

Characterization of Japanese Raku Ceramics Using XRF and FTIR

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Abstract

Japanese raku ware is characterized by the use of lead glazes, short firing times, and rapid cooling, which give it its distinctive appearance. However, this also results in a high degree of heterogeneity because the firing is too rapid for the various components in the glaze to be made homogeneous. In this study of glazes from raku and associated wares, data from elemental analysis by X-ray fluorescence (XRF) spectroscopy, and from Fourier transform infrared (FTIR) spectroscopy using a fiber-optic probe, have been combined with observations of the glaze texture using a low-powered optical microscope and physical characteristics of color and foot shape.

Keywords: ceramics, raku, analysis, composition

Introduction

Although the raku technique has been attributed to the Raku family workshop in late 16th-century Kyoto, recent scholarship suggests multiple influences and paths of development. Raku ware is characterized by the use of hand-formed bodies, lead glazes, and short firing times, which give it its distinctive appearance. Traditional raku consists of two types, red and black (Fig. 1). Black raku is fired at a higher temperature, with a glaze traditionally consisting of lead frit and ground Kamogawa stone (i.e., stone from the Kamo River) containing iron and manganese (Wilson 1995, p. 132). Red raku is fired at a lower temperature, with a transparent lead silicate glaze composed of quartzite and feldspar with a lead frit over a red-slipped body (Raku 1997, pp. 75–76).

Although the term *raku* is properly applied to ceramics produced by the Raku family workshop, ceramics (mainly bowls) that appear to have the same characteristics but were made at other workshops in the late 16th or early



Figure 1

Red (*left*) and black raku tea bowls. Taller: H. 8.8 cm, D. 15.3 cm. Freer Gallery of Art, Smithsonian Institution, Washington, D.C. (F1904.326 and F1900.87, gifts of Charles Lang Freer).

17th century have been found in archaeological excavations. Those unidentified workshops eventually ceased production, leaving the Raku family workshop to carry on and refine the technique. However, following the publication of the technical manual *Collected Raku Ceramic Secrets* in 1736, the technique spread, and many kilns around Japan produced pieces in the raku style (Wilson 2001; Pitelka 2005). Pitelka (2001 and 2005) mentions at least 43 kilns firing lead-glazed raku-style ceramics dating from the early 17th to 20th centuries. While raku in its various forms has been well studied from a stylistic perspective, few technical analyses have been performed, and the technique's lengthy popularity and widespread production, as well as the high degree of heterogeneity inherent in such a rapid firing process, make it difficult to date and attribute individual pieces to specific workshops.

The Freer Gallery of Art houses several Raku workshop wares, as well as raku-style wares produced by other Japanese workshops, most of which are assigned dates in the 18th or 19th century, following the spread of the raku technique throughout Japan. In our project, the use of nondestructive methods for studying raku ceramics was explored. The techniques chosen focused on the glazes because most of the pieces do not have unglazed areas of sufficient size for analysis and sampling was neither possible nor justifiable without an established protocol. X-ray fluorescence (XRF) spectroscopy is commonly used to differentiate ceramics by their elemental compositions, and it was chosen for this study. It is an ideal method for examining the heterogeneous glazes because of its large spot size. Its penetration depth for heavier elements (such as lead in the glaze) is much less than the thickness of the glaze, so the results are not confused by contributions from the clay body.

Infrared spectroscopy has been employed extensively to measure the degradation of glass. Studies of lead silicate glasses and ceramic glazes have shown the effects of different amounts of lead in a glass matrix, which acts as a matrix modifier but also as a matrix former at higher concentrations (Liu 1993; Gee, Holland, and McConville 2001; De Sousa Meneses, Malki, and Echegut 2006). Other studies have been able to assign fictive temperatures—the temperatures at which glass is at thermal equilibrium before quenching—to glass using the same technique (Raffaëly and others 2008). We had hoped that

these features or other information given by Fourier transform infrared (FTIR) spectroscopy analysis could be used, together with XRF, to develop a means of dating and attributing individual pieces in the Freer Gallery collection. While FTIR often requires sampling, when it is used with a fiber-optic probe, the technique can be applied noninvasively to examine the surface of an object (Fabri and others 2001). However, both XRF and reflectance FTIR spectroscopies are surface techniques, and the possible effects of surface degradation on the data must be considered. In this study, data from elemental analysis by XRF and from FTIR analysis using a fiber-optic probe have been combined with observations of the glaze texture using a low-powered optical microscope, and of foot shape, in an attempt to further characterize the Freer's raku wares.

Method

The surfaces of each piece were examined under magnification using a Wild Heerbrugg binocular microscope with an attached Olympus DP-70 digital camera. Microstructural features were noted and used to categorize the glazes, which were subdivided into groups by color (black or red). These groups were further categorized by glaze microstructure: clear with white inclusions, very degraded with bubbles and inclusions, or cloudy with large bubbles. The features of the foot of the vessel were also classified.

XRF spectra were obtained in air, using an Omega 5 spectrometer, a modified open architecture Spectrace 6000, with a rhodium X-ray tube. Measurement conditions were 35 kV for 200 seconds. Spot size was approximately 1 cm. A fundamental parameters program, EDXRF, version 1.35a, was used with standards BGIRA3, BGIRA4, Corning A, and BCR 126A to quantify the spectra (standard compositions are given in the Appendix).

Noninvasive FTIR was carried out on both the reference glasses and the raku glaze surfaces with a REMspec fiber-optic probe and an MCT A detector in reflectance mode. A Thermo Nicolet NEXUS 670 FTIR was used for the infrared source. Spectra were acquired as an average of 250–500 scans at a resolution of 4 cm^{-1} . Omnic version 6.0a software was used to collect the spectra, assign peaks, and apply a Kramers-Kronig correction over the range of 947–4000 cm^{-1} . Kramers-Kronig transforms a reflectance spectrum containing Reststrahlen bands (i.e., bands caused by discontinuities in the complex refractive index of the

sample in the region of an absorption band) into a spectrum from which absorbance as a function of frequency can be calculated, allowing comparison with transmission spectra and aiding comparisons between samples (Lang and Richwine 1993).

Although quartz was not seen at the surface in the glaze microstructures, it was measured in order to ensure that the FTIR results on the raku glazes were not derived from quartz inclusions. The peaks were similar, but displaced. The red slip underlying the clear glaze in red raku did not contribute to the FTIR spectra. A small sample of glaze with red slip obtained during the restoration of a raku bowl (AK-MAK-674) in the Rijksmuseum, Amsterdam, was analyzed using an FTIR microscope, where spectra of both the slip and the glaze in reflectance mode were taken separately. The peaks seen in the spectrum of the slip were not present in the spectrum of the glaze. The glaze spectrum taken with the microscope was similar to those taken of glaze surfaces in reflection in the fiber-optic measurements.

Results

In general, the microstructures, if separated by type of manufacture (red or black raku), were relatively uniform. Red raku glazes are mostly transparent, and they often contain white particles and bubbles that range from small ($\sim 60 \mu\text{m}$) to large ($\sim 350 \mu\text{m}$), which are usually associated with cloudy areas in the glaze (Fig. 2). Their surfaces are typically very glossy, with less surface degradation than the black raku. Black raku glazes are a translucent amber color under the microscope, and they tend to have inclusions of white particles and many small bubbles that are mostly obscured by the colored glaze itself (Fig. 3). Their surfaces are typically matte in appearance. However, glossy glazes are known to have been introduced in the early 17th century, and some of the wares had a shiny surface. Other comparative or possibly misfired raku pieces often had no inclusions or bubbles within their glazes, and the glazes were generally thinner and completely transparent. The surface characteristics were separated into five features: (1) transparent glazes with no inclusions, (2) glazes containing only white particles, (3) glazes with a severely degraded surface, (4) glazes with inclusions of both white particles and small bubbles, and (5) glazes with large bubbles (Table 1).

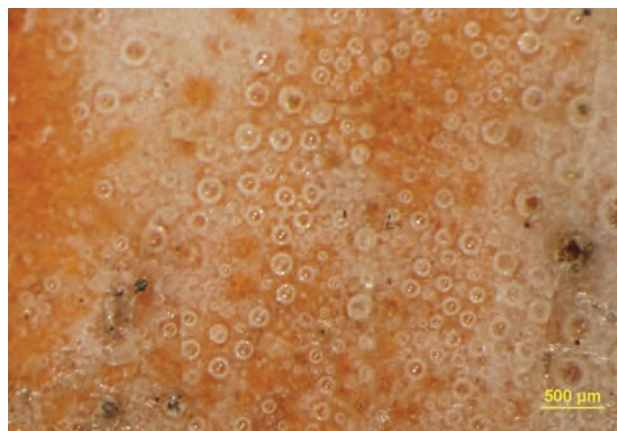


Figure 2
Optical microscope photo of glaze surface of red raku F1896.89.

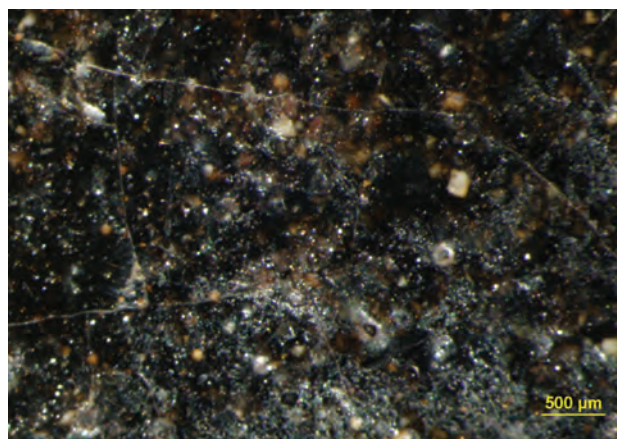


Figure 3
Optical microscope photo of glaze surface of black raku F1900.87.

The feet of the vessels were grouped into five categories: (1) those that were glazed with a central divot, (2) those that were carved with a tool, (3) those in which two or three spacer marks were visible, (4) those that had a stamped seal impression, incised inscription, or other type of signature, and (5) those that were glazed and flat.

The majority of the glazes contained lead, which varied from less than 1%¹ to greater than 50%. There were five

1. All percentages noted in this paper are mass percent, unless otherwise indicated.

TABLE 1
Data for Glazes from Raku and Associated Wares

Red Raku

<i>Acc. No.</i>	<i>Si-O-Si</i>	<i>FTIR</i>	<i>FTIR Dif. from Quartz</i>	<i>Si-O-Si Range</i>	<i>Microstructure</i>	<i>Feet</i>	<i>PbO Mass %</i>	<i>Dating</i>
F1896.89	1098	2	62	10	5	2	14	4
F1897.1	1084	2	76	8	4	4	very high	4
F1897.38	1086	2	74	8	5	2	0	4
F1899.3	1096	2	64	9	4		10	3
F1899.66	1094	2	66	12	5	4	very high	2
F1899.97	1085	2	75	0	1	5	18	4
F1900.40	1113	2	47	31	2	2	29	2
F1900.118	1108	2	52	40	1		very high	4
F1904.326	1099	2	61	3	2	1	19	4
F1905.25	1101	2	59	10	4	1	17	4
F1911.391	1122	5	38	6	5	3	23	4
F1911.392	1100	2	60	21	4	1	29	3
F1911.509	1098	2	62	12	5	1	30	4

Black Raku

<i>Acc. No.</i>	<i>Si-O-Si</i>	<i>FTIR</i>	<i>FTIR Dif. from Quartz</i>	<i>Si-O-Si Range</i>	<i>Microstructure</i>	<i>Feet</i>	<i>PbO Mass %</i>	<i>Dating</i>
F1894.16	1055	1	105	49	4	3	22	4
F1897.35	1066	1	94	50	4	4	9	4
F1897.36	1045	1	115	41	4	3	28	4
F1898.418	1070	1	90	12	4	3	12	4
F1898.437	1089	2	71	17	4	5	18	4
F1898.438	1067	1	93	8	4	1	20	3
F1898.443	1066	1	94	29	4	5	7	2
F1899.96	1110	1	50	24	4	2	9	4
F1899.100	1071	1	89	31	4		0	4
F1900.87	1040	5	120	6	3	1	0	1
F1900.103	1091	1	69	26	4	1	10	4
F1901.2	1082	1	78	29	4	4	no data	3
F1901.61	1060	1	100	27	4	4	25	4
F1901.71	1098	2	62	1	3	4	4	4
F1901.157	1094	1	66	3	4	3	19	4
F1902.53	1088	1	72	28	4	4	7	2
F1902.55	1060	1	100	48	4	5	0	4
F1902.206	1053	1	107	33	3	2	20	4
F1905.221	1072	1	88	42	3	1	10	4
F1911.389	1200	1	40	0	4	3	11	4
F1911.390	1081	1	79	30	4	3	8	4

Related or Possibly Misfired Wares

<i>Acc. No.</i>	<i>Si-O-Si</i>	<i>FTIR</i>	<i>FTIR Dif. from Quartz</i>	<i>Si-O-Si Range</i>	<i>Micrographs</i>	<i>Feet</i>	<i>PbO Mass %</i>	<i>Dating</i>
F1898.128	1071	5	89	34	1	2	71	4
F1898.510	1075	5	86	1	2	5	22	1
F1898.516	1087		74	3	2		19	3
F1899.46	1099	3	61	20	3	2	very high	2
F1899.52	1091	3	69	12	4	3	very high	4
F1900.38	1099	3	61	12	1	5	very high	3
F1900.74	1100	2	60	7	4	2	very high	4
F1900.75	1103	2	57	2	1	4	very high	4
F1900.76	1102	4	58	0	4		very high	2
F1900.102	1072	1	88	32	5	3	0	4
F1900.105	1071	4	89	31	1		22	4
F1901.76	1098	3	62	8	3		very high	2
F1901.83	1100	2	61	7	5	3	very high	4
F1901.116	1087	4	73	8	3	4	0	4
F1901.118	1105	4	55	30	4		very high	5
F1902.82	1094	4	66	34	1	2	very high	4
F1902.211	1098	3	63	11	1	2	27	4
F1902.220	1100	3	60	11	5		32	2
F1904.429.2	1099	3	61	19	4	4	25	4
F1905.217	1098	3	62	6	3		very high	4
F1905.218	1088	2	73	26	5		26	4
F1905.301	1096	2	64	10	1		17	3
F1906.27	1095	3	65	7	5		17	4
F1906.260	1099	2	61	17	1		39	2
F1907.86	1095	2	65	2	2		34	4
F1907.524	1077	4	83	20	3		0	4

Key

FTIR Numbers		Microstructure Numbers		Feet Numbers (for Tea Bowls)		Dating Numbers	
~ 1250 peak	1	Clear glaze	1	Glazed with divot	1	17th century	1
~ 1200 + ~ 1050 peaks	2	White particles	2	Carved with a tool	2	18th century	2
All 3	3	Very degraded	3	Spacer marks	3	18th–19th centuries	3
~ 1250 + ~ 1200	4	Bubbles and particles	4	Stamped/signed	4	19th century	4
~ 1200 only	5	Big bubbles/cloudy	5	Glazed only	5		

TABLE 2
Absorption Peak Locations for Fused Silica and Reference Glasses

<i>Glass Standard</i>	<i>Mass % PbO</i>	<i>Peaks, Fiber-Optic Reflectance</i>	<i>Peaks, Fiber-Optic Reflectance (after Kramers-Kronig)</i>	<i>Peaks, Microscope Transmission</i>
NBS 620	0	1272	1065	1113, 973, 760
Corning C	36	1175	1017	1104, 1001, 934, 974, 753
BGIRA 3	9.8	1241	1035	1135, 988, 780
BGIRA 4	30.4	1207	1015	1134, 983, 779
Quartz	0	1369, 1160	1260, 1160	1164, 1070, 947, 767

glazes with less than 1% PbO: three black raku (F1900.87, F1902.55, and F1899.100), one black on white painted ware (F1907.524), and one possibly misfired red raku (F1900.102).

Quartz showed bands with the fiber-optic probe at 1260 and 1160 cm^{-1} , and in transmission under the microscope at 1164, 1070, 947, and 767 cm^{-1} , while bands for the reference glasses containing lead ranged from 1015 to 1035 cm^{-1} (Table 2). The spectra of the red raku contained peaks at approximately 1200 and 1050 cm^{-1} (Fig. 4). After the Kramers-Kronig correction, the peak locations were 1100 and 1000 cm^{-1} , with occasional peaks seen in the range of 900–950 cm^{-1} (Fig. 5). Comparisons of spectra taken under the microscope in the transmission of quartz and the reference glasses resulted in numbers that were similar to, but not the same as, those derived from Kramers-Kronig-corrected spectra obtained in reflectance with the fiber-optic probe. The bands are given in Table 2. In the spectra of the black-glazed raku wares, in general only a single peak was seen at approximately 1220 cm^{-1} . The peak location was in the range of 1050–1100 cm^{-1} after the Kramers-Kronig correction, and often a shoulder, undetected in the uncorrected spectrum, was visible in the corrected spectrum. A single instance of a peak at 1200 cm^{-1} was seen for a glaze that had single measurements up to approximately 1240 cm^{-1} . Absorption by the inclusions observed in the microstructure may have shifted the peak to higher wave numbers. The variability in the Si-O-Si peak position on a single ceramic is shown in Table 1 as the Si-O-Si range.

Discussion

The results of the XRF analysis include a wide range of lead contents: from almost no lead to 98% lead oxide. It is possible to form glasses with up to approximately 90% PbO (Rabinovich 1976; Nordyke 1984). The standard with the highest lead content used in this study contained only 30% PbO, so these high values were treated as approximations, indicators of lead content much higher than that of the standards. In several of the raku wares examined in this study, the surface appeared iridescent, which could be indicative of corrosion. FTIR spectra, however, did not provide evidence of corrosion. Peaks in the spectra are similar to those of unweathered lead silicate glazes reported previously (Pilz and McCarthy 1995) and do not show the definition in the peaks at 1100 and 1000 cm^{-1} that were seen in weathered lead glazes in that experiment. In modern wares, areas of reduced lead are visible (Raku 1997). A thin surface film of lead could also result in iridescence and explain the very high lead values seen in the XRF analyses. The presence of such a layer, however, has not been confirmed. In addition, some of the high lead values were seen in analyses of red raku wares.

Both XRF and FTIR are surface measurements, but the depth of penetration is not the same in the two techniques, and their use can be complementary. Penetration depths of X-rays in materials depend on their energy, and the effective analysis depth in a lead-silicate glass is low because of the absorption of both incident and fluorescent radiation by the dense matrix. Henderson (2000)

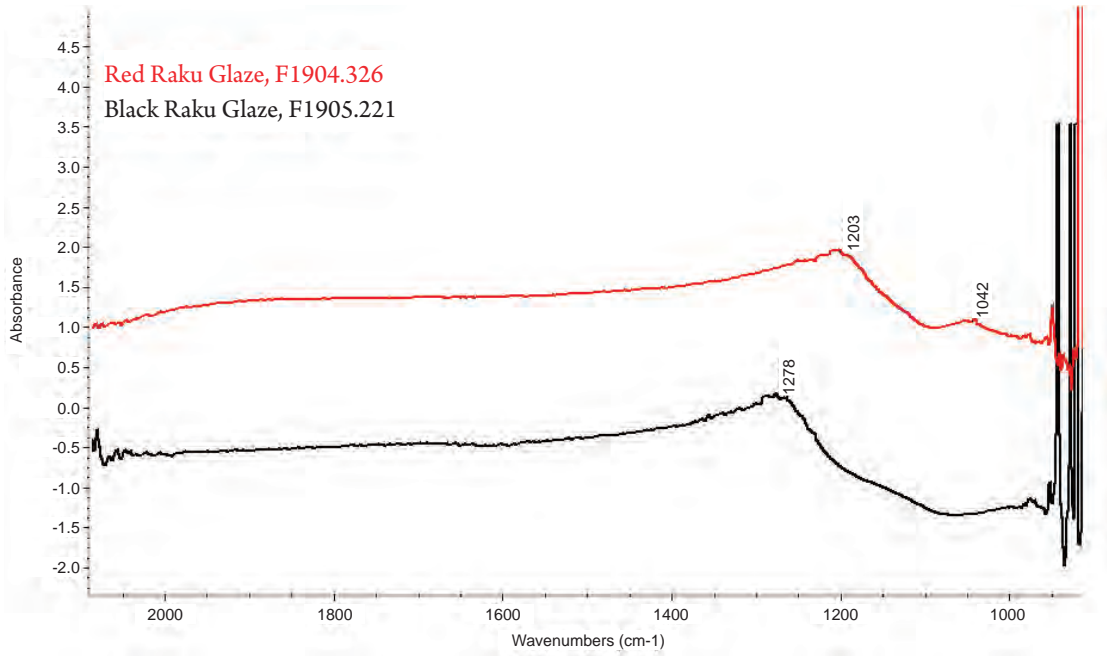


Figure 4
FTIR spectra of red (F1904.326) and black (F1905.221) raku glazes.

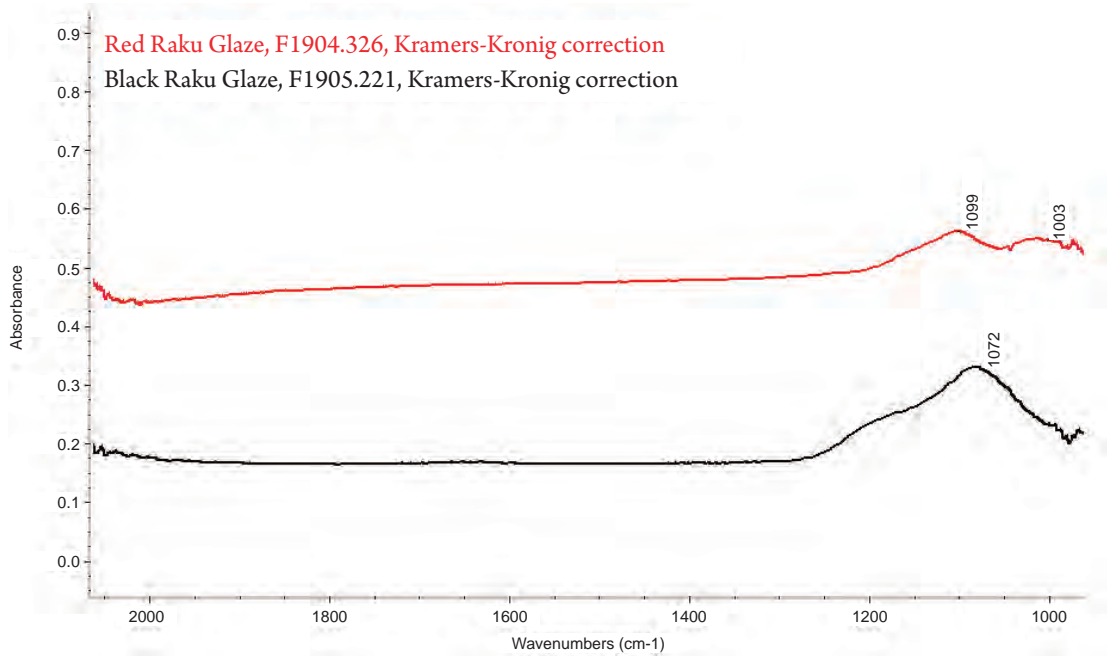


Figure 5
FTIR spectra of red (F1904.326) and black (F1905.221) raku glazes after Kramers-Kronig correction.

cites 15 micrometers as a penetration depth for dense materials; other sources give even lower estimates. Over the range of 50–750 cm^{-1} , Liu (1993) calculated a penetration depth range of 5–50 μm for infrared radiation into a lead glass from the complex dielectric constant; a reasonable estimate for penetration depth in our measurements is in the range of 50–100 μm .

The Kamo River stone that is said to have been used for the black raku is a ferromanganic rock (Wilson 1995) with a composition of 47.88% SiO_2 , 2.33% TiO_2 , 14.12% Al_2O_3 , 14.80% Fe_2O_3 , 0.52% MnO , 7.08% CaO , 4.12% MgO , 1.34% K_2O , and 3.92% Na_2O (Raku 1997, p. 75). The use of such an iron source should result in an iron:manganese ratio of approximately 28:1. In the analyses of black raku wares with more than 1% PbO , the manganese peak did not rise above the level of the background in the XRF analyses. While several of the green glazes included in the “related or possibly misfired wares” were colored by copper, two of the black glazes also had a copper content greater than 1% (F1902.206 and F1901.61, two bowls that are thought to date from the late 19th century and perhaps were made in the same workshop), and three more had approximately 0.5% (F1898.443, F1898.437, and F1900.87). A bright green glazed bowl (F1897.1), attributed to the 19th century, that contained more than 1% CuO had an FTIR spectrum similar in shape and peak position to that of the red raku type.

The FTIR spectra were similar in shape to those for lead glasses in the literature (Liu 1993); however, the peaks were offset and broader. Many of the published spectra for lead glasses focus on binary or ternary systems, and the broad peaks seen in this study may result from the inclusion of other elements in the glass structure.

In reflectance measurements, the spectra are affected by the behavior of the complex refractive index of the sample. Lead silicate glasses have discontinuities in their refractive indexes near absorption edges in the wavelength region studied. The result is Restrahlen bands, derivative-like features, in the spectra. Since the accuracy of the Kramers-Kronig-corrected spectra depend on the range over which they are calculated, the maximum range possible without including noise specific to the chalcogenide fiber used for measurement was chosen.

When analyzed, red raku yields stronger spectra than black raku. This difference derives from the 2–10 times

stronger signal given by red raku surfaces, which is a function of their increased specular reflectance. The FTIR spectra acquired in this study include signals from a combination of specular and diffuse reflection. Which mode of reflection has dominance in a particular spectrum is dictated by the reflectivity of the surface being analyzed. If it is highly reflective, specular reflection will be the dominant mode; if it is not, more diffuse reflection will be detected. Thus, since the black glazes are less reflective than the red and tend to be more matte, their amount of specular reflection is much lower. Both peak position and shape have been shown to depend on the type of reflection (Derrick, Stulik, and Landry 1999), and this is seen in a comparison of the reflectance and transmission spectra of the reference glasses (Table 2). For comparison with the data in this study, it was important to use reference spectra collected with the fiber-optic probe under conditions similar to those used for data collection on the raku glazes.

In the spectra, quartz has a primary Si-O-Si bridging peak at 1160 cm^{-1} . The reference glasses had more bands than quartz because other cations were present (Liu 1993), and at least a second peak appears as a result of the action of the modifier on the silica matrix (Si-O-X or the nonbridging peak). The changes in the structure may also be modeled using structural units based on silicon and oxygen. The locations of the absorptions in a spectrum describe the structural units present. Peak shifts occur from higher to lower wavelengths as the glass structure is disrupted with the addition of modifiers from an undisrupted network, decreasing through sheets, then chains, to SiO_4 tetrahedrons (Zaharescu, Mocioiu, and Andronescu 2008).

For glasses, FTIR peak height and location depend on the amount and type of modifiers as well as the firing temperature. As modifiers are added, the peak decreases in size and shifts to lower wave numbers, and the nonbridging peak grows. With high lead contents, above about 40 mol-% (~ 32 mass %) in a binary system (De Sousa Menezes, Malki, and Echegut 2006), however, lead contributes to both the bridging and nonbridging peaks, and the bridging peak grows in height and shifts to higher wave numbers. In silicates, the frequency of absorption peaks increases with increasing fictive temperature (Agarwal and Tomozawa 1995). For the rapidly cooled black raku

glazes, the fictive temperature should be near the firing temperature. In a study of Roman window glass, Raffaëly and others (2008) found that peak location moved to increased wave numbers with increases in fictive temperature. Thus changes in firing temperature and cooling rate can shift the position of the infrared peaks. However, published shifts of the infrared peak position due to changes in composition are much greater than shifts due to fictive temperature, and as a first approximation, after examining the different types (red, black, and related wares) separately, we ignored the effect of fictive temperature in this study.

The difference between the network (Si-O-Si) peaks for the raku glazes and the peak for quartz was calculated, providing a measure of the amount of disruption of the glass network in the raku glazes. Quartz was used for a reference point, since its peak should not be measurably affected by possible differences in solidification temperatures, compared to structural changes seen in vitreous fused silica because of differences in firing and annealing temperatures.

Black raku glazes showed a general trend of increasing quartz (Si-O-Si) peak difference with increasing lead oxide content, although there was scatter in the results due to the large range of values for each object. Neither red raku glazes nor the related or possibly misfired glazes showed this trend. The values for glazes with PbO greater than 32% had smaller differences than the maximum peak difference values, supporting the role of lead as a network former at these lead oxide levels.

For all of the glazes, no peaks indicative of a crystalline lead compound were seen, supporting the traditional assumption that the lead was added as a glass frit. Tunstall and Amarasiriwardena (2002) found lead bisilicate peak positions, in the range of 1327–1429 cm^{-1} , after firing a lead glaze, showing that evidence of a crystalline lead source can remain in the glaze after firing. Considering the rapid firing used for black raku wares, it is possible that if a crystalline lead source had been used, traces would remain.

Conclusion

XRF data show broad compositional ranges for the raku glazes from the Freer Gallery collection. This is not surprising, given the number of small workshops that are

believed to have produced these wares, most of which are dated to the 18th or 19th century on the basis of style. Glaze compositions include almost no lead, very high lead, and values between these extremes. In addition, wide compositional ranges were seen for single examples of raku ware, indicating chemical heterogeneity within the glaze. Similarly, the range in Si-O-Si peak position also indicates chemical heterogeneity within a single raku ware. This heterogeneity, as well as the large numbers of production sources, makes it difficult to form groups among the objects and to arrive at conclusions regarding kilns and production periods. For nondestructive measurements of heterogeneous raku glazes, one technique is not sufficient for characterization. The use of multiple data types—including information on the shape of the foot, the glaze microstructure, and glaze chemistry, potentially at different surface depths—is a first step toward understanding these wares.

Because of the heterogeneity found in the glaze of a single ware, it is necessary to subcategorize the raku wares into visual types to understand the results of XRF and FTIR analysis. What seems to be an obvious first step—separation by color into black and red raku wares—also has a basis in the technology. The two types are known to have different manufacturing processes, and their data need to be examined separately. Correlation between lead content and FTIR peak position was not seen in the red raku wares, or in the “related or possibly misfired” wares analyzed. For several of the red raku wares, lead contents were found to be much higher than initially expected. Lack of a standard with a high lead content prevented true quantification of these glazes.

For the black raku, the FTIR Si-O-Si peak position could be correlated with the lead content of the glaze determined by XRF, providing two data sets for characterization of the wares from two different depth regions of the glaze. The correlated data sets suggest that, in this case, it may be possible to overcome the variations in data resulting from the heterogeneity within single glazes, allowing categorization of the black raku wares. Re-analysis of the high-lead glazes with additional standards might permit correlation with the FTIR results and further separation of the wares into groupings. However, the low penetration depth of X-rays into the lead glaze makes XRF a near surface technique for lead-glazed wares, and may

prevent it from providing useful data for heterogeneous glazes, such as those found on raku wares. In this case, other techniques, such as UV-VIS or Raman spectroscopy,

may prove more useful. Current work is focused on an attempt to apply statistical methods to better understand the results of the study.

APPENDIX

Standards Used (Mass %)

	SiO ₂	PbO	K ₂ O	Na ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	SnO ₂	MnO	TiO ₂	Li ₂ O	Sb ₂ O ₃
BGIRA 3	58.4	9.84	5.4	7.5	5.75	2.1	1.61	2.95	3	3.1				
BGIRA 4	42	30.4	3.87	5	4.07	1.5	3.58	3.01	3.25	3.02				
BCR 126A	57.8	23.98	10	3.58	1.033	0.512			1.036	1.02			0.495	0.29
Corning A	66.56	0.12	2.87	14.3	5.03	2.66	1	1.09	0.56	0.044	1	0.79	1.17	1.75

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References

Agarwal and Tomozawa 1995

Anand Agarwal and Minoru Tomozawa, "Determination of Fictive Temperature of Soda-Lime Silicate Glass," *Journal of the American Ceramic Society*, v. 78, no. 3, 1995, pp. 827–829.

De Sousa Meneses, Malki, and Echegut 2006

D. De Sousa Meneses, M. Malki, and P. Echegut, "Structure and Lattice Dynamics of Binary Lead Silicate Glasses Investigated by Infrared Spectroscopy," *Journal of Non-Crystalline Solids*, v. 352, no. 8, 2006, pp. 769–776.

Derrick, Stulik, and Landry 1999

Michele R. Derrick, Dusan Stulik, and James M. Landry, *Infrared Spectroscopy in Conservation Science*, Scientific Tools for Conservation, Los Angeles: Getty Conservation Institute, 1999.

Fabri and others 2001

Martha Fabri and others, "Mid-Infrared Fiber-Optics Reflectance Spectroscopy: A Noninvasive Technique for Remote Analysis of Painted Layers. Part I: Technical Setup," *Applied Spectroscopy*, v. 55, no. 4, 2001, pp. 420–427.

Gee, Holland, and McConville 2001

I. A. Gee, D. Holland, and C. F. McConville, "Atomic Environments in Binary Lead Silicate and Ternary Alkali Lead Silicate Glasses," *Physics and Chemistry of Glasses*, v. 42, pt. 6, 2001, pp. 339–348.

Henderson 2000

Julian Henderson, *The Science and Archaeology of Materials: An Investigation of Inorganic Materials*, London and New York: Routledge, 2000.

Lang and Richwine 1993

Patricia L. Lang and Lisa J. Richwine, "The Versatile Sampling Methods of Infrared Microspectroscopy," in *Practical Sampling Techniques for Infrared Analysis*, ed.

- Patricia B. Coleman, Boca Raton, Ann Arbor, London, and Tokyo: CRC Press, 1993, pp. 145–163.
- Liu 1993
Liping Liu, “Infrared Spectroscopy on Lead Silicate Glass,” *Zeitschrift für Physik B Condensed Matter*, v. 90, no. 4, April 1993, pp. 393–399.
- Nordyke 1984
John S. Nordyke, *Lead in the World of Ceramics: Research Review*, Columbus, Ohio: American Ceramic Society, 1984.
- Pilz and McCarthy 1995
Monika Pilz and B. McCarthy, “A Comparative Study of Ormocer®s and Paraloid B 72® for Conservation of Outdoor Glazed Ceramics,” *The Cultural Ceramics Heritage: Proceedings of the IV.ECERS–European Ceramic Society Conference in Riccione, Italy, October 1995*, ed. B. Fabbri, v. 14, 1995, pp. 29–37.
- Pitelka 2001
Morgan Pitelka, “Raku Ceramics: Tradition and Cultural Reproduction in Japanese Tea Practice, 1574–1942,” Ph.D. diss., Princeton University, 2001.
- Pitelka 2005
Morgan Pitelka, *Handmade Culture: Raku Potters, Patrons, and Tea Practitioners in Japan*, Honolulu: University of Hawai‘i Press, 2005.
- Rabinovich 1976
Eliezer M. Rabinovich, “Review Lead in Glasses,” *Journal of Materials Science*, v. 11, 1976, pp. 925–948.
- Raffaëly and others 2008
L. Raffaëly and others, “IR and Raman Spectroscopies: A Way to Understand How the Roman Window Glasses Were Made?” *Journal of Non-Crystalline Solids*, v. 354, no. 2, 2008, pp. 780–786.
- Raku 1997
Kichizaemon XV Raku, “The Techniques of Raku Ware,” in *Raku: A Dynasty of Japanese Ceramists*, ed. Seizo Hayashiya, Taka Akanuma, and Kichizaemon XV Raku, Japan: Raku Museum, Maison de la Culture du Japon à Paris, and The Japan Foundation, 1997, pp. 73–76.
- Tunstall and Amarasiriwardena 2002
Sara Tunstall and Dulasiri Amarasiriwardena, “Characterization of Lead and Lead Leaching Properties of Lead Glazed Ceramics from the Solis Valley, Mexico, Using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT),” *Microchemical Journal*, v. 73, 2002, pp. 335–347.
- Wilson 1995
Richard L. Wilson, *Inside Japanese Ceramics: A Primer of Materials, Techniques, and Traditions*, New York: Weatherhill, 1995.
- Wilson 2001
Richard L. Wilson, *The Potter’s Brush: The Kenzan Style in Japanese Ceramics*, Washington, D.C.: Freer Gallery of Art and Arthur M. Sackler Gallery, Smithsonian Institution, and London: Merrell, 2001.
- Zaharescu, Mocioiu, and Andronescu 2008
M. Zaharescu, O. C. Mocioiu, and C. Andronescu, “Influence of CaO Addition on the Structure and Properties of the Glasses in the SiO₂-PbO-Na₂O System,” *Journal of Optoelectronics and Advanced Materials*, v. 10, pt. 6, June 2008, pp. 1315–1319.

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Cire perdue figure made by Frederick Carder in the 1930s or 1940s, with a repair in which the epoxy is badly yellowed. The Corning Museum of Glass (59.4.426).



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