LA-UR-97-3592

TITLE:

X-RAY FLUORESCENCE SPECTROSCOPY FOR THE ELEMENTAL ANALYSIS OF PLUTONIUM-BEARING MATERIALS FOR THE MATERIALS DISPOSITION PROGRAM

AUTHORS(S):

Stewart L. Voit
Stephen T. Boerigter
Thomas L. Rising

SUBMITTED TO:

General Distribution

X-Ray Fluorescence Spectroscopy For The Elemental Analysis Of Plutonium Bearing Materials For The Materials Disposition Program.

Stewart L. Voit
Stephen T. Boerigter
Thomas L. Rising

Los Alamos National Laboratory
Technology and Safety Assessment Division
Technology Modeling and Analysis Group
TSA–7

August 7, 1997

This work conducted in support of the Nuclear Materials and Stockpile Management Program Office Los Alamos National Laboratory.

Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

X-Ray Fluorescence Spectroscopy For The Elemental Analysis Of Plutonium-Bearing Materials For The Materials Disposition Program

1. ABSTRACT

The U.S. Fissile Materials Disposition (MD) program will disposition about 50 MT of plutonium in the next century. Both of the alternative technologies for disposition, MOX Fuel and Immobilization require knowledge of the incoming composition to 1-5wt%. Wavelength Dispersive X-Ray Fluorescence (WDXRF) systems, a common elemental analysis technology with a variety of industrial applications and commercial vendors, can readily achieve this level of characterization. Since much of the excess plutonium will be packaged in a long-term storage container as part of the DOE Environmental Management (DOE-EM) program to stabilize plutonium-bearing materials, the characterization system must be implemented during the packaging process.

We describe a preliminary design for the integration of the WDXRF system into the packaging system to be used at the Rocky Flats site. The Plutonium Stabilization and Packaging System (PuSPS), coupled with the WDXRF characterization system will provide MD with stabilized plutonium-bearing excess material that can be more readily fed to an immobilization facility. The overall added expense to the MD program of obtaining analytical information after materials have been packaged in long-term storage containers could far exceed the expense of implementing XRF analysis during the packaging process.

2. INTRODUCTION

The DOE's strategy for the disposition of surplus plutonium is to pursue an approach that allows immobilization of plutonium in glass or ceramic material and burning some of the plutonium in commercial reactors in the form of mixed oxide (MOX) fuel. In December of 1994, the Department of Energy (DOE) issued the DOE Standard 3013 that provides for the safe storage of plutonium metals and oxides for at least 50 years or until final disposition. The 3013 standard encompasses the packaging and storage criteria for plutonium in metal or oxide forms containing a minimum of 50-wt.% plutonium but it does not require the characterization of the remaining matrix. Each of the disposition options recommended by the DOE are technologically unique and have requirements in addition to those associated with packaging and storage. These disposition requirements might include having a characterization strategy. In response, the U.S. Fissile Materials Disposition program (MD) has asked for a recommendation for a practical analytical technique.

3. REQUIREMENT FOR CHARACTERIZATION

The surplus plutonium that is considered for the DOE's disposition strategy is currently stored at eight sites across the country and in various forms that include plutonium metals and oxides (both high-purity and low-purity weapons grades and non-weapons grades), and various residues and materials including fuel forms, halides, and other compounds. The DOE current standard 3013-96 only encompasses containers that will hold material with plutonium metals and oxides at a minimum of 50-wt.%. The characterization of the unknown component stored in the 3013 containers could be necessary for each of the disposition options under consideration by the DOE.

3.1 MOX FUEL

The plutonium that is currently designated for the MOX fuel program originates from the pit dismantlement program at the Pantex site in Texas. The pits have a relatively high degree of purity, therefore, processing is primarily associated with removing the plutonium from the pit in an oxide or metallic form and fabrication. Specifications exist for MOX fuel and contain strict guidelines for purity. Certain elements, even at levels below 10 ppm, can have significant detrimental effects in a reactor environment due to high temperature induced migration. Analysis of the samples subsequent to storage in the 3013 containers is necessary to provide data on plutonium purity. The analysis should be used as a coarse screen to determine if a particular sample is a candidate for the MOX option. MOX processing will require supplemental analytical capability of the sample to make a final screen.

3.2 VITRIFIED WASTE FORM

The design of a successful batch for vitrification is contingent on the elemental composition of the waste. The additives for the glass frit are formulated based on the waste composition using phase diagrams. If the waste added to the stream has unknown components then it is difficult to optimize the glass for important characteristics such as chemical durability, mechanical durability, thermal stability, radiation stability, and flexibility.

High concentrations of several elements such as Al, Fe, and Ca can produce detrimental effects for glass formulations. These effects include increasing viscosity and/or redox potential leading to segregation and foaming. The levels of alkali metals must be monitored because of their effect on plutonium solubility. Elevated levels of halides and sulfates are known to move the composition from a single phase to a more undesirable multi-phase region of the phase diagram. Additional concern is associated with the presence of low Z elements. Low Z elements, such as boron that are expected glass constituents, undergo (α, n) reactions which present a significant dose concern. Present estimates on impurity requirements suggest that characterization of the waste stream to within 1-5 wt% will be necessary to allow for proper material blending. This limit will help simplify staging and batching design and will ensure that high concentrations of impurities will be diluted enough to facilitate immobilization processing.

3.3 CERAMIC WASTE FORM

Synroc-like formulations are being considered for the immobilization of plutonium and other actinide elements. The key to the success of this material as a host matrix is the ability to chemically bind the plutonium by lattice substitution in the seven sites available in the zirconolite structure. Studies have confirmed that Pu^{+3} and Pu^{+4} are the only viable valence states for substitution into the Ca and Zr sites in Synroc and the valence states are highly dependent on the processing conditions and other elements present. It has been indicated that most of the impurities can be accommodated in the desired ceramic phases except Na, K, Si, and B. These impurities tend to form a separate silicate phase with Ti and Al. A large amount of this silicate phase will not be desirable. Cl and F are also of concern since they volatize in the firing step. A significant amount can be tolerated, but if too much is present, the pellets will not densify well during the firing process.

Most of the development of Synroc has used formulations with high purity Pu and a ceramic precursor composition that is well established. Thus it is possible to tailor the waste form by modifying the precursor so the appropriate phases will be present to immobilize impurities. It is also important to use this method to refine the grain size which will increase the mechanical strength, reduce the tendency for microcracking and minimize anisotropic irradiation induced swelling. Uncertainty in the waste stream will reduce the ability to design the waste form and potentially introduce phases that are undesirable on the basis of waste form durability and leachibility. However, if impurities in the feed oxides are known to within the suggested 1-5%, precursor blends can be used to form phases with known acceptable durability.

Thus for both the vitrified or ceramic immobilization forms, it is important to know the amount of impurities present in the feed stream in excess of 5% in order to facilitate batch design, optimize durability, and reduce risk.

4. X-RAY FLUORESCENCE TECHNOLOGY

X-Ray fluorescence (XRF) is a technology that can be used for analysis of the plutonium bearing samples subsequent to storage in the 3013 containers. In XRF, a sample is subjected to an x-ray beam of sufficiently high energy. The x-rays impinging on the sample eject electrons from the inner shells of the atoms in the sample. The ejection of these electrons is followed by the emission of x-radiation from the atom at a set of wavelengths that is characteristic of the particular element. Thus each element gives rise to a characteristic x-ray spectrum. The relative amount of an element in a sample is determined by measuring the intensity of the observed x-ray fluorescence arising from the sample.

Two techniques are available for the determination and measurement of the output characteristic x-rays: energy dispersive X-ray fluorescence (EDXRF) and wavelength dispersive X-ray fluorescence (WDXRF).

In WDXRF, the emitted X-rays are dispersed based on their wavelength using diffraction. If the emitted x-ray photons from the sample are incident on a crystal at an angle θ between the crystal plane and the incident beam, the beam is diffracted with rays of equal wavelength but interfering constructively only in those directions for which the phase relationship is conserved. All rays emitted under angles different from θ cancel because they are out of phase and destructive interference occurs. The planes of a crystal are used to disperse the emitted X-ray photons from the sample based on Bragg's law:

$$n\lambda = 2\,d \sin\theta,$$

where n is an integer, λ is the wavelength of the photon, d is the lattice spacing of the dispersion crystal, and θ is the angle of incidence of the radiation. The WDXRF system is a sequential measurement, where the instrument must step through the 2θ values of the goniometer. This provides for higher spectral resolution and better sensitivity than the EDXRF system.

In contrast to the sequential nature of WDXRF, the energy dispersive system collects all the X-ray photons simultaneously onto the detector. Each photon generates an electrical pulse with an amplitude that is proportional to the energy of the X-ray photon. Further electronic processing involves amplification and analysis by a multichannel analyzer. The EDXRF system has the advantage of detecting all of the elements simultaneously, which means that analyses are rapid and unexpected elements are not missed. The major drawback is that the overall resolution of the EDXRF system is not as good as the WDXRF. Additionally, a sample that contains a radioactive component will saturate the detector on the EDXRF system further reducing the resolution.

Wavelength dispersive x-ray fluorescence allows the measurement of elements of the periodic table with a Z number greater than 4 in samples of various forms. Typical limits of detection for the low -Z elements beginning with Be can be as low as 100 ppm with the accuracy improving for the higher elements. Current software for semi-quantitative analysis can be coupled with standard samples for calibration to provide excellent resolution and accuracy for most applications.

A typical layout of a WDXRF spectrometer is shown in Figure 1. Among the important features are the x-ray tube; (1) collimators, which act as geometric beam filters, (2) masks, which reduce the shape of the fluorescent beam in front of the collimator, (3) the analyzing crystal, which is the central point of the instrument, and (4) the goniometer which, controls the rotation of the crystal and the detectors. As imposed by the conditions of Bragg's law, the crystal rotates over an angle of θ and the goniometer moves over an angle of 2θ. The rotation of the goniometer and crystal are coupled through a mechanism with a gear ratio of 1:2.

The goniometer arm carries two detectors in tandem: a flow proportional counter with two windows allowing the high-energy photons to pass to a scintillation detector. In the proportional counter, the photon enters through a window and imparts its kinetic energy to other atoms in the gas creating a series of electron-cation pairs. The resulting ions and electrons are collected and the current is proportional to the intensity of the incident photon. This detector is used for longer X-ray wavelengths of the lighter elements ($Z < 27$). The scintillation detector consists of a thallium doped sodium iodide crystal on the front of a photomultiplier tube. The X-rays from the sample strike the sodium iodide crystal and generate photons that illuminate the photocathode of the photomultiplier. The photons generate photoelectrons that are amplified and detected. The energy exchange, in this detector, takes place in a medium of higher density so it is only efficient for higher-energy photons (short wavelength) for elements with $Z > 25$.

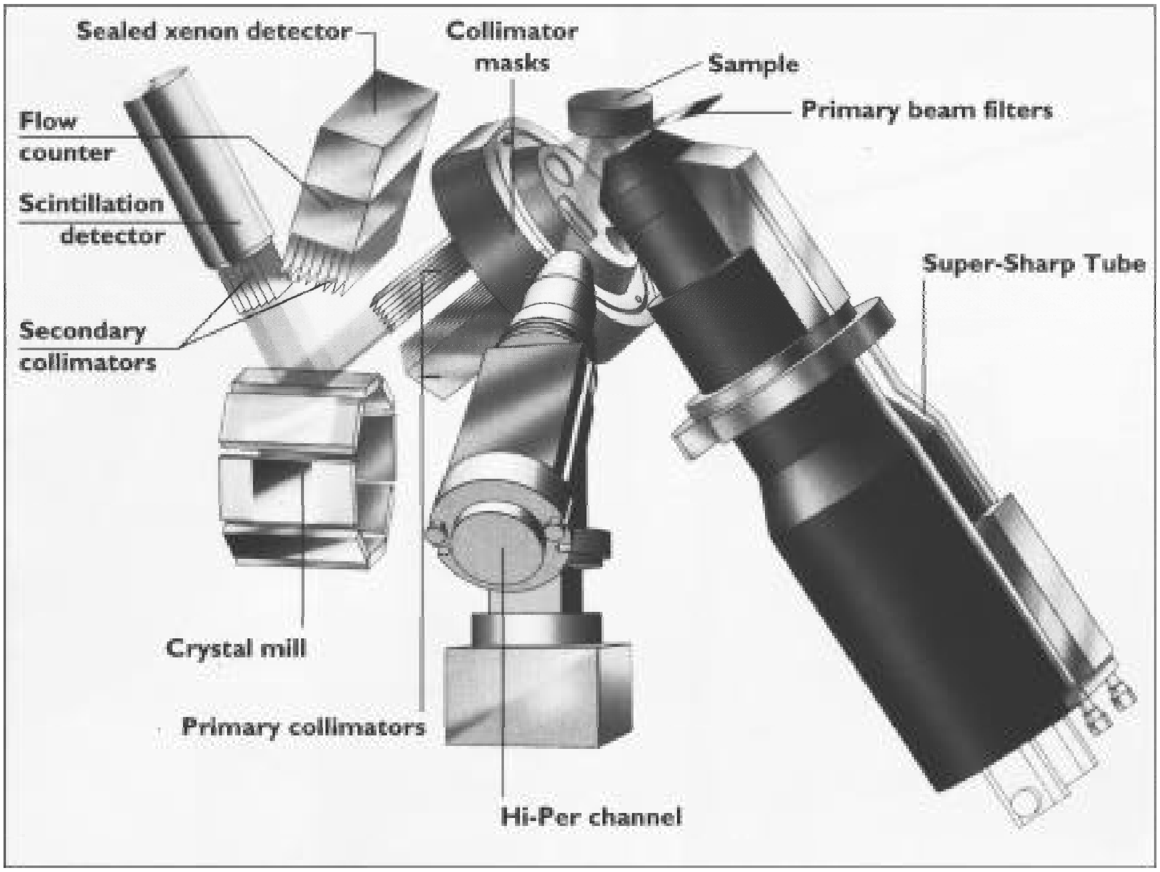

Figure 1. WDXRF Spectrometer

Information on some important features of the main WDXRF commercial instruments is summarized in Table 1 and a list of vendors is given in Appendix A. The Limit of Detection (LOD) is referenced to Na in a light matrix (e.g. plastic) for a 100 second counting time. The Oxford unit uses a combined wavelength and energy dispersive system to achieve a LOD for most elements, however this system may receive interference from a sample with a radioactive source.

Table 1: Listing of Commercially Available WDXRF Instruments

VENDOR	ARL	SEIMENS	PHILIPS	RIGAKU	DIANO	OXFORD
Type	WDXRF	WDXRF	WDXRF	WDXRF	WDXRF	WD/EDXRF
Analyzing Range	Be - U	Be - U	Be - U	Be - U	B - U	Be - U
Limit of Detection	20 ppm	15 ppm	10 ppm	3 ppm	100 ppm	50 ppm
Crystal Exchanger	9	8 or 10	8	10	4 or 6	10
Sample Changer	multiple	multiple	multiple	6	multiple	10
Sample Size (dia x h)	2.0” x 1.2 “	2.0” x 1.8”	2.0” x 1.8”	2.0” x 1.2”	1.9” x 1.6”	1.5” x 1.3”
Generator	3 kW	3 kW	4 kW	3 kW	3 kW	3 kW
Cost	$200,000	$215,000	$210,000	$200,000	$185,000	$140,000

Several alternative technologies that are able to provide similar analysis are listed below. Each of the techniques, although established in other applications, has limitations when compared to XRF on a merit basis.

- Inductively coupled plasma (ICP) emission and mass spectrometry techniques provide greater routine sensitivity but they require all samples to be dissolved in solution.
- Glow discharge mass spectrometry has similar sensitivity to ICP methods but is able to handle solid samples. However, closely matched standards are required for quantitative analysis.
- Atomic absorption is a single-element flame or furnace-based method that is simpler and cheaper than XRF but is more labor intensive for more than one or two elements.
- Atomic fluorescence compares with furnace atomic absorption for sensitivity but commercial instrumentation is limited and it requires similar sample preparation to ICP.
- Prompt gamma activation analysis offers high sensitivity but is still in the developmental stages for this application.

XRF is a more practical technology for this application and will provide the information needed to be able to blend for both vitrification and ceramification without the additional expense and effort required for these other analytical methods.

5. WDXRF APPLICATION FOR THE MD PROGRAM

5.1 CONFIGURATION OF WDXRF FOR GLOVE BOX OPERATIONS

The sample preparation for XRF analysis must be performed within a glove box environment. The sample needs to be mixed, bound, and pressed before it can be bagged-out for analysis. Sample mixers and automatic hydraulic presses are commercially available and designed specifically for use in conjunction with the XRF system. The XRF instrument can be maintained in an uncontaminated environment so that any repair or calibration can be done without contamination concerns. A sample preparation process flow is given below.

- Prior to preparation, the matrix will be calcined per DOE-STD-3013-96 packaging criteria.

- After calcination, several grams of the matrix will be extracted. Typically the amount extracted will be several times the amount needed for analysis so that a representative sample can be obtained and any heterogeneity can be accounted for.

- The matrix will then be placed in a mixer with a binding agent. The mixer is an impact grinder that uses a ball pestle to reduce particle size. The binder is introduced to reduce clumping thus allowing for uniform particle size. Additionally, it helps to prevent the sample disc from crumbling, breaking, and releasing of respirable particulate.

- The sample is mixed for several minutes (depending on particle size) to blend the binder and sample to create a homogeneous mix.

- After mixing, the sample is transferred to a holding cup that will be placed in the press.

- The sample is removed from the press and placed into a sample cup. Multiple samples can be prepared and taken to the XRF instrument, which can reside in an uncontaminated environment.

- After analysis, the sample is bagged-in to the glove box and recalcined to remove the binder. The characterization process is complete and the matrix is ready for packaging.

5.2 INTEGRATION OF WDXRF WITH THE PUSPS SYSTEM

The plutonium stabilization and packaging system (PuSPS) is proposed for the processing of feed materials in compliance with the DOE-STD-3013-96. A prototype is currently being built for use at the Rocky Flats Environmental Technology Site (RFETS) and is shown schematically in Figure 2.

The PuSPS system processes the feed material in two phases: stabilization and packaging. The stabilization phase includes calcination of the material in a furnace to remove water and organics then verification with LOI testing. After stabilization, the material will be automatically transferred to the tipping/dispensing/fill area that begins the packaging phase. The material is poured into the material container which is then put inside the inner can. The inner can resides outside of the glove box but is connected by a sphincter seal that allows the material container to be inserted while maintaining a contamination free exterior. The inner can is laser welded closed and placed into the final outer container which is also laser welded.

The sample preparation that is described in section 5.1 will be most efficiently integrated in the stabilization phase of the PuSPS system. Following calcination, material will be extracted for both LOI testing and XRF preparation. The XRF machine can handle multiple samples, therefore, up to 24 samples can be prepared and bagged out at one time. After the samples are processed for XRF analysis per the above criteria, the material will be reintroduced into the transfer glove box and processed in the furnace to burn off the binder and any absorbed organics.

The sample press and mixer should reside in the transfer glove box near the LOI testing area. The items are compact and can be easily glove handled with no interference to the operation of the PuSPS system. The dimensions of the items are listed in Appendix A. The PuSPS that is currently being assembled at RFETS was designed with little additional space therefore these items should be located in one of the existing glove boxes adjacent to the PuSPS system that were used in previous operations. Minor modifications to the transfer glove box in future PuSPS designs will allow for the incorporation of the sample press and mixer into the system. Additionally, the XRF instrument can be located in an uncontaminated area due to space and maintenance issues.

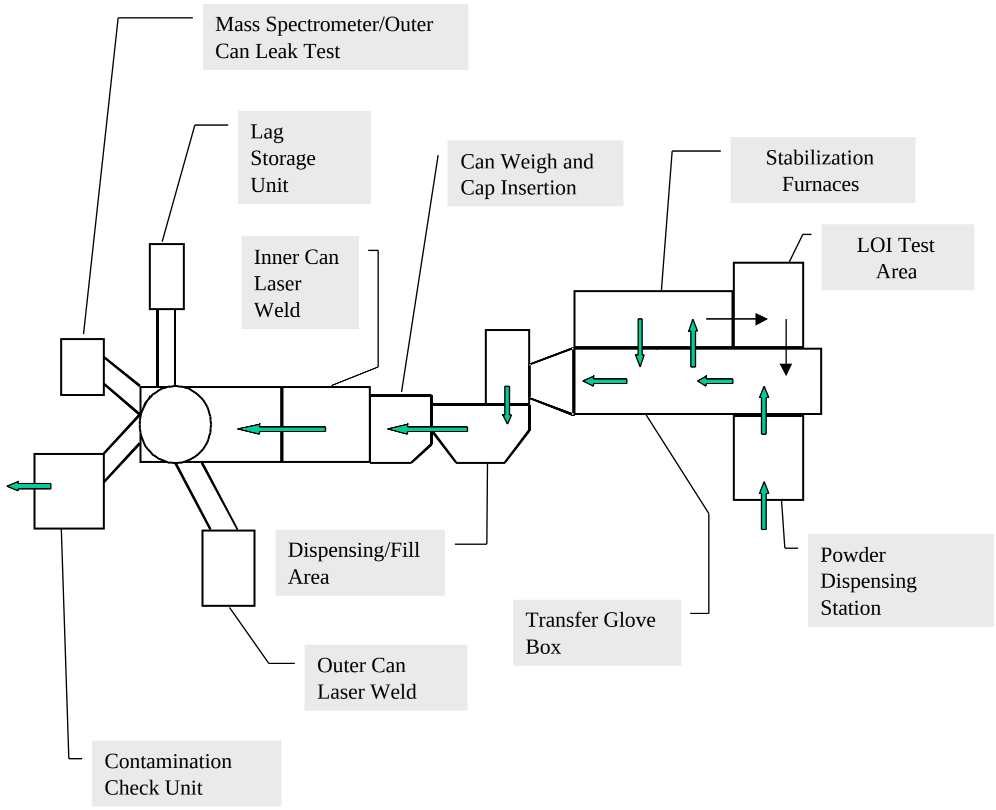

Figure 2. Schematic of PuSPS System at RFETS.

6. SUMMARY

The U.S. Fissile Materials Disposition program will disposition about 50 MT of plutonium in the next century. Both of the alternative technologies for disposition, MOX Fuel and Immobilization require knowledge of the incoming composition to 1-5wt%, which WDXRF can readily achieve. Use of WDXRF technology to obtain this analytical information before these materials are packaged into long-term storage containers will provide the elemental composition knowledge. Failure to use XRF, or some other appropriate analytical technique, could lead to failed fabrication batches, damaged equipment, and a great deal of unneeded expense and delay. This cost avoidance could undoubtedly far exceed the expense of implementing XRF analysis.

7. BIBLIOGRAPHY

1. G.J. Havrilla, "X-ray Fluorescence Spectrometry" Handbook of Instrumental Techniques for Analytical Chemistry. Prentice Hall, 1997.
2. R.E. Van Grieken, "Handbook of X-Ray Spectrometry" Marcel Dekker, Inc. 1993.
3. R. Tertian, "Principles of Quantitative X-Ray Fluorescence Analysis". Heyden, 1982.
4. G. Wicks, Westinghouse Savannah River Site. Private conversation.
5. H. Li, Pacific Northwest National Laboratory. Private conversation.
6. A. Jostsons, Australian Nuclear Science and Technology Organization. Private conversation.
7. DOE/ROD for the Storage and Disposition of Weapons-Usable Fissile Materials.
8. DOE-STD-3013-96.
9. D.S. Goldman, "Nuclear Waste Glass Composition Limitations" ANS International Meeting on Waste Management. August, 1984.
10. A. Jostsons, "Surplus Plutonium Disposition Via Immobilization in Synroc". International Topical Meeting on Nuclear and Hazardous Waste management. August, 1996.
11. E.R. Vance, "Excess Pu Disposition in Zirconolite-Rich Synroc". Materials Research Society vol. 412, 1996.

APPENDIX A

1. SAMPLE PREPARATION EQUIPMENT

1.1 SPEX 8000-D Mixer/Mill

Capability: Reduction of solids to analytical finess and blending a wide range of powders.
Size: 22 x 15.25 x 11 inches.
Vendor Address: SPEX Industries Inc.
3880 Park Avenue
Edison, NJ 08820
(908) 549-7144

1.2 Chemplex 30 Ton Force SpectroPress

Capability: Programable load, dwell time, and bleed rate ensure reproducibility.
Size: 26 x 16.25 x 14.25 inches.
Vendor Address: Chemplex Industries Inc.
3091 Sewaaler Street
Stuart, Fl 34997-5923
(800) 424-3675

2. XRF VENDORS

2.1 Applied Research Laboratories
55 Cherry Hill Dr.
Beverly, MA 01975
(508) 524-1000

2.2 Diano Corporation
30 Commerce Way
Woburn, Ma 01801
(617) 935-4310

2.3 Oxford Instruments Inc.
130A Baker Ave. Ext.
Concord, MA 01742
(508) 371-9009

2.4 Philips Electronic Instruments Company
85 McKee Dr.
Mahwah, NJ 07430
(201) 529-3800

2.5 Rigaku/USA Inc.
Northwoods Business Park
199 Rosewood Dr.
Danvers, MA 01923
(508) 777-2446

2.6 Siemens Industrial Automation Inc.
Analytical X-Ray Instruments
6300 Enterprise Ln.
Madison, WI 53719-1173
(608) 276-3000