Gamma-Ray induced thermoluminiscence of majolica pottery as an indicator of its provenience

J. E. VAZ, and J. M. CRUXENT

The thermoluminescent emission induced by gamma-ray irradiation in samples of majolica pottery was analyzed to determine if their artificially-induced thermoluminescence (TL) could be used as an indicator of provenience. It has been recognized for some time that an independent method of determining the provenience of pottery would be of significant value to the archaeologist. Two analytical methods are currently in use for the determination of provenience in pottery: neutron activation analysis using gamma-ray spectrometry [1], and optical spectroscopy [2]. Some work has also been carried out in the utilization of Mössbauer spectroscopy [3, 4] in provenience problems. These methods are based on the fact that the chemical composition of clays used in the manufacture of pottery depends on the source rocks, and in the geochemical conditions that produced the sediment. These two factors will give rise to clays with enough variation in their minor, and trace-element content to allow distinction between the sources of the raw materials used in the preparation of the paste.

The TL measurements presented here were carried out in the clay matrix of majolica pottery manufactured in pottery centers in Europe, and Mexico. This type of pottery is a porous pottery of soft paste with a hard covering of opaque, vitreous material. It was wheel-made in Europe from the XV to the XVII century, and in several places in

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[1] I. PERLMAN, F. ASARO, Archaeometry 11,21 (1969).
[2] H. W. CATLING, Archaeometry 6, 1 (1963).
[3] D. R. COUSINS, K. G. DHARMAWARDENA, Nature 223, 732 (1969).
[4] N. H. J. GANGAS, A. KOSTIKAS, A. SIMOPOULOS, J. VOCOTOPOULOU, Nature 229, 485 (1971).

the New World after the Conquest. The origin of the samples, and other pertinent data are presented in Table 1.

The clay matrix of the sherds was ground and sieved, and the 74-177 μm fraction was used for the TL measurements. Portions of the samples were irradiation with gamma rays from a Cesium-137 source until their TL output reached saturation. After irradiation with 2×10^6 Roentgens of gamma radiation, the samples were kept in the dark at room temperature for 48 hours to allow the low-curve peak to stabilize. The gamme-ray induced TL of 18 mg aliquots of the material was measured in a nitrogen atmosphere with a TL analyzer. The samples were heated linearly from room temperature to 500° C at 10° C s^{-1}. The reproducibility of the measurements is within ± 5 %.

Figure 1 shows a set of glow curves obtained from samples from each of the pottery manufacturing centers studied. Glow-curve measurements of each of the samples that were analyzed are presented in Table 1 where the glow-curve peak temperatures, the peak-intensity ratios, and the area under the glow curve are shown.

In the preparation of the paste used in the manufacture of pottery, the clay is mixed with tempering in the form of impure sand. Both of these constituents of the paste will emit TL when the clay matrix of the sherd is heated after being irradiated with nuclear radiation. This property of the material has been used[5] to date ancient pottery because the minerals found in the clay matrix can accumulate some of the energy released by the radioactive decay of U, Th, and K-40 impurities present in their crystal lattices. In addition, the TL output of any one of the mineral constituents of the paste depends on the concentration of trace elements within the crystal that act as activator, or luminescent centers. It is, therefore, reasonable to assume that the shape of the glow curve obtained after irradiation of the clay matrix with gamma rays depends on the type of clay, and on the tempering used to make the pot, as well as on the concentration of trace elements in these two constituents of the paste.

If these assumptions are correct, it should be possible to use gamma-ray induced TL to distinguish or relate pottery sherds found in an archaeological context. By irradiating the clay matrix with gamma rays until its TL output is saturated, one is assured that each of the thermoluminescent mineral fractions in the paste is contributing fully to the total TL output. Analyses of the natural TL output of the clay matrix would not have been suitable to this study because the low levels of natural TL measured in the samples depend on the radioactive-impurity content of the specimen, its age, and the environmental conditions under which it was preserved.

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[5] M. J. Aitken, D. W. Zimmerman, S. J. Fleming, Nature 219, 442 (1968).

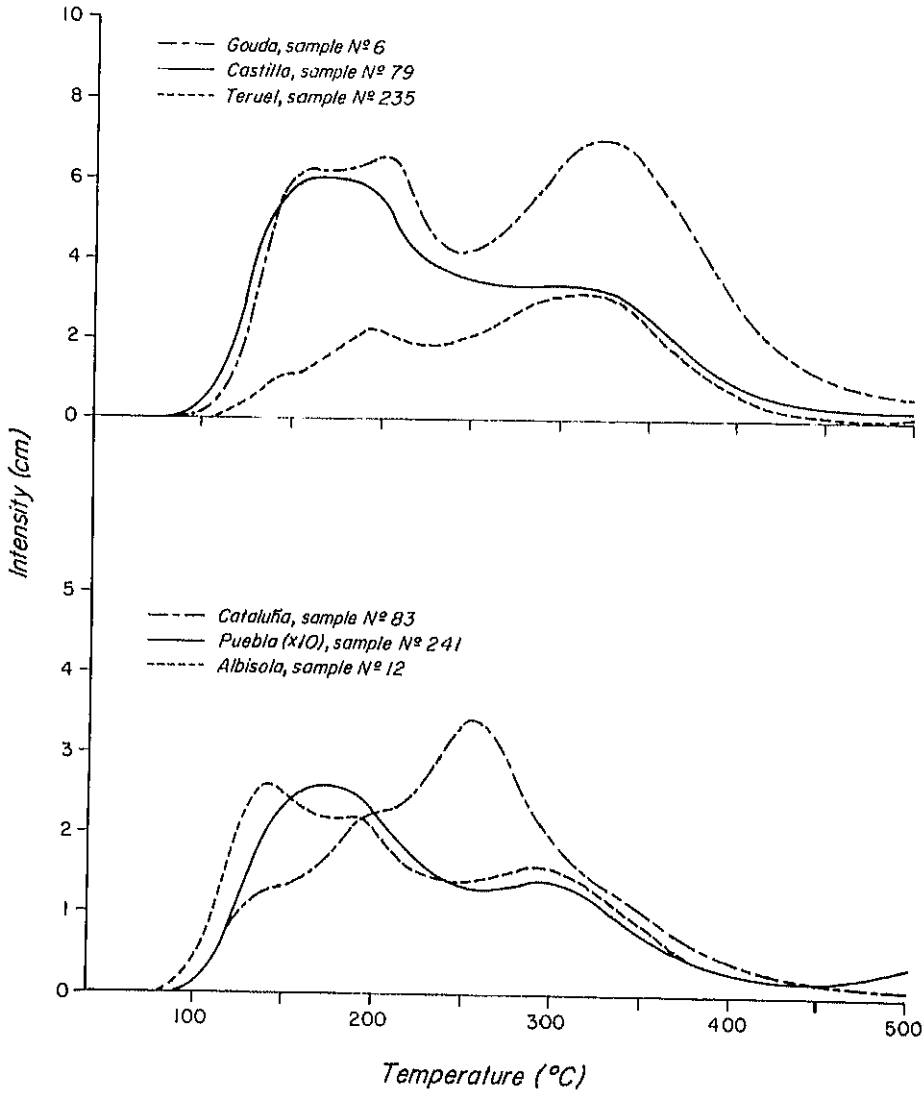

FIGURA 1.—*Representative gamma-ray induced TL glow curves of each of the pottery manufacturing centers studied.*

The results of the TL measurements presented in Figure 1, and in Table 1 show that the assumptions discussed earlier are reasonably valid. It is evident from the data presented in Table 1 that the glow-curve measurements are similar, within relatively narrow limits, in the samples of majolica pottery from the same locality. However, these measurements are substantially different in the same type of pottery manufactured in diferent localities. These differences are more clearly seen in the curves shown in Figure 1.

Among the samples from any one of the six different localities studied, the largest variation in the TL measurements is found in the measurement of the area under the glow curve. This variation appears to be due mainly to changes in the transparency of the material produced by the baking of the pottery. It should also be pointed out that although the samples from Teruel, Spain, range in age from the XV century to the XVIII century, the TL spectra are very similar from sample to sample. This similarity indicates that the source of the raw materials used in the preparation of the paste was the same throughout the years. It is probable that the same comment can be made about the samples from the other localities studied, but we do not know with certainty the approximate date of manufacture of most of these samples.

The results obtained to date indicate that the gamma-ray induced TL of majolica pottery is specific to the locality where the artifacts were made. It is possible in principle to apply the TL technique described here to classify according to origin other types of pottery found in archaeological sites. This would require a systematic study of the characteristic TL spectra of the principal types of pottery. It is hoped that analyses similar to the one presented here could be used to complement typological studies [6] of majolica pottery found archaeologicallll in the Americas.

Instituto Venezolano de Investigaciones Científicas. Caracas.

[6] J. M. Goggin, Spanish Majolica in the New World (Yale University Publications in Anthropology, No. 72, 1968).

[7] We thank V. Betancourt for technical assistance, and G. Bemsky for aditing the manuscript.

Table I. TL measurements in majolica pottery

Sample	Locality	Century	Peak temperature (°C)	Peak intensity ratio *	Glow-curve area (nC)
18	Teruel, Spain		125,180,300	a) 1.6, b) 2.3	8.8
19	" "	XIV-XV	"	a) 1.4, b) 2.4	4.6
20	" "	XV	"	a) 1.2, b) 2.2	6.3
27	" "	XIV-XV	"	a) 1.1, b) 1.7	7.1
28	" "	XIV-XV	"	a) 1.4, b) 1.7	19
31	" "	XIII-XIV	"	a) 1.1, b) 1.8	3
35	" "	XIII-XIV	"	a) 1.6, b) 2	6.5
36	" "	XV	"	a) 1.2, b) 2.4	9
37	" "	XIII-XIV	"	a) 1.2, b) 3.1	5.2
38	" "	XIV-XV	"	a) 1.4, b) 2.3	6.2
39	" "	XVIII	"	a) 1.6, b) 2.8	6
41	" "	XVIII	"	a) 1.6, b) 2.3	9.6
42	" "	XVIII	"	a) 1.4, b) 2.8	3.5
43	" "	XVI	"	a) 1.4, b) 2.4	10.6
44	" "	XIII-XIV	"	a) 0.9, b) 2	4.5
56	" "		"	a) 1.7, b) 2.6	12.9
235	Teruel, Spain	XV	125,180,300	a) 1.4, b) 2	6.2
7	Albisola, Italy	XVII	135,185,300	a) 0.7, b) 0.8	5
8	" "		"	a) 0.5, b) 1	6.3
9	" "		"	a) 0.7, b) 1	7.3
10	" "		"	a) 0.7, b) 0.9	3
12	" "		"	a) 0.7, b) 0.9	4.3
13	" "		"	a) 0.8, b) 0.9	3.9
48	" "	XVII	"	a) 1.1, b) 1.1	2.2
54	" "		"	a) 0.4, b) 1.1	6
3	Cataluña, Spain	XVII	125,190,245	a) 1.6, b) 1.8	12
33	" "		"	a) 3.8, b) 1.8	12
34	" "		"	a) 2.5, b) 1.5	10.6
83	" "		"	a) 1.5, b) 1.7	5.1
89	" "		"	a) 2 , b) 1.9	4.6
29	Castilla, Spain		160,275	a) 0.7	10.6
30	" "		" "	a) 0.6	9.3

Table 1. TL measurements in majolica pottery (Cont.)

Sample	Locality	Century	Peak temperature (°C)	Peak intensity ratio *	Glow-curve area (nC)
45	Castilla, Spain		160,275	a) 0.6	11.4
47	" "		" "	a) 0.6	9.7
55	" "		" "	a) 0.5	9.8
77	" "		" "	a) 0.9	10.5
78	" "		" "	a) 0.5	7.4
79	" "		" "	a) 0.6	10.4
80	" "		" "	a) 0.9	5.8
82	" "		" "	a) 0.7	8
6	Gouda, Holland	XVII-XVIII	135,180,300	a) 1.1, b) 1.1	4.9
24	" "	XVIII	"	a) 1.1, b) 1.1	7.3
57	" "		"	a) 1.4, b) 1.3	16
58	" "		"	a) 1.1, b) 1.1	8.6
65	" "		"	a) 1.2, b) 1.2	11.2
66	" "		"	a) 1.4, b) 1.2	34.6
68	" "		"	a) 1.3, b) 1.2	10.5
70	" "		"	a) 0.9, b) 1	9.5
59	Puebla, Mexico		160,285	a) 0.3	1.1
60	" "		" "	a) 0.4	0.6
241	" "		" "	a) 0.6	0.6
240	" "		" "	a) 0.4	0.4
237	" "		" "	a) 0.3	0.7
239	" "		" "	a) 0.2	0.8
242	" "		" "	a) 0.2	0.6

* a) Ratio of the high temperature glow peak to the middle temperature glow peak

b) Ratio of the middle temperature glow peak to the low temperature glow peak