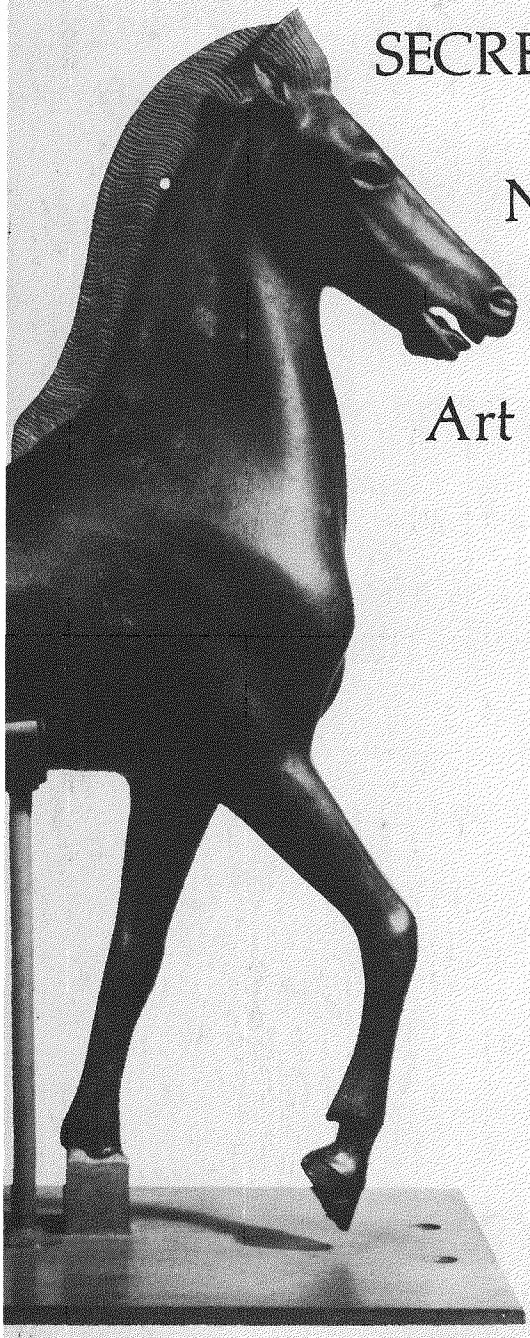


SECRETS OF THE PAST:

Nuclear Energy Applications in Art and Archaeology

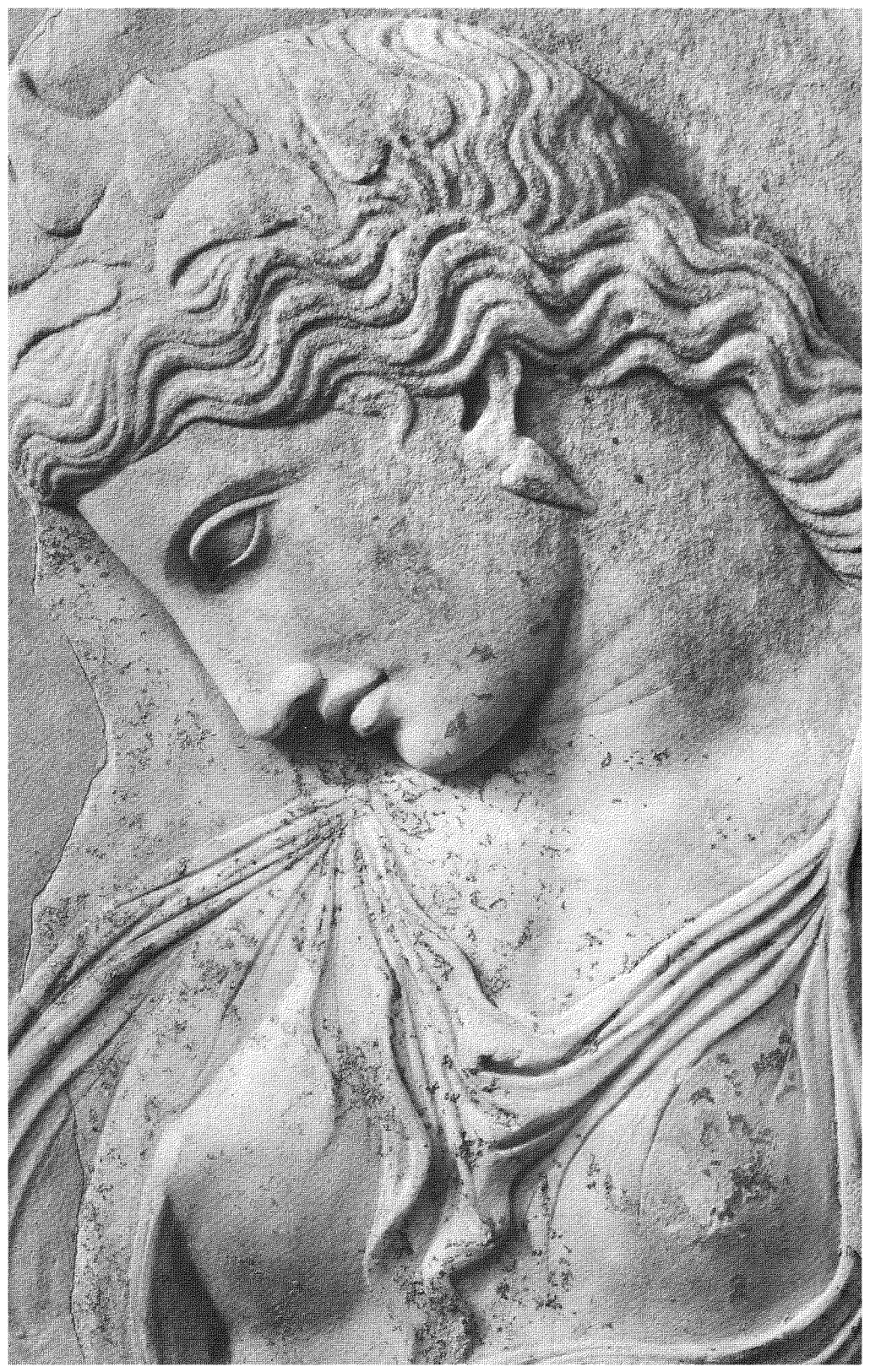
by Bernard Keisch

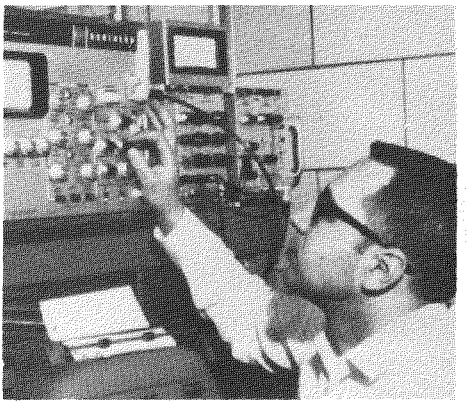
WORLD OF THE ATOM SERIES

ATOM

Art reminds us what a creator man has been, and how little, comparatively, a destroyer.

Bernard Berenson





The Author

Dr. Bernard Keisch received his B.S. degree from Rensselaer Polytechnic Institute and his Ph.D. from Washington University. He has been a Fellow with the Division of Sponsored Research of Carnegie-Mellon University in Pittsburgh since 1966. He is presently engaged in a project that deals with the applications of nuclear technology to art identification. This is jointly sponsored by the Atomic Energy Commission and the National Gallery of Art. Previously he was a nuclear research chemist with the Phillips Petroleum Company and senior scientist at the Nuclear Science and Engineering Corporation. He has contributed articles on art authentication to a number of journals. For the AEC, in addition to this booklet, he has written "The Atomic Fingerprint: Neutron Activation Analysis" and "The Mysterious Box: Nuclear Science and Art".

The Cover

This 15-inch tall bronze horse was purchased in Paris by the Metropolitan Museum of Art of New York in 1923. It was thought to be about 2400 years old and was considered one of the finest ancient bronzes in existence. In 1967 X-radiography showed an unusual internal construction that caused some doubt regarding the authenticity of the piece. (See pages 101 and 102.)

The World of the Atom Series

Nuclear energy is playing a vital role in the life of every man, woman, and child in the United States today. In the years ahead it will affect increasingly all the peoples of the earth. It is essential that all Americans gain an understanding of this vital force if they are to discharge thoughtfully their responsibilities as citizens and if they are to realize fully the myriad benefits that nuclear energy offers them.

The United States Atomic Energy Commission provides this booklet to help you achieve such understanding.

UNITED STATES ATOMIC ENERGY COMMISSION

Dr. James R. Schlesinger, Chairman
James T. Ramey
Wilfrid E. Johnson
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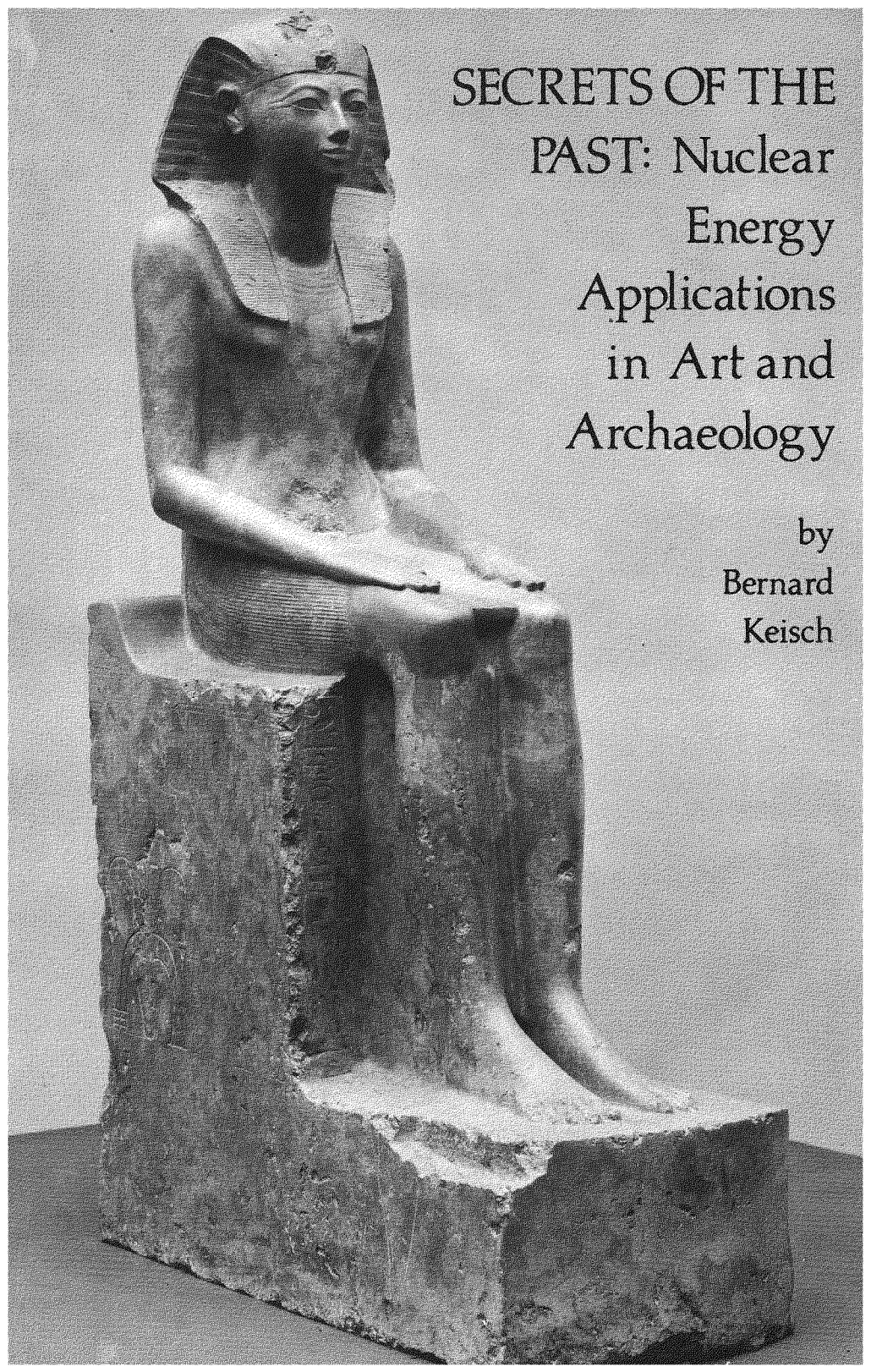

SECRETS OF THE PAST: Nuclear Energy Applications in Art and Archaeology

by Bernard Keisch

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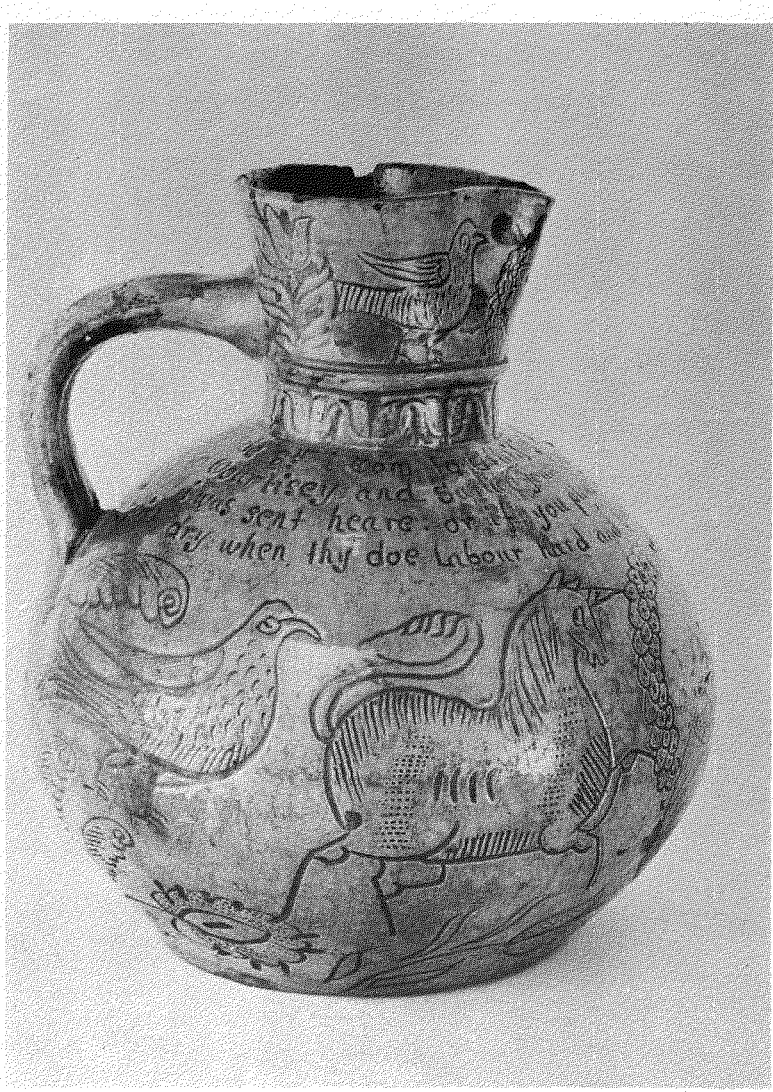
1972

The 16-inch-wide Sacro Catino is in the Cathedral of San Lorenzo in Genoa, Italy. For centuries it was revered as the Holy Grail. X-ray fluorescence analysis indicates that the bowl does not fit the usual formula for Roman glass of Christ's time but is typical of later Islamic ware. During the Crusades it was acquired by Genoese sailors in Palestine and later shattered. Part of it is still missing.



A harvest jug, made in North Devon, England, and used in Sussex County, Delaware. It is 11 inches high and bears the date 1698. The inscription reads: "Kind Sr: i com to Gratifiey your Kindness Love and Courtisey and Sarve youre table with Strong beare for this intent i was sent heare: or if you pleas i will supply youre workmen when in harvist dry when thy doe labour hard and swear good drinke is better far then Meat".

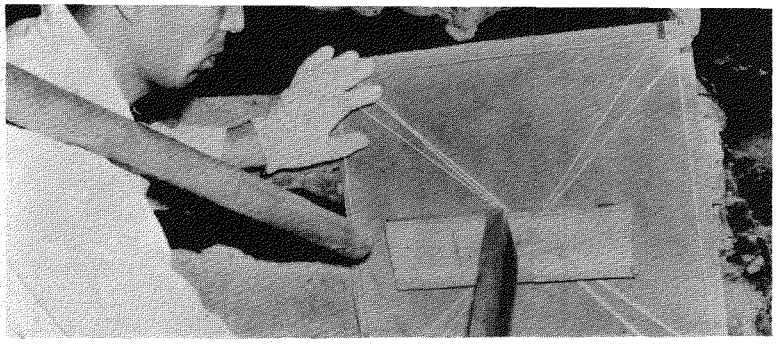
Introduction

ART AND ARCHAEOLOGY HAVE MUCH IN COMMON

Archaeology is the study of history through the observation of antiquities and relics. While many of the "antiquities" that are studied are not art in the usual sense (artifacts such as arrowheads, tools, plain pots), a large number are art in every sense (decorated pottery such as the jug on the left, sculpture, carvings, etc.). On the other hand, while much art is modern and has nothing to do with archaeology, there is quite a bit that belongs equally to the realms of the art historian and the archaeologist.

Experts in these subjects often have a great deal in common. Both have an interest in displaying objects, preserving them so that they do not deteriorate, repairing and restoring them when they have been damaged or have deteriorated, and accurately identifying the time, place, and method of their creation.

There are many methods by which nuclear science can be used to aid in the study of art and archaeology. Many of these methods are applicable to both fields while some are unique in their application. The material presented here has been divided between the two fields primarily to help organize it. You will also find that most of the methods using nuclear science deal with the *identification* and *dating* of objects.



Gamma radiography is often used to examine large industrial castings and welds in pipes. Kenzo Toishi of the National Research Institute of Cultural Properties in Tokyo applied this technique to look for defects in casting and structural damage in the Great Buddha at Kamakura, which was built in 1252 A.D. Some holes and cracks were discovered. Also revealed was the fact that the 13th century artisans had attached all the castings by supplementary mechanical supports in addition to conventional butt joins. Without these extra supports the statue would have long since collapsed from earthquake shock. The cobalt-60 source is in the box suspended from the platform to the left of the statue. Sheets of X-ray film sealed between thin layers of iron recorded the results. Above, the film is placed against the inner surface of the wall.

WHY STUDY ART AND ARCHAEOLOGY?

Man enjoys beauty. While one hardly needs to present proof of this, one such proof might rest upon the large crowds that visit art museums and galleries.

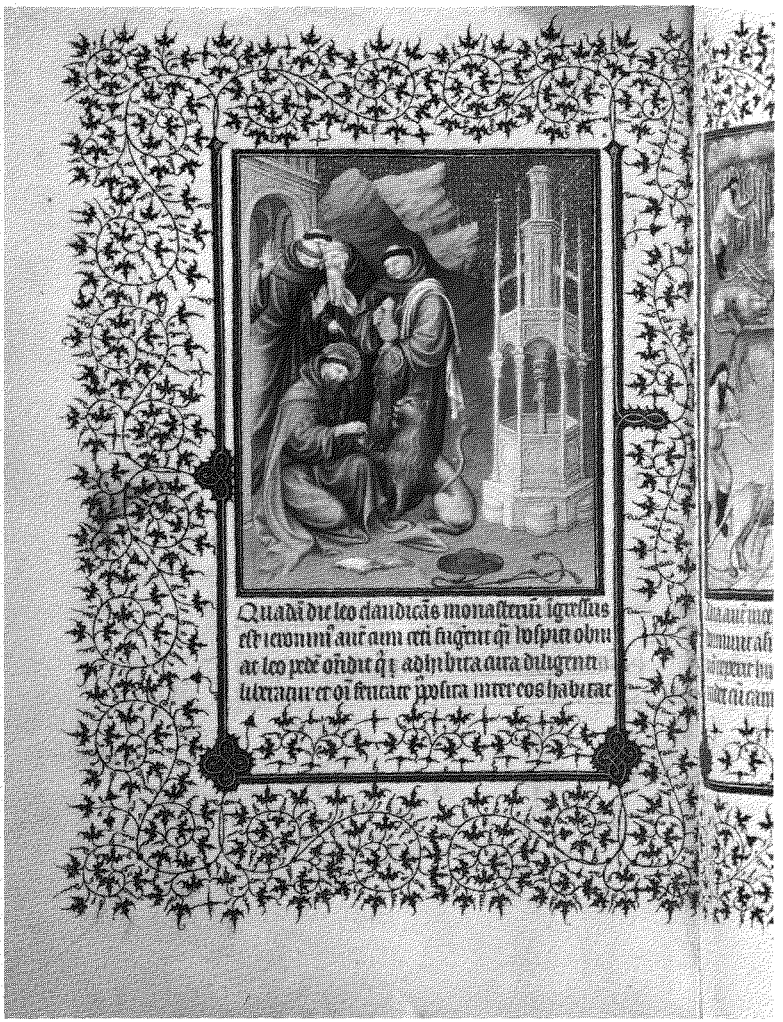
It is equally obvious that man is curious about his origins. Even in our times, when "practical" problems press from all sides, much time and effort are devoted, by professional, amateur, and casual observers, to the study of the origins of man. From the earliest recorded times, our mythologies and religions have presented us with "pre-histories" as man seeks out his links with the past.

At the present time in our society, there are practical aspects to be considered as well. Because of the increasing number of persons with leisure time and money to spend, the collection of objects of art and archaeology has also become a big business. Further, this business is one that is vulnerable to promoters of fakes and forgeries. And that is a crime that hurts not only the immediate victim, but in more subtle ways, society as well.

Another aspect of our present society with which we are increasingly concerned relates to the conservation of objects. The ravages of air pollution have already left their mark on many works of art. The exhibition of objects for audiences of millions is a recent development. For hundreds of years, much art was kept in dark vaults where only the privileged few could enjoy it. Now we have modern, well-lit museums that in themselves are works of art. But, unfortunately, these modern edifices often promote deterioration of works of art or of priceless antiquities through the fading action of light and through the exposure of materials to cyclic changes of moisture and temperature.

The scientific study of art and archaeology may be divided into four classes:

(1) Dating and identification of objects as a means of establishing historical fact.



A page from the 15th century Très Riches Heures de Duc de Berry *(Very Rich Hours of the Duke of Berry), a small illuminated prayer book. These works of art were made for, and enjoyed by, only a few privileged persons.*

(2) Dating and identification of objects as a means of seeking out fakes and forgeries.

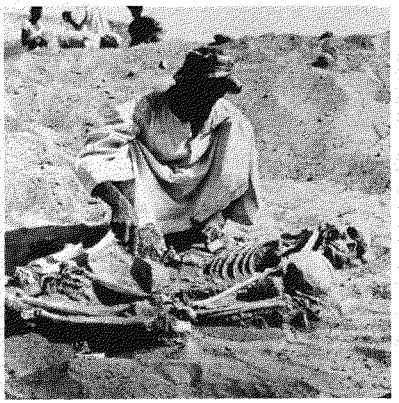
(3) The restoration of objects.

(4) The conservation of objects.

HOW ARCHAEOLOGISTS WORK: THEIR METHODS AND MATERIALS

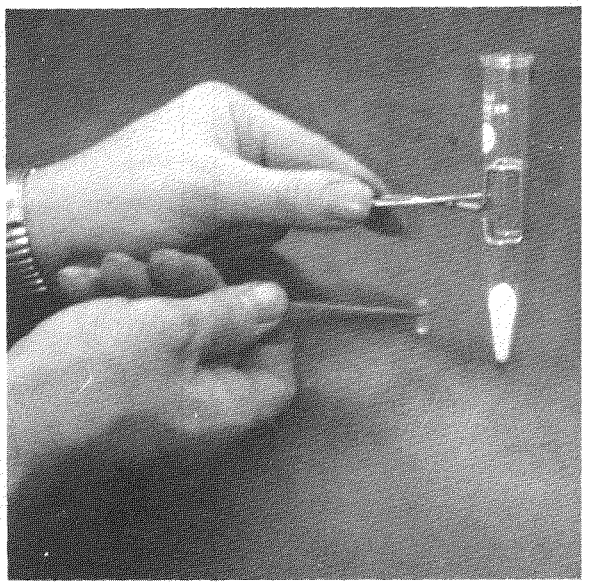
Until the blossoming of nuclear technology following World War II, archaeologists were quite limited in the tools available for pursuing their studies. Their techniques were essentially those of classification and deduction. Many theories were based upon a combination of chemical analysis, some educated guesswork, and a line of reasoning that was often uncertain. One very important fact associated with any artifact is its age. Yet, for a long time, the age of an object depended upon a consideration of its relationship to similar objects and to the layers of soil and rock in which it was found.

By providing accurate methods for dating objects and materials, nuclear dating techniques, particularly carbon-14 dating (described in a later section), marked the real beginning of archaeology as a scientifically based subject.



A 14,000-year-old burial site being uncovered in the area of the Aswan Reservoir in Sudan. To determine the age of such ancient remains, archaeologists search for every scrap of associated wood or charcoal that could be used for age measurement of the isotope carbon-14.

Nuclear techniques can also help answer other important questions for archaeologists. These questions are concerned with where things were made, how they were made, and how tools, techniques, objects, and information were disseminated among the peoples of the earth. The answers to such

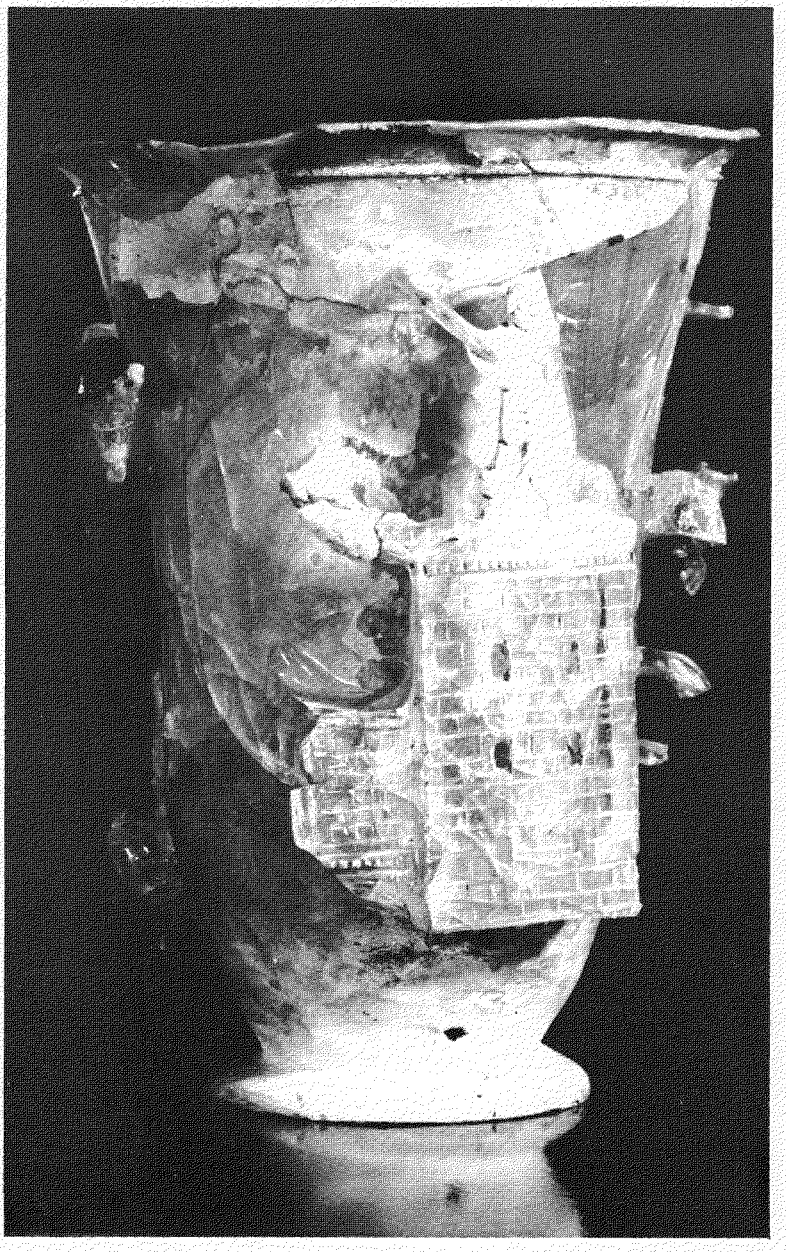


Typical samples for analysis. The large tube contains a quantity of sam ple needed to measure 0.1% of a minor component in it when ordinary chemical procedures are used. More modern methods can measure concentrations far lower than that in the sample at the bottom of the tiny gelatin capsule in the photograph.

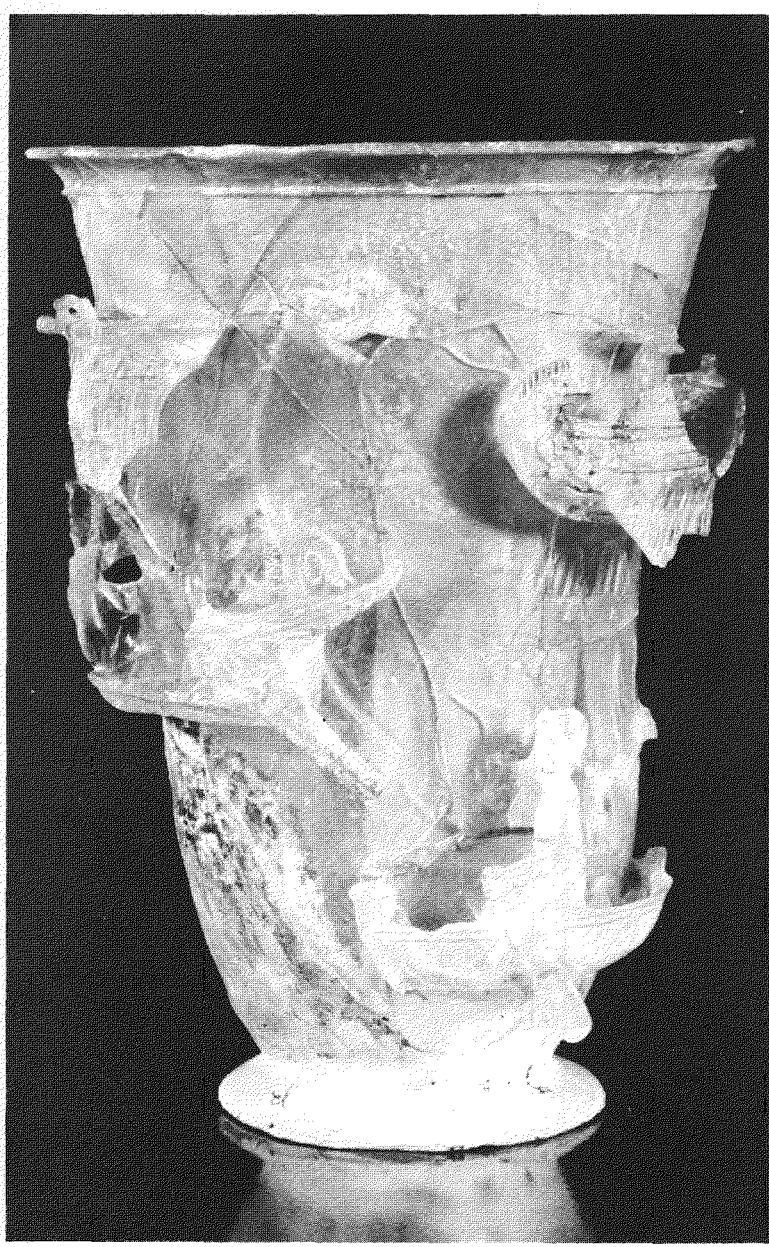
questions can tell us a great deal about the lives and times of our ancestors.

A completely detailed list of materials of archaeological interest would be quite varied. However, most of these can be classed as wood, stone, metals, bone, pottery, textiles, or glass. Many of these materials have been further classified by ordinary chemical analyses, by style, and by the location in which the objects were found.

Nuclear techniques can now provide factual evidence to help classify collections of objects as well as accurate information on dates of production or ultimate geographical source. Of particular value is the fact that such new techniques provide chemical analyses of samples that are much smaller than those required previously. In the past, objects might have been disfigured or destroyed by older techniques that required larger samples.



The sea god Poseidon stands on the Lighthouse of Alexandria, Egypt, one of the wonders of the ancient world. Boats ply the opposite side of this 7½-inch-high glass beaker, which

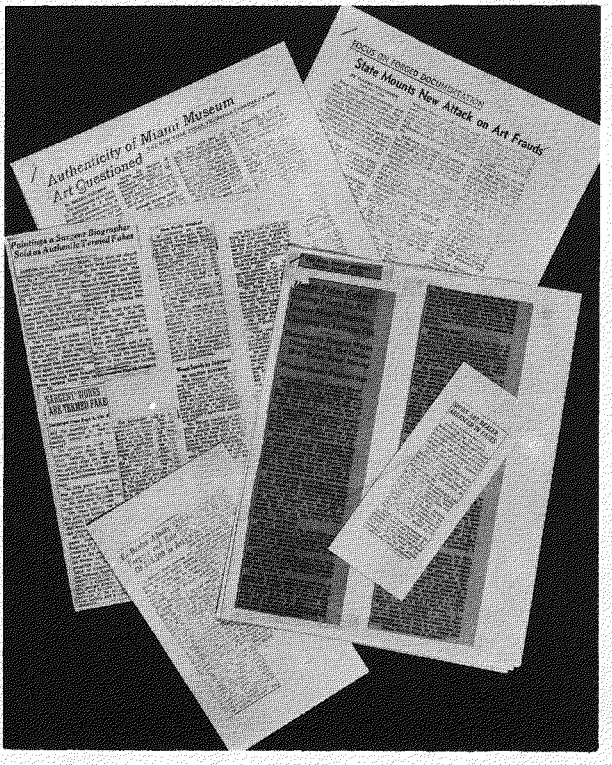


was found in Begram, Afghanistan. Emission spectroscopy analysis indicates that this 1700-year-old object was made in the upper Euphrates Valley.

ART: THE NEED FOR ACCURATE IDENTIFICATION

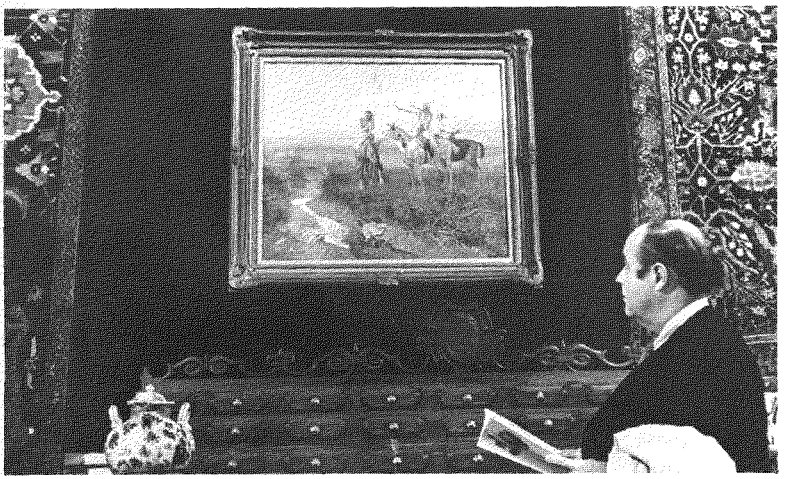
Our newspapers often describe the sale of a single painting for hundreds of thousands, or even millions, of dollars. The sale of works of art amounts to hundreds of millions of dollars annually. No one knows how much of this business involves fakes and forgeries. Occasionally, an important case becomes public, but this is only the tip of the iceberg.

There was a time, hundreds of years ago, when a copy of a painting was valued as much as the original. However, many

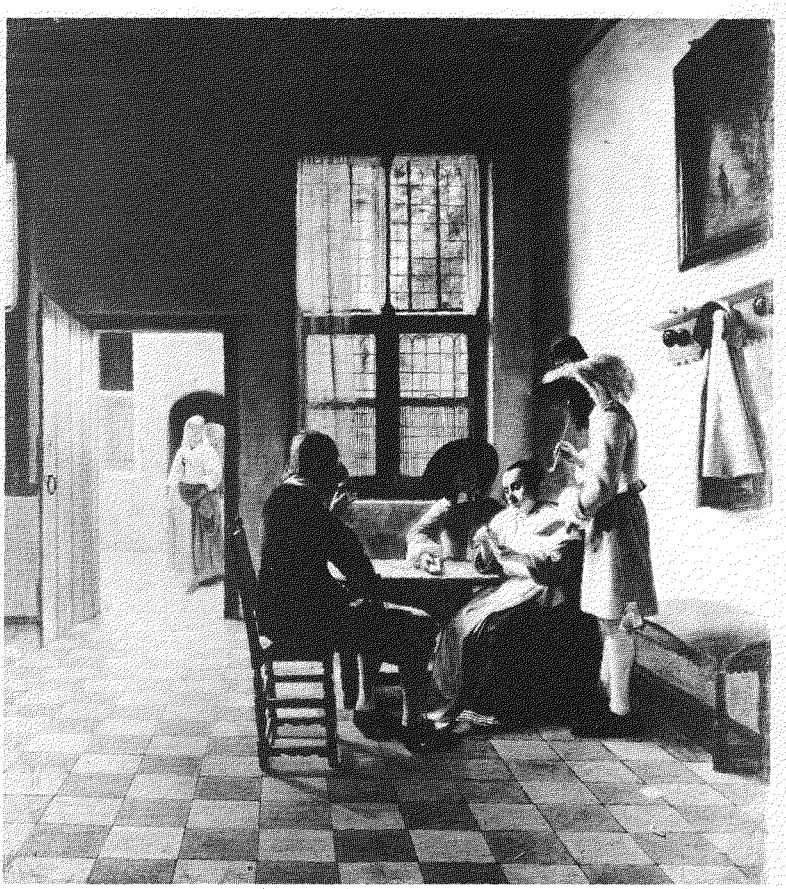


A selection of newspaper clippings. These are a sampling of the "sensational" stories that have been published in the last few years. Many more such stories were made public and still more occurred but were not publicized.

of today's "collectors" collect the artist *not* the painting. That is, they do not necessarily buy something because they like it, but only because they believe they are buying quality in a signature.



Above, a collector of Western American art examines a Charles M. Russell painting, "The Sun Worshipers", which sold for $75,000 in 1971. Below, at Philadelphia's Freeman Gallery another Russell painting, "A Range Mother", is sold at auction for $90,000.



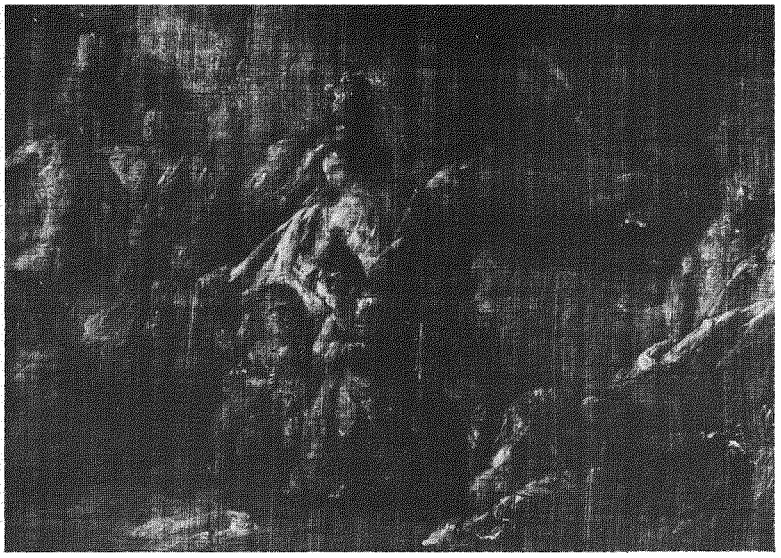
An authentic Pieter de Hooch work, "The Card Players", painted in the 17th century.

A forgery of a Pieter de Hooch picture painted in the 20th century by Han Van Meegeren. *(See pages 79-86.)*

Photograph (above) and X-radiograph (right) of an 18th-century German oil painting. Such X-radiographs enhance the senses of the art expert by making visible the underlying

While this situation has worsened with the recent expansion of the market, forgeries have been produced and sold whenever customers were available. Realizing this, the prudent buyer consults experts whose opinion regarding authenticity is much sought after. Today, as in the past, visual judgment is often enough to detect anything but the most painstaking forgery. Gradually, during the early part of the 20th century, various practical and scientific aids were also applied; X rays to make the artists' brushwork visible, solvent tests to determine whether an oil paint is as hard as its alleged age would require, and finally, the identification of the pigments and other materials of the work to determine whether the alleged artist could have produced the questioned work.

Unfortunately, the clever forger learned these methods as quickly as the experts and also learned to produce work that could pass the battery of tests. For example, he learned to use chemicals and heat to harden the paint in weeks instead of years, and paid careful attention to the techniques and materials of the artist whose work he was imitating.

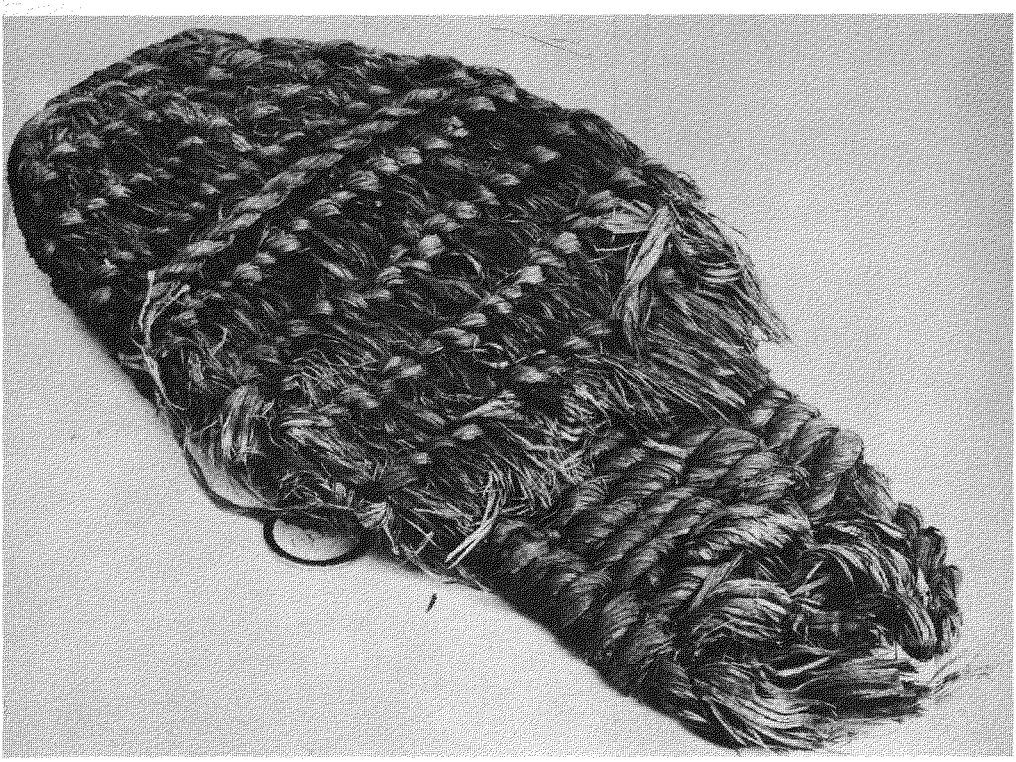


structure of the work. However, he must still rely on his judgment as to the authenticity of the work.

The question is often raised: If a forgery is so fine that it *can't* be distinguished from the real thing, isn't it just as good? There are many moral and aesthetic reasons regarding why it isn't just as good, but one practical reason involves the interest that the Internal Revenue Service has in works of art. Because of the U. S. income tax laws, works of art, bought cheaply (perhaps because they are forgeries) and donated to museums or galleries, can cost our government a large amount in revenue that otherwise would have been collected from persons with very high incomes. In 1965, for example, the total dollar value of contributions of art taken as income tax deductions was in excess of $140,000,000! What part of that involved the passing on of forgeries is unknown but was probably considerable.

The development of new tools for the identification of works of art thus has a practical as well as a moral purpose. The nuclear age has given birth to some new methods that are foolproof unless techniques are used which are so costly that the forger will eventually be discouraged.

One of a pair of 300 pairs of rope sandals found in an Eastern Oregon cave. Carbon dating revealed that they are about 9000 years old.



Nuclear Techniques in Archaeology

DATING

Carbon-14

One cannot possibly overemphasize the importance of carbon-14 dating in the field of archaeology since its discovery shortly after World War II. In spite of its limitations, its impact can be compared to that of the discovery of the periodicity of the elements in the field of chemistry. The importance of the method was recognized immediately and, in 1960, earned for its discoverer, Willard F. Libby, the Nobel Prize.

The reasoning behind the method is this. The earth is being continually bathed in cosmic radiation.* One product of that radiation, a quantity of neutrons,† reacts with nitrogen in the upper atmosphere to produce carbon-14, thus:

$$^{14}\mathrm{N}\begin{pmatrix}\text{7 protons}\\ \text{7 neutrons}\end{pmatrix} + \text{one neutron} \rightarrow {}^{14}\mathrm{C}\begin{pmatrix}\text{6 protons}\\ \text{8 neutrons}\end{pmatrix} + \text{one proton}$$

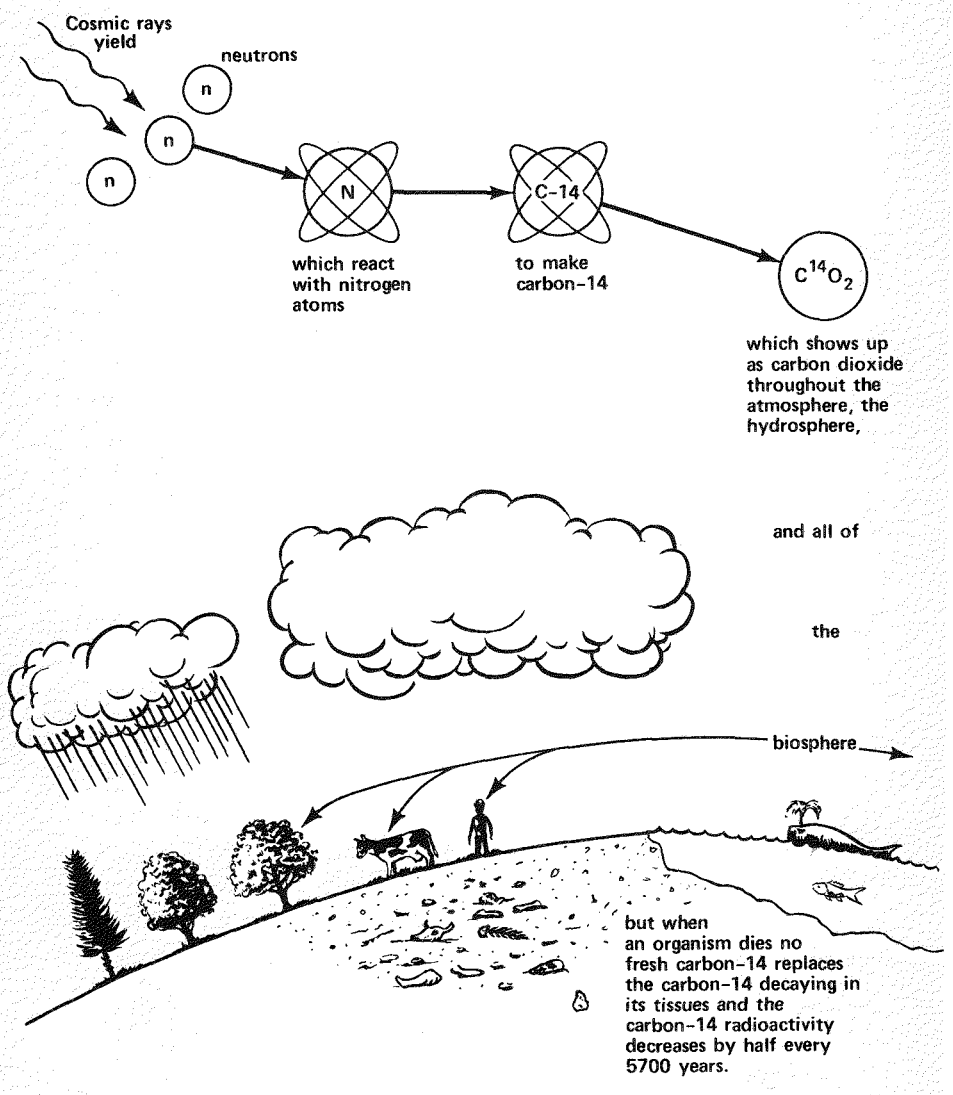
Since the flux of neutrons has been nearly constant for the last several thousand years, the rate at which carbon-14 has been produced by this means has been just as constant.

The carbon-14 atoms react chemically with oxygen to form carbon dioxide, which eventually mixes, throughout the atmosphere, with ordinary carbon dioxide. (Ordinary carbon atoms contain 6 protons and 6 neutrons and are not

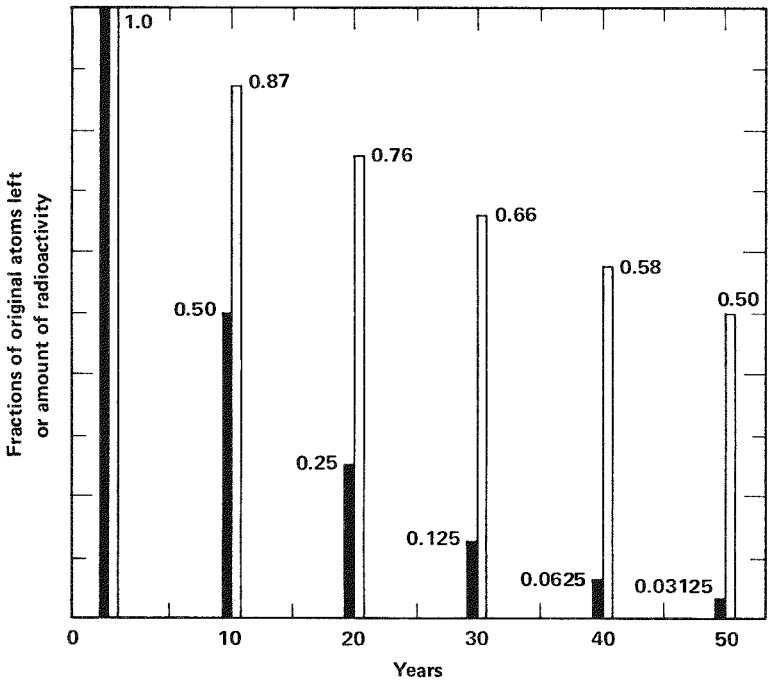
*See *Space Radiation*, another booklet in this series.

†For definitions of this and other "nuclear" words used here, see *Nuclear Terms, A Brief Glossary*, another booklet in this series.

radioactive.) Carbon dioxide in our atmosphere is incorporated into living tissue by growing vegetation. Animals that eat vegetation, and the animals that eat vegetarians, etc., also eventually contain carbon-14.



Carbon-14 dating.



Half-life of radioactive isotopes. The graph shows the decreasing radioactivity of two different isotopes over a period of 50 years. The open bars show this decrease for one with a half-life of 50 years while the dark bars are for a 10-year half-life.

The end result is that all living things (the biosphere) must contain carbon-14 in the same concentration that occurs in the atmosphere during their lifetime. But carbon-14 has a *half-life* of about 6000 years*, and when an organism dies and ceases to participate in the biosphere, its carbon-14 supply is no longer being replenished by freshly produced carbon-14 through the food chain. The concentration of carbon-14 in its tissues thus begins to decrease.

The nature of radioactivity is such that we may express the rate at which a radioactive substance disappears in terms

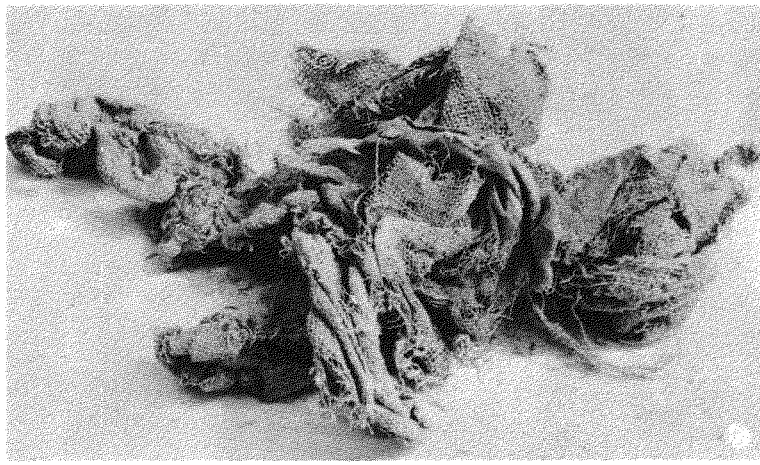
*Actually 5730 years.

of its half-life. In this case, it means that after 6000 years, one-half of the carbon-14 atoms will have disappeared. After a second 6000 years, half of that remaining after the first 6000 will have disappeared, or *three-quarters* of the original number will be gone.

Up to about 1900* the concentration of carbon-14 in our atmosphere and biosphere was such that the radioactivity of each gram of carbon was about 15 disintegrations per minute (dpm). This way of expressing radioactivity, dpm per gram, is called "specific activity". Put another way, for our present case, 15 dpm per gram means that in among the 5×10^{22} (50 thousand million million million) atoms of carbon-12 in 1 gram, there are about 6.5×10^{11} (650 billion) atoms of carbon-14 of which 15 "disappear" by radioactive decay each minute.

Thus, 6000 years after an organism dies, the carbon-14 specific activity will be 7.5 dpm per gram; in 12,000 years, it will be 3.75 dpm per gram, and so on. By using large samples

*Since 1900, man has disturbed the natural supply of carbon-14 in various ways; more of this later.



Carbon-14 dated this linen wrapping from the Dead Sea Scroll containing the Book of Isaiah at about 1900 years.

(if they are available!) and efficient instruments for measuring the radioactivity, it has been possible to date objects made of wood, for example, that are as much as 50,000 years old. Most carbon-14 dating, however, is done on objects that are no more than 10,000 to 15,000 years old.

Most of the objects dated by this method are made of wood. It is also possible to date objects of bone, textiles, ivory, and iron. (It is possible to date iron because iron contains a few percent of carbon which, in old samples, came from wood charcoal.)

While Dr. Libby in his original work used a device to measure the radioactivity of carbon-14 called a "screen-wall counter", nearly all the measurements made today are obtained with one of two more modern instruments. These are the *gas proportional counter* and the *liquid scintillation counter.*

The choice of which one of these to use depends to a great extent on the size of the sample available. The problem is that in any device for measuring radioactivity, there is a "background" that is due to natural radiation.* In other words, even with no carbon-14 present, a small amount of radioactivity will be detected.

The gas proportional counter has the advantage of having a low background. This is obtained by using a massive steel or lead shield and an electronic "trick" called anticoincidence counting. The counter itself consists of a tube, usually metal, down the center of which is strung a fine wire that is charged to a high voltage. The sample is introduced in the form of a gas produced from the carbon in the sample. This gas is usually either carbon dioxide or methane (a carbon-hydrogen compound, CH_4). When carbon-14 in the sample decays, the radiation it emits produces free electrons in the gas. These electrons are collected by the wire where an electrical pulse is generated.

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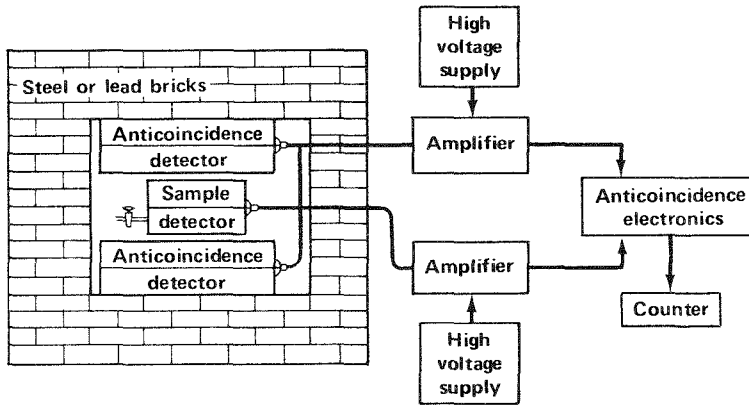
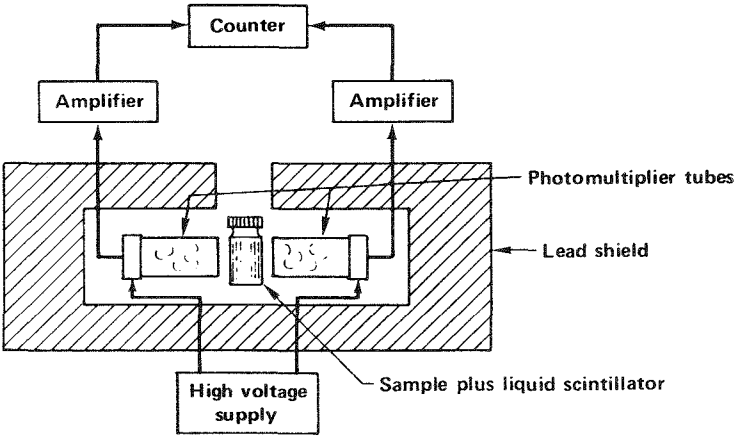
*See *Nature's Invisible Rays,* another booklet in this series.



A gas proportional counting system for the measurement of small amounts of carbon-14. A sample, prepared in the form of carbon dioxide or methane, is used to fill the sample detector in the center of the shield. While the shield protects the detector from much of the natural radiation from materials in the laboratory or cosmic rays (background radiation), it is also necessary to use the anticoincidence system shown. This works by automatically cancelling the detection of any radiation that comes from the outside and thus triggers an anticoincidence detector and the sample detector at the same moment. Actually the system is not perfect and a small amount of the background gets through.

An anticoincidence counter is arranged to completely surround the sample counter. Then any radiation detected in both counters at the same time is automatically eliminated from the count because it must have originated *outside* the carbon-14 counter. The disadvantage of the gas proportional counter is that it must be made quite large to accommodate a large sample since the gas is of a relatively low density. And when the counter becomes large, the background goes up, the shield and anticoincidence counter become still larger and the advantages are generally outweighed by these factors.

The liquid scintillation counter, on the other hand, cannot be made to have a low background but can handle



A liquid scintillation counter used for carbon-14 measurements. The sample is combined with a mixture of chemicals that emits flashes of light (scintillations) when radiation passes through it. The flashes are detected and converted into electrical pulses by photomultiplier tubes that "look" at the bottle of liquid. Because the sample is in the form of a liquid (much denser than a gas) far more sample can be placed in this counter than in a gas-filled counter. Below, a sample bottle is about to be lowered into the counter so that it can be "looked at" by the photomultiplier tubes. Another is resting on the rim of the shield. The entire assembly is in a freezer cabinet because cold temperatures reduce the electronic "noise" that may interfere with the measurement.

large samples quite easily. In this system, the carbon in the sample is chemically converted to an organic liquid like benzene. Other special chemicals are then dissolved in the benzene. These special chemicals have the property of emitting flashes of light (scintillations) when radiation passes through them. The solutions are placed in clear glass or plastic bottles that are monitored with one or more special electronic tubes called photomultipliers. These convert the scintillations into pulses of electricity that can be measured. Low backgrounds cannot be obtained because there is a certain minimum amount of *electrical* "noise" in this system that is always present. Nevertheless, for large samples, this disadvantage is overcome because the liquid is a relatively dense physical state.

Thousands of measurements have now been made and all sorts of additional refinements to the techniques mentioned above have been developed.* The measurements are not easily made, but the information gained is certainly worth the effort. Unfortunately, the types of materials on which carbon-14 dating can be used are usually not very durable. Thus, other methods have been developed and applied and still others will be sought in the future.

Thermoluminescence

In 1960 George C. Kennedy first used radiation-induced thermoluminescence for the dating of ceramics of archaeological interest. This method was eventually refined by workers at Oxford University and at the University of Pennsylvania and has become an extremely valuable tool. One reason it is so valuable is because bits of pottery (called potsherds), which are quite durable, are almost always found at "digs", or archaeological sites.

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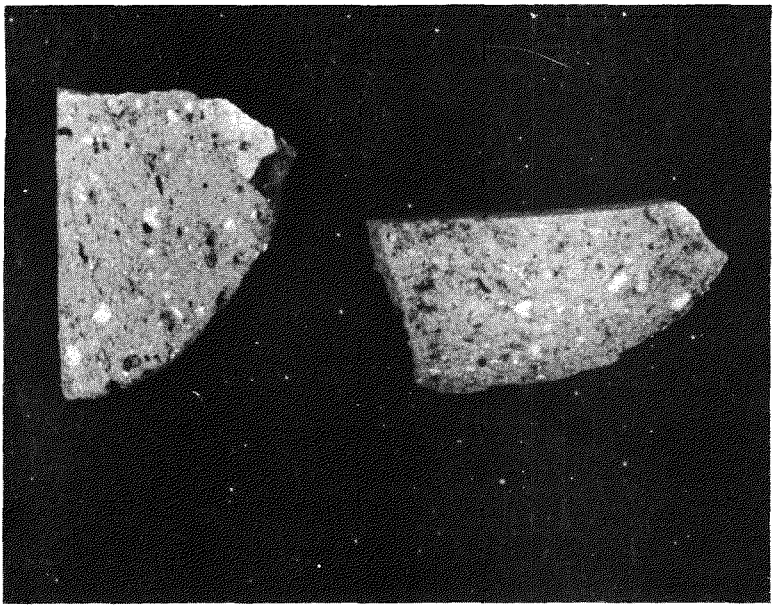
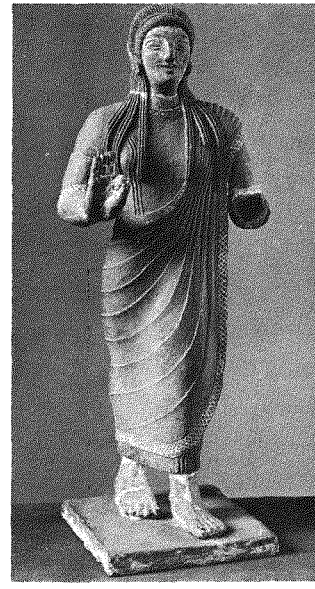
*For more detail on carbon-14 dating, see *Nuclear Clocks*, a companion booklet in this series.

The method itself is based on the principle that radiation distorts the electronic structure of insulating materials and so stores energy within the material. This process may be likened to the stretching of a spring. When the material is heated to a certain temperature the forces holding the electrons "out of place" begin to "loosen", the structure relaxes as a stretched spring would, and the stored energy is released. This released energy is emitted in the form of light. The radiation that produces this deformation comes mainly from naturally radioactive materials like uranium, thorium, and potassium, which are present in the pottery in low concentrations. The soil in which the pottery was buried also contains naturally radioactive material that affects the pottery in the same way. Cosmic radiation also contributes to the radiation "damage".

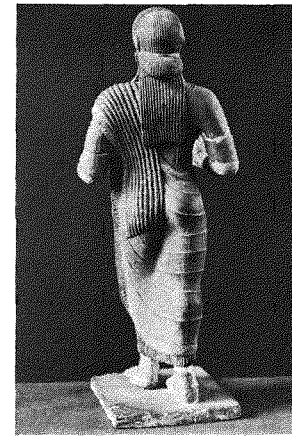
As time passes, more and more energy is stored in the material and thus the system acts like a clock. The clock is



Samples of potsherds excavated at Drake's Bay, California.



A terra-cotta statuette originally thought to be of Etruscan origin between 510 and 490 B.C. Chemical tests revealed that the statue could have been made in Italy, but did not give any hints as to its age. After the statue was placed on display, a number of art historians suspected that it was a fake based on the hair style, the draping of the chiton, the scale, and the thickness of the plinth. Thermoluminescence dating disclosed that the statue was of modern origin.



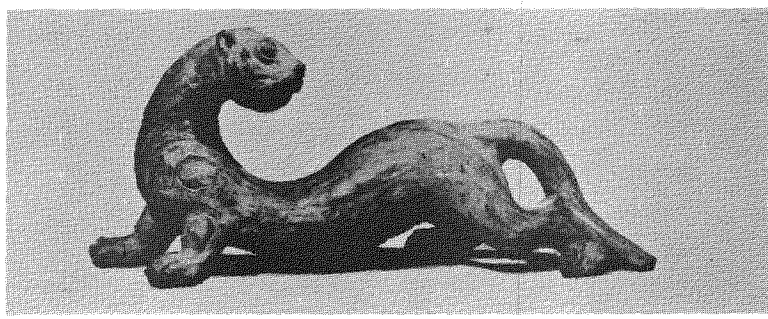
started at "zero", which is the last time the material was heated to the temperature at which the system "relaxes" (a process called annealing). In the case of pottery, this is the time when the pottery was baked as the final step in the manufacturing process.

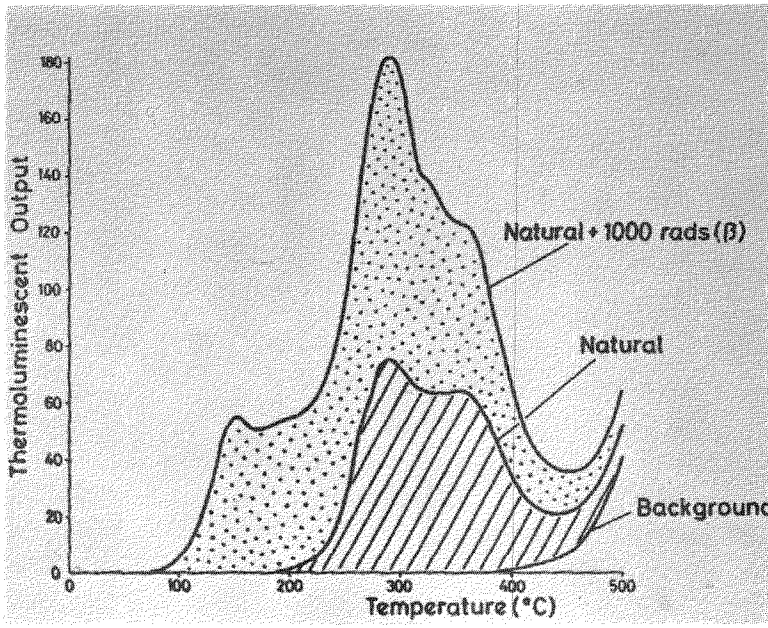
To read the clock for a potsherd years after it was started, one must know or measure at least three important things.

1. How much radiation "ran the clock" since it was started. This information is obtained by measuring the radioactive constituents of a sample of the potsherd and the soil in which it was buried, estimating the small contribution of cosmic radiation, and calculating an annual radiation dose.

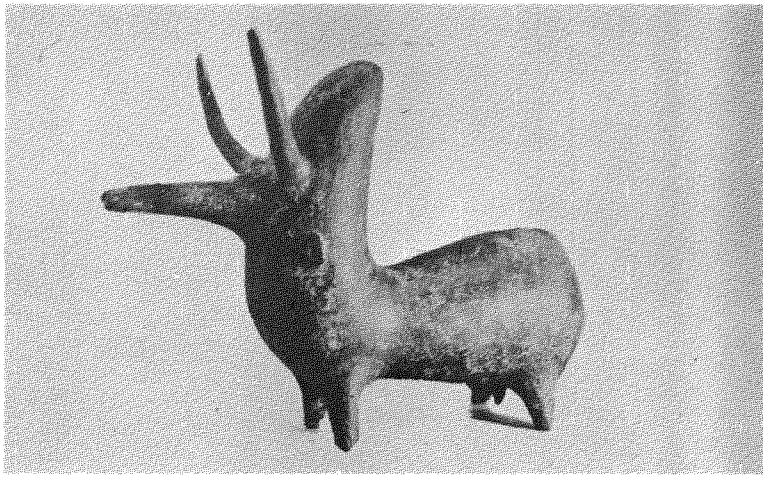
2. The amount of energy stored in the sample must be measured. To measure this, a small amount of very fine powder taken from the sample is spread in a very thin layer and attached to a block of metal. A light-measuring device (called a photomultiplier) is set up so that it faces the sample. The metal block is then electrically heated so that its temperature (and that of the sample) rises slowly and steadily. The temperature and the light emitted are continuously measured and recorded to give a thermoluminescence curve. Any material that is heated begins to emit light, or glow, when it gets hot enough. The trick here is to measure the *extra* light emitted by the pottery. (See the curves in the figure on the next two pages.) The shaded area between the curves represents the radiation-induced thermoluminescence.

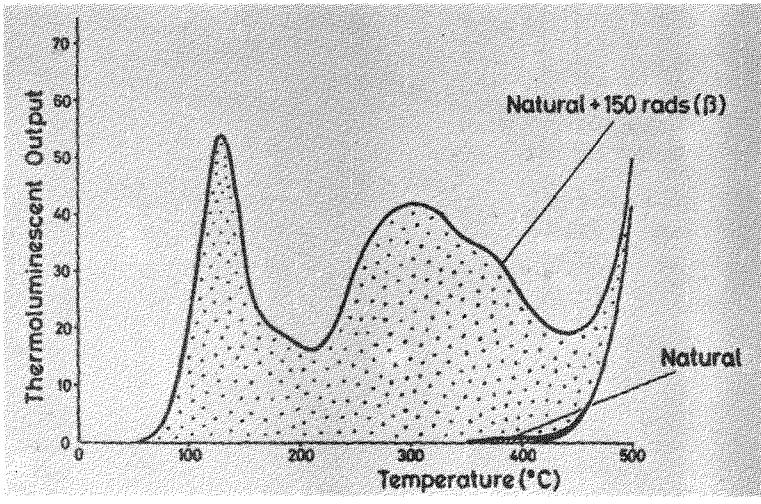
3. The susceptibility of the sample for radiation-induced thermoluminescence. This is determined by measuring the artificially induced thermoluminescence produced by irradiating the sample with a *known* quantity of radiation after the original measurement is complete.



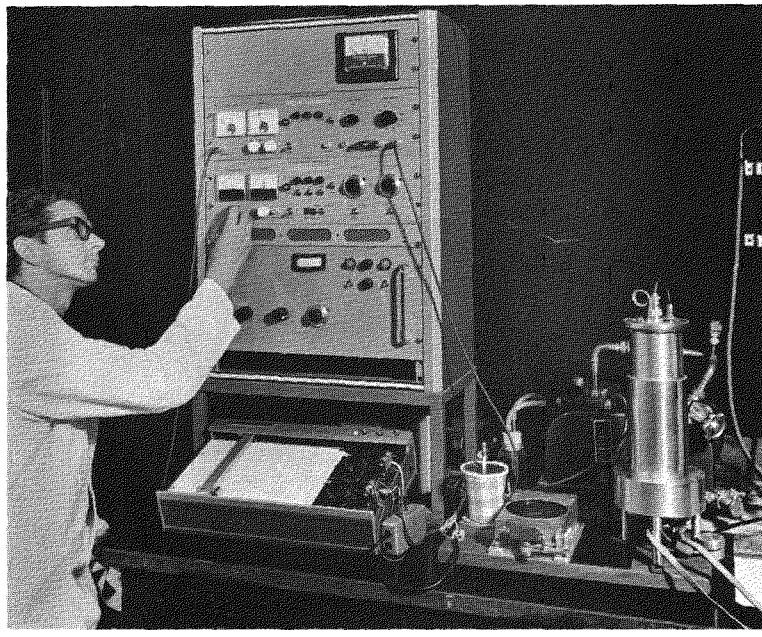


Thermoluminescence curves of two objects. The graphs show the light output obtained from samples taken from the two objects above them. The lowest curve in each case is the light output from a sample of material that yields no thermoluminescence (the background). The middle curve shows the light output when the sample itself is heated. The top curve is obtained from the same sample after it had been exposed to the known amount of radiation indicated in the diagram. For the object on the left, it required quite a bit of radiation to produce the natural effect depicted by the hatched area. For





the object on the right very little natural thermoluminescence was obtained even though the induced thermoluminescence (dotted area) was considerable. Hence the object on the left is old and that on the right is of relatively recent manufacture. Exact dating also requires an estimate of the rate of natural radiation received by the object during its lifetime. This is determined by measuring the amount of radioactive minerals present in the object and in the soil in which it was found buried.



Thermoluminescence dating equipment. The large cylinder on the right contains a temperature-controlled oven and a photomultiplier tube. As the sample is slowly heated through a controlled temperature range, the light output is measured and plotted on the chart recorder (lower left) as a function of the temperature.

Relating these three factors in an equation such as:

$$\text{Age} = \frac{\text{radiation dose per year}}{\text{natural thermoluminescence} \times \dfrac{\text{artificial dose}}{\text{artificial thermoluminescence}}}$$

gives the age of the piece.

It takes careful work and attention to detail to obtain an accurate date by this method. For example, the sample must be powdered carefully because grinding it too hard and fast may heat it enough to emit light prematurely. Nevertheless, the techniques have been worked out, and quite a number of dating problems have been solved in this way.

Other ceramic items besides potsherds can and have been dated. Terra-cotta statuary and ceramic figures have also been analyzed, and forgeries have sometimes turned up.

Fission-Track Studies

Another dating method based upon radiation damage was developed by Robert L. Fleischer, P. Buford Price, and Robert M. Walker at General Electric and Washington University in the early 1960s. In this case, advantage is taken of the fact that uranium-238, one of the natural isotopes of uranium, occasionally splits into two parts just as uranium-235 does in a nuclear reactor. This spontaneous fission, as it is called, occurs only rarely, however. For example, in every million years only 84 out of a million million ^{238}U atoms in a rock sample will fission. Counting these will yield the age of the rock.*

Whenever a fission occurs in a rock or piece of pottery, the two parts of the split atom leave a tiny trail of damage in the crystal structure of the material. If this happens close to the surface of the specimen, the trail will penetrate the surface and can then be detected in the following manner.

A small area of a thin slice of a specimen to be dated is cleaned and polished. This area can be as small as 1 millimeter square or even smaller. Then, for a short time, a chemical solution is applied that attacks the surface and begins to dissolve away the substance. The kind of chemical and the time it is allowed to remain on the surface for this etching process depend on the material.

After a while, the tracks become enlarged to such size that they can be observed with an ordinary microscope. By counting these holes, or etch pits, in a known area, one obtains the number of fissions that occurred in that area since the rock was formed or since the pottery was fired.

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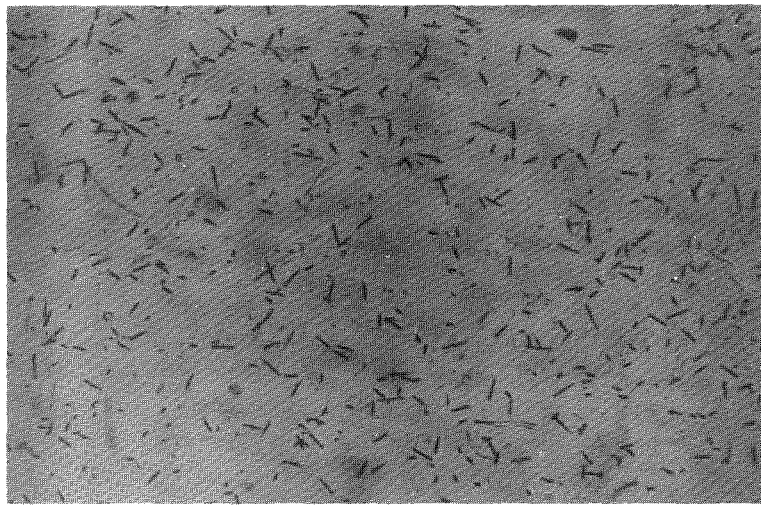
*See *Nuclear Clocks*, a companion booklet in this series.



Tracks of uranium fission from a fossil antelope bone fragment from Hopefield, Cape Province, South Africa.

(Just as in the case of thermoluminescence dating, annealing the material by heating it to an elevated temperature repairs the radiation damage.)

The next step in the method is to determine how much uranium is present in the area where the tracks were counted. By irradiating the specimen with a known quantity of neutrons in a nuclear reactor, one can cause the uranium-235 atoms to fission. Because the ^{235}U is always present in the same proportion to the ^{238}U, the number of new fission tracks in the area previously observed is a measure of the amount of ^{238}U in that area and may be easily calculated.

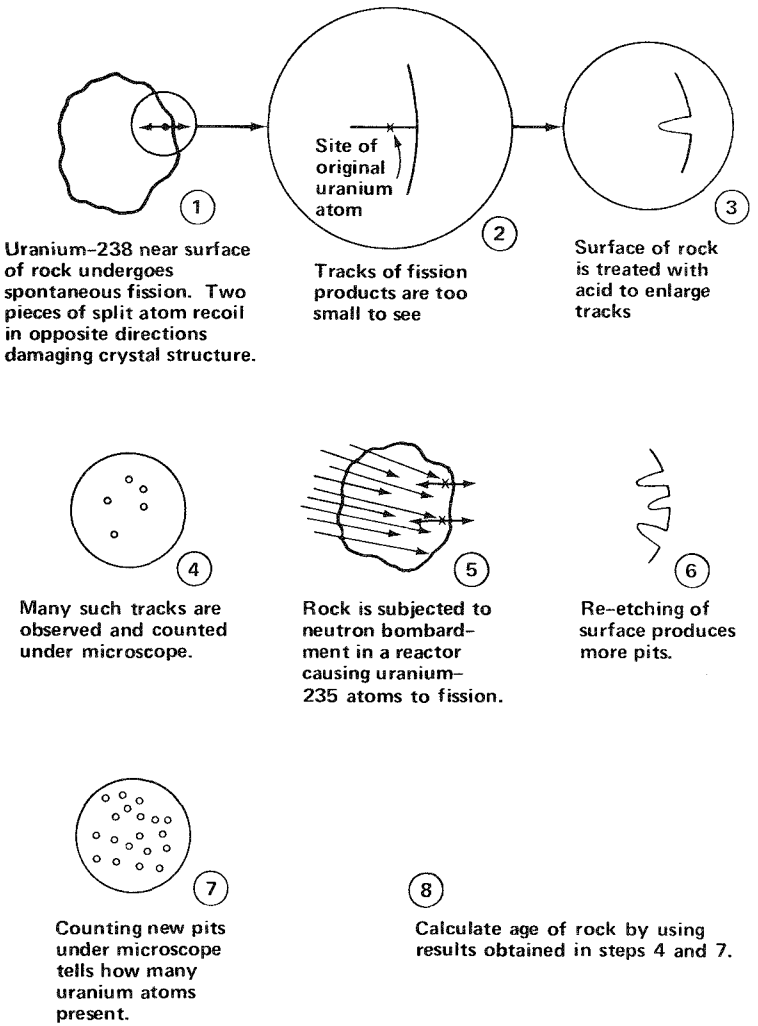
Then, the following equation may be used to calculate the age of a potsherd:

$$t = \frac{N_t}{N_u} \times 1.2 \times 10^{16}$$

where t is the time since the specimen was fired, N_t is the number of natural tracks observed in a given area, N_u is the

number of ^{238}U atoms in that same area, and 1.2×10^{16} is a constant related to the known rate of spontaneous fission of ^{238}U.

Usually the accuracy of this dating method depends on the number of natural tracks that can be observed, which, in



Fission-track dating.

turn, of course, depends on the age of the object and the amount of uranium it contains. Most rock and clay contain between 1 and 100 parts per million of uranium; the table below shows the minimum age that can be measured with an uncertainty of 10% in such rocks.

Glass can also be dated in this way, but because glass is a relatively "recent" invention of man, only glass to which uranium has been added deliberately as a coloring agent can be dated. A typical concentration might be approximately 1% and Robert Brill at the Corning Museum of Glass in New York has actually dated samples of glass that are between 20 and 120 years old.

With a uranium concentration of	One can determine* ages as recent as
1 part per million	100,000 years
100 parts per million	1,000 years
1%	10 years

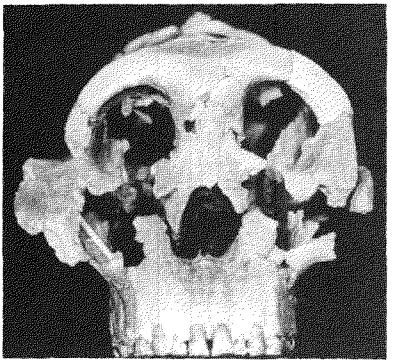
*By counting tracks in 1 square centimeter.

Potassium–Argon

Although this technique is rarely used in archaeological problems, it is included here because it has been used to help establish the oldest evidence of man's existence.* Generally speaking, it is practical only for potassium-bearing rocks that are at least 50,000 to 100,000 years old.

The method is based on the radioactive decay of potassium-40, a naturally occurring isotope with a half-life of approximately 1.5 billion years. As it decays, argon-40, an isotope of a "rare" gas, is produced and is trapped in the rock. The older the rock, the more argon-40 is present. The required measurement is accomplished by melting the rock

*See *Nuclear Clocks*, a companion booklet in this series.



Fossil skull of Zinjanthropus, nearly 2,000,000 years old, discovered in 1959 by Dr. L. S. B. Leakey in Olduvai Gorge, Africa. Accurate dating of this earliest human ancestor was done by the potassium-argon method.

and analyzing the emitted gases for argon-40 and other argon isotopes. A potassium analysis is also required and from the excess argon-40 (compared to the "normal" amount in an ordinary mixture of argon isotopes) and the potassium content, the age of the rock, since it was last melted, can be calculated.

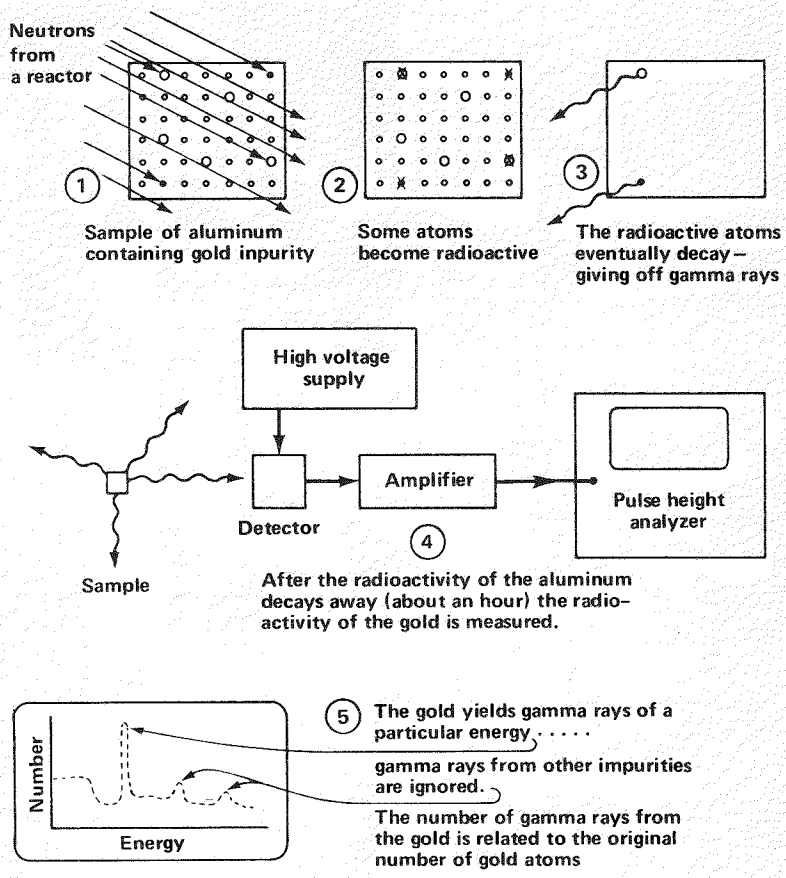
FINGERPRINTING

Neutron Activation Analysis

The term "fingerprinting" is used here to describe unique patterns in some measurable property that occur by accident and may be used to identify a common source of two or more materials. Three methods based on this kind of distinction are described here; there are others.

Neutron activation analysis (NAA) is an extremely sensitive analytical technique by which it is possible to detect and measure small quantities of a great number of elements.* When an element is present in a very low concentration, for example less than 0.01%, it is said to be a "trace" element. Trace elements occur in almost every substance, are usually

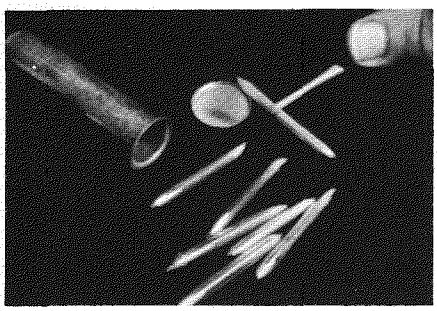
*See *The Atomic Fingerprint: Neutron Activation Analysis*, a companion booklet in this series.

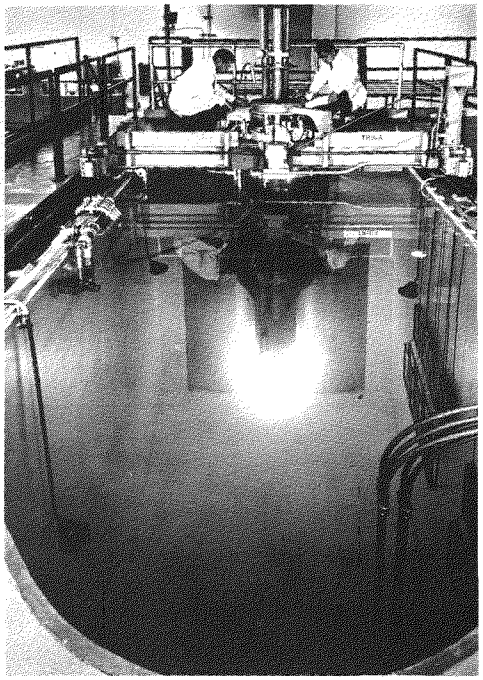


Neutron activation analysis.

present only by accident, and do not affect the useful properties of the substance. The concentrations of such trace elements may constitute a "fingerprint".

The measuring of trace element content of archaeological materials may be useful for the following purposes. The question often arises: Was a certain type of pottery, found in a particular area, produced from locally obtained materials or was it imported from a second area, where similar pottery is found? While the gross chemical properties of clay deposits found in the two areas may be practically indistinguishable,

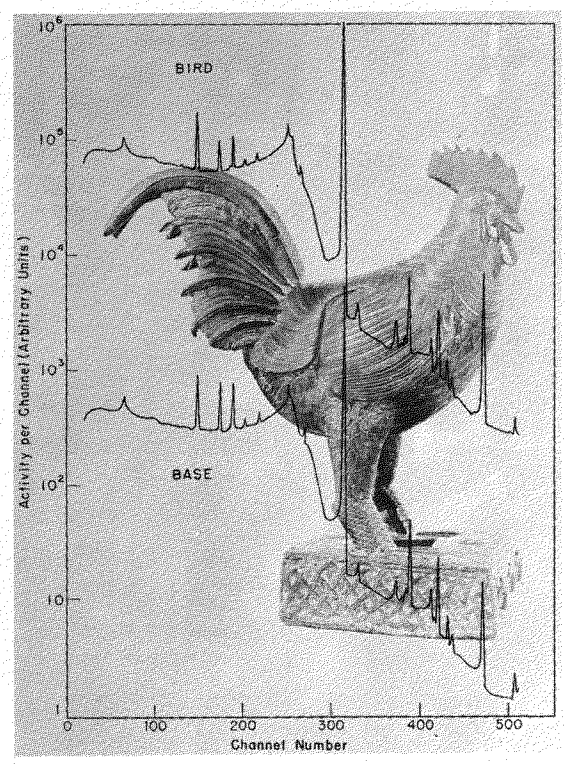




Above, quartz vials containing samples are sealed in the aluminum can on the left. They are then bombarded with neutrons in a reactor like the one on the right.

the chance that the trace element content will be the same is very small. Thus, a comparison between the trace element concentration of the clays and of the pottery found in the two areas should yield an answer to the above question.

While trace elements may be determined by ordinary chemical methods, large samples would be required that might ruin valuable objects. The power of NAA is that such analyses may be obtained using only very small samples. Because NAA does not change the appearance or composition of a subject to any significant degree, it sometimes can be (and has been) used nondestructively. That is, a whole object, such as a coin, may be irradiated and analyzed without the removal of a sample. The main disadvantage to this technique is that the object becomes radioactive and remains so for some time before it can be safely returned to a collection.



Neutron activation analysis of a brass rooster. This 18th-century brass rooster was made by the Benin people in the part of Africa that is now Nigeria. It was constructed of two parts, the bird itself and the base, and a question was raised as to whether the two parts were made by the same people. Superimposed on the photograph are the gamma-ray spectra obtained when samples taken from the two parts were activated by neutrons in a reactor. Notice how similar the shapes of the two spectra are. Each peak represents a gamma ray of a particular energy and can be identified as coming from a particular element in the brass. The height of each gamma ray is related to the quantity of that element present. In all, seven elements were identified and found to be in almost identical concentrations in the two parts of this sculpture. This tends to prove that the two parts, although made separately, were made at the same time and place.

Analysis by neutron activation is performed in the following manner. When the atoms of an element are bombarded by neutrons in a reactor, some of them will absorb a neutron.* In most cases, this will result in some fraction of these atoms becoming radioactive. For example, in the case of sodium:

$$^{23}_{12}\mathrm{Na} + ^{1}_{0}\mathrm{n} \approx ^{24}_{12}\mathrm{Na} + \text{energy}$$

This equation represents the fact that a sodium nucleus with 12 protons and only 11 neutrons absorbs a neutron to become a sodium nucleus with 12 neutrons. The sodium-24 is radioactive and eventually decays:

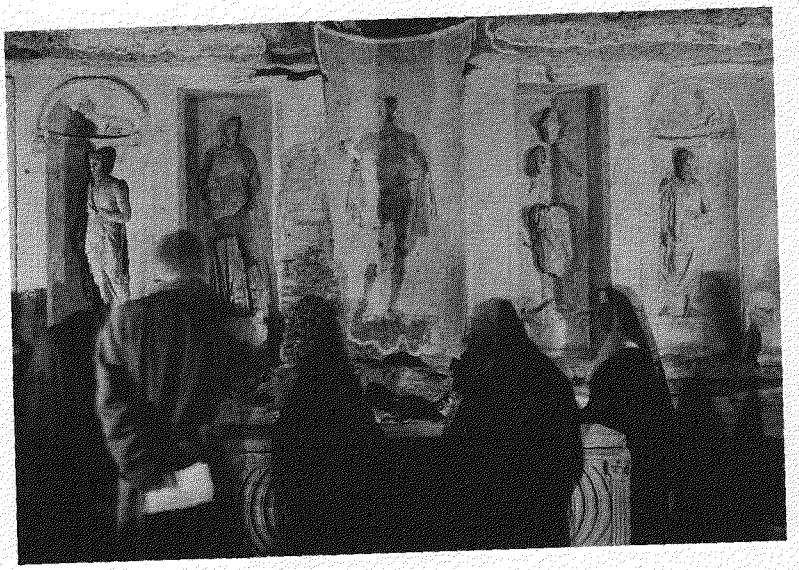
$$^{24}_{12}\mathrm{Na} \rightarrow ^{24}_{13}\mathrm{Mg} + \beta^{-} + \text{energy}$$

Each sodium-24 atom that decays to a magnesium atom (with 13 protons and 11 neutrons) emits a beta particle (β^{-}, a free electron) and energy mostly in the form of gamma rays. The number and energy of the gamma rays is unique for the decay of sodium-24 and thus constitutes a kind of signature. Furthermore, measuring the half-life of the sodium-24 (15 hours) is also a means of identification.

Thus, when a material containing some sodium is irradiated by neutrons in a nuclear reaction, one may (a) show that sodium is present by later observing the energies of gamma rays from sodium-24, and (b) determine how much is present by measuring how many such gamma rays are emitted.

In practice, there are sometimes pitfalls and interferences. Nevertheless, with modern electronic techniques, many ele-

*Other nuclear particles, such as protons or deuterons, as well as high-energy gamma rays or neutrons from sources other than reactors can be used also. The principles are the same as for NAA but one of these techniques might be more convenient or better suited to a particular problem.



Stucco figures line the walls of the 1800-year-old mausoleum of the Valerii, a wealthy Roman family. The tomb is directly beneath St. Peter's Basilica. Outline of the vanished central sculpture suggests the god Apollo. Above, nuns, blurred in a time exposure, move about a marble sarcophagus in the lavish chamber. Below are perfume vials found in the mausoleum during excavations between 1939 and 1950. Neutron activation and emission spectroscopy analysis of the bottles shows components typical of glassware produced in the first century. This seems to bear out the Roman Catholic belief that the grave of the Apostle Peter lies below his basilica. Church tradition holds that St. Peter died a martyr's death in Rome about 64 A.D.

ments can be determined simultaneously without chemical separation of any kind. The sensitivities for many elements are very good, that is, quite small quantities of a particular element can be detected and measured. In some cases (gold, for example), as little as a millionth of a millionth of a gram can be determined.

There have been many applications of NAA to archaeological problems. The first of these was described in 1956 by Edward Sayre and Richard Dodson of Brookhaven National Laboratory. Much work remains to be done. Here are two examples of more recent efforts.

One example of the application of NAA to archaeology by determining trace element distributions may be found in the work of Isidore Perlman and Francesco Asaro at the University of California. These workers have refined their techniques of analysis and data interpretation (using computers) to a remarkable degree and have analyzed over 1000 potsherds. While they admit that much remains to be done, they present some intriguing results obtained on sherds found at certain archaeological sites.

Some of their research involves fragments obtained at two ancient sites in Israel: Tell Ashdod and Tell Eitun, which

are some distance from each other. Three different styles that date from different periods were found at both sites. Their research shows that the Philistine sherds at both places probably came from the same place but that the others, Cypriote and Mycenaean styles, came from various places. (See the table.) It is hoped that further study of sherds originating at possible sources for these unusual samples will reveal something about the nature of the trade routes of the time.

A second example of archaeological problem-solving by the use of NAA involves the source of material for Indian arrowheads made of obsidian. At the University of Michigan, Adon A. Gordus was able to pinpoint the source of the

CONCENTRATIONS OF 20 ELEMENTS IN POTSHERDS FOUND AT TELL ASHDOD AND TELL EITUN AS DETERMINED BY NEUTRON ACTIVATION ANALYSIS

(Parts per million unless shown as percent)

Element	Ashdod Philistine	Eitun Philistine	Eitun Mycenaean	Eitun Cypriote	Ashdod Mycenaean	Ashdod Cypriote
Mn	780	730	800	870	960	780
Na%	0.67	0.71	0.87	0.69	0.59	1.16
U	2.5	2.3	2.5	3.3	2.6	1.34
Lu	0.46	0.45	0.51	0.44	0.39	0.38
La	29	28	32	43	32	9.1
Ti%	0.67	0.63	0.66	0.50	0.44	0.34
Sb	0.40	0.34	0.45	0.71	0.88	0.23
As	4.5	4.9	3.8	8.3	2.3	1.3
Fe%	3.86	3.70	4.0	4.8	5.3	6.3
Sc	12.8	13.0	13.7	18.8	21.4	37
Co	19	17	18	23	29	34
Ta	1.20	1.14	1.13	1.31	0.02	0.36
Cs	1.6	1.6	1.8	7.9	9.2	0.68
Cr	126	117	127	154	251	186
Hf	13	12	11	5.2	3.9	22
Th	8.0	7.3	7.8	13.8	112	2.5
Ba	390	560	370	380	375	145
Rb	53	53	51	150	158	31
Zn	142	140	210	209	292	262
Ca%	6	7	10	3.6	11	4

material used by the Hopewell Indians, a group that inhabited what is now Ohio, Indiana, Illinois, Michigan, and Wisconsin during the period 300 B.C. to 500 A.D.

The puzzle was that while obsidian arrowheads were found in Hopewell burial mounds, the closest sources of that material are in the Western U. S., Mexico, and Alaska.

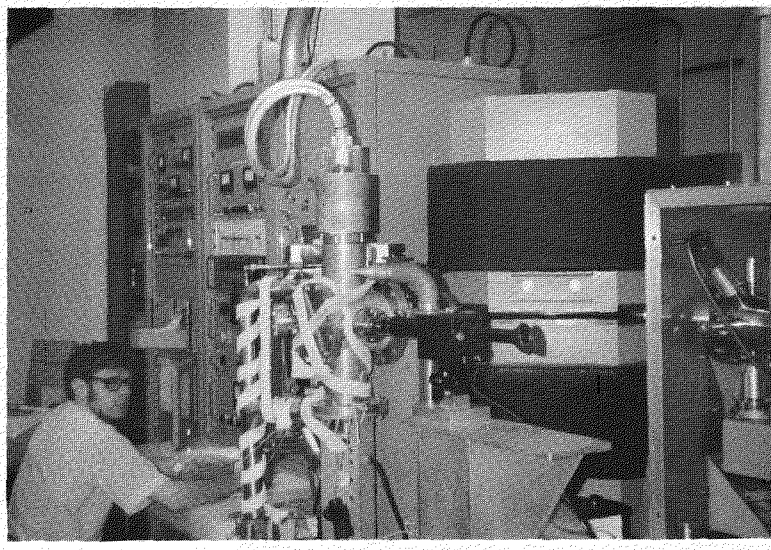
Using NAA, Gordus analyzed the arrowheads and the obsidian from all the North American sources for two elements, sodium and manganese. He found that only three sources contained these two elements in concentrations similar to those of the arrowheads. He then used NAA to check approximately 15 other elements in these sources and found that only the composition of obsidian from one source, Obsidian Cliff in Yellowstone National Park, corresponded to the composition of the arrowheads.

Spark Source Mass Spectrometry

At the Los Angeles County Art Museum, Thomas J. Cairns uses another technique to examine artifacts for patterns of trace element concentrations. While the general idea of obtaining "fingerprints" is the same, this relatively recently developed method of measurement is quite different; a spark-source mass spectrometer is used.

In this machine, a sample from an artifact, let us say a tiny metal chip, is subjected to a very hot, electrically produced spark. With this treatment, a small part of the metal is vaporized and the individual atoms become electrically charged or ionized. This process takes place at one end of a curved metal tube that has been evacuated to a very low pressure. The metallic ions are accelerated in an electrical field of about 1000–2000 volts in such a way that a narrow beam of ions travels down the tube.

At the point where the tube bends, there is a magnetic field that bends the path of the ions. The important point is that the amount that the path of an ion bends is determined, in part, by its mass. The arrangement produces a separation



A mass spectrometer used to measure lead isotope ratios. In the center is the part of the apparatus where the sample of the lead is ionized. Just to the right of it can be seen the massive magnet that bends the path of the lead ions. At the extreme right is the detector that measures the intensity of each separate beam of ions.

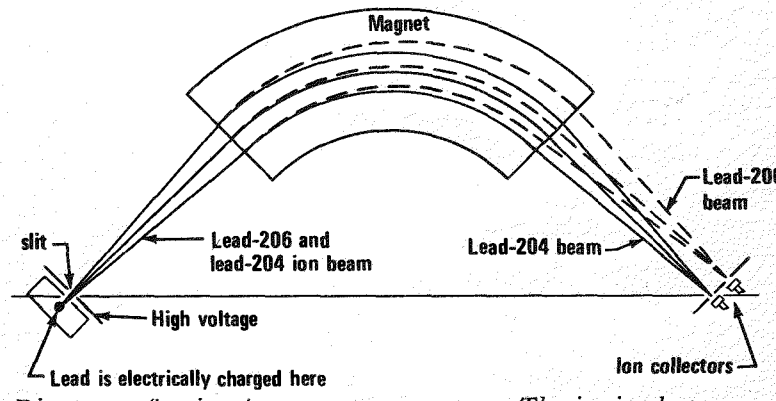


Diagram of a simple mass spectrometer. The ionized atoms of lead travel in a beam at the same speed. The heavier atoms bend less than the lighter ones when the beam passes the magnet. Thus two beams emerge instead of one. Actually there are four isotopes of lead so there will be four beams.

of ions, according to their mass, into numerous beams. The beams eventually strike a photographic plate that, upon developing, shows a series of lines corresponding in position to the masses of the ions which struck the plate. The intensity or blackness of each line is a function of the concentration of the element at that mass number.

Thus, means are at hand to measure the kind and concentration of elements present in a small sample. While there are complications in the interpretation of the mass spectra obtained by this method (for example, there are contributions from more than one element at many mass numbers), it is extremely sensitive and versatile. At the present time, the instrument in Los Angeles is being used to examine a collection of bronzes, having a common source, to determine what patterns of trace element concentrations exist in these items.

Lead Isotope Ratios

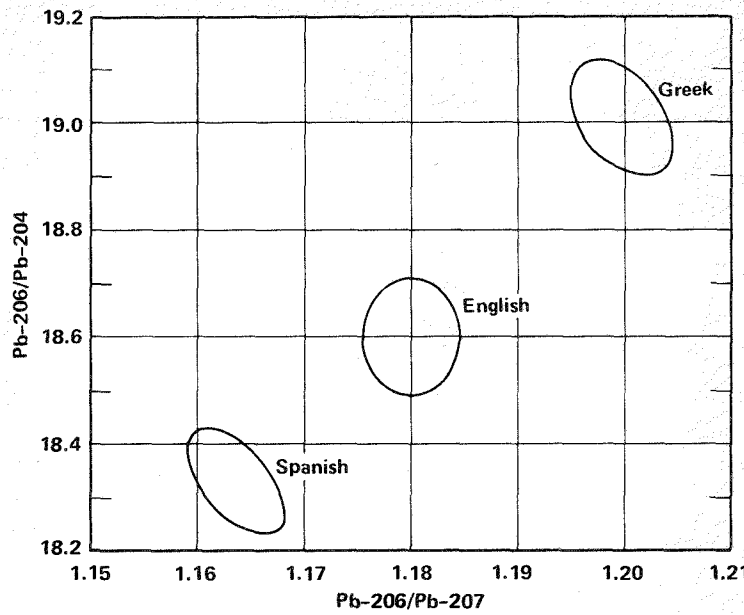
There is another type of information about certain artifacts that can also be used as a kind of "fingerprint".

Lead metal has been used by man in one form or another for thousands of years. It is present in things made mainly of lead, but also as a minor constituent of many alloys including bronze and brass. In addition, glazes containing lead have been used in pottery, and glass sometimes is colored by having lead compounds added to it.

The "fingerprint" for lead is the relative amounts of the four stable (nonradioactive) isotopes of lead found in nature: lead-204, lead-206, lead-207, and lead-208.

While many elements occur in nature as mixtures of two or more isotopes, and a few of these mixtures show variations, only lead occurs with a very large variety of isotope mixtures. The reason is as follows.

Of the four isotopes mentioned above, three are the stable end products of natural radioactive decay series. (One of these is shown in the figure.) The series that end with



Lead isotope ratios for three sources. The diagram shows one convenient way of plotting the ratios of the lead isotopes obtained for three ancient sources of lead. Lead from Spain, England, and Greece will have isotope ratios that fall within the indicated areas on the diagram. While certain other locations might yield ratios similar to these, this kind of information can help pin down the source of an object that contains or is constructed of lead.

lead-206, lead-207, and lead-208, begin with uranium-238, uranium-235, and thorium-232, respectively. The ratios of the lead isotopes in any given lead ore deposit were initially determined by the timing of the geological event that took place when the deposit was being formed. (The age of these deposits may actually be determined from the isotope ratios and other information.*)

The relative amounts of the isotopes in a sample of lead can be determined with a mass spectrometer that is similar in

*The dating of rock by this method is described in *Nuclear Clocks*, a companion booklet in this series.

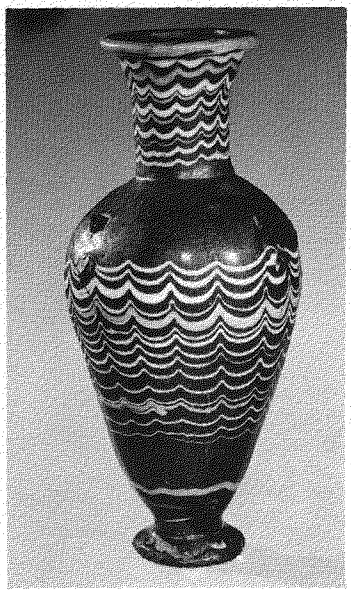
operation to that described for spark-source mass spectrometry above. There are some differences, however, because we are now interested in very precise measurements of only four isotopes rather than a whole spectrum. In this instrument, the lead (an almost invisible amount) is usually placed on a wire that is electronically heated so that lead vaporizes and is ionized. The four separated beams, which are obtained, bombard a metal plate one at a time. By slightly varying the beam accelerating voltage to focus each mass on the plate in succession, the number of ions of each mass striking the plate may be measured with a device called an electrometer. With much care and with many refinements, measurements can be reliably made to within a fraction of 1%.

Many measurements have been made by geophysicists on lead ore deposits throughout the world. Robert Brill at the Corning Museum of Glass and N. Grögler at Bern University in Switzerland and their co-workers have used this information and data obtained on archaeological materials to try to determine the source of lead used in some interesting objects.

The Swiss workers, for example, were able to trace the sources of lead used in Roman piping (the earliest known use of lead for this purpose) to various ancient mines in England, Spain, Central Europe, etc., depending on where the pipe was found.

Brill and his co-workers were able to classify the sources of ancient lead used in metallic objects as well as in glass. (In the latter, lead was sometimes added along with other chemicals to produce bright red and yellow opaque glasses.) In his work, Brill found that he could plot the ratios of lead isotopes in a way that grouped the data in clusters, depending on their source. (See the figure.)

While this plot covers only a fraction of the range of ratios found in nature, the ratios obtained from lead coming from some ancient sources are shown. As shown here, the group with the lowest ratios is typical of ore from the Roman workings in Rio Tinto, Spain. The middle group is typical of



Ancient Egyptian glass vessel (circa 1400–1350 B.C.). Some of the light colored threaded decoration is a yellow opaque glass colored with flakes of a lead-containing pigment. Isotope determinations on lead extracted from this pigment in similar glass objects proved that the pigment was made of lead mined locally in Egypt. Lead in similar objects from Mesopotamia contains a different isotopic composition.

Roman mines in England and Wales. The highest group is typical of the famous mines at Laurion in Greece. Ratios similar to these can be obtained from mines in other places, but the information still gives valuable clues as to the source of some objects.

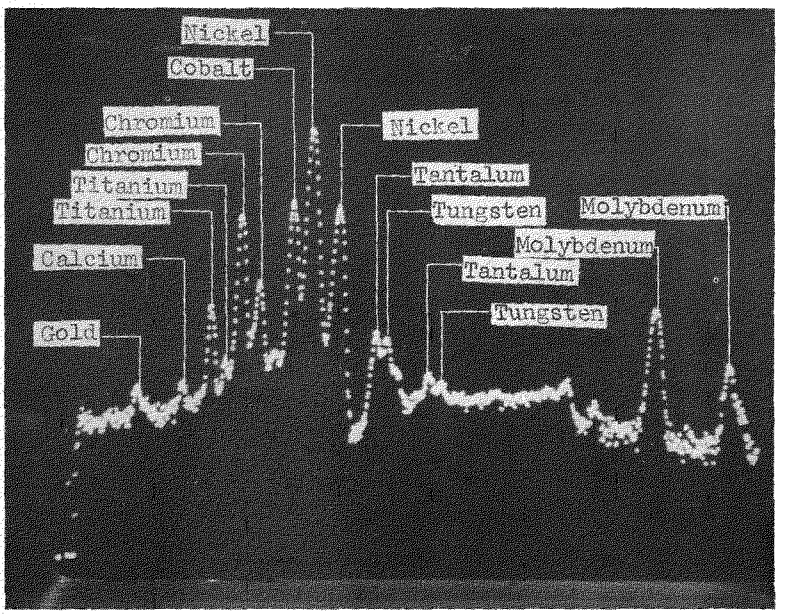
Many of the objects analyzed by Brill fall neatly into one of these groups showing, for example, that a number of artifacts found in Greece were produced from locally obtained materials. On the other hand, some Roman objects found near Florence, Italy, were made of lead that appears to be Spanish in origin.

The main disadvantage in studying lead isotope ratios in archaeological objects is that these ratios are not entirely unique to any given lead mine. However, the method can be used to prove that the lead in an object did *not* come from a particular place. And when the information obtained is used in conjunction with other information (trace element patterns, etc.) it can be quite useful in establishing the ultimate source of material and, indirectly, the trading habits of the peoples who created them.

GENERAL ANALYSIS

X-Ray Fluorescence and Diffraction

While it may often be possible to obtain special answers using the "unusual" methods described thus far, there is often a great deal of information that can and should be gathered using "ordinary" analytical techniques. Thus, in such crafts as metal-working and ceramics, much has been learned about the basic technology of our ancestors simply by using classical chemical analysis on large numbers of

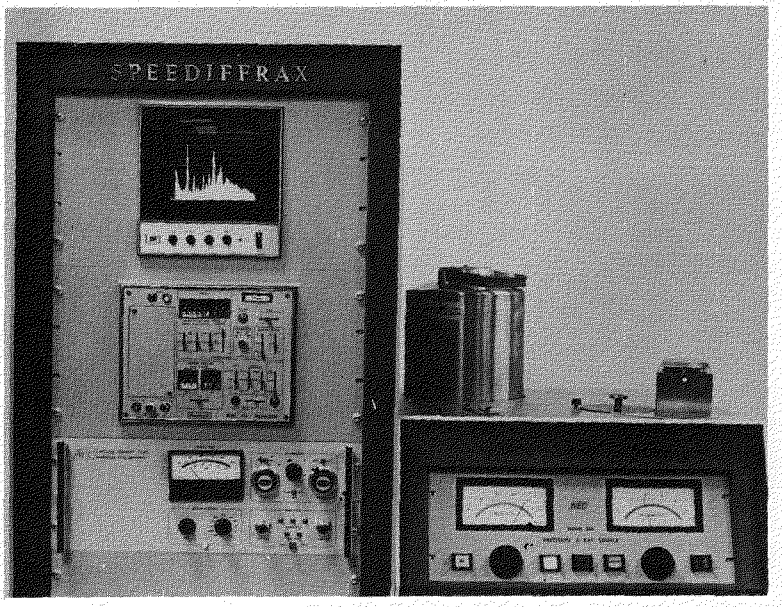


An X-ray fluorescence spectrum. This is the result obtained when a mixture of metals is bombarded with X rays and the X rays given off by the metal are analyzed with a device called a lithium-drifted silicon detector. Each peak corresponds to an element present in the mixture and its height is proportional to the amount of the element present. The analyzed sample is unharmed and often need not be separated from the object.

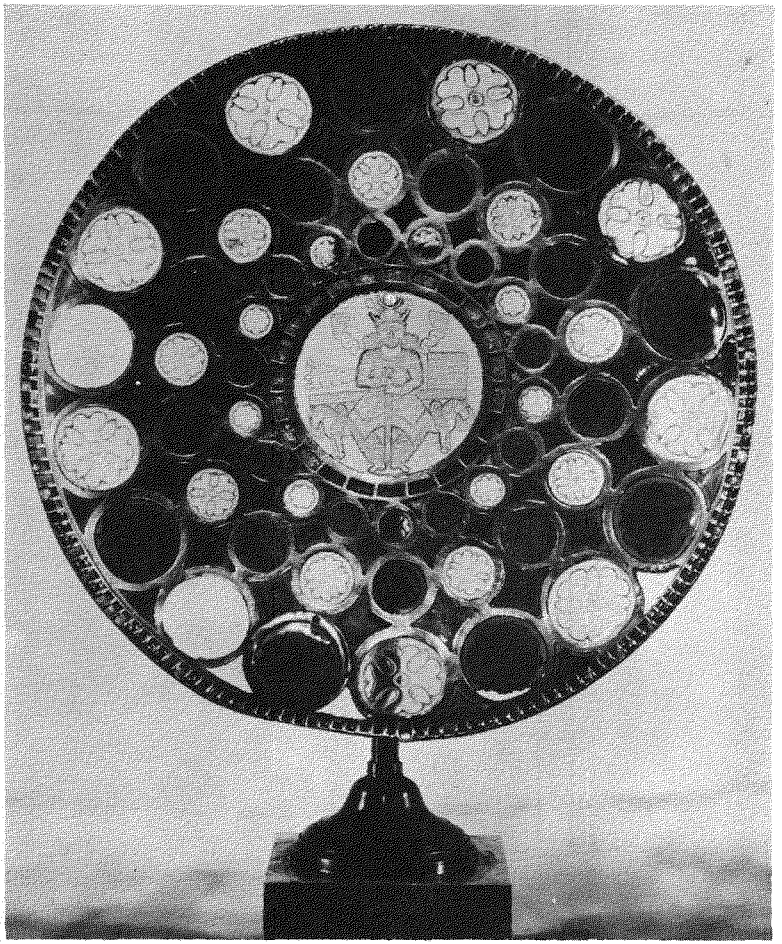
archaeological objects. Analysts have become proficient at applying these techniques to reasonably small samples. Often these methods are painstakingly tedious and so modern technology has once more come to the rescue.

While we all know the value of X rays in "seeing" inside an object, X rays are also a valuable probe for the measurement of many elements and the identification of compounds. One technique used to detect and measure elements in an object is called "X-ray fluorescence".

The principle behind it is that the nuclei of any target element bombarded with X rays of sufficiently high energy become excited and emit X rays having an energy characteristic of the element and with an intensity roughly propor-



Modern X-ray fluorescence equipment. In this instrument the detector is of a type developed originally for nuclear applications and the source of X rays is a conventional tube. Isotopic X-ray sources could be used as well. The pattern displayed on the screen corresponds to the impurities in a piece of natural quartz.



The Cup of Chosroes I. Solid gold rings hold gemlike medallions in a priceless plate named for a 6th century A.D. Persian king. X-ray fluorescence determined the source of this glass plate.

tional to the amount of that element present in the target. Not very long ago, X-ray fluorescence required a rather bulky bit of machinery and an analysis took quite a bit of time. Part of that equipment is an X-ray generator that is sometimes still used, but can be replaced by a compact radioactive source. Such a source, made from a man-made

radioisotope, americium-241* for example, can be shaped into a ring so that a sample can be bombarded efficiently by X rays† with an energy, in this case, of 62 keV‡.

The measuring part of the machine used to be a special crystal that reflected X rays of only one energy at each angle to which it was rotated. Thus, a scan of a complete energy range required a series of measurements at many different crystal angles.

Now, however, a special detector is available that sorts the energies electronically. This *lithium-drifted silicon detector* permits an analyst to make one simultaneous measurement of an entire range of energies.

While the analytical data obtained this way does not give information on trace element concentrations the way neutron activation analysis does, it is very useful for rapid, quantitative analysis of the major constituents in many materials. It has been used, for example, to trace the gradual devaluation of ancient coins by measuring the decrease in gold content in more recently minted coins. An important feature of this type of analysis is that it is nondestructive.

X-ray diffraction is another useful analytical technique. It is used to determine what chemical *compounds* are present by telling the analyst something about their crystal structure. It works by producing patterns of scattered X rays that vary according to the spacing and arrangement of the atoms of a crystal. In studying ancient metallurgical procedures it can also indicate the process by which a material was formed. For example, a cast coin will yield a different X-ray diffraction pattern than a struck coin because of the difference in crystal structure. Since forged coins are often cast and genuine coins are usually struck, you can see that this would be a very useful technique.

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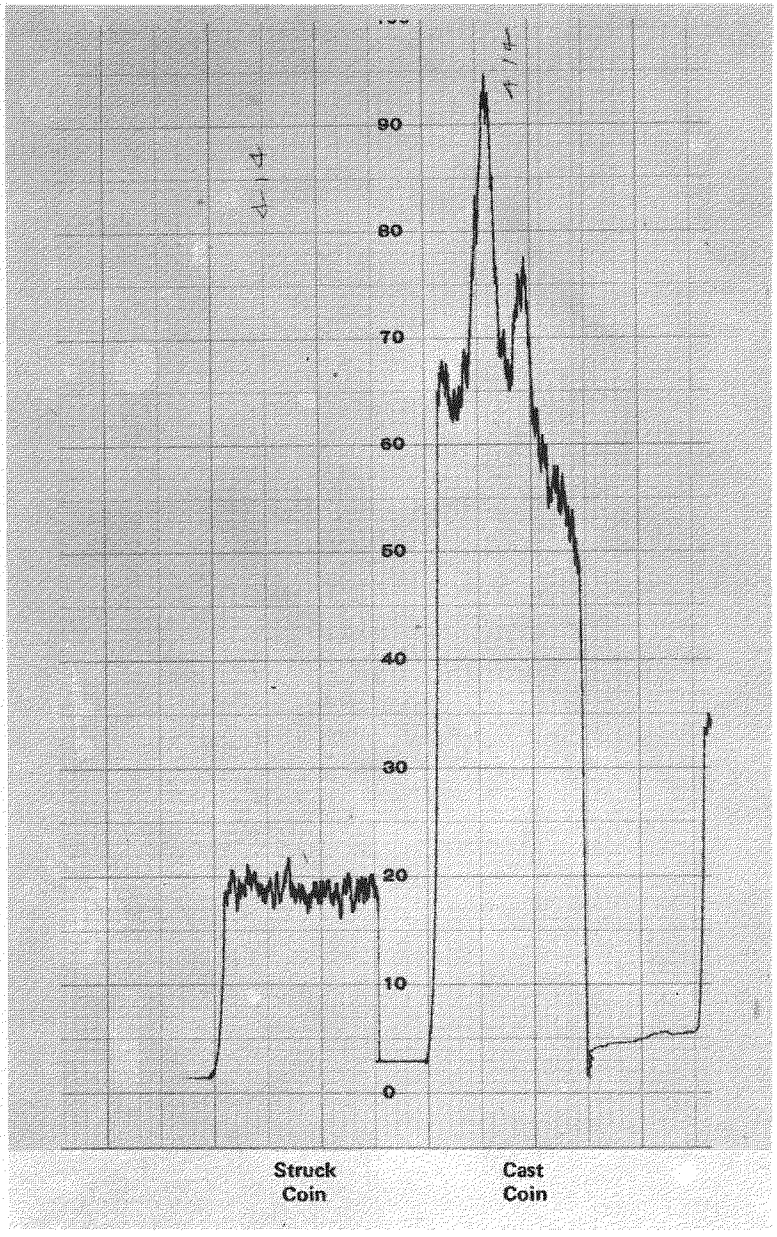
*See *Synthetic Transuranium Elements*, a companion booklet in this series.

†Strictly speaking these are gamma rays, but once emitted, X rays and gamma rays are indistinguishable.

‡KeV = one thousand electron volts.



X-ray diffraction patterns obtained from struck and cast coins of similar composition. Only the struck coin is likely to be genuine.

SPECIAL ANALYSES

Beta-ray Backscattering

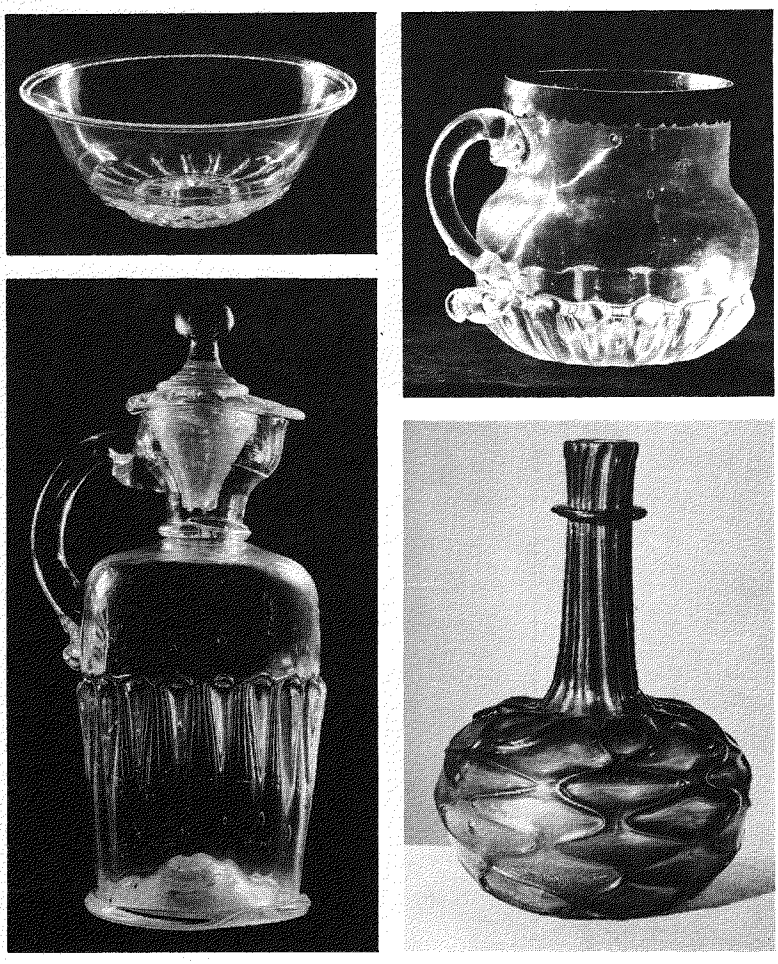
A few workers have made interesting use of a well-known principle of nuclear science. Beta rays, which are actually energetic electrons, are emitted by many radioactive atoms. When beta rays strike a surface, some penetrate to a shallow depth and are absorbed, but some also bounce off or, in more technical terms, are "backscattered". For reasons having to do with the numbers of electrons in the atoms of the scattering surface, elements having a higher atomic number are more efficient scatterers.

This idea has been used as a means of measuring the amount of lead (an element with the high atomic number of 82) in leaded glass and in pottery (both consisting mostly of low atomic number elements) that has been finished with a lead glaze. For example, the English produced a famous crystal glass, called Ravenscroft after the Englishman who produced it, toward the end of the 17th century. Analyses of several pieces from that time and from a century later showed that the amount of lead present was increased later on.

The use of this method is very simple and does no harm to the piece being examined. A beta-ray emitting radioisotope is allowed to "shine" on the surface being analyzed and a Geiger counter measures the beta rays that are reflected; the more lead there is in the surface, the more scattered radiation is measured by the counter.

Mössbauer Effect

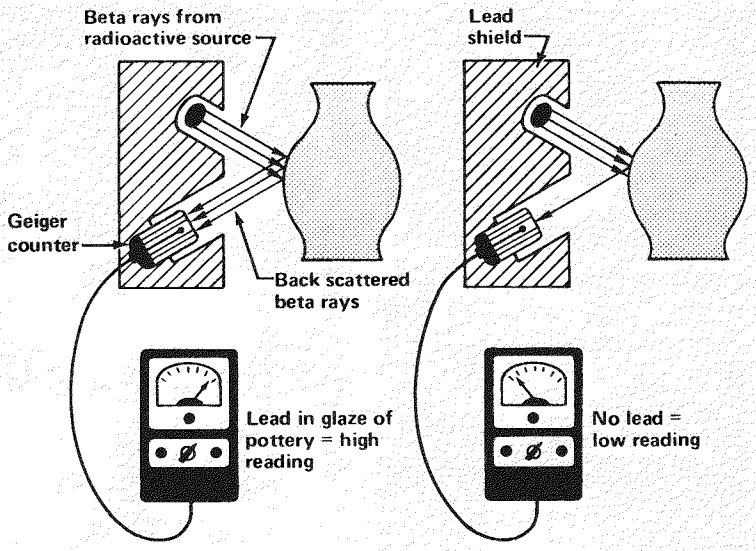
In the late 1950s, Rudolf Mössbauer discovered the key to a method in which the *nuclear* properties of certain elements can be affected by their *chemical* and *physical* circumstances. While relatively few elements can be studied by this means, iron happens to be the easiest. This is a



Samples of Ravenscroft glass.

fortunate circumstance since iron compounds, especially oxides, have been used to add color to pottery for thousands of years.

The reason for the interest in iron oxides as a pigment is the rich variety of colors that can be obtained by simple variations in the chemical state of the iron. Thus, colors obtainable vary from yellow to brown, red, and black, with many variations. Most pottery clays contain at least some



Detecting heavy metals by beta-ray backscattering.

iron oxide and the conditions at the time of firing the pottery can chemically change the oxides and thus control the color of the finished ware.

The theory behind the Mössbauer Effect is rather complex, so we will only describe "how" rather than "why".

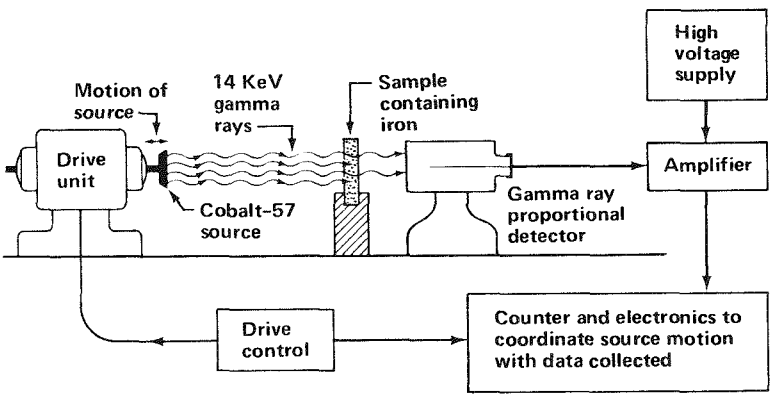
In the case of iron, one begins with a specially prepared radioactive source containing cobalt-57 that decays to a natural, *non*radioactive isotope, iron-57. The radiation from the cobalt-57 is allowed to pass through a thin layer of sample (naturally containing all the nonradioactive isotopes of iron) and then falls upon a detector where the amount of radiation is measured. While part of any radiation is absorbed when passing through any material, some of the radiation from the cobalt-57 is very special in this case.

This special radiation, which consists of gamma rays with an energy of about 14 keV, tends to be *preferentially* absorbed by the nuclei of iron-57 atoms because it is *exactly* the right energy. Scientists call this *resonance absorption.* The "exactness" is very important; the slightest alteration can

destroy the resonance absorption. For example, moving the radioactive source even slightly while making the measurement can do it.* And so can a difference in the chemical state of the iron.

As a matter of fact, in making a Mössbauer effect measurement, scientists deliberately move the radioactive source at various velocities and measure the radioactivity reaching the detector at each one. If the iron in the sample is

*This is called the "Doppler Effect" and is the same effect that changes the apparent pitch of the whistle on a moving train as heard by a stationary observer.



Mössbauer Effect spectrometry. The specially prepared cobalt-57 radioactive source is moved back and forth at carefully controlled velocities. The radiation from the source is allowed to penetrate a sample containing iron and a detector measures the amount of radiation that passes through the sample. An electronic device measures the amount of radiation reaching the detector and coordinates this information with the velocity of the source. This results in a Mössbauer Effect spectrum as shown in the figure on page 67.

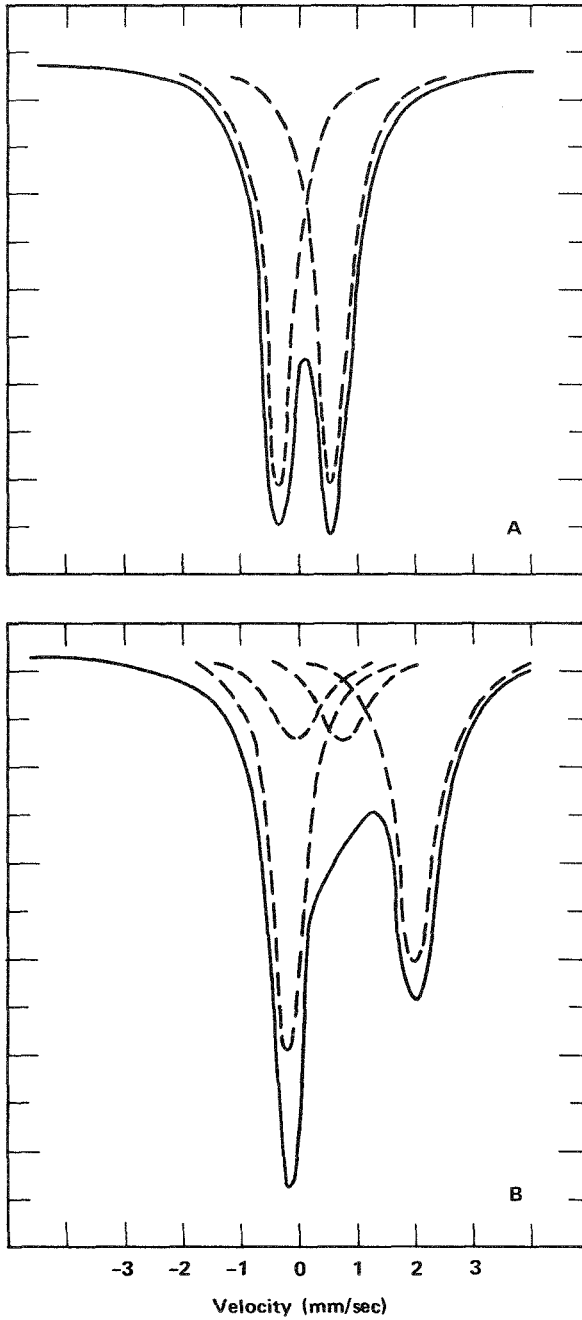
at a particular chemical state, different from the iron atoms in the decaying source, then a certain velocity will exactly compensate for the difference and restore the resonance absorption.

A graph showing the measured radioactivity at each of many velocities is called a Mössbauer effect spectrum. There may be one or more dips in it depending on how many and what kinds of iron compounds are present.

D. R. Cousins and K. G. Dharmawardena in England have studied some medieval English pottery by this means. They concluded that one could estimate the firing temperatures of the pottery as well as tell the difference between pottery that was similar in appearance but from different sources.

One piece that they examined was red outside and black inside. They showed that this was a result of oxidizing conditions during the firing of the ware. These workers believe that they will eventually be able to reconstruct some of the ancient practices so that we will know more about the technology of the people who made this pottery.

Mössbauer Effect spectra. These two spectra were obtained with apparatus similar to that shown in the preceding figure. The horizontal scale is the velocity of the source and the vertical scale is the relative amount of radiation reaching the detector. The upper curve is that obtained for a buff-colored pottery containing iron in a fully oxidized condition. The lower curve is that obtained for black pottery in which only part of the iron has been completely oxidized. The solid curves represent the data as obtained from the measurement while the dotted lines represent the component parts of the curve as contributed by the different chemical states of the iron atoms present in the samples. With this data it is believed that information can be obtained regarding the condition under which the firing of the pottery took place—for example, the temperature of the kiln.

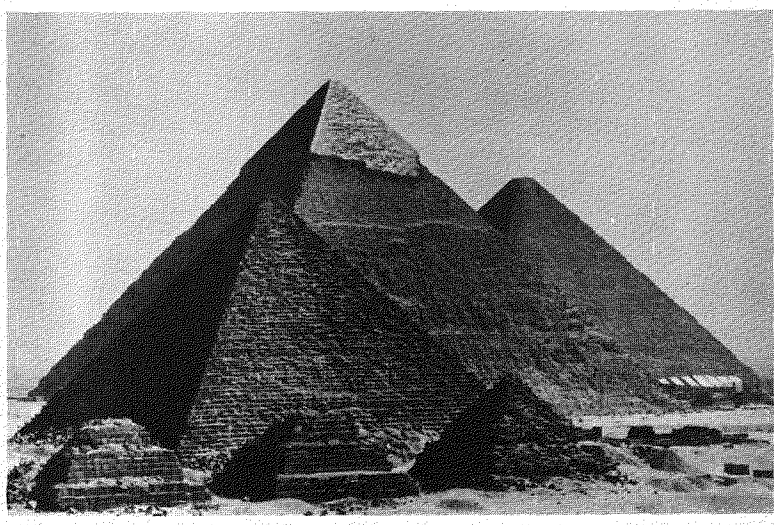

A
B
-3
-2
-1
0
1
2
3
Velocity (mm/sec)

A SPECIAL TECHNIQUE: "X-RAYING" THE PYRAMIDS

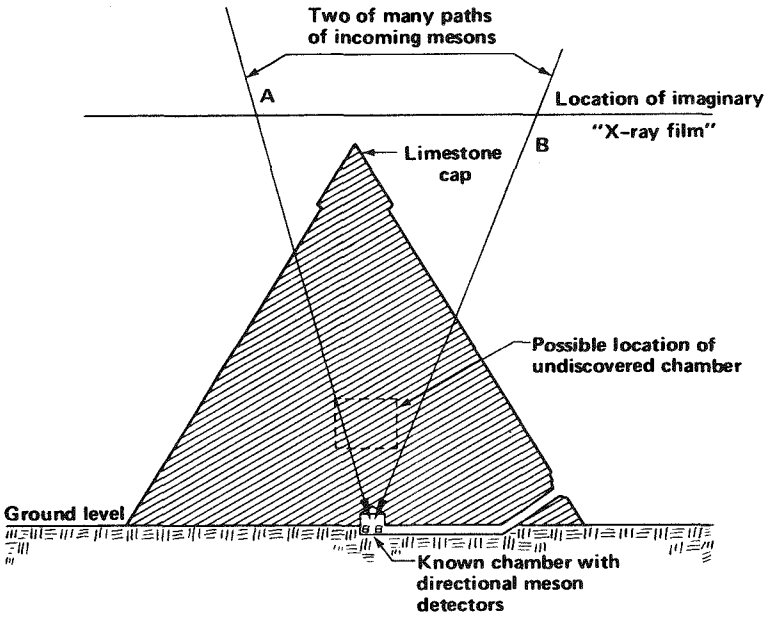
The use of X rays to "see inside" parts of the human body is well-known to everyone who has had a physical examination or has visited the dentist. The use of X rays to examine archaeological objects is also quite common and is accomplished in a manner similar to the application of medical X rays. For many years, enormous X-ray machines have also been used to detect flaws in large metal objects.

Recently, however, what amounts to the biggest "X-ray" job of all was performed on one of the pyramids in Giza in Egypt. Actually, cosmic rays and special detectors were used in place of the usual X-ray machine and photographic film but the principle and the results were quite similar.

It seems there was some question about the possible existence of a hidden chamber in the Second Pyramid of Chephren. This pyramid, which is about the same size as the Great Pyramid of Cheops, did not have as complex an internal structure as Cheops. In the latter, a hidden upper



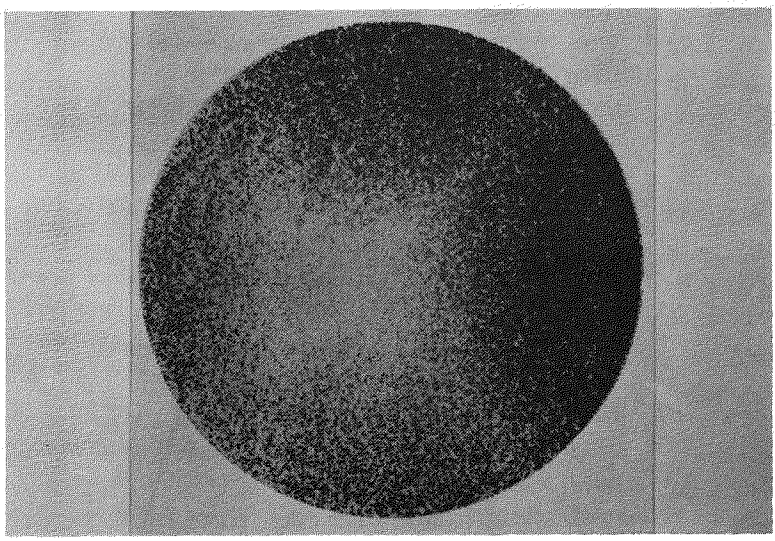
The pyramids of Giza. Left to right, the Third Pyramid of Mycerinus, the Second Pyramid of Chephren, and the Great Pyramid of Cheops.



Simplified diagram of an experiment to X-ray a pyramid. Incoming mesons are detected by apparatus that is capable of telling which direction the meson came from. By tracing back the paths of millions of mesons coming from all directions to the points where they intersect an imaginary plane, one can compute a picture like an X-radiograph on that plane. If mesons following path A passed through a hidden chamber there would be fewer of them lost by adsorption in the rock than if there were no chamber present in the indicated position. Mesons traveling along path B would be unaffected.

chamber was discovered in the 19th century, 3400 years after its construction. But in Chephren's pyramid, there is only one known chamber and archaeologists have been wondering for over a hundred years if a secret, hidden chamber remains undiscovered.

In 1960, a group of scientists headed by Dr. Luis Alvarez of the University of California began an experiment to determine whether an undiscovered chamber exists in



An "X-ray" picture of a pyramid. This photograph was produced by computer from the information obtained by detecting many mesons arriving at a detector beneath the pyramid of Chephren in Egypt. The four corners of the pyramid are apparent, but there is no shadow corresponding to a possible hidden chamber in the rock.

Chephren's pyramid. They planned to use the highly penetrating components of cosmic rays called *muons* that arrive at the earth's surface from all directions.* To produce an "X-ray picture" it was necessary to place a special detector system in the chamber located under the center of the base of the pyramid.

The detection system consisted of devices called *spark chambers* and *scintillation counters* that enabled the scientists not only to detect the arrival of a muon but, most important, to tell exactly the direction from which it had arrived.

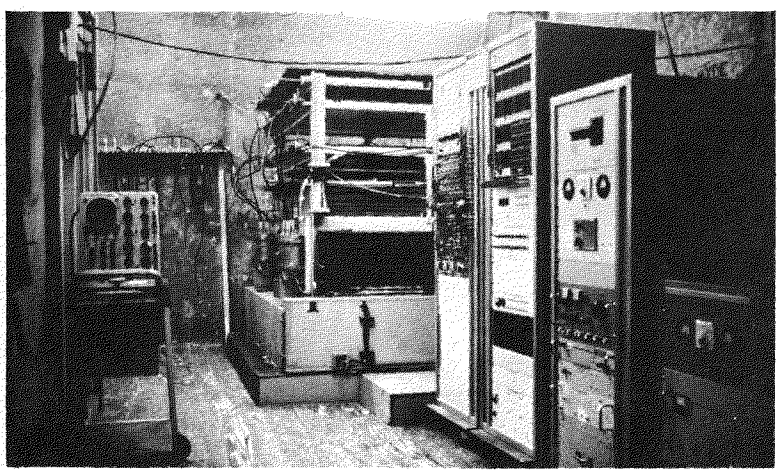
*See *Space Radiation*, another booklet in this series.

In 1968 the collection of data began. Some 700,000 muons were detected and recorded on magnetic tape that was later fed into a computer.

The computer turned the process "inside out". By pretending the detector was the source of the muons (the "X-ray machine"), and by tracing each one back to an imaginary plane above the pyramid (the "X-ray film"), the computer was able to build up a picture on that plane. The greater the number of muons coming from a given point on the plane, the less stone they passed through on the way into the detector from that point.

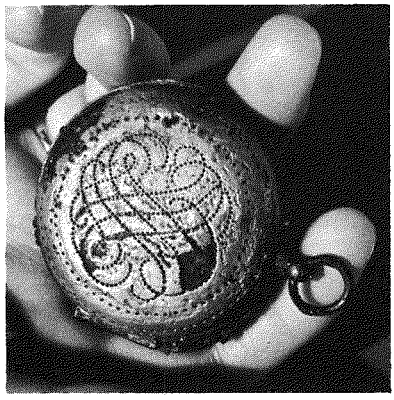
The resulting picture, which was corrected for various geometric factors in the detector construction and location, clearly showed the four corners of the pyramid. The computer also was able to "see" the limestone cap that covers the point of the pyramid.

And, finally, it proved that no hidden chamber exists in a large portion (the most likely location) of this pyramid even though a room half the size expected would have been easily "seen".



The equipment in place in the Belzoni Chamber under the pyramid. On the right is the detection apparatus containing the spark chambers.

Twenty minutes before noon on June 7, 1692, an earthquake swallowed the city of Port Royal, Jamaica. Diving expeditions in the late 1950s salvaged a number of 17th century artifacts including this watch. A limey encrustation (upper left) clung to its glassless face. An X-ray photograph (upper right) of the matrix, which had molded tightly to the watch's dial, showed traces of the vanished hands (marked by arrows), which had stopped at 11:43 a.m. before the first heavy earth shock or plunge into the sea halted the works forever. Brass gears, as bright and uncorroded as the day they were made, fell out when the watch was opened. Minute silver studs, fitted into the perforated design in the bottom photograph, once held in place a leather sheath. The exact time of the earthquake was not known until this watch was recovered.



Nuclear Techniques in Art

DATING

Natural Radioactivity in Lead

One of the most important pigments used by artists in the past is lead white. This compound, which is a basic lead carbonate, has been used in painting since the dawn of history and only during the last century has it been supplanted by other white pigments. Lead also often occurs as a metal (mixed with other metals) in statues made of bronze or brass.

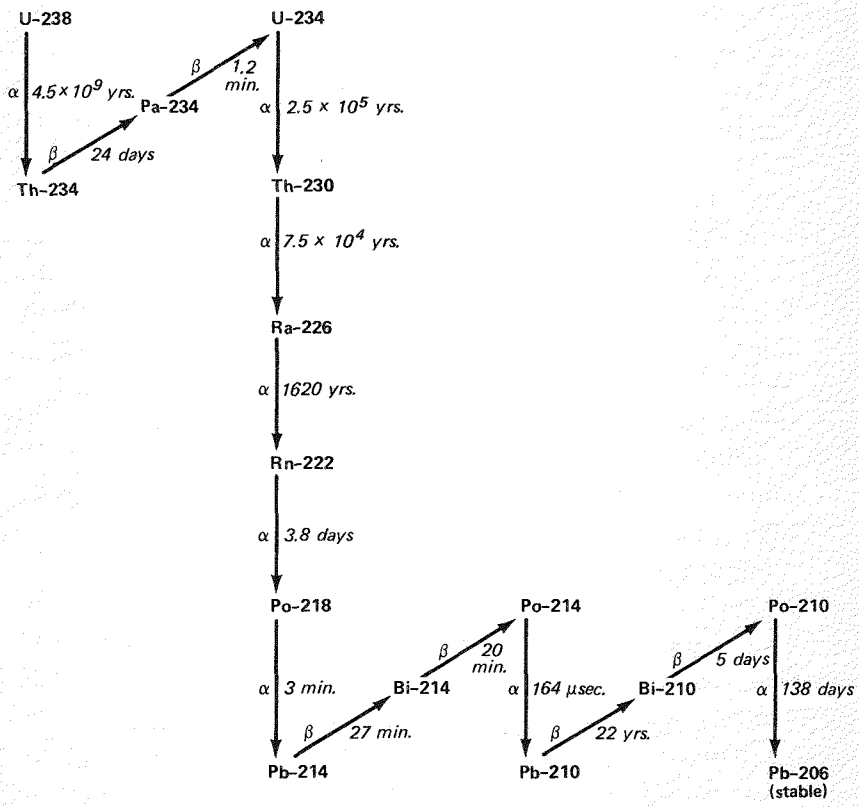
Twenty or thirty years ago, a method for dating lead and its compounds was proposed but the science of that time was not capable of making it work. In the last few years, a technique for roughly dating lead white was developed at the Carnegie-Mellon University with the support of the National Gallery of Art. More recently, supported also by the United States Atomic Energy Commission, researchers at Carnegie-Mellon applied the method to metals as well. The method is described below.

Almost all rock, including lead ore, contains small amounts of uranium. The individual atoms of this radioactive element disintegrate to become atoms of thorium, which in turn decay further. Eventually, through many such steps, they become nonradioactive isotopes of lead. Nearly all the uranium (more than 99%) consists of the isotope with mass 238. The main path for the decay of uranium-238 leads to the nuclide radium-226 with a half-life of 1600 years (half of it disintegrates in 1600 years; half of the remainder, in another 1600 years; etc.); and to the nuclide lead-210, a direct descendant of radium-226 with a half-life of 22 years.

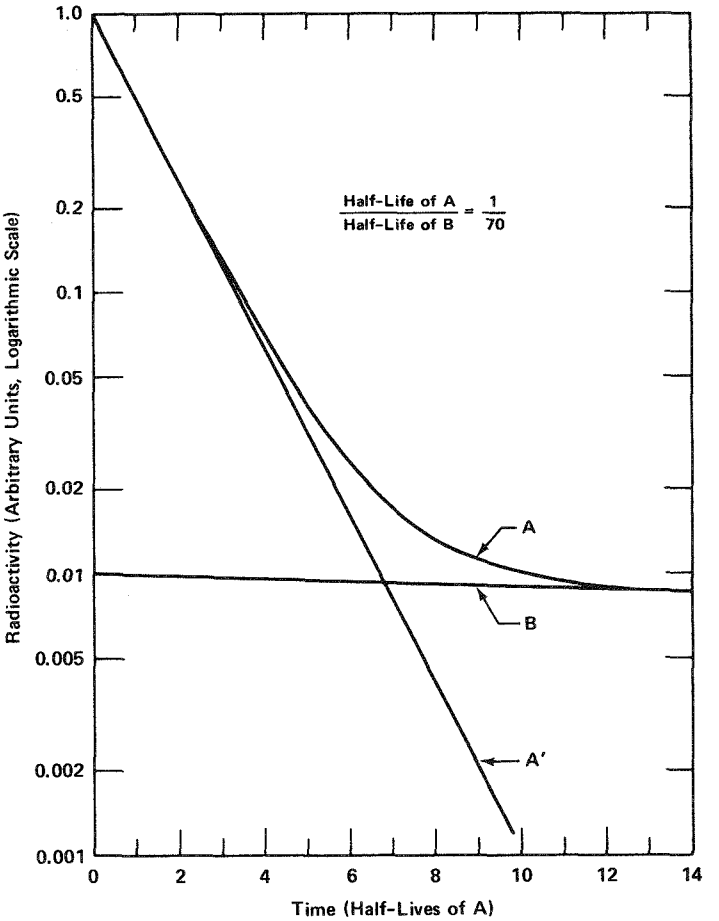
The laws of radioactive decay (and growth) state that, in time, all members of a chain beginning with a long-lived ancestor, such as uranium-238, will be present in amounts

having a mathematically precise relationship. This equilibrium relationship exists in the ancient rocks of the earth. Specifically, in lead ore the concentrations of radioactive lead-210 and of radium-226 (expressed as disintegrations of nuclei per unit time per weight of ore) will be equal.

The next important point is that when the ore is smelted, any lead-210 present remains with the lead metal, while most of the radium-226 is removed with the slag. From that moment on, the lead-210, no longer being replenished by its



The Uranium Series. In this simplified diagram, the double vertical arrows represent alpha radioactivity and the single slanted arrows represent beta radioactivity. The times shown on the arrows are the half-lives for each step.

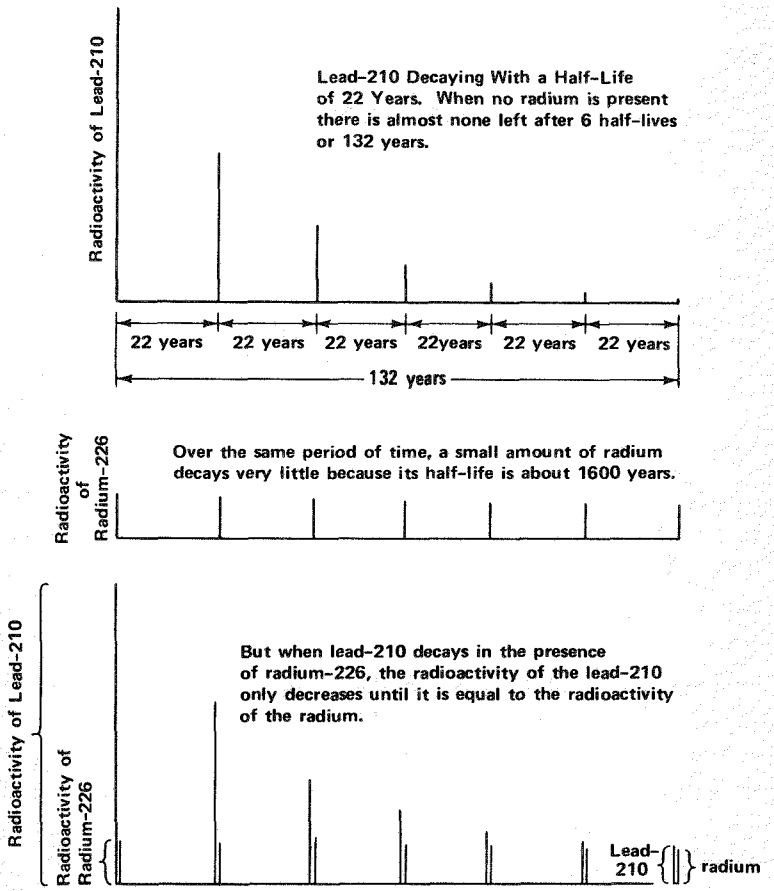


longer-lived ancestor, begins to decay with 22-year half-life and will continue to do so until it once more reaches an equilibrium relationship with the much smaller amount of radium-226, which somehow survived the smelting process.

The figure illustrates a simplified version of the radioactivity relationships. The scale along the bottom is the time in terms of the half-life of A, the short-lived "daughter". The "parent", B, has a half-life seventy times longer than A in this illustration. Curve B shows the activity of the parent

beginning at an amount $1/100$ of that of A. (This would represent 99% removal of B at time zero.) During the period shown, a relatively small fraction of B decays. Curve A would represent the activity of A, if all of B had been removed at time zero. Curve A′ shows the actual case; that is, eventually the activity of A "levels off" at the new activity of B.

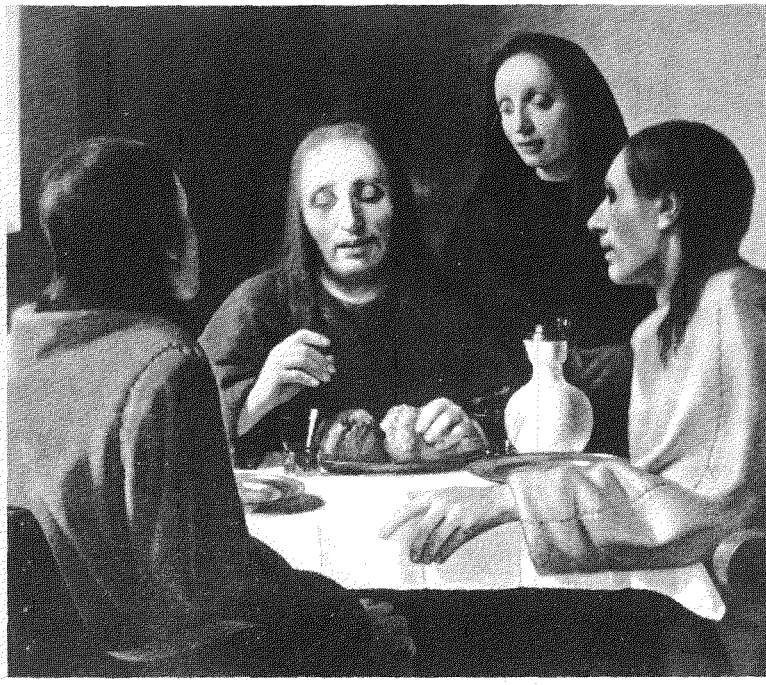
In the case of lead-210 and radium-226, despite the short-lived nuclides through which the radium must decay before becoming lead-210, a similar relationship holds. Thus, a *modern* sample of lead, that is, lead produced only a few lead-210 half-lives ago, will exhibit a *difference between* the concentrations of radioactivity of lead-210 and radium-226



that it contains. In old lead, there will be no such difference.

Measurements of the concentrations of radioactivity of lead-210 and radium-226 in a sample of lead, therefore, give the information needed to apply the method.

Recently this method was used to solve a problem that had its beginnings in 1937. In that year, an artist named Han Van Meegeren "found" a painting by the famous 17th-century Dutch artist Vermeer and was paid the equivalent of approximately $250,000 for it. This painting, entitled "Christ and His Disciples at Emmaus", was proclaimed the greatest work of Vermeer and given a place of honor in the Boymans Museum at Rotterdam.



The Van Meegeren forgery "Christ and His Disciples at Emmaus". The artist sold it in 1937 as a genuine Vermeer. In 1968 the measurement of lead-210 and radium-226 in a small portion of the lead white in the upper corner proved beyond doubt that it was of modern origin.

Over the next few years (on into World War II) Van Meegeren "discovered" several other valuable paintings. At the end of the war a Vermeer—"A Woman Taken in Adultery"— was found in the collection of the Nazi leader Hermann Göring, and this painting was traced to Van Meegeren. Since it was considered treason to have sold a national treasure to the Nazis, Van Meegeren was in serious trouble.

Soon after his arrest, Van Meegeren shocked the art world by stating that he had not only forged the painting found in Göring's possession, but also a host of others including the renowned Emmaus painting. It seemed that the artist, furious with the critics for some unkind words about his own paintings, claimed that he painted the Emmaus to fool them. "Spurred by the disappointment of receiving no acknowledgement from artists and critics. . . ", he said, "I determined to prove my worth as a painter by making a perfect 17th century canvas." He then painted six "Vermeers", two "De Hoochs", one "Terboch", and one "Hals".

Naturally many critics, with their reputations at stake, believed that he was now lying to save his skin. A court-appointed commission of experts studied the works in question and decided that Van Meegeren really was the creator of those paintings.

During this time Van Meegeren painted a final Vermeer, "Jesus Among the Doctors", under the watchful eye of the experts.

Among the clues to the forgeries were:

1. An old painting has only three layers—varnish, paint, and ground. Van Meegeren's had five—the three from the old one and two that he added.

2. Cobalt blue crystals in two of his paintings. This blue was not discovered until the 19th century. Van Meegeren had used what he believed to be pure ultramarine blue (the kind that Vermeer used) but it had been diluted with the modern cobalt blue.

3. Radiographs of genuine and Van Meegeren Vermeers revealed that surface cracks extended below the surface in the real paintings, while in the fakes many cracks (which Van Meegeren had made by rolling the painting around a tube) were only on the surface. He had also filled these cracks with black ink (simulating the dust of centuries) and this ran underneath the paint and was visible in the radiographs.

4. The presence of Bakelite.

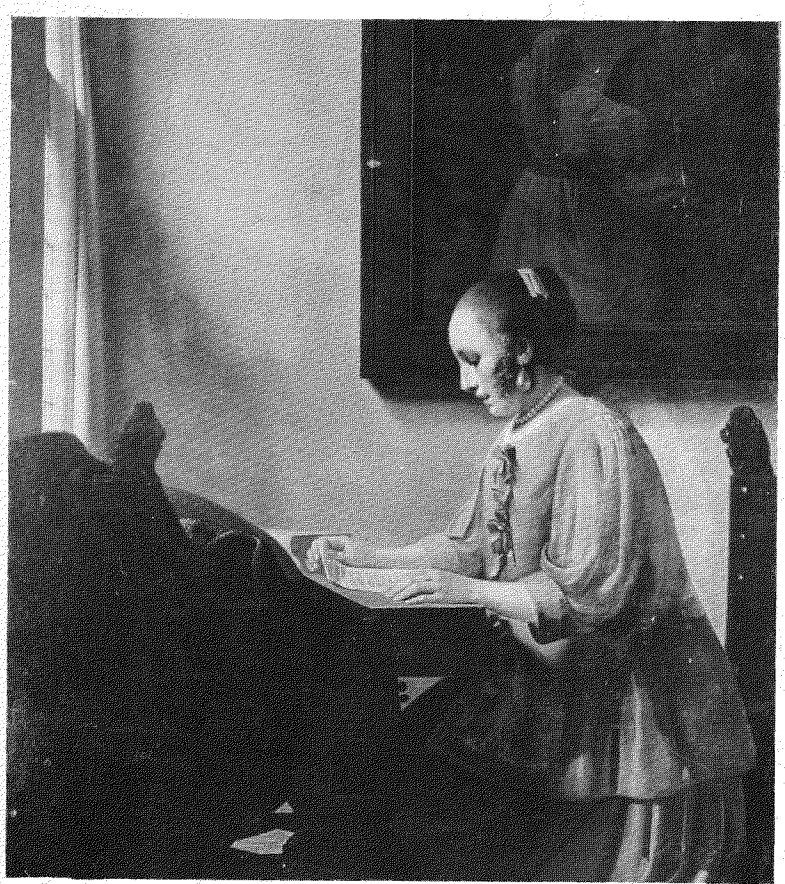
However, the evidence on the Emmaus was not as conclusive as on the others and even up until 1968, there were some who believed the Emmaus was genuine.

The new technique for lead dating was, therefore, applied to the Emmaus and to a few other Van Meegeren paintings. In every case, a large excess of lead-210 over radium-226 was found, thus proving the lead white in these paintings could not have been produced much before the 20th century.

Han Van Meegeren, who was convicted of fraud and died in prison shortly after his trial, was indeed telling the truth!

Han Van Meegeren listens to the evidence at his trial in Amsterdam in 1946. In the background is his painting "The Blessing of Jacob", which was sold in 1942 as the work of Vermeer.

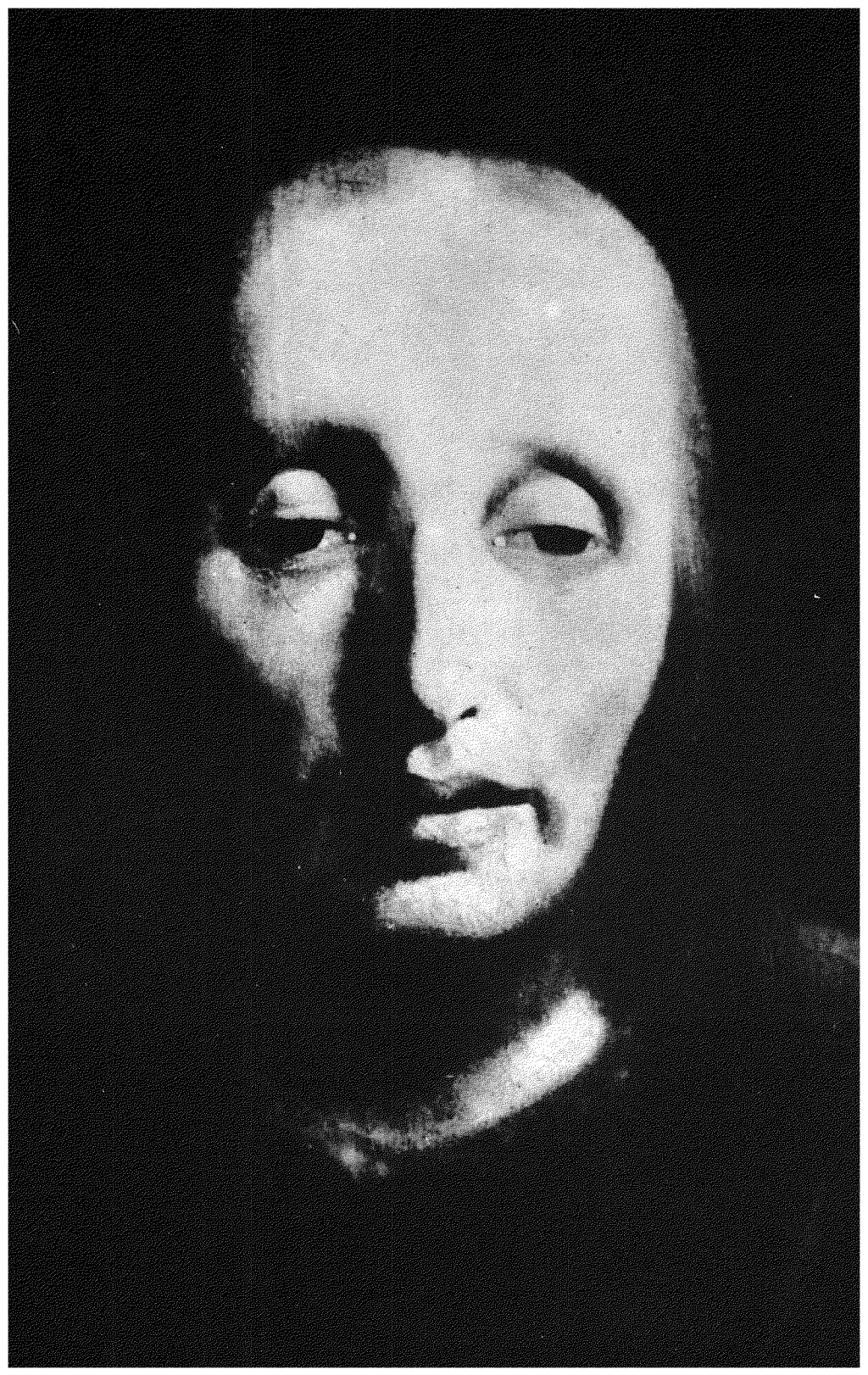
"A Woman Writing", a genuine Vermeer.



A Van Meegeren forgery of a Vermeer.

"The Love Letter", an authentic Vermeer painting.

A Van Meegeren forgery of a Vermeer. Note the similarity in the musical instrument and the pattern of the floor (reflected in the wall mirror of the forgery).



◊ *Head of Christ, a fake Vermeer painted by Van Meegeren.*

Carbon-14 and Recent Forgeries

When we discussed the use of carbon-14 dating in archaeology, we briefly mentioned the fact that man has disturbed the levels of carbon-14 in the biosphere. Work has recently begun at Carnegie-Mellon University to make use of these "disturbances" in the detection of recent forgeries.

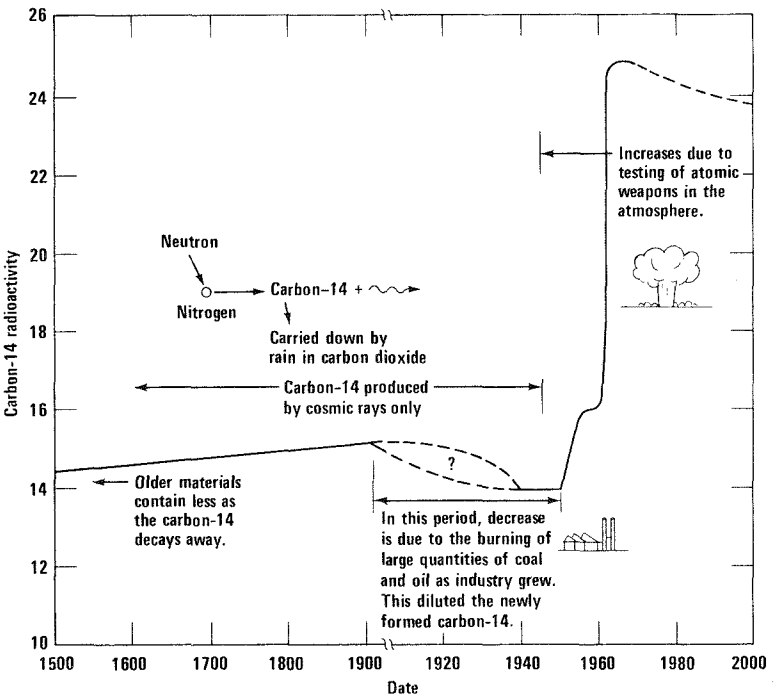
Much has changed in the "business" of producing fake works of art since the days of Van Meegeren. Because of dating methods like that based on the natural radioactivity of lead white and generally better techniques for the examination of paintings, forgers no longer attempt to fake a very old, rare painting. Instead, they produce forgeries of works supposedly painted during the last hundred years. Their job is very much simplified because they need not simulate great age, most of the pigments are still in use, and the painting technique is easier to imitate. The result is that, since World War II, an unknown but large number of forgeries of late 19th-century and early 20th-century paintings have been produced. Since these do not command the fabulous prices of the old masters, the business tends toward large numbers and little intensive examination is given to such works.

The levels of carbon-14 in the atmosphere and biosphere have also changed during this period. You will recall, from the description of carbon-14 dating, that the natural level of carbon-14 is fairly constant at about 15 disintegrations per minute per gram of carbon. It turns out that after about 1900, man began to use huge amounts of coal, oil, and gas, thus diluting the natural carbon-14 with inactive carbon from ancient deposits of these fuels. The net effect was a decrease, by a few percent, of the specific activity of carbon-14 in the atmosphere. Following World War II, however, nuclear weapons began to be tested in the atmosphere and these tests produced additional carbon-14. By the early 1950s, the increases had overcome the dilution by fossil fuel combustion

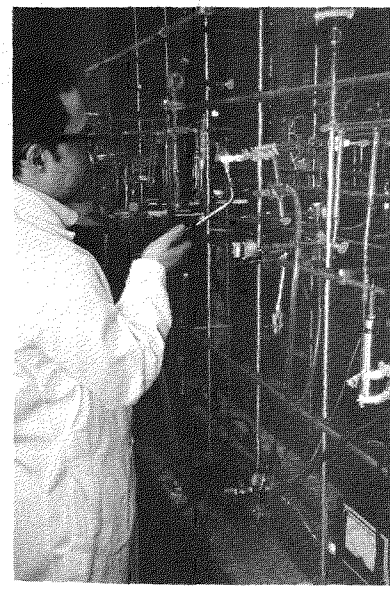
and were rising fast. By 1962, the concentration of carbon-14 in the atmosphere had about *doubled* since 1900!

Many artists' materials are produced from natural products growing in our atmosphere. These include wood, paper, canvas, and linseed oil. The latter is produced from the flax plant shortly after each growing season, and the oil has a limited useful life; that is, it must be used fairly soon after it is produced.

Because of the large sample required to achieve the necessary accuracy (the detection of only a few percent decrease in a few hundred years), dating paintings by ordinary carbon-14 methods is out of the question. The distinction between old and modern linseed oil (which



The changing concentrations of carbon-14 in our atmosphere. High levels of carbon-14 in linseed oil and other painting materials will indicate that a work of art is only a few years old.



Preparing the carbon in linseed oil for a carbon-14 determination. A sample of linseed oil is being burned in oxygen inside a glass tubing system. This will be converted to carbon dioxide. After the gas is purified carefully, it will be placed in the detector at the extreme right of the picture. This will be sealed and placed in a counting system such as that shown in the figure on page 30.

involves a doubling of radioactivity) can be made, however, with a relatively small sample. Using a miniature version of the gas-filled counter detection system described in the section on carbon-14 dating, these differences have been measured on samples of linseed oil weighing as little as 30 milligrams.

Similar techniques can be applied to other natural materials and the day of the successful modern forger may be almost over.

Identifying Pigments

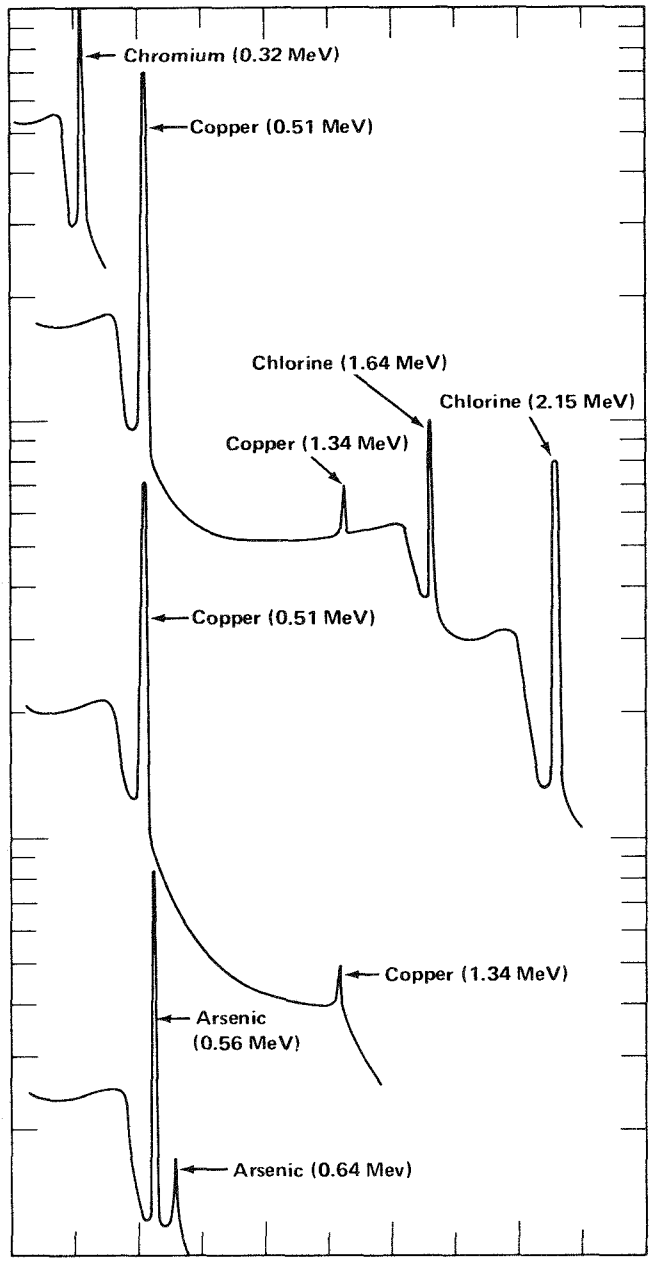
One of the earliest scientific methods used to determine the authenticity of a painting was devised by Martin De Wild, a Dutch chemist-conservator, some 50 years ago. This method relies on the identification of each of the pigments in a particular painting *plus* the knowledge of when these pigments were used by painters. While the original work of pigment identification was accomplished by painstaking

microchemical techniques, and these techniques are still in use, several modern methods have recently been developed for this purpose.

Neutron activation analysis has been used to identify the major elements in extremely small samples of paint as an aid to pigment identification. The method may help answer such questions as: Is a green pigment in a painting (a) malachite (ancient), (b) chrome green (19th century), (c) paris green (19th century), or (d) phthalocyanine green (a modern dye)? The major elements present in each of these pigments are; (a) copper, (b) chromium, (c) arsenic, and (d) copper and chlorine, respectively. Using activation analysis, it would be an easy matter to spot the activation products of these elements. In this case, the presence of any of these pigments except the first would rule out the possibility of the painting being more than 150 years old.

While activation analysis requires the removal of a very small sample, a closely related method requiring no sampling is called neutron activation autoradiography and was devised by Edward Sayre and Heather Lechtman at Brookhaven National Laboratory. In their method, these workers irradiated a whole painting with a relatively small dose of neutrons. Then photographic film was placed in contact with the painting at various times after irradiation and for gradually increasing periods. The radioactivity induced in the painting produces a picture in much the same way as an X ray. In this case, however, the resulting photograph varies with the time elapsed since the irradiation.

Neutron activation analysis of pigments. These gamma-ray spectra would be similar to those obtained if one irradiated four different green pigments with neutrons and measured the activation products. From the top down, they are chrome green, phthalocyanine green, malachite, and paris green. Only the third one should be present in a painting produced before the 19th century.


Chromium (0.32 MeV)
Copper (0.51 MeV)
Chlorine (1.64 MeV)
Chlorine (2.15 MeV)
Copper (1.34 MeV)
Copper (0.51 MeV)
Copper (1.34 MeV)
Arsenic
(0.56 MeV)
Arsenic (0.64 Mev)

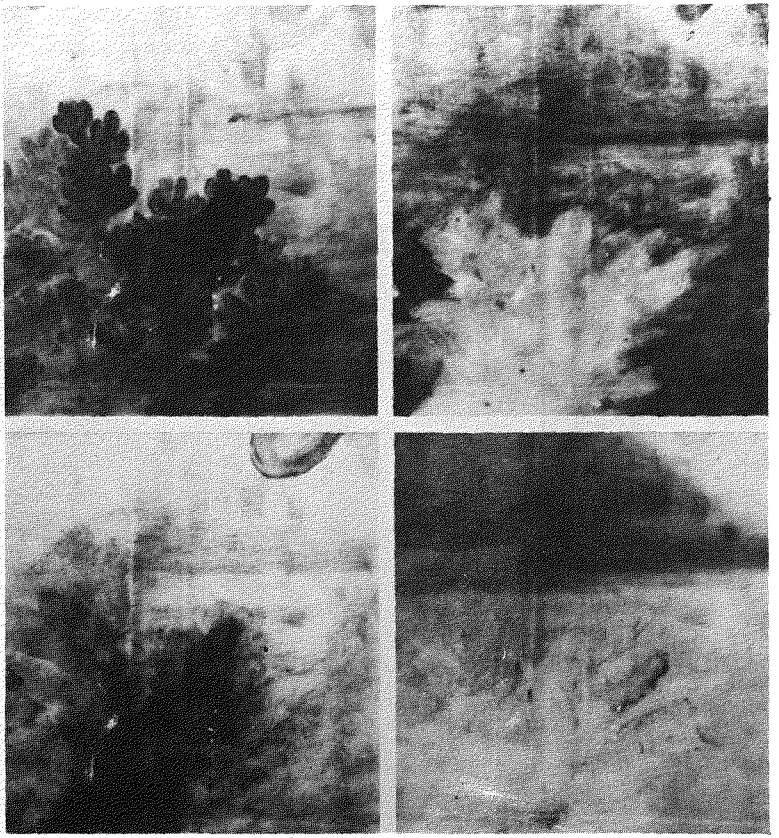
At first, the greatest darkening of the film is produced by the presence of elements whose induced radioactivity has a short half-life and is most intense shortly after the irradiation. Later films are darkened most where the radioactive isotopes have slightly longer half-lives and so on.

Thus, for example, a few minutes after irradiation, radioactive aluminum might show up in certain areas of the painting to indicate the use of a dye incorporating aluminum oxide as a mordant*. After a few hours, areas containing manganese and copper (which may indicate umber and azurite, respectively) would be indicated and finally, after many days, the location of any cobalt blue on the painting might be observed. The "autoradiographs" thus obtained not only yield information about the presence (or absence) of certain pigments, but also give valuable information about the technique used by the painter. In this respect the method has its greatest utility. The information obtainable is comparable to that obtained using X rays. However, while the latter reveals the structure (brushstrokes, for example) of the paint that mainly contains lead white pigment, neutron activation autoradiography yields such information about paint containing almost any pigment.

One drawback to this method is the fact that the whole painting is irradiated and made slightly radioactive. While this procedure has been shown to be safe for both the painting and persons viewing it later on, museum directors are understandably reluctant to submit important paintings to such treatment.

The use of X-ray fluorescence, on the other hand, can be used to detect major concentrations of elements in a painting with no more effect upon the painting than the taking of an X-ray photograph. The latest developments in this field (see page 57) include the use of a radioactive isotope as a source

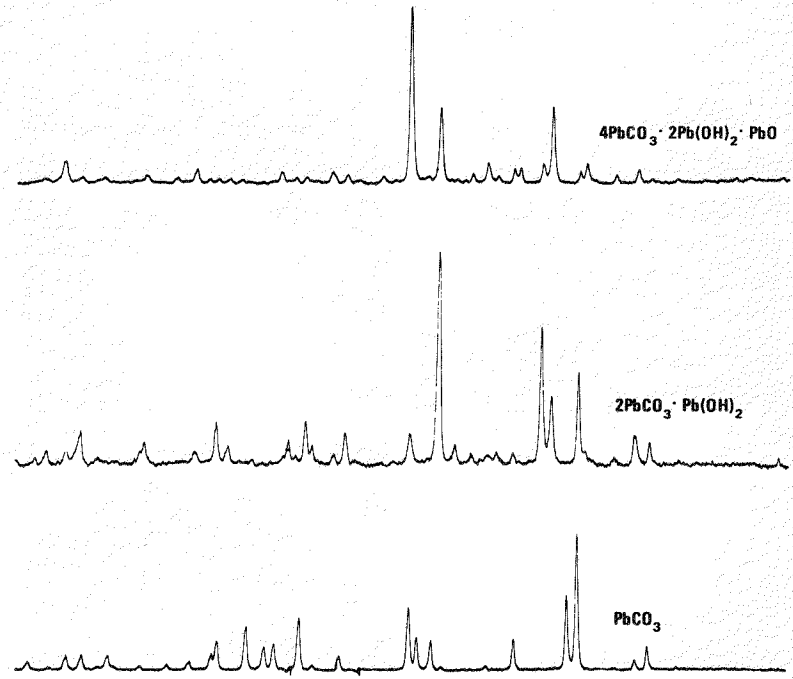
*A mordant is a substance that, by chemical reaction, helps attach a dye to a fabric by making it insoluble.



Neutron activation autoradiography. The four pictures represent a series of exposures of a section of a painting after activation by neutrons. These exposures were made at successively longer times after the irradiation. Upper left, a few minutes; lower left, a few hours; upper right, next day; lower right, a few months. At these successive times, various pigments can be identified in various areas of the painting.

of X rays and a special detector originally developed for use in nuclear physics. The equipment now available permits the analyst to determine the major constituents in any small area of a painting without sampling at all.

While the techniques described above all yield information on *elemental* composition, *positive identification of a*



X-ray diffraction patterns from three different lead compounds that might occur in lead white. The middle one is the ideal lead white produced for over 2000 years. While some of the bottom compound may be found mixed with it, the compound shown at the top is only a 20th century invention.

pigment must rest upon other techniques. One such technique is that of X-ray diffraction. X rays are allowed to strike a small sample taken from a work and are bent (or diffracted) in ways that are unique for each chemical compound. The diffracted X rays are usually allowed to strike a photographic film where a pattern of light and dark bands is formed. By comparison with patterns obtained from known pigments, almost any pigment can be identified. This method has been used, for example, to tell the difference between various lead white samples that have similar elemental composition (lead, carbon, hydrogen, and oxygen), but are actually different compounds manufactured by various methods.

FINGERPRINTING

Neutron Activation Analysis

Just as in archaeology, artists' materials may also be "fingerprinted" by measuring concentrations of accidental trace elements. One pigment that has been studied for trace element content by using neutron activation analysis is lead white. Activation analysis is used because of the ability to measure low concentrations of impurities in very small samples with this method.

Lead white is an important subject for this technique because of its common use and also because neutron activation does not yield much radioactivity from the main elements in this material (lead, carbon, oxygen, and hydrogen). Results obtained by Johannes Houtman and J. Turkstra in The Netherlands, first seemed to show that one could tell if a sample of lead white was produced prior to the 19th century. The samples that these workers analyzed from older Dutch and Flemish paintings contained higher concentrations of certain elements, like silver and copper, than modern lead white did.

However, Franz Lux and Lothar Braunstein in Germany found that old Italian works contained lead white that was as pure as most modern material. At the present time, research on the possibility of using neutron activation analysis to "fingerprint" sources of lead white is still going on. At Carnegie-Mellon University it has been found that much care must be taken to separate the lead white from other pigments and the oil in the paint in order to get good results. It is hoped that eventually patterns of trace element concentrations will be found that will be characteristic of a particular artist or a group of artists who worked at the same place and during the same time period.

Another pigment that has been studied by neutron activation analysis is ultramarine blue. From ancient times in the East and Mideast up through the time of the Renaissance

in Europe, this beautiful pigment was made by painstakingly separating fine blue particles from the crushed semiprecious stone, lapis lazuli. This gem-like material is found in only a few places. At the time it was used to produce the pigment, almost all of it came from a remote region of Afghanistan. Naturally, it was quite expensive and was only used by the best artists for their most important works.

In the 19th century, during the flowering of chemistry, French and German workers managed to produce an artificial ultramarine by heating clay, sulfur, and soda ash under carefully controlled conditions. Chemically, there is no real distinction between the natural and the artificial product. But telling them apart is a useful means for deciding if a painting containing this pigment was produced before the early 19th century.

Distinguishing between these two types can be accomplished by studying the shapes of the particles, but this requires careful study and a subjective judgment on the part of the analyst. Using neutron activation analysis at Carnegie-Mellon University, differences in some of the trace elements contained in the materials have been observed that appear to offer an objective means of telling them apart. It may even be possible to distinguish between various sources of the natural and artificial products by this means. For example, the artificial product often contains far larger concentrations of the elements cesium and thorium than does the natural material.

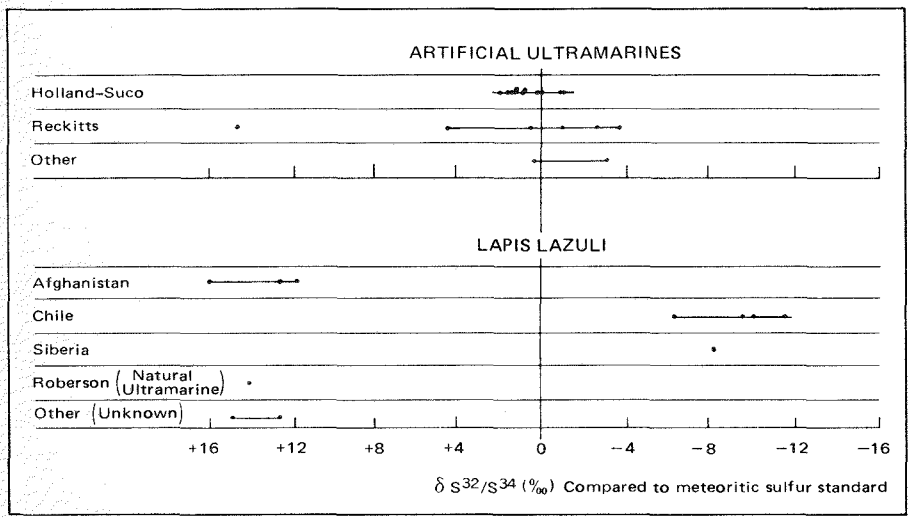
Isotope Mass Spectrometry

Another means of distinguishing between different types and sources of ultramarine blue is isotope mass spectrometry. At Carnegie-Mellon University, the ratios of sulfur isotopes* have been measured in samples of ultramarine and lapis lazuli.

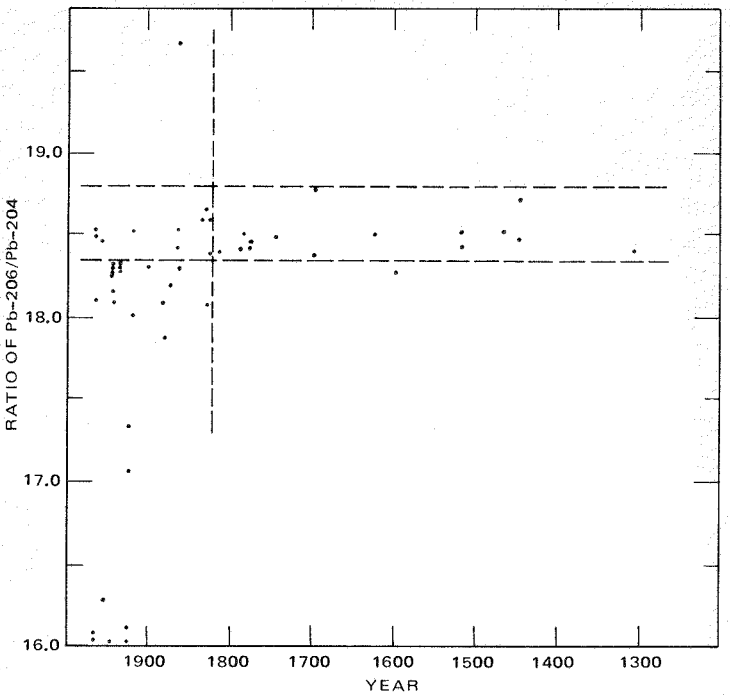
*Chemically, ultramarine is a type of material called a "zeolite" containing several percent of sodium sulfide.

Sulfur, an important constituent of ultramarine blue, as found in nature consists of a mixture of 4 isotopes with atomic weights of 32, 33, 34, and 36. About 95% of the atoms in ordinary sulfur have an atomic weight of 32 and about 4% have an atomic weight of 34. But this ratio of 95:4 or approximately 23, varies slightly depending on the source of the sulfur and the type of mineral deposit in which it occurs.

It turns out that the sulfur in synthetic ultramarine made today comes mostly from sulfur deposits along the Gulf Coast of the United States. These deposits have distinctly different isotope ratios than do the three major deposits of



Sulfur isotope ratios in samples of ultramarine and lapis lazuli. The graph shows the isotope ratios measured for sulfur in a series of samples of artificial ultramarine and lapis lazuli (the source of natural ultramarine). The horizontal scale is the difference between the sample and the accepted standard. During the period when this blue pigment was in use and was not yet produced artificially, the only known source was in Afghanistan. Notice the distinctly different isotope ratio obtained for this material.



Lead isotope ratios for lead white. This diagram shows the ratio of lead-206 to lead-204 as found in a number of samples of this widely used white pigment. The ratios are plotted as a function of the age of the pigment (known approximately). It appears that before the mid-19th century, the sources of lead were restricted to ore deposits having a relatively narrow range of isotope ratios. After that time, new sources came into use, such as those in the Western Hemisphere or in Australia. You can see the value of this information in determining the age and source of the lead in a painting.

lapis lazuli in Afghanistan, Siberia, and Chile. In fact, preliminary results show that the deposit in the ancient mines of Afghanistan can easily be distinguished from the more recently mined deposits.

This technique can also be extended to other sulfur-bearing artists' materials such as the red pigment, vermilion

(mercury sulfide), or plaster of paris (calcium sulfate hydrate). It can also be used for two other "light" elements, carbon and oxygen, in which natural variations of isotope ratio have been observed.

In addition, the variations in lead isotope ratio discussed in connection with archaeological lead can also be used to "fingerprint" the source of lead used to make lead white. At Carnegie-Mellon University it was found that prior to the 19th century the lead isotope ratios in this pigment were restricted in range because all the lead came from a relatively small area of the world. Later on, mines in Australia, the United States, Canada, and many other countries produced lead with larger variations in isotope ratio. One possibility that remains to be explored is the idea that a given artist's supply of white lead may have come from one place and, hence, the lead in all his paintings would have similar isotope ratios.

Two major advantages in the use of isotope ratio measurements to identify the sources of pigments are that (1) very small samples, invisible (or nearly so) to the naked eye, may be used, and (2) impurities, such as other pigments, do not interfere with the measurement as they do with other techniques.

GENERAL ANALYSIS

X Rays to See More

One of the earliest attempts to improve on the judgment of art experts was to give them more to look at. X-ray photographs of paintings give additional information about the process by which these works were "constructed". In some cases, X rays reveal an underlying painting that might prove (a) that the top painting is a fake, or (b) that the artist did not like his first effort and reused the canvas to save money.

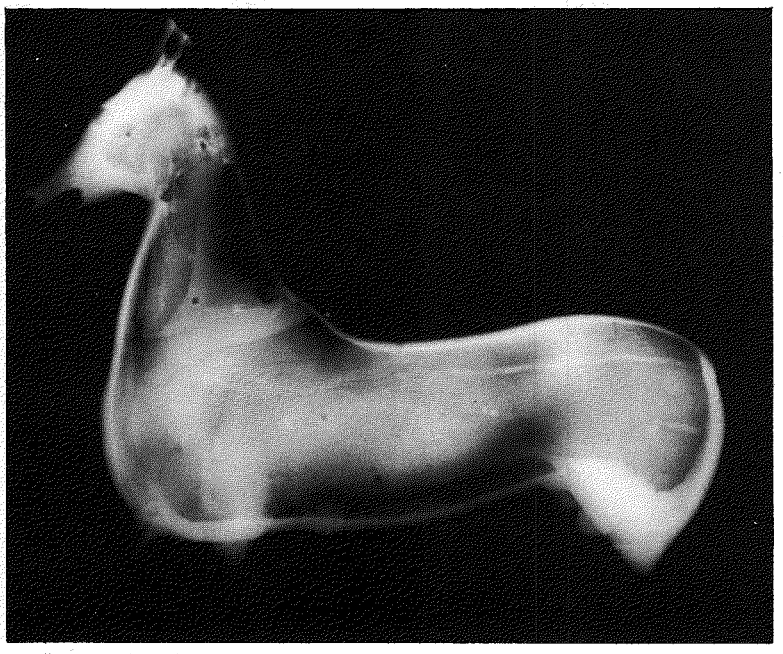
Because X rays are stopped more efficiently by elements with high atomic numbers, the lead white used in most old paintings generally shows up quite well. X-radiographs usually reveal the underlying brush strokes used by the artist

and in rare cases even his fingerprints. Such X rays are obtained with machines similar to those used for medical purposes.

The art experts then attempt to judge whether the brush strokes in a questionable painting indicate a technique similar to those in a genuine work by the same artist. Such judgments, like the judgment of the visible painting itself, are not always infallible and often lead to disagreement among the experts.

Recently, an object was X-rayed using a technique that would have been extremely difficult, if not impossible, before radioisotopes became abundantly available.*

At the Metropolitan Museum of Art in New York City,



Photograph and gamma radiograph of a bronze horse, 15 inches tall, which was purchased in Paris by the Metropolitan Museum in 1923 and is thought to be 2400 years old. It is considered by scholars to be one of the finest ancient bronzes in existence. In 1967 X-radiography caused certain questions to be raised about the authenticity of the horse.

there is a bronze statue of a horse that for many years held a place of honor as a fine example of early Greek art. One day, an official of the Museum became suspicious when a study of

*For more information about modern X-radiography, see *Nondestructive Testing*, another booklet in this series.

the horse using tiny magnets revealed the presence of iron at certain locations.

An X ray of the horse by ordinary techniques would have revealed nothing because of the thickness and density of the object. The use of the radioactive isotope iridium-192, however, provided gamma rays of sufficient penetrating power to reveal the presence of iron wires inside the horse.

Because the technique of using iron wire to support cores (to provide hollow spaces within the object) was thought to be a much more recent development, it was thought that the horse might be a modern forgery. Studies of the techniques used for casting by the ancient Greeks are under way to determine the authenticity of the horse.

There is little difference in the basic principles of radiography as practiced with X-ray machines decades ago and that using isotopic gamma-ray sources such as the one described above. However, the use of isotopes has made the examination of certain types of objects not only more convenient but sometimes possible for the first time. Beta rays have also been used for very thin materials (as have very low-energy X rays) because of the relative ease with which they are stopped. Somewhat different is the use of neutrons for radiography. In this case, while the radiation may be as penetrating as X rays, the stopping power of the examined material varies in such a way that components different from those detected by X rays may be seen. The method of "neutron activation autoradiography" described on page 90 is also a radiographic technique but with the extra advantage of providing identification of the elements present in the subject (flat objects only).

RESTORATION OF OLD PHOTOGRAPHS

While there are those who will deny photography the "right" to be called art, few will deny that the preservation

of fine photographs, particularly those of historical significance, is of great importance.

Eugene Ostroff, the curator of photography at the Smithsonian Institution, has studied some of the very early (mid-19th century) pieces in his care. Many of these represent efforts made during a period when the chemistry of the image-fixing process was imperfectly understood. The result was that these early prints had faded away until little or no image was visible.

An ingenious procedure for reprinting such old photographs was devised. This process, involving neutron activation of the image-forming silver deposits remaining in the paper, works even if no visible image is left. While the method is not always useful and, hence, is somewhat specialized, some success has been achieved in a number of cases.

The method is applied by bombarding the photograph for a short time in a section of a nuclear reactor having a known neutron flux. The photograph, with its silver now made radioactive is removed from the reactor and placed in contact with a fine-grained modern photographic film. The radiation from the old silver has an effect on the film similar to that of light and an image is thus produced on the film.

Mr. Ostroff and his co-workers have been able to produce clear images, undoubtedly similar to the original, where only badly faded ones existed before. In one case, "an image of a standing man dramatically emerged" from a completely faded William Henry Fox Talbot* photograph where "the paper contained no visible image." This was obtained with a 2- to 3-second irradiation and a 5-minute "autoradiographic" exposure.

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*William Henry Fox Talbot (1800–1877), an English pioneer of photography, invented a process at the same time as the French painter and inventor of the daguerreotype Louis Jacques Mandé Daguerre (1789–1851).

William Henry Fox Talbot (1800–1877), English antiquarian, physicist, and pioneer in optics and photography.

An early photograph restored by neutron activation. This 19th century picture, which is in the Smithsonian Institution, was exposed to neutrons and then placed in contact with modern photographic film. The originals had been taken by Talbot who began his career in 1834.

CONSERVATION OF WOOD AND OTHER POROUS MATERIALS

An important function of art museums is preservation (or conservation) of the priceless treasures housed within their walls. Artists' materials are often quite fragile and old objects in particular show the ravages of climate, weather, light, handling, and even air pollution.

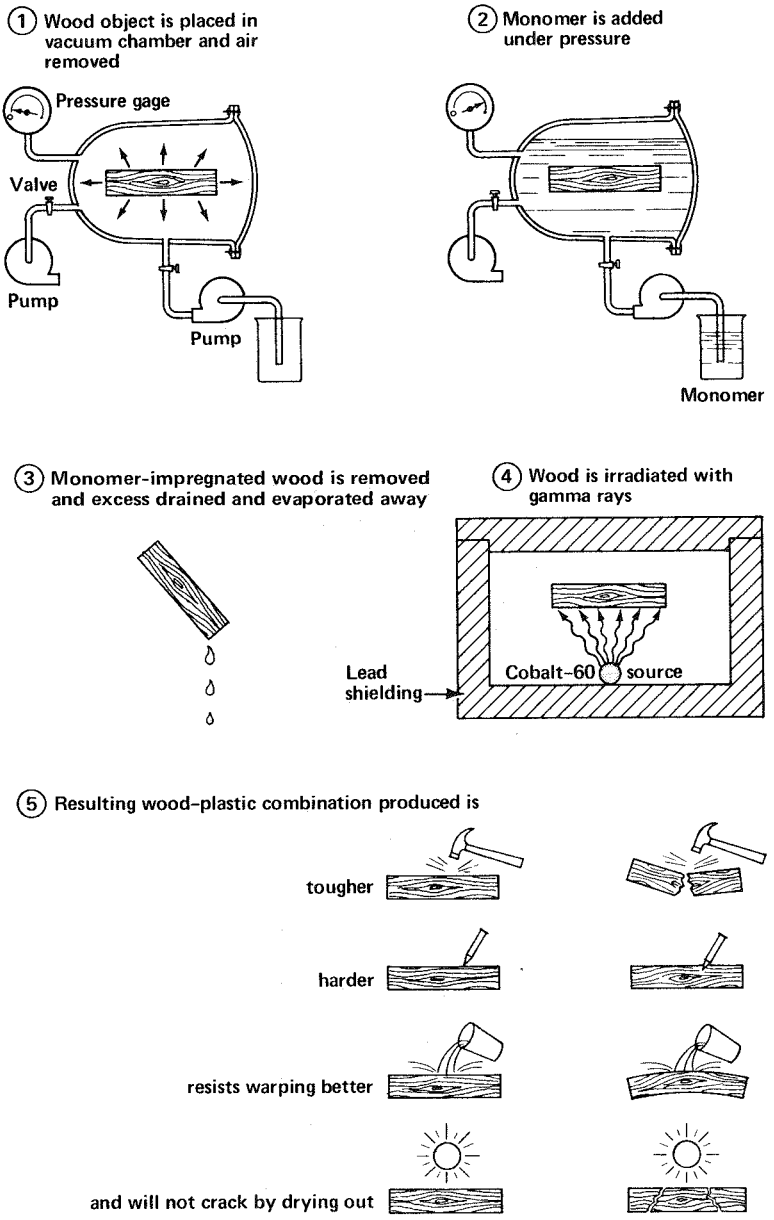
One material that has been frequently used by artists and that is quite susceptible to climatic conditions is wood. When wood dries out, it shrinks in an uneven way that may cause it to warp and crack. Naturally, a panel painting can become distorted and often will lose paint by flaking. Wood carvings are, of course, also highly susceptible to this kind of damage.

While many techniques have been developed to strengthen panels and to restrain the warpage, none have been wholly satisfactory. Many of the world's great museums have installed elaborate air conditioning systems, solely for the purpose of maintaining "comfort" for the art (not for the people). Many smaller museums and other repositories for works of art, however, cannot afford this expensive equipment.

In recent years, scientists, supported by the Atomic Energy Commission, have developed a whole new technology that can provide a better "wood". The procedure is to impregnate wood with a "monomer", a substance that can be made to "weld" its simple molecules into large ones called "polymers".* This process, called "polymerization" is induced by irradiating the wood-monomer combination with penetrating radiation from an isotope such as cobalt-60 or from a device such as an X-ray machine. The resulting wood-polymer material is much stronger and harder and no longer as vulnerable to changes in moisture and temperature.

While some art conservators have recognized that a stabilization process of this kind would be a valuable

*Plastics are an example of polymers with which we are all familiar.



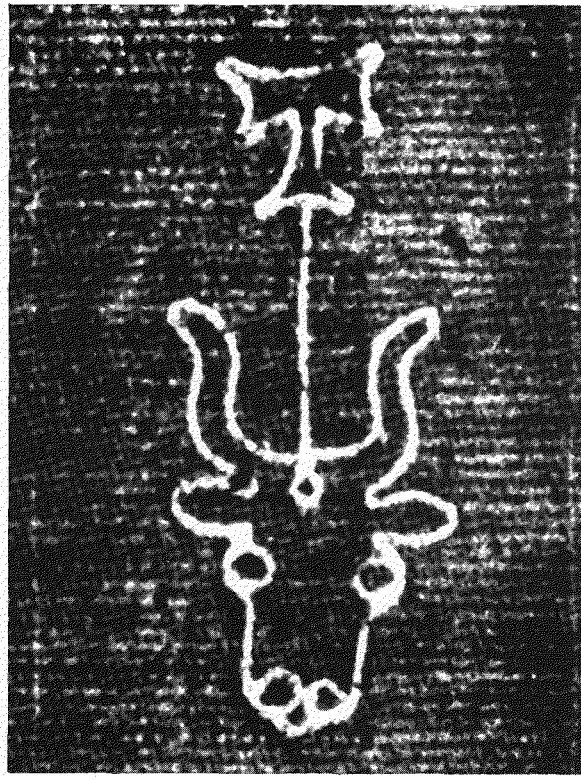
Making a combination of wood and plastic. Experiments have been started to use this system for the restoration of art made of wood.

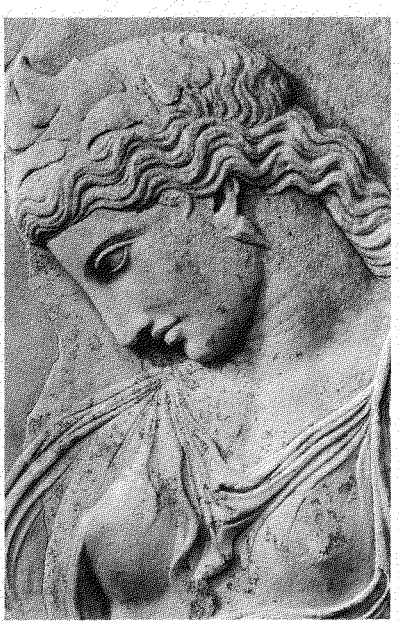
development, only a little work has thus far been accomplished along these lines. R. A. Munnikendam in the Netherlands has shown, for example, that the water of the wood of old, waterlogged ships can be replaced by a suitable monomer in a stepwise process. Then when the material is irradiated, a permanent, strong wood-plastic is obtained that will no longer be damaged by the drying-out process and yet is quite similar in appearance to the original object.

In view of the even more recent development (at Brookhaven National Laboratory) of radiation-induced concrete-polymer combination, it has also been suggested that works in stone, like marble, could be preserved by sealing the surface in this way. Marble is susceptible to staining because of the porous nature of this material. Once stained, it is difficult to clean without damaging the surface. The preservation of textiles, paper, leather, and other fragile materials has also been suggested.

◊ *This 14th century wooden madonna and child has been preserved by monomer impregnation and radiation polymerization by the French Atomic Energy Commission and the International Council of Museums.*

Of special interest to art historians is the need to know the exact date of early printed books. One way is to determine the age of the paper on which the book was printed. The molds used for watermarks, each with its own unique design, had a "life" of only a few years before they deteriorated beyond use. Ordinary methods of studying watermarks had not been satisfactory. A new technique, which is simpler than any camera and guaranteed not to harm the books, uses beta radiography to produce clear sharp pictures that are to scale. A small sheet of carbon-14 impregnated Perspex (a hard plastic) is placed on one side of a watermark and a piece of X-ray film on the other. Thirty minutes later the picture has been "taken". Other beta sources are quicker, but more costly and shorter-lived. Carbon-14 will work satisfactorily for 5000 years after which it is advisable to invest in another sheet of Perspex. On the right is a beta radiograph of a page from Caxton's Golden Legend, *circa 1484.*





Summing Up: What the Future Holds for the Past

As you can see, there are many new tools that are being developed for art and archaeology as extensions of the techniques of nuclear science. Most of these had their beginnings only in the last few years. As a result, much work remains to be done in order to fully develop these new methods and to prove their reliability and usefulness.

Already at least one method, carbon-14 dating, has really revolutionized the field of archaeology. In addition to the wealth of information derived from this dating method, scientists from many fields have now been attracted to the problems of both art and archaeology. This can only lead to more fruitful applications of scientific methods to these problems.

Finally, there has been a gap between the "two cultures" of art and science, which, in the past, has prevented understanding between two large segments of our civilization. Now at last, mutual interest between these two groups may begin to bridge the gap as each learns the other's "language" and begins to see the meaning of the other's profession.

Reading List

Because of the diverse nature of the material in this booklet, no attempt is made to provide a comprehensive guide to the literature. For general information about the fundamentals of nuclear science, the reader is referred to:

A Bibliography of Basic Books on Atomic Energy, a companion booklet in this series, and to those other booklets indicated as footnotes in the text.

For more specific information, the following references provide an entry to the literature of the field.

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PHOTO CREDITS

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Contents page	Statue of Queen Hat-Shepsut, ca. 1485 B. C. The Metropolitan Museum of Art, Rogers Fund and contributions from Edward S. Harkness, 1929.

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A terra-cotta portrait of the Etruscan god Apollo.

It was no easy matter, moving the cover, but finally it was lifted upright then allowed to fall heavily on the other side. And then something happened that I have never forgotten and that will remain before my eyes as long as I live. I saw resting within the coffin the body of a young warrior in full military panoply, with helmet, spear, shield, and greaves. Observe that it was not a skeleton that I saw, but a body, complete in all its limbs, and stiffly outstretched as if freshly laid in the grave. This apparition endured, but for a moment. Then everything seemed to dissolve in the light of the torches. The helmet rolled to the right, the round shield fell into the now sunken breast-piece of the armor, and the greaves suddenly collapsed flat on the ground, one to the right, one to the left. The body that had remained untouched for centuries had suddenly dissolved into dust when exposed to the air. . . a golden dust was suspended in the air and about the flame of the torches.

Augusto Jandolo describing the opening
of an Etruscan sarcophagus

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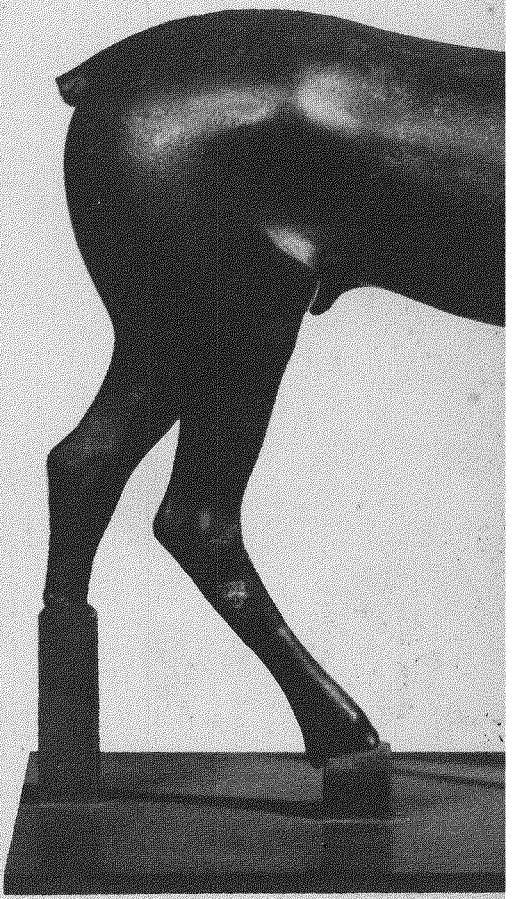
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