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Refinement in Methods of Neutron Activation Analysis of Ancient Glass
Objects through the Use of Lithium Drifted Germanium Diode Counters *

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Abstract

The non-destructive analysis of archaeological objects by means of neutron activation followed by gamma-ray spectroscopy has been limited by the relatively low resolution obtainable with crystal scintillation detectors. The relatively broad spread of photopeaks of high activity overlaps and masks nearby peaks of lesser activity, limiting the number of component elements that can be detected and measured. The new lithium drifted germanium diode solid state detectors, which record photopeaks with nearly ten times the resolution of large crystal scintillation detectors, provide promise of largely overcoming this problem.

With the new detectors it has been possible to determine non-destructively the concentrations of some rare earth oxides in ancient glasses. Of these the concentration of europium oxide, although below spectrographically detectable limits, showed a pronounced and significant reverse correlation with the concentrations of magnesium and potassium oxides. It has been suggested that the alkali used in the preparation of ancient glasses which are characterized by low concentrations of magnesium

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or potassium oxides might have been natron, the naturally deposited sodium carbonate from the lakes of the Wadi Natroun in Egypt. If natron contained a sufficiently high concentration of europium oxide its use in these glasses would be indicated. However specimens of both ancient and modern natron were found not to contain the relatively high europium concentrations which characterize the low magnesium and potassium ancient glasses.

Introduction

Neutron activation analysis has proved a practical method for the analysis of ancient artifacts which in many instances can be carried out in a nondestructive way on the artifacts themselves¹. In such procedures all or a portion of the ancient objects are exposed to a beam of neutrons which will nearly uniformly penetrate the objects and transmute a minute fraction of the atoms within them into radioactive forms, i.e. radioisotopes. As the transient radioactivity that has been induced throughout the objects decays away some of the high energy particles emitted in this process can be detected beyond their surfaces. The induced radioactivity will eventually diminish to the extent that the objects essentially return to their original condition.

From the nature and quantity of such emitted particles a determination of the concentrations of some of the components of the activated objects can be derived. Because gamma rays are emitted from most neutron activated nuclei and come off with characteristic and well-defined energies they are most frequently measured for such determinations. In the past the sodium iodide crystal scintillator has been the most useful device for measuring

gamma rays. With this detector and appropriate supplemental electronic equipment it has been possible to separate the measured gamma rays according to their individual energies into a spectrum. The gamma rays contributing to a particular energy peak in such a spectrum usually will have been emitted by a radioisotope of a particular chemical element. To the extent this is true the peak will indicate the presence and concentration of this element independent of the other components of the activated object. This method of analysis has been restricted, however, by the relatively low energy resolution of crystal scintillators. Their response is such as to record a monochromatic gamma ray as a broad peak. For example, the scintillation counter photopeak associated with a gamma ray of a million electron volt energy will extend over a range of more than one hundred thousand kilovolts. The photopeak of gamma rays of even roughly similar energies when measured this broadly will therefore interfere with each other. In past nondestructive activation analyses a photopeak was properly trusted as representing a gamma ray from a single radioisotope only if it decayed with the precisely correct half life for that isotope.

The recently introduced lithium drifted germanium diode solid state counters² to a great extent overcome this disadvantage of scintillation counters because their resolution is an order of magnitude better. Figure 1 shows a comparison of the spectrum of the two gamma rays of cobalt 60 is of 1.17 and 1.33 million electron volt energies measured by a large sodium iodide scintillating crystal and a relatively small germanium diode. The difference in the breadth of photopeaks is indeed striking. That this sharpening in gamma ray measurement can be of immediate value in the nondestructive analysis of ancient glasses is demonstrated in

Figure 2. This figure shows, for the same region of energy as Figure 1, the gamma ray spectrum measured by a germanium diode of a neutron activated ancient glass specimen. The gamma ray spectrum of the activated ancient glass clearly includes photopeaks arising from gamma rays other than those of cobalt 60 which are resolved from the cobalt 60 peaks by the germanium diode counter but which would have overlapped them in a spectrum obtained by a scintillation counter. It is apparent the new counters will permit the separate measurement of many additional elements.

A germanium diode is constructed by effectively bringing into contact a slab of the semiconducting element germanium containing a small concentration of another element capable of releasing electrons into its crystal structure with a germanium slab containing an element which removes electrons from it. At the plane of contact electrons will tend to migrate from the electron excess side to the electron deficient side creating a thin intermediate layer in which the ground electronic state of the germanium crystal lattice has been exactly satisfied. At low temperatures this intermediate layer has high electric resistivity because the usual charge carriers within it have been exactly neutralized. For this reason it is called the depletion layer, having been depleted of excess electrons or electronic vacancies. However the transversal of this depletion layer by a high energy gamma ray photon will result in electronic excitation which temporarily permits electricity to flow through the layer. The quantity of electricity passed through the normally resistant barrier is proportional to the amount of energy lost by the particle within the layer. A sharp photopeak results from complete absorption of the photon energies within the measuring layer. Partial

loss of particle energy results in a broad spectrum band called the Compton band which first appears some two hundred kilovolts below the photopeak. Figure 1 shows the accompanying Compton bands as well as the photopeaks of the cobalt 60 gammas. Of course, the larger the depletion layer the greater the likelihood of the complete absorption of particle energy which contributes to the desired photopeak. The distribution of ionic charges within the germanium diode layers is such that the spontaneously occurring depletion layer is very narrow. The thickness of the layer can be increased, however, by applying an electric potential to the diode and by allowing metallic lithium to diffuse from the electron excess side into the intermediate layer while the diode is heated and an electric current is flowing through it. In such lithium drifted germanium diodes depletion layers with as much as a centimeter depth have been produced. Although the partial Compton interactions often have provided a troublesome background in the use of the small germanium diodes first available it is to be hoped that the newer larger detectors will to a great extent overcome this difficulty. The larger germanium detectors also promise to overcome in part another disadvantage of the smaller detectors, that is, a very low counting efficiency. The solid state detectors will probably continue to be characterized by low sensitivity, however. Another disadvantage of the present detectors is that they must be maintained and operated at low temperatures, otherwise the thermal noise level would be high and the lithium might further drift in an undesirable way. The low temperature is usually maintained by mounting the detector in thermal contact with a metallic rod that extends into a reservoir of liquid nitrogen.

"Trace-Trace" Concentrations of Europium and Cerium in
Ancient Soda Lime Glasses

For some time an extensive analytical study of ancient glass has been undertaken at Brookhaven National Laboratory in collaboration with Mr. Ray Winfield Smith.³ Some forty-five institutions throughout the world, mostly museums and other repositories of archaeological materials have generously provided specimens of well-established provenance and date for this study. The specimens which now number more than four hundred were selected to sample reasonably uniformly the glass produced in western Asia, Europe and North Africa from the middle of the second millenium B. C. through the end of the first millenium A. D.

A number of significant compositional correlations have been observed among these specimens but the most fundamental aspect of our data has been the extent to which the specimens can be divided into large basic groups upon the basis of their compositions. About 98 percent of our specimens have had basic compositions very similar to modern "soda-lime" glasses. The predominant alkali in these glasses is sodium oxide, which occurs in about 15 to 20 percent concentration, and the predominant alkaline earth calcium oxide, 5 to 10 percent. With but a few exceptions these major components show no significant variations in concentrations. However, the related minor constituents potassium and magnesium oxides occur in two quite separate ranges of concentrations. The separation of these some four hundred specimens into a group characterized by relatively high magnesium and potassium concentrations and a group with relatively low concentrations of both elements can be made without reference to the origins or dates of the individual specimens. A plot of the numbers of specimens against the logarithm of their magnesium oxide concentrations

shows a separation into two well-resolved and defined peaks. Such a plot is shown in the lower part of Figure 3. The best fitting Gaussian curves are superimposed upon the histograms showing that the peaks plotted in this way have normal chance distribution. If the potassium oxide concentrations of the two groups of specimens which have been separated upon the basis of their magnesium oxide contents are similarly separately plotted they also distribute into different although more overlapping Gaussian peaks.

In the upper part of Figure 3 the specimens under the solid curve at lower potassium oxide concentrations are the same specimens that are grouped under the solid low magnesium oxide curve. Similarly the same specimens are included under the dotted curves with higher potassium as well as magnesium concentrations. The potassium distributions are more broad and overlap more than do the magnesium distributions but they clearly show the existence of a pronounced and consistent correlation between the magnesium and potassium concentrations. The very few specimens which show an indeterminate intermediate magnesium concentration can be designated as to their proper group on the basis of their potassium concentrations.

As would be expected the occurrence of these two basic compositional types of ancient soda-lime glasses conforms to a distinct chronologic and geographic pattern. For example, all of our second millenium B. C. glass specimens have been of the high magnesium type. This includes specimens from Egypt, Greece, and southwestern Iran. The low magnesium formulation is first encountered in glass of the first millenium B. C. from relatively western find sites, although specimens from as far east as Persepolis

have been of this type. During the first half of the first millenium A. D. glass of the older high magnesium formulation appears to have been plentiful only in areas extending eastward from the Mesopotamian region. From within the maximum geographic limits of the Roman Empire practically all of the glass finds are of the low magnesium type. However many of the early Islamic glass makers seem to have returned the older high magnesium tradition to more western areas. One finds a large fraction of Islamic glass from sites as far west as the countries bordering the Eastern Mediterranean to be of the high magnesium type. Thus the two formulations would appear to characterize two distinct traditions on glassmaking, both of which were followed in many different areas for many centuries. Because the correlation between the magnesium and potassium concentration is so consistent in these many regions and over these long periods one feels the characteristic change in the concentrations of both elements must have been controlled by the same raw material. Because potassium is one of the elements significantly involved it would seem likely that a different alkali was used in the two types of glass.

One can theorize as to the nature of the alkalis that might have been used. The concentrations of magnesium and potassium in the low magnesium glass are sufficiently small that they could have arisen from clay and other soil contaminants in the sand used for this glass. The alkali used in this glass could, therefore, have been nearly devoid of both magnesium and potassium. Such an alkali is natron, the naturally occuring mixture of sodium salts, predominately sodium carbonates, that naturally deposits in the lakes of the Wadi Natroun in lower Egypt. Natron has been commercially exploited in Egypt since early Dynastic times and indeed Pliny⁴ mentions the use of "nitrum" in Roman glassmaking.

As for the high magnesium glasses, Turner⁵ has suggested several alkalis which contain sufficiently high magnesium and potassium concentrations that had they been used for glass manufacture in antiquity they would have produced glass of this formulation. These alkalis include the ashes of certain desert plants and the residue that is obtained upon the evaporation of Nile river water. Thus it can be seen that the major component analyses indicate a number of possible alkalis which might have been used in the different traditions of ancient glassmaking.

The first approach to an evaluation of the usefulness the lithium drifted germanium counters in the nondestructive analysis of ancient glass was a detailed study of the spectra obtained from various activated ancient glass specimens. Of particular interest in these spectra were a group of four photopeaks in the energy region of 150 kilo electron volts. The four peaks at 122, 133, 145 and 160 keV arise from the radioisotopes europium 152, hafmium 181, cerium 141 and scandium 47 respectively. A typical spectrum of these photopeaks as measured on an ancient glass specimen is presented in Figure 4. It shows that the photopeaks are just well separated by the high resolution germanium counter. The property of this group of photopeaks which caught ones attention was that the relative heights of the europium and cerium peaks appeared to be distinctly different in the low and high magnesium glasses. The decision was made to determine whether this difference was systematic and significant. If such a compositional pattern existed it might provide an additional clue tending to differentiate between the raw materials used in the two types of glass.

The quantitative determinations were made on entire fragments of ancient glass of about one half gram in weight. The fragments were irradiated for an entire reactor cycle, a period of nearly three weeks, in the N-9 irradiation facility of the Brookhaven research reactor. The thermal neutron flux in this facility 1.1×10^{13} neutrons per square centimeter per second. Following activation the specimens were left at the reactor for a period of one week to allow the short lived activities to decay away and then were repeatedly counted at periodic intervals during the following several weeks. The counting was carried out with

a germanium diode which had been purchased from the Canadian branch of the Radio Corporation of America. The depletion layer of this detector was 2 millimeters thick and 18.5 millimeters in diameter. The gamma ray spectrum was recorded by a 254 channel pulse height analyser. A diagram of the detector and photograph of the complete counting equipment are presented in Figures 5 and 6.

Decay curves were plotted to confirm that all the measured peaks were diminishing with correct half lives. The scandium 47 peak has complex decay characteristics because it is produced as a daughter radioisotope in the decay of calcium 47 which in turn is formed by the activation of calcium 46. The mathematics of the decay of such complex activities and decay situations has been worked out by Robinson.⁶ It was very fortunate that this peak which is ultimately produced from calcium occurred in the energy region of interest because the calcium concentrations of all of our glass specimens had been determined by spectrographic means. Therefore the scandium 47 peak could serve as an internal standard. From the relative number of counts in the europium, cerium and scandium peaks and a knowledge of the pertinent activation cross section and decay characteristics one could calculate the relative concentrations of europium, cerium and calcium in the activated specimen. Such factors as the exact-integrated neutron flux received in the specimen will cancel out in these computations. Then from the known calcium concentrations all of the relative concentrations could be charged to absolute concentrations. The activation cross sections used for these calculations were 5900 barns for europium 151, 0.59 barns for cerium 140 and 0.25 barns for calcium 46. The half lives employed were 12.7 years for europium 152, 32.5 days for cerium 141, 4.7 days for

calcium 47 and 3.43 days for scandium 47. Some of these measured constants are as yet not too well determined. Any errors in them will of course result in errors in the calculated absolute concentrations but they would not affect the relative concentrations of the same element in different specimens. Of course, the primary concern is with the significant differences that occur between different glass types and the relative differences would not be affected by possible constant factor errors in the calculation.

The selection of specimens for analysis was made with the attempt to sample both the geographic and chronologic distribution of the two glass types. The specimens are listed in Table I, where their magnesium, potassium and phosphorous oxide contents are given. The analyses show that the specimens do indeed belong to one or the other of the compositional types and also that the phosphorous concentrations too tend to show a correlation with the magnesium concentrations.

Eight specimens of each type were analyzed. The high magnesium specimens include two second millenium B. C. specimens, one from southwestern Iran and one from Egypt, also a Parthian specimen and five early Islamic specimens selected to cover geographically the Islamic areas from Iran to Tunisia. Specifically the early specimen from Iran was a fragment of wall decoration from the Elamite Ziggurat at Tschoga-Zambil which was supplied to us by Professor Ghirshman. The early Egyptian specimen was supplied to us by the Metropolitan Museum of Art from XXth dynasty material that had been excavated at Lisht. The Parthian specimen was supplied by Professor Erdmann from material that had been excavated at Ktesiphon. The early Islamic glasses include specimen excavated at Susa supplied by Professor Ghirshman, one from Iraq supplied by the Bagdad Muscum, a vessel fragment from Raqqa in Syria supplied by the

Selection of Specimens

Specimen Number	Site of Discovery	Probable Period of Manufacture	Concentration of Oxides in Percent			
			Magnesium	Potassium	Phosphorous	
970	Tshoga-Zambil	Elamite	3.7	1.38	0.158	
814	Lisht	XX th Dynasty	3.2	2.6	0.083	
929	Ktesiphon	Parthian	6.6	2.7	0.182	
674	Susa	{ Islamic of about 9 th - 10 th centuries	3.9	2.5	0.088	
681	Iraq		4.5	1.86	0.089	
774	Raqqa		5.2	1.32	0.180	
752	Fostat		3.2	1.58	0.26	
964	Sabrah		4.5	1.29	0.43	
			Average	4.4	1.90	0.184
706	Pompeii	1 st century	0.62	0.87	0.079	
857	Castra Praetoria- Rome	1 st century	1.02	0.81	0.098	
867	Athens	ante - 267 A. D.	1.02	0.91	0.085	
630	Karanis	2 nd - 4 th cent. A. D.	0.98	0.42	0.069	
745	Valerian tomb beneath St. Peters	4 th century	1.17	0.49	0.085	
892	Rhens	4 th century	1.58	0.60	0.072	
568	Lommersum	7 th century	1.26	0.56	0.076	
773	Raqqa	9 th - 10 th century	0.71	0.34	0.061	
			Average	1.04	0.63	0.078

Services of Antiquities at Damascus, a fragment from Fostat supplied by the Museum of Art at Cairo, and a glass factory fragment from Sabrah supplied by the Tunisian Services of Antiquities.

The low magnesium glass specimens include a specimen from Pompeii supplied by the Archaeological Services there, a first century vessel fragment from the Castra Praetoria in Rome supplied by the Museo Delle Terme, a glass vessel from a house in Athens which was destroyed in the Herulian raids of 267 A. D. supplied by the Stoa Museum at Athens, a specimen from the Roman-Egyptian spa at Karanis supplied by the Kelsey Museum of the University of Michigan, a glass fragment from the fill that was dumped into the cemetery beneath St. Peters in Rome at the time of the construction of the original Constantinian basilica, two specimens from the Rhine and Moselle region supplied by the Rheinisches Landes Museum at Bonn, one from a 4th century grave at Rhens and one from a 7th century grave at Lommersum, and finally a glass floor tile from an Islamic palace at Raqqa supplied by the Services of Antiquities at Damascus. The two specimens from Raqqa were selected as examples of the two types of glass found at the same geographic site under conditions datable to the same period. In general the specimens in each group come from many widely separated geographic areas and are datable to many different centuries. Any consistent trend among them, therefore, should relate to the basic glass formulations rather than to any specific geographic or chronologic variation.

The europium and cerium concentration found in these specimens are listed in Table II. It is apparent in these data that the europium oxide concentrations in the low magnesium glasses is consistently and

Europium and Cerium Analyses

Specimen Number	Concentration of Oxides in Parts per Million		Ratio of Concentrations
	Europium	Cerium	Europium/Cerium
High Magnesium Specimens			
970	0.029	3.7	0.0079
814	0.022	2.8	0.0079
929	0.068	10.8	0.0063
674	0.025	3.3	0.0076
681	0.034	3.9	0.0087
774	0.044	7.6	0.0058
752	0.044	8.3	0.0053
964	0.055	9.8	0.0056
Average	0.040 ± 0.016	6.3 ± 3.2	0.0069 ± 0.0013
Low Magnesium Specimens			
706	0.115	9.0	0.0128
857	0.142	10.3	0.0138
867	0.192	13.4	0.0143
630	0.101	6.6	0.0153
745	0.097	7.7	0.0126
892	0.168	8.7	0.0193
568	0.149	9.4	0.0159
773	0.088	6.5	0.0135
Average	0.132 ± 0.037	9.0 ± 2.2	0.0147 ± 0.0022
Differences Between Types			
Average	0.091 ± 0.040	2.7 ± 3.9	0.0078 ± 0.0025

significantly higher than in the high magnesium glasses. The cerium oxide concentrations in the two groups of specimens was more nearly the same so that the ratio of the europium oxide concentrations to those of cerium oxide are also significantly different for the two glass types. This last observation is a little surprising because both belong to the rare earth group of elements and to a great extent their compounds have similar chemical properties. One rather expects the relative proportions of the rare earth elements to be somewhat constant in nature. However, both europium and cerium ions can have unusual valence states which might lead to their individual chemical separation. In assessing these observations it is well to keep in mind that the original identification of the two glass types is not based upon the relatively few europium and cerium determinations but rather upon the analysis of more than four hundred specimens by quantitative spectrographic means. Rather the eight specimens of each type analyzed in this study constitute a statistically significant sampling of these two glass groups, as the data themselves indicate.

One can now argue that at least one raw material used in the fabrication of low magnesium glass probably contained significantly more europium oxide than the corresponding raw material used in the high magnesium glasses. One immediately asks whether this raw material could have been natron. The low concentrations of magnesium and potassium oxides in the low magnesium glass by themselves provided only necessary indications that natron might have been used in the production of this glass. However if natron were found to have a high europium concentration which was consistent with the relatively high concentrations of europium in the low magnesium glasses it would constitute rather positive evidence that natron was so used.

To test this hypothesis we were fortunate in obtaining specimens of both ancient and modern natron. The Metropolitan Museum of Art supplied us with natron from the 11th dynasty tomb of Neket Re and from the burial pits of Tut-Ankh-Amun. These natron specimens were contained in the original small cloth bags in which the material was used in the process of mummification. The Tut-Ankh-Amun specimen was discolored with an organic material and caked. We expected that specimen to be slightly contaminated. The Neket Re specimen was white and free flowing and appeared to be in a pure condition. The Corning Museum of Glass very generously provided five specimens of modern natron taken directly from various lakes in the Wadi Natroun. Glass specimens were activated and analyzed coincidentally with these specimens. Quantitative determinations of the europium and cerium concentrations in the natron specimens were obtained by direct comparison of the photopeaks in the natron and glass specimens. In this way any absolute errors would apply equally to the natron and glass specimens and hence cancel out in comparison between them.

The results of these determinations are given in Table III. The europium concentrations were lower in both the ancient and modern natrons than in either of the two types of glass. Also the europium oxide to cerium oxide ratio in the natrons is significantly lower than that observed in the low magnesium glass. Obviously whatever was the source of a high concentration of europium oxide in the low magnesium glasses it was not natron.

Although the observations that the low magnesium glasses are characterized by a relatively high europium concentration and by a high

Europium and Cerium Concentrations
in Some Natron Specimens

Specimen Source	Concentration of Oxides in Parts per Million		Ratio of Concentrations
	Europium	Cerium	Europium/Cerium
Ancient Specimens			
Tomb of Neket Re (11th Dynasty)	0.003	0.3	0.0084
Burial pits* of Tut-ankh-Amun (18th Dynasty)	0.02	2	0.0089
Modern salt deposits from the Wadi Natroun			
Lake El-Bida	0.002	0.3	0.0043
Lake El-Zaagig	0.0004	0.2	0.0023
Lake El-Zugm	0.00004	0.007	0.0054
Lake Abu-Gabara	0.0006	0.1	0.0062
Lake El-Fasda	0.002	2	0.0008
Salt used in a Wadi El-Natroun Glass factory	0.001	1	0.0013

* Specimen contaminated with organic matter.

ratio of europium to cerium did not lead to proof of the use of natron in those glasses, as we might have hoped, they do contribute in a quite positive way to the study of ancient glass. 1) They indeed demonstrate that the higher resolutions of the lithium drifted germanium diodes can be of practical value in the non destructive neutron activation analysis of ancient artifacts. 2) The europium concentrations measured were in the range of tenths to hundredths of parts per million, which is well below the sensitivity range of most analytical methods. It is most interesting and encouraging to discover that significant differences occur at these very low level, "trace-trace", concentration ranges. 3) In future studies of determination of the raw materials of ancient glass manufacturing europium and cerium concentrations should now provide criteria for judging the probability of the use of various substances in the formulation of these ancient glasses of the soda-lime type.

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References

1. E. V. Sayre and R. W. Dodson, Neutron Activation of Mediterranean Potsherds, *Am. J. Archaeol.* 61, 35 (1957); E. V. Sayre, A. Murrenhoff and C. F. Weick, The Nondestructive Analysis of Ancient Potsherds through Neutron Activation, Brookhaven National Laboratory Report 508 (T-122) April 1, 1958; V. M. Emeleus, The Technique of Neutron Activation Analysis as Applied to Trace Element Determination in Pottery and Coins, *Archaeometry* 1, 6 (1958); C. M. Kraay, Gold and Copper Traces in Early Greek Silver, *Archaeometry* 2, 1 (1959); V. M. Emeleus, Neutron Activation of Samian Ware Sherds, *Archaeometry* 3, 16 (1960).
2. A. J. Tavendale, Large Germanium Lithium-drift p-i-n Diodes for Gamma Ray Spectroscopy, *I. E. E. E. Trans. Nuclear Sci.* NS-12, 255 (1965).
3. E. V. Sayre and R. W. Smith, Compositional Categories of Ancient Glass, *Science* 133, 1824 (1961).
4. Pliny, *Natural History*, Book XXXI, Chapter 46, Book XXXVI, Chapters 65 and 66.
5. W. E. S. Turner, Studies in Ancient Glasses and Glassmaking Processes V. Raw Materials and Melting Processes, *Trans. Soc. Glass Tech.* 40, 277 (1956).
6. W. Robinson, The Equations of Radioactive Transformation in a Neutron Flux, *J. Chem. Phys.* 17, 542 (1949).

Figure 1.

COBALT-60 GAMMA RAY SPECTRUM MEASURED
BY A LARGE CRYSTAL SCINTILLATOR AND A
GERMANIUM DIODE

Figure 2

Figure 3. Distributions of magnesium and potassium oxides in some ancient "soda-lime" glass specimens. The same specimens are included under the solid curves and the dashed curves in the two sets of distributions.

Figure 3

Figure 4

PORTION OF GAMMA RAY SPECTRUM
OF NEUTRON ACTIVATED
ANCIENT GLASS

Figure 5

GERMANIUM LITHIUM DRIFTED DIODE

Figure 6.

The complete counting assembly.

- A. Lead and plastic shielding housing for the detector. The germanium diode itself is at the bottom of this housing.
- B. Liquid nitrogen reservoir for cooling the diode.
- C. Equipment for measuring temperature of the counter and maintaining an insulating vacuum throughout the cooling system.
- D. Amplifier and power supply.
- E. Multichannel analyzer and recorders.