The Earliest Known Use of a Material Containing Uranium

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FOR obvious reasons there has arisen in the past two years a considerable and widespread interest in uranium and its compounds, as is well indicated by the appearance of a very large number of items and articles on the subject in newspapers and general magazines in addition to those that have appeared in scientific publications. A not inconsiderable proportion of these items or articles, especially those in the popular press, convey, or at least tend to convey, the impression that the application of uranium and its compounds to the arts is solely a development of the past few years. Both the element and a large number of its compounds were, of course, investigated in detail in the 19th century and applied to various uses, though our knowledge of uranium minerals and compounds really had its beginning in the late 18th century.[1] What does not appear to be generally known, however, even among historians of chemistry, is that some evidence exists for the use of a uranium mineral or compound by the Romans in Italy soon after the beginning of the Christian Era. The purpose of this paper is to call attention to this evidence and to examine it critically.

Some forty years ago, while excavating the Imperial Roman Villa on Cape Posilipo on the shore of Naples Bay, R. T. Günther [2] of Oxford University discovered a remarkable glass mosaic mural in a niche in the wall of a substructure on the eastern side of the Gaiola hill. This niche was set in from the plane of the wall surface about five inches, and the flat back wall of the niche and its sloping sides and its top were evidently covered originally in their entirety with glass tesserae composing the mosaic mural. The bottom of the niche was apparently left undecorated. The mosaic on the back wall of the niche was still largely intact, and the whole of the original design could with certainty be determined. This consisted of a background of bright blue tesserae representing the sky, against which was a centrally placed plant, evidently a reed of some sort, delineated in opaque green glass. Two other plants of uncertain identification were placed one on each side of the central plant. Above the three plants hovered a dove rendered in opaque white glass. The leaves of the plants were treated in a very realistic manner, two different colors of green glass being used for the shading with small pieces of blue-black glass inserted to show up the leaves in greater contrast. At the bottom of the design was a conventional representation of a trellis consisting of diagonal lines of yellow tesserae crossing each other on a blue ground. Around the whole picture ran lines of white and blue glass tesserae and one of cockle shells. The glass mosaic decoration of the sides of the niche was much less complete, but enough remained to indicate with considerable certainty the original design. This consisted principally of small crosses placed vertically and in alternate colors against a background of black glass. Each cross was formed of four tesserae, the alternate crosses

[1] Klaproth (*Crell's Chemische Annalen* 1789, Part 2, 387–403) named the element and believed that he had isolated it, though he actually obtained only a lower oxide and mistook it for the metal. In spite of further studies by such eminent chemists as Arfvedson, Berzelius, and Richter this error, curiously enough, persisted for over 50 years, until Péligot (*Compt. rend. Acad. Sci. Paris 13* (1841), 417–426) isolated elemental uranium for the first time.

[2] *Archaeologia 43* (1912), 99–105. This article is illustrated with architectural line drawings and a color plate of the glass mosaic mural.

being composed of four yellow tesserae surrounding a blue one and four white tesserae surrounding a yellow one. An inlaid rectangular border consisted of spirally twisted black glass rod containing a thread of yellow glass. Around this was an outer border of cockle shells.

Shortly after its discovery, specimens of two kinds of colored glass from this remarkable mosaic mural were given to J. J. Manley [3] of Oxford University for chemical analysis. One of these specimens was pale green in color and the other bright blue. The actual analysis of the specimen of pale green glass was entrusted to a student, E. G. Laws of Magdalen College. In the course of the analysis of this green glass small amounts of a substance were encountered that could not at first be identified, but finally it was decided that this substance was a uranium oxide. However, some uncertainty exists as to the proportion present in the glass as indicated by the following statement in the report:

> As the quantity of uranium oxide obtained for weighing was 1.7 milligrams only, the difficulty of determining the exact amount present will be apparent. It is believed that notwithstanding the great care bestowed upon the work, the nature of the experimental errors led us to over-estimate the quantity of uranium oxide. Taking all the circumstances into due consideration, it would therefore appear that the best plan is to state the weight of uranium oxide as a difference. By this method, the percentage of uranium oxide present in the glass was found to be 1.25. The percentage deduced from the weighed oxide (1.7 mg.) was equal to 2.58.

The complete analysis of the green glass is given as follows:

Silica	62.11%
Iron Oxide	2.70%
Alumina	1.76%
Lime	8.90%
Magnesia	2.90%
Uranium Oxide	1.25%
Potassium Oxide	20.38%
	100.00%

The term "uranium oxide" in this statement of the analytical results is ambiguous. In view of the color and acidity of the glass it is likely that the uranium was present largely in the quadrivalent state. Hence it would have been better to express the uranium content of the glass more definitely as uranium dioxide (UO_2). It may also be remarked that the 1.7 milligrams of oxide that was obtained in the course of the analysis was in all probability in the form of uranosic oxide (U_3O_8) which on calculation to uranium dioxide would have given the direct percentage of 2.48 instead of the 2.58 stated in the report. The term "iron oxide" is also ambiguous. It seems likely that the percentage given is that of ferric oxide as determined directly by weighing, but in view of the color of the glass and the normal valency state of iron in a glass of this type the analytical result should have been calculated to ferrous oxide and so stated. The lack of consistency in the nomenclature of the other components is less objectionable since it involves no ambiguity in the stated percentages. This published analysis is also open to criticism because the percentages of the components of the glass are all given through the second decimal place, an apparent degree of accuracy for which no justification exists in view of the weights of the samples that were taken for the various analytical determinations. Thus, it is stated in the report that the complete analysis was made on a sample weighing only 0.167 gram, meaning in all probability 0.1670 gram since the weighing was evidently to the fourth decimal place in grams. From the data above cited on the quantity of uranosic oxide found by weighing and the corresponding stated percentage in the glass it may be calculated that the

[3] "Analyses of Green and Blue Glass from the Posilipan Mosaic," *Archaeologia 43* (1912), 106–108.

weight of the sample in which the uranium was determined must have been 0.0659 gram, which leaves only 0.1011 gram for any other sample or samples. It is therefore evident that the percentage results should not be stated beyond the first decimal place. On the basis of the above criticisms the results of the analysis of the green glass would be better stated as follows:

Silicon Dioxide	62.1%
Aluminum Oxide	1.8%
Ferrous Oxide	2.4%
Uranium Dioxide	1.5%
Calcium Oxide	8.9%
Magnesium Oxide	2.9%
Potassium Oxide	20.4%
	100.0%

It will be noted that as a result of the recalculation of the iron content in terms of ferrous oxide the percentage of uranium dioxide expressed by difference is now a little higher and hence a little nearer the percentage indicated by direct weighing.

However, the exact quantitative composition of the glass is, after all, a matter of minor importance as compared to the presence of uranium as a coloring agent in a glass of such undoubted antiquity. Was uranium actually present at all in this ancient glass? Unfortunately, the analysts give no details as to the qualitative tests or methods by which they established the presence of uranium so that it does not seem possible now to answer this question beyond the possibility of doubt. On the other hand, they appear to have been absolutely convinced as to the correctness of their finding. In respect to their discovery of the presence of uranium in the glass they state: "It must be confessed that this conclusion was at first accepted with some degree of reluctance and skepticism; but the new evidence as supplied by additional tests finally convinced us that the opinion we had already formed as to the nature of the body was correct and indisputable." These additional tests included the experimental preparation of a glass of the composition determined by analysis. It was found that this experimental glass resembled the original in general appearance, and that the omission of uranium oxide in its preparation resulted in a glass that was noticeably darker in color.

The colors of the two green glasses of the mosaic mural as shown in the color plate published by Günther also tend to confirm the reported experimental findings. One of these glasses is decidedly dark green and could not have been the "pale green" glass that was analyzed. The other, the one analyzed, is actually a light yellowish green, a coloration typical of a glass containing uranium. On the whole, therefore, it seems reasonably certain that this ancient green glass did contain uranium in the approximate proportion stated.

The sample of blue glass, the actual analysis of which was entrusted to a student, W. B. Shaw, was found to be a cobalt glass containing the unusually high proportion of 4.2% cobalt as the oxide. Otherwise this glass was found to have the same general composition as the green glass, except of course that it contained no uranium.[4]

Was the presence of uranium in the green glass purely accidental or was it more or less intentional? In the opinion of Manley the presence of uranium was an accident: "We may conclude almost certainly that the use of a sand having uranium as one of its constituents was merely accidental." However, he does make the following reservation: "It is of course quite possible that the maker observed that by using sand

[4] It is unfortunate that careful chemical analyses were not made of all the different colored glasses in this remarkable mosaic mural. The information thus obtained would probably have added a great deal to our meager knowledge of the composition of Roman colored glass. It is perhaps too much to hope that any samples of these glasses can now be obtained for chemical examination.

from a particular locality he was able to manufacture a green-tinted glass that was more appreciated and sought after than the green glass produced with the aid of other kinds of sand. If there is any truth in this conjecture, we should naturally expect to find other specimens of the same glass in the neighborhood." That the presence of uranium in this glass was wholly accidental is certainly the easiest and most obvious conclusion to draw, a conclusion that at first glance seems the only tenable one.

However, there are certain considerations that throw doubt on this conclusion. The fact that this is the sole specimen of Roman glass in which uranium has been detected does not really, as Manley seems to imply, lend much support to the argument that its presence was entirely accidental since only a few specimens of Roman colored glass have been analyzed anyway. That the uranium was introduced into the glass by the use of a uraniferous sand may be seriously doubted. Aside from the question of the rarity of such a raw material as compared to distinctive uranium minerals there is both literary and technical evidence that the general procedure in the manufacture of ancient colored glass was to add the coloring agent as a separate ingredient.[5] Pliny,[6] for example, explicitly states that the coloring agents were added separately, and he mentions copper as such an ingredient. In the manufacture of ancient blue glasses colored with cobalt, such as the one examined by Manley and Shaw, there can be little doubt that the cobalt was added separately in the form of a compound or mineral, any hypothesis that it was accidentally added in the form of a cobaltiferous sand being untenable in view of the virtual non-existence of such sand. Cobalt minerals, like uranium minerals, are rare, and if the ancients were able to locate cobalt minerals and use them for the coloring of glass then it is reasonable to conclude that they were equally capable of locating uranium minerals and applying them to the same purpose. Thus it appears probable that the uranium was separately added in the form of a mineral in the manufacture of the green glass in question, and this being so it cannot be said that the coloration of the glass by this means was an entirely accidental procedure. Of course, the true nature of the uranium mineral used for the purpose could not have been appreciated by the ancient workers any more than they could appreciate the true nature of other mineral substances they used in the arts. Nevertheless, it would appear probable that they recognized it as a peculiar and distinct kind of a mineral substance, and they may have even given it a distinct name.

On the basis of archaeological and historical considerations Günther[7] concluded that this glass mosaic mural, of which this uranium glass was a part, could be dated sometime in the neighborhood of 79 A.D. In the light of our present knowledge of the composition of ancient materials this date may then be taken as fixing the approximate time of the first use of uranium glass and the approximate time of the first use of any kind of a material containing uranium.

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[5] An exception must of course be made for much of the ancient glass colored by iron alone since this element must often have been accidentally introduced from the raw materials and utensils.

[6] *Historia Naturalis 36*, 193

[7] *Loc. cit.*