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#6

DEVELOPMENT OF AN ON-LINE, REAL-TIME ALPHA RADIATION MEASURING INSTRUMENT FOR LIQUID STREAMS

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1. INTRODUCTION

The U.S. Department of Energy (DOE) has expressed a need for an on-line, real-time instrument for assaying alpha-emitting radionuclides (uranium and the transuranics) in effluent waters leaving DOE sites to ensure compliance with regulatory limits. Due to the short range of alpha particles in water (~40 îm), it is necessary now to intermittently collect samples of water and send them to a central laboratory for analysis. A lengthy and costly procedure is used to separate and measure the radionuclides from each sample. Large variations in radionuclide concentrations in the water may go undetected due to the sporadic sampling. Even when detected, the reading may not be representative of the actual stream concentration. To address these issues, the Advanced Technologies Group of Thermo Power Corporation (a Thermo Electron company) is developing a real-time, field-deployable alpha monitor based on a solid-state silicon wafer semiconductor (U.S. Patent 5,652,013 and pending, assigned to the U.S. Department of Energy). The Thermo Water Alpha Monitor (Figure 1) will serve to monitor effluent water streams (Subsurface Contaminants Focus Area) and will be suitable for process control of remediation as well as decontamination and decommissioning (D&D) operations, such as monitoring scrubber or rinse water radioactivity levels (Mixed Waste, Plutonium, and D&D Focus Area). It would be applicable for assaying other liquids, such as oil, or solids after proper preconditioning. Rapid isotopic alpha air monitoring is also possible using this technology.

This instrument for direct counting of alpha-emitters in aqueous streams is presently being developed by Thermo Power under a development program funded by the DOE Environmental Management program (DOE-EM), administered by the Federal Energy Technology Center (FETC). Under this contract, Thermo Power has demonstrated a solid-state, silicon-based semiconductor instrument, which uses a proprietary film-based collection system to quantitatively extract the radionuclides of interest from the water sample. The new instrument permits extremely sensitive counting of alpha-emitters in water, and it also provides high-resolution alpha spectrometry so that individual radionuclides can be identified and assayed simultaneously, based on their different alpha energies. The specialized film captures a broad (or narrow by choice of film) range of alpha-emitting radionuclide ions dissolved in the liquid. The radionuclides are captured on or near the film's surface, forming a very thin source for high resolution spectrometry.

Based on results to date, readily observable peaks are evident at very low levels, to 10 parts per trillion (15 femto Curies per liter) natural uranium. With an analysis time of under 30 minutes, depending on the concentration and statistical accuracy, this new technology represents a significant (by more than a factor of 1,000) advance toward rapid identification and quantitative assay of alpha-emitters in aqueous streams, both on-line and in real time. When commercialized, the new system will be more cost-effective than present methods of analysis with a simple payback period of less than five months, and often as short as several weeks.

Figure 1. Thermo Alpha Monitor (TAM)

This report details the program's accomplishments to date. Most significantly, the Alpha Monitoring Instrument was successfully field demonstrated on water 100X below the Environmental Protection Agency's proposed safe drinking water limit – down to under 1 pCi/l. During the Field Test, the Alpha Monitoring Instrument successfully analyzed isotopic uranium levels on a total of five different surface water, process water, and ground water streams (the primary water types of interest to the DOE). As an example of the user demand for such an analytical instrument, a portion of the Field Test for the Alpha Monitoring Instrument was on the DOE's Oak Ridge Reservation, at two test locations in the Y-12 Site's Bear Creek Valley.

The isotopic detection limit was extended to 10 parts per trillion natural uranium (15 fCi/l), or 1/2,000th the Environmental Protection Agency's (EPA) drinking water limit of 20 ppb, which is well under the program's goal of 30 pCi/l. In addition, the technology has responded to 20 ppb natural uranium (30 pCi/l) in under 30 minutes, well under the program's goal of a 1- to 12-hour instrument response time. Laboratory testing successfully quantified isotopically 1.5 pCi/l (2 ppb) total uranium in Carlisle, Massachusetts potable groundwater, comparing quite favorably with 0.68 pCi/l levels of soluble uranium and 1.35 pCi/l total uranium that were measured by conventional analysis methods. Laboratory testing also successfully isotopically analyzed a 600 ppb uranium sample obtained from the DOE's Fernald, Ohio site.

In addition, the instrument has been used to isotopically detect thorium (^{232}Th) at 100 parts per trillion (17 femtocuries per liter), as well as lesser amounts of thorium daughters. Overall, the technology has demonstrated a linear dynamic range over greater than six decades of concentration, from 10 parts per trillion (15 fCi/l) to 10 parts per million (15,000 pCi/l) natural uranium, including levels of natural thorium between 100 parts per trillion (17 fCi/l) and 1 part per million (172 pCi/l).

The key recommendation of this Final Report is to continue development of the on-line, real-time alpha monitor for liquids by using the lessons learned in the successful field test to improve the functionality of the instrument, and then to conduct one or more deployments. Site personnel at the Oak Ridge Reservation Y-12 Bear Creek Valley and at the Los Alamos National Laboratory Process Waste Treatment Plant have expressed an interest in hosting such initial deployments, in order to reduce operating costs and improve data quality. These deployments would serve to prove the utility of the instrument when operated by non-Thermo Power personnel in extended duration field tests. Obtaining such credible, long-term end-user experience is the imperative next step toward the commercialization of the instrument.

2. TECHNICAL SUMMARY

2.1 THE NEED

The DOE must ensure that on-site process waters and effluent waters leaving contaminated DOE sites do not affect the safety or health of its employees, contractors, or the public (see Table 1). Alpha-emitting radioisotopes, such as $^{238}U/^{234}U$ and ^{239}Pu, are rated by the U.S. EPA as Class A carcinogens with very low regulated limits in water. Uranium also has a high chemical toxicity. The EPA-proposed maximum concentration limit (MCL) for uranium in public drinking water supplies is 20 ppb (approximately 30 pCi/l), equivalent to an emission of 67 alphas per minute in one liter of water. For reference, the world's sea water has a uniform uranium concentration of 3.3 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 preserved (by the addition of acid), entered into a chain-of-custody infrastructure, packaged for shipping, and then sent to a central laboratory for analysis. The analytical procedure involves separation and concentration of the alpha-emitting radionuclides from the water sample, 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 QA/QC protocols, converted to the radionuclide concentration, pCi/l, and reported to the requester.

Shortcomings of this current approach are summarized below:

(A) Current Approach Gathers Intermittent Information Only

Only intermittent data are available on the alpha-emitting radionuclide concentrations in the water stream. Further, only a limited number of samples are taken because of the high cost of analysis and cost-reduction desires of the DOE. High excursion of alpha-emitting radionuclides could occur between samples without anyone being aware of it.

Results of analyses at the Fernald site[1] indicate such wide variations. In 1992, 46 samples were taken from Paddys Run, sample location W-10DD, and analyzed for total uranium (and other contaminants). The minimum uranium concentration measured was 0.41 pCi/l, the maximum was 1,800 pCi/l, and the average was 480 pCi/l. What was occurring in between these 46 samples (an average of one every 7.9 days) will remain unknown.

[1] 1992 Fernald Site Environmental Report, FEMP-2290 Special UC-707, June 1993, U.S. DOE (Table 12, Page A-20).

TABLE 1

PERTINENT RADIOACTIVITY STANDARDS AND RECOMMENDATIONS

IAEA Safety Series; No. 46 (1978)	Monitoring of airborne and liquid radioactive releases from nuclear facilities to the environment: recommendations ISBN 9201231784	International Atomic Energy Agency
IEC 60768 (1983-01)	Process stream radiation monitoring equipment in light water nuclear reactors for normal operating and incident conditions	International Electrotechnical Commission
IEC 60861 (1987-12)	Equipment for continuously monitoring for beta and gamma emitting radionuclides in liquid effluents	International Electrotechnical Commission
IEC 61306 (1994-08)	Nuclear instrumentation – Microprocessor-based nuclear radiation measuring devices	International Electrotechnical Commission
IEC 61311 (1995-10)	Radiation protection instrumentation - Equipment for continuously monitoring beta and gamma emitting radionuclides in liquid effluents or in surface waters	International Electrotechnical Commission
Title 10 CFR Part 20	Standards for Protection Against Radiation	NRC
Title 10 CFR Part 820	Procedural Rules for DOE Nuclear Activities	DOE
Title 10 CFR Part 834	Radiation Protection Of The Public And The Environment	DOE
Title 10 CFR Part 835	Occupational Radiation Protection	DOE
Title 10 CFR Part 1021	DOE NEPA Regulations	DOE
Title 40 CFR Part 141, 142	National Primary Drinking Water Regulations; Radionuclides; Proposed Rule	EPA
Title 40 CFR Part 260 – 272	Resource Conservation and Recovery Act Hazardous Waste Regulations (RCRA mixed-waste regulations)	EPA
Policy 441.1	Department Of Energy Radiological Health And Safety Policy	DOE-S-1
Policy 450.1	Environment, Safety And Health Policy For The Department Of Energy Complex	DOE-EH
Policy 450.2A	Identification, Implementation, And Compliance With Environment, Safety And Health Requirements	DOE-EH/GC
Policy 450.3	Authorizing Use Of The Necessary And Sufficient Process For Standards-Based Environment, Safety And Health Management	DOE-EH

TABLE 1 (Continued)

PERTINENT RADIOACTIVITY STANDARDS AND RECOMMENDATIONS

Policy 450.5	Line Environment, Safety And Health Oversight	DOE-DP
Policy 450.6	Environment, Safety And Health	DOE-EH
Order 210.1	Performance Indicators And Analysis of Operations Information	DOE-EH
Order 231.1	Environment, Safety, And Health Reporting	DOE-EH
Order 232.1A	Occurrence Reporting And Processing Of Operations Information	DOE-EH
Order 440.1A	Worker Protection Management For DOE Federal And Contractor Employees	DOE-EH
Order 451.1A	National Environmental Policy Act Compliance Program	DOE-EH
Order 5400.1	General Environmental Protection Program	DOE-EH
Order 5400.4	Comprehensive Environmental Response, Compensation and Liability Act Requirements	DOE-EH
Order 5400.5	Radiation Protection of the Public and the Environment	DOE-EH
Order 5440.1E	National Environmental Policy Act Compliance Program	DOE-EH
Order 5480.4	Environmental Protection, Safety and Health Protection Standards	DOE-EH
Order 5480.11	Radiation Protection for Occupational Workers	DOE-EH
Order 5480.19	Conduct Of Operations Requirements For DOE Facilities	DOE-EH
Order 5484.1	Environmental Protection, Safety and Health Protection Information Reporting Requirements	DOE-EH
Order 5820.2A	Radioactive Waste Management	DOE-EM
Manual 231.1-1	Environment, Safety, And Health Reporting Manual	DOE-EH
Notice 441.1	Radiological Protection For DOE Activities	DOE-EH
Notice 441.4	Extension Of DOE N 441.1, Radiological Protection For DOE Activities	DOE-EH
HQ Order 250.1	Civilian Radioactive Waste Management Facilities--Exemption From Departmental Directives	DOE-RW
Executive Order 12580	Superfund Implementation	DOE-EH

When D&D or site remediation efforts are underway and the site is disturbed (by excavation, washing, etc.), continuous, rather than intermittent, monitoring is essential to ensure no public hazard. In addition, the off-gas scrubbers needed on Mixed Waste thermal treatment systems have a DOE-identified need for controlling and monitoring alpha activity levels; no commercial instrumentation exists to fill that analytical need.

(B) High Cost of the Current Approach

The end-to-end analysis cost for isotopic uranium in drinking water is approximately $300 per sample; for total uranium, the cost is approximately $135 per sample. The majority of this cost involves taking the sample, numbering it, properly preparing it for transport to the laboratory, and logging in and evaluating the results. These sampling/processing costs average approximately 200% of the direct analysis cost for each sample. Seven thousand and thirty-four (7,034) surface and ground water samples were taken and analyzed at Fernald in 1992, an average of 19.3 per day, resulting in an annual analysis cost of approximately $2.1 million. In addition to the high cost, these samples were spread over many sampling locations, restricting the data available at each location. High cost of the current approach is a strong impediment to increasing sampling frequency for obtaining more complete data.

There is a growing emphasis on cost reduction within the federal government. One approach to reducing the cost of environmental monitoring would be to decrease the frequency of sampling while continuing to use existing analytical technology. Although this approach would certainly reduce immediate costs of analysis, much information would be lost compared to even the relatively sparse data collected today. There is clearly an opportunity now for the introduction of "better, faster, and cheaper" alpha-monitoring technology. The Thermo Water Alpha Monitor would address budgetary constraints in a very different manner by both reducing costs and improving data quality, while providing analyses as needed.

(C) Time Delay Between Sampling and Data Availability with the Current Approach

After submission of a sample, several days usually pass before the sample is analyzed and the results transmitted. The laboratory generally operates with a backlog of samples, which are analyzed in sequence on a production basis.

For immediate analysis, the total sample cost is much higher than $300 per sample for uranium isotopic analysis. While an immediate procedure can be used in an emergency, the number of "rush" samples must be limited because of their high cost.

This time delay can have serious consequences. Firstly, changes can be occurring to the water's composition, which may not be detected for days. Secondly, in thermal treatment, D&D, or site remediation operations, the time delay can result in wasted effort and slow progress since the operating personnel are ignorant of current conditions. The total operations cost remediation can thus be greatly increased due to inefficient operation, in contrast to what is possible with immediate availability of analyses of uranium (or other alpha-emitting radionuclide) concentrations.

(D) The Current Approach is Prone to Errors

Due to the many steps involved and the production analyses, many opportunities exist for mistakes and other errors to occur in the current process. Improper sampling procedures can be used, the analysis can be faulty, and the data reduction or reporting can be inaccurate. Such errors are difficult to detect, and quality assurance is always an important part of environmental monitoring. Elimination of the many sequential manual steps involved in the conventional approach, by use of automatic on-line monitoring, will reduce the opportunity for errors.

(E) No Process Control Exists for Waste Processing and Decontamination Operations

In addition to improved environmental monitoring for alpha-emitting radionuclides, improved process control is required. At the Idaho National Engineering Laboratory, for instance, a Plasma Arc thermal treatment system for vitrifying mixed waste is being developed. At Fernald, an Advanced Wastewater Treatment Plant will be used to remove uranium from site waters to below proposed EPA drinking water limits. With the current analytical approach of sampling and central laboratory analyses, the same difficulties result as with environmental monitoring. Modern chemical processing plants utilize on-line, real-time analytical equipment for process control and operation. Availability of such an instrument for uranium and other alpha-emitting radionuclides will be of great benefit for process control and monitoring.

For reference purposes, Figure 2 summarizes the DOE's two trillion liters of liquid radioactivity releases of 1993, averaging 6 pCi/l, that were reported by the various DOE Operations Offices. Approximately 400,000 liquid sample alpha analyses per year are performed for both these effluent waters, as well as for on-site monitoring. The present end-to-end cost per alpha analysis is ~$300, for an annual total in excess of $100,000,000. Approximately 30% of this cost is for the actual analytical work (charged by laboratories), while the remainder is handling or overhead. (Appendix 1 contains a cost savings analysis for the Thermo Water Alpha Monitor).

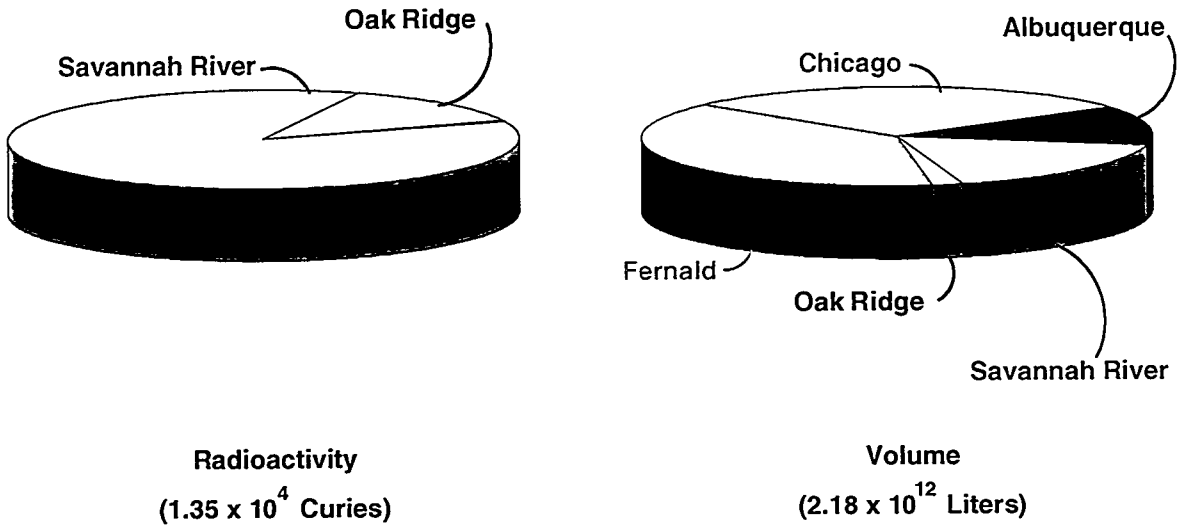

Figure 2. DOE Complex-Wide Liquid Radioactivity Releases (1993)

2.2 PRESENT STATE-OF-THE-ART TECHNOLOGY

2.2.1 Summary

This section attempts to quantify the technology gap that exists between present state-of-the-art technology and the needs of the DOE for monitoring alpha-emitting radionuclides in liquid samples. Both on-line and off-line instruments and methods are surveyed. While the major emphasis of this survey is the evaluation of instruments which are commercially available, devices and technologies under development are also surveyed. Conclusions drawn from examining these systems indicate that a factor of approximately 1,000 improvement in detection limits for on-line instrumentation is required in order to meet DOE needs.

Commercial devices and methods examined by this survey include:

1) EG&G Ortec's LB/BAI9126 Alpha/Beta/Gamma Monitoring System,
2) Eberline Instruments OLAM,
3) Canberra Industries Inc.'s In Line Real-time Water Monitoring Systems,
4) Conventional radiochemical laboratory analysis methods,
5) ORDELA, Inc.'s PERALS spectrometer,
6) Quantrad Systems' Liquid Analyzer System,
7) EG&G Ortech's LB 506 AT (Specially Modified),
8) Canberra Inc.'s Flow Cell Scintillator Analysis System, and
9) Two analytical (non alpha-detecting) analytical systems that will undergo a user-based performance evaluation at the DOE Fernald (Ohio) site.

Alpha monitoring instrumentation that is not yet commercially available includes:

1) Los Alamos' LRAD for Radioactive Liquid Waste,
2) Westinghouse Savannah River's patented fiber optic Sol-Gel Indicator (SGI) technology,
3) SCUREF'S Flow-Cell Scintillation Counting,
4) Lawrence Livermore's Fiber Optic Analytical Methods,
5) Los Alamos' Fiber Optic Analytical Methods, and
6) The University of South Carolina's research titled, "Development of a Fiber-Optic Uranium Sensor Employing Fluorescence Quenching and a Second-Order Photo-oxidation Effect."

Of the six known alternative on-line devices (both commercially available and under development), none have the capability of monitoring alpha radioactivity at drinking water levels. Of the commercial "off-line" devices and methods, 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 are sensitive enough to monitor drinking water levels of uranium. By contrast, the Thermo Water Alpha Monitor, as shown by Thermo Power Corporation, has the unique capability of performing isotopic on-line analyses of alpha-emitting radionuclides at well below drinking water levels. The Thermo Water Alpha Monitor goes beyond the DOE's required factor of 1,000 enhancement to a factor of 2,000,000, or a detection limit of 10 parts per trillion (15 fCi/l) natural uranium.

2.2.2 Commercial Devices

Commercial alpha-monitoring instrumentation has been divided into two categories: on-line devices and off-line devices.

Commercial On-line Devices

This section examines commercial on-line alpha monitoring instruments. Included are:

1) EG&G Ortec's LB/BAI9126 Alpha/Beta/Gamma Monitoring System,
2) Eberline Instruments OLAM, and
3) Canberra Industries Inc.'s In Line Real-time Water Monitoring Systems.

1.) EG&G Ortec – LB/BAI9126

EG&G Ortec's LB/BAI9126 Alpha/Beta/Gamma Monitoring System is designed for effluent and drinking water applications. In the Ortec 9126, a large-area proportional counter is used to measure radioactivity leaving the surface (top 40 micrometers) of a water sample. The proportional counter used in the 9126 can discriminate between alpha and beta radioactivity. Four inches of lead shielding are used; total system weight is 3,300 pounds (1,500 kg). One of these units is installed at the Oak Ridge National Laboratory's Process Waste Treatment Plant,

but is not used for detecting alpha-emitters (it responds only by giving false alarms during high radon level conditions on rainy days). The approximate price of the 9126 is $75,000.

EG&G Ortec's LB/BAI9126 technology will not permit detection of alpha radioactivity at drinking water levels.

2.) Eberline Instruments – OLAM

Eberline Instruments acquired the rights to OLAM from the Oak Ridge National Laboratory. OLAM pumps a thin layer of sample between two solid scintillating materials and measures the alpha radioactivity emanating from the top 40 micrometers of the sample. OLAM is no longer actively marketed by Eberline Instruments. While it was being sold, the detector cost approximately $30,000 and the required electronics cost $5,000, bringing the total system cost to $35,000.

The technology involved will not detect alpha radioactivity at drinking water levels.

3.) Canberra Industries – In Line Real-time Water Monitoring Systems

Canberra Industries Inc. has installed several custom-designed In Line Real-time Water Monitoring Systems for environmental monitoring of ^{235}U, fission products, and activation products in water. Canberra's stated sensitivity of 1 ppm ^{235}U translates to a radioactivity level of 2,162 pCi/l, equivalent to a naturally-occurring uranium concentration of 3.2 ppm. This system detects gamma emissions above 100 – 300 keV and is not applicable to samples containing low-gamma yielding alpha-emitters. For reference purposes, a count time of 60 minutes is used to sample the water. Costs for these systems are on the order of $80,000.

The technology involved will not detect alpha radioactivity at drinking water levels.

<u>Commercial Off-line Devices/Methods</u>

This section examines commercial off-line, alpha-monitoring instruments. Included are:

1) Conventional radiochemical laboratory analysis methods,
2) ORDELA, Inc.'s PERALS spectrometer,
3) Quantrad Systems' Liquid Analyzer System,
4) EG&G Ortech's LB 506 AT (Specially Modified),
5) Canberra Inc.'s Flow Cell Scintillation Analysis System, and
6) Two analytical (nonalpha-detecting) analytical systems that will undergo a user-based performance evaluation at the DOE Fernald (Ohio) site.

1.) Conventional Radiochemical Laboratory Analysis Methods

The most rapid forms of conventional radiochemical laboratory analysis involve moderate sample preparation followed by counting for » 30 minutes on a silicon-based semiconductor detector. Sample preparation takes perhaps 4 to 48 hours and usually involves either a macroprecipitation of the dissolved material using neodymium fluoride or a boiling off of the sample's water. Drinking water levels of radioactivity can be accurately measured using a one-gallon sample size. Drawbacks of the conventional method include the extensive manual processing involved and the need for qualified technical personnel to perform and oversee the analysis, leading to a high per-sample cost. The nuclear instrumentation portion of the capital cost ranges from $6,000 for a one-channel alpha spectroscopy system to $30,000 for a system capable of eight simultaneous alpha counts.

As such, conventional radiochemical laboratory analysis methods are capable of isotopic detection of alpha-emitters at drinking water levels, requiring multiple sequential handling operations and a resultant high cost. These methods are not suited for continuous or semi-continuous analysis.

2.) ORDELA – PERALS

ORDELA, Inc. manufactures the PERALS (Photon/Electron-Rejecting Alpha Liquid Scintillation) spectrometer. Analysis with the PERALS method begins with solvent extraction of the sample, using extractive liquid scintillator cocktails, followed by bubbling with argon to remove oxygen, a chemical quench agent. Finally, the prepared sample is counted on the PERALS. Sample preparation times are quoted as 30 minutes for simple (water-based sample) extraction, and four hours for soil samples. Method sensitivity (MDA) for uranium in water is quoted as approximately 1 pCi/l in four hours (equivalent to 1 ppb natural uranium). A complete PERALS system costs $21,250.

The PERALS spectrometer is capable of off-line isotopic measurements of low-level alpha-emitters at drinking water levels; the main drawback of the PERALS method is the need for disposal of secondary mixed waste (spent liquid scintillator cocktail).

3.) Quantrad – Liquid Analyzer System

Quantrad Systems manufactures a Liquid Analyzer System that performs an in situ deposition of dissolved radionuclides directly onto a silicon-based semiconductor detector. Consequently, the deposited radionuclides are analyzed as they build up on the detector's surface. After sufficient counting time has passed, the detector is cleaned with concentrated acid and a new analysis is begun. Known deficiencies of this method include: inevitable catastrophic failure of the detector due to sample or acid leaks (analyzer lifetime averaging only a few hundred hours), slow response time (days of counting for samples 1,000X stronger than drinking water

limits), severe degradation in detector performance prior to catastrophic failure, production of secondary mixed waste (spent concentrated acid), and poor repeatability and stability of instrument calibration. The cost of a Quantrad system is $12,995.

The technology involved will not permit detection of alpha radioactivity at drinking water levels unless extremely long count times (in excess of weeks) are used.

4.) EG&G Ortech – LB 506 AT (Specially Modified)

EG&G Ortech is selling a flow cell scintillator analysis system that uses a liquid scintillator to analyze samples of water. It involves a technology similar to the PERALS; EG&G claims a sensitivity of at least 100 pCi/l. EG&G sells what amounts to a modified life sciences laboratory instrument that is a custom-engineered product. The 506 costs approximately $25,000; the total price is approximately $50,000.

EG&G claims the 506 to be capable of off-line isotopic measurements of low-level alpha activity at near-drinking water levels; the main drawback of this method is the need for disposal of secondary mixed waste (spent liquid scintillator cocktail).

5.) Canberra/Packard – Flow Cell Scintillation System

Canberra/Packard Inc. is selling a flow cell scintillation analysis system that uses a liquid scintillator to analyze samples of water. It involves a technology similar to the PERALS; Canberra claims a sensitivity of 30 pCi/l (uranium drinking water limit). Canberra claims that only one part of liquid scintillator is needed for each part of sample (1:2), which is much less than the 2:1 or 3:1 ratios needed by competitors' systems. The Flow Cell Scintillation System costs $20,000 to $35,000.

Canberra claims the Flow Scintillation System to be capable of off-line isotopic measurements of low-level alpha activity at drinking water levels; the main drawback of this method is the need for disposal of secondary mixed waste (spent liquid scintillator cocktail).

6.) Fernald Field Test of Two Analytical Systems

Although not capable of detecting levels of regulatory interest of short-lived radionuclides (short-lived relative to ^{238}U) such as plutonium, analytical systems are commercially available that claim three-minute response time at 5 ppb natural uranium levels. They would not be useful for sites with plutonium contamination, as the NRC water limit for ^{239}U is 3.2×10^{-4} ppb, significantly under these analytical method limits of 5 ppb. These systems include at least one based on absorptive stripping voltammetry. As site characterization has apparently revealed nonenriched (natural) uranium to be the primary contaminant of interest,

it may be appropriate for Fernald to utilize such nonradiochemical instruments for off-line analyses.

Rapid off-line detection of low-level heavy metals at drinking water levels is claimed for these two analytical systems; they would not be capable of detecting short-lived alpha-emitting radionuclides such as plutonium nor would they be capable of discriminating between naturally-occurring uranium samples and those enriched in or depleted of ^{235}U.

2.2.3 Devices Under Development

Alpha-monitoring instrumentation that is not yet commercially available has been divided into two categories: on-line devices and off-line devices.

On-line Devices Under Development

This section examines on-line alpha-monitoring instruments that are not yet commercial. Included are:

1) Los Alamos' LRAD for Radioactive Liquid Waste,
2) Westinghouse Savannah River's patented fiber optic Sol-Gel Indicator (SGI) technology, and
3) SCUREF's Flow-Cell Scintillation Counting.

1.) Los Alamos – LRAD for Radioactive Liquid Waste

Los Alamos National Laboratory (LANL) has a project titled, "A Real Time Alpha-Monitoring System for Radioactive Liquid Waste." The technology is analogous to what is used in Eberline's commercial LRAD (Long-range Alpha Detector) Object Monitor. The unit detects the airborne ionization produced by the surface layer (40 micrometers) of liquid sample. Claimed liquid sample detection limit for the monitor is 100 pCi/l, but no response time is given. A field test was conducted in 1994 at the LANL Radioactive Liquid Waste Treatment Facility (RLWTF). With the RLWTF's reported influent activity level of tens of nano-Curies (equivalent to 15 ppm natural Uranium), the unit produced a measurable signal. No contemporaneous sample data was reported for this field test. LANL's recent efforts have resulted in a larger, one square meter unit that may have improved detection limits.

LANL's Real Time Alpha Monitoring System for Radioactive Liquid Waste technology will not permit detection of alpha radioactivity at drinking water levels. For samples that have sufficiently high levels of gross alpha activity, no elemental or isotopic identification of individual species is possible with this technology.

2.) Savannah River – Sol-Gel Indicator Fiber Optic Analytical Method

In 1995, Westinghouse Savannah River patented a Sol-Gel Indicator (SGI) fiber optic technology that has been incorporated into an analytical measuring system. Sol-Gel indicators were reported being incorporated into flow injection analysis cells, eliminating one reagent stream from the system. Arsenazo III was used as the indicator that allowed detection of the uranyl ion. SGI uranyl sensor response time is reported as approximately five minutes; the detection limit is stated as 1 ppm. A treatment for reversal of the uranyl sensor was developed, which allows it to be reused; the SGI coating is claimed to be viable for at least six months; no mention was made of performance degradation during that six-month coating lifetime. Savannah River indicates a need for additional refinement of the coating process to improve fabrication reproducibility. One CRADA has been completed, two CRADAs have been signed with industrial partners and the technology has been licensed by four companies. DOE-EM CMST-CP has funded some of this development effort.

This method has demonstrated in the laboratory the capability of detecting elemental uranium at 50X drinking water levels. This method would not be capable of detecting short-lived alpha-emitting radionuclides such as plutonium, nor would it be capable of discriminating between naturally-occurring uranium samples and those enriched in ^{235}U.

3.) SCUREF – Flow-Cell Scintillation Counting

The South Carolina University Research and Education Foundation (SCUREF) has a 1995 DOE-FETC ROA contract titled, "Measurement of Radionuclides Using Ion Chromatography and Flow-Cell Scintillation Counting." The project's objective is to reach on-line counting of aqueous and nonaqueous samples at minimum detectable concentrations (MDCs) that are low enough for environmental screening; off-line counting would produce MDCs that approach typical regulatory limits. No data has been reported to date on achieving these MDCs; radiochemistry work has focused on developing hardware and evaluating scintillation detector materials.

While the objective of the technology is to permit off-line detection of alpha radioactivity at drinking water levels, no supporting data has been produced to date.

Off-line Devices Under Development

This section examines off-line alpha-monitoring instruments that are not yet commercial, including:

1.) Lawrence Livermore's Fiber Optic Analytical Methods,
2.) Los Alamos' Fiber Optic Analytical Methods, and
4) The University of South Carolina's research titled, "Development of a Fiber-Optic Uranium Sensor Employing Fluorescence Quenching and a Second-Order Photo-oxidation Effect."

1.) Lawrence Livermore – Fiber Optic Analytical Method

In 1994, Lawrence Livermore National Laboratory was developing an analytical method for analyzing heavy metals using a coated fiber optic probe. Sensitivity to 1 ppm uranium was demonstrated. Due to the limited sensitivity of the method, DOE funding was eliminated.

This method has demonstrated the capability of detecting elemental uranium at 10,000X drinking water levels; no further development is ongoing at Lawrence Livermore. This method would not be capable of detecting short-lived alpha-emitting radionuclides such as plutonium, nor would it be capable of discriminating between naturally-occurring uranium samples and those enriched in ^{235}U.

2.) Los Alamos – Fiber Optic Analytical Method

In 1994, Los Alamos National Laboratory was developing an analytical method for analyzing heavy metals using a coated fiber optic probe. Sensitivity to ppm levels of uranium was demonstrated. Status of this program is unknown.

This method has demonstrated the capability of detecting elemental uranium at 10,000X drinking water levels; its development status is uncertain. This method would not be capable of detecting short-lived alpha-emitting radionuclides such as plutonium, nor would it be capable of discriminating between naturally-occurring uranium samples and those enriched in ^{235}U.

3.) University of South Carolina – Fiber Optic Analytical Method

The University of South Carolina reported at the Environmental Technical Sessions of PITTCON '96 on research titled, "Development of a Fiber-Optic Uranium Sensor Employing Fluorescence Quenching and a Second-Order Photo-oxidation Effect." No further information is available at this time, but it is likely that this method will have a similar detection limit of approximately 1 ppm.

It is not known what the elemental uranium detection capability is for this method. This method would not be capable of detecting short-lived alpha-emitting radionuclides such as plutonium, nor would it be capable of discriminating between naturally-occurring uranium samples and those enriched in ^{235}U.

2.3 THERMO ALPHA MONITOR CONCEPT

The Thermo Water Alpha Monitor is currently being developed by Thermo Power Corporation, Advanced Technologies Group. The technology involves automated, on-line, near real-time, isotopically-resolved alpha monitoring of liquids, employing the collection of radionuclides on a film substrate followed by alpha spectroscopy using a large area solid-state diode detector. The collection film may be archived for record keeping or additional analyses. Air monitoring is also possible using this technology.

The instrument has been shown to be isotopically sensitive to extremely low (ten parts per trillion, or 15 femto Curies per liter; 1/2,000th of the EPA's drinking water limit of 20 ppb total uranium) levels of a broad range of radioisotopes. Other performance data obtained during the course of this investigation have shown that on-line real-time operation is possible with a sub 15-minute response time analyzing 20 ppb (30 pCi/l) natural uranium.

The Thermo Water Alpha Monitor will provide dramatic total cost savings compared with present technology. The most dramatic savings will be through the elimination of individual sample handling and processing, the largest contributor to present monitoring costs. Additional savings will be realized through much lower cost per analysis using this technology. In a first release product, the new instrument is expected to reduce the cost per analysis by a factor of two to a factor of three, relative to analytical laboratory charges (see Appendix 1). The estimated annual savings to DOE by adopting the new monitor are at minimum (averaged over the life of the instruments, including amortization of the projected $25,000 unit capital cost):

- $36 million per year savings, 50% Thermo Water Alpha Monitor use.
- $72 million per year savings, 100% Thermo Water Alpha Monitor use.

Table 2 summarizes the salient features of the Thermo Water Alpha Monitor and performs a comparison with the monitors detailed in the previous section. A review of the table reveals that not only is the new instrument the only on-line monitor capable of analyzing drinking water levels of uranium, but its expected capital cost is less than the $39,400 average cost of all commercial monitors surveyed. In other words, not only is the Thermo Water Alpha Monitor the sole on-line instrument that meets DOE's performance requirements, but it is less expensive than the average cost for other systems.

TABLE 2

CURRENT MONITOR SUMMARY

Device/Method	Commercial?	On-Line?	Drinking Water U?	Capital Cost?	Other
Thermo Alpha Monitor	N	Y	Y	$25,000	1 ppT limit, isotopic U, 10 ppb: 15' cycle time
EG&G Ortec's LB/BAI9126	Y	Y	N	$75,000	3300 # system weight
Eberline Instruments' OLAM	Y	Y	N	$35,000	Obsolete product
Canberra Industries Inc.'s Water Monitoring Systems	Y	Y	N	$80,000	Gammas, not alphas
Conventional Radiochemical Laboratory Analysis	Y	N	Y	$6,000	Not automatic
ORDELA, Inc.'s PERALS Spectrometer	Y	N	Y	$21,250	Produces mixed waste
Quantrad Systems' Liquid Analyzer System	Y	N	N	$12,995	Not automatic
EG&G Ortech's LB 506 AT (Specially Modified)	Y	N	Y	$50,000	Produces mixed waste
Canberra/Packard Inc.'s Flow Scintillator System	Y	N	Y	$35,000	Produces mixed waste
Two Analytical (Nonalpha-Detecting) Systems To Be Evaluated at the DOE Fernald (Ohio) Site	Y	N	Y	Unknown	Can't monitor Pu or ^{235}U
Los Alamos' LRAD for Radioactive Liquid Waste	N	Y	N	N/A	Gross alpha only
Westinghouse Savannah River's Fiber Optic Sol-Gel Indicator (SGI) Technology	N	Y	N	N/A	1 ppm detection limit
SCUREF'S Flow-Cell Scintillation Counting	N	Y	N	N/A	No data yet
Lawrence Livermore's Fiber Optic Analytical Methods	N	N	N	N/A	1 ppm detection limit
Los Alamos' Fiber Optic Analytical Methods	N	N	N	N/A	1 ppm detection limit
University of South Carolina's Fiber-Optic Uranium Sensor	N	N	N	N/A	1 ppm detection limit

The Thermo Water Alpha Monitor uses a semiconductor counter, which is a form of solid-state detector. 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 (see Figure 3). The energy lost by ionizing radiation, such as alpha particles, in semiconductor detectors results in the formation of ions (electron-hole pairs).

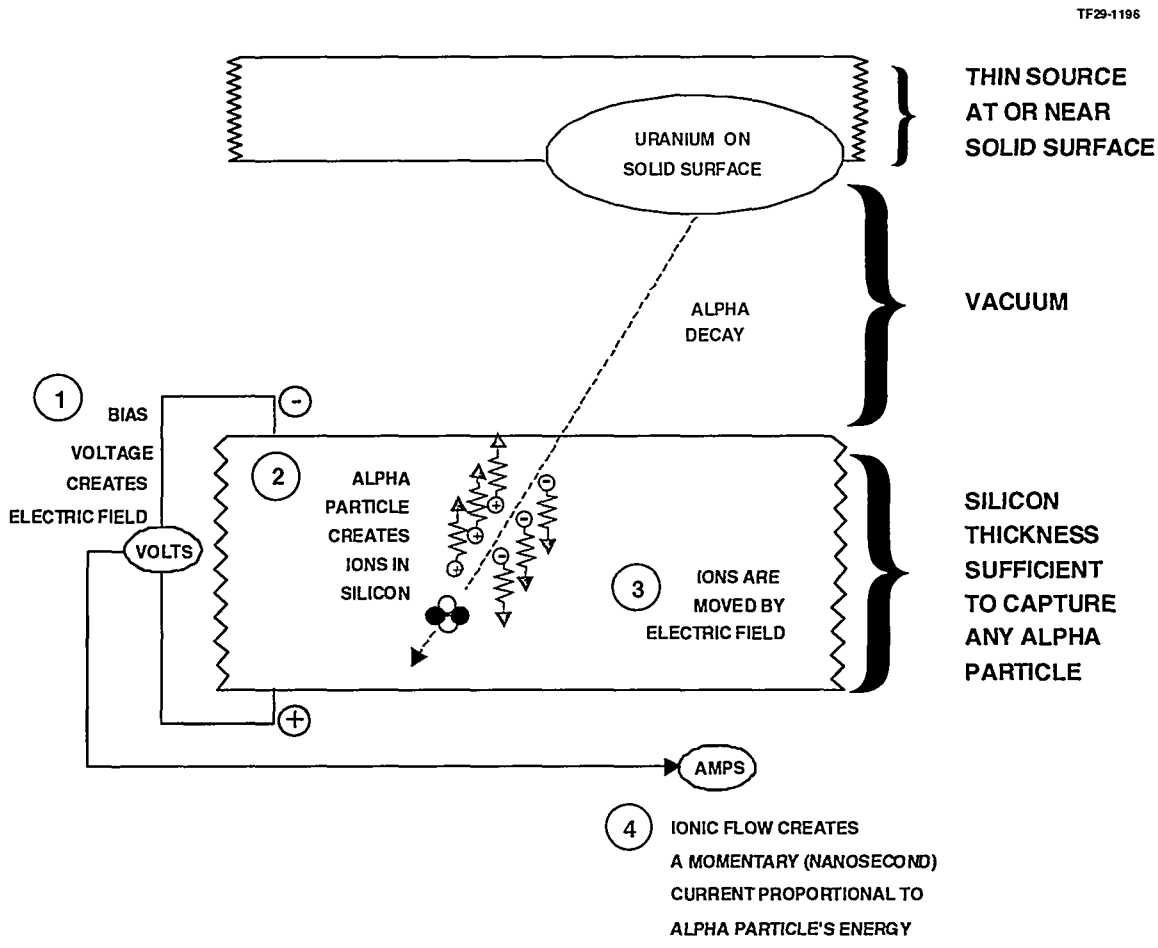

Figure 3. Silicon Diode Measurement Concept

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.

The average energy loss per ion pair for alpha particles in silicon is about 3 eV, compared with about 30 eV per ion pair for gases. Hence, an alpha particle creates about 10X as many ion pairs in the semiconductor solid as in gas, and the statistics are thus about 3X better than for gas ionization detectors. In addition, the smaller distances involved in collection allow for higher electric fields and faster collection times.

Surface barrier, diffused junction, and ion-implanted are the three predominant types of alpha counters, with extremely thin "windows" on the surface (typically equivalent to an 800 Å silicon thickness). The combination of a very thin window and short range in silicon (30 micrometers for 6 MeV alpha) results in 100% absorption of the alpha energy in the depletion region of the detector, with formation and collection of electron-hole pairs linearly proportional to the alpha energy, providing high energy resolution. Characteristics of the silicon detector for alpha particles are:

- High energy resolution, typically 15 keV FWHM for 5 MeV alphas.
- Fast pulse rise time of 5 to 10 nanoseconds.
- No apparent dead time.
- Linearity of charge collected with particle energy.
- Detection efficiency for alphas entering surface.
- 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, typically 40 micrometers for 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 itself is negligible. The planchet is then placed in front of the silicon detector and a vacuum pulled to prevent absorption of alpha energy by the air between the source and detector. Where the source/detector spacing is small and the source is smaller than the detector, 50% of the emitted alphas enter the silicon detector surface and are counted (detector efficiency). Higher energy resolution is possible using a greater source/detector spacing, although at a lower detector efficiency.[2]

Under the current DOE contract, Thermo Power has demonstrated in the laboratory a new modality which permits extremely sensitive analysis of alpha-emitters in water and provides high resolution alpha spectrometry so that individual radionuclides can be assayed simultaneously, based on their different alpha energies. This new instrument provides the basis for an on-line, real-time monitor of alpha-emitting radionuclides in water streams for both effluent streams leaving DOE sites and process streams. It is the objective of the Optional Phase II of the current program to convert the laboratory instrument into an automated, on-line, real-time instrument for alpha-emitters in water streams and to conduct field testing and demonstrations of the prototype for monitoring of uranium and other alpha-emitters. This new on-line, real-time alpha instrument for liquids will satisfy important DOE needs, as described in a preceding section.

To analyze a sample, the proprietary film is installed into the waterproof chamber (see Figure 4). The sample then passes through the film, allowing quantitative uptake of the radioactive species of interest. The alpha-emitters are captured at or near the surface of active film, forming a thin source that provides excellent alpha energy resolution during the counting step.

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[2] Increased source/detector spacing results in a more collimated path for alpha particles reaching the detector, and produces a reduced average transit through the inert window of the detector. This results in a lower average attenuation of the incoming alphas, thereby reducing the average peak width.

A small amount of de-ionized (DI) water is used for rinsing the exposed film in the waterproof chamber; subsequently, any residual liquid is withdrawn from the waterproof chamber. The captured radionuclides are adherent and are not removed from the film by a water wash. Next, the film is transferred from the waterproof chamber to a second chamber where it is prepared for the counting step. At a minimum, this preparation consists of rapid drying using one or more of the following: microwave energy, hot air, vacuum, and infrared heating.

The dry film is routed to the detector chamber for counting the radioactive decay of the species on the film's surface. The counter incorporates a solid-state, silicon-based, reverse-biased, p-i-n diode. 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; special software is used for data acquisition, analysis, and report generation (see Chapter 2.6.2). In Figures 5 and 6, results of counts for a uranium-containing solution (20 ppb of uranium) and for a residential deep well water sample are presented, indicating the excellent alpha energy resolution and the applicability to a wide range of alpha-emitting radionuclides.

After the analysis is completed and before a new sample is counted, the film is removed from the counting chamber and archived in an appropriate plastic bag. The total sample cycle is completed in under 30 minutes, which is well under the program's stated goal of a 1- to 12-hour sample cycle time.

In Figure 7, a schematic is presented for conversion of the laboratory counter to an automated, on-line, real-time alpha monitor for water streams. Water from the sample stream is pumped continuously through the instrument's sample chamber and discharged back to the stream. To provide rapid response, a large film (53.5 cm^2) and large area detector (50 cm^2) are used. Calibration, cleaning, and de-ionized rinse water are also provided and can be pumped in sequence through the instrument for calibration and cleaning between runs. Sample preparation is restricted to filtering of the sample stream, where necessary, and to pH control for optimum operation.

The field-deployed Thermo Alpha Monitor for Water is envisioned to consist of the following primary components:

- Archivable film, which quantitatively recovers the nuclides of interest from the sample of interest.
- One large area silicon detector, complete with power supply and low-noise signal preamplifier.
- One multichannel analyzer card.
- One IBM-compatible personal computer.
- Control and sequencing software complete with Remote Monitoring and Control System (RMCS) software.
- Ancillary equipment (chambers for sampling and counting, sample pumps, calibration and instrument cleaning solutions, controls, valves, automatic film handling equipment, etc.).

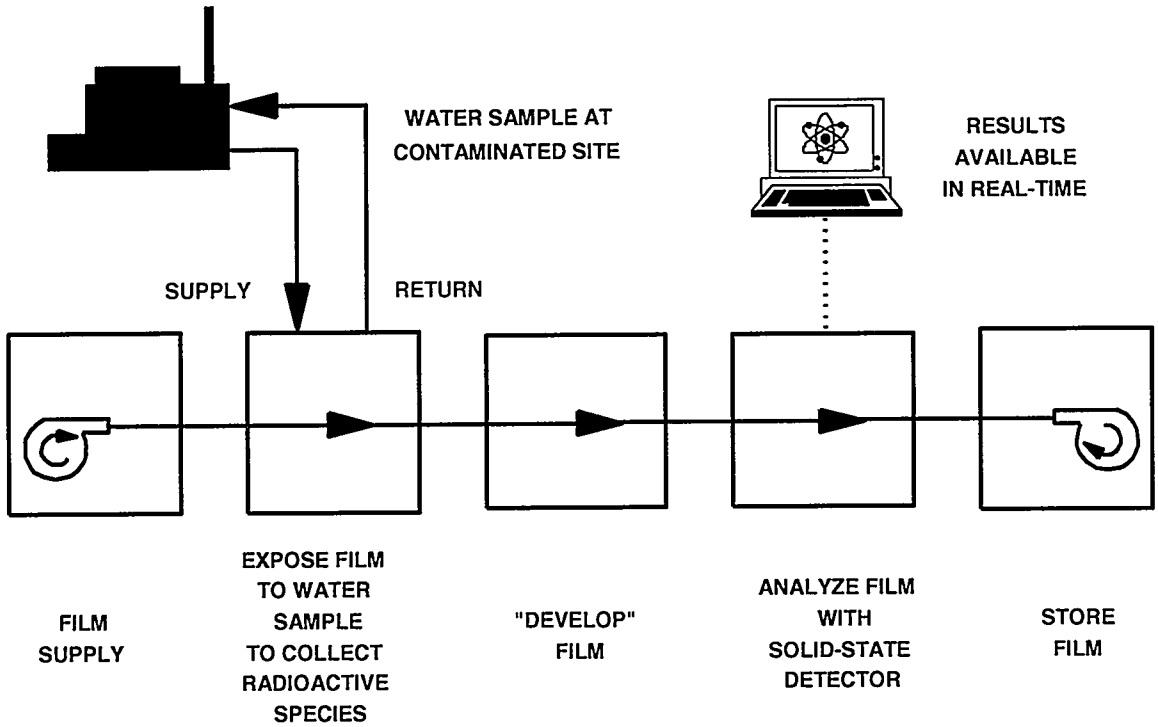

Figure 4. Thermo Alpha Monitor (TAM)

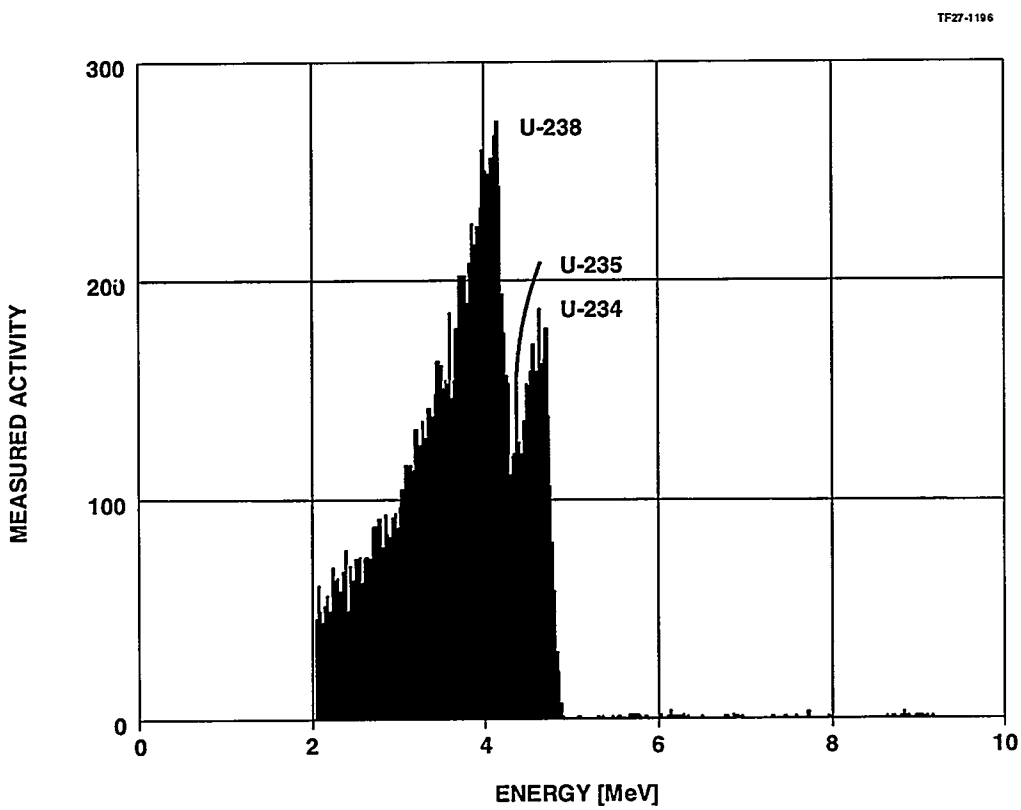

Figure 5. Laboratory Test Results – 20 Parts Per Billion Natural Uranium

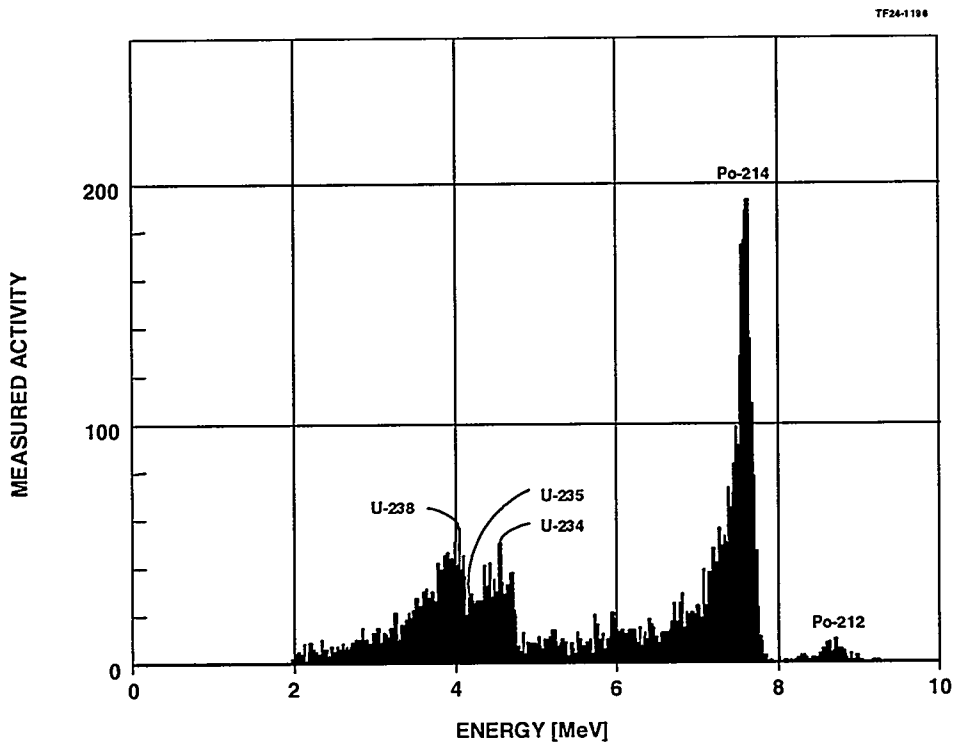

Figure 6. TAM Laboratory Test Results, Massachusetts Groundwater, 2 ppb (1.5 pCi/l) Total Uranium

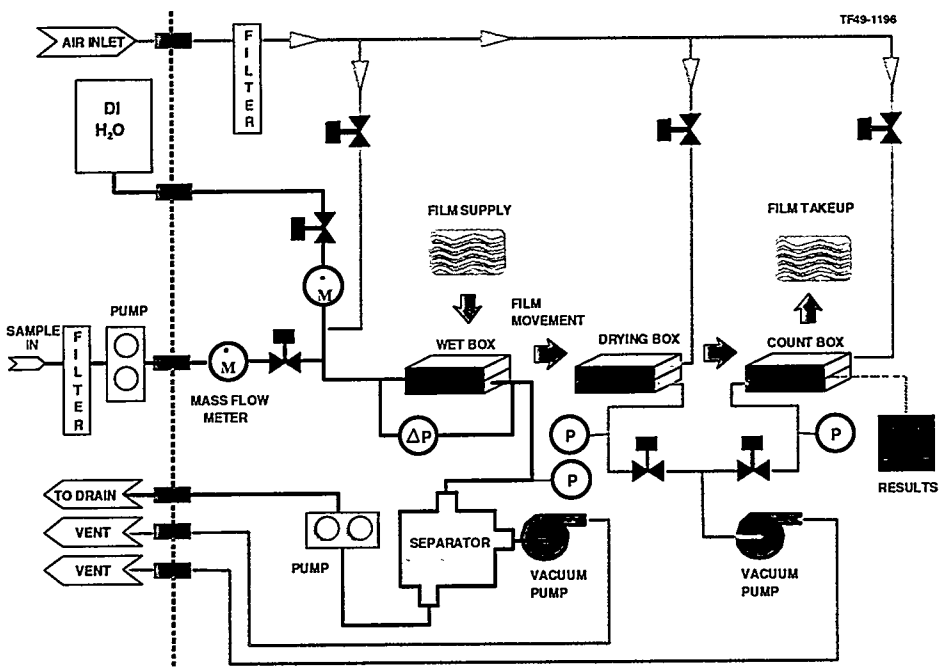

Figure 7. Thermo Alpha Monitor Schematic

During normal operation, a representative portion of the stream of interest will be pumped through a single film sample for on-line analysis, then returned to the main portion of the stream. After the sampling period, the film will be dried and then counted by the detector in order to complete the on-line analysis cycle. The instrument cycle will be designed so that the time to complete the drying and counting portion of the analysis is less than or equal to the required sampling time. This methodology will allow for uninterrupted on-line analysis, with a fresh film ready for sampling every 30 minutes.

Periodic automatic calibration, blank checks (to verify instrument cleanliness), and long background counts will be programmed according to the pertinent data quality objectives. This feature is included in order to verify off-line that the detector is still in calibration and that very low background levels exist. Should unacceptable background levels exist in the instrument, i.e., due to a significant change in the chemical makeup of the sample stream, 5% nitric acid will be available for removal of the offending radionuclide(s).

The laboratory measurements, discussed in upcoming Section 2.5, provide a firm base for predicting the field instrument response to varying uranium concentrations. The instrument will provide quantitative measurement over a very wide range of uranium in water concentrations, 10 ppT (15 femto Curies per liter) to over 10 ppm (15,000 pCi/l). Laboratory testing has verified the linear response of the instrument with uranium concentrations over the range of 10 ppT to 10 ppm. This linear response to concentration is expected on the basis of the physical phenomena taking place, and there is no reason to expect deviation at either lower or higher uranium concentrations.

The response time of the field instrument is directly related to the uranium concentration in the aqueous stream being monitored. The instrument typically will automatically total the ^{238}U, ^{235}U, and ^{234}U peaks and measure the time required to reach 10 (for approximately $\pm 40\%$ statistical accuracy) to 100 net counts (for approximately $\pm$ 15% statistical accuracy). For 1 ppb uranium, the instrument cycle time will be approximately 30 minutes. For 10 ppm U, it can be as short as approximately five minutes. An unexpected excursion from ppb to ppm levels will be detected very rapidly. For each count time to reach TC net counts, the average U concentration over the count time is given by the following relation:

$$X = \frac{0.8216\ (TC)}{(V)\ (T)}$$

where:

X = average ppb uranium concentration over the sampling period.
V = total volume sampled during the sample cycle, liters.
T = count time, minutes.
TC = total cumulative net counts in time T due to $^{238}U - ^{235}U - ^{234}U$.

This relation is based on the following factors:

(1) Detector active area of 50 cm^2, film active area of 53.5 cm^2, detector-film spacing of 0.52 cm, giving a geometrical counting efficiency of 42.13%.

(2) Quantitative extraction of U by the film, which is based on experimental data obtained between 10 ppT and 10 ppm.

(3) The 2.7:1 activity ratio of ^{234}U:^{238}U accepted by the EPA for natural uranium in drinking water, or a specific activity of 1.3 pCi/îg natural uranium.

The factor 0.8216 is the conversion factor obtained by converting counts per minute per liter to parts per billion:

$$\frac{0.450 \text{ pCi / dpm}}{0.4213 \frac{\text{cpm}}{\text{dpm}} \text{ x } 1.3 \text{ pCi / } \mu\text{g x } 1000 \text{ g / l}} = 0.8216 \text{ ppb} - \text{min} - 1 / \text{count}$$

Taking TC to be 100 counts, the count time corresponding to different uranium concentrations is given in Table 3. The instrument will respond to, and quantitatively monitor, a very wide range of uranium concentrations. At 1 ppb, the instrument's overall response time is 30 minutes. Should the level increase to 20 ppb U, the increased level could be identified in 10 minutes. Should an increase to 600 ppb U occur, only five minutes will be required to verify the increased concentration. A very large excursion of 4,000 ppb will also be verified in five minutes. The 1 ppb overall response time is reduced by 31% to 21 minutes, by use of 10 counts instead of 100. Analyses can occur below 1 ppb by allowing larger sample volumes to pass through the film and/or allowing additional counting time to transpire. The cycle time can be reduced by over three minutes by using microwave-assisted drying.

TABLE 3

INSTRUMENT CYCLE TIME VS. U CONCENTRATION

Average U Concentration Over the Sampling Time (ppb)	Volume Sampled (liters)	Required Sampling Time (Minutes)	Drying Time* (Minutes)	Count Time for TC = 100 Counts (Minutes)	Total Analysis Time (Minutes)
1	8	16	4	10.3	30.3
5	4	8	4	4.1	16.1
20	2	4	4	2.1	10.1
600	0.5	1	4	0.27	5.3
4,000	0.5	1	4	0.04	5.0

* Microwave-assisted drying has reduced this to 30-60 seconds.

In summary, the field instrument will operate on-line and provide a continuous measure of the uranium concentration in the effluent stream. For subdrinking water uranium levels near 1 ppb, a 20- to 30-minute instrument cycle time is required to reach 10 to 100 net counts (for statistical accuracy of approximately ± 40% or ± 15%). If an excursion to higher uranium concentrations occurs, the count time (and subsequent sampling times) will be reduced, with very short response times to 600 ppb excursions. It will not miss any such excursions. The instrument will also give the relative amount of ^{238}U, ^{235}U, and ^{234}U isotopes separately, if desired. The data will be available immediately to the site workers. If desired, alarms and/or diversion of the stream to a holding area can be effected for excursions above a preset limit. The instrument is expected to readily monitor other alpha-emitting radionuclides, such as ^{239}Pu and ^{241}Am, and process streams. The instrument operation is completely automatic, with only periodic replenishment of the film, calibration, cleaning, and rinsing liquids required, probably on a weekly basis. Operation will be very cost-effective.

2.4 DESCRIPTION OF INSTRUMENT

The laboratory tests provide a firm base for the field demonstration. Earlier tests used proprietary film samples that were only 1 cm^2 (0.16 in^2) in area. Figure 8 compares the size of two films that were used in later stages of laboratory testing. The smaller of these specimens has a usable area of 13.4 cm^2 (2.07 in^2), the larger film has a usable area of 53.5 cm^2 (8.29 in^2). This represents an increase in film area by a factor of 53.5, well in excess of the program's stated goal of a 10X increase in activation.

These films are designed to capture the alpha-emitting radionuclides of interest. They can be factory-tailored to capture either a broad or narrow range of chemical species of interest. Through modern mass-production techniques, all specialized film preparation chemistry can be performed at a central manufacturing plant prior to shipping the QA/QC-approved film to the Thermo Water Alpha Monitor for testing.

Normally, the analysis is performed with a sample volume between 100 cm^3 and 8,000 cm^3, depending on the sample's activity and the desired counting time. (Sample volumes as great as 42 liters have been successfully used to date.) The sample is passed through the film (Figure 8) as it is held in a waterproof chamber (Figure 9). The waterproof chamber and associated plumbing apparatus (Figure 10) are designed to withstand most acidic and basic solutions, allowing for a variety of sample preparations as well as occasional acid cleaning. In addition, appropriate materials and types of construction were selected to minimize carryover of radioactive species between analyses.

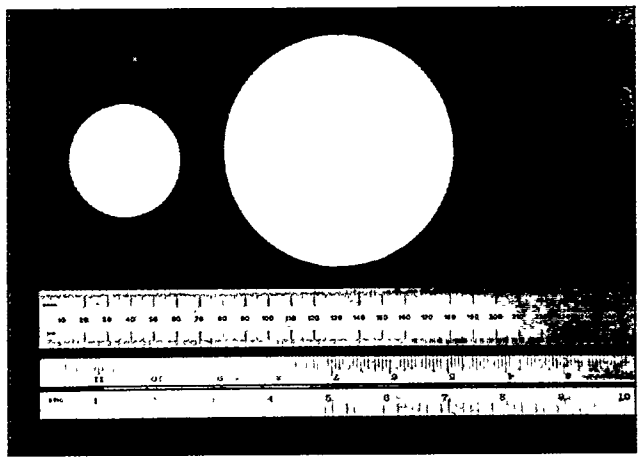

Figure 8. Sizes of Two TAM Films

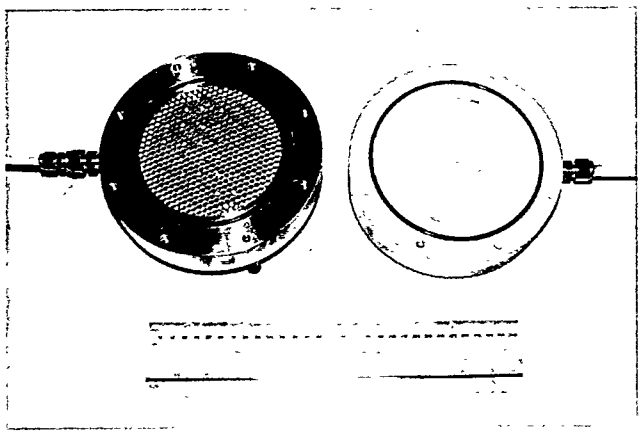

Figure 9. TAM Waterproof Chamber

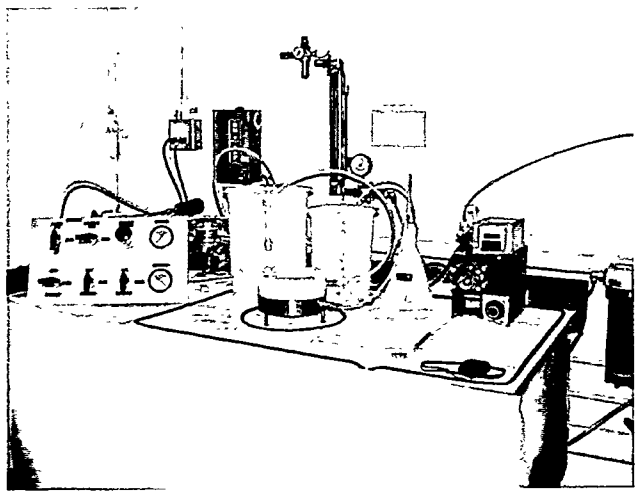

Figure 10. TAM Waterproof Chamber in Laboratory

To analyze a sample, the proprietary film is installed into the waterproof chamber (see Figure 11). The sample is passed through the film, allowing quantitative uptake of the radioactive species of interest. Quantitative extraction is provided by the high mass transfer flux of rad to the large active surface area provided by the microporous film (average equivalent particle size is less than 10 î). The alpha-emitters are absorbed at or near the surface of active film, forming a thin source that will provide excellent alpha energy resolution during the counting step. De-ionized (DI) water is then used for rinsing the waterproof chamber assembly and film between analyses. The DI water serves to minimize carryover of radioactive material between analyses, as well as remove all transferable surface radioactivity from the film. The absorbed radionuclides are adherent and are not removed by a water wash. Finally, any residual liquid is withdrawn from the waterproof chamber. The complete sampling cycle takes approximately 16 minutes to complete for an 8,000 cc sample.

Next, the film is transferred from the waterproof chamber to a chamber where it is prepared for the counting step. At a minimum, this preparation consists of rapid drying using one or more of the following: microwaves, hot air, vacuum, and infrared heating. Appropriate instrumentation (i.e., thermocouples or thermistors) are used to monitor the film for dryness. The complete preparation cycle takes approximately four minutes to complete[3].

Subsequently, the film is routed to the detector chamber for counting the radioactive decay of the species on the film's surface. The detector subsystem used in this work is illustrated in Figure 12. The counter incorporates a solid-state, silicon-based, reverse-biased, p-i-n diode. Figure 12 shows the large surface area of the laboratory detector, as well as the enclosure that is used to produce a light-tight assembly. 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 (see Figure 13); special software is used for data acquisition, analysis, and report generation (see Chapter 2.6.2). The complete counting cycle takes approximately six minutes for a high-accuracy film analysis of 8,000 cc of 20 ppb natural uranium.

After the analysis is completed and before a new sample is counted, the film is removed from the counting chamber and archived in an appropriate plastic bag. The total sample cycle is completed in under 30 minutes, which is well under the program's stated goal of a 1- to 12-hour sample cycle time.

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[3] Microwave-assisted drying has reduced this time to 30 to 60 seconds.

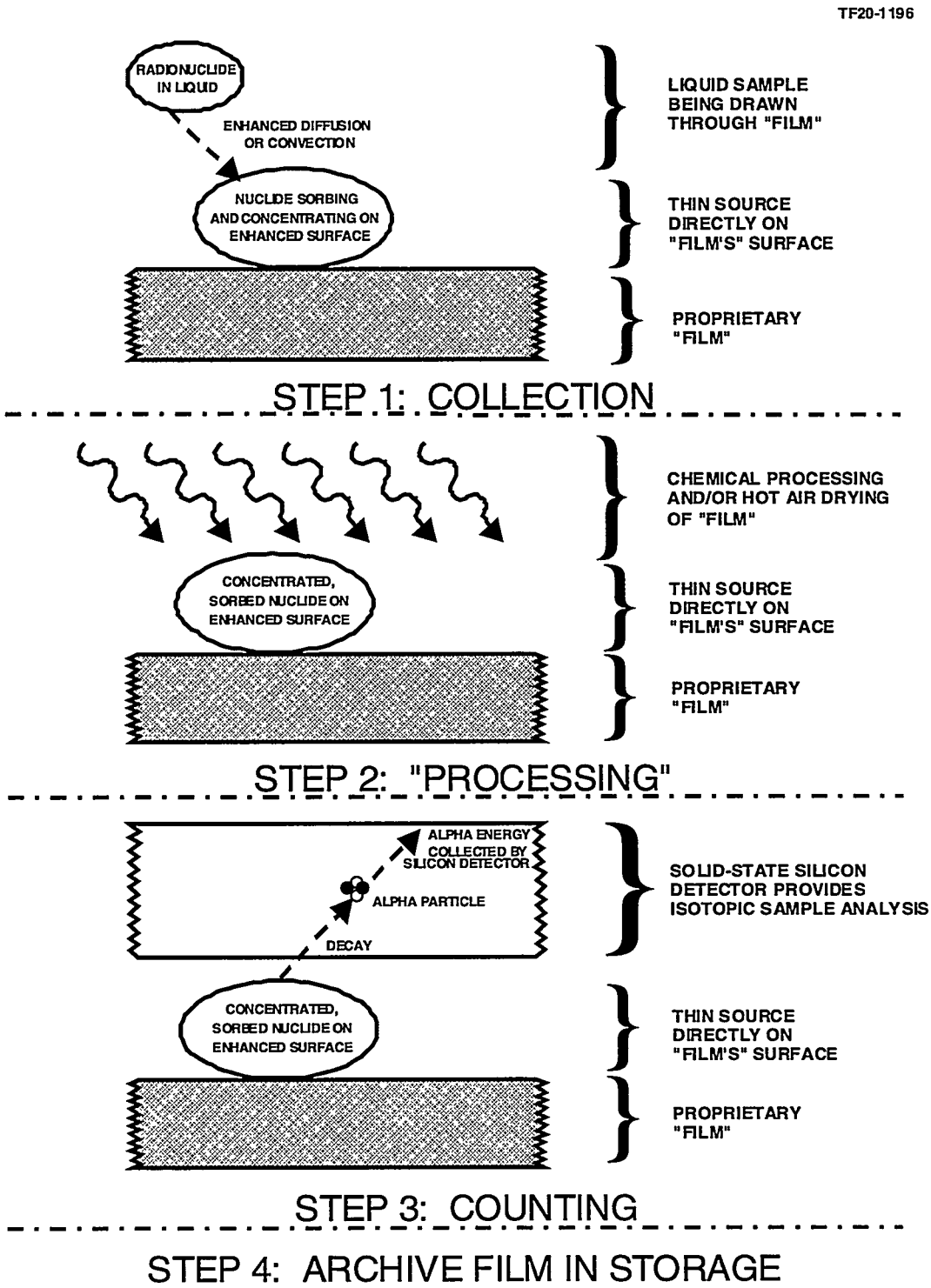

Figure 11. Basic Principle of Operation

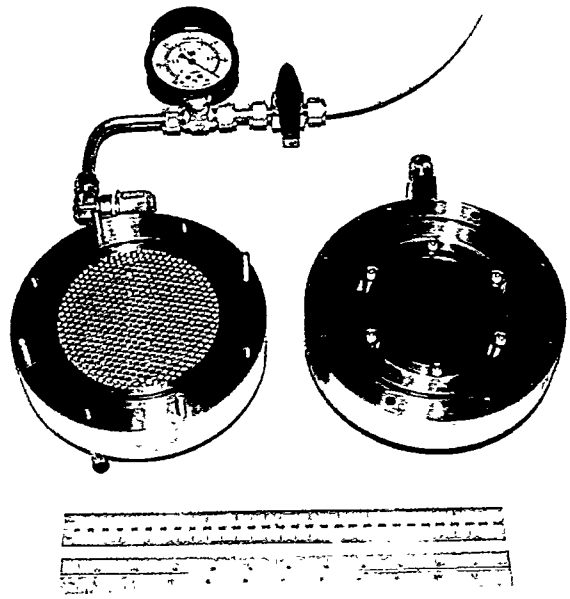

Figure 12. TAM Detector Chamber

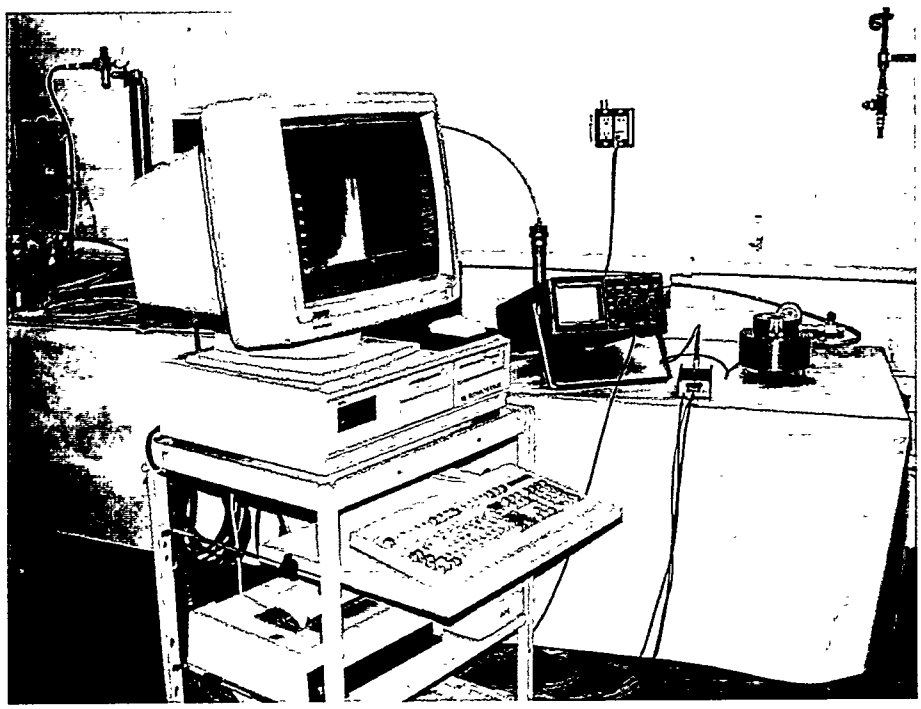

Figure 13. TAM Detector Chamber in Laboratory

2.5 LABORATORY RESULTS

2.5.1 Benchmark of Instrument Response Time

A benchmark was made of the current laboratory unit's response time analyzing eight liters of a calibration solution of natural uranium at the proposed EPA drinking water limit of 20 ppb (30 pCi/l) (see Table 4). As currently configured, 16 minutes were required to sample the test solution with a 53.5 cm^2 film; preparation of the film for analysis took four minutes, and performing accurate[4] isotopic analysis of the resultant film took six minutes, for a total of 26 minutes. In other words, the program's major goal of a sample turnaround time of 1- to 12-hours at an alpha activity level of 30 pCi/l has been successfully demonstrated.

TABLE 4

RESPONSE TIME BENCHMARK

Analysis Step	Time
Sample test solution	16 minutes
Prepare film for analysis	4 minutes
Perform isotopic analysis	6 minutes
TOTAL	26 minutes

2.5.2 Analysis of Uranium Nitrate Solutions

A commercially available, uranium atomic absorption (AA) standard solution was used to prepare 10 ppT to 10 ppm uranium solutions for testing the detector response to aqueous uranium solutions. Uranium standard solutions are prepared from purified natural uranium ore. Due to the long half-life of ^{238}U compared to ^{234}U, their relative half-lives, and their natural abundance, the activity of ^{234}U in the standard solution should be equal to the ^{238}U activity, and 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 in ore and relative activities of the three isotopes is summarized below:

Isotope	Half Life (yr)	Natural Abundance (wt %)	Alpha Activity (Relative to ^{238}U)
^{238}U	4.51×10^9	99.283	1.00
^{235}U	7.10×10^8	0.711	0.0461
^{234}U	2.47×10^5	0.0054	1.00

[4] Instead of counting to reach 100 total counts, counting until a peak height of 10 was reached.

Thus, the expected primary activities from the natural uranium standard solutions are from ^{238}U and ^{234}U, with the following alpha energies:

^{238}U	23% 77%	4.15 Mev 4.20 Mev
^{234}U	28% 72%	4.72 Mev 4.77 Mev

These tests were performed by passing a neutralized sample of the water through a 53.5 cm^2 film, drying the film, and then counting the film. The results of the count are presented in Figure 14. The ^{238}U and ^{234}U peaks are clearly evident near 4.20 and 4.77 Mev, indicating that the uranium is adhering to the surface of the film. ^{235}U is apparent in this spectrum between the ^{238}U and ^{234}U peaks.

The activities are also about the same for the two main uranium isotopes. Manual subtraction of background and deconvolution of the three overlapping curves was completed in order to quantify the isotope ratio of the sample. Results of this analysis indicate that the ^{238}U peak had 58%, the ^{234}U peak had 40%, and the ^{235}U peak had 2% of the net alpha activity – a ^{238}U:^{234}U:^{235}U isotope ratio of 1.0:0.69:0.034. These data either indicate that the sample is slightly depleted uranium or that the measured activity ratio is slightly in error.

These results for a sample of "natural" uranium clearly demonstrate the capability of the system to respond to low levels of uranium, to identify specific isotopes with the high energy resolution of the film and silicon detector, and to provide quantification of the sample's ^{235}U enrichment level (or depletion, as in this case).

2.5.3 Analysis of Fernald Site Groundwater

An acid-preserved sample of contaminated groundwater from the DOE Fernald (Ohio) site assayed at 600 ppb total uranium (the DOE free-release limit) was obtained for testing. Again, if the contamination was caused by purified natural uranium, due to the long half-life of ^{238}U and ^{234}U, their relative half-lives, and their natural abundance, the activity of ^{234}U should be equal to the ^{238}U activity and 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. These tests were performed by passing a neutralized sample of the water through a 13.4 cm^2 film, drying the film, and then counting the film. The results of the count are presented in Figure 15. The ^{238}U and ^{234}U peaks are clearly evident near 4.20 and 4.77 Mev, indicating that the uranium is adhering to the surface of the film. Negligible ^{235}U is apparent in this spectrum.

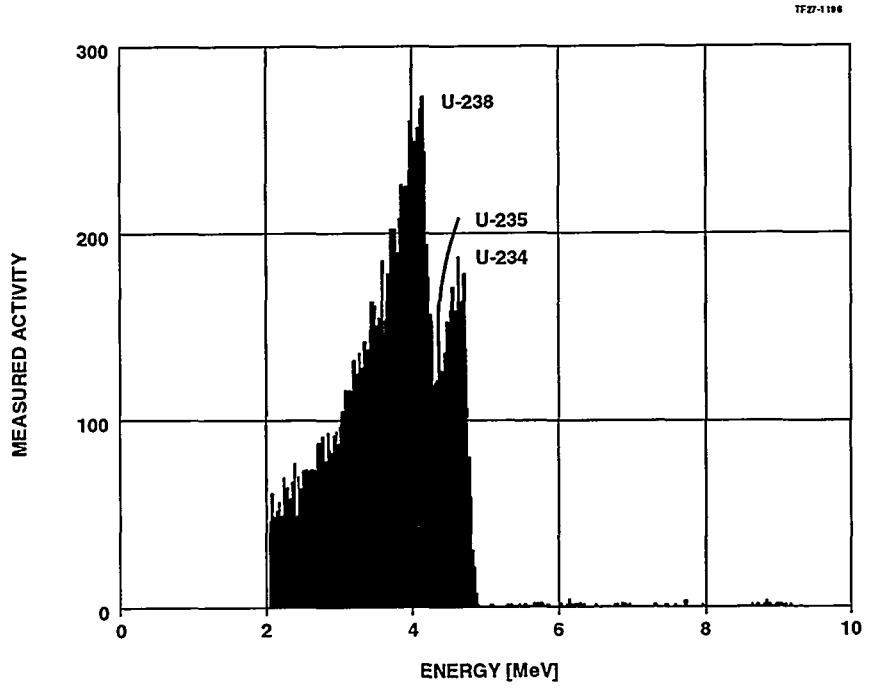

Figure 14. Laboratory Test Results – 20 Parts Per Billion Natural Uranium

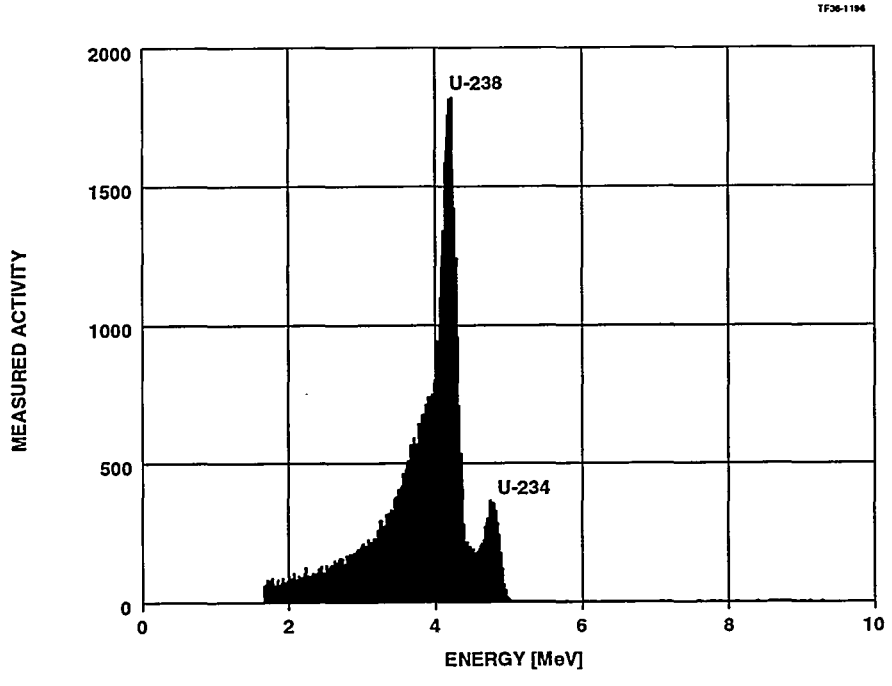

Figure 15. Laboratory Test Results, Fernald Groundwater

The activities are clearly not the same for the two main uranium isotopes. Manual subtraction of background and deconvolution of the overlapping curves was completed in order to quantify the isotope ratio of the sample. Results of this analysis indicate that the ^{238}U peak had 82% of the net alpha activity while the ^{234}U peak had 18% of the net alpha activity – a $^{238}U/^{234}U$ isotope ratio of 4.5.

A likely explanation for this $^{238}U/^{234}U$ isotope ratio of 4.5 is that this particular portion of Fernald became contaminated with depleted uranium. If it had been contaminated with natural uranium, the $^{238}U/^{234}U$ activity ratio would be 1; if it had been contaminated with enriched uranium, the ^{235}U and ^{234}U peaks would have been pronounced, relative to the ^{238}U peak. Consequently, the data conclusively shows that man-made (depleted) uranium contaminated this groundwater as the isotope ratio does not match natural uranium's.

These results for a sample of a DOE site's contaminated groundwater water clearly demonstrate the capability of the system to respond to low levels of uranium, to identify specific isotopes with the high energy resolution of the film and silicon detector, and to provide quantification of the sample's ^{235}U enrichment level (or depletion, as in this case).

2.5.4 Analysis of Tap Water (From Well) of Carlisle, Massachusetts Residence

Water from a deep well in granite at a Carlisle, Massachusetts residence was analyzed in the laboratory breadboard instrument. The water sample was transported sealed in a full sample bottle and had set less than one day before starting the count. Two liters of the unfiltered water were passed through a 53.5 cm^2 film sample placed in the sample chamber. The film was dried, then counted under vacuum by a 50 cm^2 detector.

A sample Thermo Water Alpha Monitor spectrum is provided (Figure 16) that shows the analytical results for this fresh groundwater sample. This water sample displays the isotopic presence of a high level of ^{214}Po, a uranium radon daughter that is typical of such New England groundwater samples. This isotope is part of the ^{238}U series and results directly from decay of ^{222}Rn (radon) in the well water. The alpha from ^{222}Rn is not observed, since radon is a noble gas and is not captured by the film. ^{214}Po's decay characteristics include:

^{214}Po	100%	7.69 Mev

The high level of ^{214}Po (without significant parent uranium) can be explained by the following: <u>all</u> radon gas that is evolved from the uranium-bearing granite's decay is dissolved in and carried along by the groundwater, as radon is soluble at such low levels in water. Negligible uranium is present, as little soluble uranium (or radon precursors) existed in the path of the groundwater. Radon, being an inert gas, is not adherent to the existing Thermo Water Alpha

Monitor film types and is not detected by the instrument. However, the decaying radon produces ^{214}Po. ^{218}Po, the other expected radon daughter, is not significantly present on the film, due to its short half-life and rapid decay after the film becomes dry (and the radon evaporates with the water).

Using the existing laboratory calibration, the total ^{214}Po level is calculated as 103 pCi/l, or approximately 7X the 15 pCi/l adjusted gross alpha limit of the EPA's proposed Safe Drinking Water Act (SDWA).

Finally, a second spectrum is provided (Figure 17) that shows the analytical results for the same Massachusetts groundwater sample that has been purged of radon for 10 hours (to allow the ^{214}Po radon daughter to decay). This water sample displays the isotopic presence of ^{238}U and ^{234}U that is typical of such New England groundwater samples. In addition, lesser quantities of uranium and thorium decay products are visible. In addition to the presence of previously identified ^{214}Po, ^{218}Po and ^{210}Po are present from the uranium decay series; in the thorium decay series, small amounts of ^{228}Th, ^{224}Ra, ^{216}Po, ^{212}Bi, and ^{212}Po are present:

^{210}Po	100%	5.3 MeV	Uranium Series
^{228}Th	28% 71%	5.34 MeV 5.43 MeV	Thorium Series
^{224}Ra	6% 94%	5.45 MeV 5.68 MeV	Thorium Series
^{218}Po	100%	5.3 MeV	Uranium Series
^{212}Bi	25% 10%	6.05 MeV 6.09 MeV	Thorium Series
^{216}Po	100%	6.78 MeV	Thorium Series
^{212}Po	100%	8.78 Mev	Thorium Series

Using the existing Thermo Water Alpha Monitor laboratory calibration, the total uranium level is calculated as 1.51 pCi/l (0.74 pCi/l ^{238}U and 0.77 pCi/l ^{234}U) or 2 ppb. It is interesting to note that while the dissolved uranium level of this sample is $1/10^{th}$ of the EPA's SDWA's 20 ppb, the adjusted gross alpha level of the sample (Figure 17) significantly exceeds the SDWA's limit.

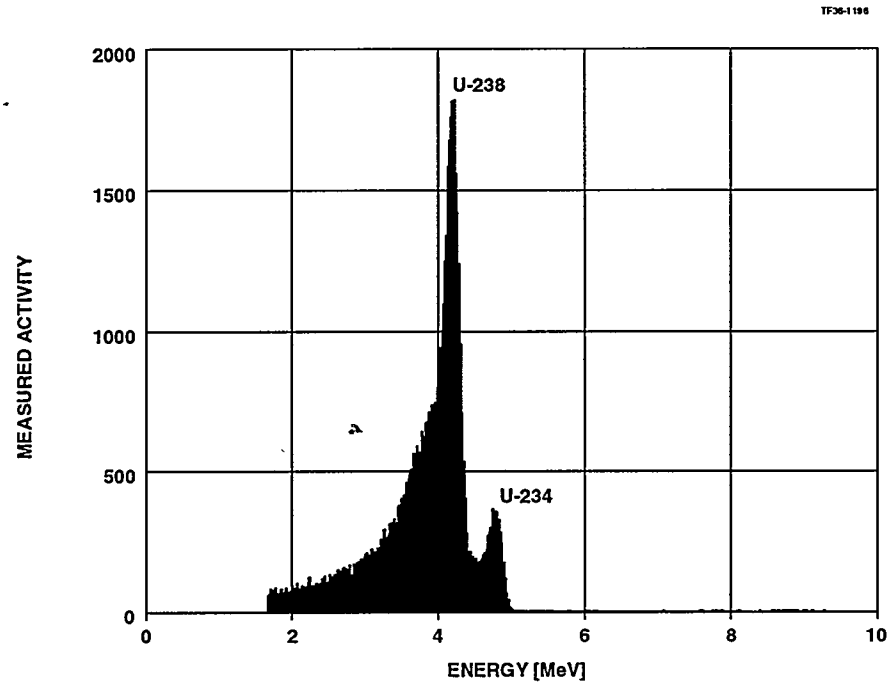

Figure 16. TAM Laboratory Test Results, Massachusetts Groundwater, 103 pCi/l Po-214

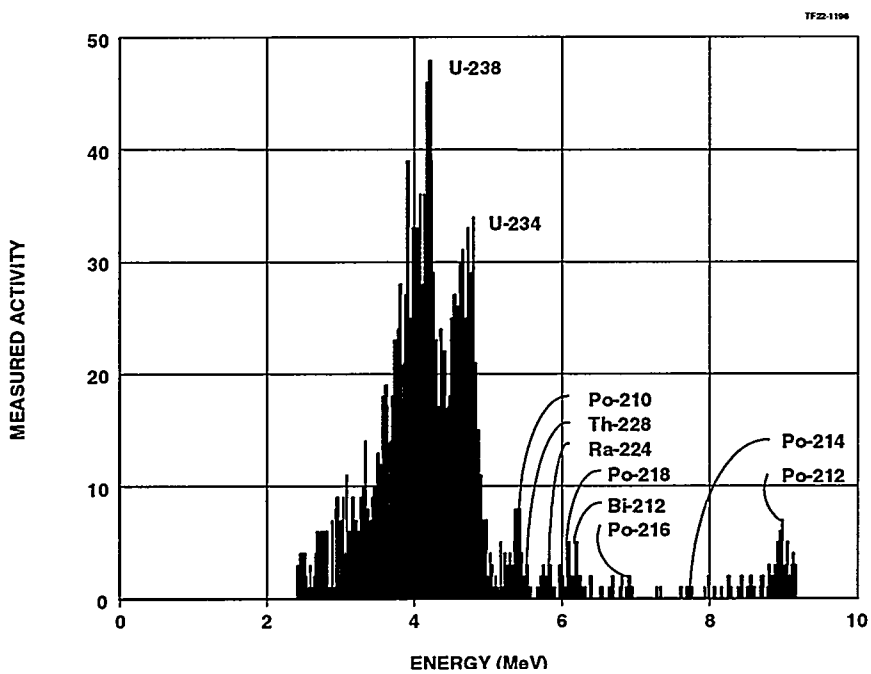

Figure 17. TAM Laboratory Test Results, Massachusetts Groundwater, 2 ppb (1.5 pCi/l) Total Uranium

Conventional radiochemical analyses were performed by a commercial laboratory on a portion of the Carlisle sample. Results for these analyses include a soluble uranium analysis of 0.68 pCi/l, and a total uranium analysis of 1.35 pCi/l. Thermo Water Alpha Monitor results compare favorably with the total uranium analysis, as they are only 12% higher than the conventional analysis results. In brief, the Thermo Water Alpha Monitor measured the total uranium of this sample, not just the soluble uranium.

These results for a potable well water sample clearly demonstrate the capability of the system to respond to very low levels of a range of alpha-emitters in a relatively short time, to identify specific isotopes with the high energy resolution of the silicon detector, and to provide a total uranium analysis of a natural groundwater sample as opposed to a soluble uranium analysis.

2.5.5 Analysis of Thorium Nitrate Solutions

In Figure 18, the result of assaying a 1 ppm thorium nitrate atomic absorption (AA) standard solution is given. The two major spectral peaks in Figure 18 are analogous to the two peaks of the uranium-containing samples: ^{232}Th is the parent of the thorium decay series, with ^{228}Th being a daughter product of ^{232}Th, just as ^{234}U is a daughter product of ^{238}U in the uranium decay series. However, Figure 18 contains a third peak, which can be identified as ^{230}Th, a member of the uranium decay series.

The presence of the third ^{230}Th peak can be explained as follows: uranium is often present in thorium ore. When the uranium-containing thorium ore was purified to produce the AA standard solution, the ^{230}Th due to the uranium remained with the ^{232}Th and ^{228}Th. Hence, there are three peaks in the spectrum. The natural abundance and relative activities of the three thorium isotopes are summarized below:

Isotope	Half-Life (Years)	Yield	Energy	Decay Series	Alpha Activity (relative to ^{232}Th)
^{232}Th	1.41×10^{10}	23% 77%	3.95 MeV 4.01 MeV	Thorium	1.00
^{230}Th	80,000	24% 76%	4.62 MeV 4.68 MeV	Uranium	-N/A-
^{228}Th	1.91	28% 71%	5.34 MeV 5.43 MeV	Thorium	1.00

The preceding table indicates that for a freshly purified thorium metal sample, the relative heights of the ^{232}Th and ^{228}Th peaks would be expected to be equal. However, for approximately every two years that the purified thorium metal sample is aged, the activity of

^{228}Th will be reduced by half (due to the presence of two beta-decaying progeny between ^{232}Th and ^{228}Th) and ^{228}Th daughter products will build. Due to the long half-life of ^{232}Th and ^{230}Th, however, the activity of these two isotopes will not have changed.

As expected, Figure 18 shows the ^{228}Th peak to be visibly less significant than the ^{232}Th peak. In addition, numerous ^{228}Th daughter products appear in the spectrum. Manual deconvolution of the three overlapping thorium curves and subtraction of background was conducted in order to quantify the isotope ratio of the sample. Results of this analysis indicate that the ^{232}Th peak has 63.8% of the net thorium alpha activity, the ^{228}Th has 28.4%, and the ^{230}Th peak has 7.8% – a ^{232}Th:^{228}Th:^{230}Th isotope ratio of 1.0:0.445:0.098. These data indicate that the sample was originally purified over two years ago and that the uranium content of the original ore was approximately 10% of the thorium.

These results for an aged sample of thorium clearly demonstrate the capability of the Thermo Water Alpha Monitor to respond to low levels of thorium, to identify specific isotopes with high-energy resolution, and to provide diagnostic quantification of a sample's elemental and isotopic makeup.

2.5.6 Robustness of Method

Linearity

Extensive laboratory data show that the Thermo Water Alpha Monitor has a linear dynamic range over six decades of uranium concentration. In addition, the instrument has proven linearity over the four-decade range of thorium concentrations that have been analyzed. Figure 19 illustrates a logarithmic plot of the calibration curve for the Thermo Water Alpha Monitor breadboard instrument, with data spanning a range of 10 parts per trillion (15 fCi/l) to 10 parts per million (15,000 pCi/l) natural uranium, and including levels of natural thorium between 100 parts per trillion (17 fCi/l) and 1 part per million (172 pCi/l). The correlation coefficient (R^2) for these data is 0.999, indicating the excellent linearity of the instrument.

Effect of pH

The operation of the Thermo Water Alpha Monitor has been shown to be unaffected by operation with slightly acidic or basic water chemistry (pH above 5). Figure 20, a plot of the measured total uranium activity of a variety of prepared samples relative to the known uranium activity, shows the larger effect on the instrument's operation caused by analyzing very acidic solutions. For example, the relative results of analyzing a uranium solution below pH 4.5 are significantly low, as the acidic solution seriously reduces the uptake of uranium by the film under test.

Such nonlinear response of the Thermo Water Alpha Monitor to sample pH can be accounted for in the Optional Phase II Field Test Monitor by one of three methods:

- Use an algorithm to model the nonconstant film response and correct the erroneous readings.
- Add base to the water sample prior to analysis to raise the pH above 5.
- Obtain an alternate film that has linear behavior for acidic solutions.

Any of these three methods will provide acceptable Thermo Water Alpha Monitor analysis results. For example, thermocouples and other instruments have nonlinear response characteristics, and their responses are commonly modeled and linearized. Automatic titrators exist that could add the proper amount of base to the incoming water sample prior to analysis, although at a penalty of increasing the operational complexity of the monitor. Three film types have been screened in the laboratory; additional film types might prove unaffected by these low pH samples.

Effort for the Optional Phase II of the current program will focus on proving the acceptability of using an algorithm to model the instrument's response to sample pH. Software correction of instrument readings is commonly performed and provides reliable results for other instrumentation. Performing additional film testing or adding an automatic titrator to the field test instrument are viewed as beyond the existing scope of work for the program.

Effect of TDS

The operation of the Thermo Water Alpha Monitor has been shown to be unaffected by operation with total dissolved solids (TDS) levels that are between 10 and 10,000X higher than the analyses of interest. Figure 21, a plot of the measured total uranium activity of a variety of prepared samples relative to the known uranium activity, shows that for TDS levels below about 100 ppm, accurate results are obtained for uranium levels between 10 ppm and 10 ppT. The instrument reports erroneous low readings when analyzing solutions with TDS levels above 1,000 ppm. For example, results of analyzing a 600 ppb uranium solution with TDS levels 2,000X greater than the uranium concentration (1,300 ppm) are significantly low, as the high TDS loading seriously reduces the uptake of uranium by the film under test.

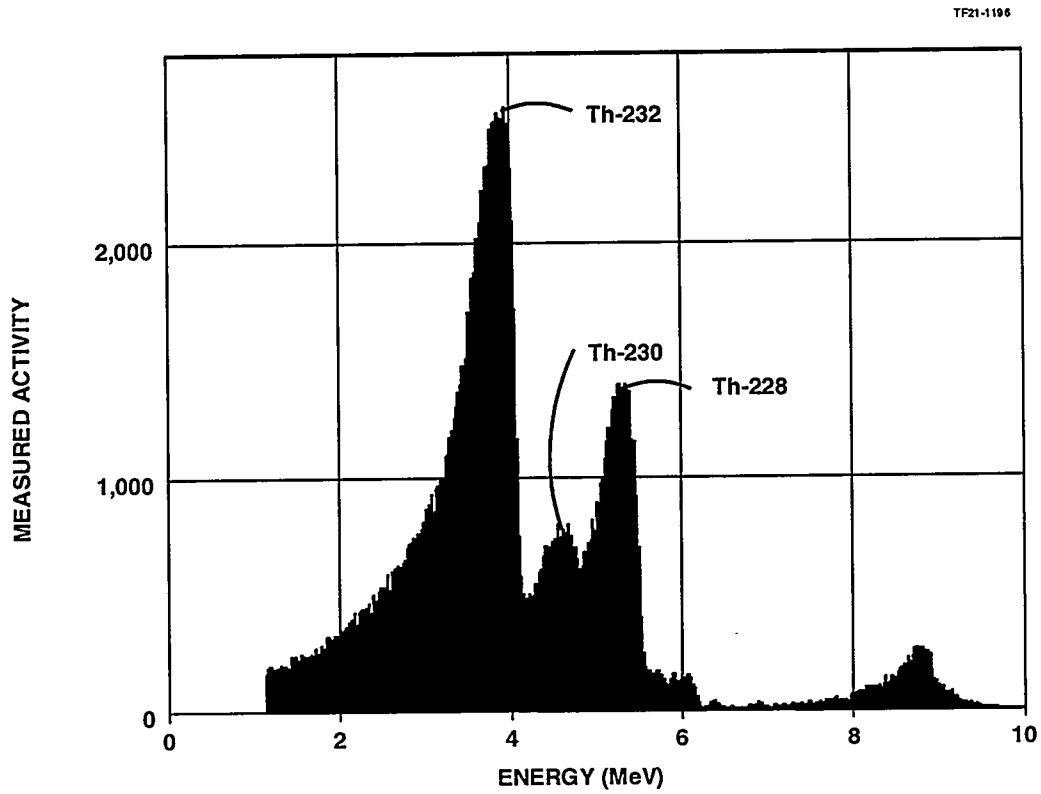

Figure 18. TAM Laboratory Test Results, 1 Part Per Million Thorium

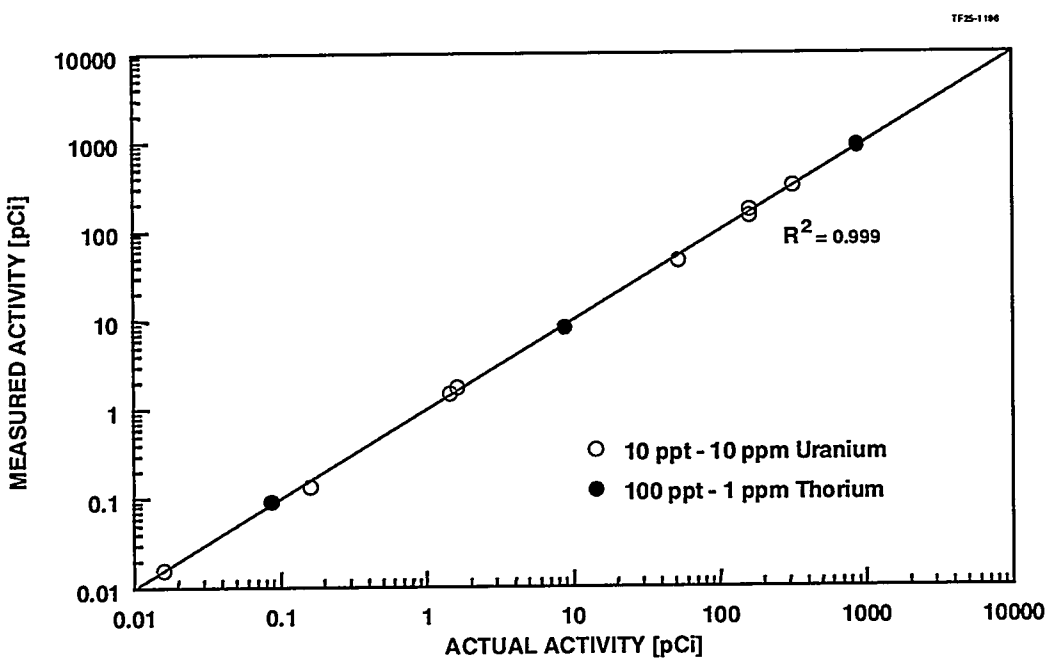

Figure 19. Broad Dynamic Range Exceeds Six Decades for Uranium and Thorium

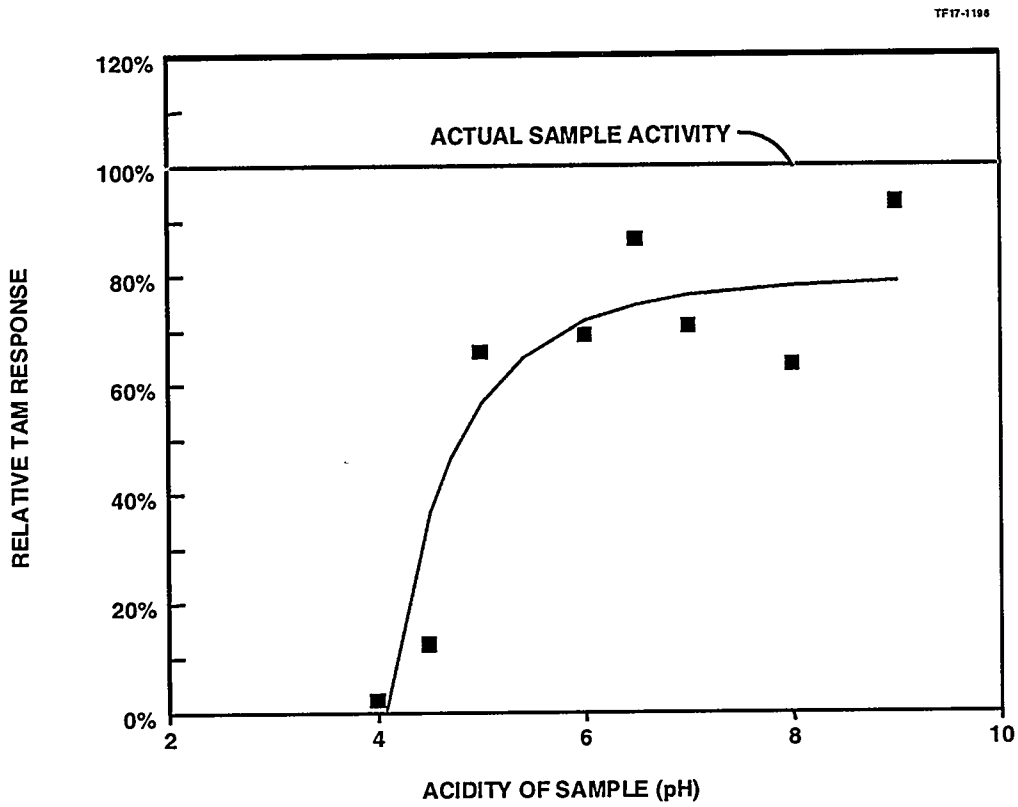

Figure 20. Illustration of TAM's Flat Response at High pH

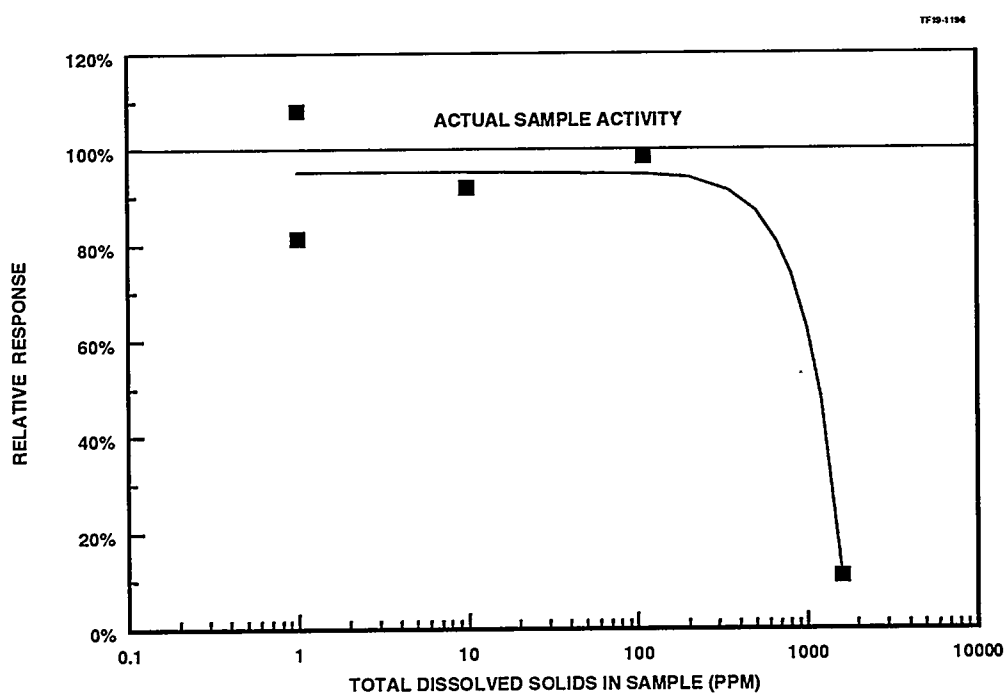

Figure 21. High Dissolved Solids' Impact on TAM Response

Similar to correcting for sample pH, such nonlinear response of the instrument to sample TDS can be accounted for in the Field Test Instrument by using an algorithm to model the non-constant film response and correct the erroneous readings. If required, the instrument to be tested in the Optional Phase II of the current program will incorporate an algorithm for correction of alpha analyses at high TDS values; the field test will validate the utility of this methodology. The algorithm is expected to involve increasing the instrument's response by dividing the unadjusted instrument response by the "Relative Response" value (see Figure 21) corresponding to the sample's measured total dissolved solids. For example, if the measured TDS is 1,000 ppm, the unadjusted instrument response would be divided by 0.55, resulting in an adjusted instrument response that is larger by a factor of 1.81.

2.5.7 Other Method Details

Deconvolution of Multiplets

Where necessary, source attenuation and deconvolution procedures have been incorporated in the data analysis/reduction procedures. The physics of alpha transmission and linear-energy-transfer (LET) of alpha particles in materials is well understood. The analysis is simplified by the fact that alpha particles travel in straight lines through materials. If required, automatic deconvolution of multiplets can be built into the Thermo Water Alpha Monitor software.

Overall, deconvolution of laboratory data has involved joining the actual Gaussian peak shape on the high-energy side of a peak with a single exponential tailing function on the low energy side. Deconvolution of multiplets employs an iterative, logical progression from the highest-energy peak to the lowest-energy peak in the multiplet: by stripping the actual and fit values of the highest-energy peak from the multiplet, then repeating the deconvolution process on the residual lower-energy peaks of the multiplet. Triplets have been deconvoluted through this process; quadryplets (or more complicated multiplets) can be deconvoluted using the existing deconvolution procedure.

To assist in illustrating the basic steps of the deconvolution procedure, the spectrum shown in Figure 14's analysis of a 20 ppb natural uranium sample will now be analyzed. An initial iteration for the parameters of the exponential tailing function is obtained from performing a linear least-squares fit on the natural logarithm of the low-energy tail of the lowest-energy peak of the multiplet. Figure 22 illustrates the resultant least-squares fit.

These parameters are then used to determine an appropriate exponential tailing function for the highest-energy peak in the multiplet. The highest-energy peak's low-energy tailing function is smoothly joined to the higher-energy Gaussian peak by adjusting the pre-exponential factor. (Occasionally, a slight adjustment is made to the exponent to improve the tailing

function's fit.) As a result, the highest-energy peak can now be defined by the actual data for the higher-energy Gaussian portion, along with the exponential low-energy tailing function (Figure 23).

Final deconvolution of the highest-energy peak occurs by subtracting both its Gaussian and exponential portions from the multiplet. If only two peaks are present, the deconvolution is complete. If a total of three peaks are present, as in Figure 24, the deconvolution procedure is repeated to separate the higher-energy residual peak from the lower-energy residual peak (fitting a tailing function to the higher-energy peak, then stripping the residual high energy portion of the next peak and the corresponding low energy tailing function). Figure 25 contains the three resultant peaks that have been completely deconvoluted from the example spectrum. The ^{238}U:^{234}U:^{235}U isotope ratio is 1.0:0.69:0.034.

These techniques are similar to commercially available algorithms that automatically deconvolute thick source alpha spectra in commercial counting applications.

Determination of Background

The best method of determining background has been to periodically perform a Blank Check, performed by analyzing a set volume of DI water with the Thermo Water Alpha Monitor. Figure 26 illustrates a typical blank check that was performed after Figure 14's analysis was completed. Generally, a Zero Count of the chamber (without any film or with an unused piece of film in place) results in an extremely low count rate relative to the Blank Check (Zero well under 0.1% of Blank, as shown in Figure 27). Consequently, zero checks need to be done much less frequently than blank checks, or only as often as a site's data quality objectives (and perhaps by the site's QA/QC system).

Counts recorded during this Blank Check will then be summed in the various regions of interest (ROI) for each nuclide detected/analyzed in each analysis. These Blank Check count rates are then subtracted from the gross count rates for each isotope, resulting in the net count rates for each nuclide of interest.

Cleaning Details

The Thermo Water Alpha Monitor field instrument will not need to be cleaned when it is analyzing multiple samples of the same stream; during these periods, a simple water rinse will be sufficient to remove transferable radioactivity from the film samples. However, when the field test instrument is moved between different field test sites, it will need to be cleaned. This cleaning will remove residual alpha-emitters from the first test site to very low levels and allow unbiased sampling of the potentially different second test site.

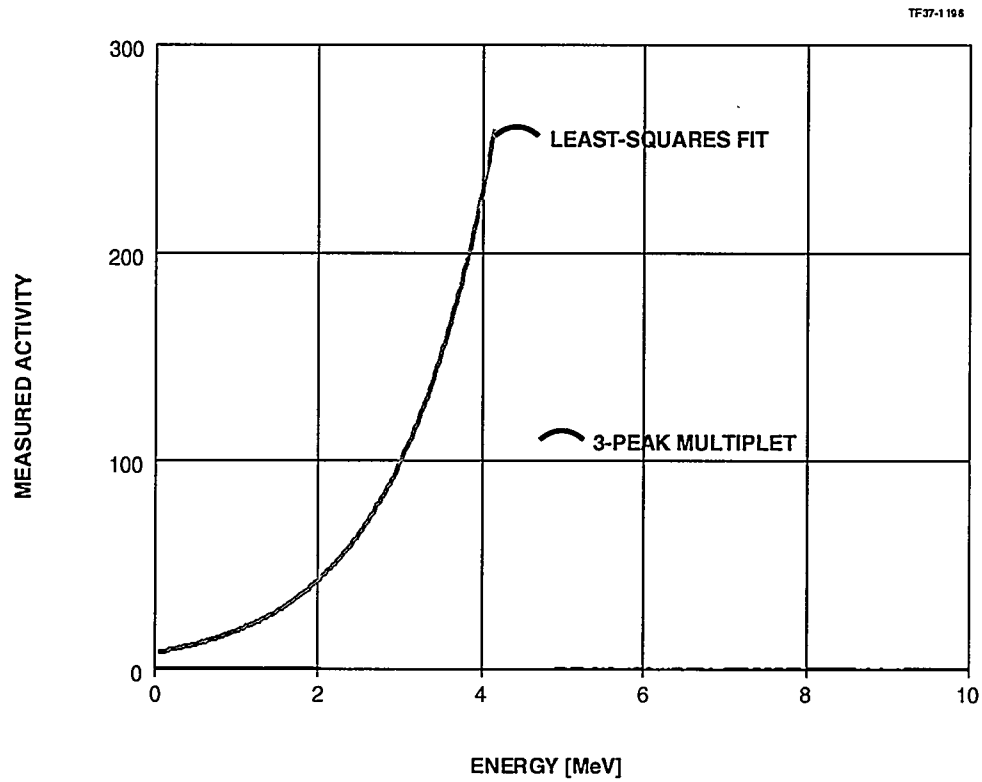

Figure 22. Multiplet Deconvolution: Logarithmic Least Squares Fit to Low-Energy Tail

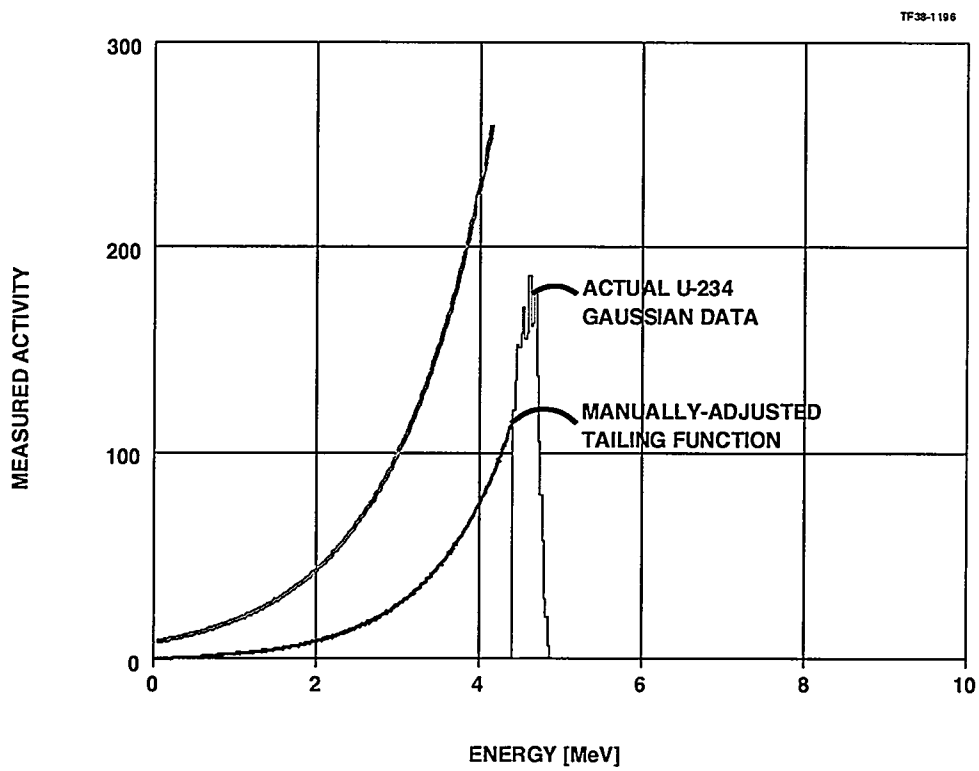

Figure 23. Multiplet Deconvolution: Manual Fit to Highest-Energy Tail

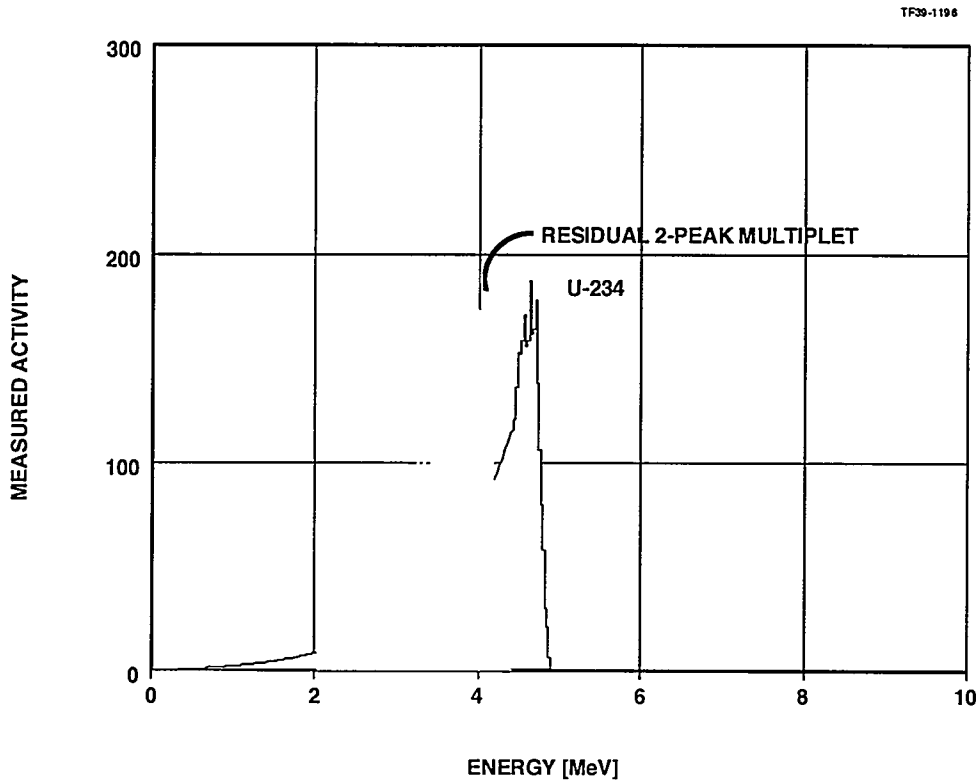

Figure 24. Multiplet Deconvolution: Resolved Peak and Residual Multiplet

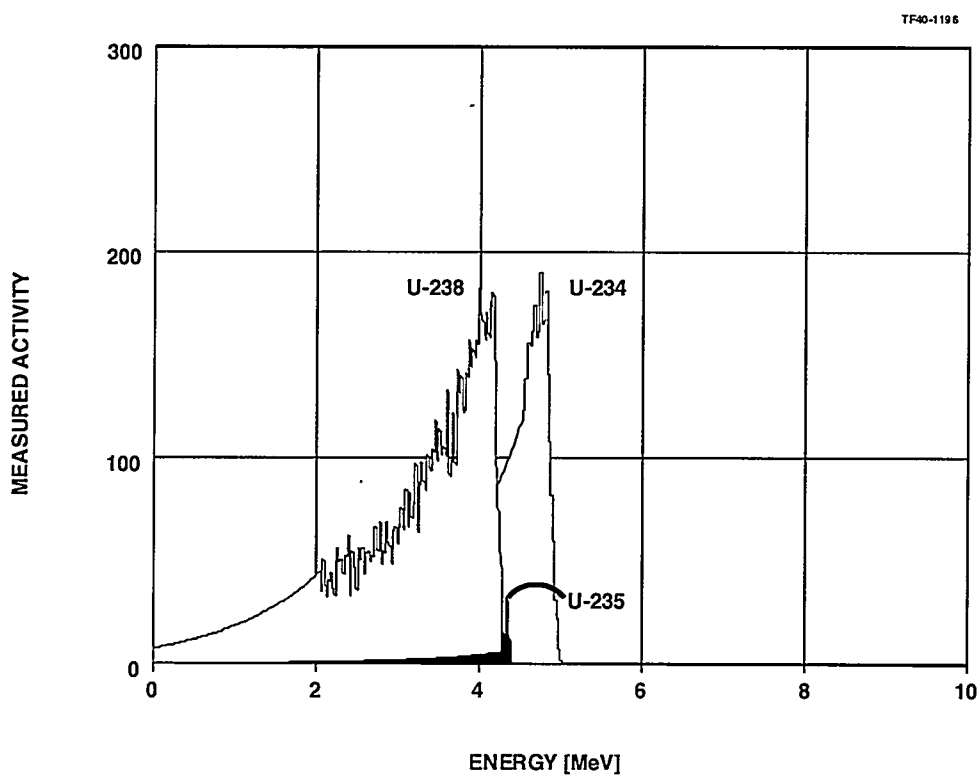

Figure 25. Multiplet Deconvolution: Three Peaks Resolved From Multiplet

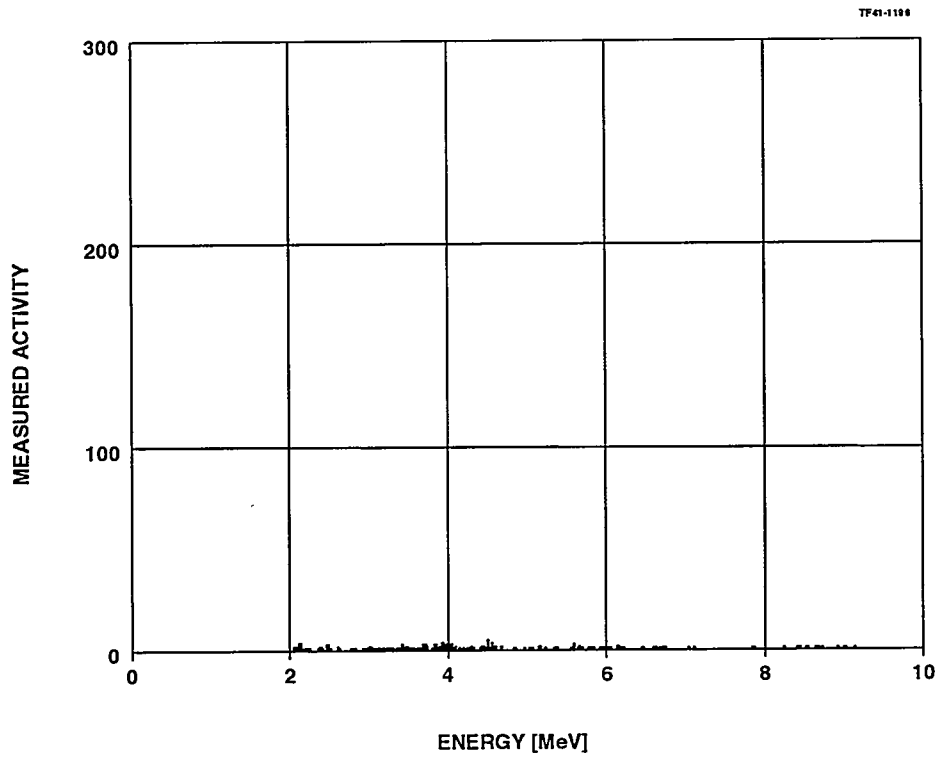

Figure 26. TAM Laboratory Test Results – Blank Check After 20 Parts Per Billion Uranium and Simple Rinse

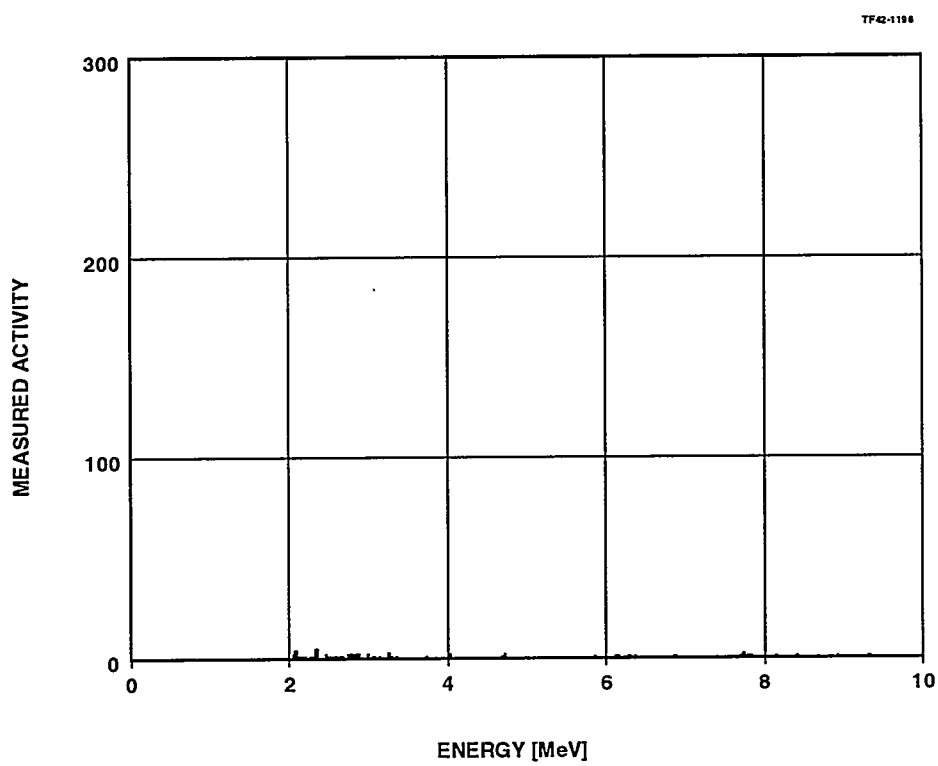

Figure 27. TAM Laboratory Test Results – Zero Check of Empty Instrument Chamber

After repeated laboratory analyses, simple DI water or soap and water wash/rinses have yielded instrument Blank Check count rates that are less than 5% of normal 20 ppb natural uranium count rates. Such low Blank Check count rates will be suitable for accurate instrument operation. To date, this has been the primary method of cleaning the laboratory breadboard unit between analyses.

For even deeper cleaning, a 5% nitric acid rinse, followed by a DI water rinse, has been found to reduce Blank Check levels to less than 0.05% of normal 20 ppb natural uranium count rates. Such nitric acid cleaning is only expected to be required after an unexpectedly high activity sample has been analyzed by the instrument, and the soap and water rinse is unable to restore the instrument to acceptable operation.

2.6 FIELD TEST INSTRUMENT DESIGN

2.6.1 Instrument Specifications

This section presents a summary of the overall requirements and needs for an On-line, Real-time Alpha Radiation Monitor for Liquid Streams. This information was obtained over the course of the project from numerous conversations and interviews with the DOE Headquarters, DOE Operations Office, M&O Contractor, and commercial laboratory personnel. A consistent theme throughout these conversations was that any new, reliable alpha-measuring instrument that allows DOE to operate better, faster, and cheaper will get widespread use across the DOE complex.

Federal government regulations provide a current framework for determining required minimum detection limits, data trending and analysis, and other features that would be required for any instrument measuring radionuclides in water. For instance, the maximum allowable concentration of natural uranium in any public drinking water stream is 20 ppb (30 pCi/liter), contained in 40CFR141, 142, the EPA's Proposed Rule for National Primary Drinking Water Regulations (the Safe Drinking Water Act (SDWA)). However, SDWA regulations also specify an adjusted gross alpha limit of 15 pCi/l; the proposed alpha-measuring instrument might also need to be capable of monitoring at this lower activity level.

Table 5 summarizes the product features required for an initial product.

TABLE 5

REQUIRED FEATURES

Key Required Feature	Technology Status
On-line operation*	Achieved
Isotopic analysis at drinking water limits	Achieved and exceeded by 2000X
Certification	TBD
Archiving	Achieved
Two- to four-hour analysis time	Achieved (26 minutes as of 6/96)
Additional desirable features	
(Portability)	(Half height rack OK now, smaller is achievable)
(Remote data access)	(In-house network to date, no issues anticipated)

* The sampling mode may be either by batch (scheduled intervals or intermittent) or continuous for time-averaged data.

Identification of Principal Criteria for the Instrument Design

1. Operating Mode

The technology will allow for installation of the instrument so as to directly sample on-line, low-level radioisotope-containing water from water streams, as opposed to the conventional technique of collecting and bottling samples for transport to a central analytical laboratory.

2. Sensitivity

The instrument will be designed to analyze for alpha radiation to the drinking water limit of 15 pCi/l gross alpha-emitters in the water stream, including a limit of 30 pCi/l natural uranium limit.

3. Response Time

The present typical two-week total, end-to-end sample turnaround time will be reduced at least to a maximum of one day. Included will be the elimination of delays currently associated with manual sampling, logging, transport, manual chemical processing and handling, and report reconciliation.

4. Isotopic Analysis

Differentiation among radioisotopes will be provided by resolving the emitted alpha energies.

5. Certification

The design will be amenable to future certification by appropriate authorities (ASTM, EPA, etc.).

6. Archiving

A means will be provided to retain analyzed samples for future verification or additional analysis.

7. Automation

The instrument will be capable of operating unattended while making multiple sample analyses.

8. Minimize Secondary Waste

In routine operation, the instrument will not increase the contaminant levels in the water undergoing analysis.

9. Instrument Environment

The alpha instrument will be designed for indoor use.

Preliminary Specifications

Detection limit	30 pCi/l natural uranium, +/-50%
Sample turnaround time	1 to 12 hours, with a settable high-level alarm
Physical size	24" w x 24" l x 48" h
Consumables	film supply, de-ionized water
Power requirement	110 VAC, 15 A, 60 Hz, 1 phase
Operating temperature	10° Celsius to 35° Celsius
Relative humidity	20% to 90% noncondensing

2.6.2 User Interface

The Thermo Water Alpha Monitor is designed to be controlled using a standard personal computer that has been integrated into the instrument's cabinet. The computer runs the Windows operating system environment. If the user has any experience using Windows-based software,

then the control panel will afford a degree of familiarity without the need to learn a new and foreign interface.

The software has different security levels, allowing varying levels of control. Instrument access is granted only upon successful entry of a password, which the user is prompted for when starting up the machine. On the lowest security level, the user is limited to viewing the operation and sequence of events as they occur. At the highest level, operating parameters such as alarm levels, run times, and instrument sequencing may be changed. At all levels of access, the user may stop the instrument's operation in case of an emergency.

Figure 28 shows the opening screen, as it appears on the computer monitor. This screen appears under two conditions: 1) the first time power is applied to the system or 2) if a new user "logs in" to the instrument. An example of a new user might be a supervisor who desires to change the instrument operating conditions, as outlined above.

Main Menu

Once the user has successfully logged into the machine, the Main Menu appears, as shown in Figure 29. Depending on security access, the user may use a mouse to click on any of the option buttons on the screen.

The **[Run Analysis]** button initiates the beginning of a sample sequence, based upon the parameters defined in the Set Up section of the software.

The **[Set Up Parameters]** button brings up an additional screen that controls the parameters under which the monitor is to operate. Some of these parameters include Sample and Count Times, high and low alarm level triggers (temperatures, flow rates, etc.), as well as Annunciation methods (audible vs. silent alarms). Additionally, the user may choose to run a single or fixed number of analyses, or to operate in a continuous mode. This latter feature is useful when the instrument is to be installed in remote locations where only periodic access will be available.

The **[Pause Run]** button temporarily suspends instrument operation without shutting down or resetting the equipment.

The **[Normal Stop]** button allows the user to stop the continuous operation of the instrument at the end of the current analysis. This prevents the user from losing the most current analysis being performed.

The **[Review Data]** button allows the user to access a database of previously collected data and review it in a variety of graphical and tabular formats. This button also leads to options for printing reports as well as for storing data on floppy diskettes.

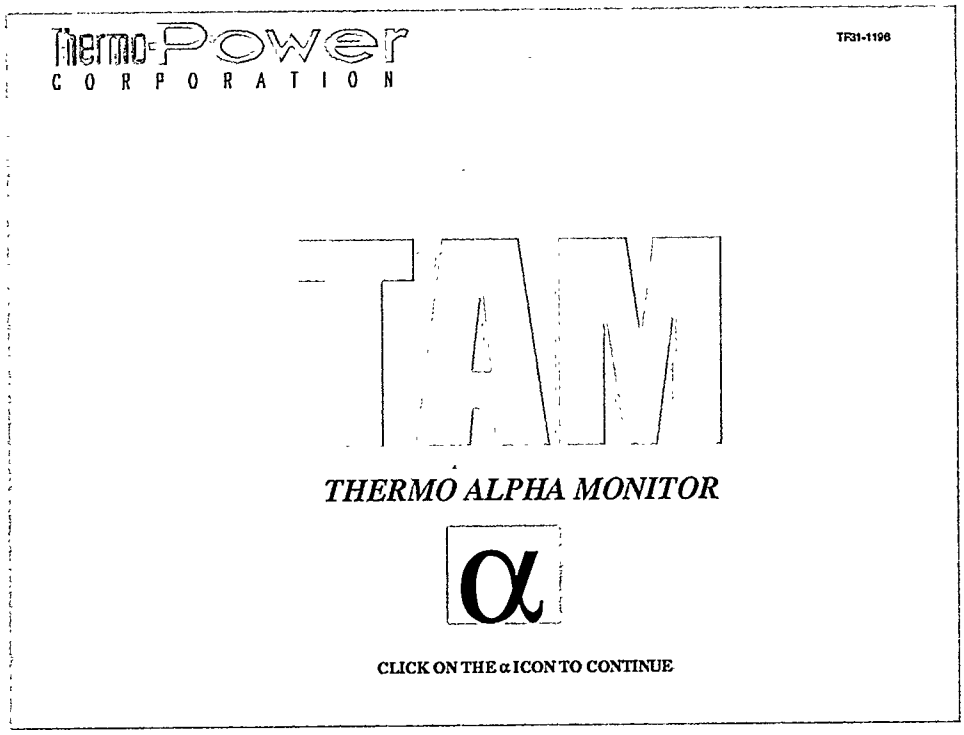

Figure 28. TAM User Interface Opening Screen

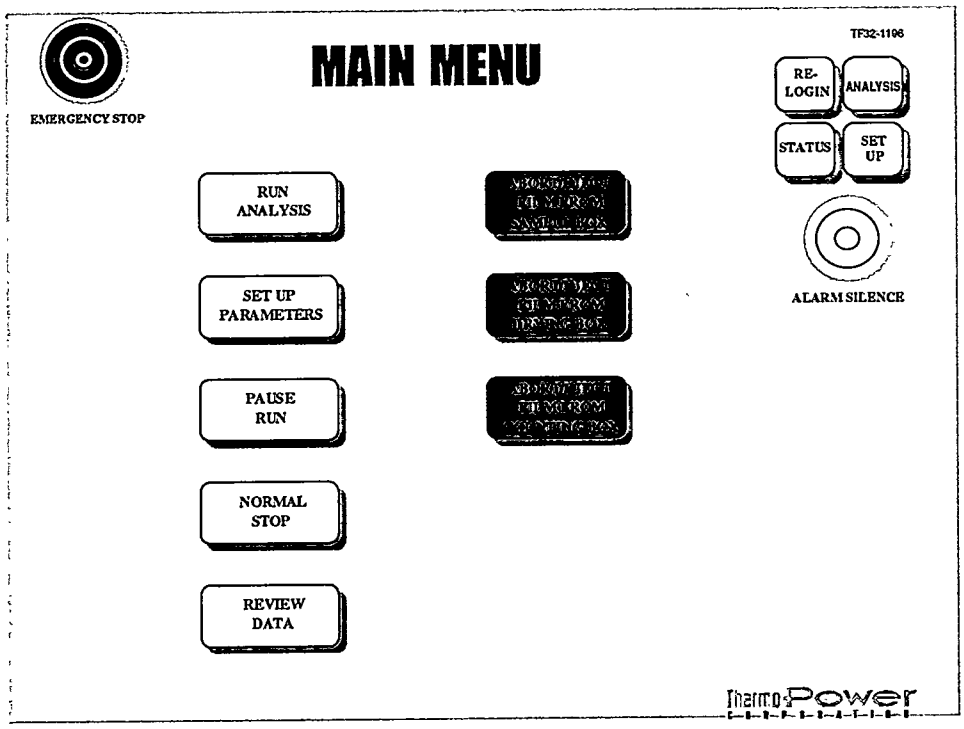

Figure 29. TAM Main Menu Screen

On the Main Menu screen there are also three **[Abort/Eject]** buttons. Pressing any of these buttons will immediately stop the selected process and eject any film from the affected chambers. For example, pressing "Eject Drying Chamber Film" ejects any film in the drying chamber without affecting the film in the sampling or counting chambers.

Also on the Main Menu, in the upper left-hand corner, there is an **[Emergency Stop]** button. This button will immediately stop all instrument processes and disconnect power to the analyzer, but not the user interface screens nor the personal computer. The **[Emergency Stop]** button can be found on all of the interface screens with the exception of the Log-in screen.

Another aspect that is common to all of the interface screens are the four buttons in the upper right-hand corner. These are quick access buttons that allow the user to directly switch to other sections/menus of the instrument's operating system. These other sections/menus are described below.

Analysis Screen

The Analysis screen presents a summary of information about present operating conditions as well as current and historical data. A sample Analysis screen may be seen in Figure 30.

On the upper third of the screen, starting from left to right, is the Last Completed Analysis indicator. This indicator show the last successful and full analysis completed. There is also a counter that indicates the number of analyses that have been completed since the last time the instrument was reset.

In the center are two sets of virtual LEDs showing the Operating Mode and any active alarms.

Three trend indicators are located on the bottom third of the screen. The left indicator shows the Gross I count for all previous runs. The middle indicator shows the Gross I count for the current run. The right indicator shows the spectrum for the current run. The Gross Current and Spectrum indicators are updated every 60 seconds, as counts are read. Alternate analysis screens can be displayed that detail isotopic data rather than gross data.

Like all of the other screens, the upper left-hand area of the screen has an **[Emergency Stop]** button and the upper right-hand corner has four **[Quick Access]** buttons to switch to other areas of the instrument's interface.

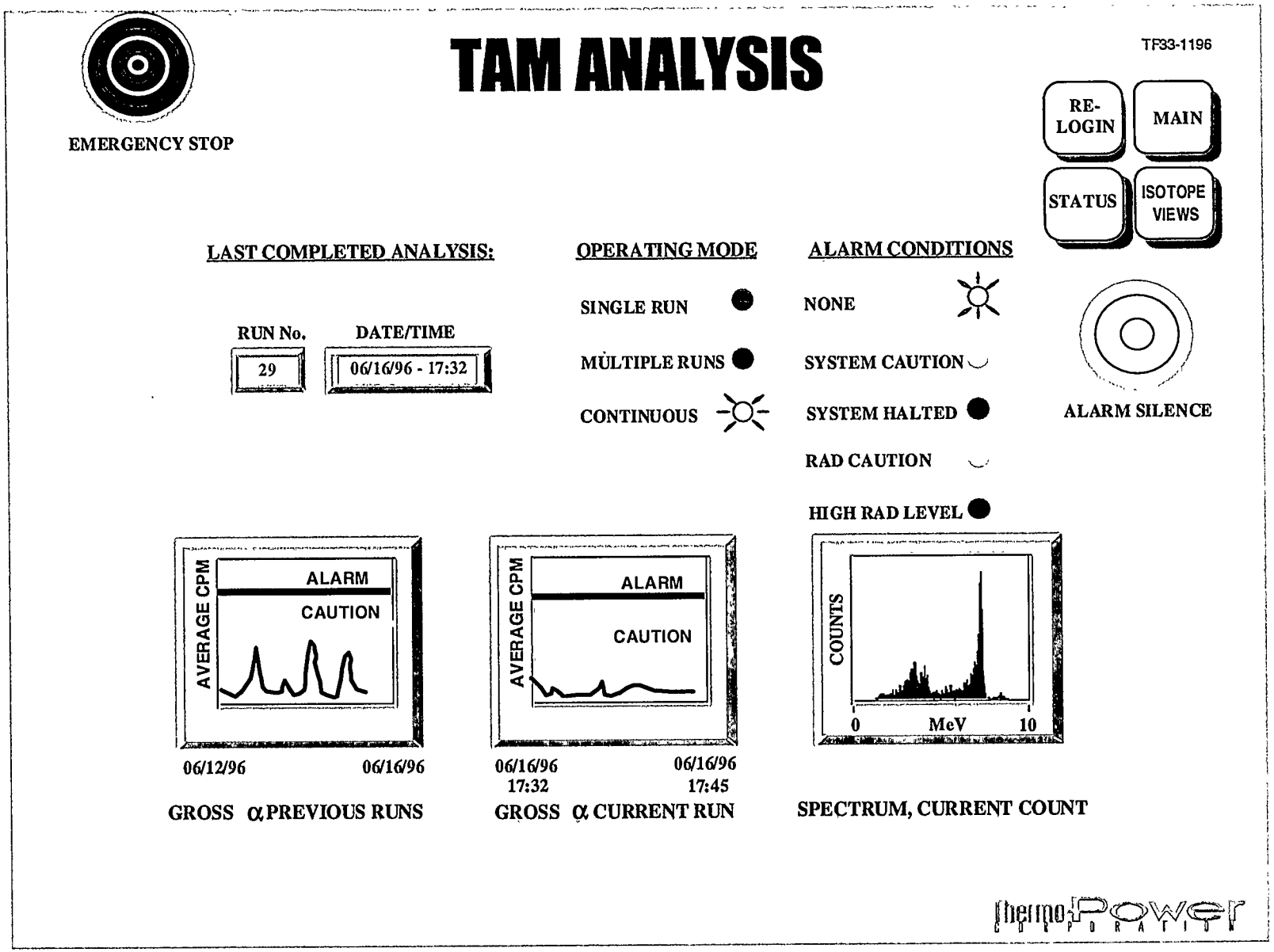

Figure 30. TAM Analysis Screen

Status Screen

The Status screen shows, in moderate detail, the current status of the instrumentation in a control panel format. Figure 31 shows a sample Status screen.

Under each chamber, there are indicator lights which show the status or mode of operation for each chamber. A green light indicates the current mode of operation. Next to each indicator light is a red LED used to indicate whether an alarm is present. Note also in the sample screen that the Drying Chamber is different from the Wet Chamber or Counting Chamber. The "split" chamber indicates that the drying chamber is currently in the open position and that no film is currently in the chamber. The Drying Chamber also has an analog temperature indicator. If the temperature rises above a preset level, the needle will change color from green to red to indicate that the temperature is too high in the chamber.

Each of the chambers is also equipped with a timer. The time indicated is always the amount of elapsed time since the last process was started or mode of operation was initialized.

On the left-hand side of the control panel are three level indicators and one status indicator. The three level indicators show the amount of material in each of the three containers. When a level reaches a preset low alarm level, the color of the indicator changes to red.

The Sample In Status indicator is green in color when the pump and filter are operating properly. If one or more pieces of equipment are not operating properly, the indicator will change to red.

Like all of the other screens, the upper left-hand area of the screen has an **[Emergency Stop]** button and the upper right-hand corner has four **[Quick Access]** buttons to switch to other areas of the instrument's interface. On this screen, there is an additional button to shut off the power to the analyzer without shutting off the power to the interface.

Detailed Component Status Screens

An additional feature of the instrument interface screens is the ability to look at the equipment and components connected to each of the chambers. By double clicking on any of the chambers on the Main Status screen, a detailed screen will be displayed. Figure 32 is an example of the Counting Chamber Status screen. On this screen, the user can determine which, if any, of the components need attention when an alarm is triggered; again, indicated by the specific color of a component changing from green to red. Pressure indicators also show the operating conditions of the air inlet filter as well as the vacuum in the Counting Chamber.

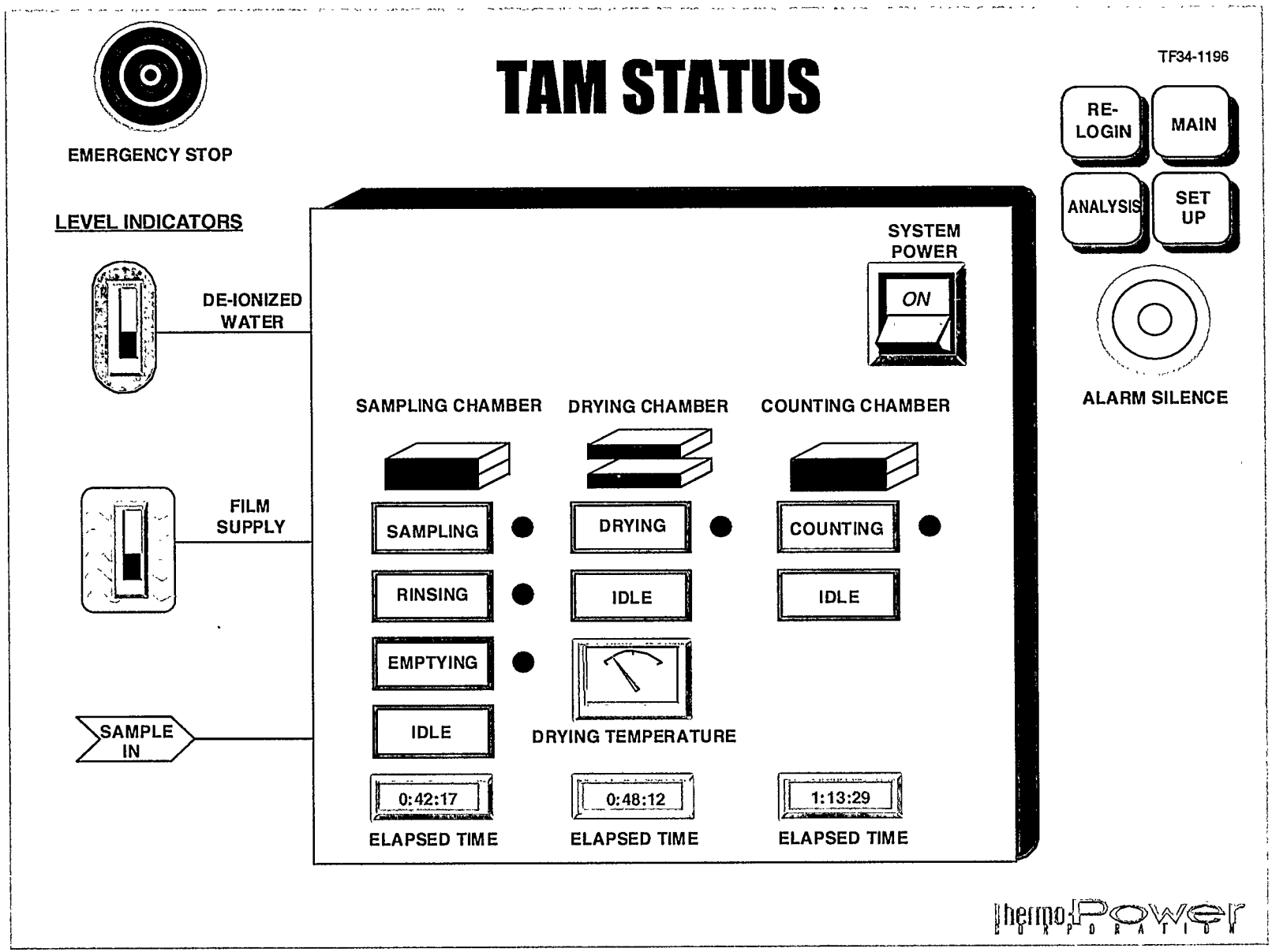

Figure 31. TAM Status Screen

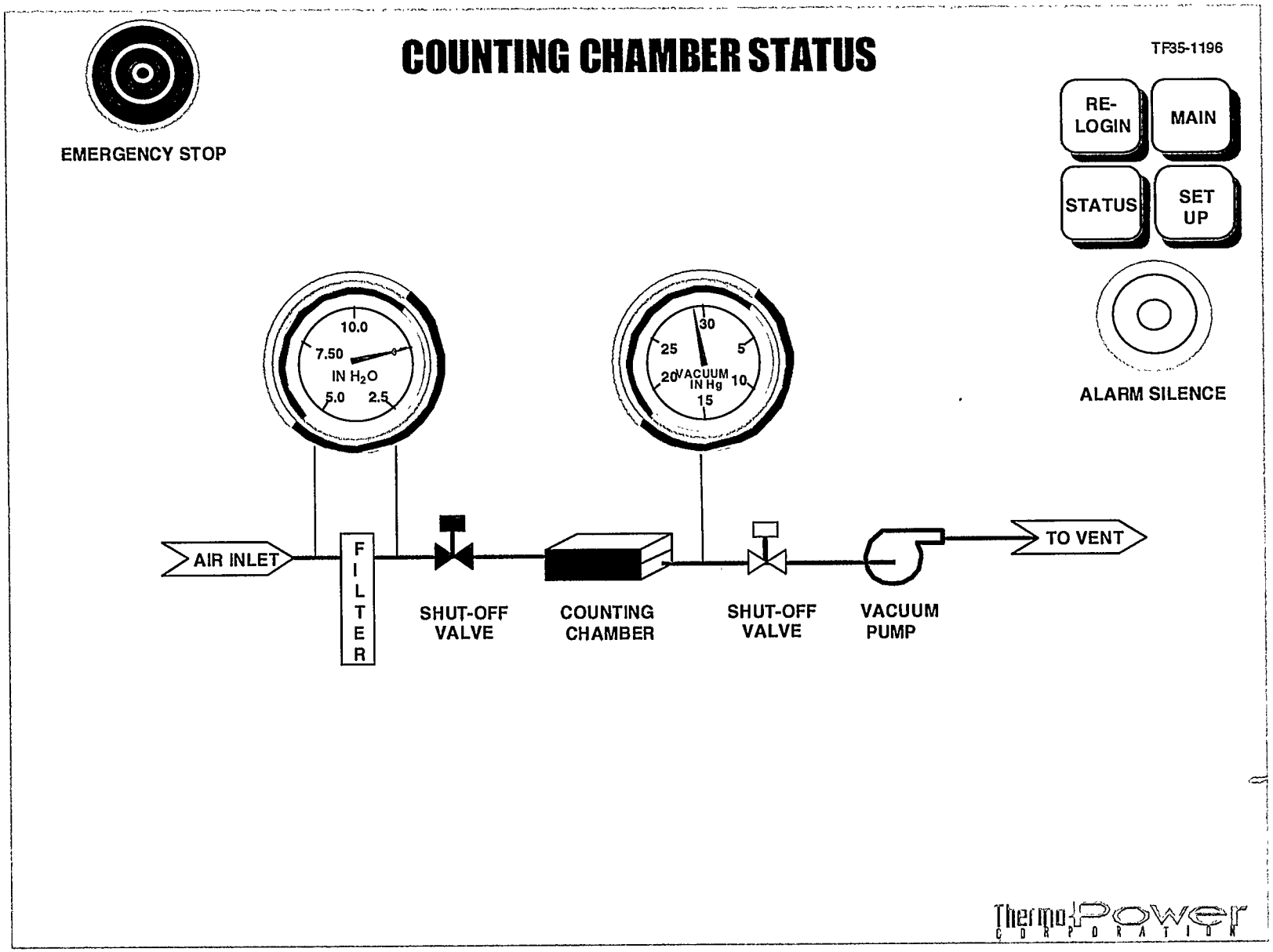

Figure 32. Representative TAM Detailed Component Status Screen

Like all of the other screens, the upper left-hand area of the screen has an **[Emergency Stop]** button and the upper right-hand corner has four **[Quick Access]** buttons to switch to other areas of the instrument's interface.

2.7 FIELD TEST

2.7.1 Site Characterization

The objective of the proposed Optional Phase Field Test was to confirm the instrument's proper operation and usefulness on a variety of contaminated waters on and near the Department of Energy Oak Ridge Reservation (DOE-ORR), Oak Ridge, Tennessee (see Figure 33), including ground, surface, and process waters.

Field testing was conducted at several Oak Ridge test locations. Monitoring with the instrument was used to determine the uranium and other radioisotope concentration variations with time, as well as any excursions above regulatory limits. At intervals, stream samples were taken and analyzed for uranium and other radioisotope concentrations by conventional means for direct comparison to the field test monitor results. The testing period covered a one week period.

Tests were conducted at five sites, in order to perform an initial evaluation of the response of the instrument to a range of water chemistries, contaminant concentrations, and radioisotopes. The ground, surface, and process water sources were selected as being representative of expected water conditions at the major areas of use across the DOE complex. Three of the sites were off the DOE-ORR, and two of the sites were on the DOE-ORR.

The primary test sites were off the DOE-ORR, located at the City of Oak Ridge Municipal Wastewater Treatment Plant (MWTP). Figure 34 illustrates the location of the MWTP relative to the DOE-ORR. Process water was available as the influent and the effluent to the MWTP, while the nearby East Fork Poplar Creek (EFPC) provided a source of surface water. Both the city's influent and the EFPC are partially derived from the DOE-ORR, as the effluent from the ORR Y-12 site is routed to the MWTP for treatment, and the source of the EFPC is on the Y-12 site. Radioactivity in these water streams is thus due to DOE-ORR discharges, as well as the several civilian/commercial users of radioactive materials in Oak Ridge. Due to the nature of their source, although significant dilution of these DOE-ORR waters occurs before reaching the MWTP, these streams remain of interest to the program.

The secondary test sites were located on the DOE-ORR reservation, in the Y-12 Plant's Bear Creek Valley (see Figures 34 and 35). The secondary test sites were a surface water source (SS-5) and a groundwater well (GW-684,) and contained water that was at background levels of uranium (30 pCi/l, or 40 - 70 ppb total uranium). Bear Creek Valley (BCV) is approximately 10.4 miles long and spans the distance from the western end of the Oak Ridge Y-12 Plant to the Clinch River to the west. BCV is mostly contained in the DOE-ORR. The eastern portion of the

valley is on ORR land, and the western portion (the Grassy Creek watershed) includes Tennessee Valley Authority and private land.

During the operation of the Y-12 Plant, solid and liquid hazardous and radioactive materials were disposed at various sites in the BCV. The primary contaminant of concern in the BCV is uranium. Over 18 million kilograms of uranium were disposed of in this watershed (the largest uranium-contaminated site in the DOE complex), and leachate from buried uranium poses a long term threat to human health and the environment. The Proposed Plan for BCV calls for excavation of some wastes, *in situ* groundwater treatment, *in situ* waste treatment, and hydraulic isolation.

Best management practices dictate that the lowest total cost monitoring option be selected for BCV. Perhaps 2/3 of the total cost of environmental monitoring is associated with the manual steps of sample collection, sample preservation, sample analysis, entry into the DOE chain of custody system, and transport to the laboratory. Consequently, a fully-automated analysis instrument represents the best method of providing low-cost long-term remote environmental data acquisition and reporting. Such an automated instrument will allow automatic data retrieval, and facile integration into an Internet-based reporting database.

2.7.2 Test Sequence

The test sequence for each site was as follows:

1.) Install and checkout the field test unit at the Oak Ridge test location. A photograph of the Field Test Unit installed at the MWTP for sampling the EFPC and MWTP effluent is provided as Figure 36; a photo of the Unit sampling the MWTP influent is shown as Figure 37; and a photo of the test installation used for sampling the surface water and ground water at the Y-12 BCV is provided as Figure 38.

2.) Operate instrument at each site to obtain one to two samples of the water stream of interest. Report the results for all alpha-emitting radionuclides detected. Take a minimum of two spot samples for analysis by conventional methods (total uranium by kinetic phosphorescence [KPA] and gross alpha precipitation) for elemental and isotopic content for direct comparison with the instrument results. Parameters to be studied in the testing included:
   a) Reliability and life of detector and instrument.
   b) Stability and reproducibility of instrument (if duplicate samples are taken).
   c) Automated operation cycle and control of instrument.
   d) Water chemistry (measure pH of sample to verify it is in an acceptable range).
   e) Radioisotope type (within limits of those available at Oak Ridge).

3.) Move instrument to next site and continue testing.

ORNL-DWG 94M-8368R2

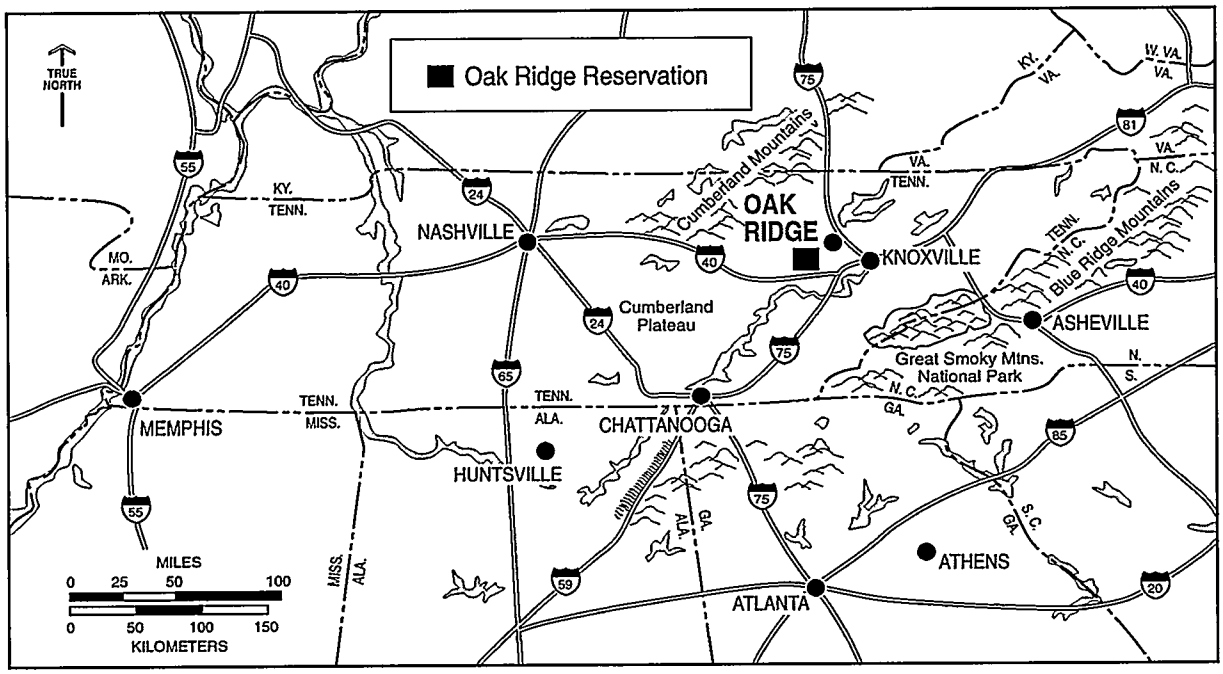

Figure 33. Location of the City of Oak Ridge

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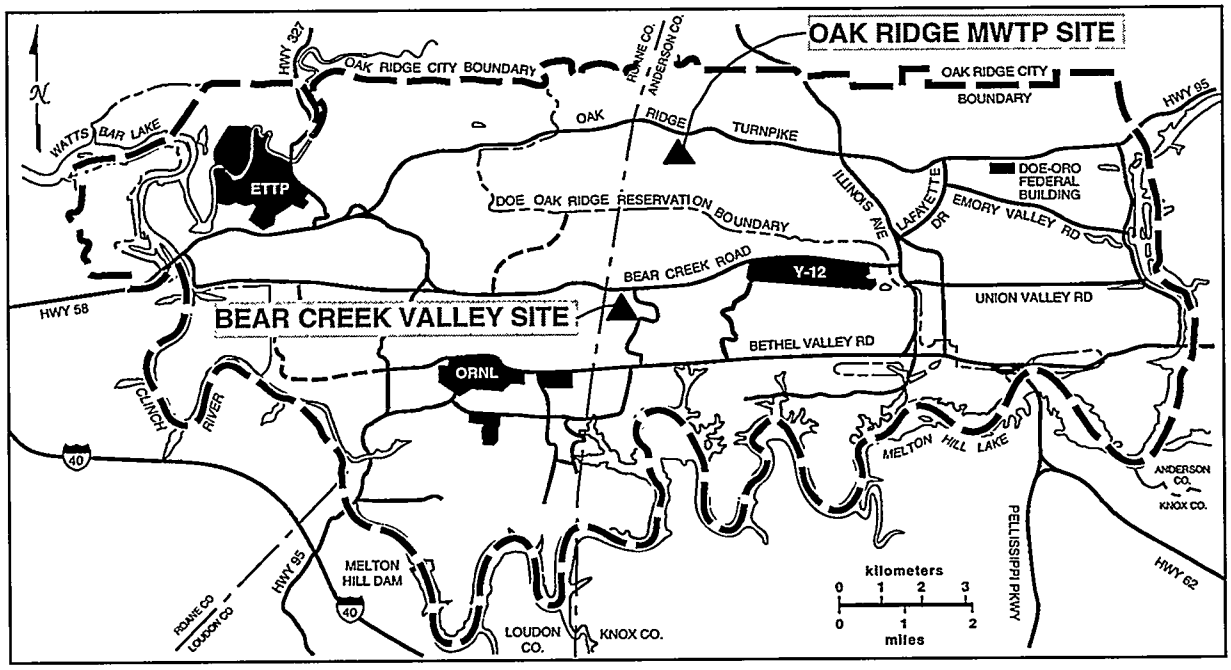

Figure 34. The Oak Ridge Reservation

Y-12 PHOTO 306208

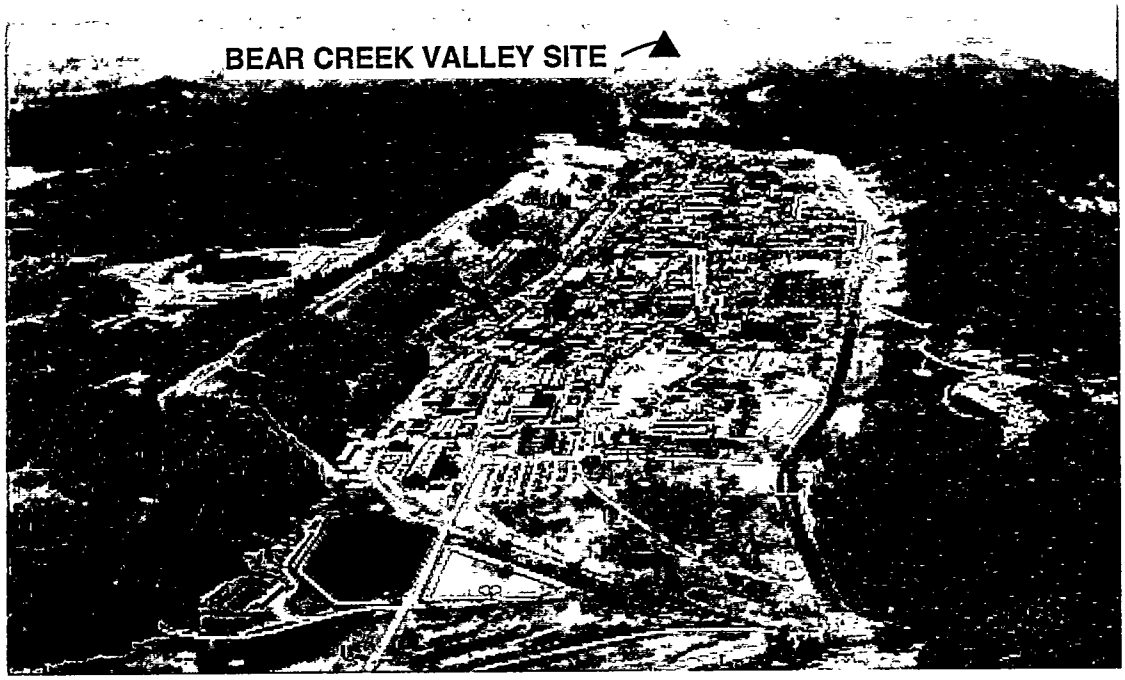

Figure 35. The Oak Ridge Y-12 Plant

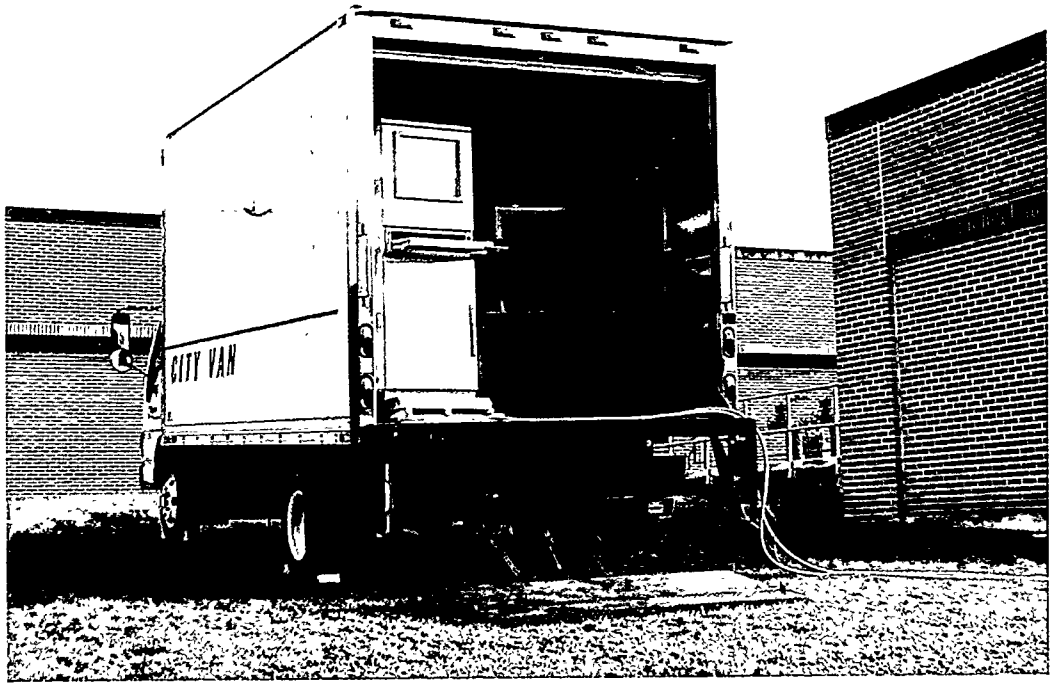

Figure 36. Field Test Unit Installed at Oak Ridge Municipal Wastewater Treatment Plant Effluent and East Fork Poplar Creek Sampling Location

Figure 37. Field Test Unit Installed at Oak Ridge Municipal Wastewater Treatment Plant Influent Sampling Location

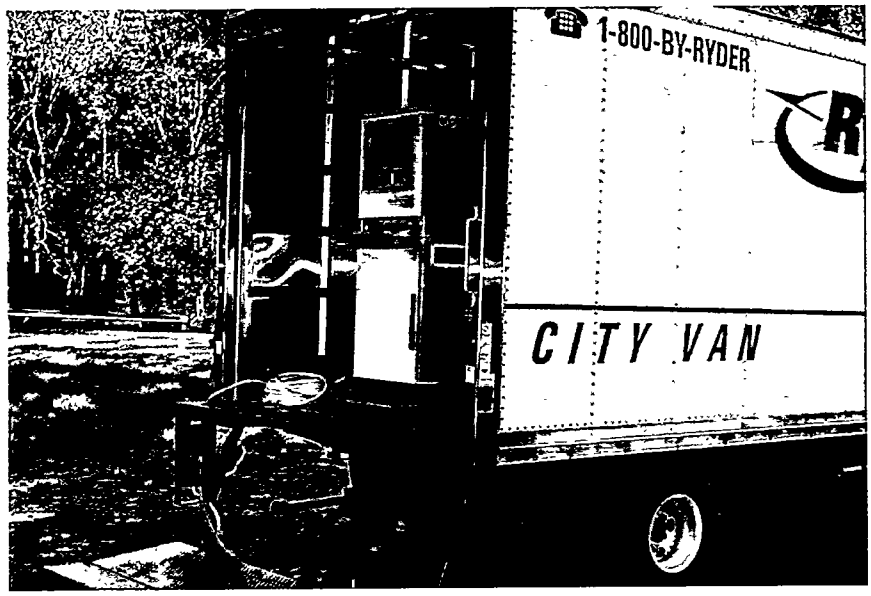

Figure 38. Field Test Unit Installed at Y-12 Bear Creek Valley

2.7.3 Test Results

Two analyses were performed at the EFPC and MWTP effluent using the field test unit. A single analysis using the alpha monitor for liquids was performed at the MWTP influent, the Y-12 BCV SS-5 site, and the Y-12 BCV GW-684 site. The acidity level (pH) of each sample was within normal operating tolerances of the field test unit. Three to four spot samples were taken during the course of almost every field test unit run, to provide repeatability results. Only a single spot sample was taken during the course of the MWTP influent field test run, due to repeated clogging of the sample pre-filter screen, which limited the amount of sample that could be obtained. Complete field test results are provided as Table 6.

TABLE 6

COMPLETE FIELD TEST RESULTS
(Results Expressed as pCi/l)

	KPA	Isotopic-Alpha	AML
MWTP Effluent "A" Sample #1	0.21	-1.4	
MWTP Effluent "A" Sample #2	0.20		
MWTP Effluent "A" Sample #3	0.27	-1.6	
Average, or Field Test Unit	0.22	-1.5	0.49
MWTP Effluent "B" Sample #1	0.23	0.38	
MWTP Effluent "B" Sample #2	0.22		
MWTP Effluent "B" Sample #3	0.22	-1.44	
Average, or Field Test Unit	0.23	-0.53	0.31
MWTP Influent Sample	0.51	-1.5	0.64
EFPC "A" Sample #1	3.7	4.0	
EFPC "A" Sample #2	3.8		
EFPC "A" Sample #3	3.8	1.8	
Average, or Field Test Unit	3.7	2.9	2.3
EFPC "B" Sample #1	3.9	2.1	
EFPC "B" Sample #1 - Duplicate	3.9	4.3	
EFPC "B" Sample #2	4.0		
EFPC "B" Sample #3	3.9	3.0	
Average, or Field Test Unit	3.9	3.1	1.8
BCV GW-684 Sample #1	22	24	
BCV GW-684 Sample #2	22		
BCV GW-684 Sample #3	21		
BCV GW-684 Sample #4	21	28	
Average, or Field Test Unit	21	26	16
BCV SS-5 Sample #1	45	60	
BCV SS-5 Sample #1 - Duplicate	45	62	
BCV SS-5 Sample #2	44		
BCV SS-5 Sample #3	45		
BCV SS-5 Sample #4	44	55	
Average, or Field Test Unit	45	59	13

Test results are summarized in Figure 39 and Table 7, where the various sites have been arranged by measured uranium levels. In addition, the replicate conventional analyses have been averaged to provide an average of either total uranium (KPA) or isotopic (alpha spectroscopy) uranium levels. A general trend is obvious in the figure, in that uranium levels measured by any of the analysis methods tend to increase from lower levels to higher levels looking from left to right across the chart. For example, isotopic uranium levels increase from below the limits of detection in the MWTP effluent and influent, up to the highest levels in the two Bear Creek Valley sites. Consequently, the field test instrument produces analysis results that follow the same trend as the conventional analysis results.

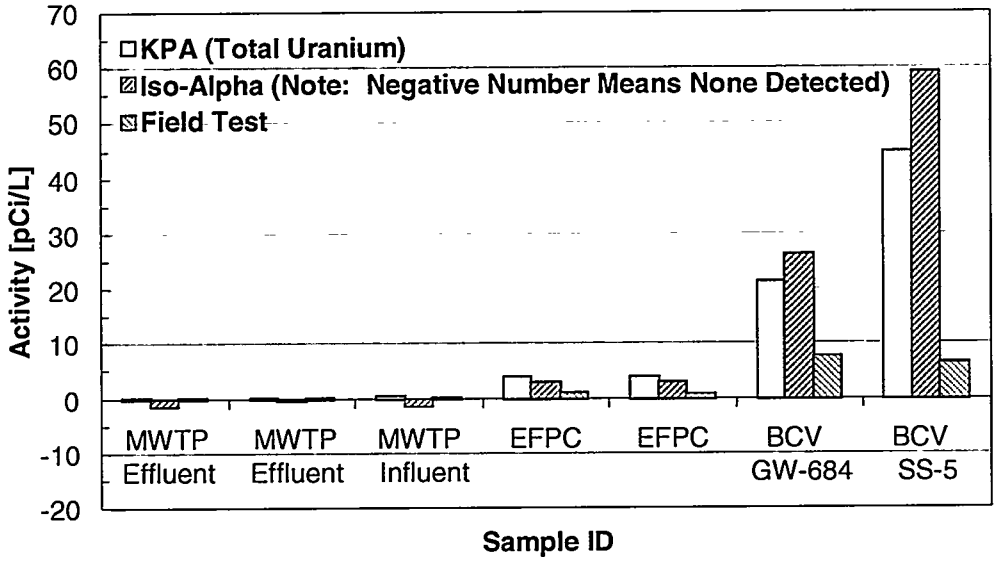

Figure 39. Average Oak Ridge Results

TABLE 7

SUMMARY FIELD TEST RESULTS
(Results Expressed as pCi/l)

	KPA	Isotopic-Alpha	AML
MWTP Effluent "A"	0.22	-1.5	0.49
MWTP Effluent "B"	0.23	-0.53	0.31
MWTP Influent	0.51	-1.5	0.64
EFPC "A"	3.7	2.9	2.3
EFPC "B"	3.9	3.1	1.8
BCV GW-684	21	26	16
BCV SS-5	45	59	13

Closer examination of the figure and data reveals that there are various differences between the various analysis methods.

- The field test instrument is able to produce reliable isotopic results at the lowest uranium levels that were measured, which were 60% above the KPA analyses. As mentioned above, the isotopic uranium analysis was unable to detect any uranium in these three MWTP effluent and influent samples. Consequently, the sample size (0.1 liter) used in the isotopic uranium analysis was not large enough to provide the required sensitivity.

- For the two highest uranium levels, the isotopic uranium analysis produced results that were 27% greater than the KPA method. The field test instrument analysis results were 49% below the KPA test results for these two BCV surface water and ground water samples.

- The KPA test results were largest for the two EFPC surface water samples. The isotopic uranium analysis results were 22% below the KPA analysis, while the field test instrument results were 47% below the KPA analysis for these two samples.

The general trends that are evidenced by these observations are that:

- Analysis results from all three methods can be ranked from lower levels to higher levels. From lowest to highest, this average ranking is as follows:
  - Oak Ridge Municipal Wastewater Treatment Plant effluent – 0.14 pCi/l
  - Oak Ridge Municipal Wastewater Treatment Plant influent – 0.28 pCi/l
  - East Fork Poplar Creek – 2.6 pCi/l
  - Y-12 Bear Creek Valley groundwater well GW-684 – 18 pCi/l
  - Y-12 Bear Creek Valley surface water site SS-5 – 37 pCi/l

- Relative to the KPA total uranium analysis method, the isotopic uranium analysis method produces results that are biased low at low uranium levels (below 10 pCi/l), and biased high at higher uranium levels (above 10 pCi/l).

- Relative to the KPA total uranium analysis method, the field test instrument produces results that are biased high at low uranium levels (below 10 pCi/l), and biased low at higher uranium levels (above 10 pCi/l).

3. ACHIEVEMENTS

With the successful completion of this program's Optional Phase II, the Thermo Power on-line, real-time Alpha Monitor for liquid streams has proven to be not only a valuable laboratory tool, but also has demonstrated the ability to become the first known field-tested instrument capable of measuring alpha-emitting radionuclides in water at parts-per-trillion (femto Curies per liter) levels. As it is an on-line real-time instrument, this accomplishment takes on even more significance. In particular, the accomplishments to date include:

- The Alpha Monitoring Instrument was successfully field demonstrated on water 100X below the Environmental Protection Agency's proposed safe drinking water limit – down to under 1 pCi/l.
- The Alpha Monitoring Instrument successfully analyzed isotopic uranium levels on a total of five different surface water, process water, and ground water streams, the primary water types of interest to the Department of Energy (DOE).
- The Alpha Monitoring Instrument was successfully tested on the DOE's Oak Ridge Reservation, at two test locations in the Y-12 Site's Bear Creek Valley.
- Extended the isotopic detection limit of the Alpha Monitor to 10 parts per trillion natural uranium (15 fCi/l), or 1/2000th the EPA's drinking water limit of 20 ppb, which is well under the program's goal of 30 pCi/l.
- Proven that the Thermo Alpha Monitor for Water will respond to 20 ppb natural uranium (30 pCi/l) in under 30 minutes, well under the program's goal of a 1- to 12-hour instrument response time.
- Isotopically detected 1.5 pCi/l (2 ppb) total uranium in Carlisle, Massachusetts groundwater comparing quite favorably with 1 pCi/l levels of soluble uranium that were measured by conventional analysis methods.
- Isotopically detected thorium (^{232}Th) at 100 parts per trillion (17 fCi/l), as well as lesser amounts of thorium daughters and uranium.
- Demonstrated a linear dynamic range over greater than six decades of concentration, from 10 parts per trillion (15 fCi/l) to 10 parts per million (15 pCi/l) natural uranium, including levels of natural thorium between 100 parts per trillion (17 fCi/l) and 1 part per million (172 pCi/l).
- Confirmed that a simple de-ionized water wash is usually capable of removing residual radioisotopes to acceptably low background levels between consecutive, nonrepetitive analyses.
- Confirmed that a 5% nitric acid flush is capable of removing heavy deposits of residual radionuclides from the instrument's wetted parts, producing acceptably low background levels between consecutive, nonrepetitive analyses.

4. REMAINING ISSUES

The remaining technical and other issues in the development of the on-line, real-time Alpha Monitor for liquid streams can be summarized as follows:

- Incorporate user feedback into an improved design, using the lessons learned from the Optional Phase II field tests.

- Determine the endurance characteristics of the Thermo Alpha Monitor for Water when it is used by non-Thermo Power personnel in a series of extended field tests; incorporate user feedback into an improved design.

- Improve our understanding of the underlying chemistry of the Alpha Monitor, through additional laboratory and/or field tests, in order to develop a peer-reviewed and agency-approved method for analyzing water streams.

- Continue the patenting of the Thermo Alpha Monitor for Water technology on behalf of the DOE.

- Disseminate the technology and utility of the Alpha Monitor within the radiochemistry, DOE Environmental Management, and other related fields in order to maximize knowledge of and interest in the technology.

- Pursue the commercialization of the Thermo Alpha Monitor for Water for liquid samples while pursuing the development of related spin-offs, such as on-line, real-time alpha monitoring of air and gas streams.

5. CONCLUSIONS

Thermo Power Corporation has proven the technical viability of an on-line, real-time alpha radionuclide instrument for aqueous sample analysis through laboratory and initial field tests of the instrument. The instrument has been shown to be isotopically sensitive to extremely low (ten parts per trillion, or femto Curies per liter) levels of a broad range of radioisotopes. Performance enhancement and other scaling data obtained during the course of this investigation have shown that on-line, real-time operation is possible, with a sub 30-minute response time analyzing 20 ppb (30 pCi/l) natural uranium.

Now that these initial field tests in Oak Ridge, Tennessee have been successfully completed, Thermo Power plans to conduct comprehensive field tests of the instrument. The purpose of these endurance tests will be to determine the endurance characteristics of the Thermo Alpha Monitor for Water when it is used by non-Thermo Power personnel in a series of one or more extended field tests. Such endurance testing is the vital next step towards the commercialization of the Alpha Monitor. Subsequently, it will be possible to provide the DOE with an instrument that has the capability of obtaining rapid feedback about the concentrations of alpha-emitting isotope contamination in effluent water streams (Subsurface Contaminants Focus Area). It will also be useful for process control of remediation and D&D operations such as monitoring scrubber/rinse water radioactivity levels (Mixed Waste, Plutonium and D&D Focus Areas).

6. POSTSCRIPT

Ongoing discussions confirm the desire of the Department of Energy's (DOE) Oak Ridge Operations to conduct additional testing. Subsequently, they plan to deploy multiple alpha monitors for liquids in the Bear Creek Valley (BCV) to assist in the required decades-long monitoring of the surface and groundwater. To that end, Oak Ridge personnel have expressed a great interest in conducting a second field test at the BCV later this year, to be followed by a more extensive field test. Exact details, including site cost-sharing, are being finalized.

A strong expression of interest in field testing the technology is continuing from personnel at the TA-50 Radioactive Liquid Waste (RLW) treatment plant at DOE's Los Alamos National Laboratory (LANL). The alpha monitoring instrument would be used to help meet the requirements of DOE Order 5820.2A, Chapter III. In brief, all waste water that is sent to any DOE radioactive liquid waste treatment plant must be characterized by the waste generator, then characterized again by the RLW treatment plant to verify the composition of their influent. Similarly, the clean effluent from any RLW treatment plant must be characterized prior to its discharge. In addition to facilitating compliance with DOE Order 5820.2A, deploying the alpha monitor for liquids at LANL would allow the RLW treatment plant to optimize the plant's operation, by diverting out of specification incoming waste water (or outgoing treated water) to a tank farm. Details of this field test and potential deployment will be finalized after LANL completes an equipment upgrade in the RLW treatment plant.

APPENDIX 1

MERITS OF TAM TECHNOLOGY

TAM, the on-line, real-time monitor for direct measurement and identification of alpha-emitters in aqueous streams, meets real DOE needs at a large number of sites. The new technology on which the monitor is based has been demonstrated in the laboratory and is the only technology capable of providing an on-line, real-time monitor with the great sensitivity required for very low activity levels. The monitor will provide continuous assay and will be of use in both:

- Monitoring of effluent water streams from DOE sites to ensure compliance with regulatory limits and

- Process control in D&D and site remediation processes, such as monitoring mixed-waste thermal treatment scrubber/rinse water radioactivity levels, soil washing, and wastewater treatment for off-site discharge.

Specific merits of the on-line, real-time monitor are discussed below.

A1.1 PERFORMANCE

Because of the very short range of alpha particles in liquids (40 micro meters), this new technology is the only approach that can rapidly identify and quantitatively assay alpha-emitters in aqueous streams. Further, the analysis method has great sensitivity and very low background and can be used to assay radionuclides at very low activity levels. The new instrument, with associated flow and counting equipment, permits on-line, real-time, automated monitoring of aqueous streams for alpha-emitting radionuclides over a very wide range, for natural uranium from less than 1 part per trillion (about 1 femto Curie per liter) to several hundred ppm's (100 ppm's □130,000 pCi/liter). The response time is, of course, faster for higher concentrations. Radionuclides can be detected at short times, with readily observable alpha peaks evident from the instrument at 10 counts per peak, corresponding to an instrument cycle time of five minutes at 600 ppb and 21 minutes at 1.0 ppb U. The statistical precision of the assay with 10 net counts in a peak is about ± 40%. The required sampling time and total count time can be varied, depending on the accuracy required in the detection and assay. For example, for 1.0 ppb U, the instrument cycle time required to achieve ± 15% accuracy (100 net counts) is 30 minutes, a factor of 1.4 higher than the above time, and ± 5% accuracy (1,000 net counts) is a factor of 5.8 higher. However, 10 net counts in a peak is sufficient to clearly and positively detect and identify a radionuclide and to provide a ± 40% estimate of its concentration.

The proposed on-line, real-time instrument provides continuous information on the aqueous stream concentration at the site. With the conventional approach of collecting a sample, preserving the sample prior to shipment, shipping to a production analytical laboratory,

separating the radionuclides from the water and plating them onto a planchet, counting the planchet, reducing the data, and transmitting the results to the requestor, several days up to weeks usually pass between collection and receiving the results. With the on-line, real-time monitor, results are available continuously, on-site and almost immediately. The conventional approach gives the concentration only at one specific time for each sample, with costs restricting the samples to infrequent intervals, often weekly or even quarterly. The concentration in between samples is not known. The continuous and immediately available data will be of great benefit in the efficient and effective operation and remediation of DOE sites, both for ensuring that water streams leaving DOE sites do not exceed regulatory limits for alpha-emitting radionuclides and for control of D&D and remediation processes, including mixed-waste thermal treatment scrubber/rinse water radioactivity levels monitoring.

A1.2 COST SAVINGS

The proposed on-line, real-time monitor will be cost-effective, relative to the use of conventional laboratory analyses, in addition to providing continuous rather than intermittent concentrations. The cost for conventional analyses has restricted the number of samples analyzed to date to less than a desirable level in many instances. As an example, 48 samples from Upper Bear Creek at the Y-12 plant at Oak Ridge were analyzed over 1991 with the following uranium concentrations:

Concentration, ppb for 48 Samples		
Maximum	Minimum	Average
848	98	224

A large variation is evident, leaving open the question of how the concentrations varied between the samples, which were taken at an average of one sample every 7.6 days. More frequent sampling would clearly be useful.

The cost savings of the new monitor is dependent upon the sampling frequency. An initial investment for the monitor, estimated at $25,000, is required. Some labor is required for operation, maintenance, and tracking/evaluation of results. With the conventional approach, each sample has a catalogue or contract cost by the laboratory, typically $125 per sample for an isotopic analysis. The overhead burden of site labor costs for collecting the sample, shipping the sample to the laboratory, and tracking/evaluation of results must be added to this conventional cost. For analysis with TAM, costs include those for operating supplies (film and de-ionized water), replacement parts (primarily detectors), and site overhead (an average of eight hours per week for replenishing supplies, calibrating and maintaining the instrument).

As illustrated in the following table, at a sampling rate as low as once per day (by conventional means), the proposed instrument would save almost $60,000 annually and pay for itself in five months.

Conventional Analysis

Sample Rate (per day)	1	6
Laboratory Cost at $100/Sample	$36,500	$219,000
Site Overhead at $200/Sample	$73,000	$438,000
Supplies	Negligible	Negligible
TOTAL ANNUAL COST	$109,500	$657,000

TAM, the On-Line, Real-Time, Automated Monitor

Sample Rate (Films per day)	1	6
Operating Supplies	$18,250	$109,500
Replacement Parts (Primarily Detectors)	$5,000	$5,000
Site Overhead at $600/Week (8 Manhours/Week)	$31,200	$31,200
TOTAL ANNUAL COST	$54,450	$145,700
SIMPLE PAYBACK PERIOD	5.4 months	0.6 months

If more frequent sampling by conventional means were desired, the cost benefits would be even more dramatic, since the cost of the on-line instrument remains constant. In addition, TAM can provide detailed information on the variation of the effluent concentration throughout the day.

Where frequent samples are not required, the instrument can be used to monitor several streams in sequence. It can also be modified to analyze batch water samples. TAM will thus be cost-effective, even where only limited samples are thought necessary and multiple streams are to be assayed.

In addition to these direct cost savings, the on-line, real-time quality of the data obtained will have important secondary cost savings. In remediation operations, immediate availability of data on process operations speeds up the remediation operations, thereby reducing costs. In addition, continuous monitoring of process streams and effluent waters will eliminate/mitigate serious accidental release of radionuclides, particularly off-site, and prevent expensive clean-up resulting from such accidental releases. In effect, the on-site personnel will have much more data available almost immediately, and this increased knowledge will facilitate and reduce the costs of remediation operations.

A1.3 REDUCING PUBLIC AND OCCUPATIONAL HEALTH RISKS

The public risk will be greatly reduced by continuously monitoring all effluent streams for uranium concentration, thereby ensuring that no streams which exceed the regulatory limit leave the site. Even short excursions to high concentrations will be rapidly detected and can be used to immediately divert the stream to a holding area and/or warn of a problem. With the current approach, one sample of the total mixed effluent per day is taken and analyzed. If some problem on-site resulted in high levels in the effluent, it could be days before the high levels were detected. The on-line, real-time monitoring will also increase the public's confidence that the remediation is being performed properly and without risk, minimizing public resistance to remediation operations and the DOE.

The monitor will have a smaller effect on reducing occupational health risks than in reducing risks to the public. Handling of samples will be minimized by the automated, on-site monitor. The solutions required for the monitor are relatively nonhazardous, with the most hazardous being dilute hydrochloric acid, which is less hazardous than many cleaning materials handled in the home.

A1.4 REDUCING ENVIRONMENTAL IMPACTS

Application of the on-line, real-time monitor to effluent waters will greatly reduce the possibility of off-site contamination by unexpected excursions of high alpha-emitting radionuclide concentrations in the effluent waters leaving the site. Such continuous and real-time monitoring will be particularly beneficial during remediation actions when the site is disturbed and unexpected releases might occur. TAM will ensure that no regulatory limits are exceeded.

A1.5 IMPROVING CLEAN-UP AND WASTE MANAGEMENT PROCESSING OPERATIONS

When used for process control, as in monitoring mixed-waste scrubber effluent, soil washing, or wastewater treatment, the on-line, real-time monitor will facilitate operating the process at peak effectiveness and minimize the effluent concentrations. The on-line data will also be useful in preventing unexpected releases due to process failures, such as bleed-through of over-loaded ion exchange columns.

On-line, real-time instrumentation is an essential base for modern, continuous process control. At the Fernald site, for example, use of the monitor for continuous uranium concentration measurements of aqueous process streams will be very useful in both soil washing and at the Advanced Wastewater Treatment Plant for control of the process and in identifying impending process failures before they occur, so that corrective actions can be taken. Without this U monitor, the plant operators will be operating in the dark, with only historic data rather than current data.

A1.6 REDUCING THE TIME REQUIRED FOR REMEDIATION AND/OR WASTE MANAGEMENT/PROCESSING

The continuous, on-line, real-time data will give the remediation/process operators the information needed for optimum performance. This current information will eliminate wasted time and effort due to delays from waiting for conventional analyses, or due to remediation/process actions not properly performed, which must be reworked or repeated. Operations always go smoother and faster when one has immediate feedback, rather than having to guess based on old data and analyses.

A1.7 MINIMIZING GENERATED OR SECONDARY WASTES

The primary waste from operation of the monitor is dilute acid, which can be neutralized with basic materials, such as limestone, and converted to innocuous and non-hazardous material. The quantities of materials required are small and can be recycled, i.e., used for multiple chemical treatment and cleaning cycles before disposal is required. No samples are taken which must be disposed of since a slip-stream of the stream being monitored flows continuously through the detector and back to the stream downstream of the monitor. The radionuclides absorbed on the film are adherent, allowing for safe and stable archiving of the film for QA/QC purposes.

We believe the disposal problems for the monitor will be less than those for the conventional analytical approach, where samples are taken and shipped to a central laboratory for analysis. In our laboratory development work, the only waste sent to a disposal service is the solid basic material used for neutralization of the acids, even though the waste was suitable for the local landfill based on current regulations.

A1.8 ABILITY TO MEET REGULATORY REQUIREMENTS

As described in Section 2, the environmental impact will be minimized by use of the monitor, with the primary waste being a small quantity of solid basic material used for neutralizing acids.

The monitor has great sensitivity, having the ability to perform measurements of alpha-emitting radionuclide concentrations at levels far below proposed regulatory limits.

The quality of the data will be excellent. The monitor includes a standard calibration solution, which is periodically used to calibrate the monitor (on the off-line instrument) and to ensure proper operation. Periodic analyses by conventional methods will be used to ensure that the monitor is operating satisfactorily and providing accurate analyses, with the monitor providing continuous measurements between conventional samples. Field experience with the monitor on particular streams will eliminate the need for these "check" samples, as the monitor becomes an accepted and standard method.