

Scintillating Phosphor Spray for Remote Detection of Tc-99 – 14183

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ABSTRACT

A scintillating phosphor spray coating was developed for wide-area assessment of radiological contamination of structures and surfaces related to decommissioned nuclear facilities. The effort concentrated on Tc-99, but is applicable to other beta emitting isotopes such as tritium and Ni-63. The scintillating phosphor is a yttrium aluminum garnet that is doped with cerium (YAG:Ce). The cerium doping levels were optimized through a series of experiments based on combustion and solid-state synthesis methods. Throughout these experiments, the performance of the scintillators was monitored using cathodoluminescence, employing an electron gun as a source of electrons to simulate beta radiation. Detection is accomplished using a filtered image intensifier that is coupled to a charge coupled device camera. A commercial Y(Al,Ga)G:Ce phosphor was identified and tested on a series of laboratory-produced debris surrogates. The detection limit for ^{99}Tc was approximated at 10 microcuries, at a standoff distance of one meter. Radioactivity levels of 35 μCi were easily detectable several meters away. The spray coating is nonhazardous, chemically inert, and easily sprayed using a commercial paint spray gun that is driven by compressed air. Since the detection system is battery powered and the sprayer may be driven by a portable compressor or compressed gas cylinder, the entire method may be field deployed in areas without utilities.

INTRODUCTION

The major objective of the scintillating phosphor spray effort was to develop a novel, highly efficient scintillator spray system that can be used to indicate the presence of beta radioactive contamination. The system is based upon radioluminescence, which is the phenomenon by which light is produced in a solid state scintillator (phosphor) by the bombardment with ionizing radiation. Such a system could reduce the time spent on hands-on surveys and analysis of samples from the field because a wide area could be assessed simultaneously. Clearly, a survey method that would facilitate rapid, less labor intensive, wide area characterization would be of significant benefit and would result in significant cost savings.

The photon emission wavelength of a particular phosphor depends on the chemical system in question. Put another way, emission in the desired wavelength range is only possible through careful design of the scintillator system, control of thermal and mechanical history, and through freedom from contamination from other elements and from lattice defects. The wavelength region of choice depends on many factors including cost, resolution, sensitivity, and availability of detectors in that wavelength range. Although there are many possibilities that could be considered, every effort was made to utilize simple, inexpensive detector systems in order to facilitate the widespread use of this system.

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The development and characterization of unique phosphors as fieldable, real-time nuclear material sensors for alpha and beta contamination remains an ongoing research effort at ORNL. The scintillating

spray effort benefitted from the significant knowledge and list of candidate materials developed under existing research efforts. The phosphor identified as optimum for Tc-99 contamination detection must emit efficiently within a given spectral window, and the emissions must be detected using currently available sensors equipped with appropriate band-pass filters, and have the capability to transmit its own emission. A non-binding spot and wide area Tc-99 contamination detection system was developed and based on the YAG:Ce scintillating phosphor system. Some consideration was given to the quality, power and cost of commercially available detectors, the ease of use and portability of the designed system, and to the presence of materials or processes that may introduce new hazards during deployment of the technique.

Yttrium aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), has interesting optical properties and thus can be utilized in a wide array of applications including light emitting diodes (LEDs).[1] YAG: Ce has a strong, broad emission centered at approx. 540 nm in the visible region resulting from the cerium dopant. Phosphors are often prepared by solid-state reactions and require high-temperature sintering for conversion to the desired phase transformation.[2,3] A major drawback of preparing the phosphors by solid-state reaction is that the product often consists of multiple phases.[4] The presence of multiple phases reduces performance of the material because the emissions may be shifted or reduced. An alternative synthetic route, such as combustion synthesis, can provide a homogenous mixture of the metal cations (Y^{3+} , Al^{3+} , Ce^{3+}) at the atomic level. Therefore, a pure YAG phase is easier to achieve without any intermediate phases.[5,6,7] Accordingly, lower sintering temperatures are required to obtain the crystalline phase desired. The amorphous precursor material transitions directly to the single phase YAG phosphor when combustion synthesis is used to prepare these materials.

METHODOLOGY

Y_2O_3 (99.99%) and Al_2O_3 (99.99%) were purchased from Beijing Chengxinligia Ltd. Co. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.999%) was purchased from Alfa Aesar. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.8%), and glycine (99%) were purchased from Sigma-Aldrich. A commercially available $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}$: Ce (YAGG: Ce) scintillator was purchased from Phosphor Technology Ltd™. All chemicals were used as received without further treatment and/or purification.

Synthesis of YAG:Ce by Solid-State Chemistry

Y_2O_3 , Al_2O_3 , and cerium nitrate were mixed in a molar ratio of $\text{Y}_{3-x}\text{Ce}_x\text{Al}_5\text{O}_{12}$ where $x = 0.01$ to 0.09 at 0.01 intervals. The Y(Ce): Al ratio was kept at 3:5. The mixtures were sintered first at 750°C for 2 hr with $5^\circ\text{C}/\text{min}$ ramp and cool down rate under atmospheric conditions in a muffle furnace. The materials were then ground using mortar and pestle to improve the homogeneity of the final product. The materials were then annealed a second time at 1600°C with $5^\circ\text{C}/\text{min}$ ramp and cool down rate with a 1-hour dwell time.

Synthesis of YAG:Ce by Combustion Synthesis

Aqueous yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.8%) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98%) solutions were prepared with well-characterized concentrations. A mixed salt solution was prepared using these two stock solutions. The amount needed from each solution was based on the stoichiometry. Next, the stoichiometric amount of cerium nitrate was dissolved in the resulting mixed salt solution in a 1L stainless steel beaker. Glycine was added to the solution. The glycine-to-nitrate molar ratio was kept constant at

1.66:1. The glycine serves two purposes. First glycine is a chelating agent that solubilizes the metal cations, ensuring their availability for reaction. Second, upon ignition, the glycine oxidizes the nitrates and releases H_2O , CO_2 , NO_x , and N_2 which promotes an amorphous YAG: Ce scintillator. Once the glycine was dissolved, the mixed salt solution was brought to a boil yielding a fluffy brown-black foam precursor. The foam was milled by mortar and pestle and then annealed at 1100 °C with a 3 °C/min ramp and cooling rate under atmospheric conditions in a muffle furnace with a 1 h dwell time.

Materials Characterization

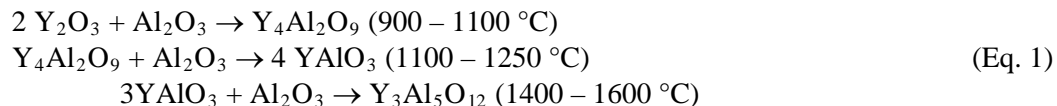
The luminescence emission properties were monitored using a prototype cathodoluminescence instrument and collected using a commercially available Ocean Optics™ spectrometer at room temperature. Cathodoluminescence was employed in an attempt to simulate beta radiation effects on the scintillating phosphors. The electron beam current was kept at 0.05 μA . The beam voltage was 10 keV. The spectra were obtained at an integration time of 10 msec with the average of 10 spectra reported. The structure and crystallinity of the YAG: Ce powders were measured by powder X-ray diffraction (XRD) on a Panalytical Xpert™ diffractometer.

Simulated Debris Tests

Various construction and demolition materials were contaminated with known amounts of Tc-99 as pertechnetate. Ammonium pertechnetate was purchased from the ORNL Isotope Business Office, dissolved in dilute NH_4OH , and certified by liquid scintillation counting. The phosphor spray was applied using a compressed-air driven high volume, low pressure spray gun for most of the debris samples. Some also had the phosphor dropped onto the dried Tc-99 contamination, and a few had the Tc liquid stock mixed with the phosphor. The spray solution was composed simply of distilled water with or without the addition of a small amount of surfactant, to aid in surface wetting. Detection of the phosphor emission was accomplished using a charge coupled device (CCD) camera that was attached to a commercially available nightvision monocular which had a custom filter adapter and 525nm bandpass filter.

DISCUSSION

The optimum doping level for Ce in the yttrium aluminum garnet (YAG) matrix was found to be 0.015 percent. The cerium substitutes for yttrium in the lattice and results in emission around 540nm. Heating studies indicated that higher heating temperatures resulted in preferential formation of the YAG phase and not the competing phases. The chemical stability of the product material is excellent. The ratio of Al_2O_3 to Y_2O_3 was found to be important for synthesis of a pure product. Excess Al_2O_3 resulted in decreased intensity of the 540nm emission and the presence of a sharp spectral feature around 700nm. Solid-state production methods produced YAG:Ce that was only about 50% pure. The purity of the material increased with heating according to the following phase transformation scheme:



In contrast, combustion synthesis produced essentially pure YAG:Ce, as evidenced by the x-ray diffraction (XRD) pattern shown in Figure 1. In addition, the particle size was lower for the combustion synthesis material. The material was noticeably lower density than that produced by solid-state

methods. Because of this, it was a better performer as a spray coating than the material produced by solid-state chemistry.

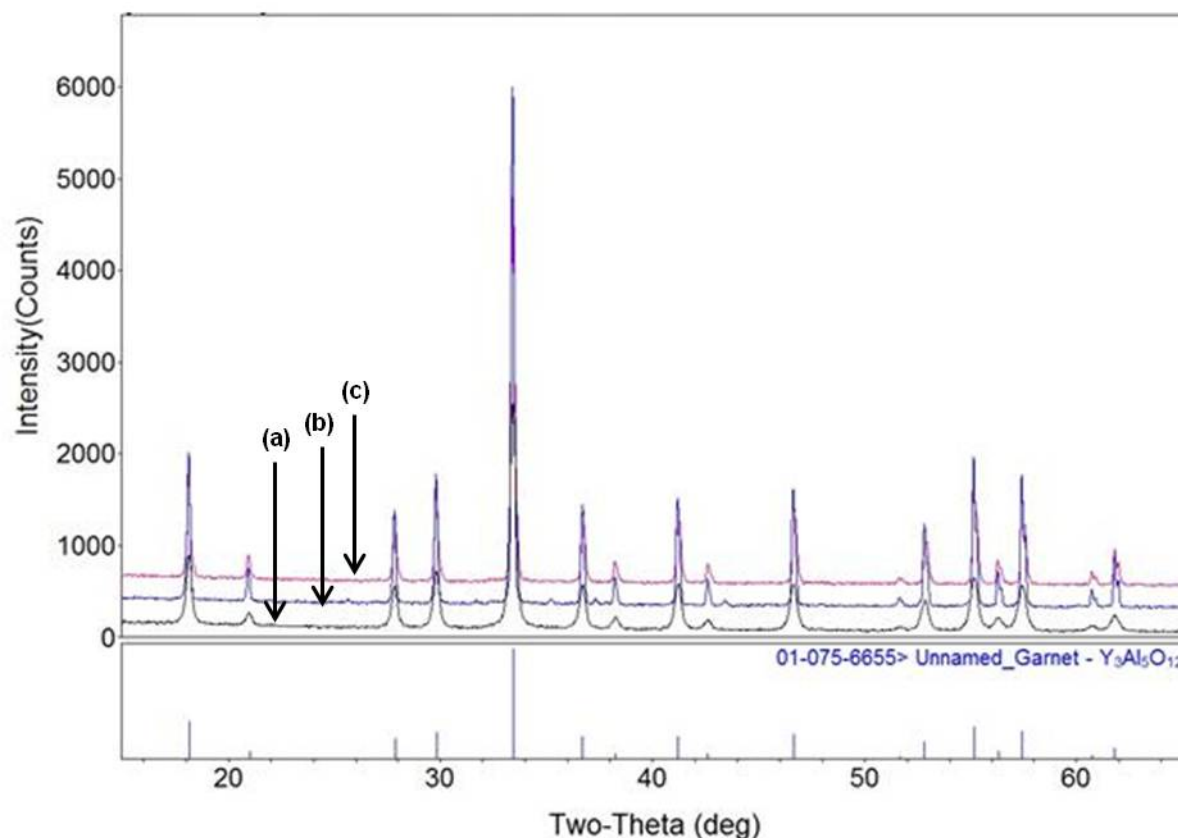


Fig. 1. XRD Patterns of YAG:0.015 Ce Prepared by Combustion Synthesis at (a) 1100 °C and then at (b) 1600 °C, and (c) Optimized YAG: Ce.

Cathodoluminescence studies were employed as a means of assessing the progress of material performance as parameters were adjusted during production. While this method did simulate beta radiation to an extent, the results did not always match what was observed when the optical detection system was employed. Minor fluctuations of the electron gun filament temperature, current, or voltage proved very difficult to control. As a consequence, the cathodoluminescence data were used qualitatively and were compared to a “witness” material that was routinely analyzed with each sample group to lessen the impact of those variations. Nevertheless, cathodoluminescence was invaluable as a multiplier of effort since several materials could be assessed in a short time. The emission spectrum under cathodoluminescence excitation for both the commercial YAG:Ce and the ORNL materials is shown in Figure 2. These data indicate that the ORNL material performance was slightly less than that for the Phosphor Technologies Ltd.TM material under cathodoluminescence interrogation. However, under beta particle irradiation by Tc-99, the ORNL material resulted in more luminescence. In order to make the Tc-99 detection system available more widely, the commercial Y₃(Al,Ga)₅O₁₂:Ce scintillator was examined alongside the ORNL materials. The Phosphor Technologies Ltd.TM material is slightly shifted to the blue (525nm) and indicates that is a slightly different version than the ORNL material.

The incorporation of gallium in the $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}$ (YAGG) scintillator system results in a blue shift to lower emission wavelength because of the perturbation in the crystal field caused by the inclusion of the larger Ga in place of some of the Al. The aluminum atoms can occupy sites that are either tetrahedral or octahedral in coordination. Gallium replaces aluminum in the matrix at both sites but probably the octahedral site is favored by atomic radius constraints.

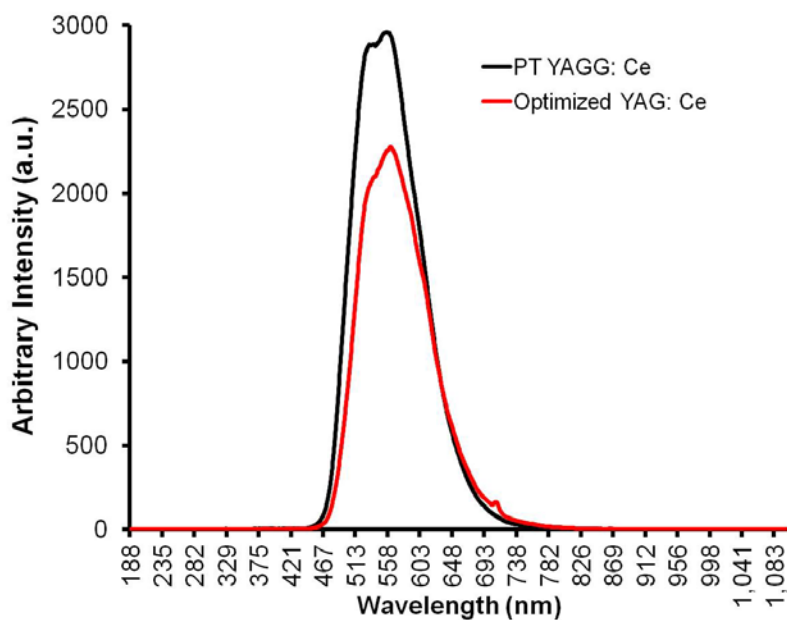


Fig. 2. Cathodoluminescence spectrum of optimized YAG: Ce scintillator prepared by combustion synthesis at 1600 °C and Phosphor Technology Ltd.TM YAGG: Ce scintillator.

Deployment, Capabilities, Assessment, and Performance of the Scintillating Phosphor Spray System

The radioactive targets and blanks were arrayed according to Figure 3 on a piece of absorbent matting after being sprayed with the YAG:Ce mixture. Although the coating was visibly more complete when the Triton X100® surfactant was used, there was little difference in performance. All of the targets had been coated with the formulation containing 0.05% Triton X100® by weight except target 7. The targets are

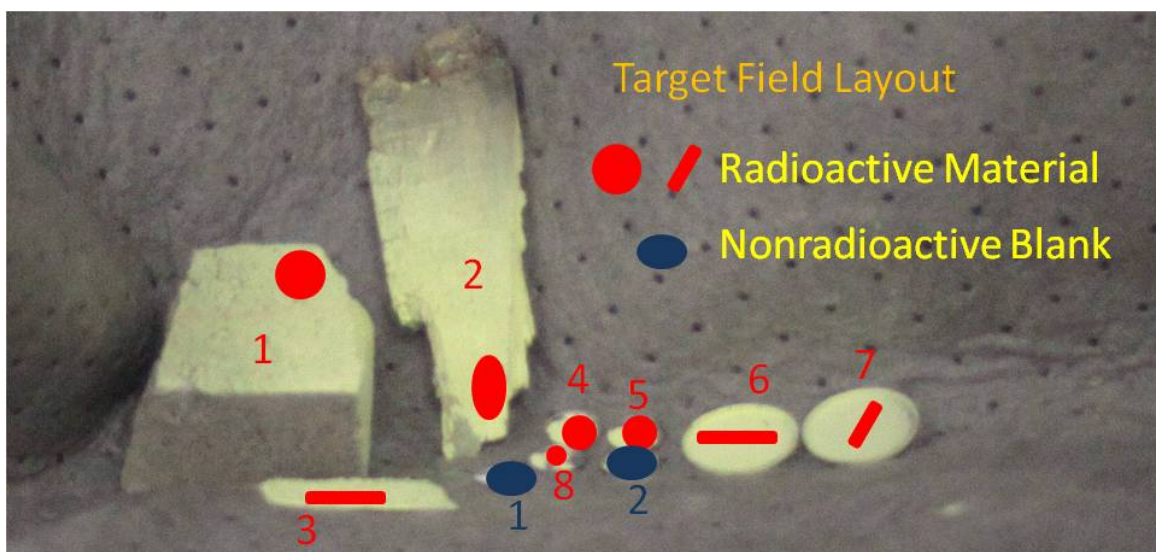


Fig. 3. Target Arrangement for Simulated Debris Evaluation.

described as follows:

1. Masonry brick with 34 μCi ^{99}Tc contamination *applied*; spot size is about 1/2" (12mm) circle
2. Weathered hardwood with 34 μCi ^{99}Tc contamination *applied*; spot size is oval about 1" (25mm) long and 1/2" (12mm) wide
3. Roofing asphalt shingle with 34 μCi ^{99}Tc contamination *applied*; spot size is about 1/2" (12mm) long and 1/4" (6mm) wide stripe
4. 1" (25mm) stainless planchette with 34 μCi ^{99}Tc contamination *mixed* with the YAG:Ce phosphor and allowed to dry; spot size is irregular circle about 1/2" (12mm) diameter
5. 1" (25mm) stainless planchette with 17 μCi ^{99}Tc contamination *mixed* with the YAG:Ce phosphor and allowed to dry; spot size is irregular circle about 1/2" (12mm) diameter
6. 2" (50mm) stainless planchette with 34 μCi ^{99}Tc contamination *applied* as a line 1" (25mm) long and about 1/4" (6mm) wide
7. 2" (50mm) stainless planchette with 34 μCi ^{99}Tc contamination *applied* as a line about 1/2" (12mm) long and 1/4" (6mm) wide; no Triton X100 in this one
8. 1" (25mm) stainless planchette with 34 μCi ^{99}Tc contamination *dried* then YAG:Ce dropped onto the surface; spot is a line 1" (25mm) long and about 1/4" (6mm) wide
1. MgO blank mixed with 100 μl pH 9 NH_4OH and dried
2. YAG:Ce blank mixed with 100 μl pH 9 NH_4OH and dried

These targets were assessed under dark conditions using the detection system shown in Figure 4. Typical settings for the camera include ISO6400, 50mm f1.4 lens using 6-second exposure, and all images were acquired using the 525nm bandpass filter. This filter was optimized for detection of the YAGG material but even so, the ORNL materials are still easily detectable as shown in Figure 5.



Fig. 4. Imaging System Components.

The effects of these different substrates and solution chemistries are demonstrated in Figure 5. The raw image has been converted to 8-bit grayscale, then the color table changed to enhance viewing contrast. Neither of these changes affects the data quality, and the technique is universally applied to all of the images taken through the intensifier. Although most of the targets have the same radioactivity applied to the surfaces, some differences in detectability are observed. Porous surfaces like the brick and wood are a bit less detectable than nonporous surfaces like the steel planchettes. This degradation in performance comes about perhaps because of two effects. First, the Tc-99 solution soaks into the surface and is less available to activate the scintillator. For this type of performance degradation, no method to mitigate the effect exists. Second, the surface contamination per unit area is less because the technetium liquid spread out along the hydrophilic surfaces of the brick and the wood. Despite these effects, both targets are still easy to observe.

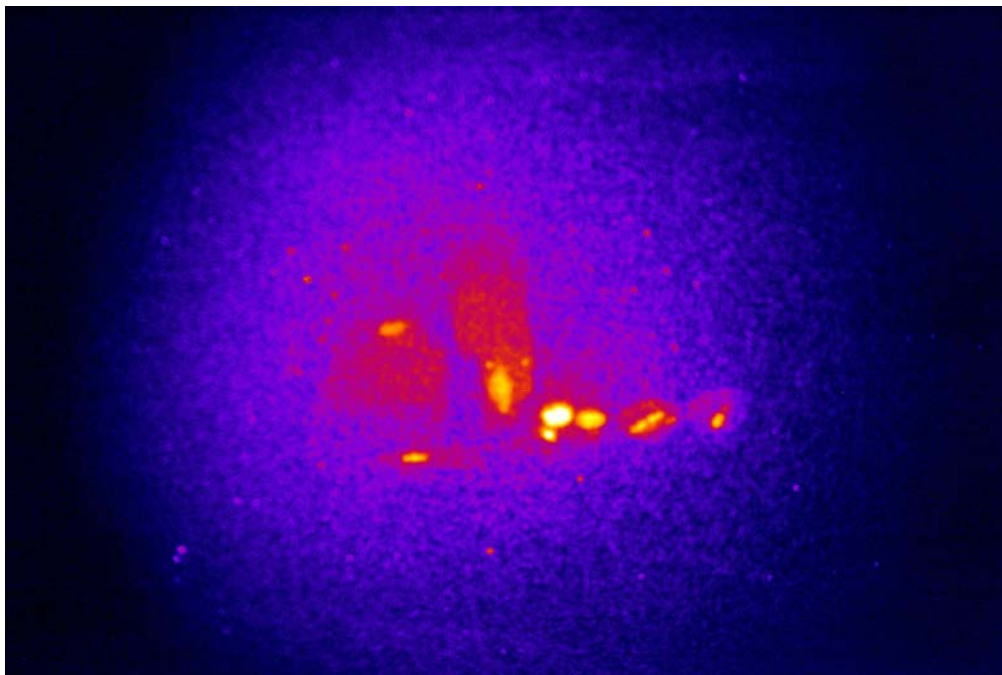


Fig. 5. Targets at 42" (1.1m) Distance

The simulated debris targets are also detected at increased standoff distance, using the same detection parameters, as shown in Figure 6.

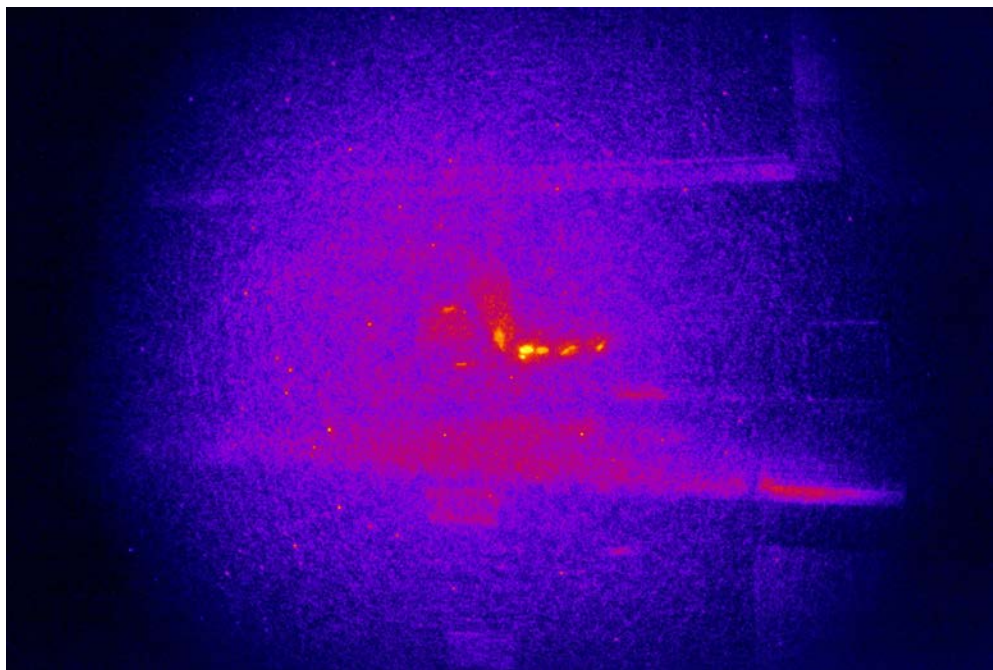


Fig. 6. Targets at 90" (2.3m) Distance

Very long standoff distances are limited by the resolution of the image intensifier system. Since these targets are small, compared to widespread contaminated areas, standoff detection distance could be much longer if wide-area systems were evaluated. The detection limit, in radioactivity, achieved during these experiments was about 10 microcuries Tc-99, and depends on several factors. Chief among them is the presence of ambient light. Although filtering over the phosphor emission helps, ambient light reduces the detection capability. Nevertheless, assessment of surfaces or structures could occur outside daylight hours, limiting background light considerably.

CONCLUSIONS

A field-deployable spray system for the detection of Tc-99 was demonstrated. The system can be used in remote areas because the detector and image intensifier are battery operated and the sprayer can be operated using a compressed gas cylinder or compressor. All of the components of the spray mixture, spraying equipment, and detection equipment are commercial off the shelf items and are inexpensive. The spray mixture is simple, nonhazardous, and easy to deploy, even in structures that have no utilities, limited fire-protection capability, and other detriments typical to decommissioned facilities.

The detection limits currently demonstrated approach 10 microcuries Tc-99. While not low enough to release materials, these levels do represent easy detection of areas of elevated or concentrated radioactivity. They may be improved by better rejection of background light, using larger-objective lenses, and perhaps by computer assisted image processing methods designed to reject background and reflection phenomena. The use of this spray detection method is expected to reduce personnel hours needed for facility characterization by assessing large areas more quickly. Because the phosphor is not sensitive to gamma-ray or neutron radiation, it may be deployed in areas having elevated levels of those radiations without degradation. Preliminary experiments have revealed that the method is sensitive to alpha radiation and to very low-energy beta radiation from isotopes such as tritium and Ni-63. These types of radiation may indicate an application that could be especially benefitted by use of this method. Future experiments should include a field trial series of experiments under realistic conditions, preferably at decommissioned facilities needing characterization.

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