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**FISCAL YEAR 1973 SUMMARY
REPORT FOR THE USAEC DIVISION OF
APPLIED TECHNOLOGY – ENVIRONMENTAL ANALYSIS**

July 5, 1973

Prepared for U.S. Atomic Energy Commission under contract No. W-7405-Eng-48

**LAWRENCE
LIVERMORE
LABORATORY**

University of California/Livermore

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Foreword

The data contained herein is a compilation of environmental analysis and feasibility studies conducted for the USAE's Division of Applied Technology. Readers who are interested in more detail regarding any item may contact the authors of the reports who are listed in the Contents.

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Edited by B. N. Odell

REPORTS

Comparison of the Absolute Borrmann Transmission of Ge and CdTe Detector Grade Crystals

Introduction

We conducted a study to compare the transmission qualities of detector grade Ge with samples of detector grade CdTe and to determine if the CdTe crystals were sufficiently ordered to allow any Borrmann transmission. If the CdTe crystals exhibit strong Borrmann effects, the implication is that the crystal order is at least as good as that of detector grade Ge. (This should be interesting to anyone trying to build radiation detectors with CdTe.)

Crystal Materials

The Ge crystal used in this study was produced prior to 1966 and, although previously used in other experiments as an x-ray band pass filter, its absolute transmission has not been measured. The crystal was 0.0365 in. thick and its etched faces were cut parallel to the (111) plane. The wafer edges had been cut so visual identification of the crystal axes was not possible. The crystal axes locations when looking on the (111) plane were located using Laue patterns. The CdTe crystal used was provided by the Environmental Analysis branch of the AEC Division of Technology.

Experimental Approach

The hardware used in the study was designed and constructed to align a developmental x-ray tube with a high resolution

silicon semiconductor photon spectrometer and, in addition, to hold the collimators and the crystal alignment holder (goniometer). Figure 1 shows all components of the experiment while Fig. 2 shows the

Fig. 1. Experimental apparatus. (Left to right: X-ray tube, alignment hardware, and detector.)

Fig. 2. Alignment hardware.

hardware. Figure 3 shows the goniometer and crystal alone. Note the flexible shaft shown attached to the goniometer in Fig. 1. The flexible shaft is attached to a servomotor to remotely control crystal angle. Figure 4 pictures the electronics associated with the x-ray tube, the detector, and the remote control unit.

The divergence of the beam using the 0.125 in. diam aluminum-lined (20 mil) tungsten collimators at ± 1 in. from the crystal was approximately 6 degrees. After accumulation of the transmitted Borrmann Peak Spectrum (see Fig. 5), the germanium crystal was removed and replaced by copper foils. Holding the beam intensity constant, the intensities of the corresponding Borrmann Peak energy component of the beam transmitted through various thicknesses of copper foil were measured and the results were plotted as shown on Fig. 6. The straight line extrapolation to zero absorber determined the

Fig. 3. Goniometer mounted crystal.

Fig. 4. Electronics.

incident flux. The experiment was repeated substituting the CdTe for the Ge crystal. The resulting Borrmann transmission, along with the incident spectrum, is shown in Fig. 7. The peak shape is non-gaussian indicating that further investigation should be considered.

Experimental Results

The transmission of 21.5 keV x-rays through the single crystal germanium used in this study was found to be 1.2×10^{-4} . This is 6×10^3 greater than expected in polycrystalline germanium. The absolute transmission measured through the CdTe was significantly higher at 3.2×10^{-3} . (This result should be useful as an evaluation tool for anyone producing high quality Ge or CdTe crystals.)

Fig. 5. Comparison of incident and transmitted beams for Ge.

Fig. 6. Variation of intensity with copper adsorber.

Fig. 7. Comparison of incident and transmitted beams for CdTe.

Thermoluminescence of Asbestos

Introduction

Asbestos concentrations in air are measured by collecting all particles on a filter, preparing the filter for phase contrast microscopy, and then counting the fibers that are longer than $5 \mu\text{m}$ as asbestos. This procedure is tedious, expensive, uncertain, and is not readily amenable to automation due to the great variety of size, form, and contrast of the images.

We began a feasibility study to determine whether thermoluminescence (TL) of irradiated asbestos offers an alternative to the current method. TL is the characteristic luminescence emitted

by a stressed material as it relaxes when heat is applied. Ionizing radiation is most often the energy source for inducing TL although mechanical work may produce a similar result.

Objectives

The initial objectives of this study were to 1) identify characteristic TL parameters that would permit quantitative analysis for asbestos fibers, 2) test for interferences by contaminating materials, and 3) determine a lower limit of detectability. This study was begun using chrysotile, a serpentine asbestos that represents more than 90% of industrial

asbestos. If successful, the study will be extended to include several varieties of amphibole asbestos.

Sample Selection

Samples of chrysotile from several sources were obtained to ensure that the results of experiments would not be due to unique properties associated with a particular locality (for example, trace element composition). One type, found at Copperopolis, California, was used to study the effects of pre-irradiation annealing and radiation dose on the TL response.

Experimental Work

Chrysotile fibers were hand sorted from admixed host rock, dispersed in water, and filtered according to the method of Badollet and Gantt.¹ The paper-like filter cake was then cut into 9-mm discs for the TL experiments. Replicate samples of asbestos discs were annealed at temperatures ranging from room temperature to 425°C to remove the luminescence naturally present as well as that mechanically introduced by grinding. Higher temperatures were not used since the available TL reader temperature is limited to 500°C and since chrysotile is known to undergo chemical and morphological changes at about 500°C.

After annealing, samples corresponding to each group of annealing temperatures were exposed to ⁶⁰Co gamma radiation doses of 10⁴R, 10⁵R, and 3 × 10⁶R. Each disc was then read out in a linearly-temperature-programmed TLD reader at 1°C/sec and the glow curve data (luminescence intensity as a function of time) stored in a PDP-11 computer that is interfaced to the reader.

A background glow curve, obtained by re-reading each disc immediately upon cooling, was subtracted from each initial glow curve. The data were recorded on paper tape and plotted on a Calcomp plotter. Samples of serpentine host rock surrounding the fiber veins and having essentially the same elemental composition were freed of fibers and run in the same way.

Observations

A broad, low-intensity peak centered at about 300°C in the TL glow curve was found for all irradiated samples. A pre-existing peak in the unannealed material interfered seriously with the radiation induced peak. It was found that this could be sufficiently reduced by annealing the asbestos discs at 275°C for 1 hr before irradiation. Gamma doses higher than 10⁴R did not materially improve the 300°C glow peak. The highest dose samples showed a broadened peak indicating saturation of the 300°C peak and the growing in of a higher temperature peak. The serpentine host rock showed a low peak at 125°C.

During the course of the work described, a sample that had been read out and left in the reader was unintentionally re-read several days later. It showed an entirely unexpected TL peak in the same region as the radiation induced peak. It was hypothesized that, in the absence of either a radiation field or mechanical excitation, this might have been the result of re-absorption from the air of bound water lost during the TL read out. This was briefly investigated for several unirradiated samples that were annealed, divided into two groups, and then allowed to stand for various times. One group was placed in

a desiccator over silica gel and the other left open to room air of about 50% humidity. After 30 hr, the samples stored in the desiccator showed no peak regrowth while those left open to the atmosphere showed a significant peak centered at 300°C.

Conclusions

The results thus far indicate that serpentine host rock does not interfere in the TL analysis. Therefore, it is possible to distinguish between the fibrous serpentine, which presents a health hazard, and the innocuous massive serpentine. However, other data indicate

that quartz, a ubiquitous mineral, does have a relatively intense, radiation-induced, glow peak in the 250°C to 300°C region.² If the peak regrowth behavior is indeed unique to chrysotile, it may offer the required technique for avoiding interferences and eliminate the need for irradiation. Failing this, spectral discrimination of the luminescence may provide a means of distinguishing between chrysotile and other minerals. Feasibility of the above depends on the TL being intense enough to provide sufficient sensitivity for the detection of chrysotile at levels of 2 fibers/cc³ of air. This has not yet been determined.

Analysis of Marine Sediment

Introduction

A Coastal Engineering Research Center (CERC) representative informally requested that 15 sediment samples brought to LLL be analyzed using existing x-ray fluorescence analysis equipment. Of the 15 samples, 4 were obtained from New York harbor sites and 11 from sites in the New York Bight Dumping Grounds. This report describes the qualitative and relative quantitative analysis performed and concludes with a summary of the findings.

Equipment

The equipment consisted of a small x-ray tube exciter, a scattering chamber/sample changer, a high-resolution Si (Li) x-ray detector with associated electronics, and a computer-based, pulse-height analyzer. Figure 8 is a schematic diagram of the system.

Sample Preparation

The samples obtained were received in the form of dry particulate (sand or silt) and as semi-liquid sludges. Dry material samples in 50 mg batches were placed between two layers of Scotch Magic Mending tape and mounted on 35-mm slide holders (our standard format). For the sludges, approximately 100 μ l drops were placed on 1/2 mil polycarbonate film and dried under heat lamps. When dry, they were sprayed with adhesive, and another layer of film was sealed over the sample. The whole "sandwich" was then mounted in a slide holder.

Analysis

The samples were exposed to silver x-rays (22 and 25 keV) and their emission spectra collected in the Nuclear Data 4420 Analyzer. Counting times were about 1000 sec (with some considerable variation),

Fig. 8. System block diagram.

Table 1. Relative intensity of interesting x-ray peaks.

Interval No.	Sample element ^a	New York Harbor ^b		New York Bight											Blank ^c
		1	2	1	2	3	4	5	6	7	8	9	10	11	
1	Ca	770	662	0	47		356	0	3,020	739	266	342	64	286	0
2	Tl	3,989	3,308	1,960	3,913	1,438	1,012	10,747	2,759	2,926	1,569	2,665	1,563	356	
3	Cr	89	570	538	299	410	122	79	215	665	451	259	140	0	
4	Fe K α	171,247	153,152	50,632	86,438	25,306	43,415	368,049	155,439	169,061	119,424	107,781	47,269	1,277	
5	Cu	1,057	2,733	1,752	2,113	1,175	2,445	7,162	2,200	2,580	1,303	1,254	962	921	
17	Zn	1,330	3,938	2,269	2,299	1,525	1,640	15,725	3,856	3,442	1,580	3,496	1,277	746	
8	Pb L α	552	1,625	162	233	0	2,212	2,734	572	1,845	159	2,032	714	239	
9	Br	1,027	1,307	908	510	44	823	735	858	3,655	1,029	2,319	554	51	
10	Pb L β	453	1,607	23	451	0	1,978	1,196	83	840	828	1,513	28	549	
11	Rb	3,892	6,520	1,344	1,171	786	1,106	6,268	6,801	2,712	1,53	1,443	1,273	0	
12	Sr	4,730	10,590	4,066	3,582	1,486	1,341	8,217	4,022	13,264	2,851	2,475	5,288	0	
14	Zr K α	15,707	36,679	19,822	22,968	8,817	5,413	37,325	11,084	11,549	7,620	5,422	8,600	0	

^aThe only elements that present a real "background" are Fe, Cu, and Zn, as can be seen in Fig. 9. The unsmoothed background subtract routine used here results in the small residuals seen in some other elements.

^bData for N. Y. Harbor numbers 3 and 4, and N. Y. Bight No. 3 are in possession of G. Carayannis (Army Corps of Engineers, Coastal Engineering Research Center, Fort Belvoir, Va.).

and the x-ray tube was operated at about 150 μ A beam current (about 1/6 of our normal maximum intensity). Spectra were plotted and analyzed qualitatively, and the net areas of x-ray peaks of interest were printed out. Figure 9 and Table 1 show the relative intensity of interesting x-ray peaks. Note that this was intended as a qualitative analysis and no effort was made to obtain real quantitative data.

The total effort expended on this job was about 6 man-hr, or 20 min per sample. This figure could be markedly reduced in a routine sampling program by: 1) developing fixtures to hold the slide frames and by pre-cutting the mounting film, 2) reducing counting time to 1-2 min by running the x-ray tube at full power, and 3) using special software to automate data reduction. It is felt that a figure of about 3-5 min per

Fig. 9. X-ray fluorescence spectrum from typical New York Harbor sediment sample.

sample will be realistically approachable.

Quantitative analysis, to an accuracy of $\pm 15\%$ and with sensitivities

around the 1 ppm level for most elements of $Z > 16$, are not difficult and will be available in the near future.

Using the Thermoluminescence of Beach Sand as A Tracer

Introduction

We performed feasibility and parameterization experiments to determine if the thermoluminescence (TL) of sand would permit its use as a tracer to study the bottom movement in harbors and beaches. If feasible, a quantity of sand could be removed from an area, be irradiated, and subsequently be dumped back into the water. Samples might then be taken at various times and locations and be washed, dried, and heated to measure characteristic TL. Diffusion and migration patterns might then be determined by comparing the TL of sampled sand and the TL of sand irradiated with the same dose as the original material.

Experimental Parameters

The scope of the experiments conducted focused on TL measurements as a function of:

- Radiation Dose - Is the basic technique feasible and is there a dose that will produce a maximum TL?
- Mechanical Agitation - Is the TL of sand affected by handling, wave pounding, or current action?
- Pre-irradiation Heat Treatment - Is there an annealing regime that will improve the TL sensitivity or reproducibility?
- Source of Sand - What effect will location have on the variability of TL glow peaks and sensitivity?

- Grain Size - Is the TL of sand affected by particle size and what effect will particle size have on translocation rates?

Experiments and Observations

Initial investigations were directed at measuring TL as a function of exposure. Figure 10 shows how TL varies with exposure for two samples collected at Half Moon Bay. Although they do not show a relative maximum, the response to additional radiation is of the functional form $Y = KX^a$ when the exponent "a" is less than 1. This indicates that an increase in exposure will result in less increase in signal than if the response were linear.

The TL effect resulting from mechanical agitation proved to be inconsequential. Figure 11 is a glow peak of unirradiated sand that contains a hump from 250° to 500°C. The hump is attributed to mechanically stimulated TL triboluminescence which should not interfere with radiation-induced TL in the 0° to 260°C region.

Samples of purified laboratory sand were annealed at 100, 200, 300, 400, and 500°C for 1 hr. Portions of the sand from each annealing were irradiated at several exposures between 300 and 1.3×10^5 R. Figure 12 shows the glow curves for the various annealing temperatures and a

maximum TL sensitivity at an annealing temperature of 200 C. The next set of experiments showed that the TL sensitivity for unannealed sand and sand annealed at 200°C are approximately equal.

Figure 13 shows the response as a function of exposure for a pre-irradiation annealing temperature of 200°C, and an approximately linear response with dose over 3 orders of magnitude.

Experiments were conducted using sand taken from four Bay Area locations selected to represent three geological regimes.³ Table 2 shows the sample locations and geological type. Two samples were taken at each location, one from above the high water mark and a second from the surf. All were washed in deionized water to remove crystallized salts that might give spurious readings and then freeze-dried. Portions of each of the samples were annealed for 1 hr at

Fig. 10. TL as a function of exposure.
X = Half Moon Bay (in surf)
O = Half Moon Bay (above high water).

Fig. 11. Glow curve of unannealed and unirradiated sand.

Fig. 12. Glow curves of purified sand at various annealing temperatures.

200°C. Both annealed and unannealed samples were exposed to 1.3×10^4 , and 6.6×10^5 R of ^{60}Co gamma rays. Some of the irradiated samples were further separated by particle size (greater or less than 28 mesh) or magnetism.

Figure 14 shows typical glow peaks of the samples taken in the surf at each location. With the exception of the

Sharp's Park sample, the integrated area under the glow peak (60°-260°C) for these samples varies by 15% from the mean. This variation compares with a 15% standard deviation for replicate readings on one sample. The variation of integrated area for samples (again excluding the Sharp's Park samples) taken above the high water mark is 44% of the

Fig. 13. Integrated TL output (90°C-210°C) as a function of exposure, purified szad and 200°C pre-irradiation annealing.

Table 2. Sample locations.

Location	Geologic regime
Stinson Beach	Late Mesozoic - Franciscan Formation
Ocean Beach	Late Mesozoic - Shelf and Slope Sedimentary
Sharp's Park	Late Mesozoic - Franciscan Formation
Half Moon Bay	Mesozoic - Intrusive Granitic

mean. This is attributed to sand above high water being contaminated with non-TL materials since, in each case, the TL was less for samples taken above high water.

The Sharp's Park samples were excluded from the above comparisons because they contain a much higher fraction of black, magnetic, non-TL material which caused the decrease in TL output.²

Fig. 14. Glow peaks of sand from various locations.

All of the samples that were size segregated, except one, showed greater TL sensitivity for smaller grain size. This is attributed to more uniform heating and less TL absorption within the grain for smaller grains. The sample that did not show increased TL sensitivity for small grains showed no significant difference in TL with grain size. This may happen because the large grains in this

sample have relatively flat faces, allowing better contact with the TL heater, thus allowing better heat transfer during a heating cycle and consequently a high TL output.

Conclusions

A TL reader, designed to read sand, may provide better results than the TL reader used in this study. It would be

required to uniformly heat "large" sand grains to eliminate particle size dependence and have its light collection and filtration optimized for sand samples. Samples exposed to 6×10^5 R of ^{60}Co gamma rays typically caused the samples to have integrated TL outputs (to 260°C) of several million counts. Unirradiated samples have essentially no signal in the

0°C to 260°C region. This suggests that it should be possible to approach dilution factors of $10^6:1$ in optimum samples read with optimal readers. Therefore, the TL of sand could be used in experiments to trace the movement of beach and harbor bottoms if the experiment can be done with dilution factors of less than $10^6:1$.

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