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Authentication by Thermoluminescence

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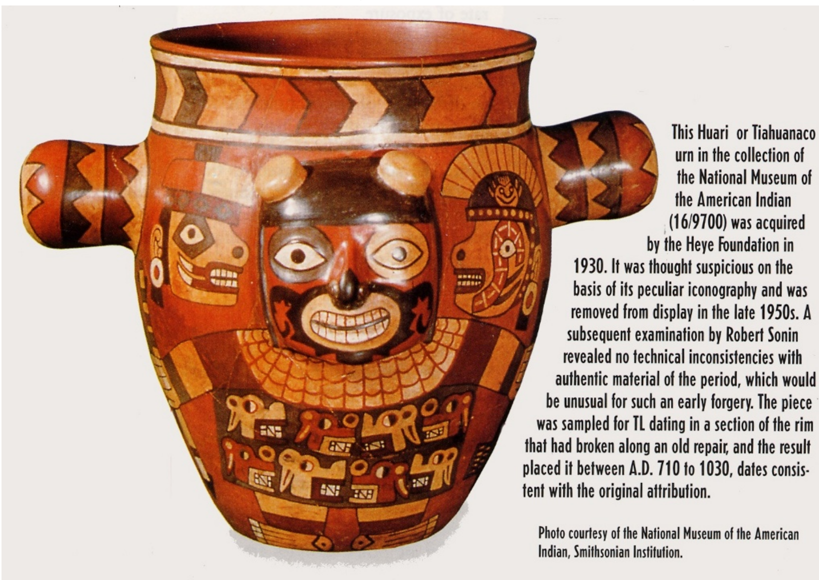
On October 28, 1663, the phenomenon of thermoluminescence was described for the first time by the renowned English chemist Robert Boyle in an address to the Royal Society. The subject of his research was a remarkable diamond that gave off a weak glow when placed on a warm part of his body. We now know that the light Boyle observed in the diamond was the result of millions of years' exposure to radiation from small quantities of uranium, thorium, and radioactive potassium present in the diamond's geological matrix. Many minerals are thermoluminescent to some degree, but most require sensitive instruments to detect and measure the glow.

The authentication of art objects by thermoluminescence (TL) dating has "name recognition" for most art collectors and professionals but is understood by few. TL dating is one of a number of physical methods that can determine the age of an object. TL dating applies only to minerals, typically clay or stone, that have been subjected at one time to intense heat (above about 500°C). The technique determines how much time has elapsed since the object was last heated. This means that TL dating is effective for clay that has been fired in a kiln, stone objects that have been heated in a firepit, or the clay cores of cast metal objects. It is the only absolute physical means of determining the age of pottery presently available. The test is not applicable to objects of carved stone, metal lacking a core, paint, textile or organic materials, although other means such as radiocarbon (carbon-14) dating may be effective for some of these.

The basic idea of TL is fairly simple, although in practice it can be quite complex. In crystalline materials such as stone) or the tiny particle of quartz and feldspar present in clay, the atoms are arranged in a regular array. Natural crystalline materials usually have defects (impurity ions. stress dislocations, and the like) that interrupt this regularity. Many of these defects attract loose electrons from naturally-occurring ionizing radiation passing through the crystal, and some of these electrons are trapped. When the mineral is strongly heated, the trapped electrons are freed. As they recombine with lattice atoms, photons are emitted, light measurable with laboratory equipment. This radiation-induced light is the thermoluminescent signal. If this measurement is repeated on the already heated sample, no light is observed. We say that the TL is "zeroed," and it is this zeroing that makes dating by TL possible. Since it is a good assumption that the radiation in and around the sample during burial has been constant, and since the TL signal can be related to radiation dose by calibrating the sample material with known radiation doses, the dose accumulated by the sample since firing can lead to an estimate of its age. The rate at which the radiation dose accumulates can be

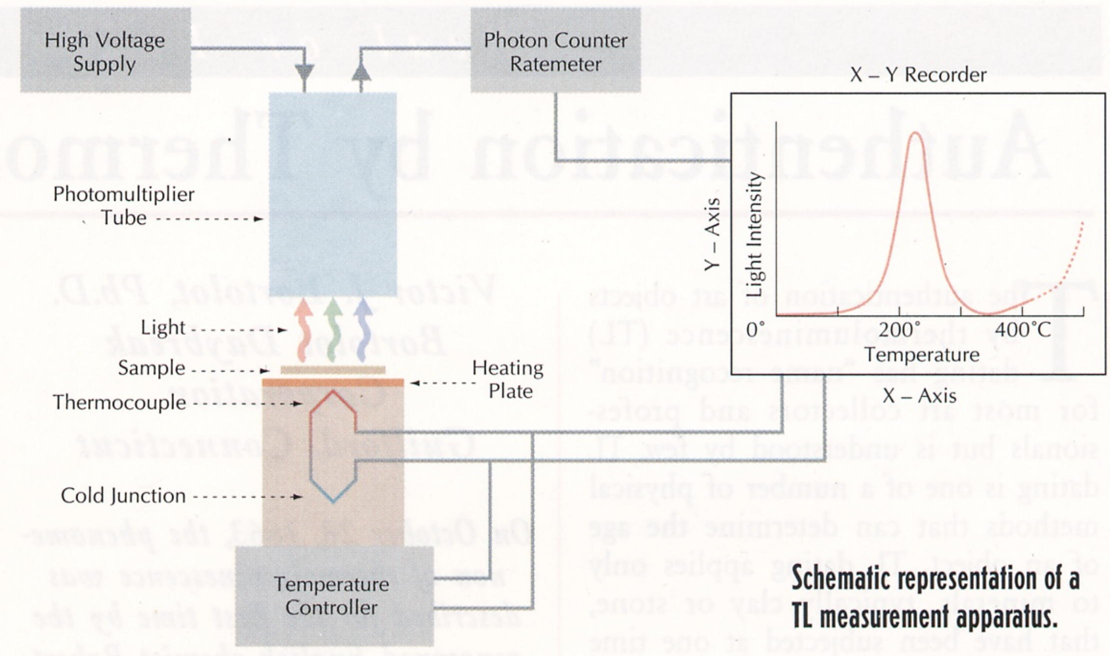


This Huari or Tiahuanaco urn in the collection of the National Museum of the American Indian (16/9700) was acquired by the Heye Foundation in 1930. It was thought suspicious on the basis of its peculiar iconography and was removed from display in the late 1950s. A subsequent examination by Robert Sonin revealed no technical inconsistencies with authentic material of the period, which would be unusual for such an early forgery. The piece was sampled for TL dating in a section of the rim that had broken along an old repair, and the result placed it between A.D. 710 to 1030, dates consistent with the original attribution.

Photo courtesy of the National Museum of the American Indian, Smithsonian Institution.

computed from measurements of the radioactive constituents of the pottery and of the burial soil. Very simply put, the radiation dose divided by the dose per year gives us the years elapsed since firing. It is important to note that unfired material like dirt or sun-baked clay will not give a valid TL age, since zeroing has not taken place. Contamination of a sample with such material will lead to impossibly ancient TL ages.

The apparatus for measuring TL is shown schematically below. The sample is placed on an electrical resistance heater and raised in temperature at a constant rate, usually 20°C/second, up to about 500°C. The sample is viewed by a sensitive light detector (photomultiplier tube), and the intensity of light given off (the TL) is plotted against temperature to produce what is called a "glow curve." A family of glow curves is obtained for identical amounts of the sample that have been subjected to a range of doses of different



Schematic representation of a TL measurement apparatus.

kinds of radiation, in order to determine the relationship between the TL signal and the radiation dose causing it, and eventually to find the dose accumulated since firing. For the most precise archaeological dating, nearly two dozen physical quantities must be accurately measured to establish the relationship between exposure to different types of radiation (alpha, beta, gamma) and to compute the rate of exposure.

Ideal TL dating circumstances involve having a number of test samples as well as a soil sample from the environment of the samples or the opportunity to place a highly sensitive TL dosimeter in the hole from which the samples were taken, so that the environmental rate of radiation dosage can be measured. Under such conditions and with an ideal sample, the uncertainty, or "error bars", is about 15 percent of the known age. When a number of associated samples can be dated and averaged, the uncertainty is typically reduced to 7 to 10 percent. Thus a potsherd fired 1000 years ago in A.D. 994 that is brought out of a controlled excavation and accompanied by a soil sample might yield a TL age of 1000+/-150 years before present (B.P.), or between A.D. 844 and 1144. When this TL age is combined with ages found for a number of other samples from the same archaeological context, the composite result might be 1000+/-70 years B.P. Unfortunately, it is not possible to achieve this precision for the majority of art objects. Usually only a very small sample may be taken from the object, and drilling, the usual method for obtaining a sample, introduces some uncertainty due to damage to the clay grains caused by the drill. It is also rare that any information about the radiation dosage of the burial soil can be obtained, as art objects are usually thoroughly cleaned. Finally, the measurement must be made regardless of whether or not the TL of the clay is "well-behaved." Some clays are hardly thermoluminescent at all; some may not have a straight-line relationship between dose and TL; spurious luminescence due to chemical or pressure effects may mask the radiation-induced TL; and occasionally a condition called "anomalous fading”, where part of the TL is unstable, may lessen the accuracy of the dose measurement.

Generally speaking, when a sample is drilled and there is no information available about the burial environment, a result with about 25 percent uncertainty may be 'expected. Up to 50 percent uncertainty may be encountered when the internal radioactivity of the sample is low and assumptions must be made about the likely ranges of major parameters. While this sort of result is hardly for precise dating, it is more than adequate for the purposes of authentication where the question is whether the piece was fired in antiquity or recently. Such a test will not necessarily differentiate between a Classical Greek terracotta and a Roman copy but it will distinguish either of these from a similar object created within the last 100 years. In some special cases, as in most Chinese clays, the properties of the clays are very uniform and some of

Detail of the foot of an Aztec incensario base showing a TL sample hole 3 mm in diameter and 8 mm deep. The object was owned by a private collector who sought to confirm its authenticity by TL dating.

In 1984 the sample yielded a date of 310 to 550 B.P. (before present). Since it cannot have been produced after the second quarter of the 16th century, these dates indicate that it was created at the close of the Aztec period.

Photos courtesy of Gallery DeRoche.

the "blanks" can be filled in with confidence. With these a 10 to 15 per cent uncertainty is possible despite the lack of associated material.

When TL dating is for routine authentication of an art object, a sample of about 50-100 mg, roughly one - third of the volume of a pencil-end eraser, is drilled out of an inconspicuous part of the object with a carbide dental burr. If the object is extremely small, the amount of the sample may be reduced but the uncertainty may increase. If the object has been restored, it may be advisable to take more than one sample as the component parts may differ in age. Sampling, if done in an inconspicuous area, does not reduce the value of a piece, and the small hole is easily repaired. When accompanied by appropriate documentation, this confirmation of authenticity by TL generally enhances an object's value considerably.

TL dating gives results only for the sample tested. The results will generally reflect the age of the entire object, but certain conditions can render a TL test invalid or give a misleading result. If the object has been subjected to extreme heat at any time after its creation, the TL date will reference that firing. This can occur when the object has been involved in a fire, or if it has been re-fired, as sometimes occurs in restoration. If the object has been restored and the test sample is taken from a filled area, the results will be misleading. An object that is a pastiche composed of unrelated fragments will not necessarily be revealed by a TL test. An object that is not composed of well-behaved TL material, such as many ceramics from West Mexico and Indonesia, usually does not successfully yield TL dates. The competence and experience of the individual performing the measurements and interpretation can also be factors in the result, especially where the sample is marginal for TL.

As with all tests for age, TL has limitations, but its value in the process of distinguishing ancient ceramics from contemporary forgeries has been proven time and time again in both public and private collections.