

CONF-961113--12

A fieldable instrument for waterborne radionuclide detection

Christopher M. Barshick, Mary L. Turner, David H. Smith

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory
P.O. Box 2008, MS-6375, Oak Ridge, TN 37831-6375

Keith D. Patch

Thermo Power Corporation, Tecogen Division
45 First Avenue, P.O. Box 9046, Waltham, MA 02254-9046

RECEIVED

DEC 04 1996

OSTI

ABSTRACT

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

In monitoring effluent water leaving its sites, the United States Department of Energy (DOE) assays for alpha-emitting radionuclides (uranium and the transuranics) to ensure compliance with regulatory limits. Because alpha emissions can only be detected over a short range in water (~ 40 μm), the conventional approach is to collect samples for processing in a central laboratory; a time-consuming and costly procedure ensues to separate and measure the radionuclides. Because of the sporadic nature of sampling processes, there is the possibility that a release may go undetected. We are addressing this issue by developing a real-time, field-deployable instrument. This device incorporates a proprietary film that selectively binds radionuclides from dilute aqueous samples. By combining the film with an appropriate alpha spectrometer, we have developed a fieldable system that can operate as an autonomous monitor in a batch or continuous manner. Laboratory results to date have been encouraging. Positive identification of uranium and plutonium has been made by resolving the energy spectrum of emitted alphas. Sensitivity for uranium is at the 10 part per trillion level (15 femtocuries per liter).

Keywords: alpha-emitting radionuclides, uranium, plutonium, proliferant activity, terrorist activity, field-deployable instrumentation.

2. INTRODUCTION

MASTER

Federal law requires that the United States Department of Energy (DOE) ensure that on-site process waters and effluent waters leaving contaminated sites do not affect the health of its employees, contractors, or the public. Some of the most stringent requirements are placed on the levels of alpha-emitting radionuclides. Radioisotopes such as ^{238}U , ^{234}U , and ^{239}Pu are rated by the Environmental Protection Agency (EPA) as Class A carcinogens, and as such have very low regulated limits in water. The proposed maximum concentration limit for uranium in public drinking water is 20 ppb (approximately 30 pCi/L), equivalent to an emission of 67 alpha particles per minute in one liter of water. For reference, the world's sea water has a uranium concentration of ca. 3 ppb.

Currently, process, surface, and ground waters at contaminated DOE sites are monitored for alpha-emitters and other contaminants by intermittent sampling. These samples are chemically stabilized (by the addition of acid), entered into a chain-of-custody infrastructure, packaged for shipping and sent to a central laboratory for analysis. The analytical procedure involves separation and

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or 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 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

concentration of the alpha-emitting radionuclides from the water either by precipitation or evaporation. The alpha-emitting radionuclides are plated on a planchet and counted in vacuum using a silicon wafer semiconductor detector. The results are subjected to quality control protocols, converted to the radionuclide concentration in picocuries per liter, and reported to the requestor.

Only intermittent data are available from this approach because only a limited number of samples can be taken (due to the high cost of each analysis). In 1993, approximately 400,000 analyses were performed at a cost of approximately \$300 per sample. The annual total costs of monitoring for alpha activity in effluent waters exceeds \$100,000,000, with only 30% of this cost going to the actual analytical work (the remainder is handling or overhead).¹ In addition to these costs, there is a time delay between sampling and the transmission of the results; this means that there is no process control mechanism available for waste processing and decontamination operations. The current approach is also prone to errors that result from the many steps involved. Such errors are difficult to detect, requiring several quality assurance steps.

2.1 Present state-of-the-art technology

A number of both "on-line" and "off-line" instruments exist for monitoring alpha-emitting radionuclides in liquids.¹ While an extensive survey of each of these devices is beyond the scope of this manuscript, a few conclusions can be drawn. Of the six known on-line devices (both commercially available and under development), none has the capability of monitoring alpha activity at drinking water levels. Of the commercial "off-line" devices, six of the seven are capable of analyzing drinking water levels, while the seventh is not sensitive enough. Finally, none of the three noncommercial off-line devices is sensitive enough to monitor uranium at drinking water levels. By contrast, the device being developed has the unique capability of being able to perform isotopic analyses of alpha-emitting radionuclides at well below drinking water levels.

2.2 Thermo alpha monitor (TAM) concept

The Thermo Alpha Monitor (TAM) is currently being developed by Thermo Power Corporation, Tecogen Division. The Oak Ridge National Laboratory is assisting in the testing of the device by providing a laboratory where isotopically-enriched samples or licensed nuclear material can be studied. The technology involves automated, on-line, near real-time, isotopically-resolved alpha monitoring of liquids. Collection of radionuclides is accomplished on a film substrate. Alpha spectroscopy is done using a large area solid-state silicon diode detector.

Figure 1 illustrates the solid-state silicon detector measurement concept. Semiconductor counters are similar in concept to ionization chambers in semiconducting materials and offer advantages in detection of nuclear radiation, particularly alpha particles. A semiconductor detector is a large surface area silicon diode of the p-n or p-i-n type, operated in the reverse bias mode. The energy lost by ionizing radiation, such as alpha particles, results in the formation of ions (electron-hole pairs). Under the influence of the imposed electric field, these charge carriers drift to the contacts of opposite polarity, producing a short-duration (nanosecond) flow of electrical current. This electrical current is processed as the analytical signal.²

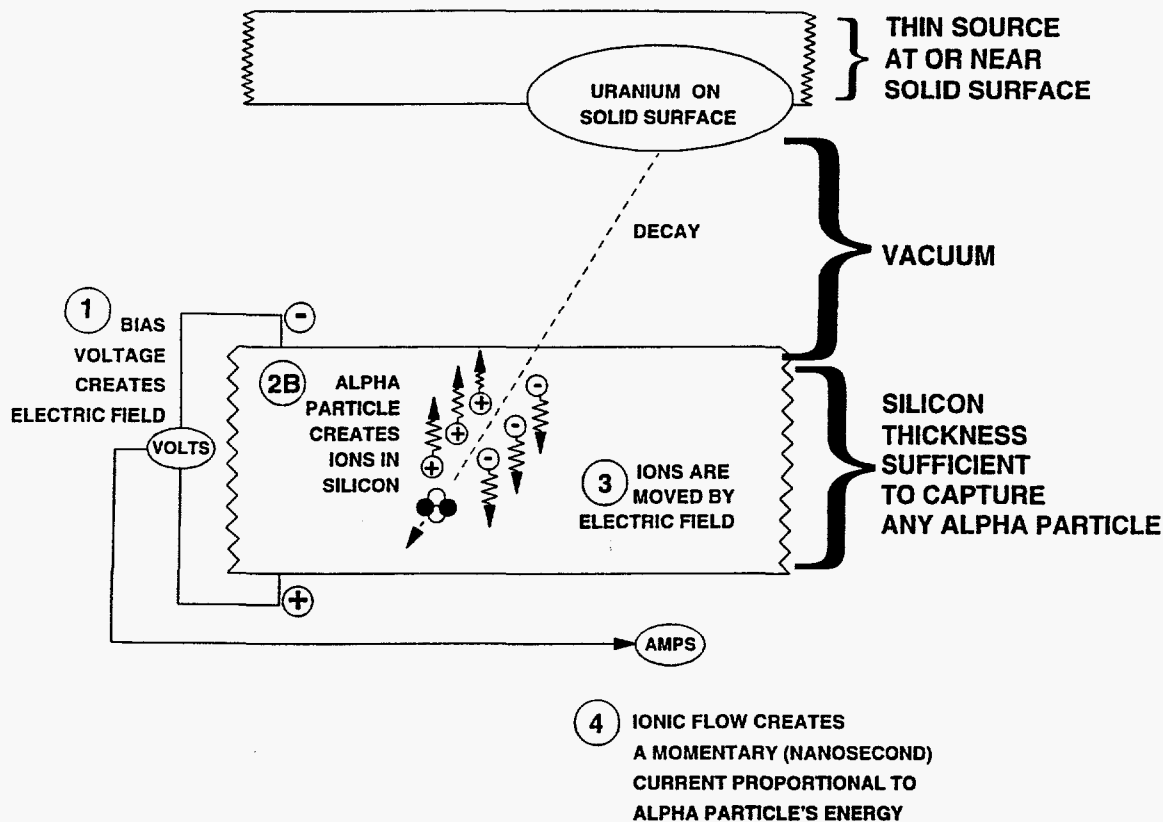


Figure 1. Solid-State Silicon Detector Measurement Concept

The average energy loss per ion pair for alpha particles in silicon is about 3 eV, compared with about 30 eV per ion pair in a gas. Hence, alpha particles create about 10X as many ion pairs in semiconductor solids as in gases; the statistics are thus 3X better than for gas ionization detectors. Silicon also provides a smaller ion capture distance, allowing for higher applied electric fields and faster collection times.

Three predominant types of alpha counters are surface barrier, diffused junction, and ion-implanted. These devices have extremely thin "windows" on the surface (typically equivalent to an 800 Å silicon thickness). The combination of this thin window and the short ion capture distance in silicon (30 micrometers for a 6 MeV alpha) results in 100% absorption of the alpha energy in the depletion region of the detector; formation and collection of electron-hole pairs are linearly proportional to the alpha energy, providing high energy resolution. Some characteristics of the silicon detector for alpha particles are:

- High energy resolution, typically 15 keV full width at half maximum for 5 MeV alphas
- Fast pulse rise time of 5 to 10 nanoseconds
- No apparent dead time
- Linearity of charge collected with particle energy
- Excellent stability
- Very low background

For high energy resolution, it is necessary for the alpha particle emitted by a radionuclide to reach the detector surface without losing any energy by passing through other materials. This is difficult because of the short range of alphas in solid/liquid materials (~40 μm in water). In conventional counting, the radionuclide is deposited on a solid surface (planchet) as a very thin layer so that self-absorption in the source is negligible. The planchet is then placed in front of the detector and a vacuum pulled to prevent absorption of energy by air between the source and the detector. Where the source/detector spacing is small and the source smaller than the detector, 50% of the emitted alphas enter the silicon detector surface and are counted. Higher energy resolution is possible using a greater source/detector spacing, although at a lower detector efficiency.²

3. INSTRUMENTATION

The alpha absorbing films used in the Thermo Alpha Monitor are proprietary. Physically, these films resemble a piece of filter paper. Preliminary studies used films that were 1 cm^2 (0.16 in^2) in area; current versions of the film are either 13.4 cm^2 (2.07 in^2) or, if increased sensitivity is needed, 53.5 cm^2 (8.29 in^2) in area. Throughout this investigation, several different film types were used depending upon whether the goal was selectivity (uranium versus plutonium), sensitivity, or sampling speed.

The analysis is typically performed with a sample volume of between 100 cm^3 and 8000 cm^3 , depending on the sample's activity and the desired counting time. The sample is passed through a waterproof chamber. The chamber and the associated plumbing are designed to withstand most acidic and basic solutions, permitting the analysis of a variety of samples. In addition, construction materials were selected to minimize carryover of radioactive species between analyses.

To analyze a sample, the film is installed in the chamber. The sample is then passed through the chamber, allowing quantitative uptake of the radioactive species of interest. The alpha-emitters are adsorbed at or near the surface of the active film, forming a thin source. The complete sampling cycle takes approximately 16 minutes to complete for a 8000 cm^3 sample. After subsequent processing, the film is counted by the detector. The counter incorporates a solid-state, silicon-based, reverse-biased, p-i-n diode. This detector has an active area of 50 cm^2 . The counter is connected through a pre-amp to a 1024 channel pulse height analyzer. The multi-channel analyzer is mounted in an IBM compatible personal computer that runs Windows-based data acquisition software. The complete counting cycle takes approximately one minute for a sample of 8000 cm^3 containing 20 ppb natural uranium. After the analysis is completed, the film is removed for archiving. The total analysis cycle is completed in under 30 minutes.

4. RESULTS

4.1 Analysis of Uranium Nitrate Solutions

A uranium atomic absorption standard solution (U_3O_8 stabilized in HNO_3) was used to prepare reference solutions in the concentration range from 10 parts per million (ppm) to 10 parts per trillion (ppt) to test the instrument response. Due to their respective half-lives, the activity of ^{234}U should be approximately equal to the activity of ^{238}U ; daughter products of ^{238}U other than ^{234}U would not be expected. In addition, due to its long half-life, ^{235}U would not have had time to produce any daughter

products. The natural abundance and relative activity of the three uranium isotopes are summarized in Table 1.

A sample of the 20 ppb uranium solution was sampled with the 53.5 cm² film; the analyte containing film was then counted. Figure 2 shows the resulting spectrum. The ²³⁸U and ²³⁴U peaks are clearly evident near 4.20 and 4.77 MeV. Perhaps less apparent is the ²³⁵U which falls between ²³⁸U and ²³⁴U. The activities are about the same for the ²³⁸U and ²³⁴U isotopes. Manual subtraction of background and deconvolution of the three overlapping peaks was done to quantify the isotope ratio of the sample. Results indicated that the ²³⁸U peak produced 58% of the net alpha activity; the ²³⁴U peak produced 40% and the ²³⁵U peak 2%. This gives a ²³⁸U : ²³⁴U : ²³⁵U ratio of 1.0 : 0.69 : 0.034, indicating that the sample was slightly depleted uranium or that the measured activity was slightly in error. The hypothesis that the sample was slightly depleted is consistent with the fact that a common starting material for atomic absorption standards is depleted uranium oxide.

Table 1. Half Life, Abundance, and Alpha Activity of Naturally Occurring Uranium

Isotope	Half Life (yr)	Natural Abundance (weight percent)	Alpha Activity (Relative to ²³⁸ U)	Alpha Energies	
²³⁸ U	4.51 x 10 ⁹	99.283	1.00	23%	4.15 MeV
				77%	4.20 MeV
²³⁵ U	7.10 x 10 ⁸	0.711	0.0461		
²³⁴ U	2.47 x 10 ⁵	0.0054	1.00	28%	4.72 MeV
				72%	4.77 MeV

4.2 Analysis of DOE Fernald Site Groundwater

An acid-preserved sample of contaminated groundwater from the DOE Fernald (Ohio) site (600 ppb total uranium) was obtained for testing. This sample was analyzed with a 13.4 cm² film. This spectrum is shown in Figure 3. No ²³⁵U is evident in the spectrum. The activities are clearly not the same for the two isotopes. Again, manual subtraction of background and deconvolution of the overlapping curves was done to quantify the isotope ratio of the sample. Results indicated that the ²³⁸U peak had 82% of the net alpha activity, while the ²³⁴U peak had 18%; a ²³⁸U : ²³⁴U ratio of 4.5.

A likely explanation for this ratio is that this particular portion of Fernald became contaminated with depleted uranium. If it had been contaminated with natural uranium, the ratio would have been 1; if it had been contaminated with enriched uranium, the ²³⁵U and ²³⁴U peaks would have been increased relative to the ²³⁸U.

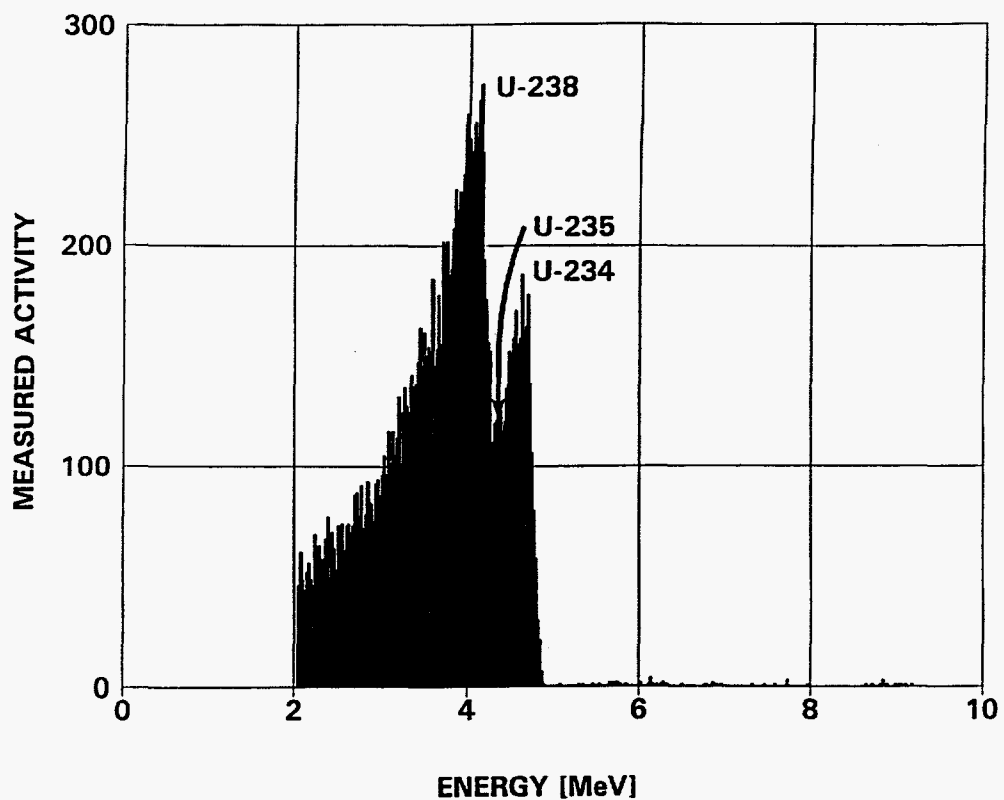


Figure 2. Measured Activity Versus Energy for a 20 ppb Uranium Reference Solution

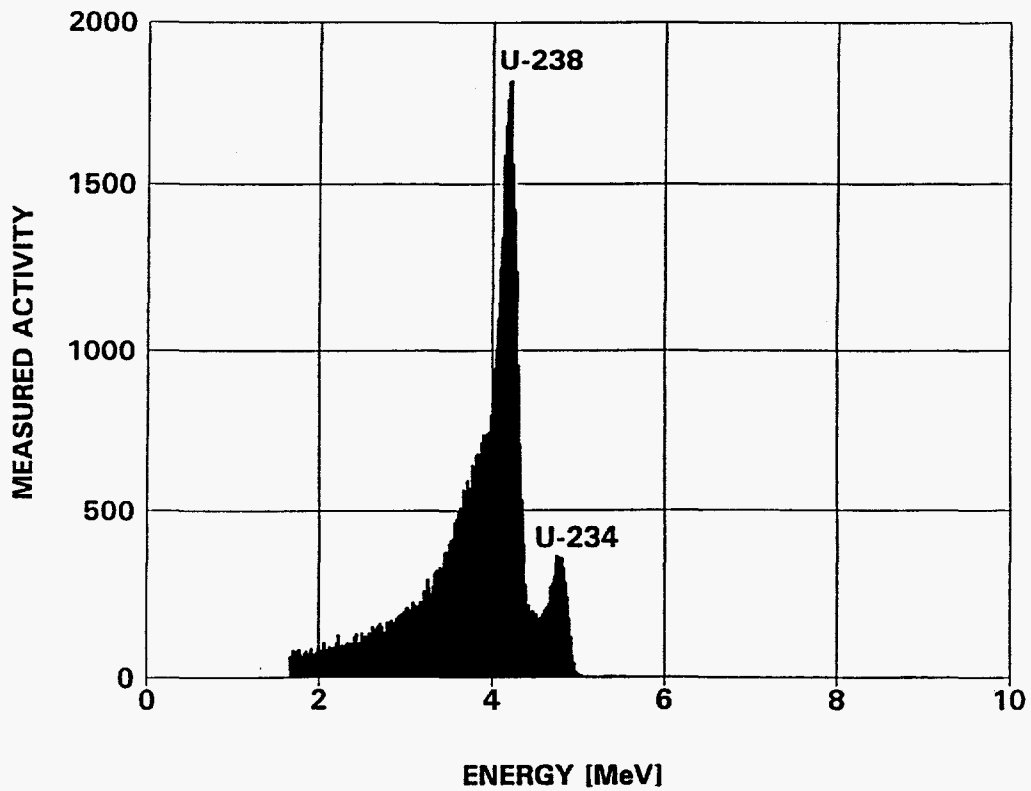


Figure 3. Measured Activity Versus Energy for a Fernald, Ohio Groundwater Sample Containing 600 ppb Uranium

4.3 Analysis of Thorium Nitrate Solutions

The results from assaying a 1 ppm solution of thorium nitrate are shown in Figure 4. The two major peaks are analogous to the two peaks in the uranium containing samples: ^{232}Th is the parent of the thorium decay series, and ^{228}Th is a daughter product of ^{232}Th . The third peak in Figure 4 is ^{230}Th (a daughter of ^{234}U). It can be seen by examining Table 2 that the relative heights of the ^{232}Th and ^{228}Th should be about equal. However, for approximately every two years that the thorium is aged, the activity of ^{228}Th will be reduced by half; ^{228}Th daughter products grow in. Due to the relatively long half-lives of ^{232}Th and ^{230}Th , the activity of these two isotopes will not change. Manual deconvolution of the three overlapping thorium peaks and subtraction of the background showed that the ^{232}Th had 63.8% of the net thorium activity, the ^{228}Th had 28.4%, and the ^{230}Th had 7.8% -- a $^{232}\text{Th} : ^{228}\text{Th} : ^{230}\text{Th}$ ratio of 1.0 : 0.445 : 0.098. This data suggests that the thorium was separated from uranium over two years ago, and that the original "ore" contained ca. 10% uranium.

Table 2. Half Life and Alpha Activity of Three Thorium Isotopes

Isotope	Half Life (yr)	Decay Series	Alpha Activity (Relative to ^{232}Th)	Alpha Energies	
^{232}Th	1.41×10^{10}	Thorium	1.00	23% 77%	3.95 MeV 4.01 MeV
^{230}Th	8.00×10^4	Uranium	N/A	24% 76%	4.62 MeV 4.68 MeV
^{228}Th	1.91	Thorium	1.00	28% 71%	5.34 MeV 5.43 MeV

4.4 Linear Dynamic Range

Results indicate that the instrument has a linear dynamic range over six orders of magnitude for uranium and over four orders of magnitude for thorium. Figure 5 shows a logarithmic calibration curve with data spanning the range from 10 ppt (15 fCi/L) to 10 ppm (15,000 pCi/L) for uranium, and from 100 ppt (17 fCi/L) to 1 ppm (172 pCi/L) for thorium. The correlation coefficient (R^2) is 0.999, indicating excellent linearity of response.

4.5 Effect of pH

The operation of the instrument has been shown to be unaffected by sampling a slightly acidic or slightly basic solution; however, the results are quite different for solutions of widely varying pH. Figure 6 is a plot of the measured total uranium activity relative to the know activity versus pH. These results show that analyzing a uranium solution below pH 4.5 significantly reduces the uptake of the analyte by this particular film. We have analyzed a second, different film that shows a similar result with low pH. A third film has complementary properties, a reduced analyte uptake at high pH and a

maximum analyte uptake at low pH.

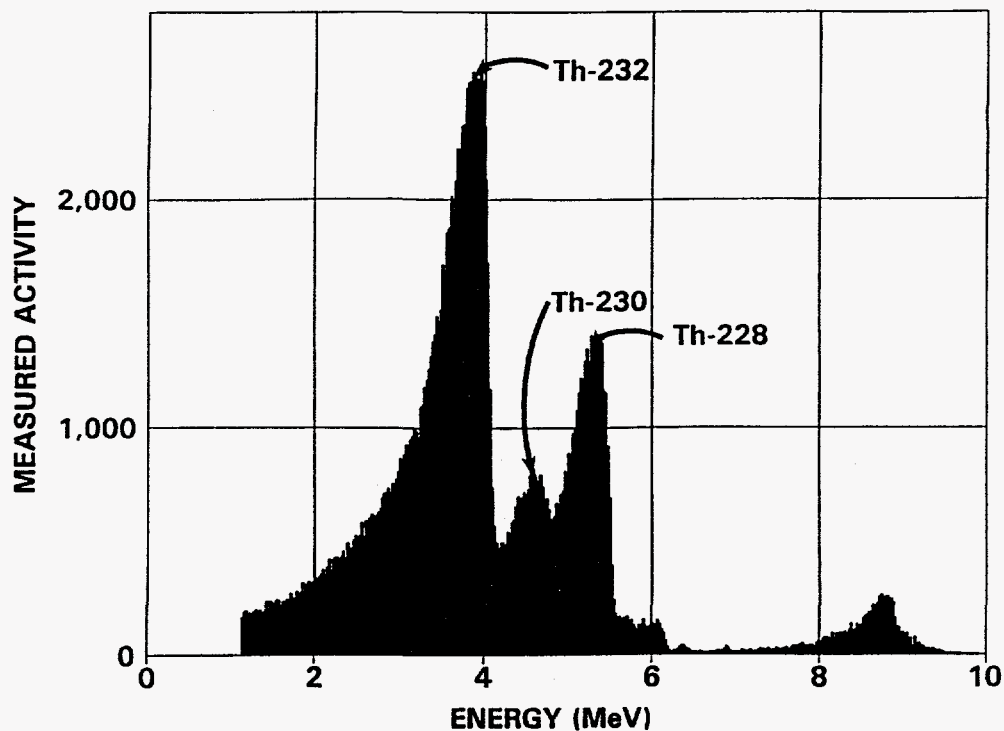


Figure 4. Measured Activity Versus Energy for a 1 ppm Thorium Reference Solution

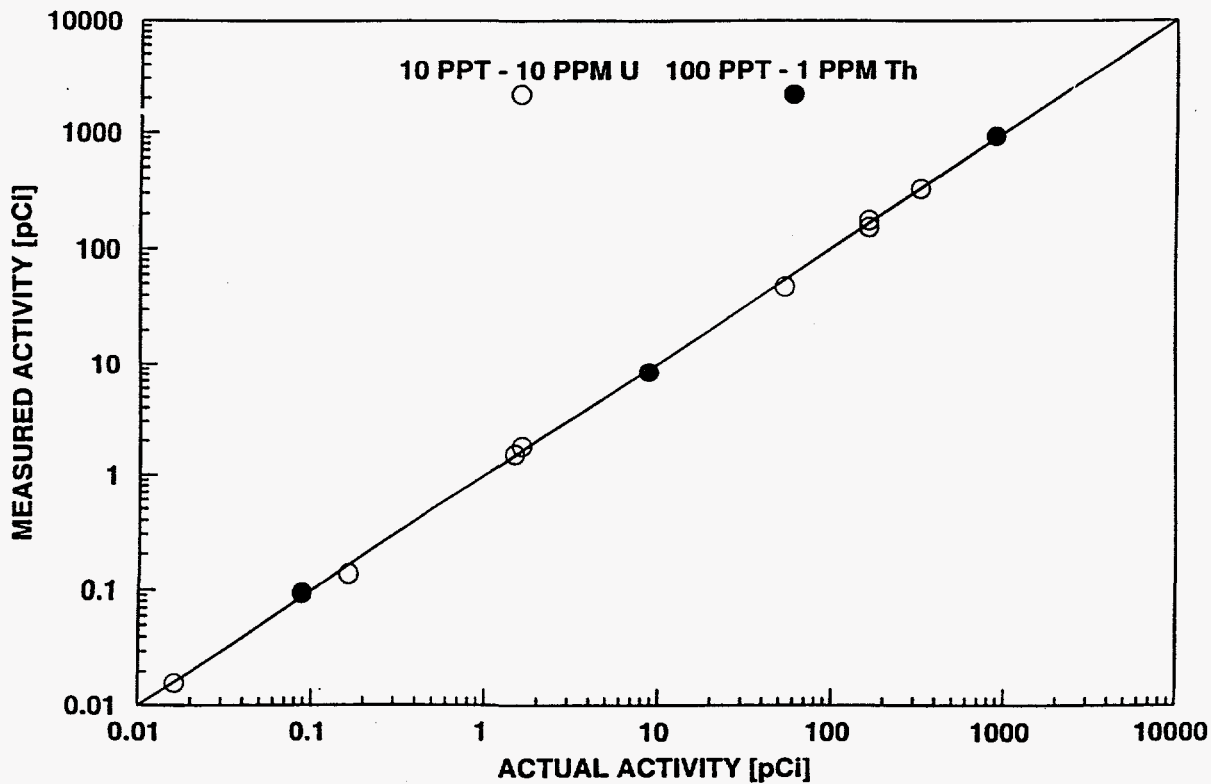


Figure 5. Measured Activity (pCi) Versus Actual Activity for Uranium (10 ppt to 10 ppm) and Thorium (100 ppt to 1 ppm) Reference Solutions

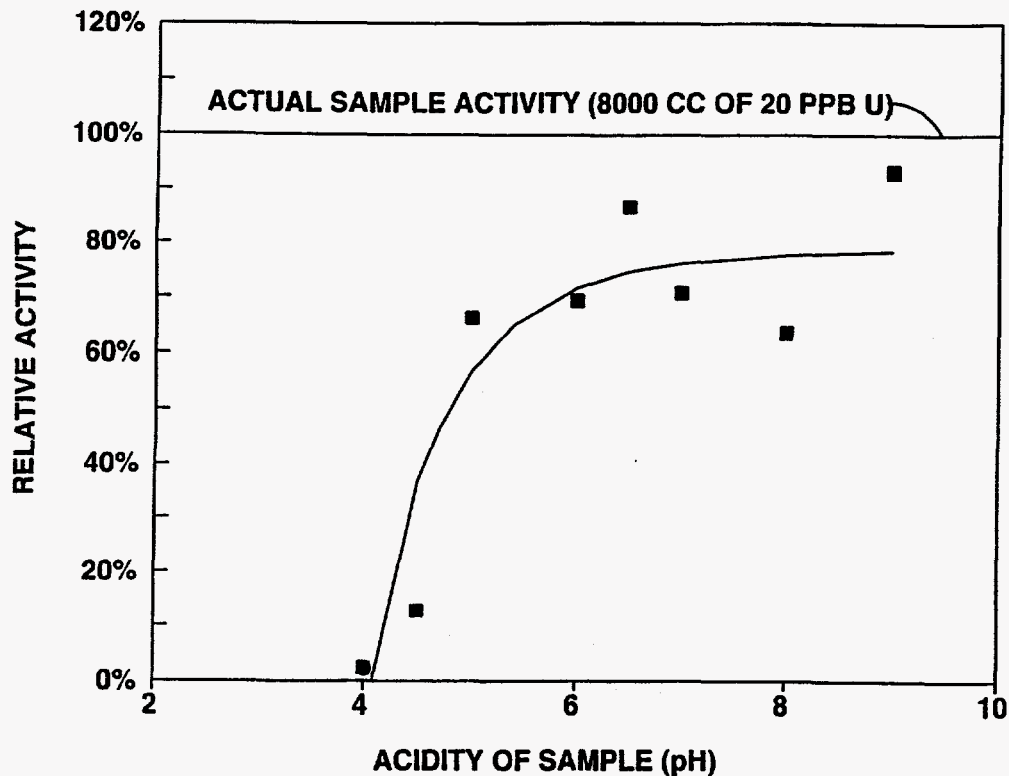


Figure 6. Effect of pH on One Film's Response to Uranium

4.6 Effect of Total Dissolved Solids

A plot of the measured total uranium activity relative to the known activity shows that for total dissolved solid (TDS) levels below 100 ppm, accurate results are obtained for uranium concentrations between 10 ppm and 10 ppt. For these concentrations, erroneously low readings are produced when analyzing solutions with total dissolved solids above 1000 ppm. It is believed the high total dissolved solids loading interferes with the uptake of uranium by the film when the analyte concentration is 10,000X less than the TDS (i.e., the TDS is 10,000X greater than the uranium concentration).

5. CONCLUSIONS

A prototype alpha-detecting instrument of extremely high sensitivity was tested. Because it is capable of measuring the most common alpha emitters to levels well below regulatory limits for drinking water, it holds great promise in the field of environmental monitoring. The fact that it can be made field-deployable and acquire results in a near-real-time framework enhances its attractiveness. Full deployment of the instrument across the DOE complex would provide annual cost savings of up to \$72,000,000 per year.¹ Further development is dependent on continuation of funding.

6. ACKNOWLEDGMENT

Research was sponsored by the United States Department of Energy, Office of Research and Development (NN-20), under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation, and the United States Department of Energy, Office of Environmental Management, Office

of Science and Technology (EM-50), under contract DE-AR21-95MC32088 with Thermo Power Corporation, Tecogen Division..

7. REFERENCES

1. "Development of an on-line, real-time alpha radiation measuring instrument for liquid streams," *U.S. Department of Energy Technical Report (draft), in fulfillment of contract DE-AR21-95MC32088*, July 3, 1996.
2. W.D. Ehmann and D.E. Vance, "Radiochemistry and Nuclear Methods of Analysis," *Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications*, Volume 116, John Wiley & Sons, Inc., New York, 1991.