Technical Appendix: Compositions of Enamels on the George Watch

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Chemical analyses were done of six different enamels from the George watch in the collection of The Metropolitan Museum of Art (acc. no. 17.190.1475) for comparison with other reported Renaissance-period enamel compositions. Analyses using an energy dispersive X-ray spectrometer (EDS) and scanning electron microscope (SEM) were done of four different translucent enamels and of two opaque enamels from the watch’s back cover and dial.

Enamels are made of glass, either produced specifically for the purpose or reused from other objects, which is fused in place onto a metal substrate. Studies of European late medieval and Renaissance enamel compositions have revealed that there was a change in the general compositions of the glass used for enameling beginning about the early fourteenth century, apparently in connection with the rise in the use of translucent enamels on gold and silver substrates. Most known enamels dating from the thirteenth and early fourteenth centuries have been found to have soda-glass compositions (a glass mixture with soda [sodium oxide] as the dominant alkali) containing relatively large amounts of potassium, magnesium, and calcium oxides. However, beginning about the early fourteenth century and continuing into the fifteenth, most of the translucent enamels analyzed can be characterized as having mixed-alkali compositions, that is, compositions with relatively high levels of both sodium and potassium. These mixed-alkali glasses are usually associated with rather low levels of aluminum, magnesium, and calcium. Magnesium and calcium serve as the main stabilizing agents for glass compositions, and the extremely low levels of these elements in many mixed-alkali enamel compositions can account for the poor condition of many enamels from this period. Little or no lead is generally found in these enamels, except for the opaque enamels, where it is associated with the addition of crystalline tin oxide as a white opacifying agent, or in opaque yellow and green enamels, where it is associated with a yellow colorant/opacifier such as lead-tin yellow. Most mixed-alkali enamels from the fourteenth and fifteenth centuries were found to have a sodium-to-potassium ratio of approximately one-to-one, or else to contain an excess of potassium over sodium. By the end of the fifteenth century, however, some enamels were beginning to be used that contained much more sodium than potassium. These enamels may be more accurately described as having soda-glass compositions with relatively large amounts of potassium, rather than being mixed-alkali. Like most of the enamels from the fourteenth and fifteenth centuries, these soda-glass enamels continued to have relatively low levels of aluminum, magnesium, and calcium. Some differences are seen between the red enamels and most other translucent enamels. In red enamels, the use of mixed-alkali compositions with relatively more potassium than sodium apparently persisted well into the sixteenth century or possibly even the seventeenth. And red enamels, unlike most translucent enamels from this period, also often contain relatively high levels of magnesium and calcium. (Unpublished analyses performed at The Metropolitan Museum of Art of fifteenth-sixteenth-century northern Italian enameled copper vessels and Limoges sixteenth-century painted enamel plaques show that at least some translucent enamels from this period also have relatively high levels of magnesium and calcium, although mostly on copper substrates rather than gold or silver.) These types of enamels appear to have been in use throughout the Renaissance period and may have continued in use until as late as the early nineteenth century. Enamels dated to the second half of the nineteenth century and later, including some attributed to the Vasters and Castellani workshops, have been found to have decidedly different compositions, usually lead-potash or lead-alkali compositions, with some different colorants and opacifiers than those found in earlier compositions.

Four translucent enamels from the George watch were examined. Quantative analyses, reported in Table 1, were performed on samples of the green, blue, and red enamels from the back cover. Non-destructive surface analyses were done on the yellow as well as on the
opaque white and green from the watch dial (only enamels with some previous loss or damage were sampled to avoid compromising undamaged surfaces). Because of various problems inherent in surface analysis, this type of analysis can only provide approximate, semi-quantitative results, which are reported in Table 2. The translucent green, blue, and yellow enamels were found to have soda-glass compositions with relatively large amounts of potassium and low levels (approximately one percent or less) of magnesium, calcium, and aluminum oxides. The blue enamel was noted as exhibiting a greater degree of decomposition than the other colors, especially the red. This is not surprising in light of the enamel compositions. The total amount of the stabilizing elements magnesium and calcium was found to be less than one percent by weight in the blue, whereas in an average stable glass it is usually about five to ten percent. While the green and yellow enamels also have low percentages of these elements, they contain large amounts of iron oxide, which can help to improve the chemical resistance of glass.

The green enamel was found to be colored with large amounts of both copper and iron oxides, while the yellow contained a very large amount of iron. The inclusion of large amounts of metallic colorants has been documented for many other translucent enamel compositions. These large amounts of colorants were apparently required to achieve the desired hue of the thin translucent layers over the metal. The dark blue translucent enamel was found to contain a relatively large amount of cobalt oxide. Cobalt is a rather strong colorant, and cobalt blue glass is generally found to contain no more than about two tenths of one percent of cobalt oxide, while the enamel tested was found to contain three times this amount. Small amounts of nickel, arsenic, and bismuth were also found in this enamel. These elements, especially bismuth, are relatively rare in glass compositions and appear to be associated with the origin of the cobalt ore used to make this enamel. Cobalt-containing glass and enamels from the thirteenth, fourteenth, and fifteenth centuries are usually found to contain small amounts of zinc, apparently from the use of a Syrian cobalt ore source rich in zinc. The fifteenth century saw the widespread reliance on European cobalt ore sources, such as those from Saxony which yielded nickel-, arsenic-, and bismuth-rich ores, for the production of glass, enamel, and the pigment smalt.
The red enamel, unlike the other translucent colors, was found to have a mixed-alkali composition with somewhat more potassium than sodium and relatively high levels of magnesium and calcium. The colorant in this enamel is a reduced form of copper oxide. A trace amount of tin oxide was also noted in this enamel. Traces of tin and lead are often associated with red glass and enamel, as they apparently act as reducing agents and help to raise the solubility of the copper oxide.

Surface analyses were also done of two opaque enamels, a white and a green. An obvious difference between these enamels and the translucent ones is that these were found to contain large amounts of lead oxide. The white enamel also contains a large amount of crystalline tin oxide, a white colorant and opacifier. Lead oxide is almost always associated with tin oxide in glasses, as it was apparently added to help the conversion of metallic tin to tin oxide. White enamels opacified with tin oxide were used at least as early as the end of the twelfth century, although generally with much smaller amounts of tin and an excess of lead to tin. White enamels from the fifteenth century and later, however, have been found to contain much higher percentages of tin, many more than twenty percent by weight, usually with an approximately one-to-one ratio of lead oxide to tin. The opaque green enamel was also found to contain tin. Analyses of some of the opacifying crystals in the enamel revealed that most if not all of the tin is present in the form of lead-tin yellow, rather than white tin oxide. Other Renaissance opaque yellow and green enamels have been found that contain either lead-tin yellow alone or a mixture of lead-tin yellow and lead antimonate yellow crystals. The green color in this enamel was achieved by the addition of some copper oxide, which by itself produces a blue or turquoise color, to yellow enamel.

Although the information currently available on Renaissance enamel compositions is somewhat sparse, all of the enamels examined from the George watch were found to be entirely consistent in composition with what is known about enamels dating from the late fifteenth to the seventeenth centuries. Unfortunately, based on current research, there appear to be few, if any, compositional criteria for distinguishing between Renaissance period enamels and enamels dating from the eighteenth or early nineteenth century. Ongoing research at the Metropolitan Museum and elsewhere will help to shed more light on the different enamel compositions of these periods.

NOTES


4. The enamels were analyzed using energy dispersive X-ray spectrometry. The three enamel samples were taken by flaking off very small pieces, on the order of a cubic millimeter in size or less, with the use of a steel scalpel. The samples were prepared for analysis by embedding them in epoxy or polyester resin and grinding with silicon carbide paper to expose the sample interiors. The cross sections were then polished with cerium oxide and given a high-vacuum carbon coating for conductivity before analysis. Weight percentages of the elements detected were calculated against well-characterized reference glasses. For EDS analysis of glasses, the relative variation in the calculated percentages for the major element oxides has been determined to be less than two percent for silicon, about five percent for sodium, potassium, and calcium, and about ten percent for magnesium, aluminum, and the metals such as copper, manganese, and iron. The minimum detection limits for the elements titanium to zinc were found to be under one tenth of one percent. The minimum detection limits for phosphorus, lead, barium, arsenic, antimony, and tin oxides, however, were found to be much higher, about one half of a percent by weight, mainly due to peak overlap problems. For details, see M. Verità, R. Basso, M. T. Wypyski, and R. J. Koestler, "X-Ray Microanalysis of Ancient Glassy Materials: A Comparative Study of Wavelength Dispersive and Energy Dispersive Techniques," *Archaeometry* 36, no. 2 (1994), pp. 241–51.
