

Title:

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Evaluation of Supercritical Fluid Carbon Dioxide Extraction as an Alternative Method for Moisture Determination in Plutonium Dioxide Powders

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ABSTRACT

Two high-purity, surrogate oxides, as well as nominally pure and impure plutonium oxides, were studied to evaluate the ability of supercritical fluid carbon dioxide to quantitatively determine moisture content. A comparison is given between the calculated weight loss by extraction, based on real-time hygrometer or FTIR measurements, and the weight loss measured by conventional loss-on-ignition (LOI).

We find a high level of agreement between the calculated and LOI measurements for the high-purity surrogate oxides, and a significant divergence of these measurements for the PuO₂ samples. We conclude that (1) the LOI measurements are not a reliable indicator for the moisture content of plutonium oxides, and (2) supercritical fluid extraction is a promising, alternative analytical method.

I. Introduction

A. Background

One of the major concerns in the packaging and storage of plutonium oxide powders is the possible generation of high internal, possibly flammable, gas pressures which may result in failure of the storage container and airborne release of oxide particles. There are four primary mechanisms which can result in pressurizations of oxide storage containers [1]: (1) radioactive (alpha) decay; (2) chemical reaction of materials within the storage container; (3) radiolytic decomposition of components within the storage container; and (4) thermal desorption of species from the stored nuclear material.

The first of the four mechanisms producing internal gas generation cannot be avoided. However, the effects of the remaining three can be greatly reduced or even eliminated if the hydrogen-bearing material (organic compounds and water) can be removed from the oxide prior to packaging. The current stabilization method for the removal of hydrogenous material from oxides is a thermal treatment where the oxide is calcined in air or an oxidizing atmosphere at 950°C or higher for at least two hours.[2] Thermal stabilization is confirmed, and the presence of volatile components detected, by the Loss On Ignition (LOI) test. The LOI test is based on heating a representative sample of previously thermally stabilized oxide in air to 1000°C or higher for at least one hour. The use of the LOI method to detect the presence of hydrogenous material has one primary disadvantage: Heating of the powders to 950°C may result in the volatilization of inorganic salts not containing hydrogen, giving an erroneously high LOI value.

B. Purpose of the Present Work

The purpose of this study is to evaluate supercritical fluid extraction as an alternate analytical method for the determination of hydrogenous content in plutonium oxides.

We have performed supercritical fluid extractions on plutonium oxide surrogates as well as pure and impure plutonium oxides to evaluate the ability of supercritical fluid extraction (SCFE) to quantitatively determine the moisture content. In this study, we will not specifically address the issue of the extraction and quantitative determination of Volatile Organic Compounds (VOC's) and Semi-Volatile Organic Compounds (SVOC's). This is done for two reasons. First, we believe that the removal of water from these oxides is a much more important problem by virtue of the larger amounts of water versus VOC's and SVOC's which are likely to be present in actual oxides. This is particularly true for oxides, which have been thermally stabilized, where the VOC's and SVOC's would be driven-off, but where there might be some re-adsorption of water prior to packaging. Second, the energetics of water adsorption is such that if we can successfully remove the water, then by virtue of water's stronger adsorption to oxide surfaces, the organic compounds should be easily removed.

In order to gauge the relative accuracy and precision of the two methods (SCFE vs. LOI) a third, independent method must be used. We therefore report results of Interstitial

Gas Analysis (IGA) and/or Thermo-Gravimetric Analysis (TGA) performed on PuO₂ samples before and after extraction. Figures 1 and 2 in Attachment 5 of the Appendix show chronological flow diagrams used in the extractions of PuO₂ and surrogate oxides, respectively, which include TGA and IGA sampling.

II. Materials Tested

- Two pure surrogate oxides (CeO₂ and ThO₂)

CeO₂ and ThO₂ -

The manufacturer's lot analysis reports the CeO₂ as 99.99 % (on a metals basis), while that of the ThO₂ as 99.99 % (on a metals basis). The particle size and specific surface areas for these materials are given in Tables 1 and 2, respectively, at the end of this report.

- Three "pure" plutonium oxides :

PEOR-3258 -

This is a nominally pure oxide, previously thermally stabilized by calcining at 950°C. The specific surface area and the average particle size is given in Tables 1 and 2, respectively, at the end of this report.

PPSL-365 -

This sample is a nominally pure oxide which had been previously thermally stabilized by calcining at 950°C. The specific surface area and the average particle size is given in Tables 1 and 2, respectively, at the end of this report.

MIS-STD-1

Another nominally pure oxide, used as a standard material of known water content. This material has been heated, prior to packaging and storage, to about 600°C. Information on the specific surface area and average particle size were not available.

- One impure plutonium oxide (ATL-27960)

ATL-27960

Information on the previous thermal history of this material are unknown. The specific surface area and the average particle size are given in Tables 1 and 2, respectively, at the end of this report.

III. Experimental

A. Hygrometer detection system

The first detection system evaluated was a hygrometer, or dew point meter. A schematic diagram of the experimental measurement system is given as Figure 3 in Attachment 6 of the Appendix.

The hygrometer, or dew-point meter, used in the initial sets of experiments is designed to measure the dew point temperature of flowing air streams. Although the gas stream in the supercritical fluid extractions is CO₂ and not air, it has been shown previously [3] that the dew point curve for water vapor in CO₂ is, within experimental error, identical to the dew point curve for water vapor in air.

A calibration curve for the hygrometer detector was constructed by extracting known volumes (and therefore weights) of water, and correlating these to integrated areas obtained from real-time hygrometer data. Table 1 in the Appendix gives the experimental extraction results. The empirical equation used to fit the data is the sum of (1) a straight line and (2) an offset, whose value is zero for zero integrated peak area and is a constant for large water contents:

$$\text{mg H}_2\text{O} = (12864 \times 10^{-3} \times \text{AREA}) + 19.2651 \left(1 - e^{-14208 \times 10^{-4} \times \text{AREA}} \right) \quad (1)$$

This particular equation was chosen because of its high degree of correlation to the experimental data, while requiring only three undetermined coefficients. The solid line in Attachment 6 of the Appendix is a plot of Eq. (1), using the known weights of extracted water, versus the integrated peak areas. Implicit in Eq. (1) is a conversion of microliters of water to milligrams of water, using an assumed density for liquid water of 1 g ml⁻¹. The statistics associated with Eq. (1) can be found in Table 2 of the Appendix. The Method Detection Limit (MDL) at the 99 % Confidence Level is 4.14 mg, which represents 0.083 weight % water in a 5 gram PuO₂ sample.

B. FTIR detection system

The second detection system evaluated was a high-pressure cell, coupled to an FTIR spectrometer. A schematic diagram of the experimental measurement system is given as Figure 4 in the Appendix (Attachment 6).

Table 3 in the Appendix gives the experimental results of the known water volume extraction experiments using the high-pressure FTIR detection system. The empirical equation fitted to these data is a straight line, Eq. (2), and is plotted against the experimental data in Attachment 6 of the Appendix:

$$\text{mg H}_2\text{O} = 1.1697 \times 10^{-6} \times \text{AREA} + 08407 \quad (2)$$

The MDL for the FTIR detection system, at the 99 % Confidence Level, is 3.53 mg, which represents 0.071 weight % water in a 5 gram PuO₂ sample.

IV. Results

The weight losses presented in this section are those calculated using the calibration curve appropriate for the detection system used.

A. CeO_2 -

The following table gives the results of supercritical fluid extractions and gravimetric weight losses for the CeO_2 surrogate materials. Path #1 (heating followed by extraction) and Path #2 (extraction followed by heating) were evaluated using the hygrometer detection system, while Path #2, at two different extraction temperatures, was evaluated using the FTIR detection system. Finally, a gravimetric weight loss measured after heating in vacuum for 24 hours are shown. The results for all of these experiments are internally consistent, showing a weight loss of 0.11 % - 0.18 %. The LOI for this material was slightly higher, at 0.22 %.

	SCFE -> vacuum heating	Vacuum heating - > SCFE	Vacuum heating for 24 hrs.
Hygrometer detection system (75°C)	0.159 % 0.190 % 0.177 % <i>Avg. = 0.175 %</i>		
FTIR detection system (75°C)	0.108 % 0.104 % 0.096 % 0.115 % <i>Avg. = 0.106 %</i>		
FTIR detection system (100°C)	0.118 % 0.128 % 0.147 % <i>Avg. = 0.131 %</i>		
gravimetric	0.143 % 0.132 % 0.131 % <i>Avg. = 0.136 %</i>	0.125 % 0.119 % 0.097 % <i>Avg. = 0.114 %</i>	0.147 % 0.177 % 0.146 % 0.152 % <i>Avg. = 0.156 %</i>

LOI = 0.224 %, 0.210 %

B. ThO₂ -

The extraction results for an as-received sample are summarized below. The agreement between LOI and SCFE is high.

	SCFE	vacuum heating ¹
FTIR		<i>0.12 %</i>
detection		<i>0.12 %</i>
system		<i>0.13 %</i>
LOI = <i>0.143 %</i>, <i>0.157 %</i>		

C. PEOR-3258 -

The extraction results for an as-received sample are summarized below. The high weight loss measured for this sample was found to be due to organic adhesives on the outside of the extraction vessel, resulting from the placement of sample-transfer stickers. However, the gravimetric weight loss measured for this sample after SCFE was 0.040 %.

	LOI	SCFE
Hygrometer	<i>0.016 %</i>	<i>0.113 %</i>
detection	<i>0.024 %</i>	
system		

¹ The scale used to weigh-out the initial ThO₂ samples has only a two-digit accuracy.

D. PPSL-365 -

The results of LOI, SCFE, and IGA analysis on the as-received material are summarized in the following figure. The as-received materials gave an average LOI of 0.345 %, while SCFE gave an average of < 0.08 %. A post-SCFE extraction sample was analyzed by TGA, giving an average, total gravimetric weight loss of 0.017 %, while IGA analysis gave a post-extraction hydrogen content less than 0.01 %.

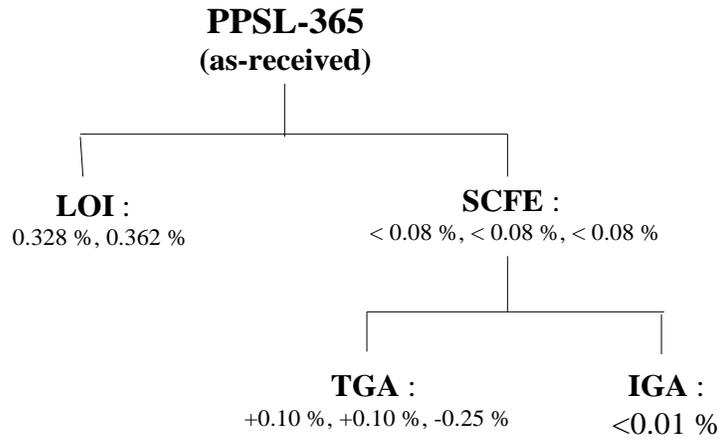


Figure 1. Weight losses measured for an as-received PPSL-365 material.

The PPSL-365 materials calcined to 600°C gave an average LOI of 0.177 %, while SCFE gave an average value of < 0.08 %. A TGA analysis of a post-extraction sample gave an average, total gravimetric weight loss of 0.017 %.

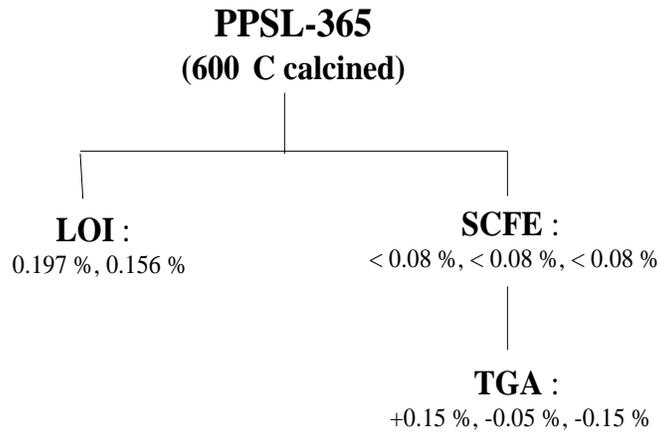


Figure 2. Weight losses measured for a 600°C calcined PPSL-365 material.

Finally, the PPSL-365 calcined to 950°C gave an average LOI of 0.044 %, while SCFE gave an average value of less than 0.08 %. Subsequent TGA analysis of the post-extracted material resulted in an average, total weight loss of 0.00 %.

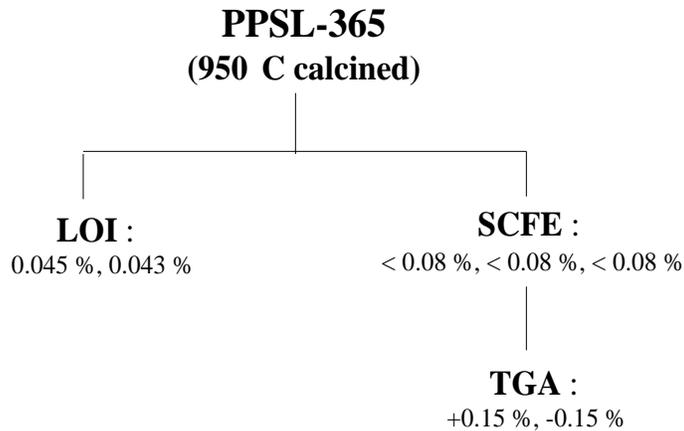


Figure 3. Weight losses measured for a 950°C calcined PPSL-365 material.

E. MIS-STD-1

The weight losses measured for the as-received materials are summarized in the following figure. The LOI and TGA results of the as-received material are in essential

agreement in that a significant weight loss is experienced by heating in air to 950°C. The LOI and TGA give gravimetric weight losses of 2.13 % and 2.80 %, respectively, while SCFE gave a value of only 0.089 %. A TGA analysis of a post-SCFE samples resulted in average, total weight loss of 0.033 %, while an IGA analysis of a post-SCFE sample gave a total hydrogen content of 0.058 %.

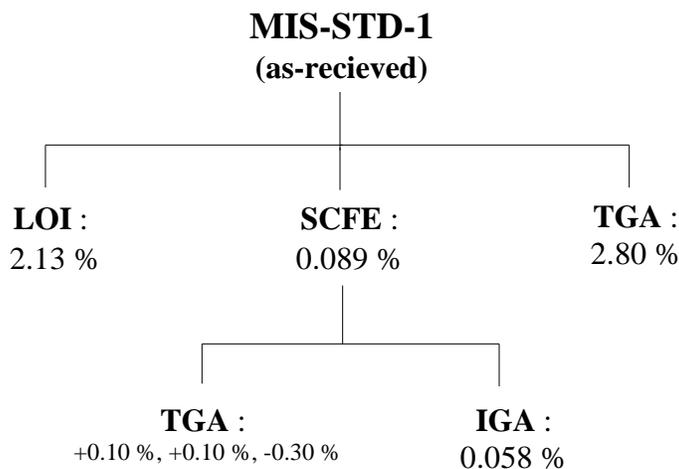


Figure 4. Weight losses measured for an as-received MIS-STD-1 material.

There appears to be a fundamental inconsistency in the set of results shown in Figure 4. The SCFE results, along with the independent, post-extraction results, indicates a low hydrogenous content, and that the LOI result is due to the volatilization of non-hydrogenous materials. However, since the TGA analysis of the post-extraction sample was run to the same final temperature as the pre-extraction samples, the same weight loss due to the non-hydrogenous material should have been recorded. The reason for this discrepancy is presently unknown.

F. ATL-27960

The results of LOI and SCFE for an as-received sample are summarized in the following table. We find that the large weight loss found gravimetrically by heating to 950C cannot be accounted for extraction, indicating that this weight loss is due to the volatilization of non-hydrogenous material.

ATL-27960	LOI	SCFE
(as-received)	4.3%	0.176 %
calcined to 600°C for 12 hours	2.4 %	-
calcined to 950°C for 2 hours	0.97 %	-

V. Conclusions

The level of agreement between LOI and SCFE for the surrogate oxides is high, indicating that, for moisture determination, supercritical fluid extraction is an effective analytical method for the quantitative determination of moisture content in oxide powders.

The results of SCFE for the PuO₂ samples is consistently lower than LOI, indicating that heating to high temperature results in the volatilization of non-hydrogenous material. It should be noted that these experiments required sample transfers from the Plutonium Facility (TA-55) to the CMR building, which probably introduced some systematic errors into the data. We feel that even better results can be achieved if the blending, sub-sampling, weighing into extraction vessels, and extractions were performed at the same site, preferably in the same glovebox. This is especially true in light of the difference in glovebox environment between the two facilities.

The use of a dew-point hygrometer to measure water vapor content in a flowing gas stream, is subject to two important constraints: (1) The method is invalid if any other constituent in the flowing gas stream condense before the water vapor, and (2) the accuracy of measurement is degraded by the presence of water-soluble materials. These factors limit the applicability of the hygrometer method to materials, which contain only water, with no organic substances. Since it is the goal of this work to evaluate supercritical fluid extraction as an analytical technique for the detection of total hydrogenous content, the FTIR detection system is recommended.

VI. Recommendations for Further Work

The FTIR detection system has been installed into the extraction system, and has been used to characterize surrogate materials. It remains to move this system into the CMR (or TA-55) and begin running PuO₂ samples. In addition, provisions for performing heat SCFE extraction cycles for PuO₂ samples needs to be made.

Additional experiments on PuO₂ samples “spiked” with organic compounds need to be performed to evaluate the quantitative determine by SCFE. Also, inorganic compounds, which may reasonably be expected to be present in impure oxides, can be added to nominally pure PuO₂ samples to verify that there is no solubilization during extraction. Finally, additional experiments on moisture uptake should be made, to investigate the efficiency of SCFE to quantify high moisture contents. The independent verification tests should continue with each of these sets of experiments

VII. Acknowledgments

The authors thank Mr. Don Vance for running the IGA analysis, and Dr. Richard Mason for providing data on the particle size, surface area and LOI analysis of the surrogate oxide and PuO₂ samples. We also gratefully acknowledge Mr. David Horrell, who initiated this work.

Table 1. Average Particle Size, Expressed as Spherical Equivalent Mean, for the Surrogate and PuO₂ powders.

	ThO ₂		CeO ₂		pure PuO ₂ : PEOR-3258	
Avg. particle size (μm)	Aliquot #1	15.4	Aliquot #1	28.1	Aliquot #1	33.2
	Aliquot #2	21.0	Aliquot #2	23.4	Aliquot #2	34.2
	Aliquot #3	17.2			Aliquot #3	32.8
	pure PuO ₂ : PPSL-365		pure PuO ₂ : MIS-STD-1		impure PuO ₂ : ATL-27960	
Avg. particle size (μm)	as received #1	12.6	Aliquot #1	-	as received	21.0
	as received #2	12.6	Aliquot #2	-		
	600° calcined #1	10.5			600° calcined #1	12.0
	600° calcined #2	21.5			950° calcined #1	16.4
	600 °950°calcined #1	10.7				
	600 °950°calcined #2	3.9				
	950° calcined #1	18.6				
950° calcined #2	18.6					

Table 2. Specific Surface Area of the Surrogate and PuO₂ Powders, Measured by 5-Point BET Method.

	ThO ₂		CeO ₂		pure PuO ₂ : PEOR-3258	
Surface area m ² / g	Aliquot #1	2.43	Aliquot #1	3.83	Aliquot #1	2.06
			Aliquot #2	3.84	Aliquot #2	1.99
			Aliquot #3	3.69	Aliquot #3	1.85
	pure PuO ₂ : PPSL-365		pure PuO ₂ : MIS-STD-1		impure PuO ₂ : ATL-27960	
Surface area m ² / g	as received #1	2.33	Aliquot #1	-	as received	15.6
	as received #2	2.32	Aliquot #2	-		
	600° calcined #1	2.36	Aliquot #3	-	600° calcined	4.3
	600° calcined #2	1.98			950° calcined	0.8
	600 °950°calcined #1	0.67				
	950°calcined #1	0.83				

VIII. References

1. "Assessment of Plutonium Storage Safety Issues at Department of Energy Facilities", DOE/DP-0123T, (1994).
2. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage", DOE/STD-STD-3013-96, (September, 1996).
3. James B. Rubin, William K. Hollis, Kennard V. Wilson, Luis A. Morales, Aaron M. Martinez, and Craig M.V. Taylor, "Extraction of Water from Oxides and Hydrates Using Supercritical-Fluid Carbon Dioxide", Los Alamos National Laboratory Report LAUR-97-2082 (June, 1997).

SUPERCRITICAL EXTRACTION OF PU-239 OXIDE, OTHER OXIDES, HYDRATES, AND HYDROXIDES

Analyte: Water, possible volatile organic compounds

Method No.: ANC 1304

Matrix: powdered PuO₂, other oxides, hydrates, and hydroxides

Procedure:

Effective Date: 12/11/96

Author: Kennard V. Wilson Jr.

Reviewed by: William Kirk Hollis

SAFETY NOTE: Before beginning this procedure, be familiar with all material safety data sheets for the chemicals listed in Sec. 7. Follow all SOP's related to the use of chemicals, radioactive material and compressed gases in the CMR; CMR-OP-AID-0015, CST-SOP5-001/X, CST-SOP-004/X, CST-SOP-005/X, CST-SOP-007/X, CST-SOP-063/X, CLS-1-OP-2,3 and 9, CST-PLA-003.X, CMR-POL-001,RX, QA-5,RX, QC-13, RX (where X is the most recent version).

1. PRINCIPLE OF METHOD

The method utilizes supercritical carbon dioxide (CO₂) to extract water and/or volatile and semi-volatile organic compounds from a powder matrix. A radioactive sample is transferred into a glovebox after receipt of the sample by sample management using proper Laboratory procedures. The sample is either received pre-weighed in an extraction vessel or in a sample container. If received in a sample container, a sample is removed, weighed and transferred into an extraction vessel. The sample is then extracted dynamically with supercritical CO₂. The temperature and pressure are controlled at the operator's desired values, within the extractor limits specified by the manufacturer.

2. ANALYTES AND LIMIT OF QUANTITATION

The analytes are water and/or volatile and semi-volatile organic compounds that may be present in the sample. Limits of quantitation will vary with analyte type.

3. SAFETY

3.1. Training Requirements

- 3.1.1. Operators must have a general knowledge of standard Laboratory practices, including the handling and disposal of corrosive, toxic and hazardous chemicals. This knowledge may be acquired by formal training, on-the-job training (OJT) or from the literature (MSDS's, manuals, etc.).
- 3.1.2. All operators must refer to the manuals provided by either the manufacturer or vendor for operational details.
- 3.1.3. All operators must have the standard required training for working at the CMR, Wing 7, laboratory in Room 7133, located inside a glovebox (see CST Operational Procedures Notebook).

- 3.1.4. Before attempting to use the Supercritical Fluid Extractor operators should be familiar with "Handling Compressed Gas Cylinders"(CST-SOP-004/2). Also refer to "Use of Chemicals" (CST-SOP-005/1) for the handling of the major types of chemical(s) to be extracted and analyzed. "Electrical Safety Awareness" and "Pressure Safety" training is also required.
- 3.1.5. When working with chemicals the guidelines specified in "Use of Chemicals" (CST-SOP-005/1) must be followed.
- 3.1.6. When working with radioactive materials the operator must follow the guidelines in "Working with Radioactive Materials"(CST-SOP5-001/1) and "Radiation Protection Practices in the CMR Facility"(CMR-POL-001, R3).
- 3.1.7. The disposal of waste will be performed in accordance with the guidelines specified in "Waste Handling Procedure"(CST-SOP-007/2).
- 3.1.8. Bagging of radioactive materials or supplies to/from glovebox to/from other areas must be demonstrated by an experienced designated individual and then observed by that individual for proper work practice. After training, the OJT form must be completed.

3.2. Safety Requirements

- 3.2.1. An experiment should not be performed if it cannot be done in a controlled and safe manner.
- 3.2.2. When working in a glovebox, with a process that requires handling radioactive materials, two persons must be present at all times.
CAUTION: Contact lenses should not be worn during experiments.
- 3.2.3. Operators are required to wear safety glasses, lab coats and 2 pair of gloves when working inside an open-front glovebox, or 1 pair of gloves when working in a closed glovebox.
- 3.2.4. No organic waste or waste containing toxic metals are to be poured down any drain. Spent waste or waste containing toxic metals must be transferred into approved containers and be collected by CST-5 personnel for proper disposal.
- 3.2.5. Special care must be taken due to the high pressures involved. A safety rupture disc on the back of the pump will blow when the system exceeds 6000 psi. A sudden relief pressure shutoff valve is used in the gas line as an added safety precaution.
- 3.2.6. The extraction system uses Supercritical Fluid Extraction (SFE) grade CO₂ or SFE-grade CO₂ mixed with a modifier such as methanol or ethanol. The carbon dioxide cylinder will have a dip tube with a helium head pressure.
- 3.2.7. Gas cylinders must be anchored with a safety strap to a solid wall, or secured to a bench or table.
- 3.2.8. Operators will routinely check their work areas for potential, developing safety problems and take appropriate corrective action.

4. INTERFERENCES

Water vapor or organics present in the CO₂, in the extraction vessels, or in the gas flow lines are possible interferences. The vessels need to be pre-conditioned by supercritical fluid extraction followed by vacuum heating. Refer to section 7 for CO₂ requirements.

5. COLLECTION AND STORAGE OF SAMPLES

Samples should be analyzed as soon as possible after being received. All samples should be stored in a desiccator or a sealed vessel with desiccant to limit adsorption of water from the atmosphere.

6. APPARATUS AND EQUIPMENT

- 6.1 The extraction unit is a stand-alone, dual chamber analytical extraction device. It consists of four modules: The Extractor, Controller, Pump, and Restrictor Temperature Controller.
- 6.2 The Extractor contains the vessel assembly and is located in the glove box.
- 6.3 The Controller contains the printed circuit boards, keyboard and electrometer, and is located outside the glovebox.
- 6.4 The Pump is of a syringe-type with 266-ml capacity. It is located outside the glovebox.
- 6.5 The Restrictor Temperature Controller maintains the restrictor at a pre-selected temperature, ranging from ambient to 240°C. It is located outside the glovebox.
- 6.6 The extraction vessels are 10-ml volume with 2- or 0.5- μ m frits, and are made of PEEK, aluminum, or stainless steel.
- 6.7 The detector is either a hygrometer or an FTIR equipped with a SFE/IR flow cell.

7. REAGENTS/STANDARDS

The extraction procedure uses: (1) SFE-grade CO₂ or equivalent, having 1 ppm water, and (2) 1 N nitric acid solution.

8. SCALE/BALANCE CALIBRATION

The scale or top-loading balance is calibrated using the internal calibration method and verified with a check weight. This is done once a day before weighing the samples.

9. QUALITY CONTROL

- 9.1. As is seen in Section 12, all calculations for both detectors are based on multipoint calibration curves. At the beginning of a sample run a known amount of water should be run to check the instrument.
- 9.2. When a known sample proves to be outside two standard deviations for either method, a new calibration curve should be generated, using 6 to 7 points.
- 9.3. Once a new calibration curve is obtained it should be tested with a known sample before proceeding with sample measurements.

10. PROCEDURE

10.1 Pre-Run Procedure

- 10.1.1. Initiate Pre-Extraction Checklist by completing personnel, matrix, and extraction fluid type.
- 10.1.2. Confirm personnel qualifications, matrix, and extraction fluid compatibility with extractor system (i.e. explosive issues and reactive extracting fluids) and complete checklist section.
- 10.1.3. Continue to complete Pre-Extraction Checklist by recording extraction temperature and pressure.
- 10.1.4. Verify Temperature and Pressure maximums on controllers and complete check list section.
- 10.1.5. Transfer sample (bulk or in extraction cell) into glovebox.
- 10.1.6. If bulk sample, transfer determined amount to an extraction cell and complete checklist section.
CAUTION: If the desired extraction temperature is greater than 80°C extra care should be exercised when handling the pre-heated extraction chamber cap.
- 10.1.7. Set extraction temperature and pre-heat the extractor to the desired temperature and record on the checklist when the temperature is stable.
- 10.1.8. Insert the end of the capillary restrictor into a collection vessel containing a

few milliliters of an appropriate collection solvent (methylene chloride has been found suitable for organic compounds) or into a detection system (such as the hygrometer) and from there into the solvent. Position the end of the tube just below the surface of the collection solvent.

CAUTION: Beware of heated restrictor.

10.1.9. Set the heated restrictor to the desired temperature depending on the collection solvent. If ice plugging occurs as the extraction progresses then increase the restrictor temperature. The operator may have to bring the restrictor further up from the collecting solvent to prevent evaporation.

NOTE: Typically 5-10 times the cartridge void volume over a period of 15-30 minutes is an excellent rule of thumb for supercritical fluid volume and extraction time. Longer extraction periods may be required if a hygrometer or another detector is interfaced.

10.1.10. Close all valves.

10.1.11. If knowledge of pump volume used at extraction conditions is known from previous runs, determine volume. If less than 100-ml continue to refill section. If greater than 100-ml continue with procedure. If volume is unknown continue to refill section.

10.1.12. Verify position of "Excess Flow Valve" (Run position) and collection containers volume and solution. Complete checklist. Continue to either section 10.3, if using a hygrometer detector or to 10.4 if using an FTIR.

10.2. Pump Refill Procedure

CAUTION: Personnel must ensure all valve are closed before filling the syringe pump to minimize the possibility if contamination due to back flow through the system.

10.2.1. Close all valves.

10.2.2. Turn "Excess Flow Valve" to the bypass position.

10.2.3. Press REFILL on the pump controller.

10.2.4. Open siphon tank valve.

CAUTION: Personnel must determine the pressure of pump reservoir before opening the "pump inlet" valve to minimize the possibility if contamination due to back flow through the system.

10.2.5. When pump pressure is below 800 psi on the pump controller open the "inlet" valve on the pump.

10.2.6. Once the pump stops allow the system pressure to stabilize.

10.2.7. Press STOP on the pump controller

10.2.8. Record the siphon tank pressure in the Tank Log Book. If the stabilized pressure is below 900 psi replace the siphon tank before the next extraction.

10.2.9. Close the "inlet" valve on the pump.

10.2.10. Close the siphon tank valve.

10.2.11. Return the "Excess Flow Valve" to the Run position.

10.2.12. If attempting an extraction return to the procedure section. If refilling the pump stop actions.

10.3. Hygrometer Procedure

10.3.1. Press the RUN button to start the pump. The pump is run up to the desired pressure.

10.3.2. Turn on the hygrometer power.

CAUTION: The order of the next two steps is critical to minimizing the possibility of back flow and contamination.

10.3.3. Open the "pump outlet" valve.

10.3.4. Open the "Supply" valve on the extractor.

10.3.5. Open the hygrometer outlet valve.

10.3.6. Once the desired pressure is reached again, the "Extract" valve is opened and the pump run at constant pressure and the extractor at the desired temperature

- until the hygrometer output is stable.
- 10.3.7. During this time the pump is refilled as necessary (Pre-Run Procedure, step 10.1.11.) using the Pump Refill Procedure (Section 10.2.), but the “Extract” valve is left open when refilling the pump.
- 10.3.8. Once the detector output is stable all the valves (“pump outlet”, “Supply”, and “Extract”) are closed except for the hygrometer outlet valve.
- 10.3.9. The pump is refilled if necessary (Pre-Run Procedure, step 10.1.11.).
CAUTION: The “Vent” valve is opened slowly and in small increments to prevent splashing of the 1 N nitric acid solution.
- 10.3.10. The vent tube is immersed in a test tube which is half-filled with dilute nitric acid(1 N) to retain any radioactive particulates that might escape from the extraction vessel.
- 10.3.11. The extraction cell is depressurized by opening the “Vent” valve.
- 10.3.12. After depressurizing the cell (gas flow out of “Vent” tube stops) close the “Vent” valve.
- 10.3.13. The extraction vessel (with sample) is weighed on the scale. This is recorded as the initial weight of the sample.
CAUTION: The extraction chamber cap is hot.
- 10.3.14. The extraction chamber cap is removed and the extraction vessel is loaded into the extraction cell.
- 10.3.15. The extraction chamber cap is replaced and tightened down.
CAUTION: The order of the next two steps is critical to minimizing the possibility of back flow and contamination.
- 10.3.16. Open the “pump outlet” valve.
- 10.3.17. Open the “Supply” valve on the extractor.
- 10.3.18. Repressurize to the desired pressure.
- 10.3.19. The valves are closed and the pump may be refilled if necessary (Pre-Run Procedure, step 10.1.11.).
CAUTION: The order of the next two steps is critical to minimizing the possibility of back flow and contamination.
- 10.3.20. Open the “pump outlet” valve.
- 10.3.21. Open the “Supply” valve on the extractor.
- 10.3.22. The entire system up to the “Extract” valve is pressurized to the desired pressure.
- 10.3.23. Once the pump pressure stabilizes the volume, shown on the LCD panel of the pump, is recorded as the initial volume (V_{int}). The initial reading on the hygrometer is also recorded.
- 10.3.24. The “Extract” valve is opened and the extraction experiment started.
- 10.3.25. Record the hygrometer output every 20 seconds for the first 5-minutes, then every minute for minutes 5 through 20, then every 5 minutes after 20-minutes until the hygrometer output stabilizes at or below the starting, baseline value.
- 10.3.26. When the hygrometer output is stable, close the “pump outlet”, “Extract”, and “Supply” valves.
- 10.3.27. Press STOP on the pump controller.
- 10.3.28. Record the remaining pump volume as the final volume (V_{fin}) and the hygrometer output as the final hygrometer output.
CAUTION: The “Vent” valve is opened slowly and in small increments to prevent splashing of the 1 N nitric acid solution.
- 10.3.29. Open the “Vent” valve and depressurize the extraction cell.
- 10.3.30. After depressurizing the cell (gas flow out of “Vent” tube stops) close the “Vent” valve.
CAUTION: The extraction chamber cap is hot.
- 10.3.31. Open the extraction chamber cap and remove the sample.
- 10.3.32. Replace extraction chamber cap and tighten down.
- 10.3.33. The sample is stored in the desiccator or in a container with desiccant until it has cooled to ambient temperature, then weighed to obtain a post-extraction (final) weight.
- 10.3.34. If this is the last run of the day, close the hygrometer outlet valve. If not, leave

the valve open and prepare for the next run (return to the Pre-Run Procedure, Section 10.1.).

10.3.35. Turn off the extractor heater control.

10.3.36. Turn off the restrictor heater control.

NOTE: Unless an extended period of time passes until the next run, the hygrometer is left on.

10.4. FTIR Procedure

10.4.1. Press the RUN button to start the pump. The pump is run up to the desired pressure.

10.4.2. Turn on the power to the FTIR instrument (power switch on rear left-hand corner when facing the front of the instrument).

CAUTION: The order of the next two steps is critical to minimizing the possibility of back flow and contamination.

10.4.3. Open the "pump outlet" valve.

10.4.4. Open the "Supply" valve on the extractor.

10.4.5. Once the desired pressure is reached again, the "Extract" valve is opened and the pump run at constant pressure and the extractor at the desired temperature.

10.4.6. At this time the data collection program (MIDAC's AutoQuant) is set up for continuous scanning with a preset method and run to establish a baseline with only supercritical CO₂ (no sample in the Extractor) .

10.4.7. After 1 or 2 minutes of data collection to establish the baseline, all the valves ("pump outlet", "Supply", and "Extract") are closed and the extraction cell depressurized.

10.4.8. The data collection is allowed to continue.

CAUTION: The "Vent" valve is opened slowly and in small increments to prevent splashing of the nitric acid.

10.4.9. The vent tube is immersed in a test tube which is half-filled with dilute nitric acid to retain any radioactive particulates that might escape from the extraction vessel. The extraction cell is depressurized by opening the "Vent" valve.

10.4.10. After depressurizing the cell (gas flow out of "Vent" tube stops) close the "Vent" valve.

10.4.11. The extraction vessel (with sample) is weighed on the scale. This is recorded as the initial weight of the sample.

CAUTION: The extraction chamber cap is hot.

10.4.12. The extraction chamber cap is removed and the extraction vessel is loaded into the extraction cell.

10.4.13. The extraction chamber cap is replaced and tightened down.

CAUTION: The order of the next two steps is critical to minimizing the possibility of back flow and contamination.

10.4.14. Open the "pump outlet" valve.

10.4.15. Open the "Supply" valve on the extractor.

10.4.16. The entire system up to the "Extract" valve is pressurized to the desired pressure. Once the pump stabilizes, as shown by the pressure reading on the pump LCD panel, the "Extract" valve is opened and the time in the program window recorded as the initial time.

NOTE: Steps 10.4.6. through 10.4.15. should be accomplished as quickly and safely as possible.

10.4.17. The absorbance display in the program window is set to observe from ~1670 cm⁻¹ to ~1570 cm⁻¹. The water peak is observed at ~1610 cm⁻¹ at 3000 psi (the region used in the method is from 1621.5 to 1590.0 cm⁻¹). The main display shows concentration (relative to the calibration standard) versus time.

10.4.18. The data collection is continued until the main screen reaches a stable baseline and the absorbance screen shows an absorbance 0.01.

10.4.19. When the baseline has stabilized, the "Extract" and "Supply" valves are closed and the program stopped and the time recorded as the final time.

- 10.4.20. The data is saved from AutoQuant into an Excel spreadsheet.
CAUTION: The “Vent” valve is opened slowly and in small increments to prevent splashing of the nitric acid.
- 10.4.21. The extraction cell is depressurized by opening the “Vent” valve.
- 10.4.22. After depressurizing the cell (gas flow out of “Vent” tube stops) close the “Vent” valve.
- 10.4.23. The sample is stored in the desiccator or in a container with desiccant until it has cooled to ambient temperature, then weighed to obtain a post-extraction (final) weight.
- 10.4.24. If this is the last run of the day continue. If not, prepare for the next run (return to Pre-Run Procedure, Section 10.1.).
- 10.4.25. Turn off the extractor heater control.
- 10.4.26. Turn off the restrictor heater control.
- 10.4.27. Turn off the heater control to the FTIR cell.
- 10.4.28. Turn off power to the FTIR instrument (power switch on rear left-hand corner when facing the front of the instrument). The switch on the power supply is left is the “on” position.

- 10.5. Conditions for extraction of water from PuO₂, surrogate oxide, and other materials are :

Extraction Pressure	3000 psig
Extraction Temperature	75°C to 100°C
Restrictor Temperature	90°C

11. CALCULATIONS AND DATA REPORTING

11.1. Hygrometer

- 11.1.1. Individual measurements of ppmv (parts-per-million-by-volume) H₂O, as reported by the LED readout of the hygrometer, versus elapsed time since the start of the extraction, will be recorded. During the initial part of the extraction, where the data is changing most rapidly, it is important that the data be recorded at closely spaced intervals so that the maximum value of ppmv is recorded.
- 11.1.2. The extraction will continue, and the data recorded, until the ppmv reading of the hygrometer falls to a value equal to or less than the starting, baseline value.
- 11.1.3. At the completion of the extraction experiment, a worksheet will be generated listing (a) the recorded values of ppmv H₂O versus elapsed time, (b) the initial vessel weight, (c) the initial vessel + sample weight, and (d) the total volume of liquid CO₂ used during the extraction, determined by the difference between the initial and final volume readings on the pump LCD panel display.
- 11.1.4. The vessel containing the sample will be removed from the extractor, as soon as this can be done safely, and transferred to a desiccator to cool for a period of not less than 6 hours. A gravimetric weight change from the extraction will be recorded.

11.2. FTIR

- 11.2.1. The data collected by AutoQuant is saved to an Excel spreadsheet. The initial and final times of the extraction are noted for use in determining what part of the data file is used for the calculations.

- 11.2.3. The extraction will continue, and the data recorded, until the concentration reading of the FTIR falls to a value equal to or less than the starting, baseline value.
 - 11.1.3. At the completion of the extraction experiment, a worksheet will be generated listing (a) the initial vessel weight, (b) the initial vessel + sample weight, and (c) the initial and final times of the extraction. The subdirectory that the data from AutoQuant is stored in is also noted.
 - 11.1.4. The vessel containing the sample will be removed from the extractor, as soon as this can be done safely, and transferred to a desiccator to cool for a period of not less than 6 hours. A gravimetric weight change from the extraction will be recorded.
- 11.3. Determination of Amount of Water in Sample
- 11.3.1. The data points obtained from either detector are placed in an Excel spreadsheet. In the case of the hygrometer they are entered manually, for the FTIR they are imported from Autoquant. The FTIR data has the additional treatment of the date/time numbers being replaced with point numbers.
 - 11.3.2. For either set of data the files are edited so that the data includes only the points collected during the actual extraction. The data is then imported into Sigmaplot and the area under the curve calculated.
 - 11.3.3. The area from the curve is then used to calculate the weight of water extracted from the equation obtained from a linear regression fit of a standard curve produced by plotting the areas produced by runs made with known amounts of water (see Section 12).

12. PRECISION AND ACCURACY

- 12.1. Tables 1 & 2 give typical calibration and statistical data for the hygrometer. Tables 3 & 4 give the same data obtained using the FTIR. Since the typical sample is 5 grams containing 0.5% (25 mg), it is well above the minimum detection limits of either method. To insure this remains so, known amounts of water are run against the standards to check accuracy of the method.
- 12.2. Confidence levels were determined from multiple extraction experiments made on a nominal water volume of 25 microliters. 25 microliters was chosen since it represents, for a 5 gram PuO₂ sample, 0.5 weight %, which is the maximum allowable adsorbate concentration specified by DOE Standard 3013. A summary of the statistical data for the hygrometer detection system can be found in Table 1 below. Since there are a small number of sample values, the standard deviation was calculated using a sample base, $n(n-1)$, rather than a population base, n^2 . The Method Detection Limit (MDL) was determined using the Student "t" test, and assuming a 2-tailed 99% confidence level. The critical value, 4.604, for the number of samples used, was multiplied by the standard deviation, 0.90, to calculate the MDL. For the FTIR calibration data the critical value for the number of samples used is 3.499. The MDL is again found by multiplying this critical value by the standard deviation, 1.01.

Table 1. Results of Supercritical Fluid Extraction, Using the Hygrometer Detection System, of Known Water Volumes.

Nominal weight of added water	Integrated Peak Area (ppmv)	Initial Gravimetric weight of added water	Gravimetric weight of extracted water	Calculated weight Of extracted water (mg)
<i>5.0 mg</i>	1821.1	-	-	<i>6.73</i>
<i>10.0 mg</i>	3059.7	<i>12.1 mg</i>	<i>7.7 mg</i>	<i>10.73</i>
<i>15.0 mg</i>	4403.7	<i>14.7 mg</i>	<i>13.6 mg</i>	<i>14.63</i>
<i>25.0 mg</i>	8547.5	<i>27.0 mg</i>	<i>22.4 mg</i>	<i>24.54</i>
<i>25.0 mg</i>	9058.9	<i>25.3 mg</i>	<i>23.9 mg</i>	<i>25.60</i>
<i>25.0 mg</i>	8879.7	<i>24.7 mg</i>	<i>23.2 mg</i>	<i>25.23</i>
<i>25.0 mg</i>	8082.8 ¹	-	-	<i>23.55</i>
<i>30.0 mg</i>	12,084	<i>28.9 mg</i>	-	<i>31.35</i>
<i>37.5 mg</i>	13,139.0	<i>36.8 mg</i>	<i>34.8 mg</i>	<i>33.19</i>
<i>50.0 mg</i>	25751.0	<i>52.4 mg</i>	<i>48.6 mg</i>	<i>51.89</i>
<i>75.0 mg</i>	43,604.0	-	-	<i>75.32</i>
<i>100.0 mg</i>	62371.0	<i>97.7 mg</i>	<i>97.0 mg</i>	<i>99.50</i>

¹ Water extracted from a sand matrix.

Table 2. Statistics for the Calibration Equation and the Method Detection Limit (MDL) for the Hygrometer Detection System.

	absolute	percent
standard deviation,	0.90	3.64
2	1.80	7.28
3	2.70	10.92
MDL confidence 99 %	4.14 mg	
MDL confidence 98 %	3.37 mg	
MDL confidence 95 %	2.50 mg	
MDL confidence 90 %	1.92 mg	

Table 3. Results of Supercritical Fluid Extraction, Using the FTIR Detection system, of Known Water Volumes.

Nominal weight of added water	Integrated Peak Area (ppmv)	Initial Gravimetric weight of added water	Gravimetric weight of extracted water	Calculated weight Of extracted water (mg)
5.0 mg	3.5104 10^6	5.1 mg	5.4 mg	4.95
10.0 mg	8.3120 10^6	10 mg	9.2 mg	10.56
25.0 mg	2.1724 10^7	25.0 mg	21.9 mg	26.25
25.0 mg	1.9408 10^7	25.1 mg	24.1 mg	23.54
25.0 mg	2.0947 10^7	25.0 mg	24.6 mg	25.34
25.0 mg	2.1021 10^7	25.0 mg	24.2 mg	25.43
25.0 mg	2.0774 10^7	25.0 mg	24.5 mg	25.14
25.0 mg	1.9958 10^7	25.0 mg	24.3 mg	24.19
25.0 mg	1.9550 10^7	25.0 mg	24.4 mg	23.71
30.0 mg	2.6880 10^7	30 mg	28.1 mg	32.28
50.0 mg	4.1071 10^7	50.1	48.1 mg	48.88
75.0 mg	6.3900 10^7	75 mg	72.7 mg	75.58
100.1 mg	8.4609 10^7	100.1 mg	98.3 mg	99.81

Table 4. Statistics for the Calibration Equation and the Method Detection Limit (MDL) for the FTIR Detection System.

	absolute	percent
standard deviation,	1.01	4.05
2	2.01	8.11
3	3.02	12.16
MDL confidence 99 %	3.53 mg	
MDL confidence 98 %	3.03 mg	
MDL confidence 95 %	2.39 mg	
MDL confidence 90 %	1.91 mg	

12.3. Given below are the equations obtained from the calibration curves generated from the above data. These are used in calculating the amount of water in analyzed samples.

HYGROMETER :

$$\text{mg H}_2\text{O} = (12864 \cdot 10^{-3} \cdot \text{AREA}) + 192651 \cdot (1 - e^{-14208 \cdot 10^{-4} \cdot \text{AREA}}) \quad (1)$$

FTIR :

$$\text{mg H}_2\text{O} = 1.1697 \cdot 10^{-6} \cdot \text{AREA} + 0.8407 \quad (2)$$

13. SOURCE MATERIALS

- 13.1. "D Series Syringe Pumps: Models 100DM, 100DX, 260D, 500D," Instruction Manual (P/N 60-1243-601), April 1993, copyright 1992, ISCO, Inc., Lincoln, Nebraska.
- 13.2. "ISCO Restrictor Temperature Controller," Instruction Manual (P/N 60-3963-003), June 1994, copyright 1993, ISCO, Inc., Lincoln, Nebraska.
- 13.3. "SFX 2-10 Supercritical Fluid Extractor Instruction Guide," (P/N 60-3863-014), November 1990, copyright 1990, ISCO, Inc., Lincoln, Nebraska.
- 13.4. "SFX-IR Interface Kit User's Guide," Instruction Manual (P/N 60-3933-121), May 1995, copyright 1995, ISCO, Inc., Lincoln, Nebraska.
- 13.5. "Grams/32 User's Guide V4.0," copyright 1991-1996, Galactic Industries Corp., Salem, New Hampshire
- 13.6. "FTIR Spectrometer Operator's Manual, M Series and Prospect•IR Systems," Revision C, July 1995, MIDAC Corp., Irvine, California
- 13.7. "MIDAC AutoQuant User's Guide," Revision B, copyright 1995-1996, MIDAC Corp., Irvine, California
- 13.8. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).
- 13.9. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

14. ATTACHMENTS

Attachment 1: *Proper Waste Disposal Practices* (2 Pages)

Attachment 2: *SCFE/heating cycle used for the PuO₂ powders* (1 Page)

Attachment 3: *SCFE and heating cycles used for the surrogate oxide powders* (1 Page)

Attachment 4: *Extraction Data Collection Sheet* (2 Pages)

Attachment 5: *Schematic Diagrams of the Extraction system, Incorporating Either the Hygrometer or FTIR Detection System* (1 Page)

Attachment 6: *Calibration curves constructed for the hygrometer (top) and FTIR (bottom) detection system* (1 Page)

Attachment 7: *CMR-OP-AID-0015: CMR Operator Aid for SFE* (1 Page)

Attachment 8: *Pre-Extraction Checklist* (1 Page)

ATTACHMENT 1

Proper Waste Disposal Practices

1. GENERAL WASTE MANAGEMENT

- 1.1. Each analyst within the section shall be given Waste Generator Training by ES&H Training (ESH-13) within 90 days of date of hire.
- 1.2. Wherever possible, the generation of waste shall be minimized through reduction, reuse, or recycling. Wherever possible, containers should be segregated to reflect the nature of the hazardous waste and the eventual waste-disposal method(s). For example, chlorinated solvent wastes should be segregated from flammable, nonchlorinated solvents and >50-ppm PCB-contaminated waste should be segregated from <50-ppm PCB-contaminated waste. This is especially important in analysis areas where the waste generated is considered to be mixed waste.
- 1.3. Categorize the waste using a Waste Profile Form (WPF).
- 1.4. Upon completion of a WPF, the waste is disposed of by completing a Chemical Waste Disposal Request (CWDR) form. Approximately 30 days is required for the disposal of waste after the completion of the listed forms.

2. SOLID WASTE

- 2.1. Solid hazardous waste, such as contaminated paper towels, pipettes, spent syringes, and glass vials, is to be collected in a covered plastic container lined with a plastic bag. The container is labeled with a hazardous waste label identifying the hazard, the type of material being stored (i.e., pipettes, paper towels, etc.) and the laboratory of origin.
- 2.2. The waste container is opened only for the time necessary to add the waste.

3. LIQUID WASTE

- 3.1. Liquid wastes, such as spent samples and spent solvents that are not reusable, are accumulated in glass or steel containers appropriate for the type of waste being stored. For example, caustic materials should be stored in glass containers whereas spent solvents that are not to be recycled should be stored in metal containers.
- 3.2. All containers storing hazardous liquid materials must be doubly contained. The container is labeled with a hazardous waste label identifying the hazard, the type of waste being stored (i.e., pipettes, paper towels, etc.) and the laboratory of origin.
- 3.3. The waste container is opened only for the time necessary to add the waste.

4. UNUSED SAMPLES

Return unused environmental samples to the Sample Management Office (SMO) for disposal.

ATTACHMENT 2

SCFE/heating cycle used for the PuO₂ powders.

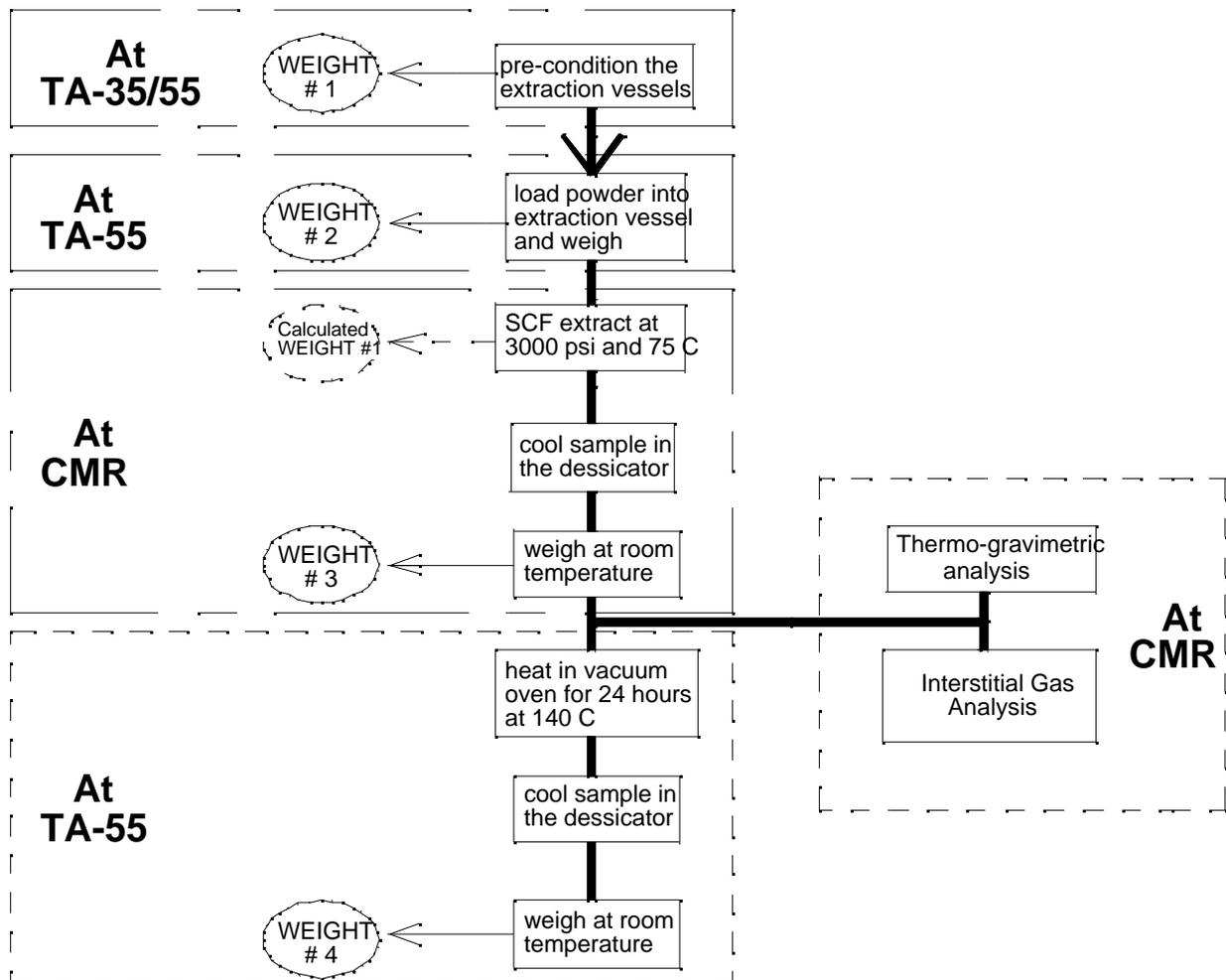


Figure 1. SCFE/heating cycle used for the PuO₂ powders.

ATTACHMENT 3

SCFE and heating cycles used for the surrogate oxide powders

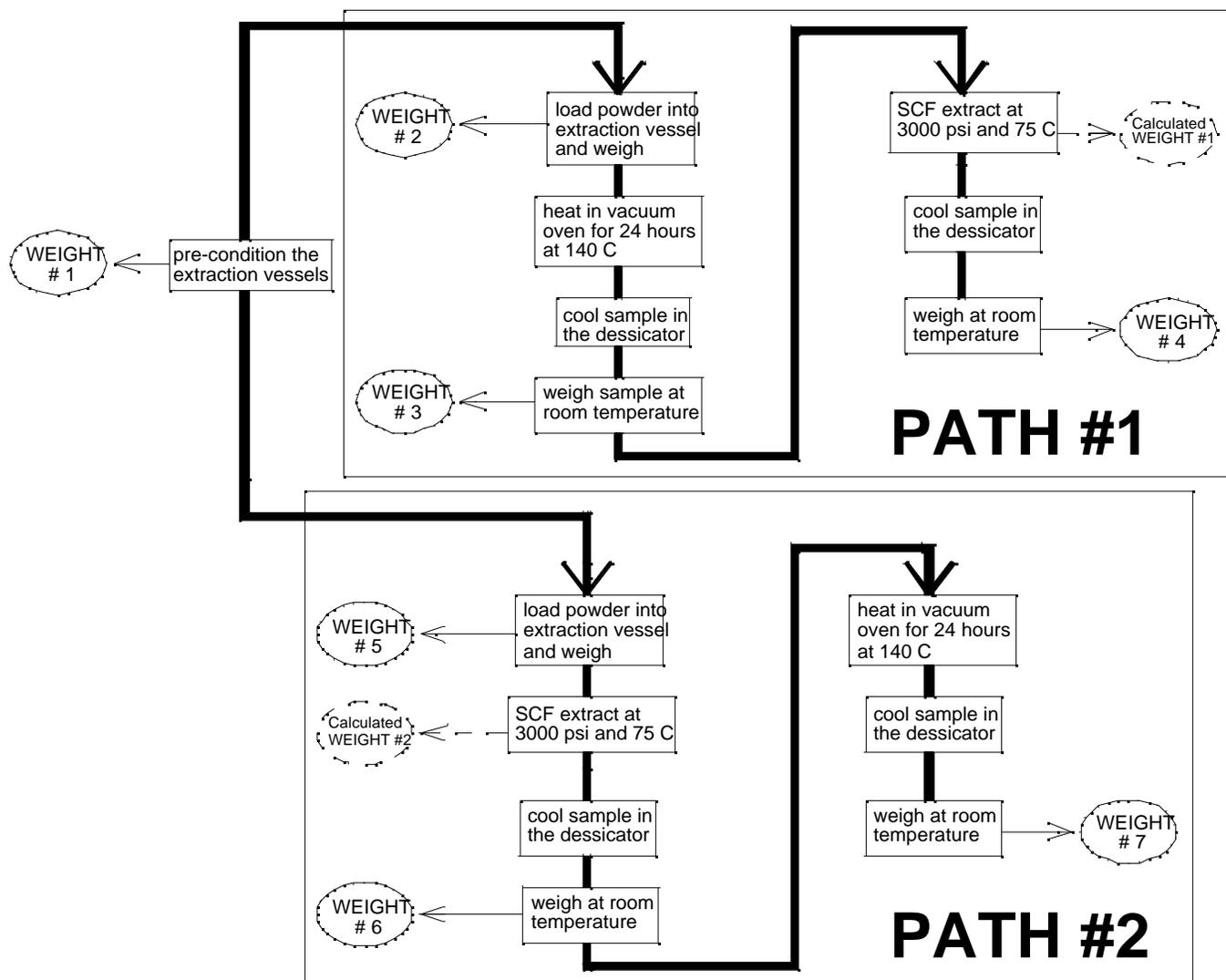


Figure 2. SCFE and heating cycles used for the surrogate oxide powders.

ATTACHMENT 4

Extraction Data Collection Sheet

Super-Critical Fluid Extraction

Sample ID

Date _____

Cartridge ID

Extraction Pressure psig

Extraction Temperature °C

Restrictor Temperature °C

Initial Vol₁ ml Initial Vol₂ ml Initial Vol₃ ml
 Final Vol₁ ml Final Vol₂ ml Final Vol₃ ml

Initial ppm ppm
 Final ppm ppm

	Weight (g)	Date
Initial Weight	<input type="text"/> g	<input type="text"/>
Final Weight ₁	<input type="text"/> g	<input type="text"/>
Final Weight ₂	<input type="text"/> g	<input type="text"/>
Final Weight ₃	<input type="text"/> g	<input type="text"/>
Final Weight ₄	<input type="text"/> g	<input type="text"/>

Time (min:seconds)	ppm	Time (min:seconds)	ppm	Time (min:seconds)	ppm
0:20	<input type="text"/>	6:00	<input type="text"/>	25:00	<input type="text"/>
0:40	<input type="text"/>	7:00	<input type="text"/>	30:00	<input type="text"/>
1:00	<input type="text"/>	8:00	<input type="text"/>	35:00	<input type="text"/>
1:20	<input type="text"/>	9:00	<input type="text"/>	40:00	<input type="text"/>
1:40	<input type="text"/>	10:00	<input type="text"/>	45:00	<input type="text"/>
2:00	<input type="text"/>	11:00	<input type="text"/>	50:00	<input type="text"/>
2:20	<input type="text"/>	12:00	<input type="text"/>	55:00	<input type="text"/>
2:40	<input type="text"/>	13:00	<input type="text"/>	60:00	<input type="text"/>
3:00	<input type="text"/>	14:00	<input type="text"/>	65:00	<input type="text"/>
3:20	<input type="text"/>	15:00	<input type="text"/>	70:00	<input type="text"/>
3:40	<input type="text"/>	16:00	<input type="text"/>	75:00	<input type="text"/>
4:00	<input type="text"/>	17:00	<input type="text"/>	80:00	<input type="text"/>
4:20	<input type="text"/>	18:00	<input type="text"/>	85:00	<input type="text"/>
4:40	<input type="text"/>	19:00	<input type="text"/>	90:00	<input type="text"/>
5:00	<input type="text"/>	20:00	<input type="text"/>	95:00	<input type="text"/>

time (cont.)

Time (min:seconds)	ppm	Time (min:seconds)	ppm	Time (min:seconds)	ppm
100:00	_____	125:00	_____	150:00	_____
105:00	_____	130:00	_____	155:00	_____
110:00	_____	135:00	_____	160:00	_____
115:00	_____	140:00	_____	165:00	_____
120:00	_____	145:00	_____	170:00	_____

Observations:

Analyst (print)	
Analyst (signature)	Date:

ATTACHMENT 5

Schematic Diagrams of the Extraction system, Incorporating
Either the Hygrometer or FTIR Detection System.

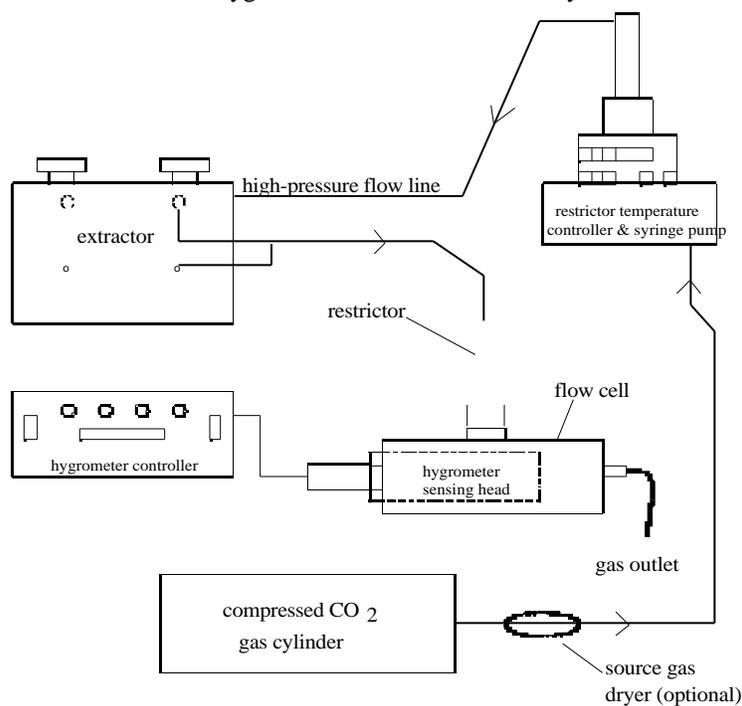


Figure 3. Schematic drawing of the supercritical extraction system, incorporating the hygrometer detection system.

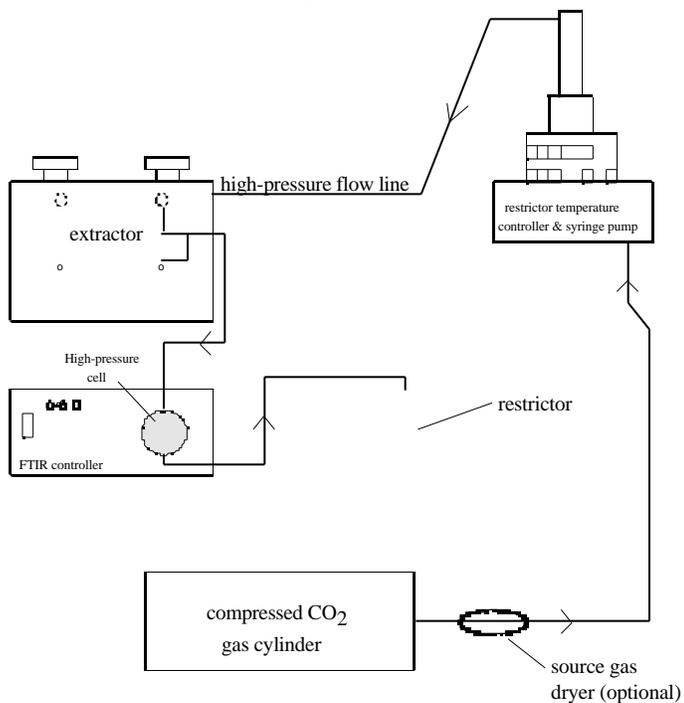


Figure 4. Schematic drawing of the supercritical extraction system, incorporating the FTIR detector system.

ATTACHMENT 6

Calibration curves constructed for the hygrometer (top) and FTIR (bottom) detection system

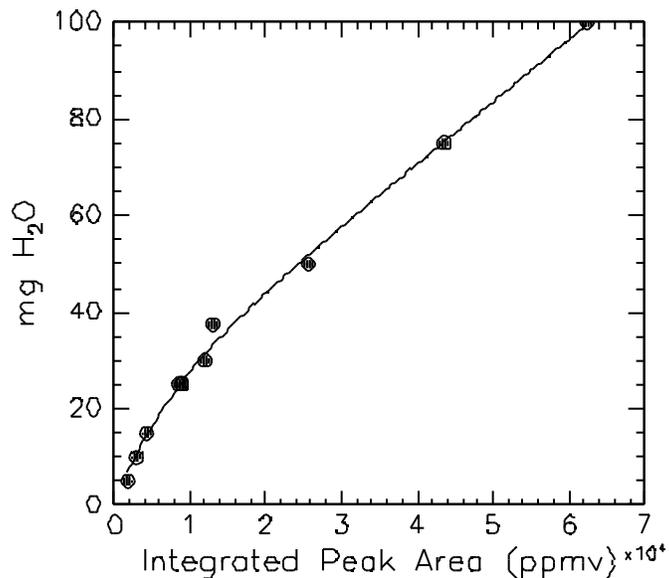


Figure 5. Plot of integrated peak areas versus known water volumes, using the hygrometer detection system (solid circles). The solid line is a plot of the empirical relation chosen to fit the data, Eq. (1).

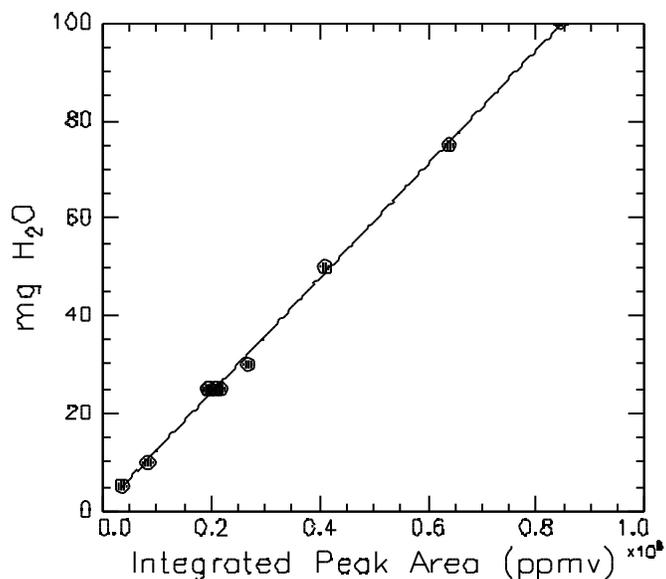


Figure 6. Plot of integrated peak areas versus known water volumes, using the *FTIR* detection system (solid circles). The solid line is a plot of the empirical relation chosen to fit the data, Eq. (2).

Hazard Potentials for SuperCritical Extractor

Use **Only** Procedure Approved Materials

For More Information Contact

W. Kirk Hollis

CST-12

5-5656

HAZARD WARNING

- FOR USE BY QUALIFIED LABORATORY PERSONNEL ONLY.
- FOR USE ONLY WITH SUPERCRITICAL TYPE FLUIDS.
- 10,000 PSI (68.9 MPA), 150⁰ C MAXIMUM.
- COMPRESSED GAS STORES DANGEROUS AMOUNTS OF ENERGY.
- DO NOT RAISE TEMPERATURE AFTER PRESSURIZATION.

IF CARTRIDGE HOLDER IS HARD TO TURN, THIS INDICATES THE UNIT IS PRESSURIZED. DEPRESSURIZE COMPLETELY BEFORE UNSCREWING TO AVOID INJURY AND DAMAGE.

DEPRESSURIZATION IS COMPLETE WHEN GAS IS NO LONGER EMITTED FROM VENTS.

EXPLOSION HAZARD!

- DO NOT PRESSURIZE EXOTHERMIC REACTIONS
- DO NOT USE REACTIVE SUPERCRITICAL FLUIDS, E.G. N₂O WITH OXIDIZABLE SAMPLE OR MATRIX.
- DO NOT EXTRACT UNSTABLE OR EXPLOSIVE SAMPLES, E.G. PICRIC ACID.

PRE-EXTRACTION CHECKLIST

1. Personnel performing extraction: _____

Are personnel unqualified?

Yes* No
* (IF YES STOP WORK)

2. Extraction Fluid

Is Extraction Fluid reactive?

Yes* No
* (IF YES STOP WORK)

3. Matrix to be Extracted

Is matrix unstable or explosive?

Yes* No
* (IF YES STOP WORK)

Estimated Amount to be extracted

_____g

4. Extractor Conditions:

Pressure (P_e)

_____psi

Temperature (T_e)

_____°C

Verify Pressure Maximum on Controller

(50 psi above P_e not to exceed 7500 psi)

Verify Temperature Maximum on Controller

(10°C above T_e not to exceed 150°C)

Confirm extractor is pre-heated?

5. Confirm Excess Flow Valve in the Run Position

6. Confirm proper solutions and volumes in vent collection and
and extraction collection containers

Personnel Signatures

1. _____

Date _____

2. _____

Date _____