LUSTER DECORATIONS are thin metallic films applied to the surfaces of ceramic objects. Since its beginnings, possibly as early as the fourth century A.D., but certainly by the ninth century, the technique of film application has seen frequent use down to the present day. In different times and at different places it has been used to produce a wide variety of colors and appearances, ranging from highly reflecting mirrorlike surfaces to faintly perceptible iridescences. Numerous kinds of colored stains and glazes have often accompanied luster effects and in some cases have so enhanced the ornamentation that these stains and glazes themselves have come to be termed “lusters” even though metallic films may not be present.

Because lusterware varies so much in style and are broadly distributed geographically—and even more so because of the somewhat complicated technologies involved in making them—there must be many cases where analysis and examination of ancient fragments would be of use to those concerned with medieval studies. The historical spread of the technique has been much discussed by art historians, and both the technology and matters of stylistic identification are usually treated as being well understood. Such may very well be the case. Laboratory studies of sufficiently large numbers of representative wares, however, would undoubtedly prove very worthwhile either for verifying the existing theories or for answering questions about problematical pieces. Analysis of the luster glazes themselves and analysis, X-ray diffraction, and petrographic examination of the fabrics would all probably be helpful.1

1 In preparing for this study, a literature search indicated that few, if any, analyses had been made of luster decoration on glass and only a few of pottery of Islamic origin. However, realizing that analyses or studies of this sort might well have been published in places familiar only to Islamic scholars, the accompanying bibliography should not be relied upon as being complete. One analytical study

The scope of the present paper, however, is not intended to be so all­
encompassing. The work described here has been confined to one very
limited aspect of luster decoration. The main objective has been to see
what could be learned about one specific group of luster glass fragments.

There are four significant lines of glass research which converge on the
group of fragments studied here. In the first place, the glasses were most
likely made in the Islamic glass factories at Fustat, near present-day
Cairo. Therefore, the analysis of the glasses themselves should be fitted
into the systematic cataloging of compositions of ancient glasses that are
being developed. Future analysis of groups of luster glasses (and their
gages) from different parts of the Islamic world might well show com­
positional differences that could be helpful in characterizing the wares
made at different factories.

Even a casual examination of the most common type of luster decora­
tion on Islamic glass, a deep transparent amber stain, suggests that it is a
silver stain. Thus Islamic luster glass can be considered to form a histori­
ical link connecting the earliest known use of silver and/or gold in ancient
glass, for coloring a small group of Late Roman dichroic glasses, with
the use of silver for making the yellow-stained glasses of the cathedral
windows of Western Europe.

The chemical formulation of the Islamic luster glazes also is of some
interest from the viewpoint of the history of chemistry, for there is at
least one extant recipe for luster glazes for pottery in the early Persian

appears in an appendix to F. Sarre, *Die Ausgrabungen von Samarra, Band II*
(Berlin), pp. 95–100. Also a series of early papers were presented by L. Franchet,
who concerned himself with the technology of Islamic luster glazes. See, for example,
(1906), 37, 227; *Trans. Brit. Ceramic Soc.*, vol. 7 (1907), 71.

The most noteworthy of these is that being compiled by E. V. Sayre and R. W.
Smith. See, for example, E. V. Sayre and R. W. Smith “Compositional Categories of
Glass Specimens with Compositions of Particular Archaeological Significance,”
(BNL-879 T-354) Brookhaven National Laboratories (July 1964). Other large,
whole bodies of analytical data are being compiled by M. A. Besborodov in Leningrad
and by the author at The Corning Museum of Glass. Analyses up to 1957 have been
tabulated and reinterpreted by Earle R. Caley in his *Analyses of Ancient Glasses,

Commission on Glass.
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literature, and others are known from Hispano-Moresque and Italian sources.

The fourth line of research is of a fundamental chemical nature, and deals with the broad question of the nature of the colorants used in ancient red, orange, and yellow opaque glasses. Two of the types of luster studied here are red opaque and yellow opaque stains.

In the sections that follow we shall review the history of luster decoration, describe the samples studied, record the results of several types of experiments, and interpret the experimental results in terms of the lines of research indicated above.

It must be added that these results can only be considered provisional, because experimental work is still in process as this paper is being prepared.

The History of Luster Decoration

Although the topic has been much discussed, leading authorities do not agree upon either the place or date of the origin of luster decoration. Indeed the discussion has at times become so lively that one not well versed in all the arguments hesitates to comment even casually upon the question. The most favored authoritative dates range from the eighth-ninth century back to as early as the fourth-fifth century A.D., and the favored places of origin seem to be Egypt, Persia, and Mesopotamia.4

Although questions of origin are sometimes finally relegated to unimportance, it does seem that in this case the question could ultimately be of considerable importance in the history of glass—even if not so in ceramics. The question is sharpened by the viewpoint of Lamm that the technique of luster decoration originated with the “glass painters of Egypt.” It would be of value to determine the place and date of origin of such a readily recognizable decoration, because this could perhaps be of help in

telling us to just what extent glass craftsmen did move around in ancient times, and more importantly it might help to clarify our pictures of the ways in which the ancient and indigenous glass industries of the Near East developed into those of the Islamic Period.

We might observe here that the recent discovery at Fustat of the earliest known dated piece of luster glass, a beaker bearing the date of 771-772,5 lends some support to the view that the technique originated with the glass painters of Egypt.

There were several well-known centers producing luster-decorated pottery, and possibly glass, during the Islamic Period. Some of these were Baghdad and Basra in Iraq, Kashan in Persia, and Fustat in Egypt. The art spread westward via North Africa, and inspired the famous Hispano-Moresque ceramics which reached an artistic peak in the fifteenth century, and to Majorca and Italy where it was incorporated into majolica ware.

**Description of Samples**

This research was prompted by a group of Islamic luster glass fragments in the collection of The Corning Museum of Glass. Unfortunately, the exact provenience cannot be rigorously proved, but since the fragments were obtained in Cairo, and since they are very similar to types of luster glass excavated at Fustat in great quantities, we believe it is reasonable to assume that they either were made in the factories known to have existed in Fustat, or at least that they came from the extensive rubbish heaps there. Thirty samples were selected for analysis from a group of approximately 700 fragments, and numerous others were examined.

There are three distinct types of glass represented. The first, the most common type of Islamic luster glass, bears a deep amber transparent stain on transparent base glasses which are either very well decolorized, or tinged with the characteristic aqua or pale greenish colors produced by iron (figs. 1, 2).

The second type is a dense yellow-orange opaque stain on either a dark blue transparent base glass or, more rarely, on a greenish glass slightly stronger in color than the aqua mentioned above (fig. 3). It should be noted that this yellow color is definitely due to a stain, that is, the color results from a fine dispersion of colorant particles beneath the surface of

5 George T. Scanlon, “Fustat, 1965,” *Newsletter*, no. 54 (June 1965), 3–6, American Research Center in Cairo.
None of the glasses used in this study has the structure of enameled glasses, where a distinct and separate body of decorative material stands raised in relief above the surface of the glass. The third type is a bright red opaque (or translucent) stain on a deep olive-colored transparent base glass (fig. 4).

Stains fitting this description have been termed “fused-in enamels,” but this is a very misleading description and is actually inconsistent with the definition of enamels. This becomes apparent, however, only after one is familiar with the chemical nature of the staining process.

Fig. 3. Fragments of blown-glass vessels, yellow opaque stain on dark blue transparent glass, 9th century, probably found at Fustat. Similar to samples 1022-1025.

Fig. 4. Fragment of blown glass vessel, bright red opaque stain on transparent olive glass, 9th century, probably found at Fustat. Similar to samples 1027-1029.
Although these descriptions have been stated in terms of pure colors, the yellow and red stains sometimes show a mottled effect containing other colors, as well as superimposed decorations in amber. On the amber-stained fragments milky halations often outline the painted designs. The fragments selected for analysis were examples of the purer, more saturated colors, free of the transient color effects, and showing no macroscopic weathering.

It is notable that only a small proportion of the fragments in the total collection actually show a distinct metallic luster. The color effects by far dominate the luster effects in the decorative motifs. Thus the use of the term "luster" in describing these glasses might be questioned. It is likely, however, that the surface appearances of these glasses could have been much more lustrous or metallic when they were new, because a loss of luster through volatilization could well have occurred over the centuries. Only about 15 percent of the fragments now show a distinct luster, in some cases mirrorlike but in most cases only ephemeral. In view of this, and because of chemical evidence presented in a latter section, we shall refer to the decorations on these glasses as stained regions rather than luster regions, keeping in mind, however, that they are commonly called luster decorations in the archaeological and historical literature.

On the basis of stylistic considerations, Richard Ettinghausen is of the opinion that the amber-stained fragments analyzed here date from the tenth to the eleventh centuries, with the decolorized base glass possibly being somewhat later than the greenish glass. He feels that the yellow- and red-stained fragments, again based on stylistic considerations, are earlier, dating probably from the ninth century or possibly the very early tenth century. Axel von Saldern, who originally cataloged these fragments, shares these views.

The fragments are all of blown vessels, with thicknesses ranging from about 1 mm up to as great as 4 mm. Rims, bases, and wall fragments are all represented. The exact shapes of the vessels have not yet been reconstructed but it is expected that they are the usual cups, beakers, bowls, and small pitchers.

A detailed catalog of the samples studied is appended at the end of this text (appendix 1, p. 375).

As supporting experiments we have also analyzed the luster glazes on four pieces of Hispano-Moresque wares, which were very kindly provided

7 Professor, Institute of Fine Arts, New York University.
8 Curator, Kunstmuseum, Düsseldorf, Germany.
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by Miss Maria Manuela de Iliveira, and a piece of seventeenth-century stained glass from Nürnberg, supplied by A. G. Frenzel.

Microscopic Examination

Microscopic examinations of many examples from this group of fragments established two important facts. The first is that the colorants within the stained regions lie beneath the surface of the glasses themselves. The colored regions do not in any case protrude or stand in relief above the surface of the base glass, as do enamel decorations. Neither could they be applied to glass which was marvered in. These stains are an entirely different class of decorations than enamels or marvered-in threads. The color of the stained zones seems for the most part not to extend much beyond a depth of 20 microns (0.02 mm) below the surface. In the case of the yellow stain, the color can be seen to be due to a dispersion of fine particles appearing to have a yellow color individually. At the highest magnification available (400X) the shapes of the particles could not be resolved, but they seemed to be approximately regular and of uniform size. The largest measure about 0.3 micron across.

The red stains were found to be due similarly to a fine dispersion of particles, again apparently of regular shapes, with the largest measuring about 0.3 micron across. These grains, however, show distinct metallic reflections. The color-producing particles are usually below a zone of transparent glass which lies just adjacent to the surface of the glass. The occasional small bubbles trapped in the colored zones are spherically shaped. Sometimes they are associated with devitrification crystals, an indication that the glass was reheated after forming, and are surrounded by zones of transparent glass. These transparent zones are undoubtedly localized zones of oxidized glass.

Representative specimens of the red and yellow glasses have been examined by Edward Korda and Raymond Fritz, both of Corning Glass Works, using a scanning electron microscope. These studies have not yet been completed, but we hope to determine more accurately just what are the shapes and dimensions of the colorant particles in each type of glass.

Chemical Analysis

Four types of chemical analysis were carried out on the selected fragments. First, X-ray emission analyses were made of masked-off stained

9 Curator, Fundação Calouste Gubennkian, Oeiras, Portugal.
regions on the fragments. This technique is well suited for this type of analysis, because the primary exciting X-radiation does not penetrate more than about 50 microns (0.05 mm) beneath the surface of the sample being analyzed. Thus the analysis obtained is essentially that of the stained surface regions rather than of the unaltered base glass below. Two independent sets of analyses were made of these stains. The first was made by Charles A. Jedlicka of Lucius Pitkin Laboratories in New York City, using a Norelco X-ray spectrograph with a tungsten target and LiF crystal. The second was by Donald Stephenson and Mrs. Dorothy Kimble of Corning Glass Works. They used a General Electric X-ray spectrograph, model XRD-6, with a chromium target and LiF and EDDT crystals. The results were only qualitative, because it would be very difficult to express the concentrations in quantitative terms. Actually, since there is obviously a variation in the compositions of the lusters, quantitative results would not be particularly more helpful anyway. A few complete scans have been made, but in most cases only partial scans were made, because we were interested primarily in establishing the presence or absence of specific elements. The effective applicability of X-ray emission analysis under the conditions used was limited to atomic numbers greater than 16, that is, to sulfur and the elements following it in the periodic table.

Before the X-ray emission analyses were carried out, Jedlicka had removed parts of the stained regions and made emission spectrographic analyses of the stains. These samples consisted of mixtures of both stained and some unstained glass, but by comparison with spectrographic analyses of the base glasses beneath the stain it was possible to determine by this independent method the principal constituents of the colorants in the stained regions. These results are summarized, along with those from the X-ray emission analyses, in table 1.

Following the analyses of the stained regions, samples were removed from the unstained regions of the same fragments and semiquantitative spectrographic analyses were made of the base glasses. These samples were analyzed with four reference glasses used routinely in our analyses.

Actually, because of their high concentrations aluminum and silicon could also be seen.

These reference glasses are the same as those being used in an international analytical round robin. They are described in “Interlaboratory Comparison Experiments on the Analysis of Ancient Glass,” paper no. 226, Comptes Rendus, II, VIIth International Congress on Glass, Brussels (1965), International Commission on Glass.
Samples of the same fragments were then analyzed by flame photometry to obtain quantitative values for Na$_2$O, K$_2$O, and CaO and MgO. Combined results of the spectrographic and flame photometric analyses of the base glasses are given in table 2. The samples there are grouped according to the colors of the base glasses and/or the types of their stained decorations.

From the analyses in table 1, it is apparent that the main constituents of all three colors of stain are silver and copper. In the eleven amber stains analyzed, silver and copper were present in about the same concentrations. Among the yellow opaque and red opaque stains there was more copper than silver in some examples, and about the same amount in others. The luster stains on the four pieces of pottery analyzed were very rich in copper but no silver was detected. 12

The minor and trace components are variable from piece to piece even among samples of the same color type. As a result, we plan more systematic and comprehensive analyses of all of these stains. The most common occurrences are tin and lead. The presence of tin is known to be beneficial for the developing of copper-red stains 13 and it could well have been so in this instance. This cannot be taken as proof, however, that the craftsmen were necessarily aware of the fact that tin has this beneficial effect, because tin would have been introduced accidentally if the original source of copper in their formulations were bronze rather than copper or copper minerals. The copper–tin ratio seems to be consistent with this explanation in the cases where we could estimate it.

12 The pottery glazes themselves were found to be essentially tin glazes containing also lead, zinc, calcium, potassium, iron, and titanium. Some also showed arsenic and were colored with cobalt.
13 For an excellent survey of the chemistry of color in glasses, as well as a very comprehensive bibliography on the subject, see W. A. Weyl, Coloured Glasses, (London: Dawson’s, 1959).
### Table 2

Analyses of Base Glasses

<table>
<thead>
<tr>
<th></th>
<th>Colorless, amber (4)</th>
<th>Pale green, amber (4)</th>
<th>Aqua, amber (3)</th>
<th>Dark blue, yellow (4)</th>
<th>Olive, red (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>64</td>
<td>64</td>
<td>58</td>
<td>61</td>
<td>59</td>
</tr>
<tr>
<td>Na₂O</td>
<td>17-20</td>
<td>17-20</td>
<td>17-20</td>
<td>17-20</td>
<td>17-20</td>
</tr>
<tr>
<td>CaO</td>
<td>7.5</td>
<td>7-8</td>
<td>12-15</td>
<td>12-15</td>
<td>9.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.8</td>
<td>4</td>
<td>1.2</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>MgO</td>
<td>2.6</td>
<td>2.5</td>
<td>1.0</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.6</td>
<td>2.2</td>
<td>2.2</td>
<td>3.0</td>
<td>7-9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.42</td>
<td>0.45</td>
<td>0.75</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.07</td>
<td>0.09</td>
<td>0.27</td>
<td>0.25</td>
<td>0.40</td>
</tr>
<tr>
<td>CuO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.1-0.4</td>
<td>—</td>
</tr>
<tr>
<td>CoO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.09</td>
<td>—</td>
</tr>
<tr>
<td>PbO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.01-0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>BaO</td>
<td>0.05</td>
<td>0.07</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>SrO</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>ZrO₂</td>
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<td>—</td>
<td>0.01</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>MnO</td>
<td>0.9</td>
<td>0.7</td>
<td>0.1-0.4</td>
<td>0.8</td>
<td>0.25</td>
</tr>
</tbody>
</table>

*At the time of publication the results of our quantitative analyses were not yet available. Therefore, the results presented in this table are composite spectrographic and X-ray emission analyses of each type of glass. The samples are described by the colors of the base glasses and stains. Numbers in parentheses are the number of analyses of each type.

A fuller investigation of the other minor-trace elements, such as gold, mercury, arsenic, and sulfur (seen only in our X-ray emission analyses and not spectrographically), might shed some light on the formulations of the stains. We might anticipate learning whether or not gold played a part in the process, whether realgar and orpiment were used, to what extent sulfur or sulfates were present, and whether the silver was introduced as an amalgam.

From the analyses of the base glasses in table 2, it can be seen that the glasses themselves are of the expected soda-lime-silica type, with the usual impurities such as K₂O, MgO, Al₂O₃, and Fe₂O₃.¹⁴

There are four noteworthy features. For the most part the K\textsubscript{2}O and MgO contents are on the order of 2–4 percent, which places them in the high K\textsubscript{2}O–high MgO type of glasses in Sayre’s system of classification.\textsuperscript{15} This is quite reasonable because of the suggested Fustat provenience. (The low K\textsubscript{2}O–low MgO type contains on the order of tenths of 1 percent of each.) These classifications are at present more applicable to earlier glasses, because relatively few examples of glasses of this late date have as yet been analyzed. Sayre has found among some Islamic weights he analyzed (15 samples) and some Islamic luster glasses (6 samples of unspecified dates) that there is about an equal division among high and low K\textsubscript{2}O–MgO types.\textsuperscript{16} Thus, along with our own results, one might see considerable promise that analysis of the base glasses might some day serve to differentiate between luster glasses from different regions and dates of origin.

A second characteristic is that the glasses have been decolorized with manganese. That manganese has been used is consistent with earlier analyses. The only exceptions are those three fragments that show the strongest greenish color. This provides an excellent example of how efficient ancient glassmakers were in their decolorizing processes. The group of eight glasses cataloged as colorless and very pale green do contain an appreciable amount of iron—about 0.45 percent. Without a decolorizer this much iron would yield a distinct green color.

A third observation is that the blue base glass is colored primarily by cobalt, and although cobalt had already been used by glassmakers for some twenty-three centuries, it usually was accompanied by more copper than is present in these glasses. This clearly indicates that a ready source of cobalt was at hand and that it was freely used, since it did not have to be adulterated with copper. One would have expected it to be adulterated if the blue glass had been made, for example, in Persia, instead of Egypt. Perhaps the most interesting result of these analyses is that the glasses bearing the yellow and red stains appear to have distinctly different base compositions from the “colorless” glasses. In the first place, the MgO values are considerably higher—up to about 5 percent—and the Al\textsubscript{2}O\textsubscript{3} in the red glass is very high, being estimated to be 7 and 9 percent. The

\textsuperscript{15} See n. 2.

number of glasses analyzed is small and one cannot therefore be com-
pletely certain yet that the results are significant, but the indication is that
the red-stained glass, and possibly the yellows, are of different origin than
the ordinary amber-stained glasses. We already suspect them of being of
earlier date but the alumina-rich composition puts one more in mind of
the glasses made in more northerly regions, for example, the region of the
Caspian Sea. This provides further encouragement for making a more
comprehensive analytical study of luster glasses. There is some reason to
believe, too, that the alumina-rich base glass might be more receptive to
copper staining.

X-Ray Diffraction

X-Ray diffraction patterns were obtained for samples representing the
three basic colors of stains. The determinations, which were made by Hans
Holland and John Geiger of Corning Glass Works, are summarized in
table 3, and the results are easily understood when compared to the
chemical analysis and observed color effects.

The amber stain is caused by colloidal particles of metallic silver. The
red stains are due to metallic copper, in one instance covered over with an
observable silver stain having a blue turbid color. The yellow-orange stains
were found to contain only Cu₂O. As explained below, the association of
a yellow color with Cu₂O, instead of its familiar red color, is probably a
particle-size effect.

Reheating Experiments

Samples of the three colors of stained glass were reheated under two
different conditions. When the base glass is heated in an oxidizing flame
just sufficiently to soften and round off the sharp edges, the color of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color</th>
<th>Phases detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>1018</td>
<td>Amber</td>
<td>AgO</td>
</tr>
<tr>
<td>1022</td>
<td>Yellow-orange</td>
<td>Cu₂O (Poss. trace AgO)</td>
</tr>
<tr>
<td>1022</td>
<td>Amber over yellow</td>
<td>Cu₂O, AgO</td>
</tr>
<tr>
<td>1024</td>
<td>Yellow-orange</td>
<td>Cu₂O, trace CuO</td>
</tr>
<tr>
<td>1027</td>
<td>Red</td>
<td>CuO</td>
</tr>
<tr>
<td>1029</td>
<td>Red</td>
<td>CuO, AgO</td>
</tr>
</tbody>
</table>
yellow and red stains disappears as the grains of the colorants go into solution. With reducing conditions the yellow is converted to a red color. Under magnification this red color can be seen to be associated with particles that appear identical to those in the red-stained glasses. In all cases, including the amber transparent stains, a film forms on the surface which shows a metallic luster or multicolored effects that resemble metal-oxide coatings. Upon more prolonged heating (1 hr at 600°C) in a closed container, the amber stain is deepened in its transmitted color, and shows a greenish yellow reflected color, due to light scattering. The yellow opaque stains tend to darken slowly upon longer heating at 600°C, but after 20 hours the yellow color disappears entirely. All the glasses blister somewhat in the stained regions upon reheating, apparently due to the evolution of dissolved gases from the stained zones.

**Fluorescence**

Under shortwave ultraviolet irradiation (2537Å), approximately two-thirds of the amber-stained glasses show a lemon-yellow fluorescence (fig. 5). In about half of these cases the fluorescence is very strong, in other cases it is only moderate, but still considerably more pronounced than the usual fluorescences of ancient glasses. The fluorescence appears only on the sides of the fragments that have stained decorations, and is much weaker under longwave (3660Å) ultraviolet. The yellow fluores-

![Fig. 5. Fragment of luster glass similar to that in figure 2, but photographed under shortwave ultraviolet irradiation. Bright regions record the lemon-yellow fluorescence from the unstained regions between the stained decorations, which do not themselves fluoresce. Stray visible light and ultraviolet filtered out. (15 min. exp., f/3.5, Plus X film.)](http://www.cmog.org)
Fluorescence is also qualitatively different from the colors usually seen and is certainly due to the presence of colloidal silver. It is very striking, however, that there is no fluorescence in the amber-stained regions themselves, although the milky halation zones outlining the amber regions do fluoresce.

It is a little puzzling why the fluorescence should be so prominent in the unstained regions of the stained surfaces. Apparently, volatilization during the firing process led to the deposition of very finely divided silver in the regions between the painted designs. The bright fluorescence there must be due more to the fine subdivision of the silver rather than to the

Fig. 6. Transmission spectra of two Islamic luster fragments similar to those in figures 1 and 2, compared to known silver-stained glass.
amount of silver present. There is much more silver present in the painted regions, but the fluorescence efficiency is much diminished because of the larger particle sizes and possibly also because the presence of copper there quenches the fluorescence.

The yellow- and red-stained glasses show no fluorescence.

Transmission and Reflectance Spectra

Transmission and reflectance spectra of the stained regions were obtained by Roland French of Corning Glass Works. These are reproduced in figures 6, 7, and 8, along with curves representative of some glasses from other periods.

In figure 6, curves $I_1$ and $I_2$ show the transmission spectra of two amber stains on the Islamic fragments. Both were run against the unstained portion of the same fragments as references, thus compensating for the aqua color of the base glasses themselves. These spectra, therefore, are of only the stain coloration. Curve $N_1$ is for the bright lemon-yellow-stained portion of the seventeenth-century Nürnberg window which on analysis for silver showed only a trace of copper. Curve $N_2$ is for an orange-stained region from the same window which contains a considerable amount of copper, as well as silver. Qualitatively, the transmissions of the two Islamic amber stains look more like the orange glass $N_2$ than the pure silver stain having curve $N_1$. The two stains must have something in common to give them similar colors and the analysis suggests that it may be the presence of copper.

Figure 7 shows reflectance spectra for one of the Islamic yellow-stained fragments (curve $YO$), and for one of the Islamic red-stained fragments (curve $RO_1$). It is believed that the rather sharp cutoff in reflectance at about 600 millimicrons, for the yellow stain, is characteristic of the color of cuprous oxide, the phase known to be present from X-ray diffraction. This is confirmed by the reflectances of two experimental glasses, also known to be colored by Cu$_2$O, which are shown in figure 8. These are two samples of the same glass given different heat treatments which, in turn, produced different colors. (This is another reason for our belief that the color of Cu$_2$O-containing glasses is dependent upon the particle sizes.) The same sharp cutoff is found on these curves, as in the yellow-stained Islamic glass.

On the other hand, the reflectance of the red-stained Islamic glass ($RO_2$ in figure 7) has a qualitatively different shape than the red Cu$_2$O-containing glass. It is known to be colored by a dispersion of metallic copper crystals, as was shown by X-ray diffraction.
Fig. 7. Reflectance spectra of yellow-opaque stained region of luster glass fragment similar to those in figure 3, and red-stained region of fragment similar to that in Figure 4.

Duplication Experiments

There are at least two, and possibly more, recipes given in the early literature for luster glazes to be applied to pottery. ¹⁷ We have selected one as a starting point for some experiments to duplicate the luster effects observed on our Islamic fragments. Of course, there is no reason to believe that the recipe we have selected should necessarily correspond to that used

by the craftsmen who decorated the pieces we happened to analyze. Nevertheless, one can hardly resist the temptation to guess at the chemicals referred to in the recipe and follow out the directions to see what will happen.¹⁸

¹⁸ We are probably not the first to have yielded to such a temptation. From the discussions of Franchet, it appears that he made some experiments as did probably the workers mentioned in n. 19.
The recipe to which we refer was recorded by Abdallah Ibn Ali Al-Kashani at Tabriz, in 1300–1301. He was one of a family of famous potters then producing luster pottery in Kashan. The recipes were part of a text translated and interpreted in 1935 by H. Ritter, J. Ruska, F. Sarre, and R. Winderlich. While this recipe was specified for luster decoration of pottery, the text does refer elsewhere to transparent wares.

The author is very much indebted to Martin Levey, a noted historian of chemistry, who retranslated the recipe from the Persian and made valuable suggestions as to the identifications of some of the chemicals involved. In general Levey’s translation agreed with that cited above, but he pointed out that the German version is not quite literal and contains some interpretations that are not explicitly stated in the Persian text.

To elaborate on all the reasoning that went into the choice of ingredients used in our experiments would require more space than is warranted here, and so we have simply presented the recipe in English, and along with this is a preparation used in one of our duplication experiments (appendix 2, p. 376).

In the first trials made, the paint was applied to small plates of a commercial soda-lime glass which approximates fairly well the analyzed compositions of the Islamic glasses. One notable difference in composition, which could have an effect on the susceptibility of the glass to taking a stain, is that the trial glasses were much lower in iron than the ancient glasses. Since iron might have been the principal internal reducing agent available to the migrated silver ions (see the chemical mechanism discussed below), the ancient glass might have taken the stain more readily. Our later trials, still under way, are being made on thin rolled sheets of experimental melts which more closely resemble the Islamic glasses, having been patterned after the analyses in table 2.

The sample glass plates, with the applied paints, were wrapped in insulation material and placed in ceramic boxes with small pieces of wood, to maintain a slightly reducing atmosphere. The boxes were placed in a large electric furnace, brought slowly from room temperature to 650°C, and held at that temperature. Draw samples were removed at various temperatures and analyzed for their chemical compositions. The results of these experiments will be reported in detail elsewhere.


20 Dept. of the History of Science, State University of New York at Albany.

21 These glasses were melted by A. A. Erickson, Manager of Melting Technology, Corning Glass Works, to whom we express our appreciation.
intervals ranging up to 13 hours. A second set of heat treatments was carried out at 600°C with times ranging up to 65 hours.\textsuperscript{22}

The sample plates of commercial glass painted with the synthetic ancient preparation, though spotty because of uneven application, developed yellow and amber stains after 15 to 30 minutes at 650°C. After more prolonged heating the surfaces tended to take on a yellow-greenish translucency. The appearance, however, was more like that of a surface-devitrified glass than a proper stained surface. In isolated spots ruby-red transparent patches appeared, but neither did they resemble the red-stained regions of the ancient glass, which have a greater opacity. No strongly lustrous metallic films were observed, but faint interference colors were sometimes seen.

The experiments on the synthetic Islamic glass produced amber transparent stains resembling the ancient ones. Occasional traces of a metallic luster showed in small unevenly spaced patches, and a pale greenish yellow opacity developed after longer heating. It did not resemble, however, the best yellow opaque stain seen on the ancient pieces, but was more like the mottled regions of less carefully painted background areas.

It was interesting to see that the ancient formulation did produce an amber stain not unlike that on the Islamic fragments. On the other hand, it must be admitted that it is not a very tricky process and almost any silver salt can be used to make a silver stain of sorts, even if not one suitable for fine decoration.

Interpretation of Results

From all of the foregoing evidence it is clear that the amber transparent decorations are essentially silver stains, and that both the yellow and red are copper stains. Both the chemical nature of these stains and the mechanisms by which they form are quite well understood,\textsuperscript{23} but there are some ramifications in the cases of these ancient examples which need to be discussed.

When a silver salt is painted onto the surface of a glass, and then fired, silver ions migrate into the glass by an ion-exchange mechanism, replacing sodium ions which occupy modifying positions in the silicate network of the glass structure. The exchange occurs readily because the silver ion is

\textsuperscript{22} The heat treatments were carried out by William Edminster and Fred Krome, both of Corning Glass Works.

\textsuperscript{23} W. Weyl, op. cit., passim.
approximate the same size as the sodium ion, and has the same charge. Under even mildly reducing conditions the migrated silver is chemically reduced and precipitates out as a colloidal dispersion of metallic silver. (The presence of ferrous ions or other reducing species appears to help the reduction along.) The glass then takes on a yellow transparent color due to the absorption of blue light by the very small silver particles. As the heat treatment continues, additional particles may form, and the existing particles grow somewhat larger, causing the yellow color to deepen to an amber, which can become strong enough to be called brown. As the particles grow beyond some critical size, the absorptive amber color is augmented by a yellowish green reflective appearance due to light scattered from the colloidal particles. As the particles grow still larger, the scattering becomes more important than the absorption, and a smoky blue-gray turbidity appears. This turbidity can become so dense that the transmission color, a dull red, can be viewed only with very intense illumination.  

In the case of copper stains, the colors are somewhat more difficult to produce and the mechanism seems to be less straightforward. Copper has less a tendency to migrate into the glass than does silver. It also appears that when the copper does get into the glass its reduction to metallic copper is more difficult to bring about, and its final state is more sensitive to chemical factors than that of the silver. Nevertheless, when the process does take place and a colloidal dispersion of metallic copper is thrown down, a transparent ruby-red stain results. If the heat treatment is extended, the particles grow to sizes that are large enough to display the color characteristics and reflection of bulk copper. The glasses then take on a livery color and eventually can grow into aventurine glasses, that is, brownish glasses in which flecks of metallic copper can be seen without the aid of any magnification.

Upon re-firing under the correct conditions, it is also known that these metals, particularly the copper, can migrate out to the surface again and deposit as a mirrorlike coating of metallic copper.

The descriptions above are sketchy as far as chemical details are concerned and there certainly are questions involved which have not been completely resolved, but in general those are the processes that occurred in the decoration of the ancient amber and red stains we have studied.

The presence, and ultimate fate, of the copper in the ancient silver stain

24 The color of the Termancia Cup in the collection of the Museo Arqueoléouco Nacional in Madrid is due to the presence of large particles of silver.
might be explained in several ways. It is possible that the copper was in
the formulation for no useful purpose but that it was merely an extraneous
constituent included for magical purposes or because the processes simply
were not understood. It is much more likely, however, that the copper did
perform a specific function, and there are two reasonable ways in which it
could have been helpful.

It must first be noted that the observed strong amber is a much more
suitable color for the decoration of such vessels than a thin yellow stain
which would not stand out as prominently. Therefore, the copper may
have contributed to deepening the silver color. The seventeenth-century
stained glass window from Nürnberg also analyzed showed a high con­
centration of copper in the orange-stained portion of the glass, whereas
the light yellow regions contained only silver. This is an indication that
copper was actually used deliberately to deepen the ordinary yellow color
of silver stains at that time. The same means might have been used for the
Islamic glasses. (See also the discussion of the transmission spectra.)

The mechanism by which the copper could alter the color of the silver
stain might involve a plating out of some copper onto the surface of the
colloidal silver crystals or of some solid solution in them. This could alter
the optical constants of the silver and cause a change of color. The X-ray
diffraction data showed only the presence of metallic silver. The silver
lines were broadened, however, due either to their small size or possibly
to the presence of copper.

A more logical explanation of the presence of copper is that whereas
the silver contributed the color of the stain, the copper was reduced in
the smoky atmosphere of the firing and was deposited ultimately on the
surface forming the overlying luster part of the decoration.

It is not quite so simple to account for the yellow and red opaque stains,
unless one is satisfied simply to dismiss them as being copper stains.

In the case of the reds, the stains are very much like the copper-ruby
stains used for making some ruby glasses today, and during the past
century. This is confirmed by both the X-ray diffraction data and
microscopic examination. It will be recalled that the Islamic red stain has
something of an opaque appearance. This is because some particles have
grown to rather large sizes. Probably these are accompanied by crystals of
colloidal dimensions, too small to be seen under the microscope. In true
ruby glasses, which are transparent, only the smaller particles are present.

It is the yellow stains that pose the most interesting chemical problems.
Our findings show the color to be due to a dispersion of very fine cuprous
oxide crystals. To make this stain was a rather tricky process. It was first necessary to introduce a good deal of copper into the glass by migration from the surface. (Note that the yellow stain sometimes occurs on base glasses that do not contain any copper to begin with.) Then the reduction had to be taken only to an intermediate state of Cu$_2$O and not taken so far as to produce primarily metallic copper. A third requirement was to arrest the growth of the cuprous oxide grains at a small enough particle size so that they would still show their yellow-orange color and not go over to the familiar bright red color characteristic of cuprous oxide in bulk phase or larger-grained dispersions.

The presence of silver could have been beneficial in creating this yellow-orange form of cuprous oxide, since it may have led to the formation of a large number of crystal nuclei which, if they acted as crystallization nuclei for the cuprous oxide, would have produced a dispersion of many small particles rather than fewer larger ones which would tend to give the red color.

To fit the yellow and red stains into the overall historical picture of yellow and red colorants used in ancient glasses, it should first be pointed out that up until this time red and yellow occurred only in true opaque glasses colored throughout, and not in the form of surface stains. Red opaques were made from the earliest times by precipitating out crystalline dispersions of cuprous oxide, which has a bright red color.\(^\text{25}\) X-ray diffraction studies of such red opaques show that they most often contain mainly Cu$_2$O but sometimes also some CuO. We have also seen a few which contain primarily CuO. Opaque yellow glasses were used in the earliest glass vessels we know, the cored vessels of the Eighteenth Dynasty in Egypt and in their counterparts in Mesopotamia. These glasses were colored by suspensions of yellow pigments,\(^\text{26}\) first lead antimonate ($\text{Pb}_2\text{Sb}_2\text{O}_7$) and after the second to fourth centuries a.d. a lead-tin oxide (“$\text{PbSnO}_3$”).

Interestingly, however, there is a class of ancient orange and yellowish orange glasses that have been shown by X-ray diffraction to contain only

\(^{25}\) The nature of these red opaques is discussed in a paper dealing with the use of lead in glasses in ancient times. R. H. Brill, “Lead Isotopes in Ancient Glass,” presented at the Fourth Congress of Journées Internationales du Verre, Venice (1967). (To be published in the forthcoming proceedings.)

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cuprous oxide. These invariably consist of very fine-grained crystals measuring not larger than about 0.1–0.3 micron across. We have found such colors in Egyptian, Iranian, Roman, and Byzantine glasses, dating from as early as about 900 B.C. up through Byzantine times. We have also accidentally made several such glasses in attempts to duplicate the ancient red opaque. Although our research on this problem is not yet complete, we are presently of the opinion that this difference of color (yellow instead of red) is a particle-size effect. This opinion is based upon direct experimental observations that fail to show the presence of any crystalline phases other than cuprous oxide in some of these glasses, and also upon theoretical considerations dealing with the color of cuprous oxide and other crystals.

This leads then to the view that the orange opaque glasses of antiquity—and the yellow stain studied on the Islamic fragments—were made by precipitating cuprous oxide and arresting the growth of the crystals at the yellow-orange stage. This does not mean to imply, however, that the glassmakers of early times could necessarily produce this orange color every time they set out to do so, because their control of their processes could not have been so precise. Undoubtedly, however, patient and determined tinkering could have substituted for precise control. The control of the Islamic glass decorators in making the yellow stains must have been much more reliable than that of the earlier makers of the bulk orange glasses. The Islamic glass decorators had to be more successful more of the time because of the economics of their production. The earlier glassmakers could always use their misfired reds and browns anyway, since they were happy to have a full color palette of mosaic tesserae, or could easily remelt their small molded figurines and start all over again. Could the secret of the Islamic glass painters' control have been in their use of silver in the stain?

The principal historical significance of the findings presented here is that this use of silver forms an important link connecting the use of silver and/or gold in coloring a small group of early dichroic glasses, and the much later separate use of silver for making yellow-stained glasses for cathedral windows in Western Europe. Depending upon the dates one accepts for these types of glass, the gap between them ranges anywhere.

27 See n. 25. Also additional unpublished results by the author.
29 This group of objects is discussed in detail in the reference in n. 3.
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from about five to ten centuries. The dichroic glasses (the Lycurgus Cup, the Termancia Cup, a diatretum fragment, and a fragment from Sardis) all have been dated from the fourth-fifth century up to the seventh-eighth century. An attribution of the invention of silver staining for cathedral windows has been made to Jacob of Ulm (Jacob Griesinger, 1407–1490) in the fifteenth century, but some windows said to be silver-stained are dated at least a century earlier. A dichroic fragment from Behnesa in Egypt is the only silver-containing glass known to this author which bridges this gap. It is dated, though uncertainly, to the ninth-tenth century. It now appears that this glass could be more directly related to the luster glass studied here, than to the other dichroic glasses mentioned above. In fact, occasional fragments of “misfired” luster glasses show a dichroism much like that seen in the Behnesa fragment.

In light of all this the use of silver in the Islamic luster glasses dated from the ninth-eleventh century helps to complete the technological link. This must be one more of the chemical arts preserved from the Greek and Roman world and later passed on to the West by Arabic alchemists and craftsmen. The careful preservation of the techniques and continuing study of the behavior of gold and silver in glasses was assured by the alchemists’ preoccupation with those metals.

The red stains are important historically because (along with the yellow) they appear to be the earliest known use of a copper stain on glass. This type of staining may have been an antecedent of the use of copper as the colorant in the ruby-stained glass windows of Western Europe, which were to appear some 250 years later. In searching for other technological connections it could well be that the red stains might not have developed from the ancient Mediterranean world at all but rather from attempts to imitate the red glazed ceramics imported into the Near East from China. Such attempts probably accounted for the early red luster glazes on ceramic wares from Samarra, Mesopotamia.

APPENDIX I

Catalog of Samples

1010 Rim fragment, colorless glass with amber stain. (51.1.145 X)
1011 Rim fragment, colorless glass with amber stain. (51.1.145 XI)
1012 Rim fragment, colorless glass with amber stain. (51.1.145 XIII)

30 This fragment is also discussed in the reference in n. 3. It is no. 691–1905 in the collection of the Victoria and Albert Museum.
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1013 Body fragment, colorless glass with amber stain. (51.1.146 XII)
1014 Rim fragment, very pale greenish glass with amber stain. (51.1.145 XIV)
1015 Rim fragment, very pale greenish glass with amber stain. (51.1.145 IX)
1016 Body fragment, very pale greenish glass with amber stain. (51.1.145 XII)
1017 Body fragment, very pale greenish glass with amber and pink (metallic) stains on both sides. (51.1.161 I)
1018 Base and pontil fragment, aqua glass with amber stain. (51.1.145 XIX)
1019 Body fragment, aqua glass with amber stain. (51.1.145 VI)
1020 Body fragment, aqua glass with amber stain on both sides. (51.1.150 II)
1021 Base fragment, pale blue glass with amber stain on both sides. Shows halo effect. (51.1.173)
1022 Base and pontil fragment, deep blue glass, with amber stain and yellow opaque stain. (51.1.159)
1023 Wall fragment, deep blue glass, with yellow opaque stain and red stain. (51.1.155)
1024 Wall fragment, deep blue glass, with dense yellow-orange opaque stain, and yellow-green streaked appearance on reverse. (51.1.152 II)
1025 Wall fragment, green glass, with dense yellow-orange opaque stained bands. (51.1.149 II)
1026 Rim fragment, pale green glass with yellowish-brown (and red-streaked) opaque stain on both sides. (51.1.149 III)
1027 Rim fragment, olive glass with red opaque stain and red-stained bands. (51.1.162 IX)
1028 Rim fragment, olive glass with red opaque stained characters on concave surface and greenish-yellowish-red mottled convex surface. (51.1.162 XIV)
1029 Rim fragment, olive glass with red opaque stained exterior and red-stained interior. (51.1.162 X)

APPENDIX 2

Early Persian Recipe

The recipe given below was recorded by Abdallah Ibn Ali Al-Kashani at Tabriz in 1300–1301. This English translation is from the German version published in 1935 by Ritter, Ruska, Sarre, and Winderlich (see footnote no. 19). The preparation process for the glaze is as follows: One takes $\frac{1}{2}$ parts yellow and red arsenic, 1 part silver or gold marcasite, $\frac{1}{2}$ part yellow vitriol from Tabas, and $\frac{1}{4}$ part burnt copper, which are pulverized and made into a paste. $\frac{1}{4}$ of this is ground together with six dirham of pure burnt and pulverized silver, and pulverized 48 hours until the powder is extremely fine. This is then dissolved in grape juice or vinegar and painted on the vessels as you wish and is put again into a second oven made especially for this purpose, and then fired there for three days with little smoke so that they take on “the color of two fires.” And when they are cooled one takes them out and rubs...
them with wet earth, so that the gold color becomes apparent. Other people add to the glaze certain things like red lead and verdigris, but instead of this, simple bloodstone with burnt silver does the same thing. The parts of this that are exposed to a constant fire will glow like red gold and shine like the sun.

From certain assumed identifications of the ingredients mentioned in the above text we prepared the mixture shown below. The materials were weighed, mixed, and ground thoroughly in a mortar and pestle with a small amount of 1:1 vinegar and grape juice. Additional vinegar-grape juice mixture, thickened with a small amount of gum arabic, was added until a paint of usable consistency was obtained.

*Mixtur Prepared to Duplicate Early Persian Recipe:*

- 3.0 silver carbonate
- 2.5 silver chloride
- 2.5 silver sulfate
- 2.0 silver sulfide
- 40.0 cupric sulfate
- 3.0 cupric sulfide
- 10.0 cuprous chloride
- 5.0 ferric sulfate
- 2.5 zinc chloride
- 0.5 zinc sulfide
- 0.5 sulfur
- 15.0 yellow ochre
- 5.0 arsenic disulfide

Cu/Ag ratio approx. 2.7
Cu/Zn ratio approx. 16.