

Lawrence Berkeley National Laboratory

Recent Work

Title

RAPID X-RAY FLUORESCENCE ANALYSIS OF ARCHAEOLOGICAL MATERIALS

Permalink

<https://escholarship.org/uc/item/41811010>

Authors

Bowman, H.R.

Giauque, R.D.

Perlman, I.

Publication Date

1967-12-04

cy 2

University of California

Ernest O. Lawrence Radiation Laboratory

RAPID X-RAY FLUORESCENCE ANALYSIS OF ARCHAEOLOGICAL MATERIALS

H. R. Bowman, R. D. Giaque and I. Perlman

December 4, 1967

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

Berkeley, California

RECEIVED
LAWRENCE
RADIATION LAB

FEB 21 1968
LIBRARY
DOCUMENTS

UCRL - 17968
cy 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Physical Review

UCRL-17968
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

RAPID X-RAY FLUORESCENCE ANALYSIS
OF ARCHAEOLOGICAL MATERIALS

H. R. Bowman, R. D. Giaque and I. Perlman

December 4, 1967

RAPID X-RAY FLUORESCENCE ANALYSIS OF ARCHAEOLOGICAL MATERIALS*

H. R. Bowman, R. D. Giaque and I. Perlman

Lawrence Radiation Laboratory
University of California
Berkeley, California

December 4, 1967

The great improvement recently in solid-state photon detectors and associated electronics has led to the development of a rather new type of X-ray fluorescence spectrometer. The instrument appears to be particularly suited to the rapid non-destructive analysis of a large number of articles and artifacts. The system takes advantage of the very high resolving power of these semiconductor detectors which make it possible to measure and distinguish the individual characteristic X-rays of various chemical elements excited in a specimen by a primary source of gamma radiation. The main features of this instrument which may appeal to the archaeological investigator are as follows.

- (1) It is relatively easy to use and operate. Many objects can simply be held in front of the detector housing for the analysis. The data resulting from these analyses are presented in a form that is relatively easy to interpret.
- (2) It provides a rapid means of non-destructive qualitative and semi-quantitative analysis of the chemical materials in a large number of artifacts. Many times only one or two minutes are needed for each analysis.
- (3) The instrument is portable. It could be taken into a museum and set up in a few minutes. It can even be taken into the field for an on-the-spot analysis of artifacts. If an object cannot be moved, then the unit can be brought up to the object to be tested.
- (4) Preliminary results indicate that the instrument can be used for quantitative analysis.

A detailed description of the equipment has been given in Science¹ where it is compared with the more conventional X-ray fluorescence analysis equipment, and only a brief description of the general principles involved will be given here. Figure 1 shows the arrangement of the

apparatus schematically. The source of gamma radiation at the lower left is usually either I^{125} or Am^{241} . Gamma rays from the source impinge on the sample to be tested while the detector is shielded by lead from the direct rays. The characteristic K X-rays and L X-rays that are excited in the sample are then detected by the X-ray detector which give rise to electrical impulses proportional to the X-ray energies. The electrical pulses are amplified and then stored in a multichannel analyzer. The stored information can be printed or plotted out at the end of the run giving a permanent record of the X-ray energy spectrum.

The X-ray detectors and the first transistor (F.E.T.) of the preamp (Fig. 1) are kept at liquid nitrogen temperature, which reduces the electronic noise and results in the very high X-ray energy resolution. The lower X-ray energy cutoff of the instrument is determined by this electronic noise as well as by the window on the detector housing and the air between the window and the sample. At present the latter two causes prevent us from detecting X-rays with energies lower than those of calcium.

In the analyses presented here we used both the lithium-drifted silicon and germanium type solid-state detectors, although either type could have been used for all of the measurements. The X-ray detectors were originally developed for nuclear spectroscopy where the products of nuclear reactions are analyzed in terms of atomic number through their self-induced X-ray energies. The X-ray fluorescence spectrometer as an analytical tool is a fortuitous product of this nuclear work.

The fact that the instrument might be of use to analyze archaeological artifacts was suggested first by Dr. Jay Frierman from UCLA who sent a large number of articles to use in an evaluation program. With the help of Dr. Robert Rodden from the University of California we were able to obtain a number of early Egyptian artifacts to further this evaluation. More than one hundred items were analyzed and a few of the results will be shown to illustrate the technique.

In Fig. 2 we show a photograph of the equipment along with a pre-dynastic Egyptian spear which is being analyzed. The accumulation of data can be seen on the oscilloscope screen even while the measurement is in progress. A plot of the results from a 2 minute analysis of this

spear is shown in Fig. 3. We are able to identify copper, arsenic and silver in the spearhead. The arsenic and silver intensities are very low compared to that of copper and represent only about 1% arsenic and 0.1% silver when these results are compared to results obtained from the analysis of standard alloys. The standard alloys were usually made by melting and mixing pure metals in a ceramic crucible. Arsenic in a range of around 1% was found in a number of the dynastic and predynastic copper artifacts.

The artifacts from this collection all came from burials and along with them were found many ore specimens including those of copper. Over 100 bits of copper ore were examined and none contained arsenic in detectable amounts. One can say for sure that arsenic in the copper objects was not accidentally introduced through copper ores of the types found and, by inference, that it was added deliberately.

X-ray fluorescence analysis is particularly sensitive to surface conditions and the surface materials. This is illustrated in Fig. 4 where the two sides of an early dynastic bronze mirror were analyzed. Side "A" indicates about a 12% tin-bronze content while side "B" indicates about 4% tin-bronze content. At first it was thought that this variation was the result of selective corrosion of side "A" shown in the photograph in Fig. 4. Further analysis using the "source target assembly" (to be described later) seems to indicate that there is a thin layer of tin on side "A." This assembly allows one to vary the energy and hence the depth of penetration of the exciter radiation. Additional useful information could be obtained by a more detailed analysis of the surface layer and of material bored from the body of the mirror. The point to be made is not that this problem has been resolved but that a very rapid scan of the X-rays did turn up a problem of potential archaeological interest.

In many cases the gamma radiation can be concentrated or focussed onto a particular part of an object to test for local nonuniformities. The article in Fig. 5 labeled "late dynastic bronze clamp" was used to demonstrate this effect. When the gamma rays were focussed onto the labeled location, exceptionally intense iron X-rays were observed. The arrows pointing to the iron on the left-side may indicate the use of an iron hinge pin and the other two locations imply the use of iron rivets or brads to fasten the hinge to a second material. The clamp or

hinge is only about 2 inches long. This technique could probably be developed so that a small beam of γ rays (~ 1 mm dia) could be used to scan an object and produce an X-ray contour plot of the different elements in or on the surface of the article. The appearance of iron on this particular object sheds considerable doubt as to whether it belongs in such an early context.

The article shown in Fig. 6 was labeled "late dynastic metal tube." The X-ray analysis on the right indicates that both the walls and the bottom of the tube were made of the same materials, namely a tin bronze with a small amount of lead that may be on the surface of the tube. The X-ray shadowgraph (in the center) suggests that the walls and the bottom were cast as one piece and also shows three separate zones of materials within the tube. These materials have the appearance of metal slags. The top zone is rich in lead, the second zone is a tin-lead composition and the bottom zone is a tin-copper mixture. One is tempted to suggest that this metal tube was used to reduce small amounts of tin or lead ores. The lower wall has either been melted or corroded away, probably melted.

Preliminary measurements indicate that the X-ray fluorescence technique can be used for more quantitative results if one is willing to sacrifice a small amount of the materials to be tested. About 100 mg of the material can be ground into a powder, incorporated into a cellulose matrix and pressed into a wafer. The wafer is then placed in a standard sample holder and attached to what is called a source-target assembly. This assembly is shown in Fig. 7. The gamma-ray source which is not critical in this method is encapsulated in a thin aluminum annular ring about 1 in. in diameter. The isotope Am^{241} was chosen in this case because of its long half life. The gamma rays and neptunium L X-rays from this source impinge upon a secondary target material which can be made of any element and excites the characteristic X-rays of that element. The targets are made from metal powders, oxides or other suitable compounds of the elements mixed with a minimum of epoxy resin. The target X-rays, which are nearly monochromatic, impinge on the wafer and in turn excite X-rays of their constituents. The target materials can be chosen to have their characteristic energy just above that of the absorption edge of the element to be determined in the wafer, thus ensuring high

analytical sensitivity. This general approach was originally developed by Rhodes and is described in more detail in his "Review of Radioisotopes in X-Ray Spectrometry"² which appears in The Analyst. The article also reviews the many difficulties encountered in X-ray fluorescence analysis. The three main sources of difficulties are due to effects usually called "matrix-absorption, matrix enhancement, and particle size." These are well known effects in conventional X-ray analysis, and the approach to their elimination is similar in both the conventional and present techniques because the effects occur in the sample.

A number of early sub-Saharan African glass beads (from Mapungubwe) were used to evaluate this method.* These analyses hopefully will give results on some of the constituents of glass which will be of some diagnostic value. The time required for the analysis of each of these specimens typically was 10-30 minutes, and improvements are quite possible by using stronger sources and X-ray detectors of higher energy resolution than the system thus far employed. The initial results are presented in Table 1 and show quite clearly that, aside from the coloring matter, a number of different types of glasses appear. The A series all contain lead, and in all except one case antimony was present, presumably added for opacity. Four of the nine specimens contain substantial amounts of arsenic.

Four of the D series contain substantial amounts of lead; the others containing smaller or undetectable quantities. All but two of the D series contain tin, but none antimony. Two of the D series (D5 and D6) contain neither lead nor tin and are very similar to the C series. The turquoise beads (D3) were visibly inhomogeneous, and further effort at segregation was attempted under magnification. The segregated beads were significantly different in copper content but otherwise seemed to be of the same type of glass. The amber beads were the only ones showing some zinc. Of special significance for archaeologists is the fact Skeleton 14 from Mapungubwe has beads of two quite different compositions, namely those of D1-4 and D5-6. The latter shows similar composition to the beads with Skeleton 23. This suggests that the beads traded up the Limpopo River to Mapungubwe came from at least two different sites.

* We are indebted to Professor J. Desmond Clark for placing these beads at our disposal and informing us of their significance.

Returning to the A series, it will be noted that the substances responsible for the colors in A-2, A-3 and A-5 were not detected by this technique. Also A-1 was significantly lower in lead than other members of the series. These beads were the only ones which were laminated, consisting of Indian red material over a colorless core. It may well be that one of the layers contains little or no lead.

In conclusion we would like to emphasize that the instrument and the techniques have only recently been developed and will no doubt be improved with further application. We believe it has a potential use in the field of archaeology, although it is still not clear which problems are most suited to it. We feel that the archaeologist himself will be able to use the instrument in the laboratory, the museum or in the field, and that perhaps he will be the one to determine the manner in which this instrument can be best applied to his problems. With this in mind we would like to restate the main features that may appeal to the archaeologist:

- (1) The equipment is relatively easy to operate.
- (2) It provides a rapid non-destructive means of identifying the elemental materials in a large number of articles.
- (3) It is portable and can be taken into museums and even into the field.
- (4) It can be used for more quantitative results when more time and care are involved in sample preparations.

FOOTNOTE AND REFERENCES

- * This work was done under the auspices of the U. S. Atomic Energy Commission.
- 1. Harry R. Bowman, Earl K. Hyde, Stanley G. Thompson, and Richard C. Jared, Science 151, 562 (1966).
- 2. J. R. Rhodes, The Analyst 91, 683 (1966).

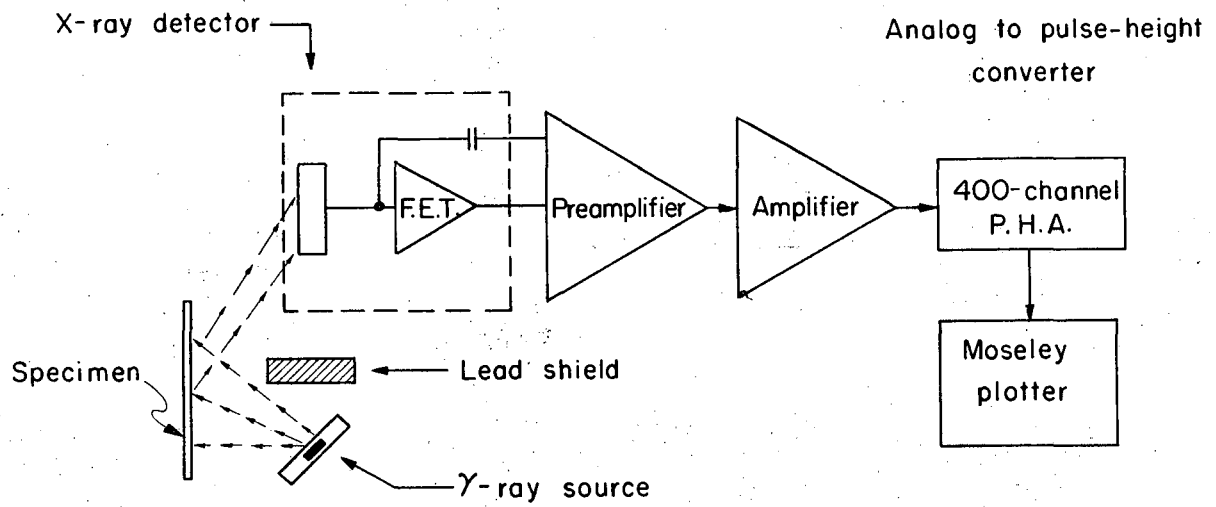
FIGURE CAPTIONS

- Fig. 1. Schematic arrangement of the apparatus for exciting and measuring the characteristic X radiation of archaeological samples.
- Fig. 2. A pre-dynastic Egyptian spearhead being analyzed with the X-ray fluorescence spectrometer.
- Fig. 3. The X-ray energy spectrum obtained from a two minute analysis of the spearhead shown in Fig. 2.
- Fig. 4. The X-ray energy spectra obtained from the two sides of an early dynastic Egyptian bronze mirror. Side "A" is shown in the photograph.
- Fig. 5. A late dynastic Egyptian bronze clamp. Iron was detected at the labeled locations.
- Fig. 6. A late dynastic Egyptian metal tube. The X-ray shadowgraph, in the center, shows the outlines of the tube walls and bottom along with three zones of material within the tube. The X-ray spectra of the outer wall of the tube shown on the right is similar to the spectra obtained from the bottom of the tube.
- Fig. 7. Schematic arrangement of the source-target assembly.

Table 1. The analysis of sub-Saharan African beads (Iron Age) using the source-target X-ray fluorescence assembly.

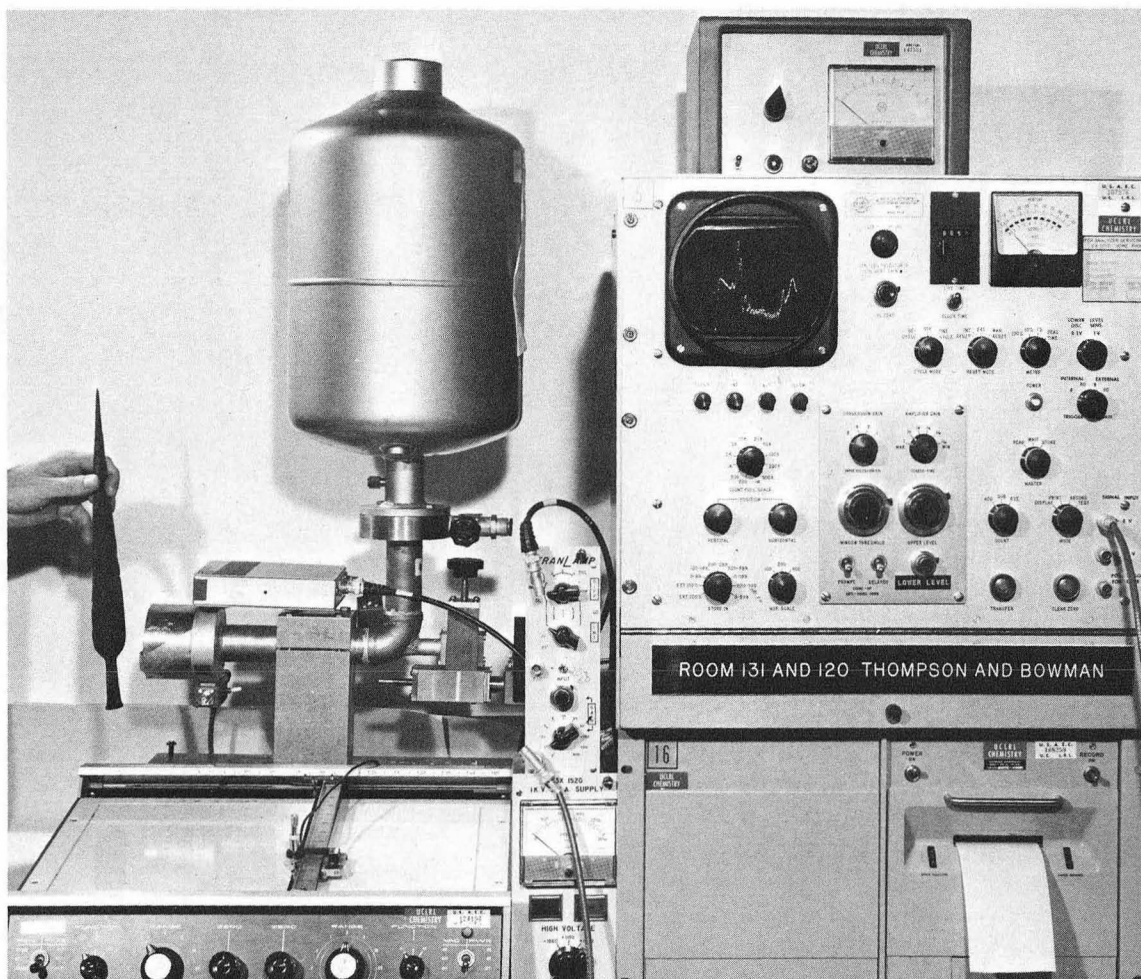
Sample No.	Sample	Sample Origination	Fe	Cu	Zn	As	Sb	St	Pb
A-1	Brownish red beads	Mapungubwe S. Limpopo, Rockshelter	1.3%	1.7%				.5%	4.3%
A-2	Pink beads	"				1.6%		.5%	25.5%
A-3	Light blue beads	"				3.7%		.1%	21.9%
A-5	Blue beads	"				2.1%		<.05%	27.4%
A-6	Long light green beads	"		1.1%				1.2%	32.5%
A-7	Dark blue beads	"		2.2%				1.8%	9.8%
A-8	Long dark blue beads	"		2.8%				.5%	10.8%
A-10	Blueish green beads	"		1.2%				2.1%	12.7%
A-12	White beads	"				4.2%		.1%	13.6%
C-1	Black beads	Mapungubwe Skeleton #23	.9%						.1%
C-2	Light blue beads	"	1.5%						<.3%
D-1	Yellow beads	Mapungubwe, Eastern Area Ex. 7, No. 1, Skeleton #14	1.0%				1.0%		5.9%
D-2	Amber beads	"	.7%		.4%		1.5%		9.5%
D-3	Turquoise beads	"	1.1%	1.5%			1.4%		.3%
D-4	Apple green beads	"	.8%	1.5%			1.2%		6.9%
D-5	Blue beads	"	1.5%						<.1%
D-6	Black beads	"	1.0%						
Maximum metal content if none reported			<.2%	<.2%	<.1%	<.1%*	<.1%	<.1%	<.1%

* <.3% if more than 5% Pb is present.



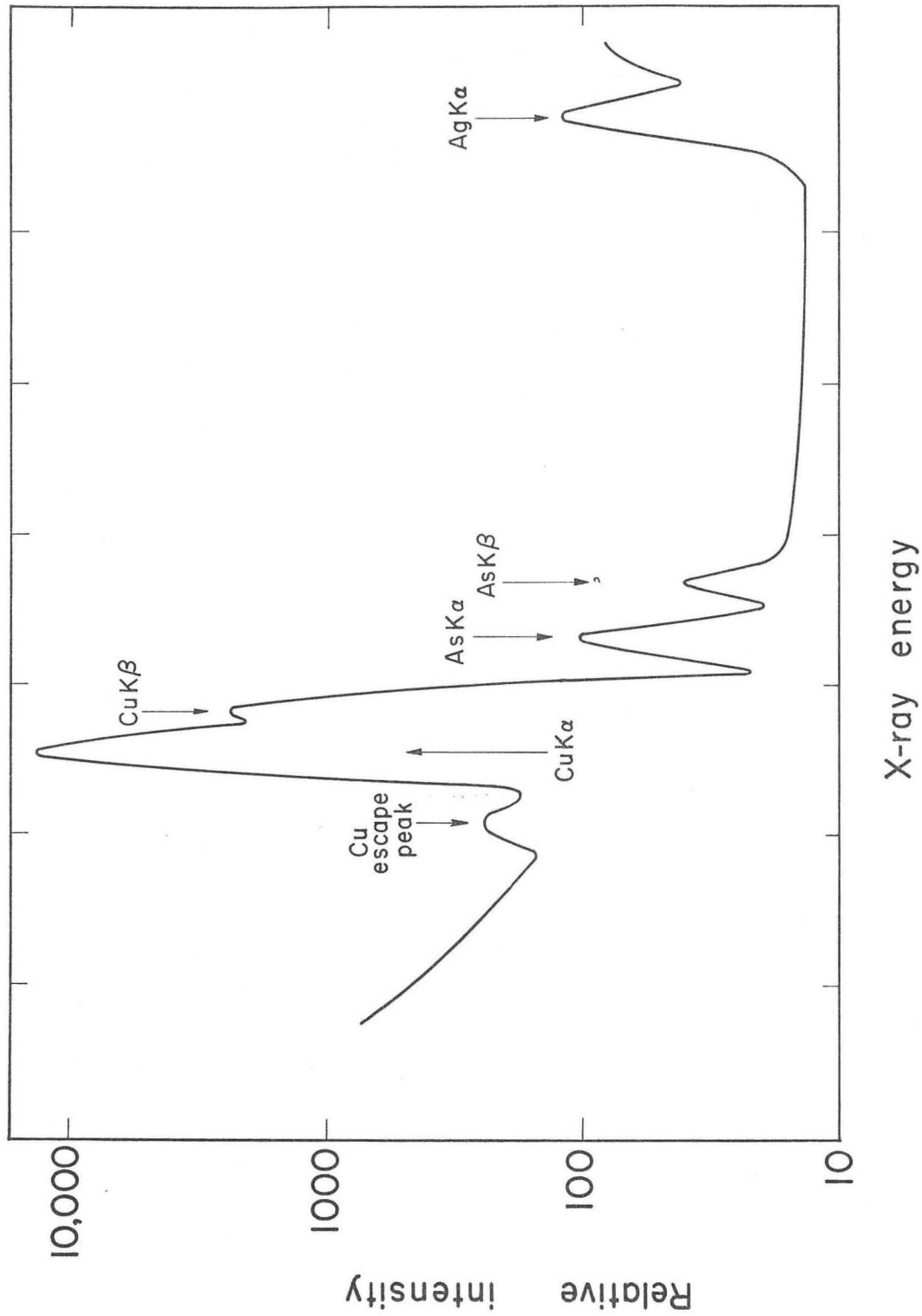
MUB-8596

Fig. 1



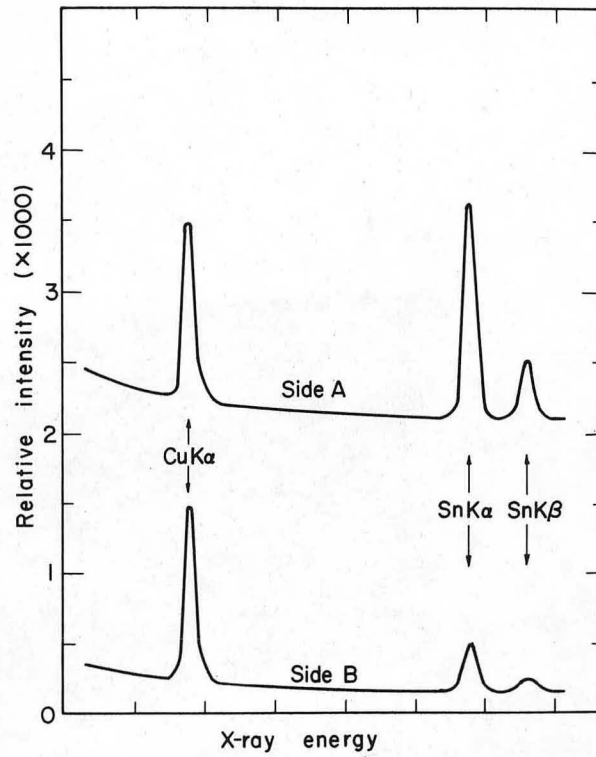
XBB 676-3244

Fig. 2



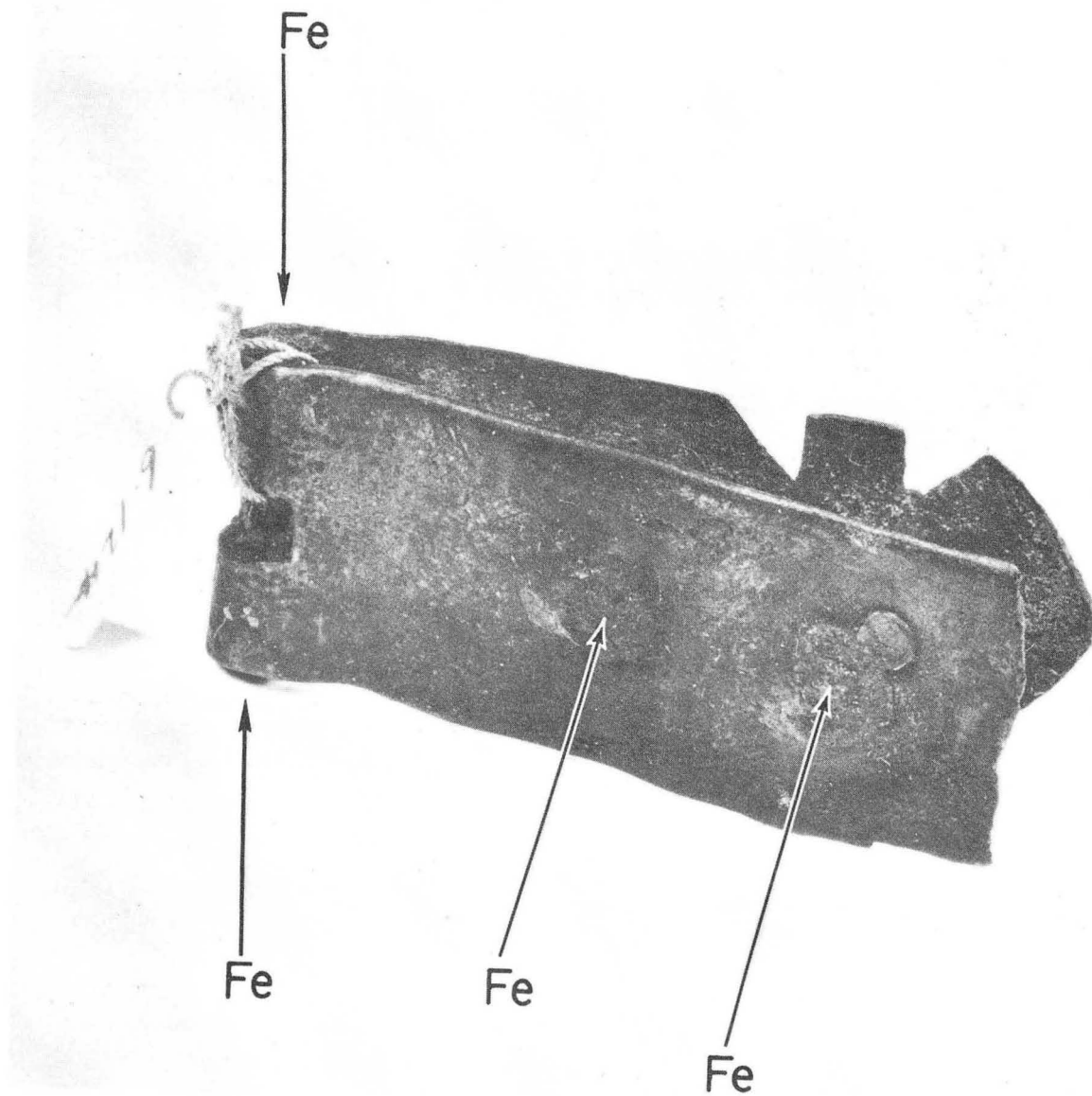
XBL 670-5380

Fig. 3



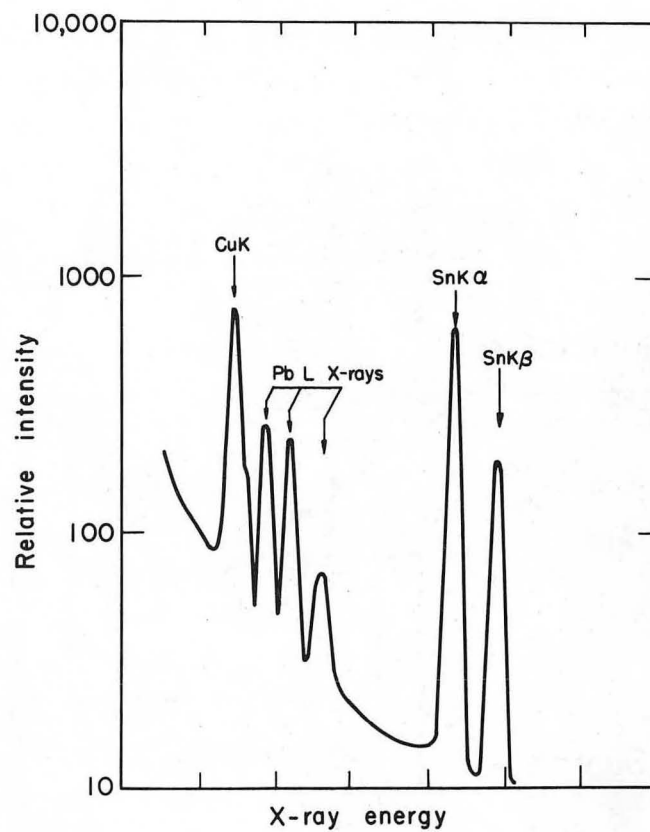
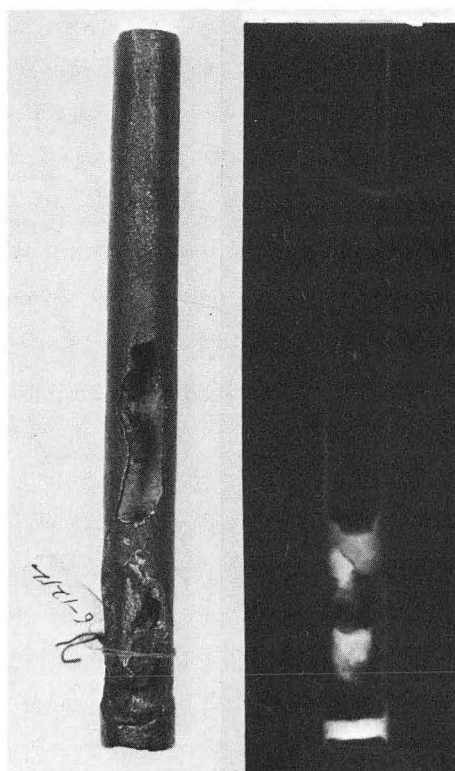
XBB 6710-6034

Fig. 4



XBB 6710-6021

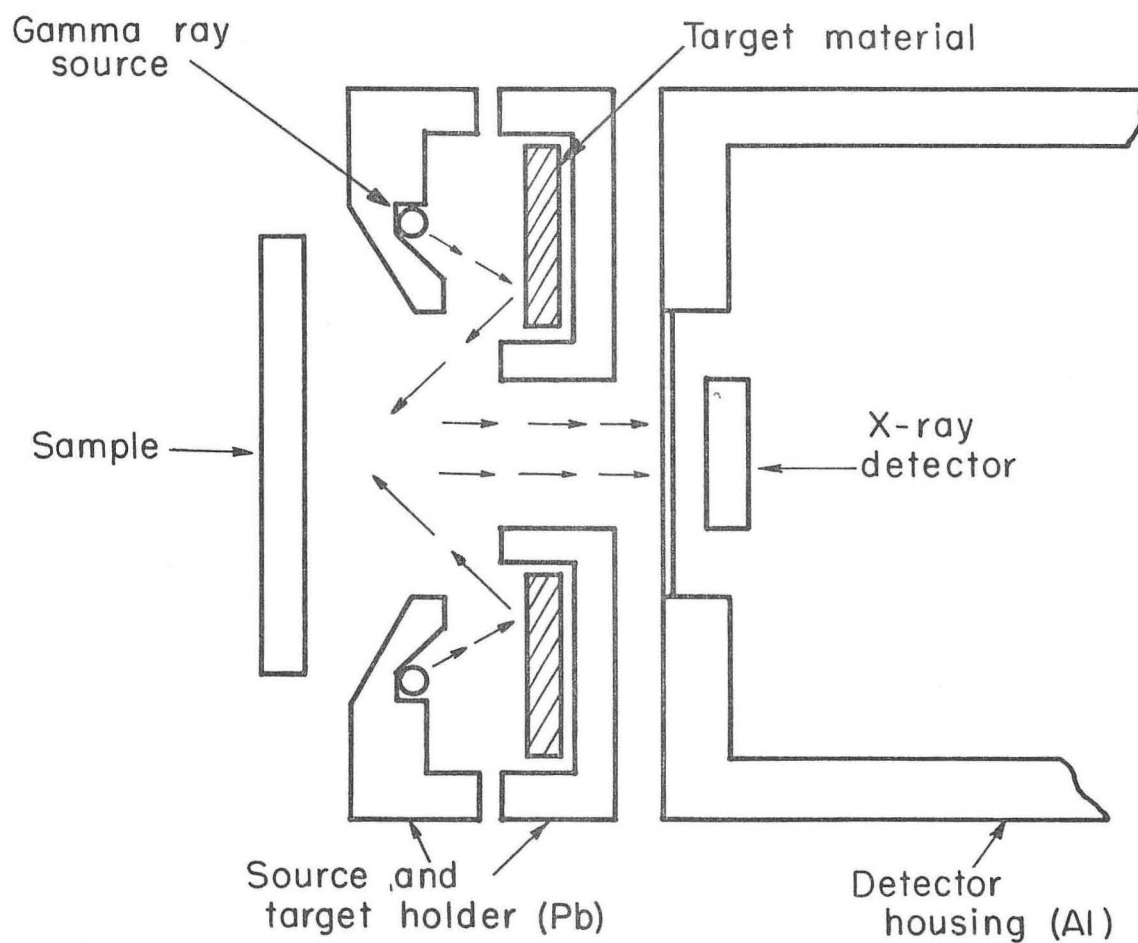
Fig. 5



XBB 6710-6033

Fig. 6

Source-Target Assembly



XBL670-5398

Fig. 7

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

