected by composition/nanostructure change of the glaze, as described in previous work). The analysis of spectra recorded in the same place with different signal-to-noise ratios and backgrounds (more than 10 spectra recorded in different places or with different objectives for each item) demonstrates that the peak position of the Q_4 component changes at random. Thus, we will only consider the signature of SiO_4 tetrahedra connected by 1, 2 or 3 Si-O-Si bridges. The main changes for these Q_1, Q_2 and Q_3 components do not seem to depend on the sample but rather on the colour of the analyzed glaze. We distinguished, more or less subjectively, two groups of signatures in the Si-O stretching massif, i) K1 group (Figs 1 and 3) characterized by the Q_2 peak forming the summit – and corresponding to green to black colour - and ii) K2 group (Figs 2 and 4), characterized by Q_3 component forming the summit and corresponding to yellow to colourless glaze. A rather similar K2' group is also recognized (Table 1). Plots of the peak component area vs. centre of gravity wavenumber (Figs 3 and 4) confirms the "validity" of our model, which can be used to assess the production homogeneity. In comparison with Iznik production (data for 12 different artefacts covering at least one century of production are given in Fig. 5), the production heterogeneity is greater (and only 5 artefacts are concerned !). The similarity between composition and nanostructure of Iznik and Kütahya glazes is however obvious from the comparison of the Q_n centre of gravity and relative area ratio given in Table 1. In the same table Savafid and Medici glazes are compared to the Iznik and Kütahya glazes. Differences are obvious. This confirms the very particular technology used by Medici' potter [9].

The polymerisation index I_P defined as $I_P = A_{500}/A_{1000}$ (with A being the area under the ~500cm^{-1} Raman band) is a useful tool to classify glassy silicates as a function of their composition/nanostructure. The relationship between I_p, the glass composition and the processing temperature is well documented [4, 9, 16]: the 1000 cm^{-1} massif dominates the spectrum of a PbO-rich Islamic glaze. Glass and glaze with intermediate [Na_2O + K_2O + CaO + PbO +…]/[SiO_2 +Al_2O_3] (flux/network former) ratios have intermediate Raman signatures. A first family (I_p < 0.3-0.5) mostly corresponds to lead-rich glazes. A second family (0.5 < I_p < 0.8) consists of some lead- or Na-based mixed enamels and glasses; a third family (0.8 <I_p < 1.1) corresponds to ancient Roman glasses and soft-paste porcelain enamels; family #4 (1.1 <I_p <1.3) and family #5 (1.3 <I_p <2.5) correspond to Ca-based glazes. Family #6 (I_p >2.5) corresponds to a K-based hard-paste porcelain glaze. I_p is strongly correlated to the processing temperature (~1400°C for I_p ~7, 1000°C for I_p ~1 and ~600°C or less for I_p ~0.3). I_p values measured for Kütahya glazes range between 0.6 and 1 (i.e. family #2); these values are slightly higher than those measured for Iznik glazes (0.4-0.8, [9]). This would indicate that higher firing temperatures were used in Kütahya production for the studied artefacts. This data are consistent with the mixed Na/Pb flux used in Ottoman glazes [17-19].

Pigment signature and technology

Black lines

Figures 6 and 7 show representative spectra recorded in different places on the artefacts. We shall first discuss the spectra of black lines and dots (Plate 1). In some places (see MNC4630[2], Fig. 7) the spectrum consists of a very strong 845 cm^{-1} peak with very weak additional bands. The signature of the glassy silicate is either not observed or very weak. Very similar signatures were observed for Iznik black lines [9] and assigned to a Cr-based compound (the symmetric Cr-O mode of CrO_4^{2-} containing compound peaks at ~840-850 cm^{-1} [2,14]).

Another type of Raman signature for the black pigment is also observed; an example is given in Fig. 6: additional strong bands are observed at ~700 and 540 cm^{-1}. This is a typical Raman signature of Fe-based spinels, a family of MOM'_2O_3 solid solutions (M= Mg, Fe, Mn, Co,..; M'= Fe, Al, Cr, V,…), a structure built of octahedra and tetrahedra. Previous quantitative analysis of Iznik and Safavid glazes [7, 17, 19, 20] show very heterogeneous compositions regarding the chromic metal content, but always a mixture of Cr, Fe and Co with addition of Mg, Si… etc. These compositions are consistent with the use of chromite ores, which was reported in ancient documents [17, 18]. Two sorts of chromite ores ($MgCr_2O_4$ and $FeCr_2O_4$) are usually found but with a variety of intermediate compositions. These compounds require high temperatures to react with silicates, forming for example uvarovite garnets (a very stable and intense green pigment) in a calcium flux [2]. It is clear that different spinel materials have been used. For instance in MNC7460[2] tile (Plate 1), the 700 cm^{-1} (Fe-based spinel) Raman signature dominates; in the bowl (MNC4630[2]) and flask (MNC6876) décors, on the other hand, the 845 cm^{-1} (Cr-based compound) signature is important. More analysis on more artefacts is required to establish a classification.

The signature of the green glazes is rather similar to that of the black lines, but its intensity is much weaker and the signature of the glassy silicate host dominates.

The use of spinel/chromite ores to draw the lines separating the different coloured regions is certainly at the origin of the famous sharpness of the Iznik and Kütahya décor. Spinel/chromite structures are nonstoichiometric compounds, which could trap many ions diffusing through the glaze, in particular Co and Cu ions, which remain dissolved in the glass structure and do not form crystalline pigments. This phenomenon hinders the crossing of the colour through the black lines.

Yellow

Yellow colour is a clear characteristic of Kütahya glazed pottery. Yellow glazes exhibit a strong and narrow peak at 670 cm^{-1}, assigned to a Cr-based silicate. A very similar Raman signature is observed for a blue pigment prepared by thermal treatment of chalk, flint and Co_2O_3 oxide. This indicates that a similar structure hosted the chromophore bond.

Red and maroon

Haematite (α-Fe_2O_3 corundum) is the base of red décor. Under green excitation, the Raman signature of haematite gives a strong peak at 1325 cm^{-1} (in addition to the 1st order signature of the corundum structure at 295, 415, 615 cm^{-1}, etc.[2, 11, 14]). As for Iznik glazes the strong signature of α-quartz is simultaneously observed, indicating that the red pigment consists of a mixture of haematite and sand. Contrarily to Iznik analysis we do not have any evidence that cassiterite was added to lighten the red colour. The presence of some magnetite (Fe_3O_4) is possible because of the rather strong intensity of the 665 cm^{-1} peak, indicating a firing under reducing atmosphere.

Blue

No specific signature is observed for the blue glaze, which is in accordance to the dissolution of the Co ions in the glass structure (so-called *couleur transparente* [2]).

CONCLUSION

This preliminary on-site study of a small selection of ceramics attributed to Kütahya production confirms the potential of the Raman technique as a non-destructive tool for the classification and understanding of the ancient technology of Ottoman potters. Contrarily to Iznik production, the Raman signature of the glaze varies a great deal. We ascribe this phenomenon to the fact that Iznik manufacturers were controlled by the *nakkashane*, the Ottoman office for décor and drawing. We thus assume that the control was applicable not only to the depicted illustrations but also to the technology. This would explain the good homogeneity of Iznik glazes' Raman signature, which became more varied only after the mid-

17th century, simultaneously with the decline of the aesthetic quality. The variation of the Raman signature of the Kütahya glazes thus reflects the autonomy of different production centres working according to the Kütahya style. The large difference between the Raman signature of Medici and Ottoman glazes confirms the very originality of the Medici technology.

Except for the yellow Raman signature, the palette of pigments seems to be very similar to that used in Iznik pottery. At least two different glaze compositions have been characterized and they seem to be associated to the achieved color. The small number of studied pieces does not permit a definite conclusion, but this point is consistent with the use of different mixtures for the colourless overglaze (which react with the pigments drawn on the piece) and coloured overglaze. The combined effect of the Q_1, Q_2 and Q_3 components'peak position, wavenumber and peak area ratio appear to be a very efficient tool to classify pottery glazes, as also seen in previous studies.

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Parameter	Iznik	Late Iznik	Kütahya 1	Kütahya 2	Kütahya 2’	Medici	Safavid
ν Q_1 / cm^{-1}	920	925	929	924	924	943	944
ν Q_2 / cm^{-1}	978	979	982	981	981	976	1016
ν Q_3 / cm^{-1}	1052	1039	1053	1054	1074	1035	1097
AQ_2/AQ_1	2.6	2.25	1.1	2	3.15	1.45	3.1
AQ_2/AQ_3	0.4	0.4	0.25	0.35	0.4	0.45	0.65
$\nu Q_2/\nu Q_1$	1.05	1.05	1.05	1.05	1.05		1.07
$\nu Q_2/\nu Q_1$	0.95	0.95	0.93	0.93	0.91		0.92

Table 1*:* Comparison of the Q_1, Q_2 and Q_3 components peak position (ν) and area ratio (AQ_i/AQ_j) for different glazes from the 16-18th century Ottoman productions, Medici porcelains and Safavid fritwares. Late Iznik corresponds to artefacts assigned from stylistic analysis to a production date after 1650. Differentiation between Kütahya 1 and 2/2’ is made by considering the summit of the Si-O stretching envelope: K1~980 cm^{-1}, K2/2’~1050-1070 cm^{-1}.

FIGURE CAPTIONS

Plate 1
Bowl (MNC4630[3]), dish (MNC6876), flask (MNC16469), tiles (MNC7460[1] and 7460[2]) assigned to Ottoman Kütahya production. A Safavid dish (MNC21840) used for comparison is shown. The tiles belong to the group of tiles originating from Saint-James Armenian Cathedral of Jerusalem and ordered by Abraham Vardapet for the Saint-Sepulchre Church (note the Bolorgir inscription). An example of the experimental set-up is shown : see, i) the optic fibre coming from the laser and that going to the spectrometer and ii) the x-y-z support. More details are given in ref 7.

Figure 1
Representative Raman spectra recorded on different samples (and for different glaze colours) classified as Kütahya 1-type.

Figure 2
Representative Raman spectra recorded on different samples (and for different glaze colours) classified as Kütahya 2 (and 2')-type.

Figure 3
Plot of the Raman peak component area vs. centre of gravity for spectra classified as from Kütahya 1-type. Q_0, Q_1, Q_2, Q_3 and Q_4 data are circled. Extra data correspond to the signature of crystalline pigments.

Figure 4
Plot of the Raman peak component area vs. centre of gravity for spectra classified as Kütahya 2 (and 2')-type. Q_0, Q_1, Q_2, Q_3 and Q_4 data are circled. Extra data correspond to the signature of crystalline pigments.

Figure 5
Plot of the Raman peak component area vs. centre of gravity for Iznik spectra (early and apogee production). Q_0, Q_1, Q_2, Q_3 and Q_4 data are circled. Extra data correspond to the signature of crystalline pigments.

Figure 6
Representative Raman spectra recorded for black and dark-green glazes for various artefacts.

Figure 7
Representative Raman spectra recorded for light coloured glazes for various artefacts.

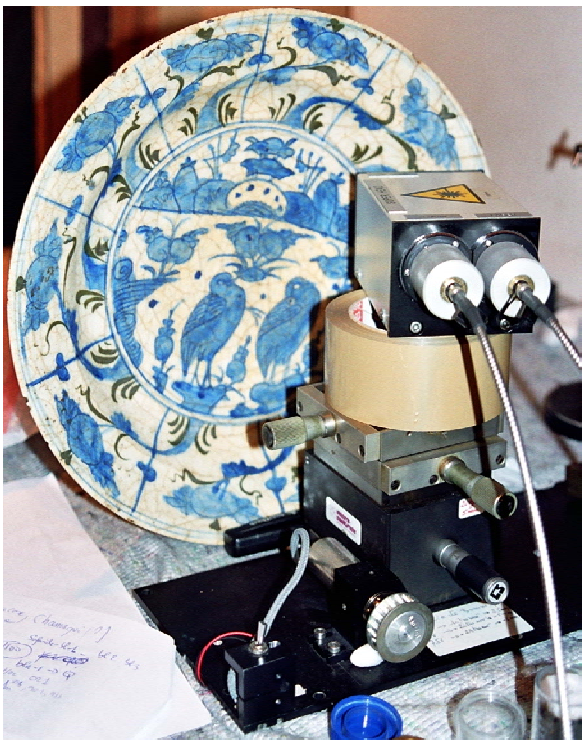
MNC4630[3]

MNC6876

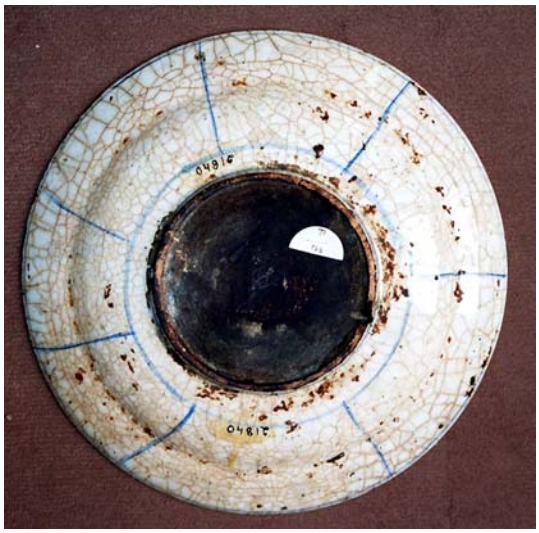
MNC16469

MNC7460[1]

MNC7460[2]



MNC21840



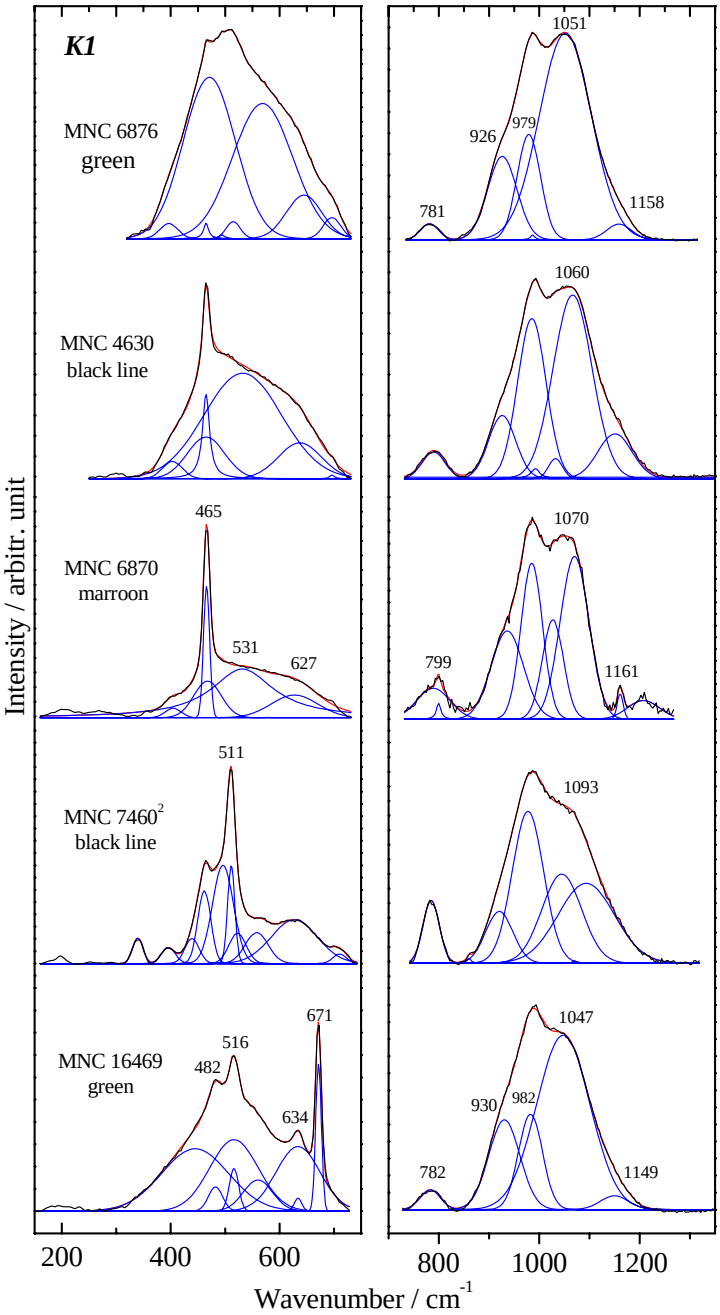

K1
MNC 6876
green
1051
926
979
781
1158
MNC 4630
black line
1060
465
MNC 6870
marroon
531
627
1070
799
1161
511
MNC 7460[2]
black line
1093
671
516
482
MNC 16469
green
634
1047
930
982
782
1149
Intensity / arbitr. unit
200
400
600
800
1000
1200
Wavenumber / cm-1

Fig. 1

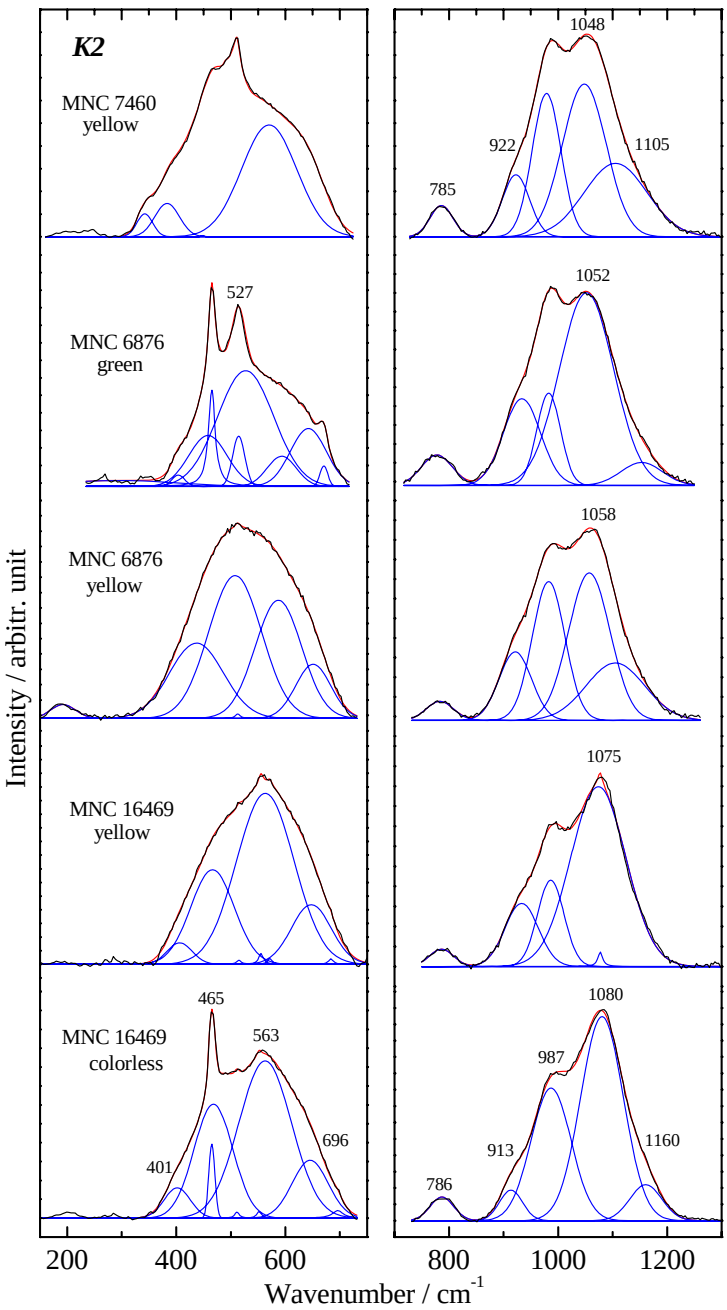

K2
MNC 7460
yellow
1048
922
1105
785
MNC 6876
green
527
1052
MNC 6876
yellow
1058
MNC 16469
yellow
1075
MNC 16469
colorless
465
563
696
401
1080
987
913
1160
786
Intensity / arbitr. unit
200
400
600
800
1000
1200
Wavenumber / cm-1

Fig. 2

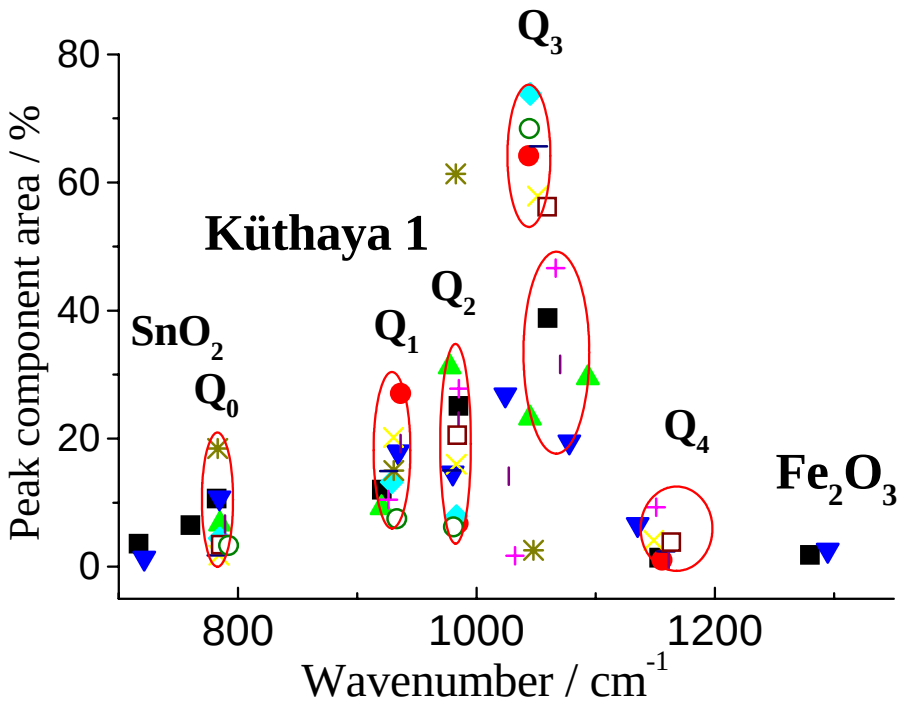

Peak component area / %
Wavenumber / cm-1
Küthaya 1
SnO2
Q0
Q1
Q2
Q3
Q4
Fe2O3
0
20
40
60
80
800
1000
1200

Fig. 3

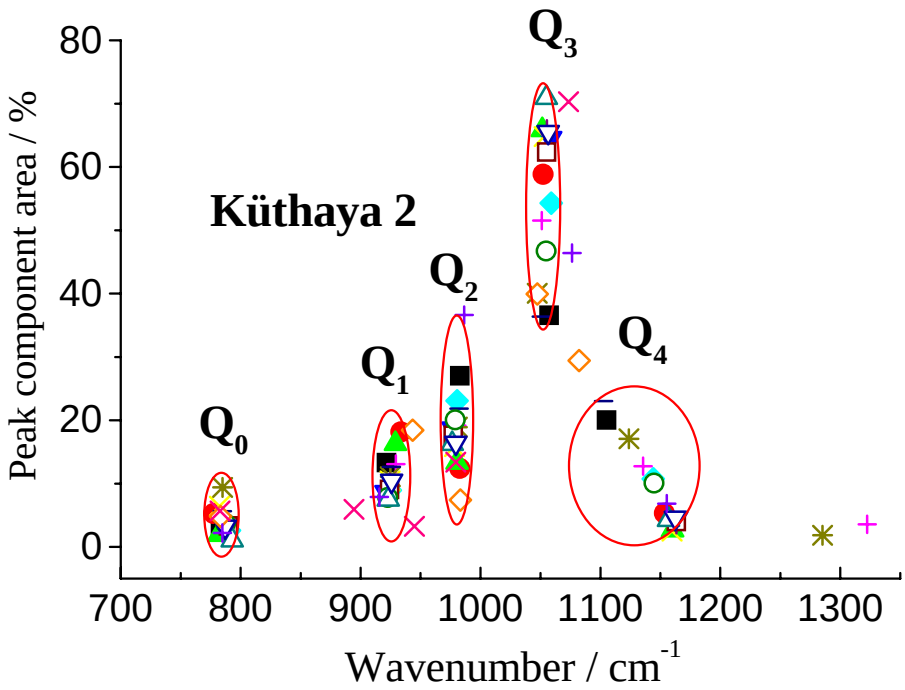

Peak component area / %
Wavenumber / cm-1
Küthaya 2
Q0
Q1
Q2
Q3
Q4
0
20
40
60
80
700
800
900
1000
1100
1200
1300

Fig. 4

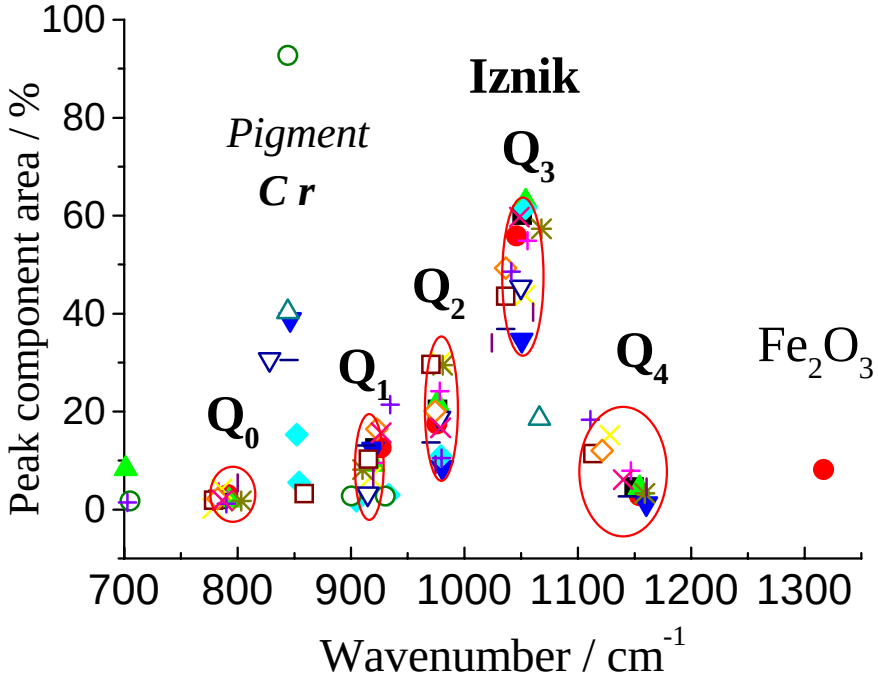

Iznik
Pigment
Cr
Q0
Q1
Q2
Q3
Q4
Fe2O3
Peak component area / %
Wavenumber / cm-1
100
80
60
40
20
0
700
800
900
1000
1100
1200
1300

Fig. 5

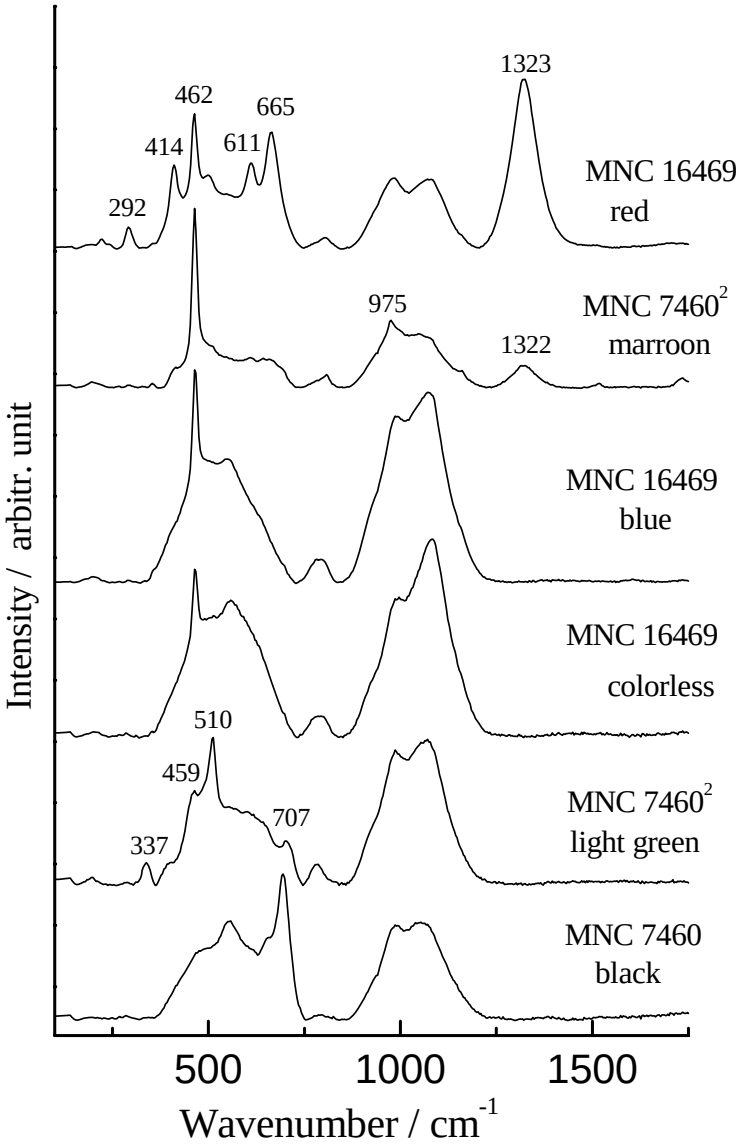
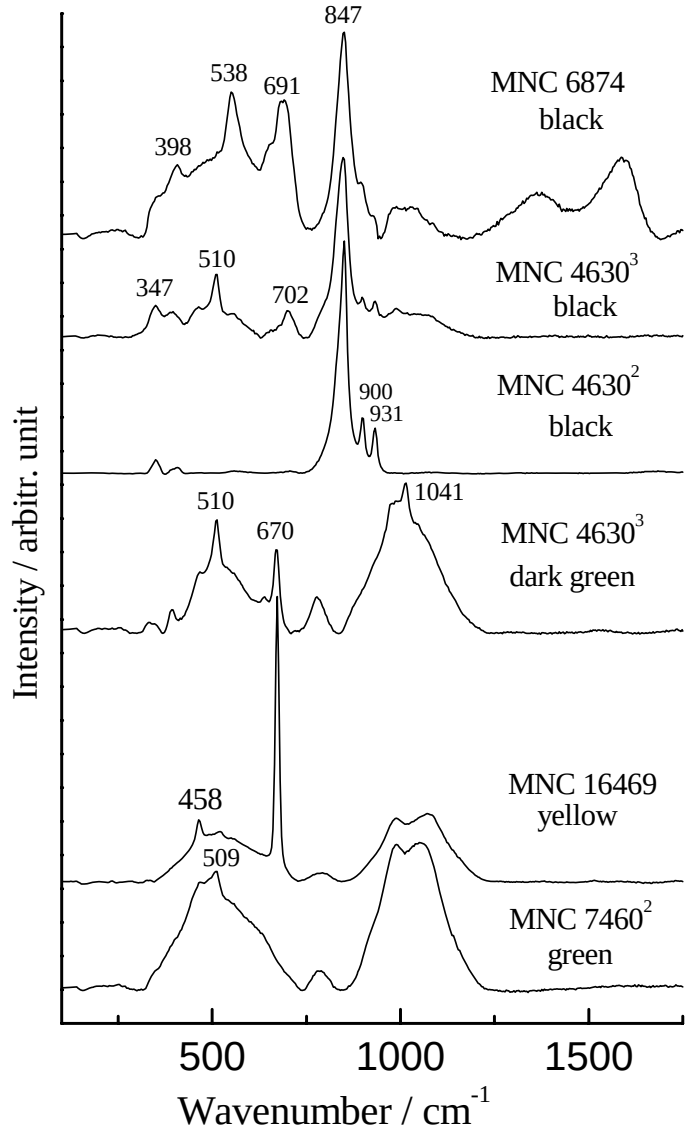

1323
462
665
414
611
292
MNC 16469
red
975
MNC 7460[2]
1322
marroon
MNC 16469
blue
MNC 16469
colorless
510
459
707
337
MNC 7460[2]
light green
MNC 7460
black
Intensity / arbitr. unit
500
1000
1500
Wavenumber / cm-1

Fig. 6


847
538
691
398
MNC 6874
black
510
347
702
MNC 4630[3]
black
900
931
MNC 4630[2]
black
510
670
1041
MNC 4630[3]
dark green
458
509
MNC 16469
yellow
MNC 7460[2]
green
Intensity / arbitr. unit
500
1000
1500
Wavenumber / cm-1