

Feasibility Study of X-ray K-edge Analysis of RCRA Heavy Metal Contamination of Sludge Packaged in Drums

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Summary

A study has been completed to assess the capabilities of X-ray K-edge analysis in the measurement of RCRA metal contamination of sludge packaged in drums. Results were obtained for mercury and lead contamination. It was not possible to measure cadmium contamination using this technique.

A typical measurement accuracy of better than 10% was achieved for the mercury- and lead-contaminated drums for concentrations ranging from 500-20,000 mg/kg, and for a measurement time of 20 minutes or less. No false positive signals were observed.

However, if one extrapolates these results on 8-gallon simulated waste drums to the more common 55-gallon drums stored at various DOE sites, a note of caution is in order. A single K-edge measurement samples only a small volume of sludge within 1 cm of the wall of the drum; the low-energy X-rays used in this analysis cannot penetrate the full thickness of a waste drum. Thus it is necessary to assume that the heavy metals are homogeneously distributed in the sludge. For larger diameter (55-gallon) drums, the region near the wall that can be penetrated will be even smaller, making the analysis more difficult.

In cases where uniformity of the sludge can be assumed, X-ray K-edge analysis can provide a quick, accurate measurement of heavy-metal contamination. This method should work even better for low-density wastes, where X-ray absorption is not as great. It should be noted that the K-edge technique can also be used to quantify radioactive contaminants such as thorium, uranium, and plutonium.

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Introduction

There are currently in storage substantial volumes of mixed waste resulting from over 40 years of nuclear weapons production at Department of Energy sites. For example, it is estimated that there are more than 135,000 55-gallon drums of transuranic (TRU) waste at INEEL[1]. Much of this material is in the form of sludge containing RCRA-identified heavy metals such as cadmium, mercury and lead. Plans are being developed for disposal of this waste in a permanent repository such as the Waste Isolation Pilot Plant (WIPP). Prior to disposal, it must be verified that these wastes meet the Waste Acceptance Criteria for the storage site.

The baseline method for analyzing RCRA metal content is to open the drum and withdraw a sample for laboratory analysis. This is obviously very time consuming and increases the risk to workers. Tests have been performed on noninvasive inspection technologies based on prompt gamma neutron activation analysis that offer the potential for faster analysis and reduced risk[1,2].

X-ray K-edge analysis is an alternative noninvasive analysis technique that can be used to quantify heavy metal contamination. The purpose of this study is to determine the sensitivity of X-ray K-edge analysis for measuring mercury and lead contamination in drums of sludge. In this report we describe the method used to evaluate the X-ray K-edge technique and present the results from a series of blind measurements on simulated waste drums. We conclude with a discussion of the feasibility of applying this analysis to the DOE legacy waste.

Method

Three identical sets of 14 simulated waste drums were prepared for Lockheed Martin Idaho Technologies Company by Rust Geotech (for details see Appendix A in Ref. 2). The simulated waste consisted of a mixture of water, sand, sodium nitrate, and Portland cement spiked with various amounts of sulfides of the RCRA metals cadmium, mercury and lead. These drums were used to evaluate different prompt gamma neutron activation analysis systems in a series of blind tests[1,2]. Seven of the drums were treated as calibration drums with the contents being revealed to the vendors. One drum contained no RCRA metals, and the remaining six drums were treated as unknowns with their contents to be determined by the vendors.

One set of these surrogate waste drums was shipped to Ames Laboratory for the purpose of determining the feasibility of using an X-ray K-edge technique to measure RCRA heavy metal contamination. The K-edge inspection technology is based on measurement of the energy spectrum of an X-ray beam transmitted through the sample. The X-ray source is an industrial X-ray tube, and the detector is a High Purity Ge (HPGe) crystal. Both source and detector are collimated to define a narrow (<1mm dia.) beam used to probe the sample[3,4]. The sensitivity of the measurement is determined primarily by the data acquisition time.

Figure 1 is a photograph of the setup used in these tests, and Fig. 2 shows a schematic diagram of the components in the system.

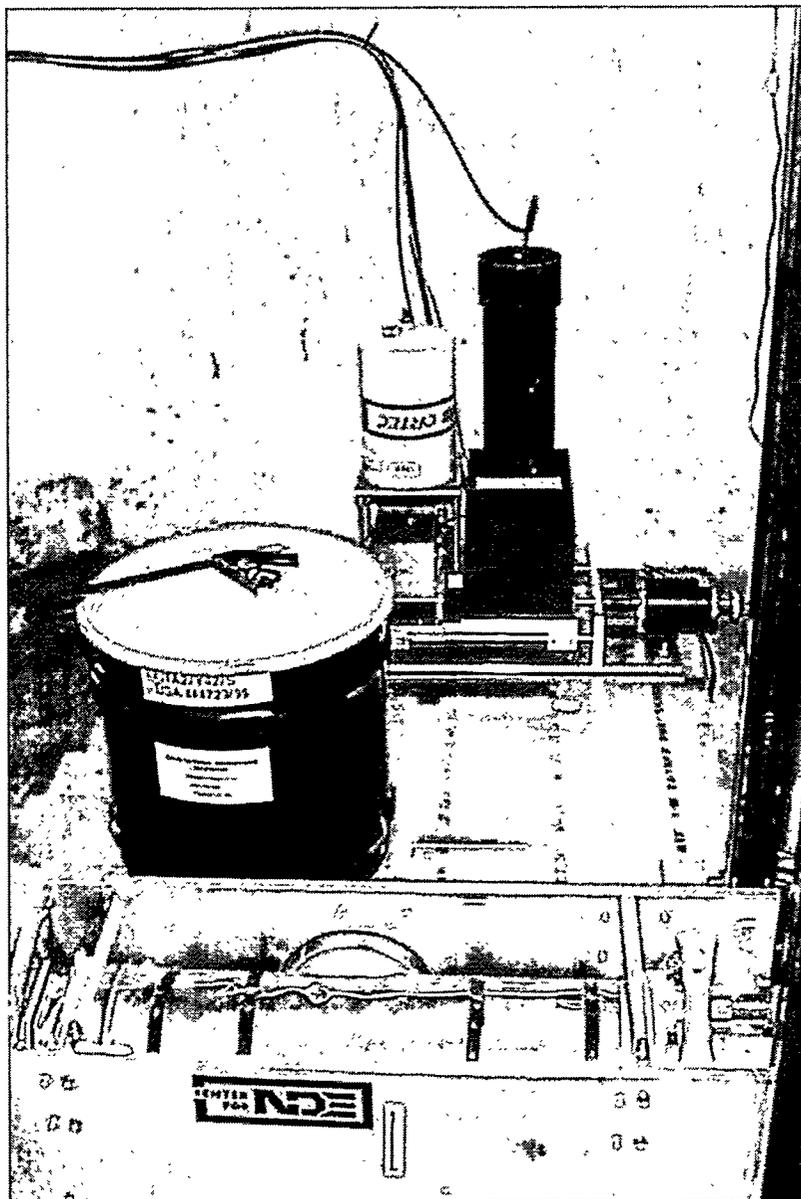


Figure 1. Setup for measuring RCRA metal contamination in 8-gallon waste drums. The X-ray tube is in the foreground and the collimated HPGe detector is behind the drum.

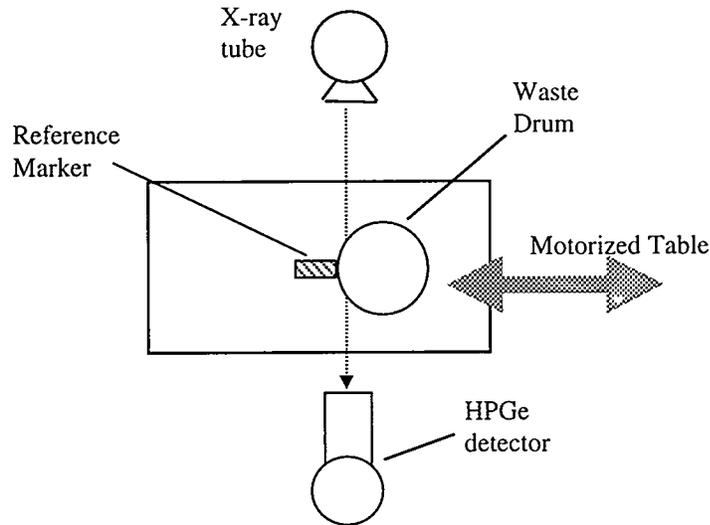


Figure 2. Setup used for K-edge analysis of surrogate waste drums.

The X-ray tube was operated at 140 kVp and 6 mA. Examples of spectra obtained for drums containing mercury, and lead, are shown in Figs. 3, and 4, respectively. The sharp drop in intensity at 83 keV for mercury and at 88 keV for lead are the characteristic K-edge signals that will be observed for these elements. For comparison, the K-edge for cadmium is at 27 keV. As can be seen in the spectra, X-rays at this energy are heavily attenuated by the walls of the drum. Therefore it is not possible to measure Cd contamination in this waste form.

The direct readout from the K-edge analysis, X_K , is in units of mg/cm^2 . To convert this to a heavy-metal concentration (mg/kg) it is necessary to know the path length of the X-ray beam through the sludge, t , as well as the density, ρ_s , of the sludge. The concentration of a given element can then be calculated from

$$C = X_K / (t\rho_s). \quad (1)$$

The density of the sludge was determined to be $\rho_s = 2.28 \text{ g}/\text{cm}^3$ based on the dimensions of the drums and the net weight as provided by Rust Geotech[2]. The path length can be calculated if the distance from the edge of the drum to the X-ray beam is measured, and the drum wall thickness and circumference are known. A diagram indicating the parameters needed for this conversion is shown in Fig. 5. The path length will be given by

$$t = \sqrt{4h(2R - h)}, \quad (2)$$

where R is the inside radius of the drum. The position of the outside edge of the drum relative to the X-ray beam can be determined fairly accurately by scanning the beam across a reference marker butted against the side of the drum. The K-absorption edge of a material such as gadolinium that is not present in the drum can be used as an alignment signal. When the Gd K-edge disappears, the X-ray beam will be situated at the edge of the drum. Using a computer-controlled motion table, the position of the drum relative to this reference position can be accurately adjusted.

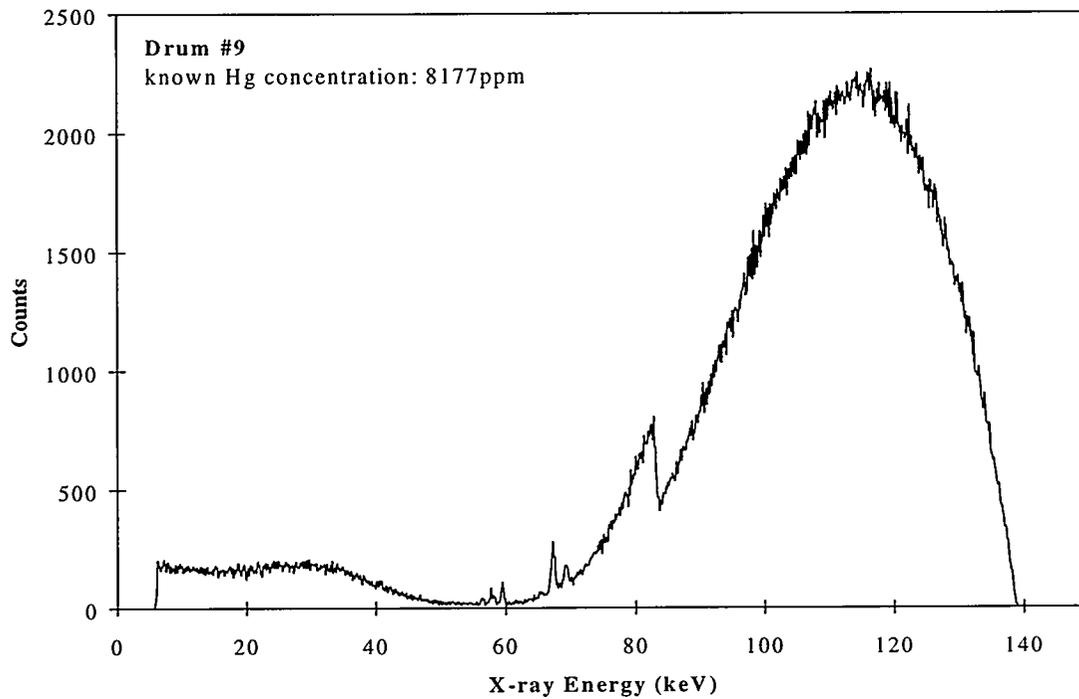


Figure 3. X-ray transmission spectrum observed for a waste drum containing mercury.

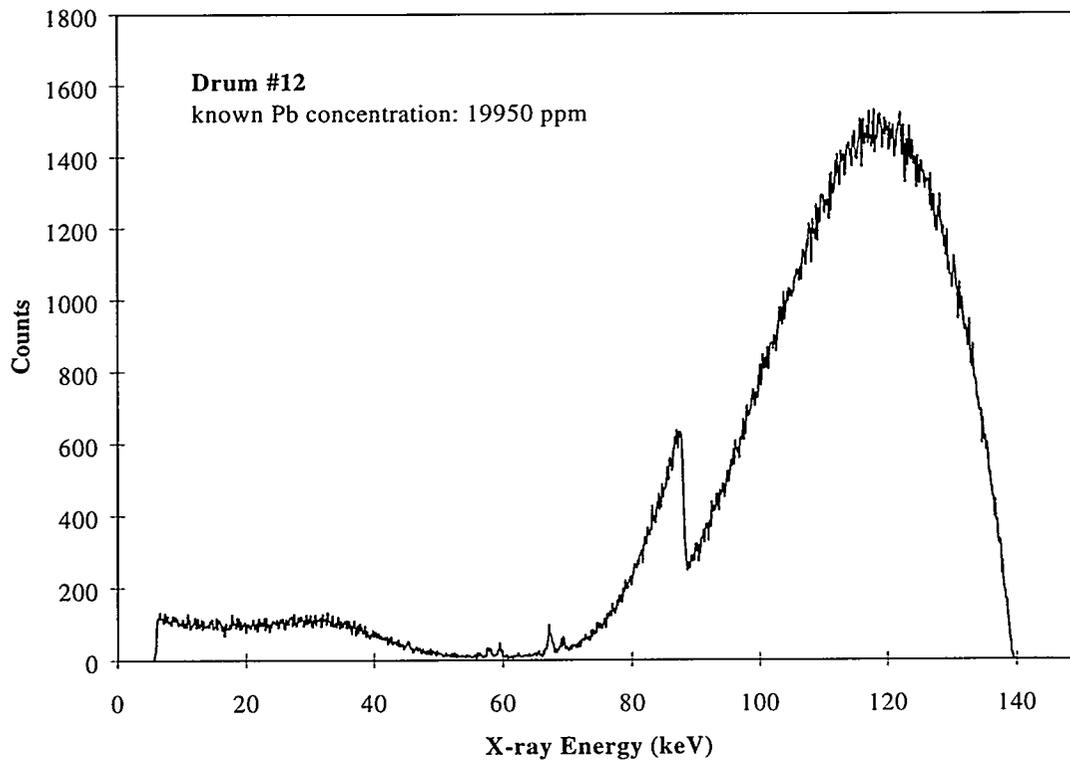


Figure 4. X-ray transmission spectrum observed for a waste drum containing lead.

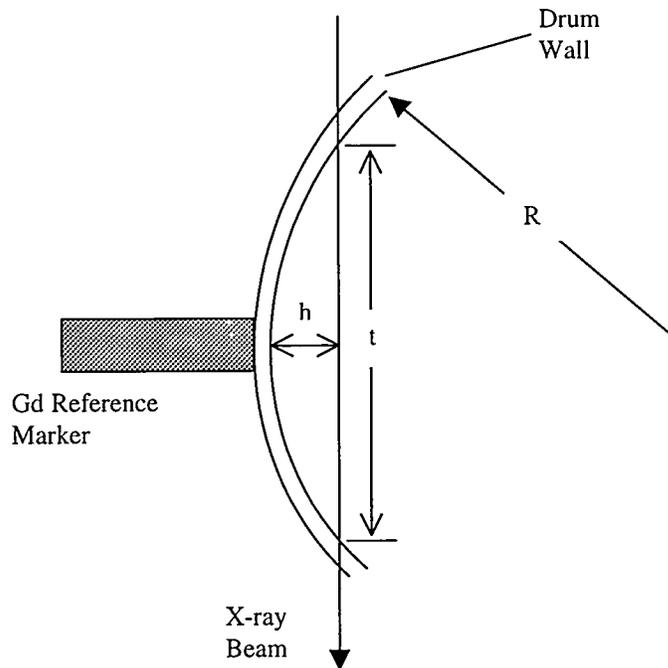


Figure 5. Geometry for X-ray K-edge analysis of a waste drum (see text for description of parameters).

Results

X-ray K-edge measurements were made on 13 of the 14 simulated waste drums (drum #14 contained only Cd). All data were acquired without specific knowledge of the drum contents. The statistical precision of the K-edge signal was monitored to determine the data acquisition time. The goal was to obtain a precision of at least 10%, which for most drums could be reached in 5-10 minutes.

To apply Eqs. 1 and 2 to determine the concentrations of Hg and Pb, one must compensate for the wall thickness of the drums. As this was not accurately known, it was decided to use one of the drums to calibrate for this value. Drum #12 was chosen as it had a strong signal for Pb. Using Eqs. 1 and 2 and the known Pb concentration, a wall thickness of 2.12 mm was calculated. This is quite reasonable considering the size of the drum (8-gallon) and the fact that four plastic bags were used as a liner in each drum. This wall thickness was then used in calculating the results for the remaining 12 drums. Where no significant signal was observed, a three sigma upper limit was estimated. The results are summarized in Table I for the 13 drums.

Multiple measurements were made on most drums, with the results being consistent. The scan time for each analysis is also shown in Table I. As can be seen, it is possible to achieve improved precision with longer scans. The errors reflect statistical uncertainty only. Additional error will be introduced by the uncertainty in the measurement of the distance of the X-ray beam from the edge of the drum, and in the estimation of the density of the sludge.

Table I. Comparison of known and K-edge measured concentrations of mercury and lead in the different simulated waste drums. Upper limits are at 99.7% CL.

Drum #	Scan Time (min)	Known Cd (mg/kg)	Known Hg (mg/kg)	Measured Hg (mg/kg)	Known Pb (mg/kg)	Measured Pb (mg/kg)
1	20	0	0	<380	0	<276
1	30	0	0	<342	0	<295
2	10	0	18,110	18,128 +/- 440	0	<1232
2	20	0	18,110	17,974 +/- 308	0	<880
3	10	0	5,835	5,258 +/- 222	0	<563
3	20	0	5,835	5,728 +/- 171	0	<420
4	20	0	583	518 +/- 106	0	<305
5	10	4,970	0	<1024	18,080	19,160 +/- 292
5	30	4,970	0	<568	18,080	18,824 +/- 172
6	10	808	0	<568	8,844	7,957 +/- 166
6	20	808	0	<502	8,844	7,890 +/- 116
7	10	291	0	<509	0	<367
7	30	291	0	<294	0	<298
8	5	0	19,820	18,563 +/- 744	0	<1981
9	5	0	8,177	8,228 +/- 351	0	<891
10	5	0	1,942	1,915 +/- 250	0	<590
11	10	0	487	803 +/- 235	0	<853
11	60	0	487	399 +/- 72	0	<175
12	5	8,181	0	<1403	19,950	CALIB.
13	5	2,123	0	<909	9,927	10,342 +/- 285

Conclusions

The X-ray K-edge technique performed very well on this set of simulated waste drums. It was possible to obtain measurement accuracy better than 10% for most samples within 20 minutes. Although cadmium could not be detected, its presence did not affect the measurement of lead contamination in the drums. Furthermore, there were no instances where false positive signals for lead or mercury were observed.

A couple of drawbacks of this technique must be pointed out. The simulated waste drums were fabricated to have very homogeneous contents, and this homogeneity was crucial for the K-edge analysis. The X-ray beam could not penetrate a thick region of the drum, so only a small volume near the wall of the drum was sampled. If contaminants in the DOE legacy waste drums are not uniformly distributed, X-ray K-edge analysis will not give an accurate measure of the average concentration in the drum. However, if the sludge can be assumed to be homogeneous within a given layer in a drum, the K-edge technique could be used to scan along the edge of the drum to map a vertical profile of the contamination.

Because the measurement was made so close to the edge of the wall of the drum, it was important to accurately compensate for the wall thickness. The use of a calibration drum enabled a precise determination of this thickness. For the legacy waste it will be more difficult to compensate for the wall thickness. Any corrosion of the drums, or differences in construction or use of liners will complicate this determination. Furthermore, for a 55-gallon drum, the distance from the edge that the X-ray beam can penetrate will be even less than for the 8-gallon drums used in this study. This will make the results more sensitive to the value used for the wall thickness.

As long as the geometry of the measurement process can be controlled to assure reasonable X-ray penetration, K-edge analysis can be a very accurate, robust technique. Multiple contaminants can be simultaneously measured, including radioactive materials, such as thorium, uranium and plutonium.

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