

1.2 Pulsed Gamma Neutron Activation Analysis (PGNAA) System for the Assay of RCRA Metals in Mixed Waste

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Abstract

The presence of certain metals defined as hazardous by the Resource Conservation and Recovery Act (RCRA) in mixed-waste drums can seriously limit the operation of waste treatment processes. Excessive concentrations of mercury, cadmium and lead in the process feed may either result in off-gas emission concentrations which exceed regulatory limits and/or interfere with the treatment process control.

Pulsed gamma neutron activation analysis (PGNAA) shows great promise as a technique for the nondestructive assay (NDA) of RCRA metals in sealed containers, and a program was undertaken to design, build and demonstrate a field-deployable PGNAA prototype capable of characterizing the RCRA metal content of 55-gallon drums containing mixed-waste sludge. The focus was on mercury, cadmium and lead since these elements are of primary concern in mixed waste.

Fabrication of the prototype was completed in March of 2001. The prototype was then calibrated for the detection of mercury using fifty-five-gallon drums of a sludge-waste surrogate (concrete) containing known amounts of mercury. Following the calibration work, the system was shipped to the Argonne National Laboratory - West site, where it was employed to assay drums of inorganic mixed-waste sludge as part of the demonstration of the technology. Data obtained from the calibration of the system and from the demonstration measurements will be presented and discussed.

PGNAA System for the Assay of RCRA Metals in Mixed Waste: A Review

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1 INTRODUCTION

Nondestructive technologies capable of detecting metals defined as hazardous by the Resource Conservation and Recovery Act (RCRA) are needed for the assay of mixed-waste drums. These hazardous constituents can potentially affect operations in a waste treatment system or disposal facility. The nondestructive assay (NDA) technologies will be employed to screen out drums containing concentrations of RCRA metals that exceed levels known to have a detrimental impact on treatment and/or disposal activities. In addition, NDA analyses can confirm existing process knowledge on the waste inventory in the drums.

In Fiscal Year 1996, a performance test sponsored by the Department of Energy's (DOE) Mixed Waste Focus Area was conducted to evaluate the capabilities of Prompt Gamma Neutron Activation Analysis (PGNAA) systems for the NDA of RCRA metals.¹ Up to that point, no practical NDA method had been demonstrated for the characterization of the hazardous components in mixed waste, although several techniques were being developed or already existed for the NDA of the radioactive components of mixed waste containers. The performance test was the first step of an effort to bridge this technology gap.

A relatively mature technology that is typically employed for bulk analysis in areas such as *in situ* well logging, process control and explosives detection,² PGNAA is based on the detection of prompt gammas emitted as a result of neutron interactions with the constituent nuclei of the sample under analysis. The principal components of a conventional PGNAA system include a neutron source, a gamma-ray detector, nuclear signal-processing electronics, and hardware / software for gamma spectroscopy. A detailed description of the technique can be found in Reference 2.

PGNAA showed merit for the NDA of RCRA metals in mixed-waste containers for the following reasons:

- Both neutrons and gamma rays can penetrate the walls of most containers (ex: 55-gallon drums) without significant attenuation, allowing for the characterization of the internal contents of a container.

- PGNAA is in theory well-suited for the detection of the important RCRA metals mercury and cadmium due to the high thermal neutron capture cross section and prompt gamma yield of these two elements.
- Since PGNAA has the ability to assay a large volume in a relatively short time, the characterization of an entire container in a timely and cost-efficient manner becomes feasible.
- In contrast to chemical sampling, the risk of creating additional waste during analysis is eliminated since the use of PGNAA does not generate secondary waste.
- PGNAA systems can be readily configured for deployment in the field.

The DOE performance test program invited private companies with existing PGNAA capabilities to participate in a study of the viability of PGNAA for the NDA of mercury, cadmium and lead. Participants were requested to perform PGNAA measurements with samples consisting of a homogeneous distribution of these metals in a surrogate waste matrix. The samples were contained in eight-gallon drums. Participants were to report the expected lower limit of detection (LLD) of each metal for real-time counting periods of 600 s and 2000 s.¹ Furthermore, in order to verify the accuracy of their measurements, participants were asked to report the concentration of “blind” samples (i.e. drums whose concentrations of Hg, Cd and Pb were unknown to the participants *a priori*).

One of the participants in this study, the Westinghouse Science & Technology Department (WSTD), used a laboratory PGNAA system to demonstrate detection of the three metals at concentration levels, in parts per million (ppm) by weight, of 487 for Hg, 485 for Cd and 9927 for Pb.³ Based on these measurement results, the projected LLDs for a 2000-s counting time were 115 ppm for Hg, 9 ppm for Cd and 4400 ppm for Pb.

The results obtained by WSTD confirmed that PGNAA was a promising method for the NDA of RCRA metals in mixed-waste containers. Consequently, a two-phase program was initiated to evaluate, build and demonstrate a PGNAA prototype capable of characterizing the RCRA metal content of contact-handled (CH) mixed-waste sludge contained in 55-gallon drums. In the first phase, potential interfering mechanisms presented by typical mixed-waste sludge constituents were studied through a combination of computational modeling and experimental testing with the laboratory (eight-gallon) system. Computational modeling was also utilized to optimize the hardware configuration of the PGNAA system for enhanced sensitivity in the analysis of 55-gallon drums. The results obtained from these studies were then used to prepare the design specifications for a field-deployable, 55-gallon drum assay prototype. This system was built, tested and demonstrated in the second phase of the program.

In addition to WSTD, other program participants were The Pennsylvania State University, the Idaho National Engineering and Environmental Laboratory, Canberra Industries (Phase 1 only) and BNFL Instruments, Inc. (Phase 2 only).

2 TECHNOLOGY

2.1 Description

The WSTD approach to PGNAA employs a pulsed 14-MeV (deuterium-tritium) neutron generator as the neutron source. Gamma-ray energy spectra are acquired with a high-purity germanium (HPGe) detector during pulsing as well as between pulses. Typically, four sequential time domains (or groups) are used, with the first group concurrent with the neutron pulse and the other three groups spanning the period between the end of one pulse and the beginning of the next. The time groups are structured so that fast neutron-induced reactions are dominant in Group 1, which is concurrent with the neutron pulse; thermal neutron-induced reactions dominate Groups 2 and 3, which occur on a time scale governed by the mean thermal neutron capture lifetime; and decay events of neutron activation products that have half lives ranging from milliseconds to minutes are prominent in Group 4. With this approach, prompt gamma rays originating from fast and thermal neutron capture reactions as well as decay gamma rays emitted by short-lived activation products can be detected with superior signal-to-background ratios. The measurements of Hg and Cd rely on the detection of thermal neutron-induced prompt gamma rays in groups 2 and 3, whereas lead measurements are based on the detection of the 1063-keV gamma ray emitted during the decay of ^{207m}Pb (half life = 0.81 s; a product of fast neutron-induced reactions in lead) in group 4. Reference 3 provides a more detailed description of the WSTD PGNAA system.

2.2 Application to Mixed-Waste Assay

As mentioned in Section 1, a laboratory PGNAA system designed and built by WSTD successfully demonstrated the detection of Hg, Cd and Pb in a surrogate waste matrix. Prior to designing and building a PGNAA prototype for the NDA of actual CH mixed-waste sludge in 55-gallon drums, several potential interference effects from mixed-waste sludge constituents on PGNAA system performance were evaluated. These included the effect of fissile isotopes such as ^{235}U and ^{239}Pu on interrogating neutron flux, background gamma radiation from radioactive components of the mixed waste (U, Pu and ^{241}Am nuclides) and background neutron radiation caused by the interaction of ^{241}Am alpha particles with matrix constituents (referred to as (α, n) reactions). The effects of matrix density, boron content and chlorine content were also studied.

The methodology to perform the study of these interference mechanisms has been reported elsewhere⁴⁻⁷, and only the main results are summarized here: The presence of U and Pu nuclides was found not to have a significant effect on the detection of Hg, Cd and Pb by PGNAA.^{4, 5} In the case of ^{241}Am , it was shown that perturbation of the PGNAA interrogation neutron flux from (α, n) reactions was at most 2.5%, while the interference effects from ^{241}Am decay gamma rays on the PGNAA Hg LLD ranged from negligible to a maximum of 18% over a range of ^{241}Am concentration levels that would include 95% of the CH mixed-waste sludge inventory.^{6, 7} The impact of waste density on photon transport and thermal neutron flux levels in a PGNAA system was found to be small over the expected density range of sludge waste.⁷ Neutron flux perturbation arising from the

presence of chlorine is also expected to be negligible for mixed-waste sludge.⁷ As expected, boron-10, by virtue of its large thermal neutron absorption cross section, significantly reduced the thermal neutron flux levels in the waste sample and may have a detrimental effect on PGNAA detection sensitivity when present in the waste matrix. This effect is common to most NDA systems based on neutron interrogation, and can also be expected from other constituents or contaminants (such as cadmium) that have large neutron absorption cross sections.

The overall conclusion drawn from the interference studies was that the radioactive, physical and chemical properties of CH mixed-waste sludge in most 55-gallon drums do not pose significant problems for the use of PGNAA to assay the drums.

2.3 Prototype Design and Fabrication

The 55-gallon drum PGNAA prototype was designed with similar pulsing and timing capabilities as those of the laboratory system. In order to optimize the mechanical design of the prototype, a computational model of a PGNAA system was developed.⁷ Studies with this model identified changes to the system configuration and to the detector shield that were implemented in the final design of the system. The model was also used to study the system's ability to detect inhomogeneous contaminant concentrations along the drum axis and to predict LLD values for Hg.

The final design of the 55-gallon PGNAA prototype was prepared by BNFL Instruments, Inc. (BII), with input from WSTD and the DOE's Transuranic and Mixed Waste Focus Area (TMFA). BII built the prototype at its facility in Albuquerque, New Mexico. The salient features of the system are

- a D-T accelerator source, with a maximum output of 10^8 n/s,
- a 40%-efficiency reverse-electrode (N-type) coaxial germanium gamma detector,
- the assay chamber, consisting of an inner compartment with 2-inch thick polyethylene walls and an outer graphite shell with a 4-inch wall thickness,
- the drum turn/lift table assembly consisting of three jackscrews for lift, a rotating base with roller balls mounted in it, and a drum platen,
- high count-rate signal-processing electronics, including four multichannel buffers for data acquisition, an ultra-high rate spectroscopy amplifier for use with the germanium detector, and a four-channel digital delay generator to correlate data acquisition with neutron generator pulsing, and
- a personal computer which provides operator interface for control of the mechanical functions of the turn/lift assembly, operation of the neutron generator, and acquisition of gamma data.

The prototype system is shown in Figure 1. Testing and calibration of the prototype after fabrication was carried out at the WSTD site in Pittsburgh, Pennsylvania. Following calibration, the prototype was transferred to the Argonne National Laboratory- West (ANL-West) in Idaho, where it was demonstrated for the assay of mercury in inorganic mixed-waste sludge.



Figure 2. PGNAA 55-Gallon Drum Prototype

3 RESULTS

3.1 Calibration

Calibration of the PGNAA prototype was performed using four 55-gallon drums containing a sludge-waste surrogate (concrete) prepared and supplied by the TMFA. The surrogate waste in three of the drums contained known concentrations of mercury (133 ppm, 424 ppm and 1345 ppm) while the fourth drum contained only the blank waste, which was assumed to have a Hg concentration of 0 ppm.

The drums were assayed in the PGNAA prototype, and a calibration function relating the intensity of the Hg 368-keV prompt gamma ray to concentration was derived from the measurement data. This function was found to be linear in the 0 - 1345 ppm range of Hg concentration.⁸

3.2 Mixed-Waste Assay Results

Eight 55-gallon drums of inorganic sludge waste were assayed with the PGNAA prototype system at the Hot Fuel Examination Facility of ANL-West. The sludge waste in these drums was produced by the secondary wastewater treatment process at Rocky Flats. These waste drums were members of a collection of inorganic sludge (IDC001) waste containers that had been sampled and analyzed destructively via chemical analysis. The drums selected for the PGNAA measurements had mercury concentrations ranging from 0 to 120 ppm. Transuranic (TRU) nuclides were present in all of the eight drums.⁸

Comparison of the PGNAA NDA measurement results with the existing chemical analysis data showed that the prototype system could reliably detect Hg at concentrations in excess of 60 ppm based on a one-hour assay.⁸ The expected LLD of the system for Hg, derived from calculations and experimental testing with surrogate samples, was of the order of 100 ppm. Thus, the Hg measurement results obtained from the NDA of actual waste drums are consistent with the projected performance of the PGNAA prototype.

It should be noted that the various components of the PGNAA prototype, including the drum turn/lift table assembly, neutron generator, gamma detector and signal-processing instrumentation, performed well throughout the demonstration at ANL-West. All measurements were completed within the schedule allocated for the demonstration.

4 FUTURE ACTIVITIES

The measurement campaign at ANL-West demonstrated the detection capabilities of PGNAA for mercury. It would be desirable to evaluate the detection limits of the PGNAA prototype system for other RCRA metals. Since experimental PGNAA data from lead and cadmium measurements have already been acquired, albeit with a laboratory system, the prototype's detection limits for these two elements can be derived. Modeling calculations are in progress to derive detection limits for other RCRA metals. Experimental measurements are also planned to verify calculation results for a limited number of these other RCRA metals.

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