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

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

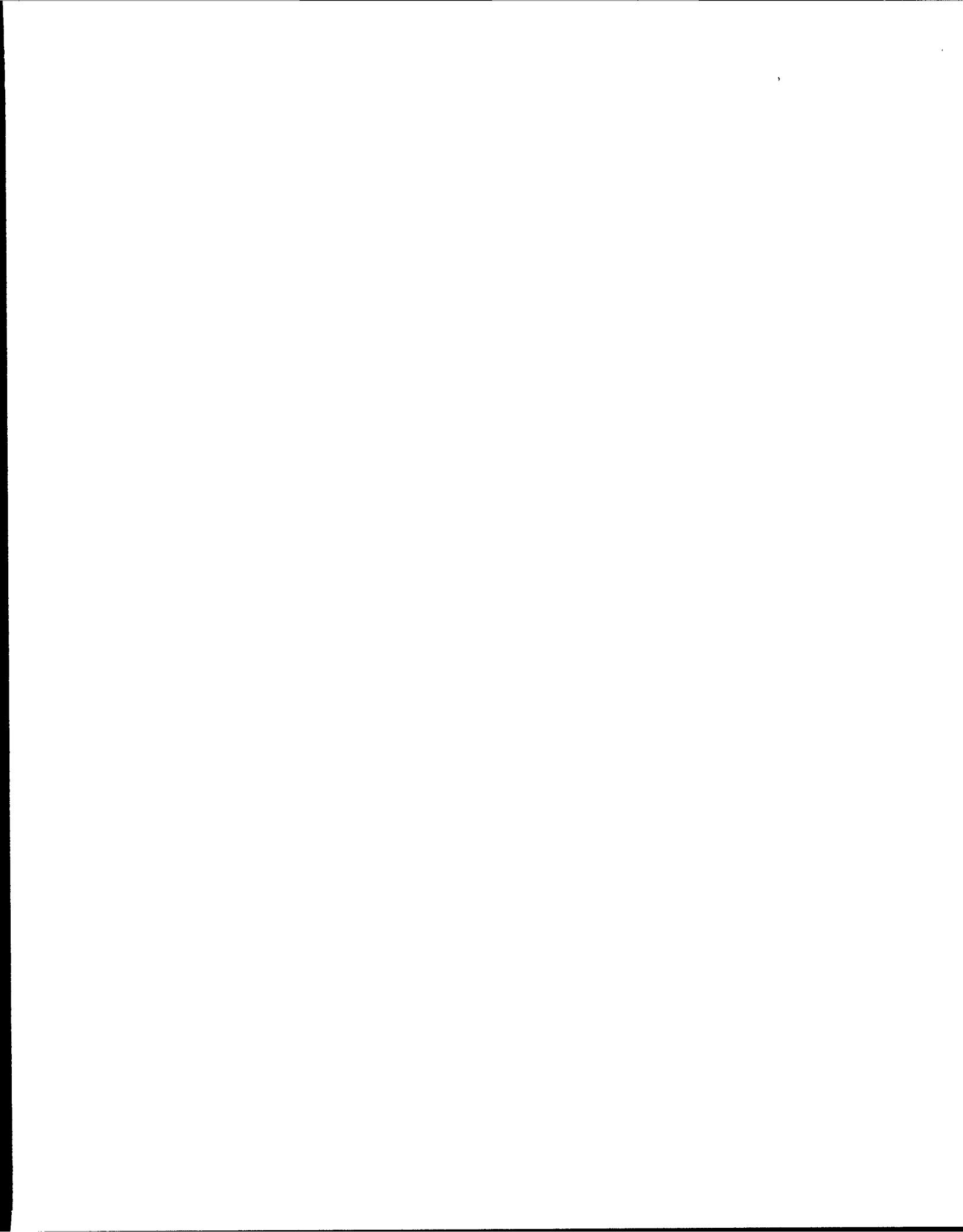
## **1. ABSTRACT**

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.



and will ensure that high concentrations of impurities will be diluted enough to facilitate immobilization processing.

### 3.3 Ceramic Waste Form

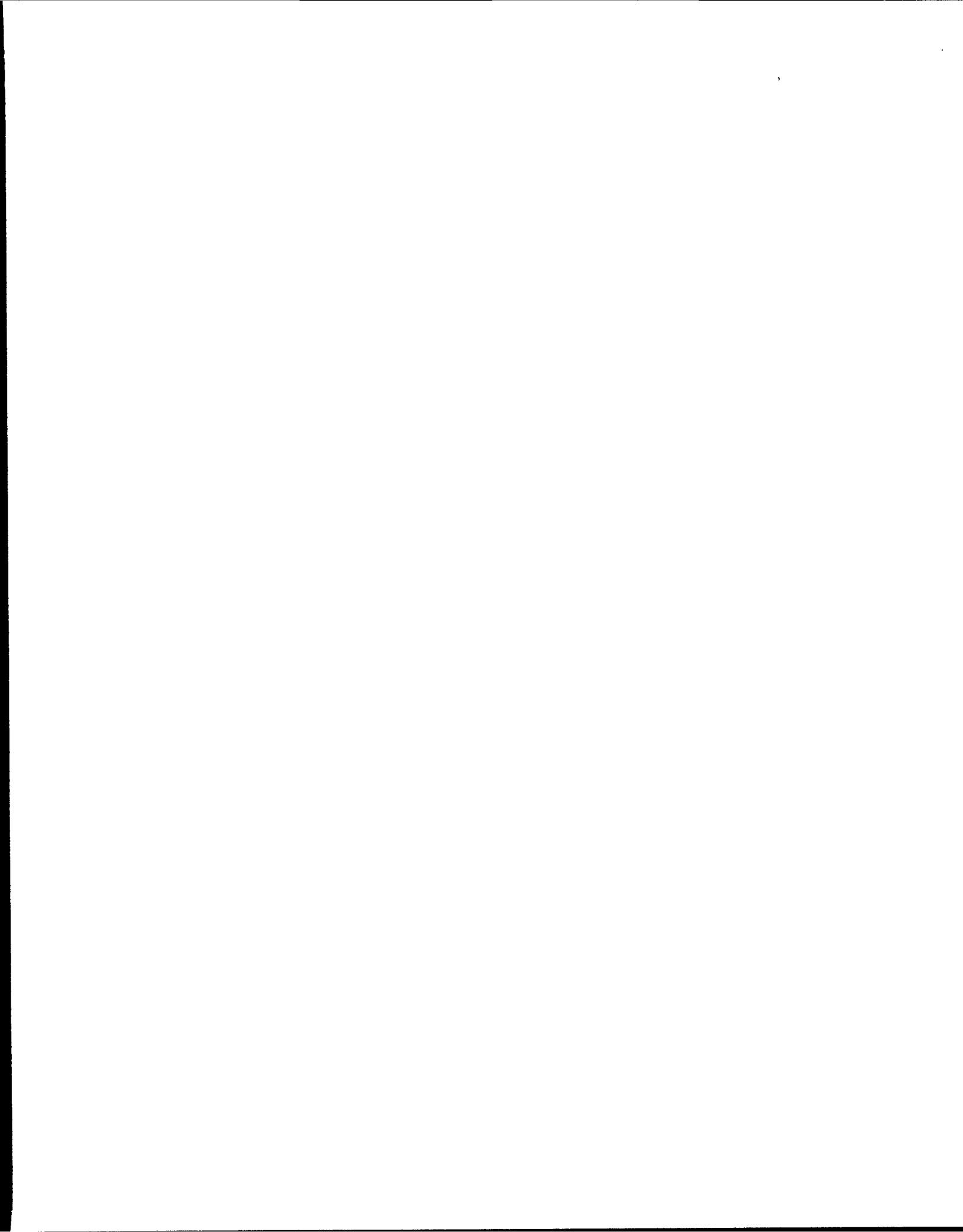
Synroc-like formulations are being considered for the immobilization of plutonium and other actinide elements. The key to the success of this material as a host matrix is the ability to chemically bind the plutonium by lattice substitution in the seven sites available in the zirconolite structure. Studies have confirmed that  $\text{Pu}^{+3}$  and  $\text{Pu}^{+4}$  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 leachability. 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.



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  $Z > 25$ .

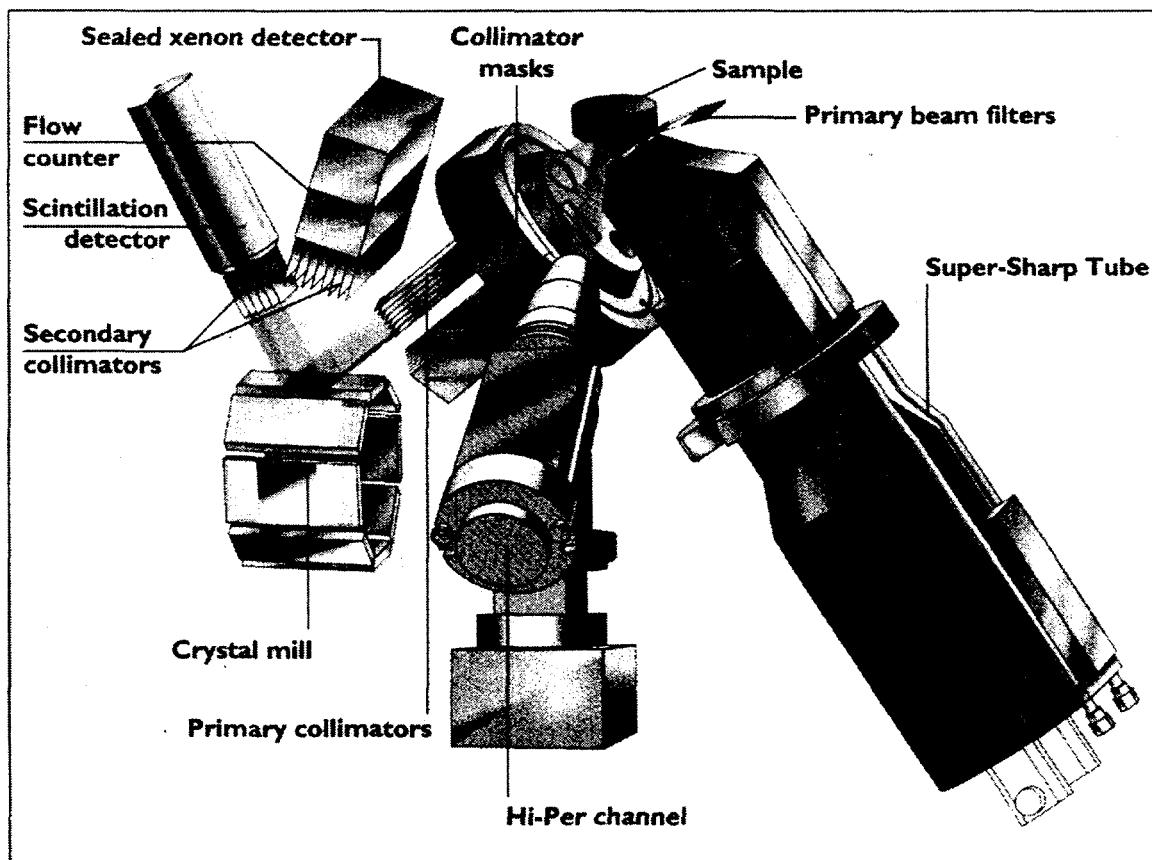
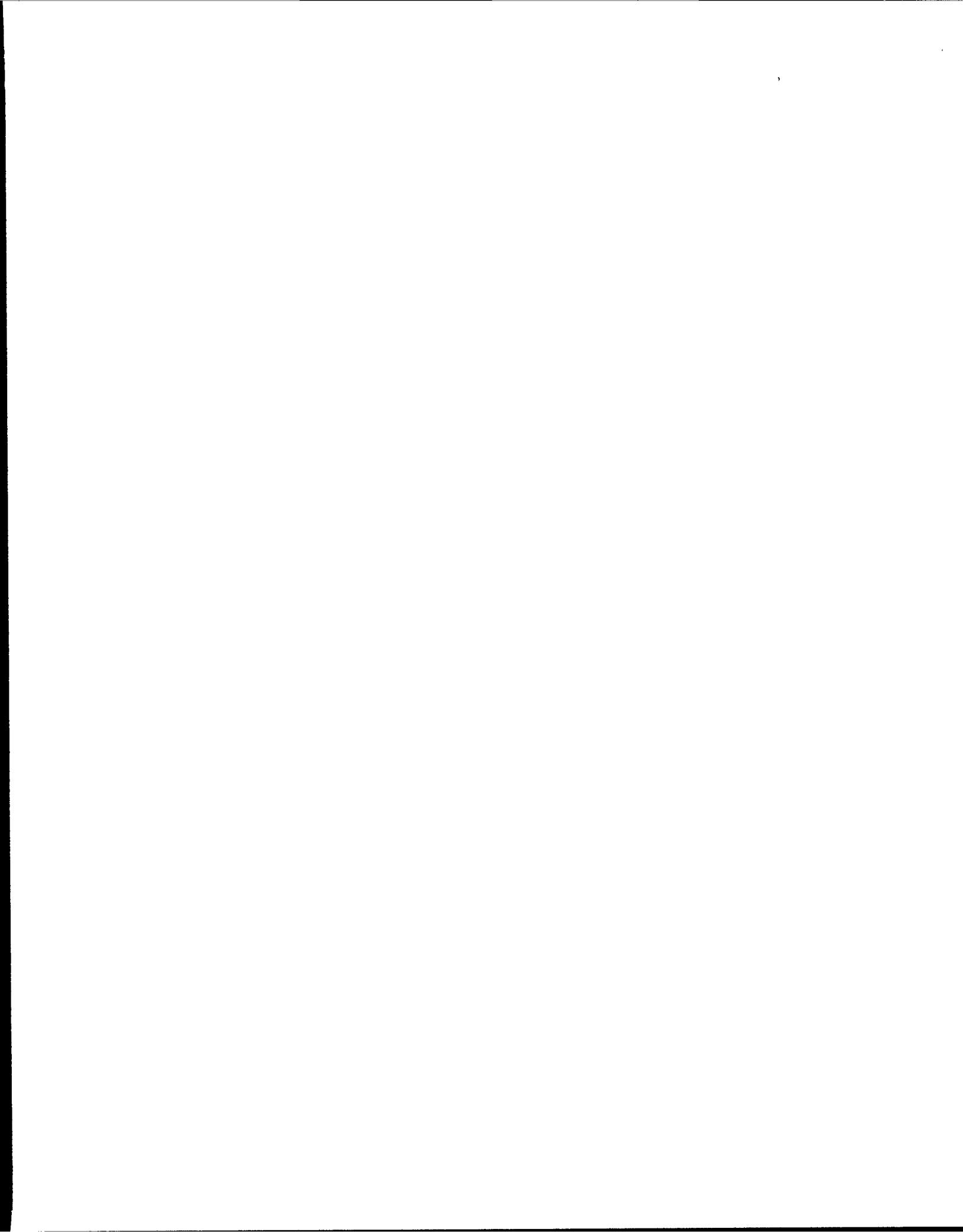


Figure 1. WDXRF Spectrometer



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.

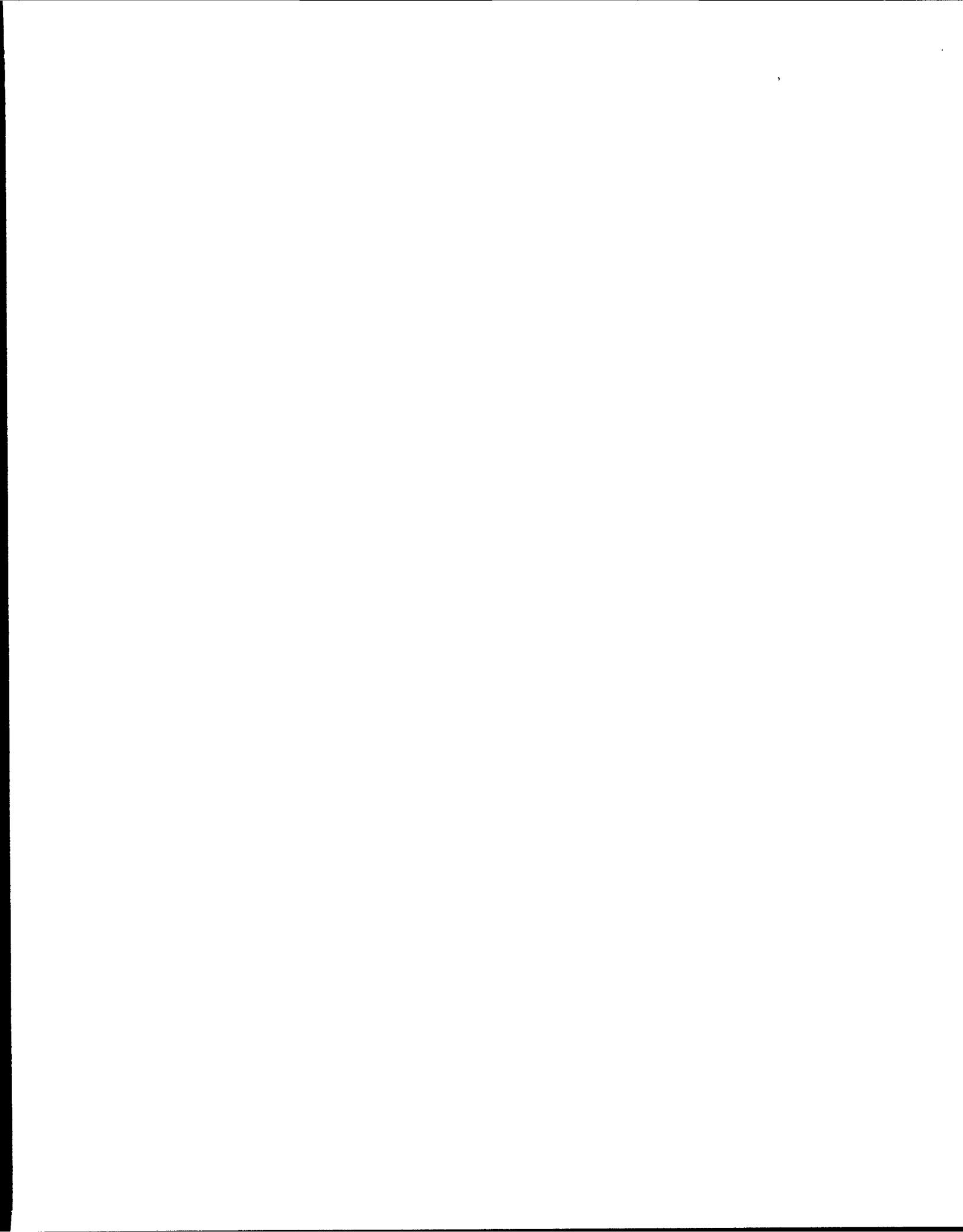
XRF is a more practical technology for this application and will provide the information needed to be able to blend for both vitrification and ceramification without the additional expense and effort required for these other analytical methods.

## **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.



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.

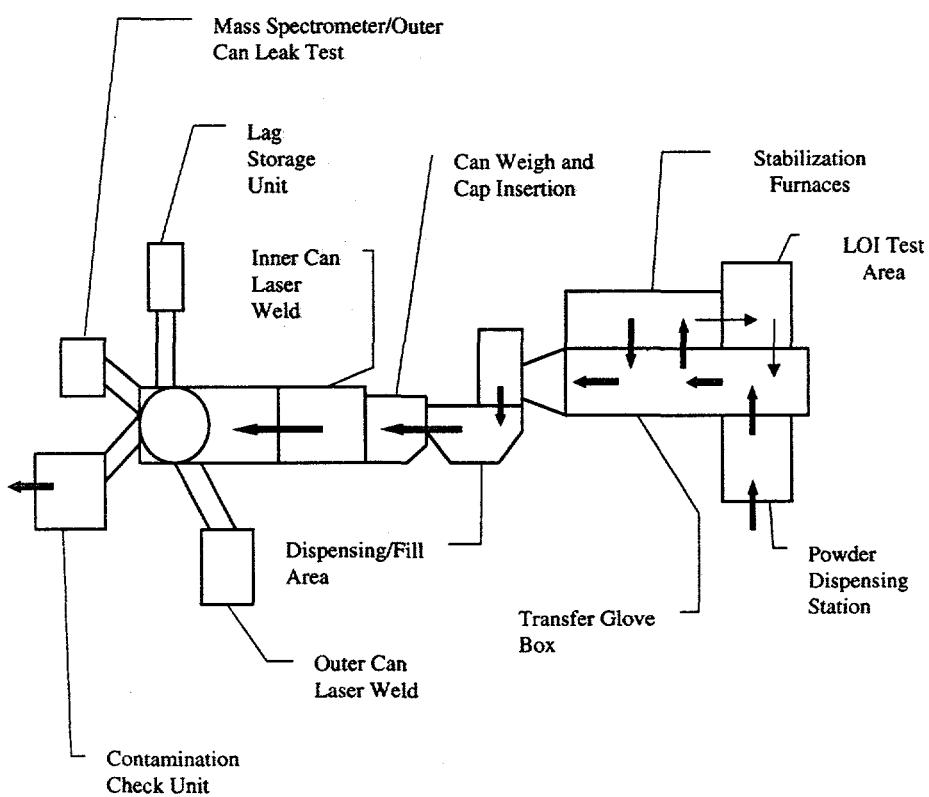
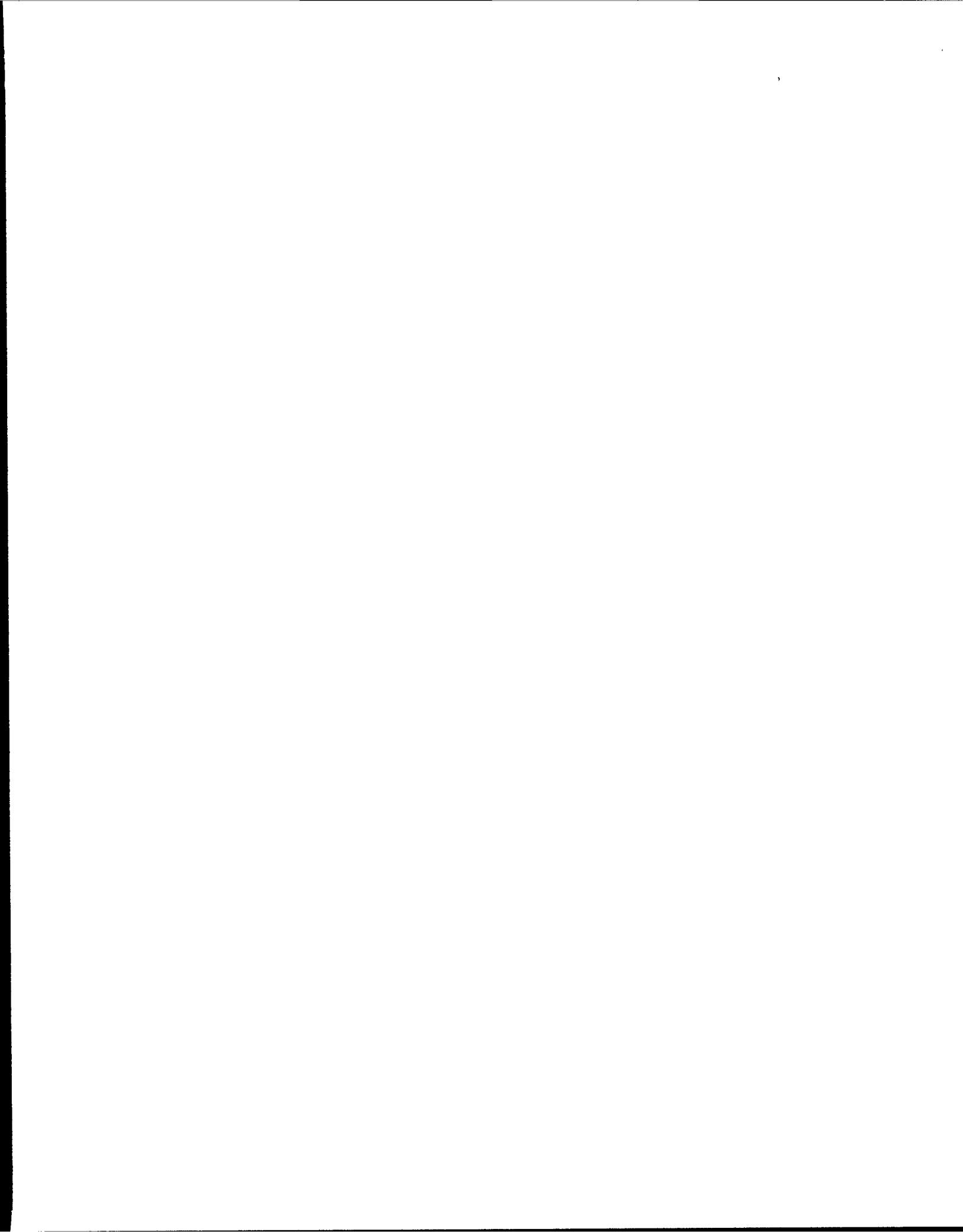
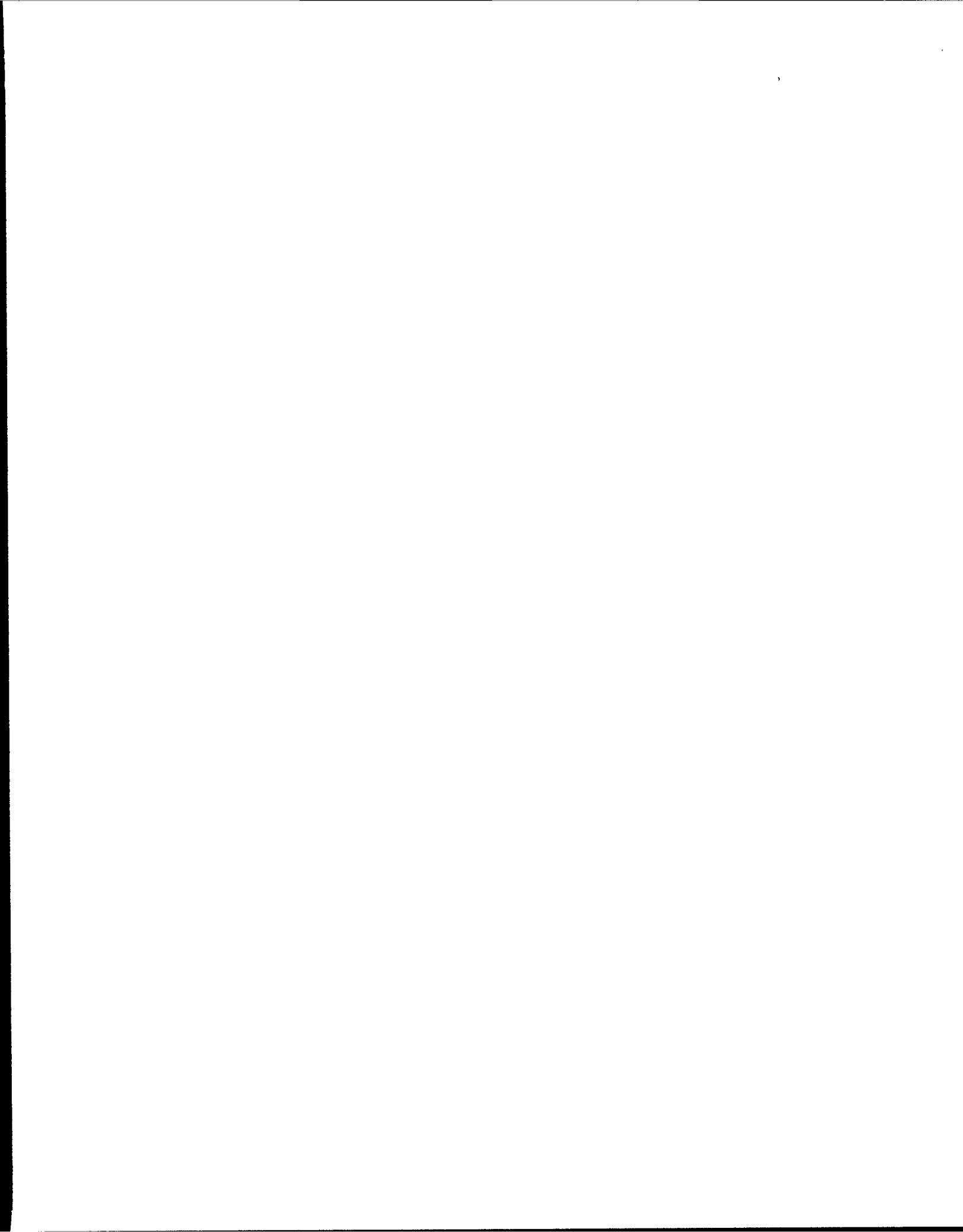


Figure 2. Schematic of PuSPS System at RFETS.



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