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7\. Abstract

This report describes the analytical tests performed on archived core composite samples form a 1985 sampling of the 241-TY-101 (101-TY) and 241-TY-103 (103-TY) single shell waste tanks. Both tanks are suspected of containing quantities of ferrocyanide compounds, as a result of process activities in the late 1950's. Although limited quantities of the composite samples remained, attempts were made to obtain as much analytical information as possible, especially regarding the chemical and thermal properties of the material.

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9\. Impact Level 4

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TABLE OF CONTENTS

APPENDIXES

LIST OF FIGURES

LIST OF TABLES

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[1] Abstracted from [Weiss 1987b]

LIST OF TERMS

101-TY	241-TY-101
103-TY	241-TY-103
AAS	atomic absorption spectrometry
DSC	differential scanning calorimetry
EPA	Environmental Protection Agency
IC	ion chromatography
ICP	inductively-coupled plasma spectrometry
PCL	Process Chemistry Laboratory
PNL	Pacific Northwest Laboratory
STG	scanning thermogravimetric analysis
SST	single shell tank
TBP	uranium recovery process
TGA	thermogravimetric analysis
TOC	total organic carbon
XRD	x-ray diffraction
XRF	x-ray fluorescence
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

Beginning in late 1954, significant quantities of potassium (later sodium) ferrocyanide and nickel sulfate were added to aqueous liquid wastes from the uranium recovery process. The uranium recovery process (TBP Process) [Sloat 1954] extracted and decontaminated uranium from the metal waste produced in the Bismuth Phosphate (Plutonium Recovery) Process. A large volume of aqueous waste, approximately equal in volume to the metal waste itself, resulted from this operation. Virtually all the radioactive fission products were present in the TBP Process waste stream. Production estimates of the quantity of highly radioactive liquid wastes from the this process ranged up to 35 million gallons. This quantity would have exceeded the storage capacity of the existing tanks.

Testing [Burns 1954, and Smith 1954] had shown that metal ferrocyanides have a good affinity for cesium. If introduced into slightly basic waste solutions, these compounds cause the cesium to be precipitated as mostly sodium nickel cesium ferrocyanide [$NaCsNiFe(CN)_6$]. An excess of ferrocyanide was added to ensure complete scavenging of the cesium. The resulting supernate was then removed and cribbed to the soil column. Estimates of scavenging efficiency indicated that virtually all the cesium (and remaining strontium) would precipitate in a small sludge volume. A sludge volume of only ten percent of the aqueous waste volume would free up large amounts of tank space.

The above process was conducted primarily at the U Plant (TBP Plant) in the 200-W area, and with tank wastes associated with T Plant (200-W) and B Plant (200-E area). Tanks selected to receive the sludge were chosen primarily for their proximity to available cribbage. The availability of sludge removal facilities, for possible future recovery of the cesium, was also a consideration. The ferrocyanide precipitate is currently estimated to be distributed among twenty-four of the single shell tanks (SSTs).

In 1984, work done at the Pacific Northwest Laboratory (PNL) [Burger 1984] indicated that potentially explosive mixtures of ferrocyanide, nitrates, and nitrites may reside in these tanks. Follow-up work is currently defining these explosive parameters [Burger 1990]. None of the known or suspected "ferrocyanide tanks," however, is believed to be at a temperature sufficiently high to cause a reaction.

2.0 GOALS AND RESULTS

2.1 STUDY OBJECTIVES

In 1985, core samples of tanks 241-TY-101 (101-TY) and 241-TY-103 (103-TY), both suspected ferrocyanide tanks, were obtained and transferred to the 222-S Laboratory for analysis. In both cases, core composites were blended from weighted fractions of the recovered core segments. All analytical work was performed on these composites. Analyses were not performed on individual segments or observed layers, in accordance with the waste characterization plan [Bowton 1985] for the 1985 work. Analyses performed and results obtained are detailed in two supporting documents [Weiss 1987a, Weiss, 1987b, and Winters, 1988]. Copies of the core composite final results are attached as Appendixes A and B. Although six cores were obtained from 103-TY, analytical data was obtained only from composites 31XC000 and 32XC000. Samples of core composites (101-TY and 103-TY) were separately packaged and stored for archive purposes in the 222-S Laboratory.

The objective of the analytical plan is to perform analyses that were not done in 1985 or since, especially those which may help in the speciation the cyanide compounds present. Synthetic cesium nickel ferrocyanide and reagent-grade potassium ferrocyanide also have been analyzed by several methods, to guide evaluation and interpretation of the analytical techniques and results. Previous analytical work [Weiss 1987a, Weiss 1987b, and Mitchell 1980] indicates no attempt was made to determine the actual cyanide compounds present in the sludge. Of course, this work predated the current hazard concerns. The chemistry and energetics of the ferrocyanide oxidation reaction can change with the form of the cyanide complex. Attempts to speciate the cyanide in the sample have been made.

Overall, these additional analytical tests will be used to gain a preliminary understanding of the reactivity of the ferrocyanide waste in a SST. Valuable additional information on ferrocyanide waste behavior is a further objective. It must be understood by the reader, that since these samples are composites, the information presented below may not be representative of any particular tank layer (ie. sludge or crust), and the data must be viewed with this fact in mind.

2.2 A NOTE ON THE COMPARISON OF 1985 AND CURRENT RESULTS

The 1985 results [Weiss 1987a and Weiss 1987b] were reported on a wet weight basis while the current results are reported on a dry weight basis. The reader may wish that the results for the 1985 set of analyses and the current round of analyses were reported in the same format, i.e. wet or dry weight basis. The reason for this apparent loss of information is that the percent water determinations were performed very differently, and so what constitutes the "dry" or "wet" sample is defined differently by the methods used, as explained below. To compare values based on either wet or dry sample weights for both the 1991 and 1985 sets of data would be misleading. The 1985 "weight loss" was measured from ambient to 400° C, at which temperature there is appreciable non-water loss (see thermal analysis section). The current (1992) round of analyses were based on sample dried at 120° C, which would only drive off water and lighter organic volatiles. The percent water was derived from drying at 120° C and so is different than a "weight loss" derived from heating to 400° C. However, one can make the assumption that the two "percent water" numbers are comparable. This assumption yields the conversion factors shown in Table 2-1.

Table 2-1. Approximate Conversion Factors for the Comparison between 1985 and Current Data.

TY-101	TY-103
1.77 g wet "1985 results" solids/g dry "1992 results" solids	2.05 g wet "1985 results" solids/g dry "1992 results" solids
3.12 g wet "1985 results" solids/g dry soluble "1992 results solids	3.53 g wet "1985 results" solids/g dry soluble "1992 results solids
4.09 g wet "1985 results" solids/g dry insoluble "1992 results" solids	4.89 g wet "1985 results" solids/g dry insoluble "1992 results" solids

Example: nitrite, TY-103

7510 μg nitrite/g wet solids * 3.53 g wet solids/g dry soluble "1992 results" solids = 26000 μg nitrite/g dry soluble "1992 results" solids

These conversion factors have errors associated with them, that are not well known, and so must not be used to generate comparison data with more than two significant figures. The errors associated with these conversion factors include, but are not limited to, the weight loss above the 120° C drying temperature, $NaNO_3$ weight loss and decomposition above 300° C (see thermal analysis section for further details).

3.0 ANALYTICAL PLAN

3.1 OVERVIEW/SCOPE

As indicated in the previous section, many analyses have already been performed on the core composite sample [Weiss 1987a and Weiss 1987b]. In 1988, portions of archive samples were used to determine the cyanide concentration in the two tanks [Winters 1988]. The total cyanide found by a low acid distillation and pyridine barbituric acid spectrophotometric method was 3580 ± 242 μg/g wet solids in 101-TY and 2660 ± 663 μg/g wet solids in 103-TY where the standard deviations are used to represent the uncertainties.

The 222-S Laboratory (WHC) and PNL performed (in late 1991) additional sample analyses on the archive samples remaining from the tank core composites of 101-TY and 103-TY and also performed analyses on synthetic and reagent-grade known materials. The synthetic and reagent material analyses are summarized schematically in Figure 3.1. The tank composite analyses are summarized schematically in Figures 3.2 and 3.3. Synthetic samples and reagent-grade materials containing ferrocyanide were analyzed by many of the same methods as the tank samples, to provide technique validation and result evaluation data.

Each archive sample was dried to a constant weight at 120° C, and a small portion (0.5 - 0.8 gram) was set aside for various analyses. A water leach was performed on the remaining material. The insoluble fraction, remaining after the water leach, was dried and weighed to determine the percent dissolved. Both the soluble and insoluble fractions underwent additional analytical analyses to determine the thermodynamic, kinetic, and chemical properties of the sample. Similar analyses on the synthetic and pure reagents are compared to those from the tank core composites. The soluble fraction was made up to 100 mL prior to further analyses.

3.2 QUALITY ASSURANCE AND LABORATORY PROCEDURES

The data produced by the tests described in this report may be used to support waste tank safety decisions. Impact Level 4 is assigned, according to WHC-CM-1-3, *Management Requirements and Procedures*, MRP 5.43, "Impact Level."

The sampling and analysis work performed for this plan conforms to WHC-SD-CP-QAPP-001, "222-S Quality Assurance Project Plan." This document describes the laboratory procedures, laboratory records, and the control of records, equipment, materials and measurements for analytical laboratories.

Specific analytical procedures for those analyses performed within the 222-S Laboratory organization are detailed in Section 4.0 and listed in the reference section. There were no major deviations from any of these approved procedures, except the elimination of carbonate because of insufficient sample.

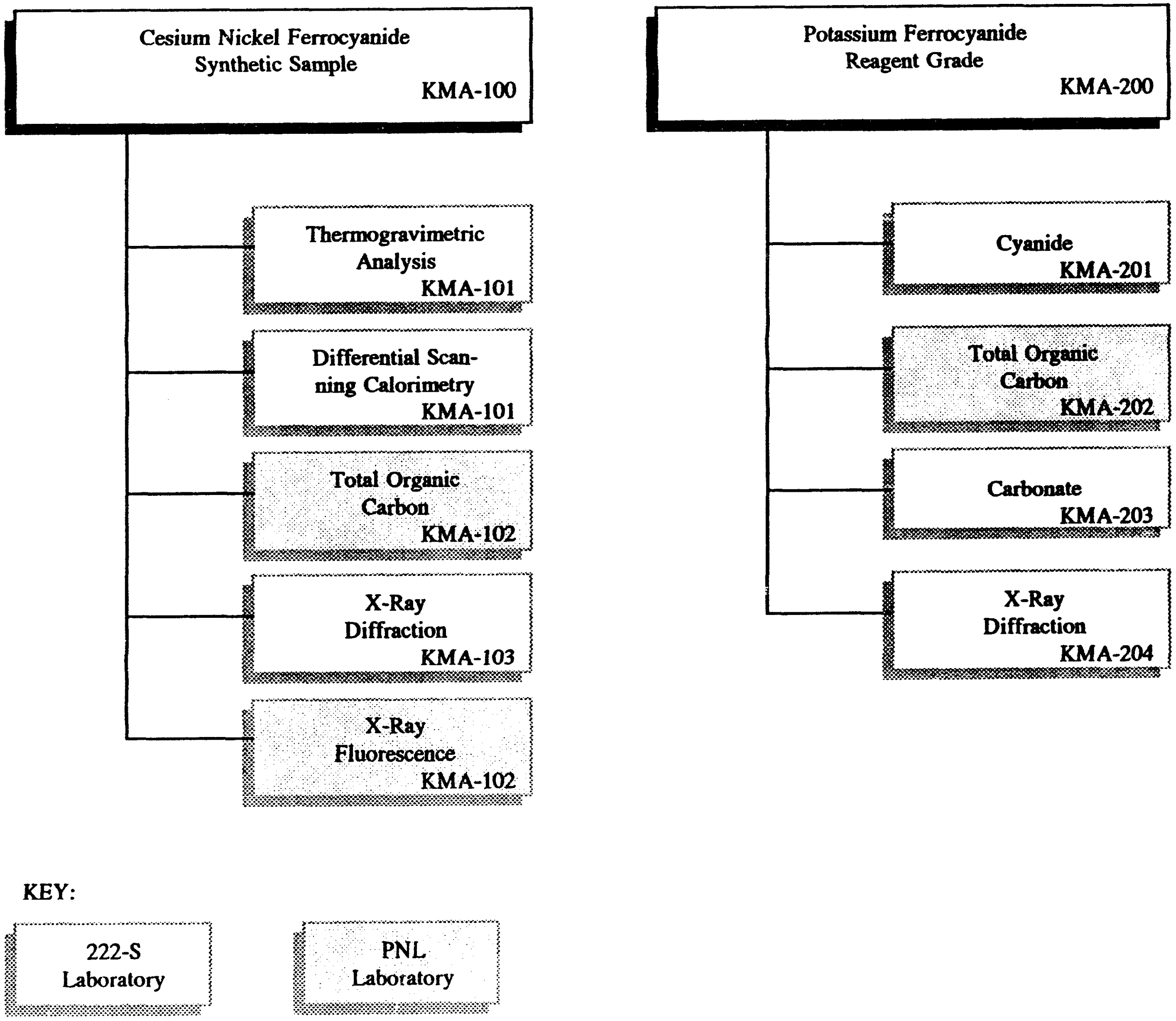

Figure 3.1. Known Material Analyses.

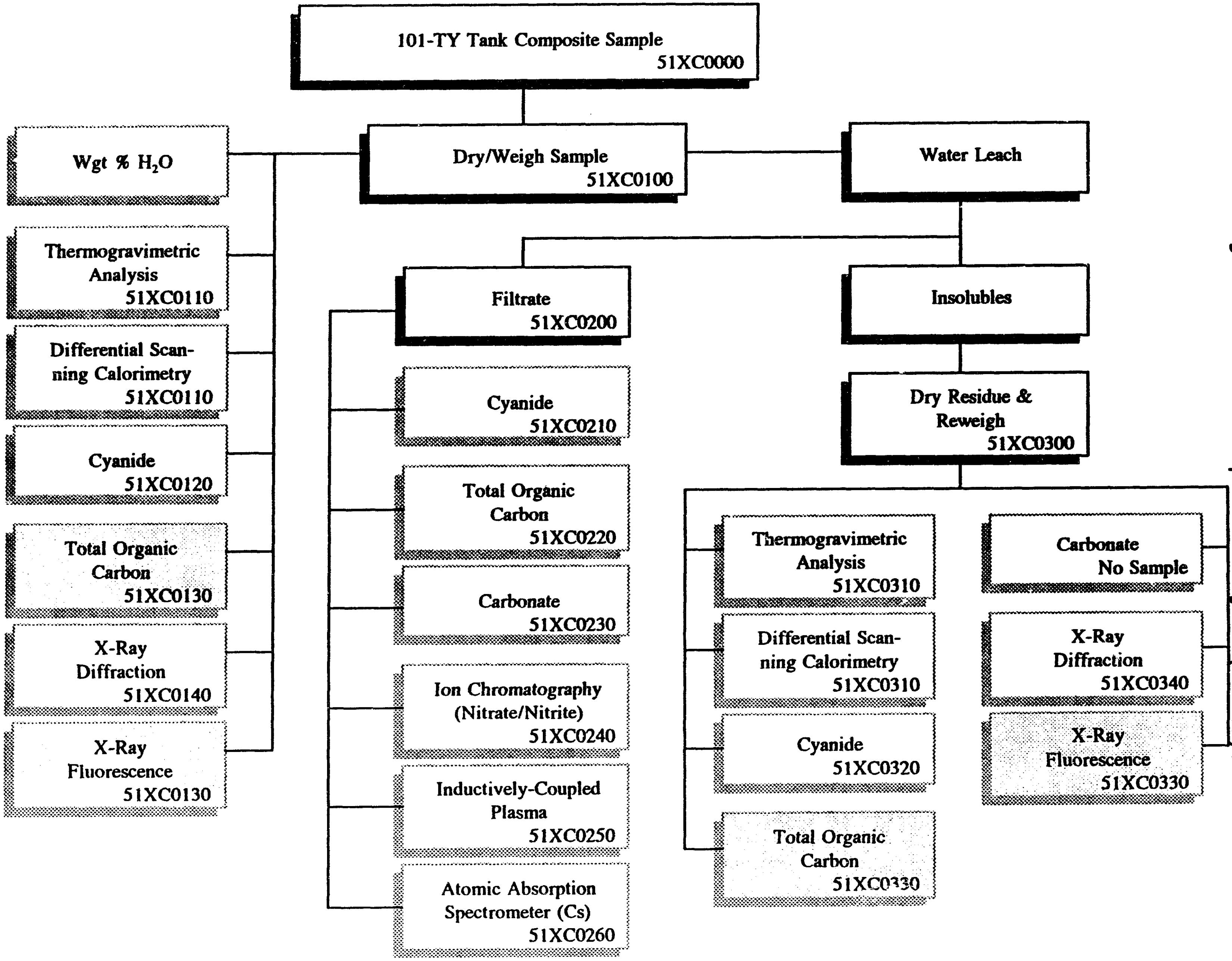

Figure 3.2. Tank Composite Analyses (TY-101).

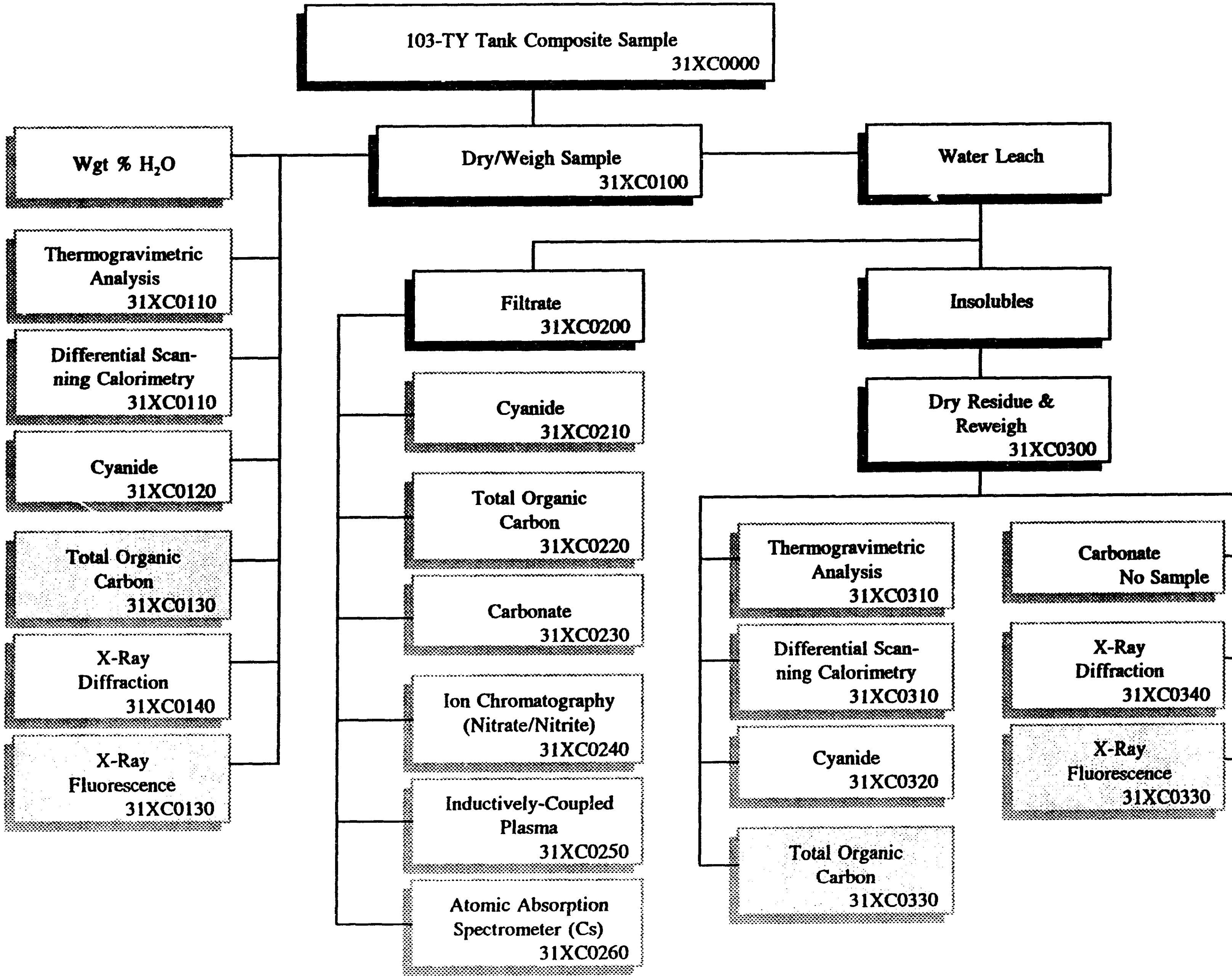

Figure 3.3. Tank Composite Analyses (TY-103).

The following desk instructions (Bechtold 1990b, Bechtold 1990c, Bechtold 1990d) governed the general laboratory work by the Process Chemistry Laboratory (PCL) at the time that the analyses were performed:

- Process Development Group Laboratories Testing
- Laboratory Notebook Documentation
- Identification and Control of Items

Additional specific desk instructions governed individual procedures performed by the PCL for analyses such as differential scanning calorimetry (DSC), scanning thermogravimetric analysis (STG), and others. Process Chemistry Laboratory is no longer using these documents for quality assurance and laboratory procedure purposes, and is in the process of converting these documents into formal laboratory procedures (LO-xxx-xxx, and LA-xxx-xxx type documents).

Procedures used by the 222-S Laboratory (Process Development Support Unit and other 222-S organizations) are listed in Section 6.1.

The methods used to submit samples for analysis to PNL, and the procedures used for the various analyses, are given in the PNL document, PNL-MA 70, "Procedures for Quality Assurance Program." This is the PNL laboratory Quality Assurance manual, and it addresses the issues delineated in the NQA-1 manual [ASME 1989]. The total organic carbon (TOC) analyses performed by PNL did not meet the requirements of the Westinghouse Hanford Company (WHC) test plan [Smith 1991]. Westinghouse Hanford Company delivered the test plan to PNL. Pacific Northwest Laboratory failed to use the WHC test plan during the development of the PNL test instructions.

3.3 ANALYTICAL PRIORITIES

The quantity of sample available from each tank was limited, estimated to be less than 5 grams for each tank. The analyses were performed according to the priorities set forth in the test plan [Smith 1991]. The WHC Senior Chemists' Panel discussed these priorities in March 1991 [Brehm 1991].

3.4 SPECIFICS

3.4.1 Description of Remaining 101-TY Composite Sample

The archived sample of 101-TY composite (51XC0000) [Weiss 1987b] consisted of approximately 3-5 grams of a relatively dry powder. Previous analyses done on this material indicate that it is indeed a composite; all layer-specific information has been lost in the compositing process. The remaining utility of the sample is chiefly its use in attempts to speciate the cyanide content into likely candidates.

3.4.2 Description of Remaining 103-TY Composite Sample

The archived sample of 103-TY consisted of a composite (31XC0000) of approximately 5 grams. Prior analyses of this material [Weiss 1987a and

Winters 1988] indicate that it contains several crystals and may not be homogeneous. Previous cyanide analyses by Winters [Winters 1988] showed an unusually wide variation between duplicates, which may be an indication of such inhomogeneity.

3.4.3 Preparation of Archived Samples

1. Test Plan [Smith 1991, Appendix C] instructions were followed to dry and prepare the archive material for further analyses.
2. The remaining sample was weighed out. Aliquots (approximate total 0.6 gm) were set aside for analyses on the direct solids.
3. The remaining material was weighed and an overnight water leach performed and test plan [Smith 1991, Appendix D] instructions used for detailed guidance.
4. The filter with solids was dried to constant weight and the solubility percentage of the composited material was calculated.
5. The dried material remaining after step 4 was weighed out for analyses on the insoluble water leach residue.

3.4.4 Description of Synthetic and Reagent Materials

Synthetic and reagent-grade materials containing ferrocyanide were analyzed by several methods. It was intended that the results obtained provide insight and information on the speciation of cyanide compounds in the core composite samples. Reagent grade potassium ferrocyanide [$K_4Fe(CN)_6 \cdot 3H_2O$] and a synthetic cesium nickel ferrocyanide [$Cs_2NiFe(CN)_6 \cdot xH_2O$] were used for these tests. The $Cs_2NiFe(CN)_6 \cdot xH_2O$ was prepared as described in WHC-N-421 pages 8 and 9 and WHC-N-341-1 pages 40-42 (See Appendix F). Neither the reagent grade potassium ferrocyanide nor the synthetic [$Cs_2NiFe(CN)_6$] were treated (dried, centrifuged, etc.) in any way.

4.0 ANALYTICAL METHODS/TECHNIQUES AND ASSOCIATED RESULTS

This section provides brief descriptions of the analyses performed by the 222-S Laboratory and PNL on the samples described in Section 3.0. All analyses performed, and the associated results, are listed here in order of priority.

4.1 THERMAL ANALYSES: TGA AND DSC

Thermogravimetric analysis (TGA) is a measurement of weight changes of a system or compound as a function of increasing temperature. This method heats a portion of the sample from ambient to 450° C while measuring the mass as a function of time and temperature.

Differential scanning calorimetry. The amount of electrical heating energy required to keep the sample and an inert reference at the same temperature as they are both heated at a constant rate. Energy is evolved in the sample if the organic-nitrate reaction commences. Energy is absorbed when water is driven off and in melting. The instrument records the heating difference as a milliwatt change, (allowing easy conversion to joules). Differential scanning calorimetry can provide an observed reaction starting temperature, an onset temperature, and the enthalpy of the reaction. The technique is similar to that used previously to determine softening points for the original tank samples [Weiss 1987a and Weiss 1987b]. To provide additional information on ferrocyanide waste reactivity, the test was extended to higher temperatures.

The following information, taken from Bechtold [1992a], reports the results of DSC and TGA of the archived samples from ferrocyanide watchlist tanks TY-101 and TY-103, as prepared according to Smith [1991]. Also included are the results for a synthetic compound cesium nickel ferrocyanide, $Cs_2NiFe(CN)_6 \cdot xH_2O$ [Smith 1991]. The TY-101 and TY-103 samples are composites from cores taken in 1985, stored at 222-S since that time. Smith [1991] discusses the origin of these samples in detail. The synthetic cesium nickel ferrocyanide was prepared by PCL as described in Jewett [1990] (see Appendix F).

Process Chemistry Laboratory utilized its own thermal analysis instrument in this work, (Perkin-Elmer model DSC-2/TGS-2) and logged the analyses in WHC-N-522 [Bechtold 1990]. Aliquots of each sample between 3 and 10 mg in size were analyzed in duplicate. The aliquots were placed in open, pre-fired stainless steel or platinum pans under 40-50 cc/min flowing nitrogen cover gas, and analyzed from 40 to 500° C at a temperature scan rate of 10° C/min.

Tables 4-1, 4-2, and 4-3 identify the specific samples analyzed by number and description. The tables also provide the averages of significant results of duplicate analyses and their associated standard deviations. The instrumental traces from which these results were derived are attached for your edification as Appendix D.

The TGA and DSC traces show in general that the tank waste composites retain approximately 10% moisture to temperatures as high as 275° C in some cases. Above that, the next prominent event is associated with the melting of sodium nitrate, which is accompanied by significant weight loss in the vicinity of 225--320° C. This event has been noted before in thermal analyses of synthetic ferrocyanide sludges in Bechtold [1992b], Bechtold [1992c], and Bechtold [1991], where the associated weight loss has been shown to involve cyanide. It is interesting to note the feature is more prominent in the TY-101 samples, which have been shown in Winters [1988] to contain the greater amount of total cyanide.

Furthermore, only the TY-101 samples showed any exothermic tendency. This was a small exotherm, it occurred near 400° C, and it was not reproducible in duplicate to any precision.

Otherwise, the tank composite samples underwent a general decomposition and weight loss above 300° C which gave no indication of completion at the 500° C analysis limit. There was also a discrete endotherm within this range which remains unassigned.

Water leaches of the TY-103 tank waste samples weakened the nitrate-melting features in the remaining residue, as expected. However, water leaching made these same features more prominent in the residues of TY-101 composite--a surprising result.

The TGA and DSC traces of $Cs_2NiFe(CN)_6 \cdot xH_2O$ have very few identifiable features other than probable moisture loss to 275°C followed by general high-temperature decomposition. These are even less informative than the trace of synthetic sodium nickel ferrocyanide, discussed in Smith [1991]. The percent moisture in this material is consistent with a hydration number $x \cong 2.2$. It should be noted that $Cs_2NiFe(CN)_6 \cdot xH_2O$ is known to have variable stoichiometry [Loos-Neskovic 1984] and variable waters of hydration, and as such is not an ideal reference material.

In conclusion, the thermal analysis of TY-101 and TY-103 composites show the presence of moisture and sodium nitrate, and indirectly infer the presence of total cyanide. Also, some traces are consistent with, but do not prove, the presence of $Al(OH)_3$. The significance of the weak tendency for TY-101 samples to exotherm is unknown, due to the fact that these are composites. The thermal analysis of cesium nickel ferrocyanide does not yield a useful feature for identifying it in actual waste samples.

4.2 CYANIDE

Cyanide was determined using a micro-distillation technique, followed by the chloramine T-pyridine-barbituric acid spectrophotometric determination (WHC procedure LA-695-102). The detection limit of the procedure is dependent on the distillation blank. With careful control to minimize blank values, a lower detection limit of 0.01 μg CN^-/mL is possible. This method is sensitive

Table 4-1. TY-101 Thermal Analysis Results.

Assignment	51XC0110 TY-101 Dried Composite Duplicate Average	51XC0110 Standard Deviation.	51XC0310 TY-101 Dried Water Leach-Insoluble Residue Duplicate Average	51XC0310 Standard Deviation
TGA Temp. Range (°C) Total H_2O Weight Loss	ambient--235		ambient--225	
TGA Total H_2O Weight Loss (%)	9.88	0.71	12.46	0.04
TGA Temp. Range (°C) Melt $NaNO_3$ Weight Loss	235--320		225--325	
TGA Melt $NaNO_3$ Weight Loss (%)	2.52	0.25	4.07	0.33
TGA Temp. Range (°C) Decomposition Weight Loss	320--499		325--499	
TGA Decomposition Weight Loss (%)	3.62	0.18	1.75	0.06
DSC Temp. Range (°C) Total H_2O Endotherm	44--150		44--225	
DSC Total H_2O Endotherm (calorie/gram)	33.33	5.22	57.56	10.83
DSC Temp. Range (°C) Melt $NaNO_3$ Endotherm	237--316		215--335	
DSC Melt $NaNO_3$ Endotherm (calorie/gram)	30.06	3.02	50.20	28.60
DSC Temp. Range (°C) Decomposition Endotherm	357--391		393--479	
DSC Decomposition Endotherm (calorie/gram)	2.6	∞	23.32	9.16
DSC Temp. Range (°C) Exotherms	389--429		none	
DSC Exotherms (calorie/gram)	-3.23	5.54	none	

Table 4-2. TY-103 Thermal Analysis Results.

Assignment	31XC0110 TY-103 Dried Composite Duplicate Average	31XC0110 Standard Deviation	31XC0310 TY-103 Dried Water Leach-Insoluble Residue Duplicate Average	31XC0310 Standard Deviation
TGA Temp. Range (°C) Total H_2O Weight Loss	ambient--175		ambient--210	
TGA Total H_2O Weight Loss (%)	10.49	0.05	11.15	0.11
TGA Temp. Range (°C) Melt $NaNO_3$ Weight Loss			210--320	
TGA Melt $NaNO_3$ Weight Loss (%)			2.19	0.11
TGA Temp. Range (°C) Decomposition Weight Loss	175--499		320--499	
TGA Decomposition Weight Loss (%)	9.45	0.24	2.65	0.30
DSC Temp. Range (°C) Total H_2O Endotherm	44--162		44--215	
DSC Total H_2O Endotherm (calorie/gram)	20.90	0.95	55.26	1.16
DSC Temp. Range (°C) Melt $NaNO_3$ Endotherm	213--318		240--303	
DSC Melt $NaNO_3$ Endotherm (calorie/gram)	32.36	1.52	6.26	0.77
DSC Temp. Range (°C) Decomposition Endotherm	338--435		336--440	
DSC Decomposition Endotherm (calorie/gram)	11.35	6.81	22.67	3.26
DSC Temp. Range (°C) Exotherms	none		none	
DSC Exotherms (calorie/gram)	none		none	

Table 4-3. Thermal Analysis Results Synthetic $Cs_2NiFe(CN)_6 \cdot xH_2O$.

Assignment	KMA101 Synthetic $Cs_2NiFe(CN)_6 \cdot xH_2O$ Duplicate Average	KMA101 Standard Development
TGA Temp. Range (°C) Total H_2O Weight Loss	ambient--275	
TGA Total H_2O Weight Loss (%)	6.84	0.14
TGA Temp. Range (°C) Melt $NaNO_3$ Weight Loss	Not Applicable	
TGA Melt $NaNO_3$ Weight Loss (%)	Not Applicable	
TGA Temp. Range (°C) Decomposition Weight Loss	275--499	
TGA Decomposition Weight Loss (%)	4.58	0.96
DSC Temp. Range (°C) Total H_2O Endotherm	Not Integratable	
DSC Total H_2O Endotherm (calorie/gram)	Not Integratable	
DSC Temp. Range (°C) Melt $NaNO_3$ Endotherm	Not Applicable	
DSC Melt $NaNO_3$ Endotherm (calorie/gram)	Not Applicable	
DSC Temp. Range (°C) Decomposition Endotherm	Not Integratable	
DSC Decomposition Endotherm (calorie/gram)	Not Integratable	
DSC Temp. Range (°C) Exotherms	Not Applicable	
DSC Exotherms (calorie/gram)	Not Applicable	

to certain types of ferrocyanide compounds, which give a low value for CN^-. The reader is reminded that this method is a modification of the Environmental Protection Agency (EPA) Contract Laboratory Program method for cyanides, and as such, may not be suitable for high alkalinity, high cyanide tank wastes. It's use is predicated on the fact that it is the accepted laboratory procedure.

In 1988, total cyanide was measured on the composite 101-TY and 103-TY archive samples, using a low-acid hydrogen cyanide distillation procedure [Winters 1988]. The total cyanide found in the 241-TY-101 and 241-TY-103 samples was 3580 ± 242 and 2660 ± 663 µg CN/g wet solids, respectively.

Table 4-4. 1992 Cyanide Analysis Results.

	Laboratory Sample #	PCL Sample #	Sample Description	Results
TY-101	R736	51XC0210	Water Leach	4.2ppm as filtrate 730 µg/g dry soluble solids
	R744	51XC0320	Leach Residue	9920 µg/g dry insoluble solids
	R741	51XC0120	Direct	3390 µg/g dry solids
TY-103	R737	31XC0210	Water Leach	5.4 ppm as filtrate 900 µg/g dry soluble solids
	R745	31XC0320	Leach Residue	8240 µg/g dry insoluble solids
	R742	31XC0120	Direct	2430 µg/g dry solids

All instrument standards were acceptable (all within 5% of the nominal value, with a slight bias towards low recovery), and all blanks were free from contamination. No good estimate of precision is available, as only one run was done for each of the samples. All of the above numbers have been arbitrarily adjusted to 3 or fewer significant figures because of the lack of information on data precision. (See Table 4-4.) A check for precision, performed by comparing the weight corrected sum of the insoluble and soluble material cyanide values against the value for the direct solid, reveals that the sum of the two (insoluble and soluble) values is greater than the value for the direct solid. For both TY-101 and TY-103 the "sum" value is about 1500 µg/g dry solids higher than the direct solids value.

A known material (potassium ferrocyanide trihydrate) was also analyzed by this procedure, to test method's ability to recover a stoichiometric amount of cyanide in the ferrocyanide complex. The potassium ferrocyanide yielded 26.3 weight percent CN (262500 µg/g dry solids), which represents a 71% recovery of cyanide from this compound. Note that the samples from the tanks have **not** been corrected for this recovery. The actual sample recoveries are likely to be higher, as the method is optimized for smaller amounts of cyanide, and could be overloaded by the very high cyanide content found in a pure known material. The potassium ferrocyanide value is useful mainly as a cautionary note for cyanide recoveries.

It can be seen that a majority of the cyanide in these samples is in an insoluble form, which could be, but is not limited to, ferrocyanide type complexes.

4.3 TOTAL ORGANIC CARBON/WHC METHOD LA-344-101; PNL METHOD PNL-ALO-380, REV 0

In the WHC method, TOC concentrations are determined when liquid samples are heated to 850-900° C in the presence of oxygen after a sample preparation of acidification and sparging. This sample preparation removes carbonate and may remove some cyanide (see preparation method for cyanide analyses) in the process. Any carbon remaining in the sample aliquot is converted to carbon dioxide and swept by the oxygen stream to a coulometer. Several traps are employed in the gas flow to remove interferences from sulfur oxides, hydrogen halides, and oxides of nitrogen. The carbon dioxide is collected and quantitatively measured with the coulometer. The coulometer generates base to automatically titrate the carbonic acid. (See Table 4-5 for results.)

Solid samples were analyzed by the PNL, apparently using a method without sample preparation. The PNL method is therefore effectively a total carbon method, and cannot be directly compared to the WHC method. Cyanide is demonstrably part of what is quantitated (see known material results), and at the temperatures used some carbonate may be detected [Schiefelbein 1992]. Additional TOC analyses were conducted on the synthetic samples to determine to what extent this method recovers any of the cyanide complex as organic carbon. The method used was not the method requested in the WHC test plan [Smith 1991], but was specified in PNL test instruction #124.

Table 4-5. 1992 Total Organic Carbon Analysis Results from WHC and PNL Laboratories.

	Laboratory Sample #	PCL Sample #	Sample Description	Results
TY-101	92-04437	51XC0130	Direct Solids	0.683% C dry solids 6830 μg/g dry solids
	R750	51XC0220	Water Leach Filtrate	0.0182 g/L filtrate solution 0.32 % C dry soluble solids 3200 μg/g dry soluble solids
	92-04338	51XC0330	Leach Residue	0.078% %C dry insoluble solids 7,800 μg/g of dry insoluble solids
TY-103	92-04339	31XC0130	Direct Solids	0.893% C dry solids 8903 μg/g dry solids
	R748	31XC0220	Water Leach Filtrate	0.0265 g/L filtrate solution 0.44 % C dry soluble solids 4400 μg/g dry soluble solids
	92-04340	31XC0330	Leach Residue	0.925% C dry insoluble solids 9250μ/g dry insoluble solids
$Cs_2NiFe(CN)_6$	92-04341	KMA-102	$Cs_2NiFe(CN)_6$	10 % C dry solids 100,000 μg/g dry solids
$K_4Fe(CN)_6$	92-04342	KMA-202	$K_4Fe(CN)_6$ $\cdot 3H_2O$ Reagent Grade	14.6 % C 146,000 μg/g reagent grade material

The R750 and R748 values have been corrected for the **method** blank (supplied by PCL) value as well as the instrument blank, and as such, do not reflect WHC Laboratory Customer Communication System output. All PNL values (92-xxxxx) were reported as blank corrected values.

Total organic carbon analyses were previously performed on the water leach and acid leach fractions of the original 101-TY and 103-TY core composites, with the following 1985 results [Weiss 1987a and Weiss 1987b]:

FRACTION	**241-TY-101 CC51XC**	**241-TY-103 CC31XC**	**241-TY-103 CC32XC**
WATER	253 μg/g	496 μg/g	990 μg/g
ACID	410 μg/g	219 μg/g	501 μg/g

The results for the synthetic $Cs_2NiFe(CN)_6$ and reagent grade ($K_4Fe(CN)_6$) materials show that considerable CN is being quantitated as total organic carbon. The fraction of carbon in $K_4Fe(CN)_6 \cdot 3H_2O$ measured as TOC is 85.7%. $Cs_2NiFe(CN)_6$ is unsuitable for precise measurement of method accuracy, because it cannot be prepared stoichiometrically pure form [Loos-Neskovic 1984] and it also has variable numbers of waters of hydration. The relative standard deviation varied from 0.3% to 7%.

4.4 CARBONATE/[WHC PROCEDURE LA-622-101]

In this method, carbon dioxide is sparged from an acidified sample and absorbed in a solution of weak organic base. Base is electrically generated in a coulometer to titrate the acidic carbon dioxide. Carbonate analyses were conducted on the water leach solution and synthetic samples to determine if any of the cyanide complexes are recovered as carbonates.

Table 4-6. 1992 Carbonate Analysis Results.

	Laboratory Sample #	PCL Sample #	Sample Description	Results
TY-101	R763	51XC0230	Filtrate, Water Leach	0.0499 g/L 0.00867 g/g dry soluble solids 0.00492 g/g dry solids
TY-103	R764	31XC0230	Filtrate, Water Leach	0.0340 g/L 0.00569 g/g dry soluble solids 0.00331 g/g dry solids
$K_4Fe(CN)_6$	R785	KMA-203	$K_4Fe(CN)_6 \cdot 3H_2O$ Reagent Grade	0.019 g/L 0.19 g/g $K_4Fe(CN)_6$ $*3H_2O$

No carbonate analyses were performed on the solid tank samples, due to a lack of sample material. (See Table 4-6 for results.) Carbonate was detected in the pure potassium ferrocyanide, indicating that cyanide is detected by this method. Cyanide is sparged from the sample as hydrogen cyanide, an acid, and titrated by the coulometrically generated base, thus giving a false indication for carbonate.

Some carbonate data was obtained from the original core composite water leaches, with the following 1985 results [Weiss 1987a and Weiss 1987b]:

241-TY-101 CC51XC	241-TY-103 CC31XC	241-TY-103 CC32XC
Not determined	7320 µg/g	4780 µg/g

4.5 PERCENT WATER (SAMPLE DRYING AT 120° C)

Drying the samples to constant weight before taking sample aliquots provides a common ground for comparing the analytical data. (See Table 4-7 for results, see Appendix E for raw data). While in storage, these archive samples lost moisture, making direct comparisons of recent and early data difficult. Although the drying conditions are only expected to remove entrained and hydrated water, any originally present volatile organic compounds are likely to have been lost, if they had not already been lost during storage. See Smith [1991, Appendix C], for details on the method used.

Table 4-7. Percent Water Results.

Tank	PCL Sample #	Sample Description	Results
TY-101	51XC0100	Direct Archive	5.87 % ave. water loss 0.19 Std. Dev.
TY-103	31XC0100	Direct Archive	4.78 % ave. water loss 0.07 Std. Dev.

4.6 SOLUBILITY (WATER LEACH)

The sample(s) were dried and weighed before and after the water leach, to determine percent water solubility. The method used may be found in Smith [1991, Appendix D]. (See Table 4-8 for results.)

Table 4-8. Solubility Results.

Tank	PCL Sample #	Sample Description	Results
TY-101	51XC0100	Archive, Direct Dried	43.27 % insolubles 56.73 % solubles
TY-103	31XC0100	Archive, Direct Dried	41.94 % insolubles 58.06 % solubles

4.7 ATOMIC ABSORPTION SPECTROSCOPY/[WHC PROCEDURES LA-505-121, -121, -122, -123, and -124]

Atomic absorption spectrometry (AAS) was be used to determine the soluble concentrations of alkali metals in the water leach fraction, including cesium. In atomic absorption, the sample is aspirated into a flame. Absorbance of the resonance line by the sample is proportional to the concentration of the element in the liquid sample. Quantitative analyses are performed by comparing the absorbance of the unknown sample to absorbencies of known concentrations of that particular element. (See Table 4-9 for results.) Spikes, containing known quantities of the elements of interest, can be used to correct for various spectral interferences. See Appendices A and B for comparisons to earlier work.

These less-than values are consistent with the cyanide concentrations listed elsewhere in this report. Assuming that the cesium is in the form of $Cs_2NiFe(CN)_6$, the expected cesium concentration based on cyanide is 900 ug/g dry solids. During the cesium precipitation process, ferrocyanide was added in excess to ensure cesium scavenging so one would expect an excess of cyanide (and thereby ferrocyanide). The cyanide and cesium concentrations are consistent with this assumption.

Table 4-9. Atomic Absorption Spectrometry Results for Cesium.

Tank	Laboratory Sample #	PCL Sample #	Sample Description	Results
TY-101	R753	51XC0260	Filtrate, Water Leach	<0.0001 M as filtrate <2000 µg/g dry soluble solids <1300 µg/g dry solids
TY-103	R754	31XC0260	Filtrate, Water Leach	<0.00001 M as filtrate <200 µg/g dry soluble solids <100 µg/g dry solids

4.8 ION CHROMATOGRAPHY/[WHC PROCEDURE LA-533-105]

Ion chromatography (IC) was used to determine the nitrate/nitrite concentrations in the water leach solutions. Inert (non-oxidizers) anions present (phosphate, sulfate, etc) can also be determined. (See Table 4-10 for results.) In IC, anions of interest are separated by a strong basic anion exchanger. They are then directed to a strongly acidic cation exchanger, and are changed to a high conductivity acid form. The anions separated in their acid form are changed to a weak acid with eluent and measured by a conductivity cell during elution. Some anions are bound more tightly than others and can be identified by their retention times on the column.

Nitrite concentrations are used to determine the oxidizing potential of the tank contents.

Table 4-10. 1992 Ion Chromatography Results.

Tank	Laboratory Sample #	PCL Sample #	Sample Description	Results Anions	ppm as filtrate	µg/g dry soluble solids
TY-101	R728	51XC0240	Filtrate, Water Leach	Fluoride	141	24520
				Chloride	16.3	2830
				NO_2^- (Nitrite)	71.4	12400
				NO_3^- (Nitrate)	3640	633000
				(63% Nitrate by weight dry solubles)		
				PO_4^{-3} (Phosphate)	391	68000
				SO_4^{-2} (Sulfate)	91.1	15800
TY-103	R726	31XC0240	Filtrate, Water Leach	Fluoride	116.3	2730
				Chloride	23.6	3960
				NO_2^- (Nitrite)	181	30340
				PO_4^{-3} (Phosphate)	494	82810
				SO_4^{-2} (Sulfate)	228	38200

Nitrate and nitrite concentrations determined on the original tank core composites are detailed below.

WATER WASH FRACTION

ANALYTE	241-TY-101 CC51XC	241-TY-103 CC31XC	241-TY-103 CC32XC
NO_3^-	1.45 E3 μg/g	1.29 E5 μg/g	1.49 E5 μg/g
NO_2^-	Not Determined	7.51 E3 μg/g	8.10 E3 μg/g
NO_3^-/NO_2^-	NA	17.2	18.4

ACID WASH FRACTION

ANALYTE	241-TY-101 CC51XC	241-TY-103 CC31XC	241-TY-103 CC32XC
NO_3^-	Not Determined	6.04 E3 μg/g	6.95 E3 μg/g
NO_2^-	Not Determined	Not Determined	Not Determined
NO_3^-/NO_2^-	NA	NA	NA

4.9 ICP SPECTROMETRY/[WHC PROCEDURE LA-505-151]

Inductively coupled plasma (ICP) analysis was used to determine the concentrations of metals present in the water-soluble fraction. The cation:anion balance is essential in verifying the accuracy of the analytical data. (See Table 4-11 for results.) See Appendix A for comparisons with previous results.

The blanks showed some contamination or interferences for aluminum and silicon. The high concentration of sodium found in R758 (a TY-101 filtrate sample) is consistent with the high level of nitrate found by IC.

Table 4-11. Inductively Coupled Plasma Results From the Filtrate Solution of the Water Leach.

Tank	Laboratory Sample #	PCL Sample #	Results Elements	µg/L of filtrate	µg/g dry soluble solids
TY-101	R760	51XC0250	Aluminum	420	699
			Barium	<7.8	<1.3
			Chromium	6840	1190
			Iron	1300	226
			Phosphorus	121000	21000
			Silicon	18100	3150
	R753	51XC0260	Aluminum	13000	2260
			Boron	4730	823
			Chromium	12500	2170
			Iron	3150	547
			Calcium	20600	3580
			Phosphorus	156000	27100
			Silicon	36500	6350
			Sulfur	45800	7964
			Zinc	23100	4020
			Magnesium	44100	7670
			Sodium (35% Sodium by weight-dry soluble solids)	2040000	355000
TY-103	R758	31XC0250	Aluminum	927	162
			Barium	<7.8	<1.3
			Chromium	16700	2800
			Iron	2040	341
			Nickel	1100	184
			Phosphorus	156000	26150
			Silicon	7740	1240
	R754	31XC0260	Aluminum	972	126
			Chromium	13000	2180
			Nickel	1280	214
			Calcium	13300	2230
			Phosphorus	162000	27160
			Sulfur	99300	16600
			Silicon	23100	3870
			Zinc	3210	538

4.10 X-RAY DIFFRACTION/[WHC PROCEDURES LA-507-151]

X-ray diffraction (XRD) is primarily used in the identification of crystalline compounds. The crystalline substance produces a characteristic diffraction pattern that is a fingerprint of its atomic and molecular structure. While this technique can qualitatively determine which species is present, it is limited to crystalline phases that constitute greater than 10% of the sample by weight. Quantitation by this method is fraught with uncertainty, and no quantitation was attempted.

Diffraction patterns of synthetic cesium nickel ferrocyanide and potassium ferrocyanide were collected and compared to patterns reported in the literature. They also were compared to patterns of the dry core composite samples and insoluble fractions.

The samples that were washed (insoluble residue, 51XC0340 and 31XC0340) tended to be amorphous in character, with only $Al(OH)_3$ likely being present in the TY-101 sample (51XC0340). The direct samples (51XC0140 and 31XC0140) contained $Al(OH)_3$ and $NaNO_3$, with the TY-101 sample being the only one with an unambiguous correlation between the peaks and library assignments (See Appendix C for raw data). No evidence for $Fe(CN)_6$ species was seen, which is not surprising, since cyanide (and therefore $Fe(CN)_6$) is a minor constituent <1% in these samples, and therefore would not be seen in an XRD.

4.11 X-RAY FLUORESCENCE

Bombardment of many substances by x-rays often causes emission, or fluorescence, of secondary x-rays specific to the elements within the substance. Qualitative and semi-quantitative analyses of the original samples and insoluble fractions were attempted, specifically to identify and determine the metals present (Cs, Ni, Fe). (See Table 4-12 for results.) Comparable data were collected for the synthetic and reagent-grade materials and used for comparison and evaluation. (See Table 4-13 for results.) The values for direct solids (51XC0130 and 31XC130) are in terms of the dry solids, while the values for the insoluble solids (51XC0330 and 31XC330) are in terms of dry insoluble water leach residue.

Table 4-12. X-Ray Fluorescence Analysis.

LAB SAMPLE #:		92-04337		92-04338		92-04339		92-04340	
PCL SAMPLE #:		51XC0130		51XC0330		31XC0130		31XC0330	
TANK:		TY-101				TY-103			
SAMPLE DESCRIPTION:		Direct Solids		Insoluble Solids		Direct Solids		Insoluble Solids	
TARGET Ti									
UNITS	EL	Results	±	Results	±	Results	±	Results	±
%	AL	6.79	0.57	13.83	0.95	1.57	0.39	2.60	0.53
%	SI	4.27	0.26	7.53	0.43	2.89	0.19	3.21	0.24
%	P	8.58	0.45	14.16	0.73	5.58	0.29	4.39	0.24
%	CA	0.080	0.005	0.159	0.009	0.110	0.006	0.153	0.009
TARGET Ag									
UNITS	EL	Results	±	Results	±	Results	±	Results	±
%	CA	0.091	0.023	0.212	0.050	0.172	0.077	< 0.20	
PPM	CR	1880	140	2890	220	2780	210	2200	180
PPM	MN	105	18	352	44	369	46	512	63
%	FE	2.47	0.17	7.31	0.51	6.03	0.42	9.57	0.67
%	NI	0.370	0.026	1.092	0.077	0.590	0.042	0.875	0.062
PPM	CU	41.3	6.8	100	17	48	13	< 41	
PPM	ZN	51.3	4.7	156	13	206	17	384	31
%	BI	3.88	0.27	10.57	0.74	3.70	0.26	10.85	0.76
%	U	0.178	0.012	0.430	0.030	3.27	0.23	8.80	0.62
PPM	SR	172	12	446	32	688	49	1392	100
PPM	ZR	369	26	970	68	696	49	2630	100
TARGET Gd									
UNITS	EL	Results	±	Results	±	Results	±	Results	±
PPM	RU	< 5.3		< 8.6		< 12		< 27	
PPM	AG	< 4.2		< 5.6		< 5.4		< 11	
PPM	CD	< 4.7		< 6.7		< 3.8		< 6.9	
PPM	SN	7.1	2.8	< 7.0		9.9	2.3	14.3	4.1
PPM	SB	< 6.4		< 8.7		< 5.4		< 9.0	
PPM	TE	< 7.5		< 8.7		< 6.0		< 9.7	
PPM	I	< 9.3		< 11		< 7.6		< 13	
PPM	CS	14.1	5.1	< 13		< 8.6		< 15	
PPM	BA	33.9	7.3	33.7	9.2	91.2	8.9	268	22
PPM	LA	< 16		< 20		< 13		27	11
PPM	CE	377	29	832	61	317	25	886	65

Table 4-13. X-Ray Fluorescence Analysis/Standards.

	USGS-AGV-1					1633A FLYASH				
EL	UNITS	VALUE	±	UNITS	KNOWN	UNITS	VALUE	±	UNITS	KNOWN
TARGET Ti										
Al	%	6.83	0.47	%	8.9	%	14.60	0.83	%	14
Si	%	27.5	1.4	%	27.6	%	26.1	1.3	%	22.8
P	%	0.112	0.046	%	(.21)	%	0.136	0.04		
Ca	%	3.50	0.18	%	3.55	%	1.338	0.06	%	1.11
TARGET Ag										
Ca	%	3.50	0.25	%	3.55	%	1.339	0.099	%	1.11
Cr	PPM	< 53		PPM	12.2	PPM	188	41	PPM	196
Mn	PPM	697	53	PPM	763	PPM	298	32	PPM	190
Fe	%	4.32	0.30	%	4.73	%	9.36	0.66	%	9.40
Ni	%	< 0.001		PPM	(18.5)	%	0.012	0.002	%	127
Cu	PPM	64.7	5.6	PPM	59.7	PPM	126	10	PPM	118
Zn	PPM	83.9	6.5	PPM	84	PPM	232	17	PPM	220
Bi	%	< 0.001		PPM	.057	%	< 0.001			
U	%	< 0.001		PPM	1.88	%	0.00	0.00	PPM	10.2
Sr	PPM	659	46	PPM	657	PPM	772	54	PPM	830
Zr	PPM	220	16	PPM	225	PPM	237	17		
TARGET Gd										
Ru	PPM	< 4.4				PPM	< 3.2			
Ag	PPM	< 5.5		PPM	.11	PPM	< 3.6			
Cd	PPM	< 5.8		PPM	.09	PPM	< 4.1		PPM	1.0
Sn	PPM	< 6.9		PPM	4.2	PPM	5.4	2.5		
Sb	PPM	< 8.1		PPM	4.5	PPM	< 5.8		PPM	7
Te	PPM	< 9.0		PPM	< 1	PPM	< 6.5			
I	PPM	< 11				PPM	< 8.2			
Cs	PPM	< 13		PPM	1.4	PPM	< 9.1		PPM	11
Ba	PPM	1206	86	PPM	1208	PPM	1222	86	PPM	1500
La	PPM	35.4	9.8	PPM	25	PPM	69.9	8.9		
Ce	PPM	57	12	PPM	63	PPM	157	15	PPM	180

Since the accuracy of the data is often not as good as the reported precision for the standards (which are well behaved, well characterized, materials), the accuracy of the sample data is also probably less than the reported precision. As a result, care should be exercised when using this data to the full reported number of significant figures.

5.0 CONCLUSIONS

The data presented in this report clearly support the following conclusions:

- There is little cyanide (and therefore little ferrocyanide) in these tanks.
- The thermal activity of these samples in the form of exotherms is minimal.
- The major molecular constituents in these tanks are sodium nitrate, other nitrates and aluminum hydroxide.
- The major water soluble constituent is sodium nitrate.
- The cyanide that is present, is largely in an insoluble form. This implies that the cyanide is largely in the form of ferrocyanide complexes, but does not prove that ferrocyanide is the form in which cyanide exists.

6.0 222-S LABORATORY ANALYTICAL PROCEDURES

ANALYSIS	WHC PROCEDURE NO.	TITLE
Cyanide (CN^-)	**LA-695-102**	Microdistillation and Spectrophotometric Determination of Cyanide
Total Organic Carbon	**LA-344-101**	Determination of Carbon in Solutions and Solids by Combustion and Coulometry
Carbonate (CO_3^-)	**LA-622-101**	Determination of Carbonate in Solutions and Solids by Coulometry
Atomic Absorption Spectrometry	**LA-505-122**	Sample Preparation and Analysis, High Activity AA-6 Atomic Absorption Spectrophotometer
	LA-505-121	Operating Procedure for the High Activity AA-6 Atomic Absorption Spectrophotometer
	LA-505-123	Process Quality Control and the Atomic Absorption Spectrophotometer
	LA-505-124	Application of the Method of Standard Additions to Atomic Absorption
Ion Chromatography [NO_2^-, NO_3^-]	**LA-533-105**	Anion Analysis on DIONEX Model 4000i
Inductively-Coupled Plasma Spectrometry	**LA-505-151**	Inductively Coupled Plasma (ICP) Emission Spectrometer Operations and Analysis
X-Ray Diffraction	**LA-507-151**	Operation of the D/MAX Diffractometer
X-Ray Fluorescence	**LA-507-131**	Qualitative Elemental Analysis Using the Rigaku S/MAX
	LA-507-121	Sample Preparation for X-Ray Fluorescence

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APPENDIX A

CORE COMPOSITE RESULTS FROM THE 1985 ANALYSES - TANK 241-TY-101[2]

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[2] Abstracted from [Weiss 1987b]

Table A-1. TY-101 Core Composite - 51%CXXXX.

COMPONENT	REPORT UNIT	REPORT VALUE Direct	REPORT VALUE Water	REPORT VALUE Acid	REPORT VALUE Fusion	REPORT TOTAL	MAXIMUM TOTAL
Density	g/mL						
Aluminum	µg/g		3.90E+01	1.34E+04	1.56E+04	2.91E+04	2.91E+04
Barium	µg/g		< 3.92E-01	1.67E+01	1.91E+03	1.92E+03	1.92E+03
Bismuth	µg/g		< 8.63E+00	2.65E+04	7.17E+02	2.72E+04	2.72E+04
Cadmium	µg/g		< 1.96E+00	3.14E+00	5.52E+00	8.66E+00	1.06E+01
Chromium	µg/g		4.24E+02	5.00E+02	7.48E+03	8.40E+03	8.40E+03
Iron	µg/g		5.31E+01	1.30E+04	2.71E+04	4.02E+04	4.02E+04
Lead	µg/g		< 6.36E+00	1.57E+02	6.08E+01	2.18E+02	2.24E+02
Manganese	µg/g		< 1.57E+01	3.83E+01	5.04E+02	5.42E+02	5.58E+02
Nickel	µg/g		7.67E+01	8.95E+02	4.12E+03	5.10E+03	5.10E+03
Phosphorus	µg/g		5.39E+03	1.91E+04	7.56E+02	2.53E+04	2.53E+04
Silicon	µg/g		3.22E+02	6.57E+02	3.77E+04	3.87E+04	3.87E+04
Silver	µg/g		< 7.85E-01	< 9.81E-01	< 2.08E+00	0.00E+00	3.85E+00
Sodium	µg/g		7.50E+04	3.33E+04	1.30E+04	1.21E+05	1.21E+05
Zirconium	µg/g		< 3.61E+00	< 4.51E+00	3.77E+02	3.77E+02	3.85E+02
Arsenic	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Mercury	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Selenium	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Uranium	µg/g		1.12E+01	2.29E+03	3.74E+01	2.33E+03	2.33E+03
Chloride	µg/g		7.57E+02			7.57E+02	7.57E+02
Fluoride	µg/g		3.37E+03	0.00E+00		3.37E+03	3.37E+03
Nitrate	µg/g		1.45E+05	0.00E+00		1.45E+05	1.45E+05
Sulfate	µg/g		< 5.49E+03	0.00E+00	0.00E+00	0.00E+00	5.49E+03
Nitrite	µg/g		0.00E+00			0.00E+00	0.00E+00
Cyanide	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Carbonate	µg/g		0.00E+00			0.00E+00	0.00E+00
TOC	µg/g		2.53E+02	4.10E+02		6.63E+02	6.63E+02
Free Hydroxide	µg/g		2.12E-01			2.12E-01	2.12E-01
Ph	log(1/M)		8.20E+00			8.20E+00	8.20E+00
EDTA	µg/g		0.00E+00	0.00E+00		0.00E+00	0.00E+00
HEDTA	µg/g		0.00E+00	0.00E+00		0.00E+00	0.00E+00
Mass Loss							
Room to 400 C	µg/g	4.35E+05				4.35E+05	4.35E+05
400 to 1000 C	µg/g	1.60E+05				1.60E+05	1.60E+05

COMPONENT	REPORT UNIT	REPORT VALUE Direct	REPORT VALUE Water	REPORT VALUE Acid	REPORT VALUE Fusion	REPORT TOTAL	MAXIMUM TOTAL
Pu-239,40	µCi/g		< 5.73E-04	1.19E-01	7.17E-02	1.90E-01	1.91E-01
Total Alpha	µCi/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
C-14	µCi/g		< 3.88E-04	< 4.85E-04		0.00E+00	8.72E-04
Pu-241	µCi/g		0.00E+00	0.00E+00	0.00E+01	0.00E+00	0.00E+00
Sr-90	µCi/g		< 1.93E-04	1.22E+01	2.79E-01	1.24E+01	1.24E+01
Tc-99	µCi/g		4.35E-03	3.01E-03	< 0.00E+01	7.36E-03	7.36E-03
Total Beta	µCi/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Am-241	µCi/g		< 3.65E-04	< 2.21E-03	< 1.05E-02	0.00E+00	1.30E-02
Co-60	µCi/g		< 1.11E-04	< 5.09E-03	< 4.77E-03	0.00E+00	9.97E-03
Cs-137	µCi/g		2.63E-04	1.63E-01	1.21E-01	2.84E-01	2.84E-01
I-129	µCi/g	< 4.70E-05				0.00E+00	4.70E-05
Total Gamma	µCi/g		2.63E-04	1.63E-01	1.21E-01	2.84E-01	2.84E-01
Visual		NOTE 1	NOTE 2	NOTE 3	NOTE 4		
Volume (total)	mL	0.00E+00				0.00E+00	0.00E+00
Mass (total)	g	3.65E+01				3.65E+01	3.65E+01
Photograph							
Radiation	mR/h	1.00E+01	1.00E+00	4.00E+00	< 7.20E+01	1.00E+01	1.00E+01
Specific Heat	J/g deg C	6.00E-01				6.00E-01	6.00E-01
Soft. Point	deg C	2.76E+02				2.76E+02	2.76E+02
Bulk Density	g/mL	1.64E+00				1.64E+00	1.64E+00
Part. Density	g/mL	9.24E-01				9.24E-01	9.24E-01
Viscosity							
25 C	cP	> 1.00E+04				> 1.00E+04	
40 C	cP	> 1.00E+04				> 1.00E+04	
70 C	cP	> 1.00E+04				> 1.00E+04	
Particle Size	µm	NOTE 5					

NOTE 1: Butterscotch colored, creamy

NOTE 2: Only two water washes, solids would not centrifuge out of third wash, continued with acid washes. Yellow solution.

NOTE 3: Bright yellow solution.

NOTE 4: Green solution, green gel-like solids scraped off filter.

NOTE 5: 8.2 MEAN POPULATION; 12.5 AT 50% OF TOTAL BY WEIGHT

APPENDIX B

CORE COMPOSITE RESULTS FROM THE 1985 ANALYSES - TANK 241-TY-103[3]

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[3] Abstracted from [Weiss, 1987a]

Table B-1. TY-103 Core Composite - 31XCXXXX.

COMPONENT	REPORT UNIT	REPORT VALUE Direct	REPORT VALUE Water	REPORT VALUE Acid	REPORT VALUE Fusion	REPORT TOTAL	MAXIMUM TOTAL
Density	g/mL						
Aluminum	µg/g		1.32E+01	1.43E+01	1.46E+03	1.48E+03	1.48E+03
Barium	µg/g		3.19E-01	5.54E+01	5.32E+02	5.79E+02	5.79E+02
Bismuth	µg/g		<6.88E+00	2.41E+04	2.29E+01	2.42E+04	2.42E+04
Cadmium	µg/g		<1.56E+00	3.04E+00	< 1.12E+00	3.04E+00	5.72E+00
Chromium	µg/g		3.53E+02	4.80E+02	3.80E+01	8.71E+02	8.71E+02
Iron	µg/g		7.07E+01	2.14E+04	6.93E+02	2.22E+04	2.22E+04
Lead	µg/g		<5.07E+00	5.14E+02	7.15E+00	5.21E+02	5.26E+02
Manganese	µg/g		<1.25E+01	1.40E+02	< 8.94E+00	1.40E+02	1.62E+02
Nickel	µg/g		4.34E+01	1.39E+03	5.32E+02	1.97E+03	1.97E+03
Phosphorus	µg/g		9.88E+03	1.89E+04	2.97E+02	2.91E+04	2.91E+04
Silicon	µg/g		7.01E+01	3.84E+02	1.05E+03	1.50E+03	1.50E+03
Silver	µg/g		< 6.26E-01	1.25E+00	1.70E+00	2.95E+00	3.57E+00
Sodium	µg/g		7.82E+04	3.30E+04	3.98E+03	1.15E+05	1.15E+05
Zirconium	µg/g		<2.88E+00	< 4.11E+00	4.16E+02	4.16E+02	4.23E+02
Arsenic	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Mercury	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Selenium	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Uranium	µg/g		5.82E+01	1.92E+04	2.18E+01	1.93E+04	1.93E+04
Chloride	µg/g		1.04E+03			1.04E+03	1.04E+03
Fluoride	µg/g		1.91E+03	0.00E+00		1.91E+03	1.91E+03
Nitrate	µg/g		1.29E+05	6.04E+03		1.35E+05	1.35E+05
Sulfate	µg/g		7.81E+03	< 4.57E+02	0.00E+00	7.81E+03	8.27E+03
Nitrite	µg/g		7.51E+03			7.51E+03	7.51E+03
Cyanide	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Carbonate	µg/g		7.32E+03			7.32E+03	7.32E+03
TOC	µg/g		4.96E+02	2.19E+02		7.15E+02	7.15E+02
Free Hydroxide	µg/g		1.68E+02			1.68E+02	1.68E+02
pH	log(1/M)		1.12E+01			1.12E+01	1.12E+01
EDTA	µg/g		0.00E+00	0.00E+00		0.00E+00	0.00E+00
HEDTA	µg/g		0.00E+00	0.00E+00		0.00E+00	0.00E+00
Mass Loss							
Room to 400 C	µg/g	5.12E+05				5.12E+05	5.12E+05
400 to 1000 C	µg/g	1.48E+05				1.48E+05	1.48E+05
Pu-239,40	µCi/g		< 1.77E-04	1.84E-01	5.59E-03	1.90E-01	1.90E-01
Total Alpha	µCi/g		< 1.56E-03	0.00E+00	0.00E+00	0.00E+00	1.56E-03
C-14	µCi/g		< 7.57E-04	0.00E+00		0.00E+00	7.57E-04
Pu-241	µCi/g		0.00E+00	0.00E+00	0.00E+01	0.00E+00	0.00E+00
Sr-90	µCi/g		1.31E-02	1.15E+02	6.17E-02	1.15E+02	1.15E+02
Tc-99	µCi/g		1.01E-02	5.00E-03	< 0.00E+00	1.51E-02	1.51E-02
Total Beta	µCi/g		0.00E+00	4.83E+02	1.71E+01	5.00E+02	5.00E+02

COMPONENT	REPORT UNIT	REPORT VALUE Direct	REPORT VALUE Water	REPORT VALUE Acid	REPORT VALUE Fusion	REPORT TOTAL	MAXIMUM TOTAL
Am-241	µCi/g		< 1.28E-03	< 3.73E-02	< 9.34E-04	0.00E+00	3.95E-02
Co-60	µCi/g		1.19E-03	1.35E-03	< 1.15E-03	1.19E-03	3.69E-03
Cs-137	µCi/g		1.13E-03	9.03E-01	9.87E+00	1.08E+01	1.08E+01
I-129	µCi/g	< 4.90E-02				0.00E+00	< 4.90E-02
Total Gamma	µCi/g		2.31E-03	1.13E+00	9.87E+00	1.10E+01	1.14E+01
Visual		NOTE 1	NOTE 2	NOTE 3	NOTE 4		
Volume (total)	mL	0.00E+00				0.00E+00	0.00E+00
Mass (total)	g	3.86E+01				3.86E+01	3.86E+01
Photograph							
Radiation	mR/h	5.00E+01	3.50E+00	5.00E+00	7.20E+01	5.00E+01	5.00E+01
Specific Heat	J/g deg C	2.91E-01				2.91E-01	2.91E-01
Soft. Point	deg C	2.87E+02				2.87E+02	2.87E+02
Bulk Density	g/mL	1.70E+00				1.70E+00	1.74E+00
Part. Density	g/mL	6.89E-01				6.89E-01	6.89E-01
Viscosity							
25 C	cP	> 1.00E+04				> 1.00E+04	
40 C	cP	> 1.00E+04				> 1.00E+04	
70 C	cP	> 1.00E+04				> 1.00E+04	
Particle Size	µm	NOTE 5					

NOTE 1: Brown sludge with a few octahedral crystals
NOTE 2: Yellow solution. Only two water washes--the third would not centrifuge out the solids
NOTE 3: Dark yellow-gold solution.
NOTE 4: Light yellow solution.
NOTE 5: 12.2 MEAN POPULATION; 30.1 AT 50% OF TOTAL BY WEIGHT

Table B-2. TY-103 Core Composite - 32XCXXXX.

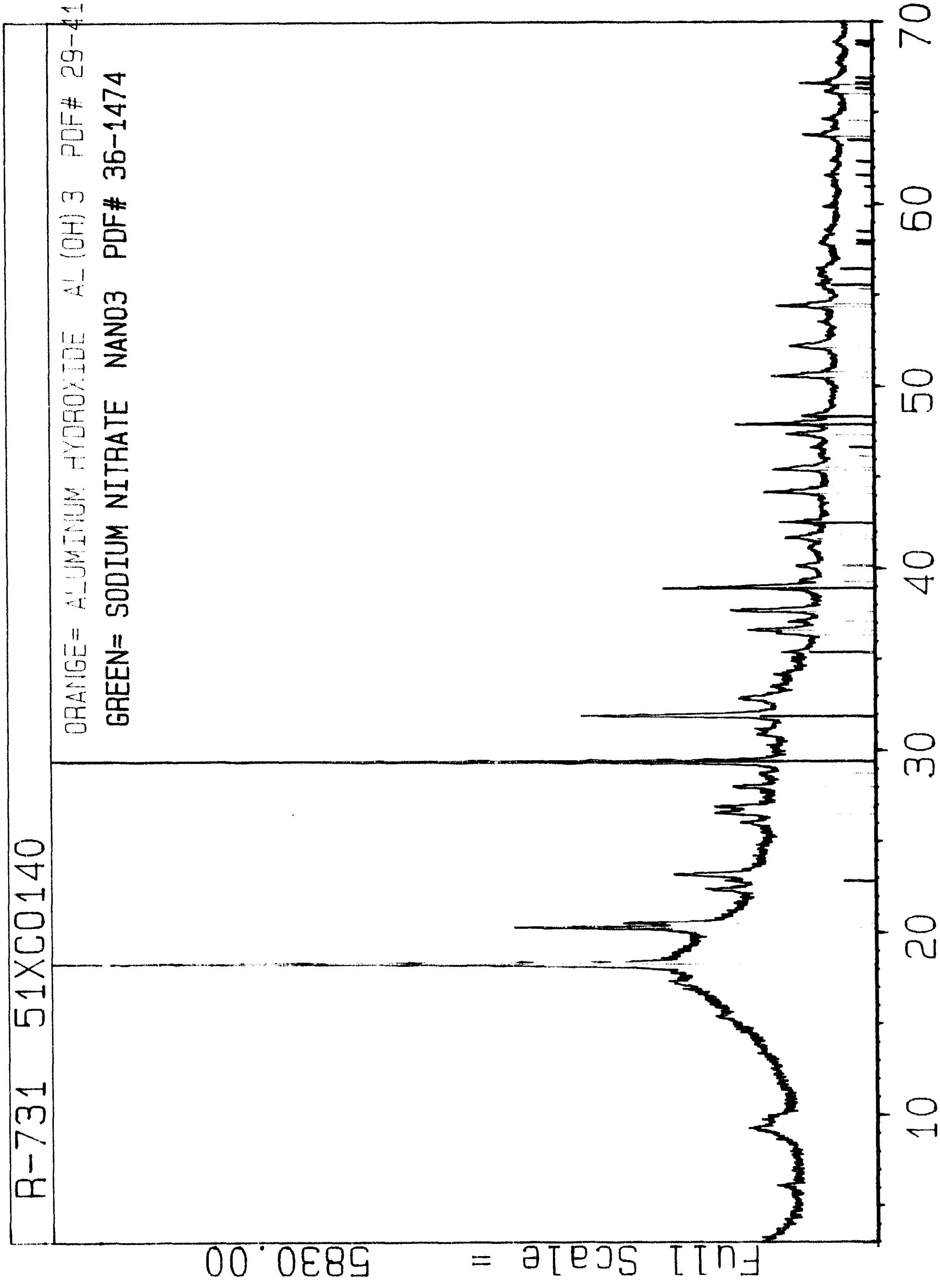
COMPONENT	REPORT UNIT	REPORT VALUE Direct	REPORT VALUE Water	REPORT VALUE Acid	REPORT VALUE Fusion	REPORT TOTAL	MAXIMUM TOTAL
Density	g/mL						
Aluminum	µg/g		2.24E+00	3.78E+03	4.28E+02	4.22E+03	4.22E+03
Barium	µg/g		7.07E+00	4.13E+01	4.52E+02	5.01E+02	5.01E+02
Bismuth	µg/g		<7.07E+00	2.74E+04	5.51E+00	2.74E+04	2.74E+04
Cadmium	µg/g		<1.61E+00	4.87E+00	< 1.15E+00	4.87E+00	7.62E+00
Chromium	µg/g		4.06E+02	5.88E+02	8.73E+00	1.00E+03	1.00E+03
Iron	µg/g		1.56E+02	2.26E+04	1.05E+03	2.38E+04	2.38E+04
Lead	µg/g		<5.21E+00	4.41E+02	< 2.23E+01	4.41E+02	4.68E+02
Manganese	µg/g		<1.29E+01	1.38E+02	< 9.18E+00	1.38E+02	1.60E+02
Nickel	µg/g		6.36E+01	1.35E+03	1.12E+03	2.53E+03	2.53E+03
Phosphorus	µg/g		6.31E+03	1.46E+04	5.28E+01	2.10E+04	2.10E+04
Silicon	µg/g		7.26E+01	5.14E+02	8.82E+03	9.40E+03	9.40E+03
Silver	µg/g		< 6.43E-01	7.44E+00	< 9.18E-01	7.44E+00	9.00E+00
Sodium	µg/g		7.39E+04	2.86E+04	3.42E+03	1.06E+05	1.06E+05
Zirconium	µg/g		<2.96E+00	< 4.22E+00	4.45E+01	4.45E+01	5.16E+01
Arsenic	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Mercury	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Selenium	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Uranium	µg/g		4.14E+01	1.62E+04	6.06E+00	1.62E+04	1.62E+04
Chloride	µg/g		1.20E+03			1.20E+03	1.20E+03
Fluoride	µg/g		<8.60E+02	0.00E+00		0.00E+00	8.60E+02
Nitrate	µg/g		1.49E+05	6.95E+03		1.56E+05	1.56E+05
Sulfate	µg/g		9.26E+03	5.33E+02	0.00E+00	9.80E+03	9.80E+03
Nitrite	µg/g		8.10E+03			8.10E+03	8.10E+03
Cyanide	µg/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Carbonate	µg/g		4.78E+03			4.78E+03	4.78E+03
TOC	µg/g		9.90E+02	5.01E+02		1.49E+03	1.49E+03
Free Hydroxide	µg/g		8.68E+01			8.68E+01	8.68E+01
pH	log(1/M)		1.09E+01			1.09E+01	1.09E+01
EDTA	µg/g		0.00E+00	0.00E+00		0.00E+00	0.00E+00
HEDTA	µg/g		0.00E+00	0.00E+00		0.00E+00	0.00E+00
Mass Loss							
Room to 400 C	µg/g	5.25E+05				5.25E+05	5.25E+05
400 to 1000 C	µg/g	1.53E+05				1.53E+05	1.53E+05
				1.75E-01			
Pu-239,40	µCi/g		< 1.72E-04	0.00E+00	1.35E-03	1.77E-01	1.77E-01
Total Alpha	µCi/g		< 1.60E-03		0.00E+00	0.00E+00	1.60E-03
C-14	µCi/g		< 7.78E-04	< 4.55E-04		0.00E+00	1.23E-03
Pu-241	µCi/g		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sr-90	µCi/g		8.94E-03	1.05E+02	2.38E-02	1.05E+02	1.05E+02
Tc-99	µCi/g		1.13E-02	5.07E-03	< 0.00E+00	1.64E-02	1.64E-02
Total Beta	µCi/g		< 4.91E-02	4.44E+02	3.48E+01	4.82E+02	4.82E+02

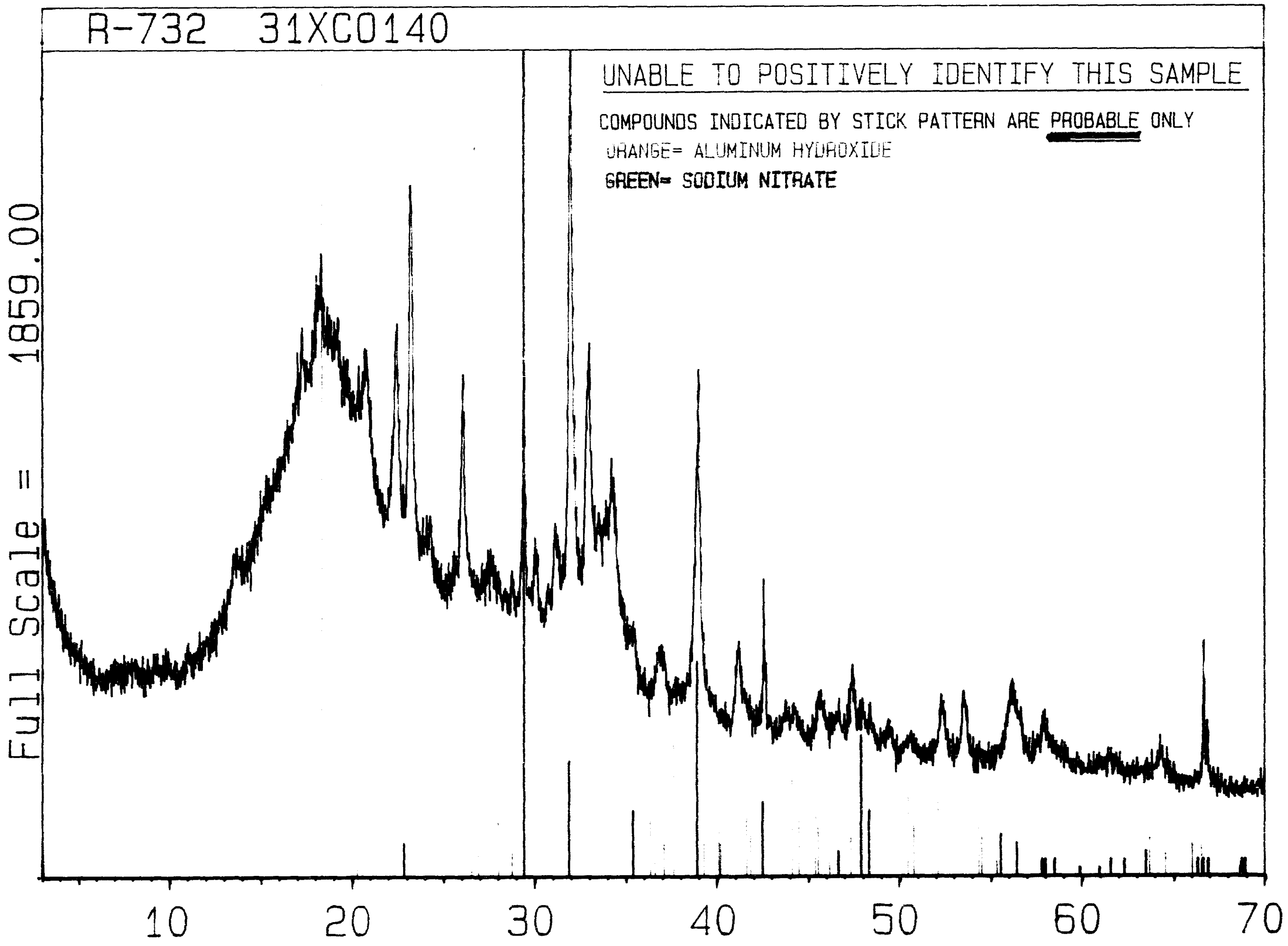
COMPONENT	REPORT UNIT	REPORT VALUE Direct	REPORT VALUE Water	REPORT VALUE Acid	REPORT VALUE Fusion	REPORT TOTAL	MAXIMUM TOTAL
Am-241	µCi/g		< 9.64E-04	< 2.48E-02	< 1.02E-03	0.00E+00	2.68E-02
Co-60	µCi/g		9.00E-04	< 2.76E-03	< 1.01E-03	9.00E-04	4.67E-03
Cs-137	µCi/g		< 5.14E-04	2.00E+00	2.27E+01	2.47E+01	2.47E+01
I-129	µCi/g	< 2.70E-03				0.00E+00	2.70E-03
Total Gamma	µCi/g		1.41E-03	1.91E+00	2.27E+01	2.46E+01	2.46E+01
Visual		NOTE 1	NOTE 2	NOTE 3	NOTE 4		
Volume (total)	mL	0.00E+00				0.00E+00	0.00E+00
Mess (total)	g	4.58E+01				4.58E+01	4.58E+01
Photograph							
Radiation	mR/h	1.00E+02	3.00E+00	4.50E+01	7.20E+01	1.00E+02	1.00E+02
Specific Heat	J/g deg C	3.37E-01				3.37E-01	3.37E-01
Soft. Point	deg C	2.87E+02				2.87E+02	2.87E+02
Bulk Density	g/mL	1.70E+00				1.70E+00	1.70E+00
Part. Density	g/mL	7.54E-01				7.54E-01	7.54E-01
Viscosity							
25 C	cP	> 1.00E+04				> 1.00E+04	
40 C	cP	> 1.00E+04				> 1.00E+04	
70 C	cP	> 1.00E+04				> 1.00E+04	
Particle Size	µm	NOTE 5					

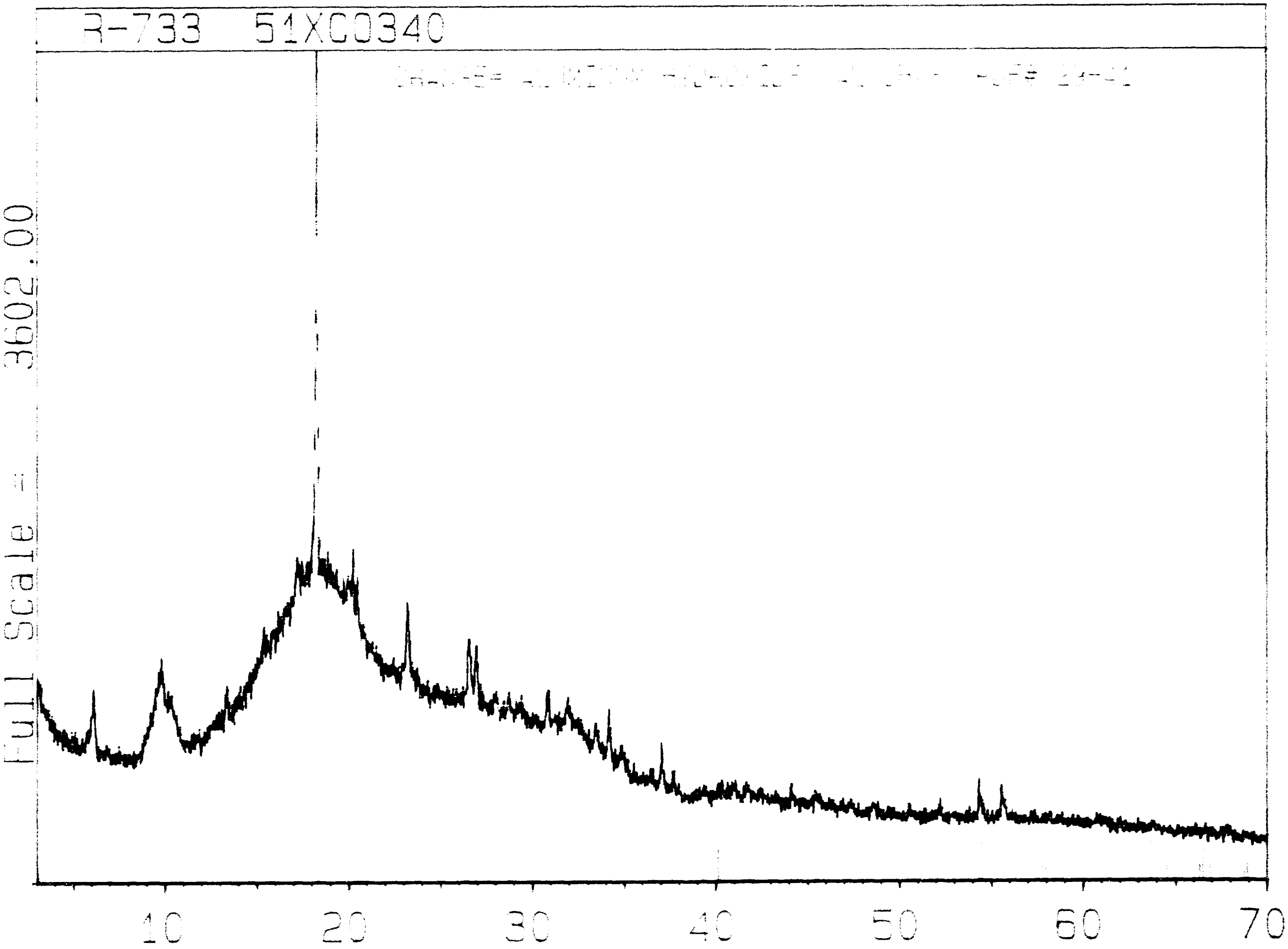
NOTE 1: Brown sludge with octahedral and needle crystals
NOTE 2: Yellow
NOTE 3: Dark yellow-gold solution.
NOTE 4: Solution: Faint yellow color. Filter: yellow film which would not scrape off.
NOTE 5: 8.3 MEAN POPULATION; 12.0 AT 50% OF TOTAL BY WEIGHT

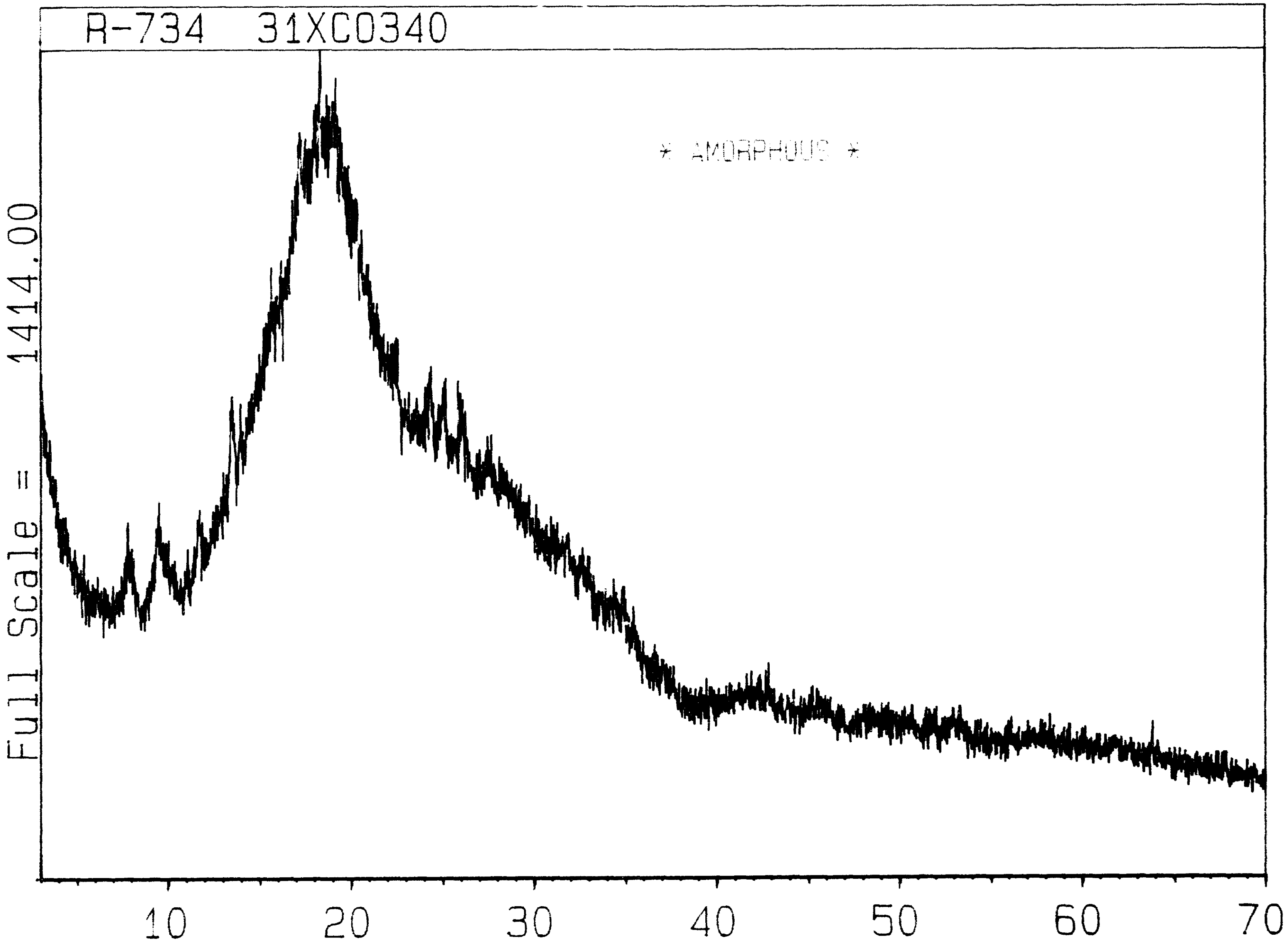
APPENDIX C

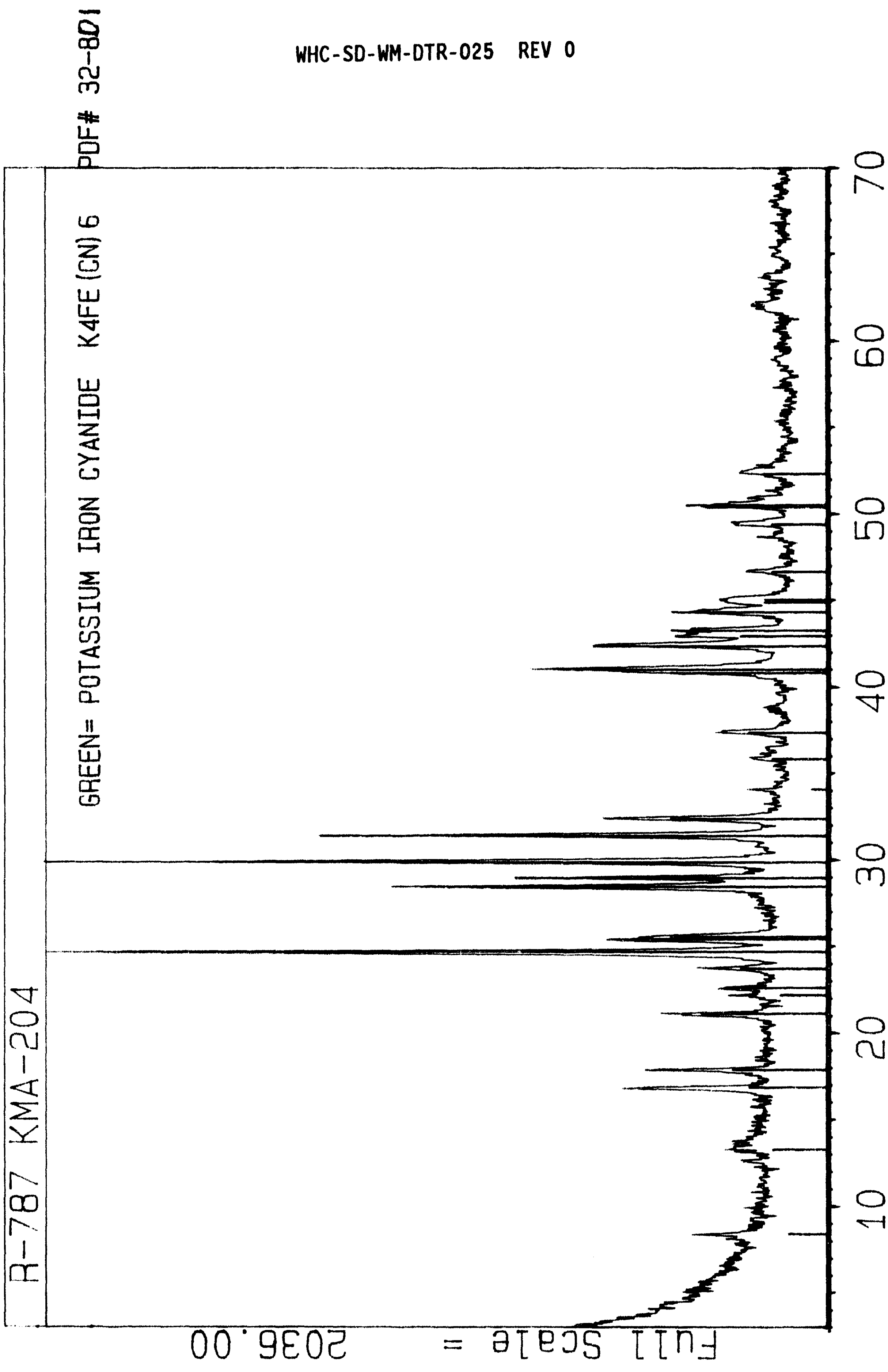
X-RAY DIFFRACTION DATA

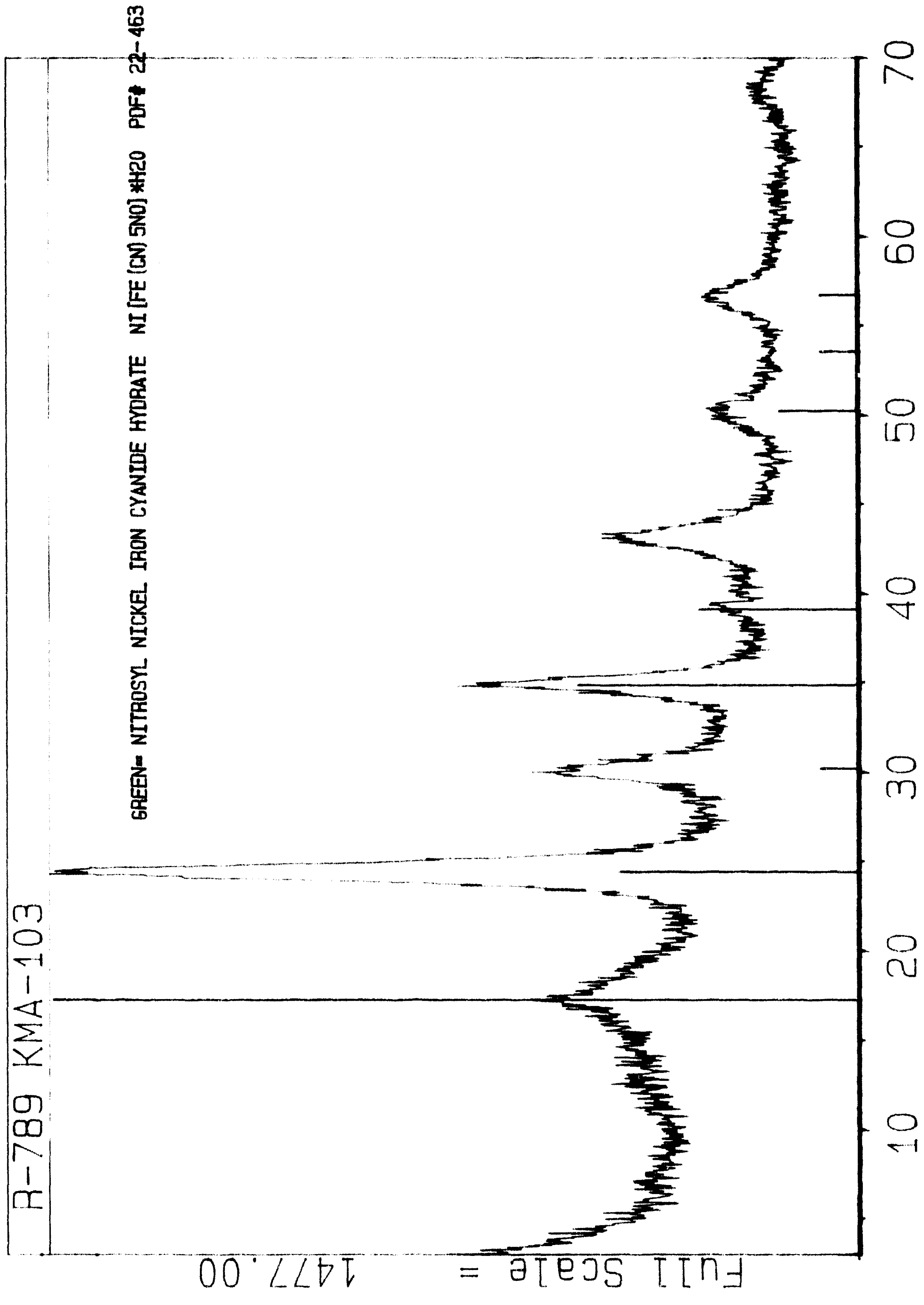

R-731 51XC0140
ORANGE= ALUMINUM HYDROXIDE AL(OH)3 PDF# 29-41
GREEN= SODIUM NITRATE NANO3 PDF# 36-1474
Full Scale = 5830.00
10
20
30
40
50
60
70

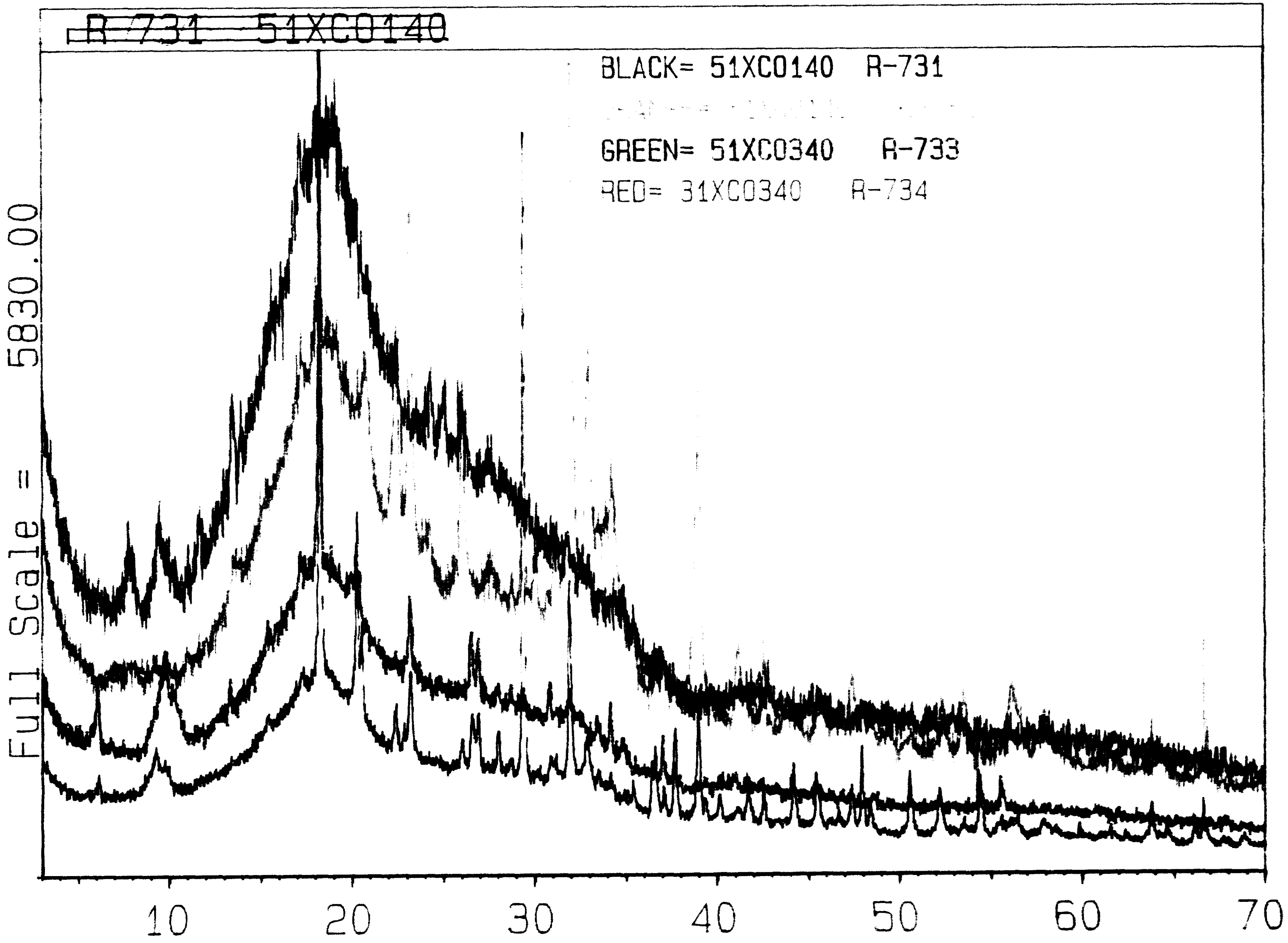

R-732 31XC0140
UNABLE TO POSITIVELY IDENTIFY THIS SAMPLE
COMPOUNDS INDICATED BY STICK PATTERN ARE PROBABLE ONLY
ORANGE= ALUMINUM HYDROXIDE
GREEN= SODIUM NITRATE
Full Scale = 1859.00
10
20
30
40
50
60
70


R-733 51XC0340
Full Scale = 3602.00
10
20
30
40
50
60
70


R-734 31XC0340
* AMORPHOUS *
Full Scale = 1414.00
10
20
30
40
50
60
70

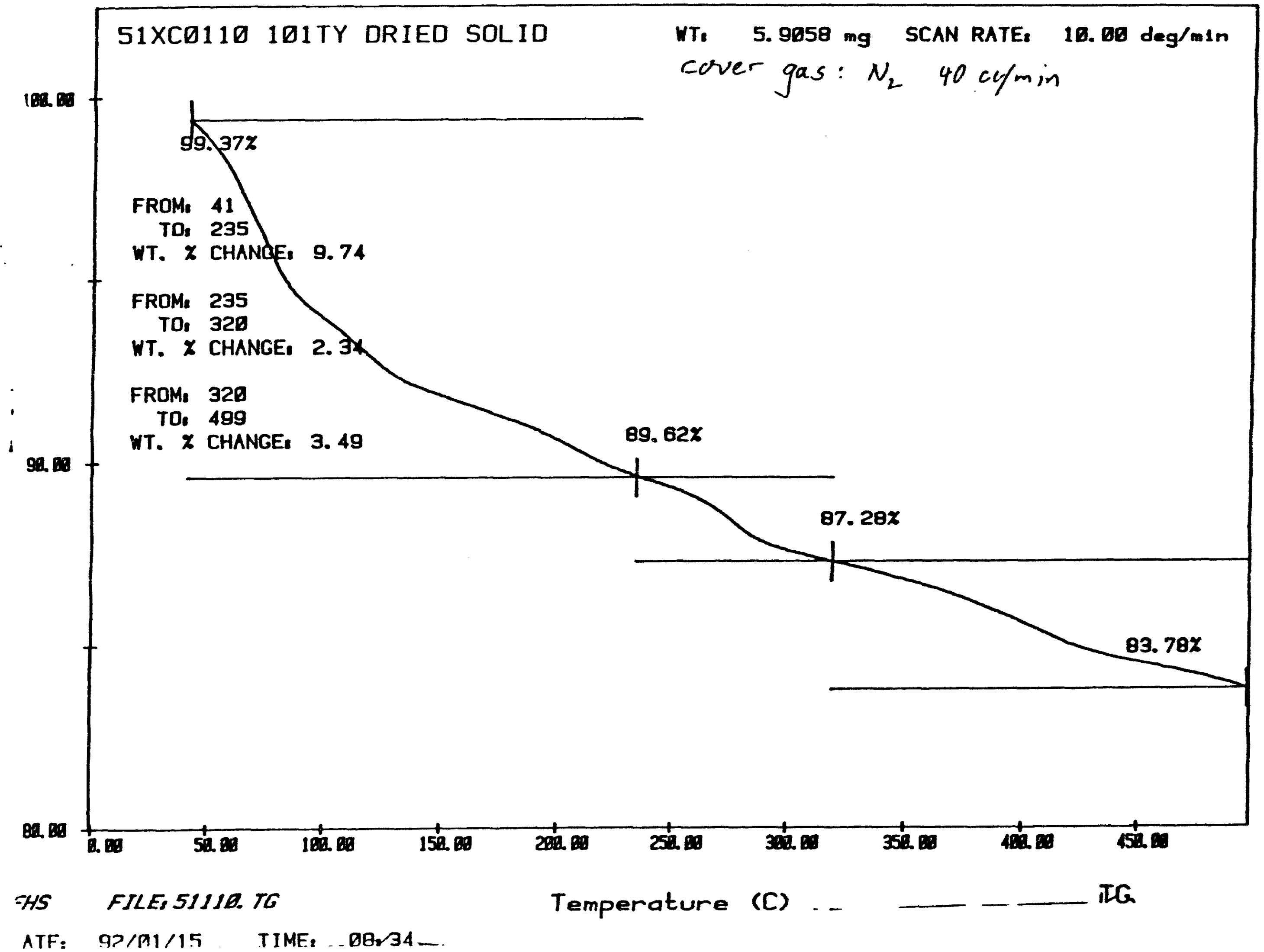

R-787 KMA-204
GREEN= POTASSIUM IRON CYANIDE K4FE(CN)6
PDF# 32-801
Full Scale = 2036.00
10
20
30
40
50
60
70

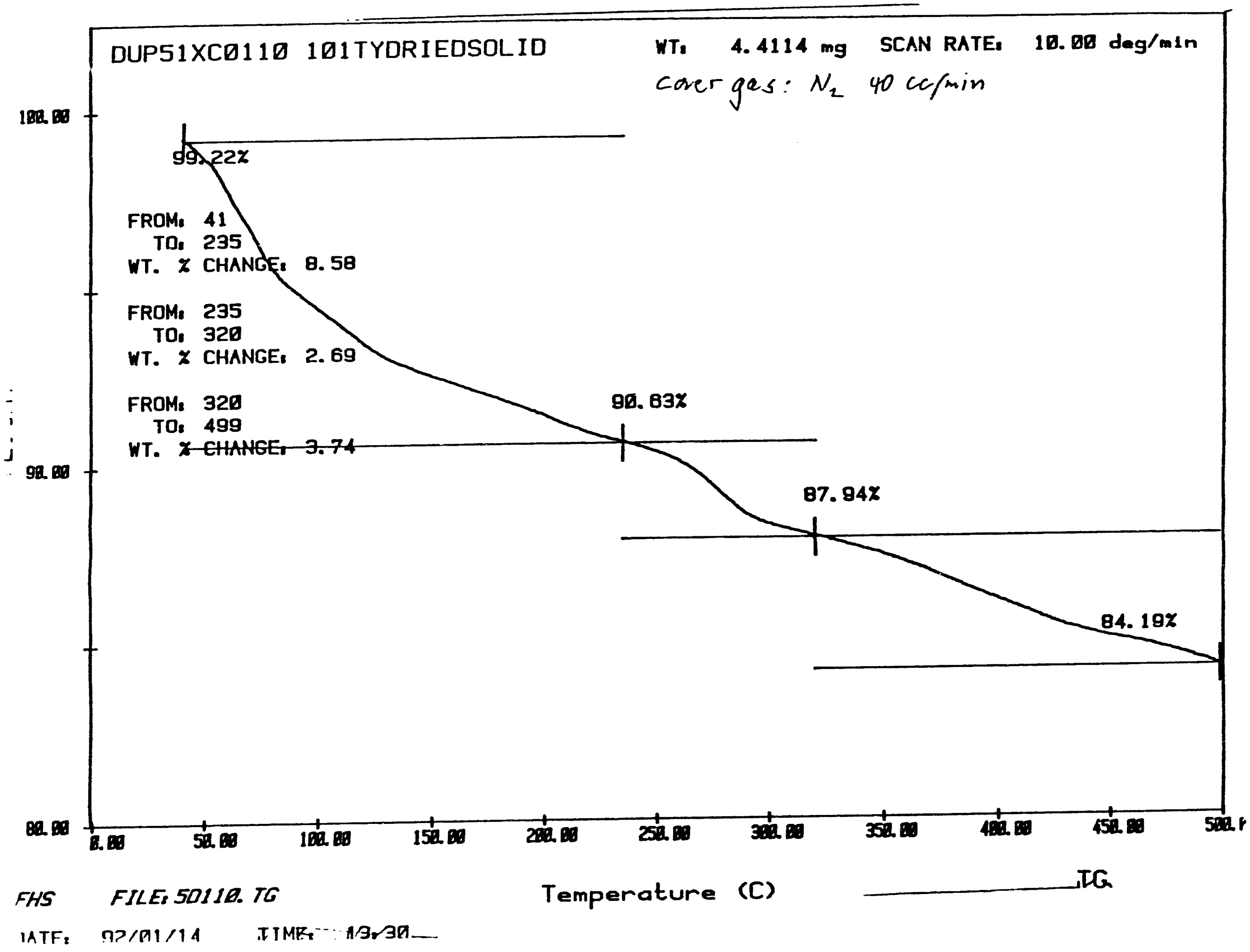

R-789 KMA-103
GREEN= NITROSYL NICKEL IRON CYANIDE HYDRATE NI[FE(CN)5NO]*H2O PDF# 22-463
10
20
30
40
50
60
70
Full Scale = 1477.00

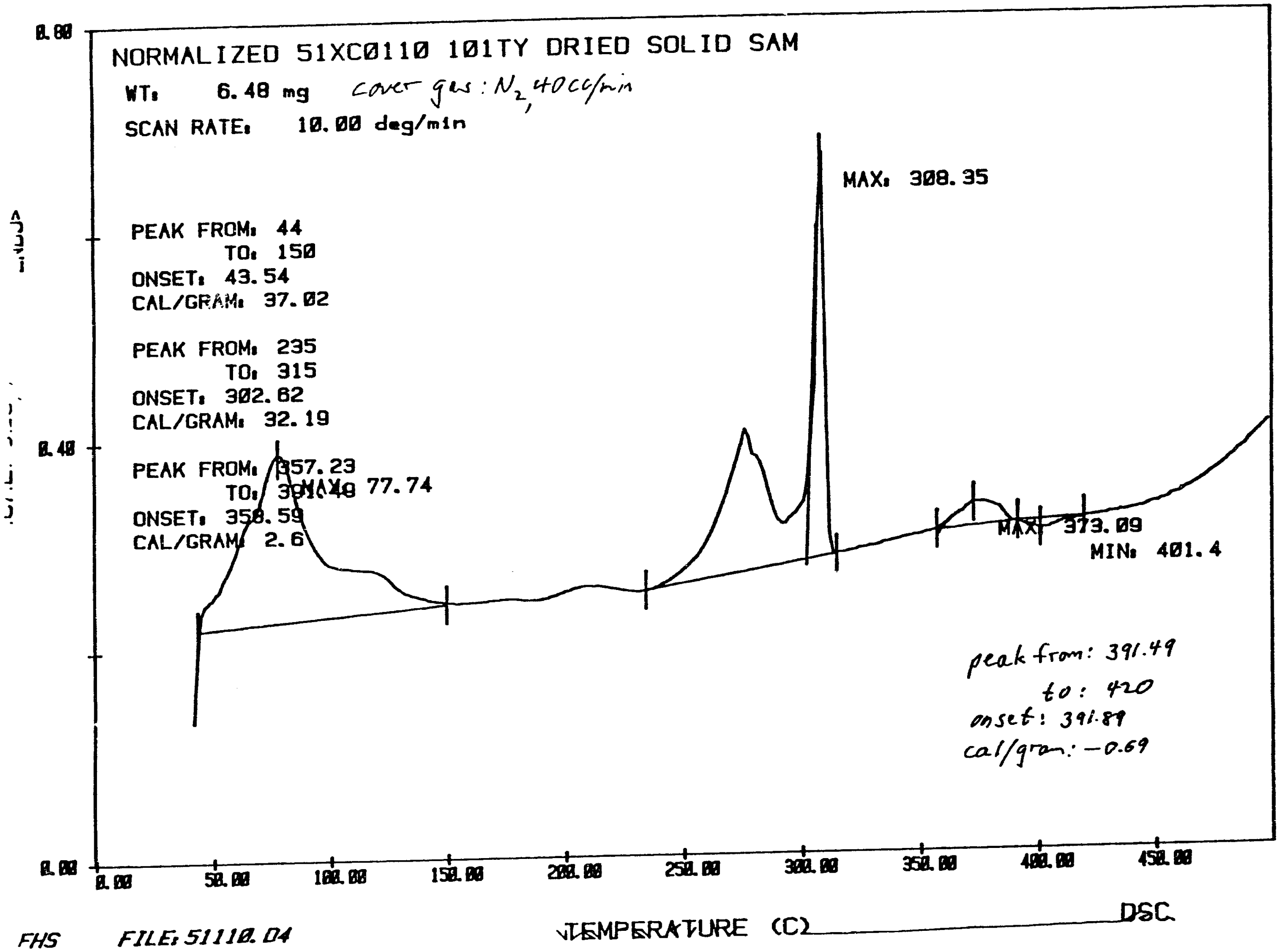

~~R-731 51XC0140~~
BLACK= 51XC0140 R-731
GREEN= 51XC0340 R-733
RED= 31XC0340 R-734
Full Scale = 5830.00
10
20
30
40
50
60
70

APPENDIX D

THERMAL ANALYSIS RAW DATA PLOTS AND TRACES

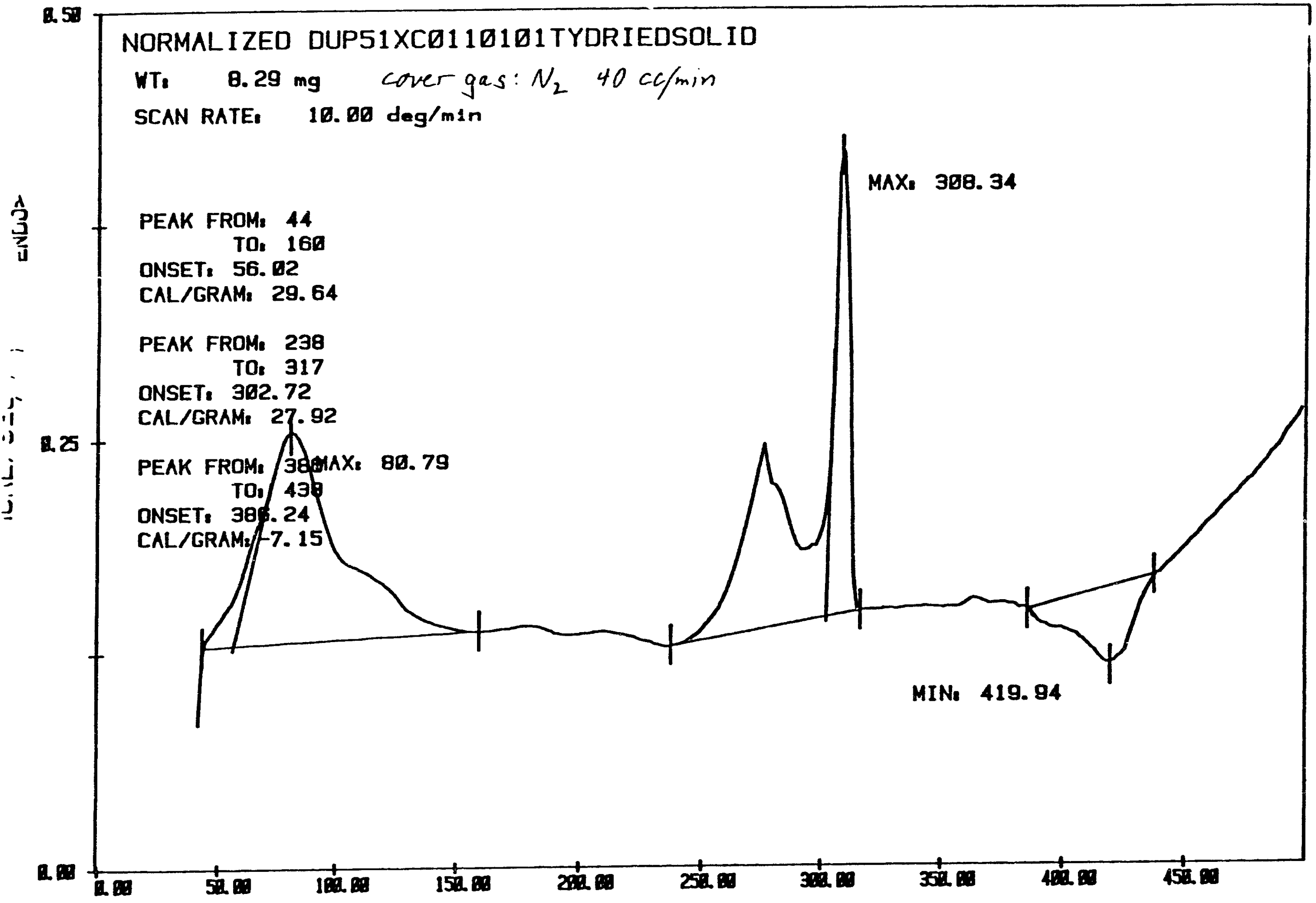

51XC0110 101TY DRIED SOLID
WT: 5.9058 mg
SCAN RATE: 10.00 deg/min
cover gas: N2 40 cc/min
99.37%
FROM: 41
TO: 235
WT. % CHANGE: 9.74
FROM: 235
TO: 320
WT. % CHANGE: 2.34
FROM: 320
TO: 499
WT. % CHANGE: 3.49
89.62%
87.28%
83.78%
100.00
90.00
80.00
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
Temperature (C)
TG
HS
FILE: 51110. TG
ATE: 92/01/15
TIME: 08:34


DUP51XC0110 101TYDRIEDSOLID
WT: 4.4114 mg
SCAN RATE: 10.00 deg/min
cover gas: N_2 40 cc/min
99.22%
FROM: 41
TO: 235
WT. % CHANGE: 8.58
FROM: 235
TO: 320
WT. % CHANGE: 2.69
FROM: 320
TO: 499
WT. % CHANGE: 3.74
90.83%
87.94%
84.19%
100.00
90.00
80.00
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.0
Temperature (C)
TG
FHS
FILE: 50110.TG
DATE: 92/01/14
TIME: 13:30



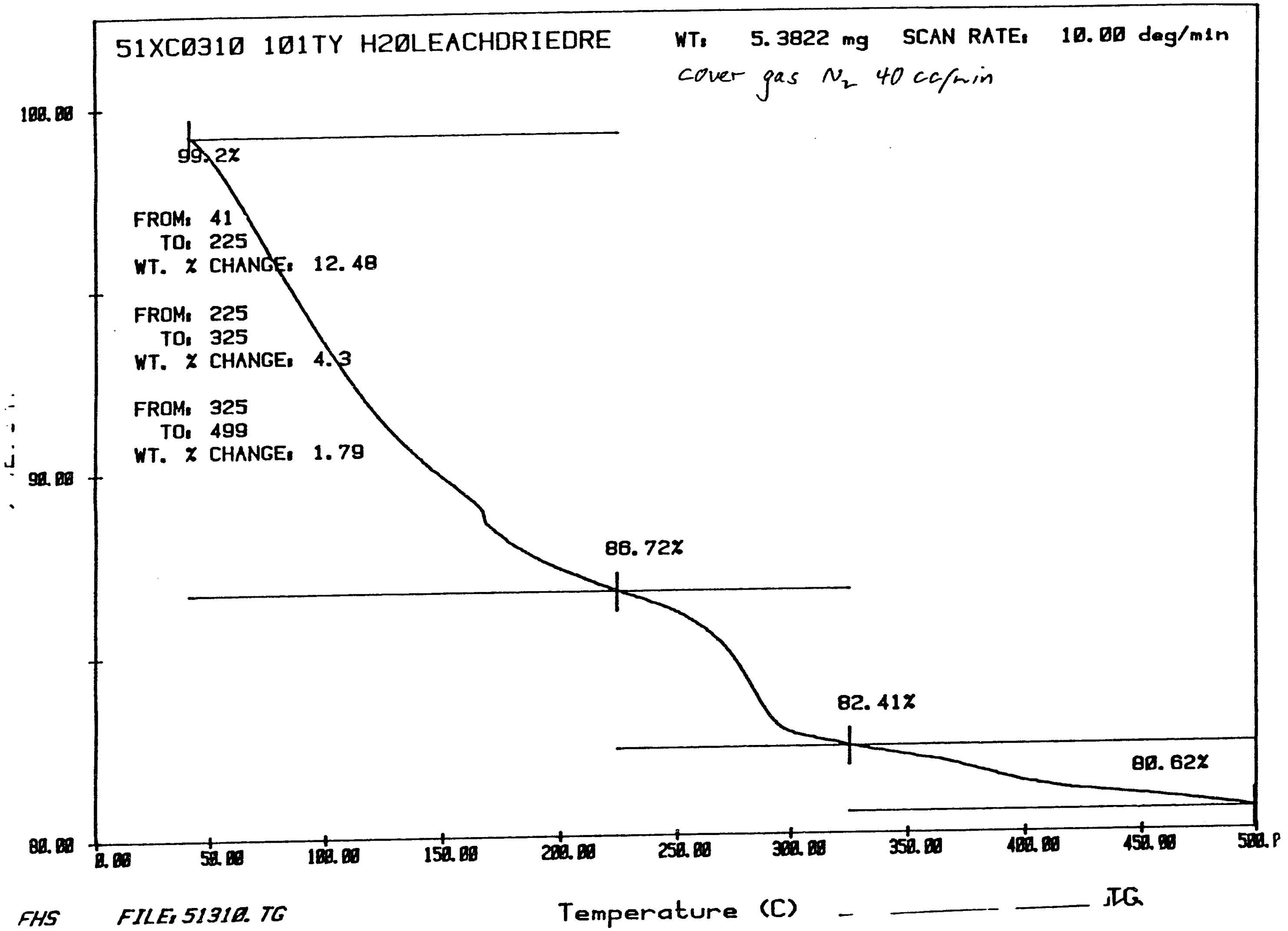
FHS FILE: 51110.04

DATE: 92/01/21 TIME: 14:53



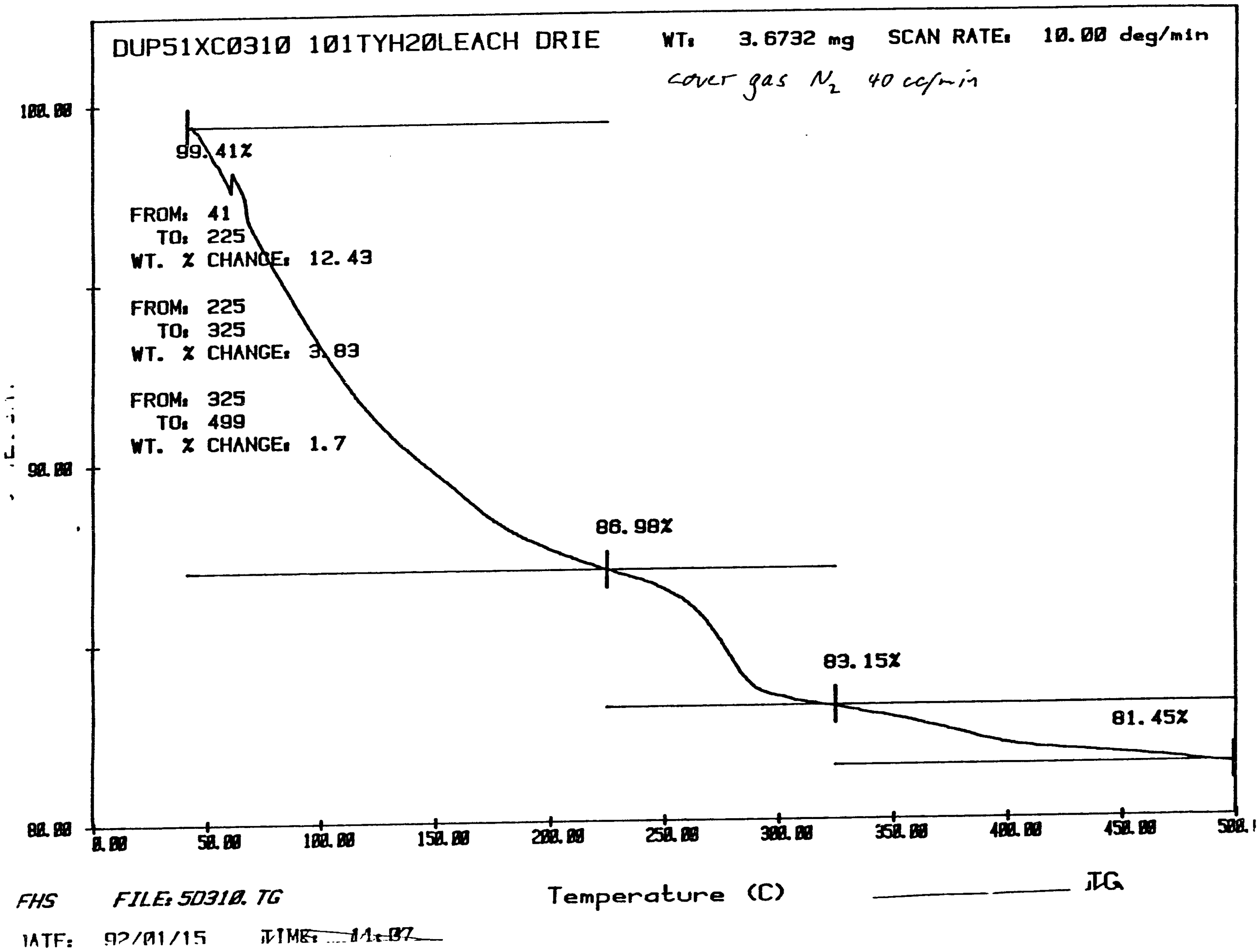
FHS FILE: 50110.D4 TEMPERATURE (C) DSC

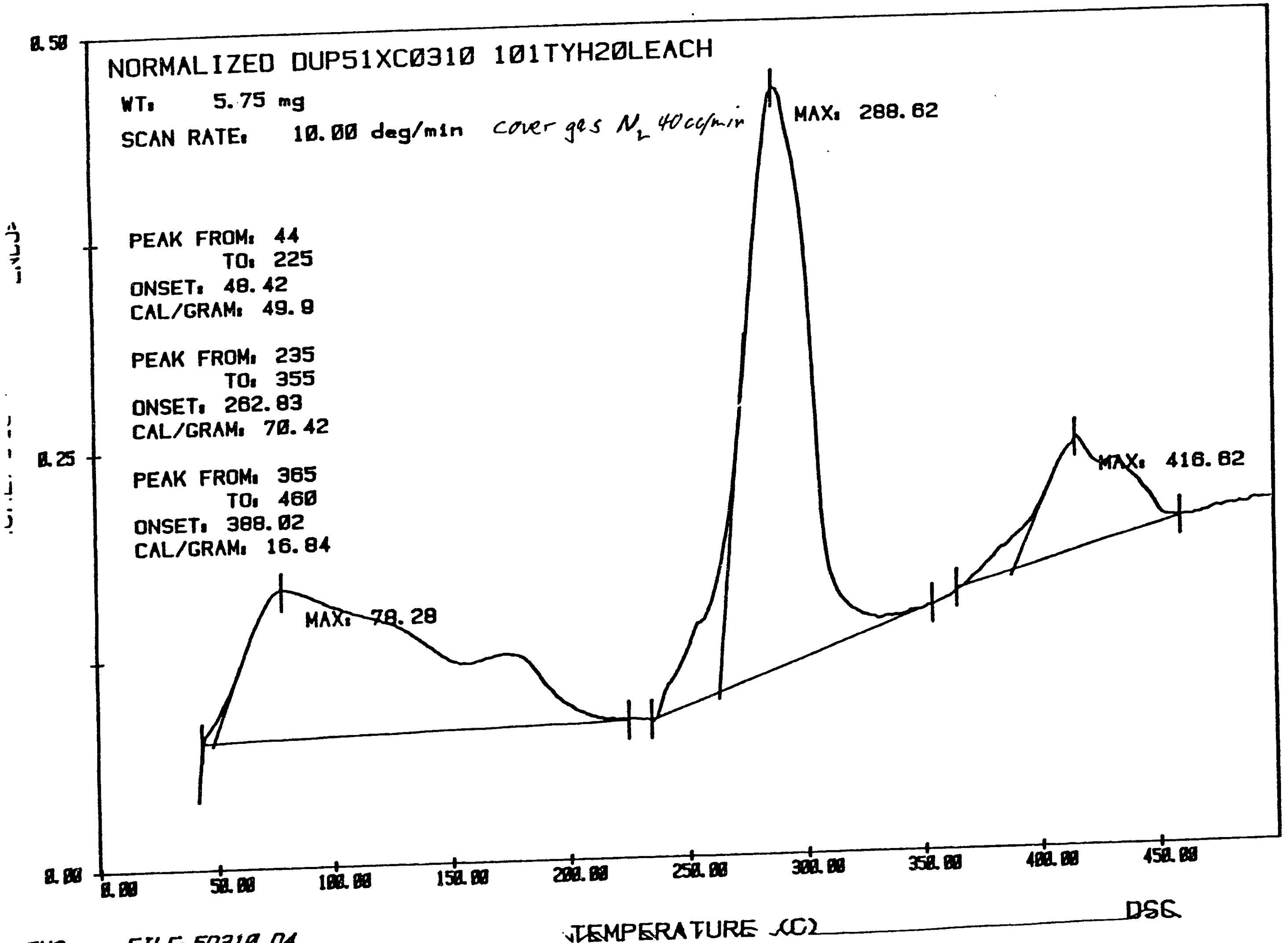
DATE: 92/01/22 ~~TIME: 10:08~~



FHS FILE: 51310. TG

DATE: 92/01/15 TIME: 10:00


DUP51XC0310 101TYH20LEACH DRIE
WT: 3.6732 mg
SCAN RATE: 10.00 deg/min
cover gas N2 40 cc/min
100.00
99.41%
FROM: 41
TO: 225
WT. % CHANGE: 12.43
FROM: 225
TO: 325
WT. % CHANGE: 3.83
FROM: 325
TO: 499
WT. % CHANGE: 1.7
90.00
86.98%
83.15%
81.45%
80.00
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.0
Temperature (C)
TG
FHS
FILE: 5D310. TG
DATE: 92/01/15
TIME: 11:07



NORMALIZED DUP51XC0310 101TYH20LEACH

WT: 5.75 mg

SCAN RATE: 10.00 deg/min cover gas N_2 40cc/min

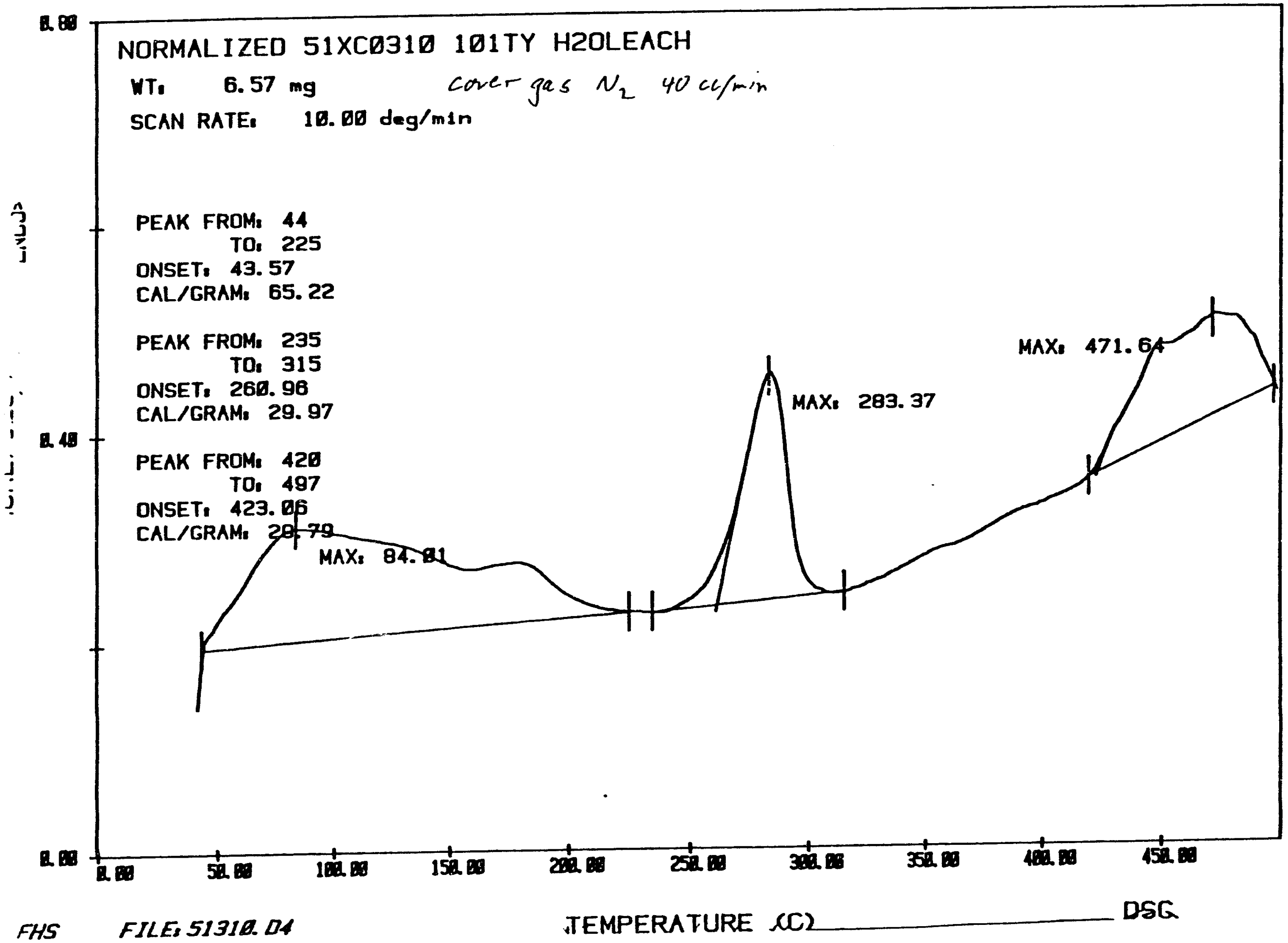
PEAK FROM: 44
TO: 225
ONSET: 48.42
CAL/GRAM: 49.9

PEAK FROM: 235
TO: 355
ONSET: 262.83
CAL/GRAM: 70.42

PEAK FROM: 365
TO: 460
ONSET: 388.02
CAL/GRAM: 16.84

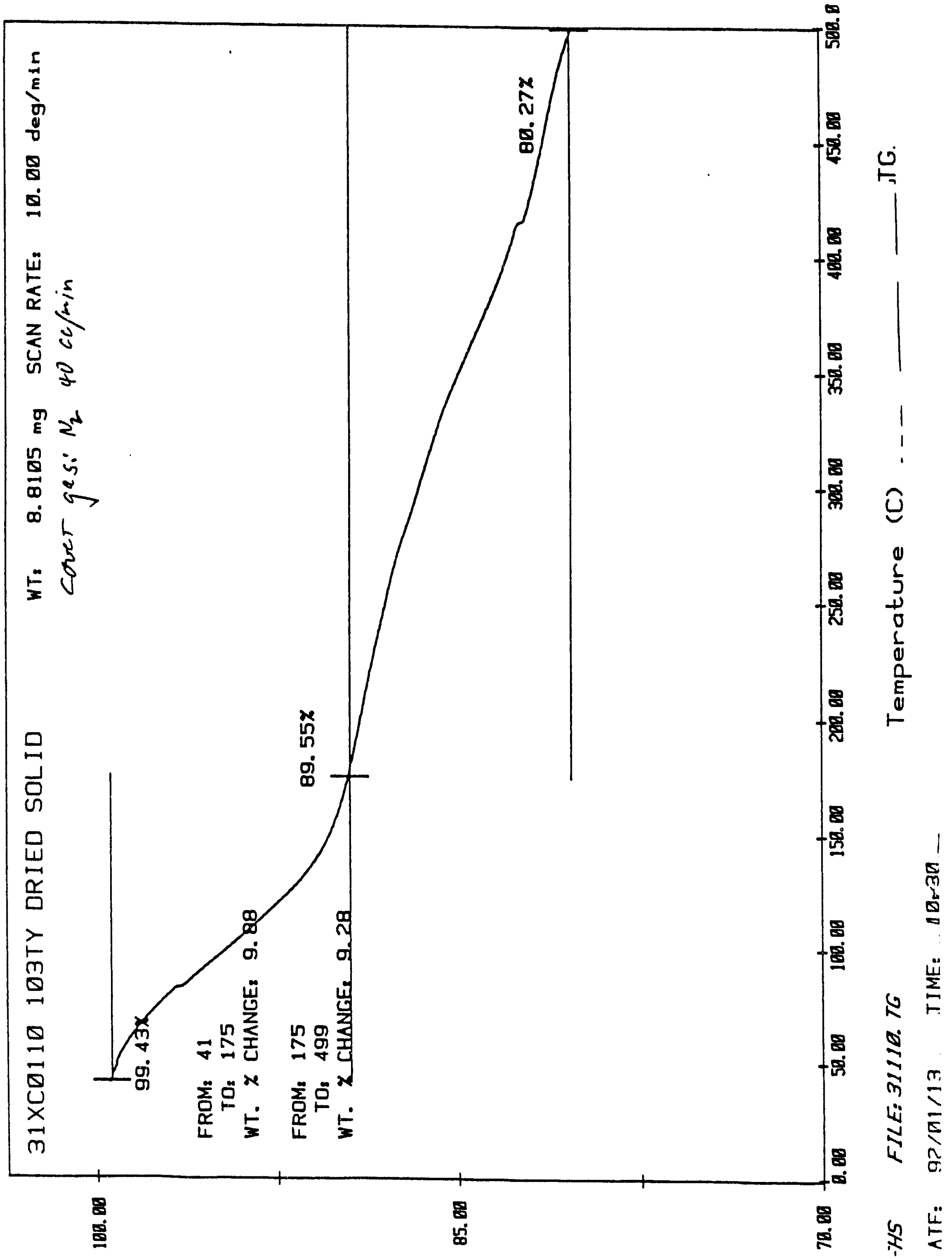
FHS FILE: 50310.04

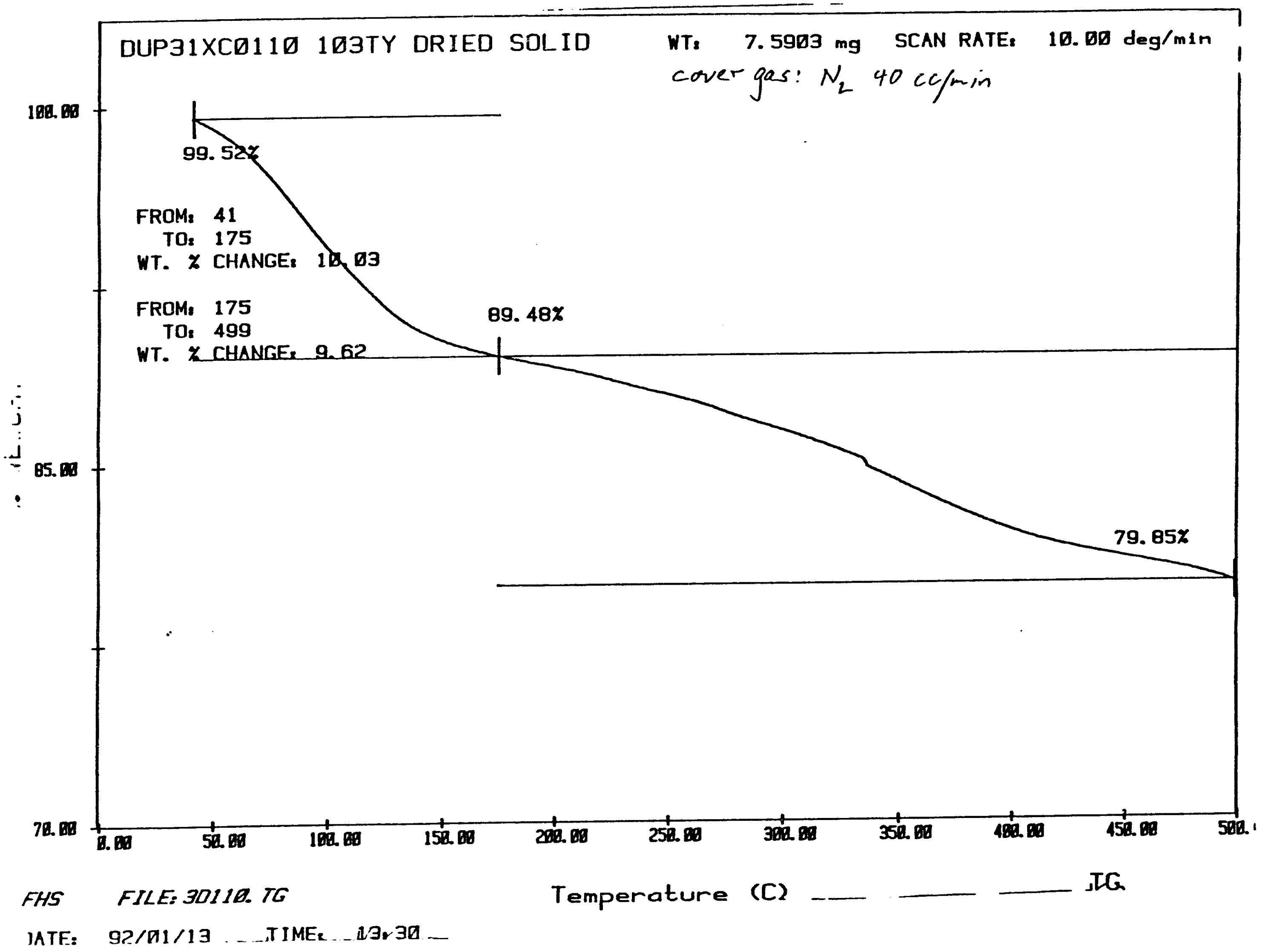
DATE: 92/02/04 TIME: 11:28

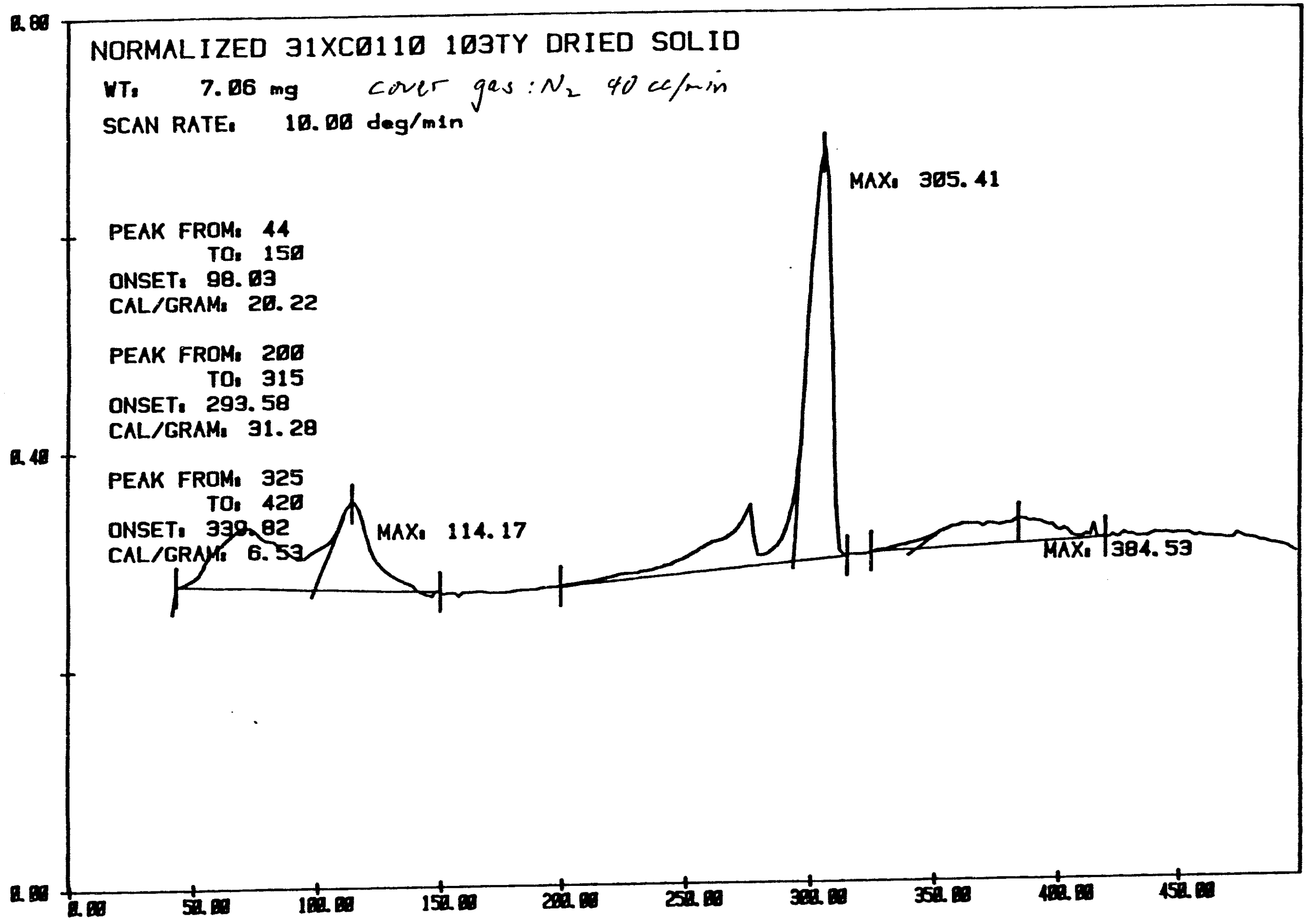


FHS FILE: 51310.04

DATE: 92/01/22 ~~TIME: 13:40~~


31XC0110 103TY DRIED SOLID
WT: 8.8105 mg
SCAN RATE: 10.00 deg/min
Cover gas: N2 40 cc/min
99.43%
89.55%
80.27%
FROM: 41
TO: 175
WT. % CHANGE: 9.88
FROM: 175
TO: 499
WT. % CHANGE: 9.28
100.00
85.00
70.00
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.0
Temperature (C)
TG
FILE: 31110.TG
92/01/13
TIME: 10:30


DUP31XC0110 103TY DRIED SOLID
WT: 7.5903 mg
SCAN RATE: 10.00 deg/min
cover gas: N_2 40 cc/min
100.00
85.00
70.00
99.52%
FROM: 41
TO: 175
WT. % CHANGE: 10.03
FROM: 175
TO: 499
WT. % CHANGE: 9.62
89.48%
79.85%
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.
Temperature (C)
TG
FHS
FILE: 30110.TG
DATE: 92/01/13
TIME: 13:30



NORMALIZED 31XC0110 103TY DRIED SOLID

WT: 7.06 mg cover gas : N_2 40 cc/min

SCAN RATE: 10.00 deg/min

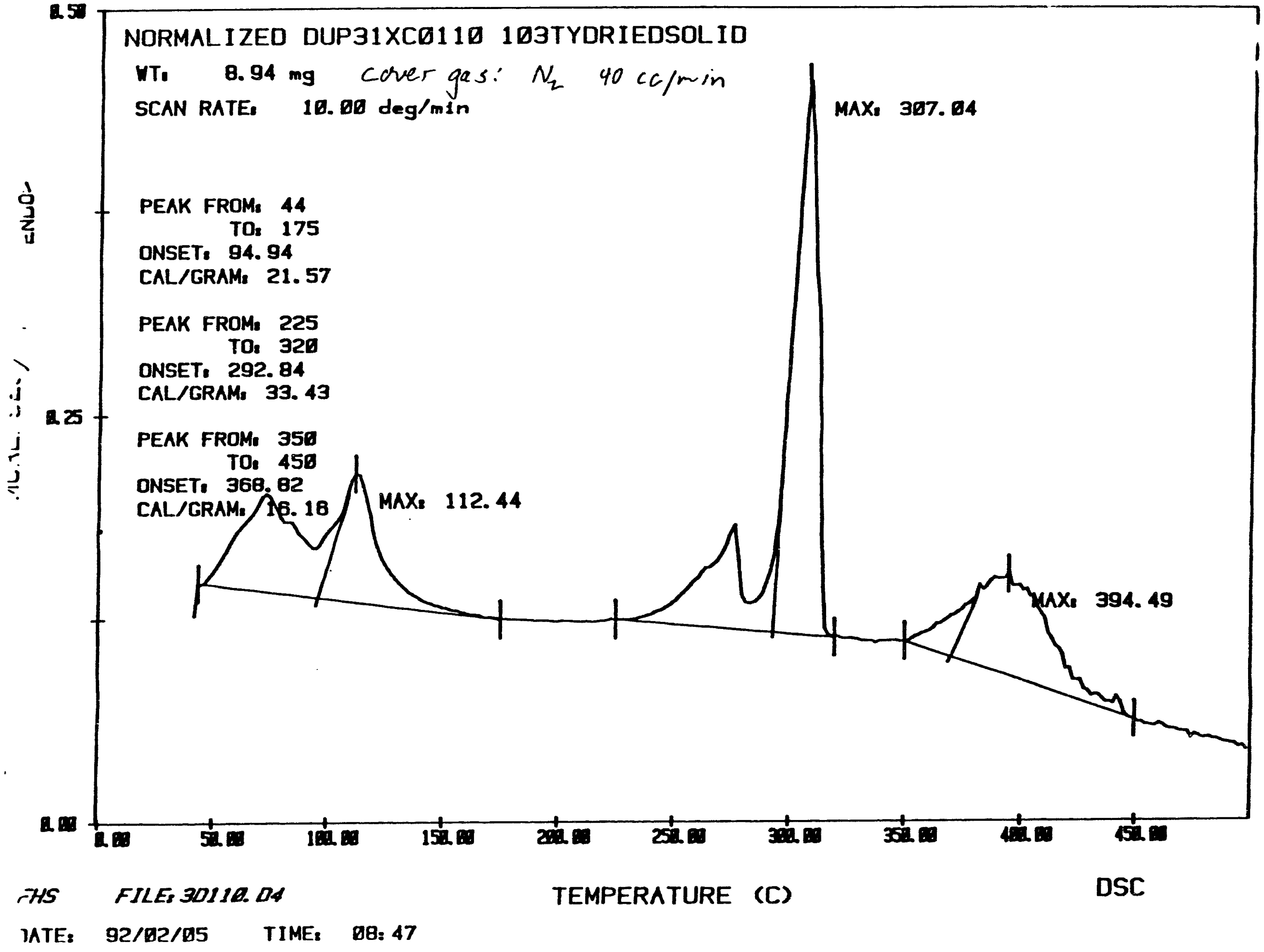
PEAK FROM: 44
TO: 150
ONSET: 98.03
CAL/GRAM: 20.22

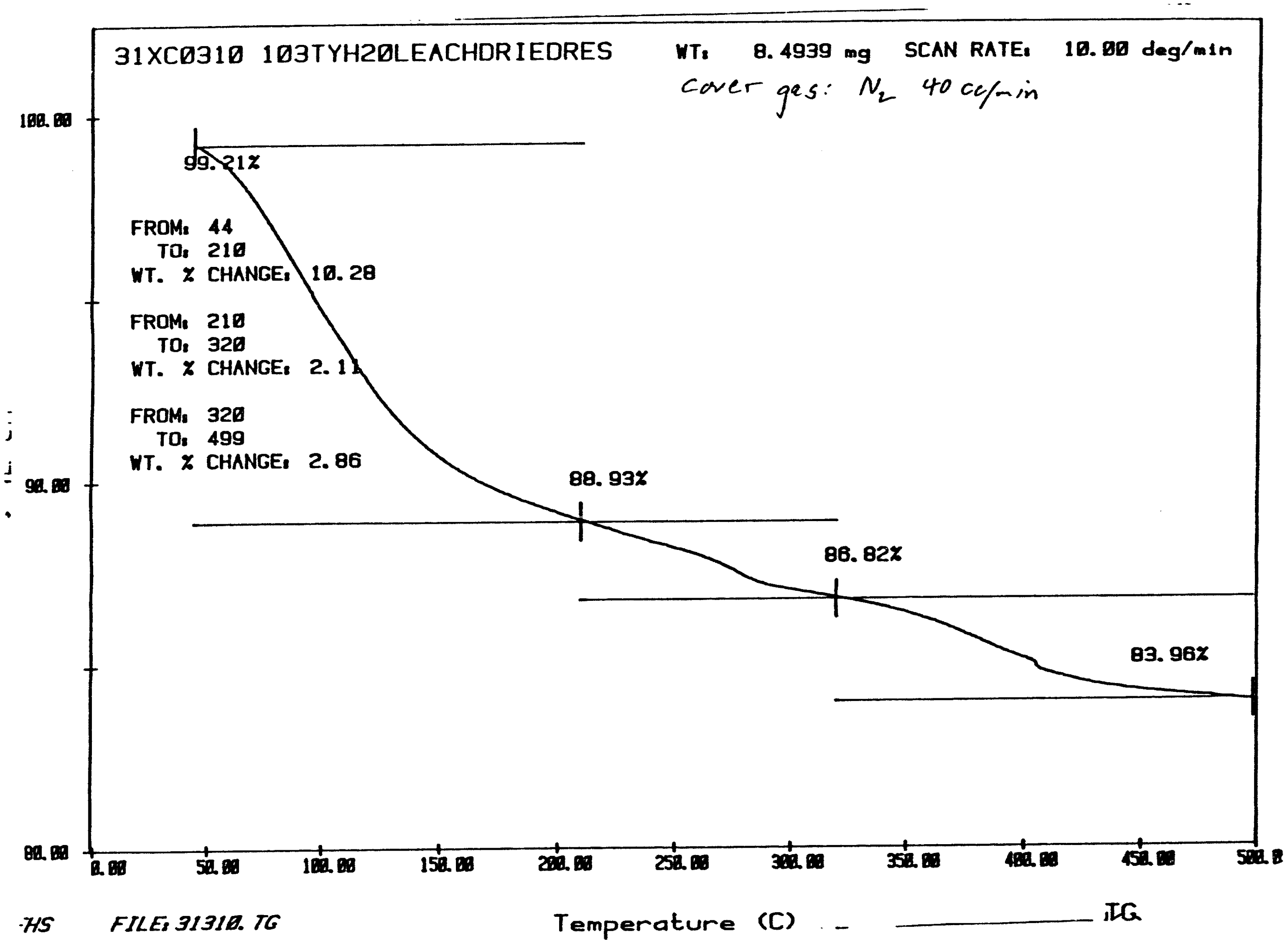
PEAK FROM: 200
TO: 315
ONSET: 293.58
CAL/GRAM: 31.28

PEAK FROM: 325
TO: 420
ONSET: 339.82
CAL/GRAM: 6.53

HS FILE: 31110.04 TEMPERATURE (C) DSC

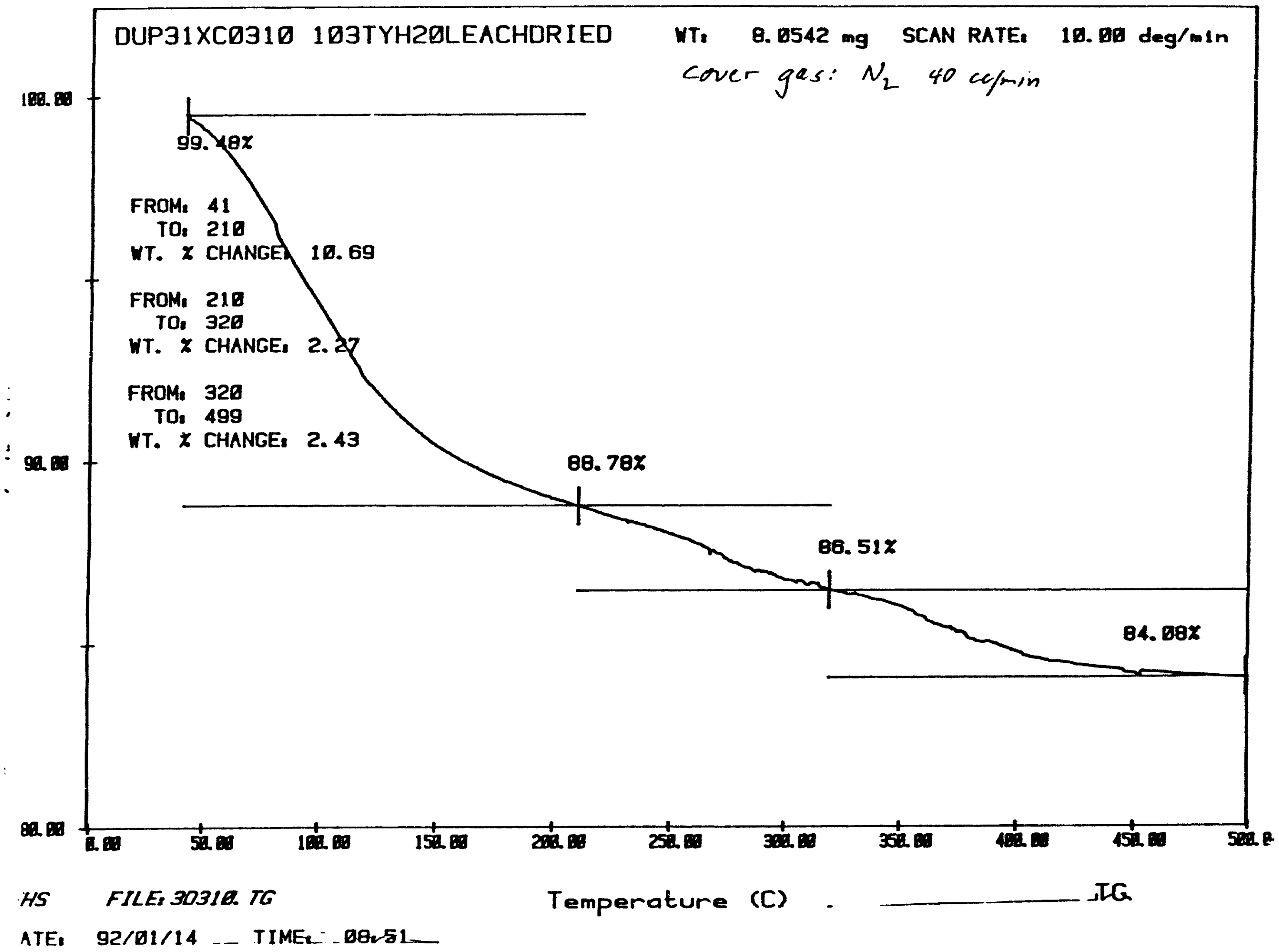
ATE: 92/02/04 TIME: 14.08

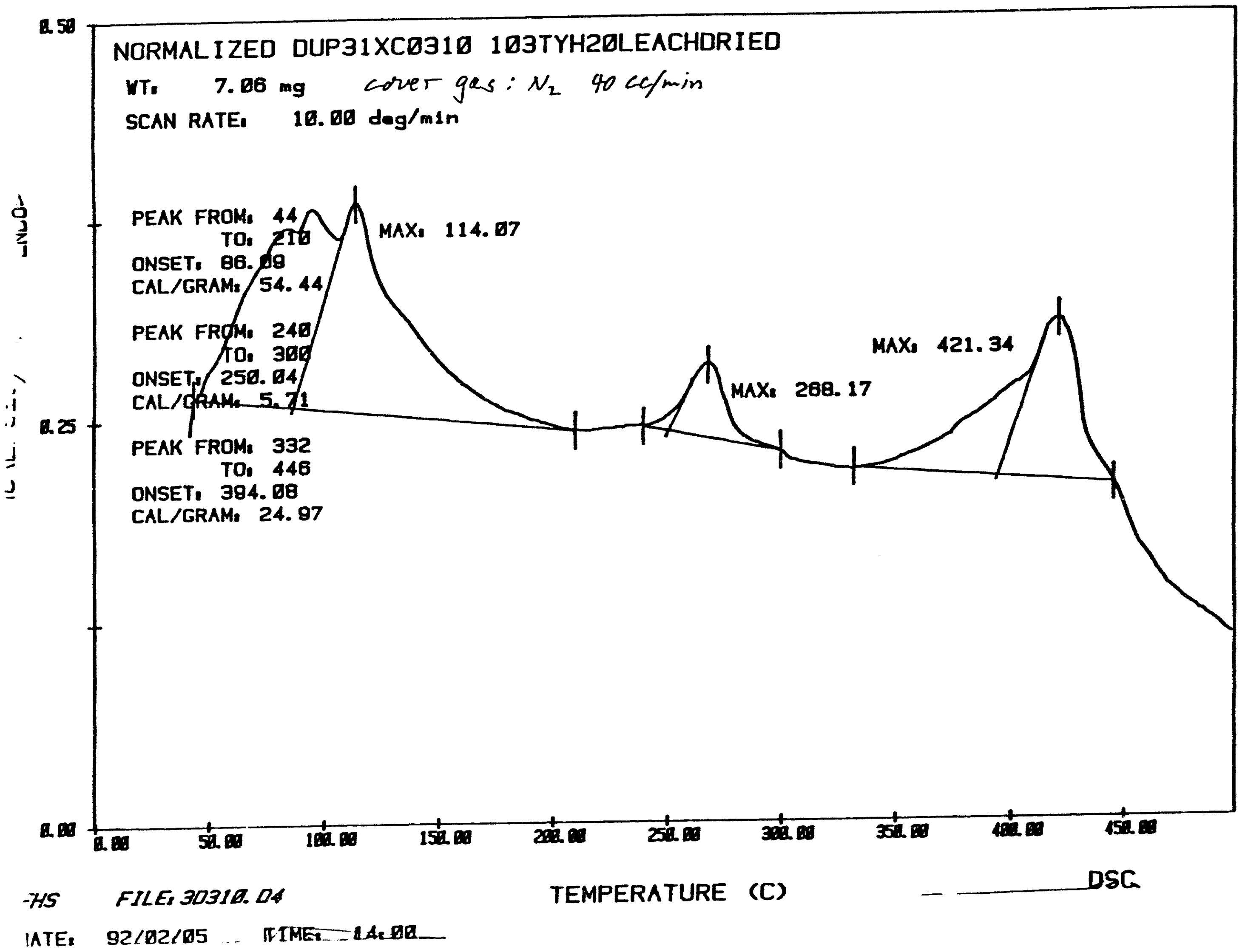

NORMALIZED DUP31XC0110 103TYDRIEDSOLID
WT: 8.94 mg
cover gas: N_2 40 cc/min
SCAN RATE: 10.00 deg/min
PEAK FROM: 44
TO: 175
ONSET: 94.94
CAL/GRAM: 21.57
PEAK FROM: 225
TO: 320
ONSET: 292.84
CAL/GRAM: 33.43
PEAK FROM: 350
TO: 450
ONSET: 368.82
CAL/GRAM: 16.18
MAX: 112.44
MAX: 307.04
MAX: 394.49
ENDO
0.50
0.25
0.00
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
TEMPERATURE (C)
DSC
FHS
FILE: 30110.D4
DATE: 92/02/05
TIME: 08:47



HS FILE: 31310.TG

ATE: 92/01/14 TIME: 07:15


DUP31XC0310 103TYH20LEACHDRIED
WT: 8.0542 mg
SCAN RATE: 10.00 deg/min
cover gas: N2 40 cc/min
100.00
90.00
80.00
99.48%
FROM: 41
TO: 210
WT. % CHANGE: 10.69
FROM: 210
TO: 320
WT. % CHANGE: 2.27
FROM: 320
TO: 499
WT. % CHANGE: 2.43
88.78%
86.51%
84.08%
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.0
Temperature (C)
HS
FILE: 30310. TG
ATE: 92/01/14
TIME: 08:51
TG



NORMALIZED DUP31XC0310 103TYH20LEACHDRIED

WT: 7.06 mg cover gas: N_2 40 cc/min

SCAN RATE: 10.00 deg/min

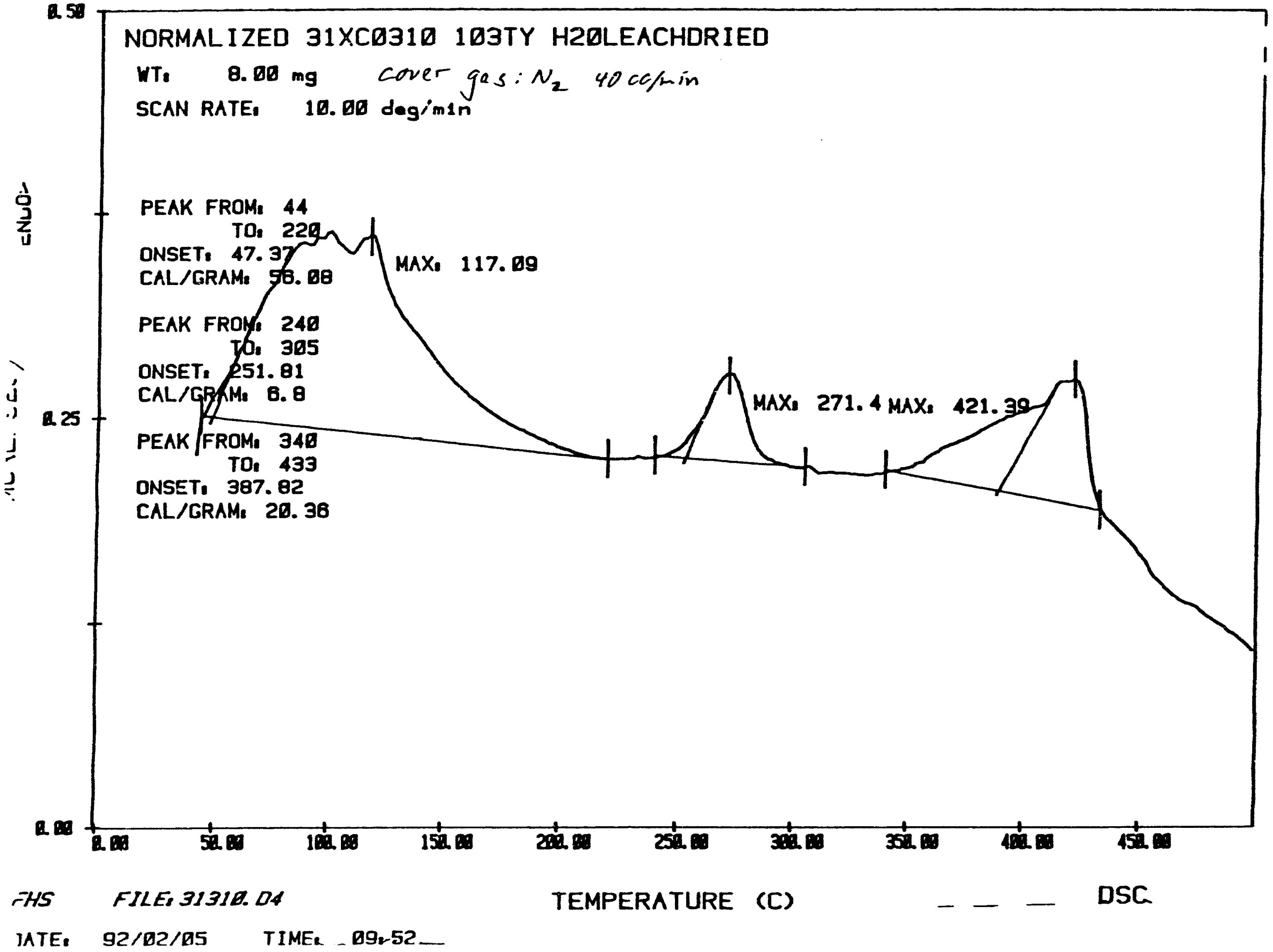
PEAK FROM: 44
TO: 210
ONSET: 86.09
CAL/GRAM: 54.44

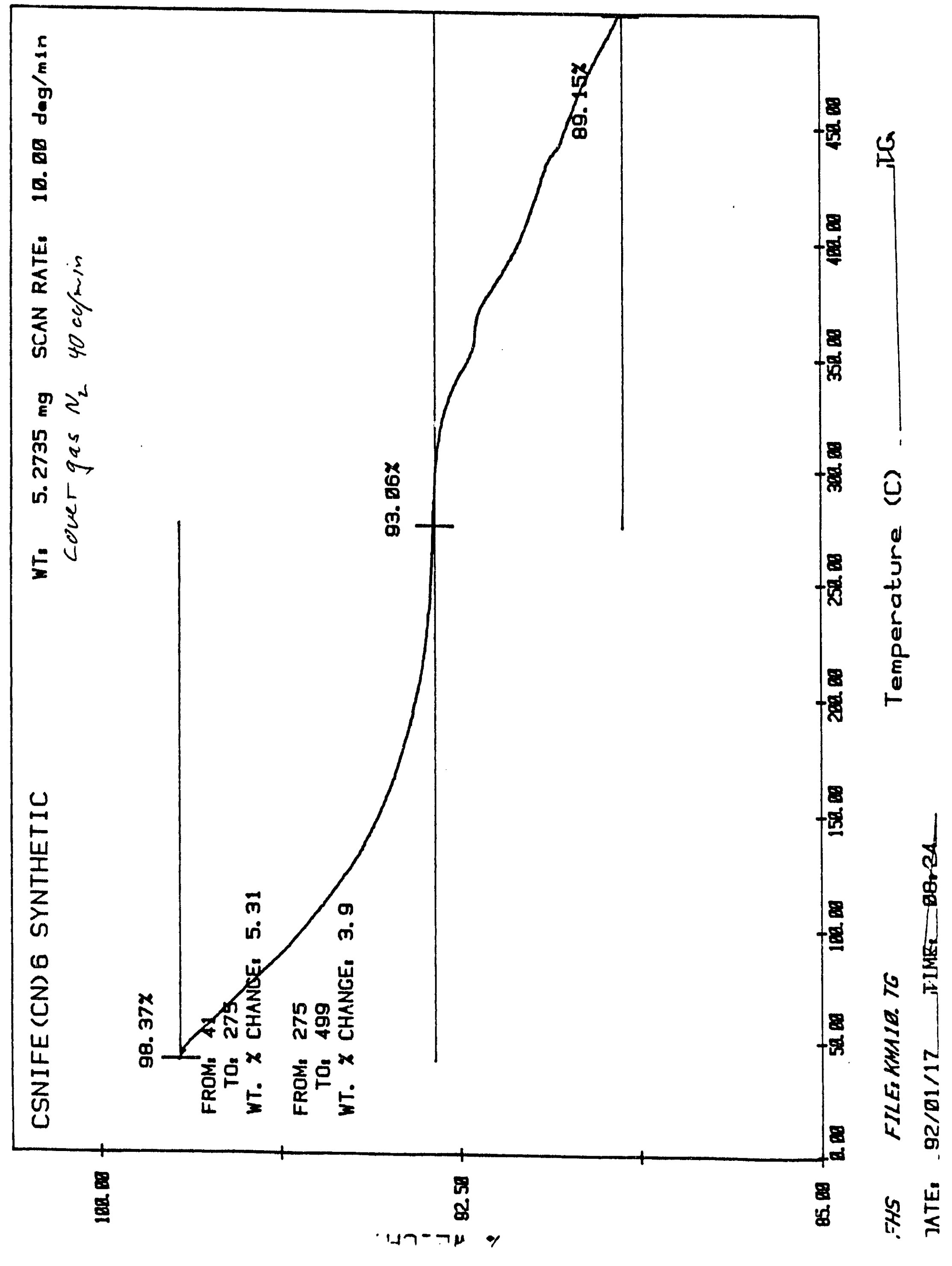
PEAK FROM: 240
TO: 300
ONSET: 250.04
CAL/GRAM: 5.71

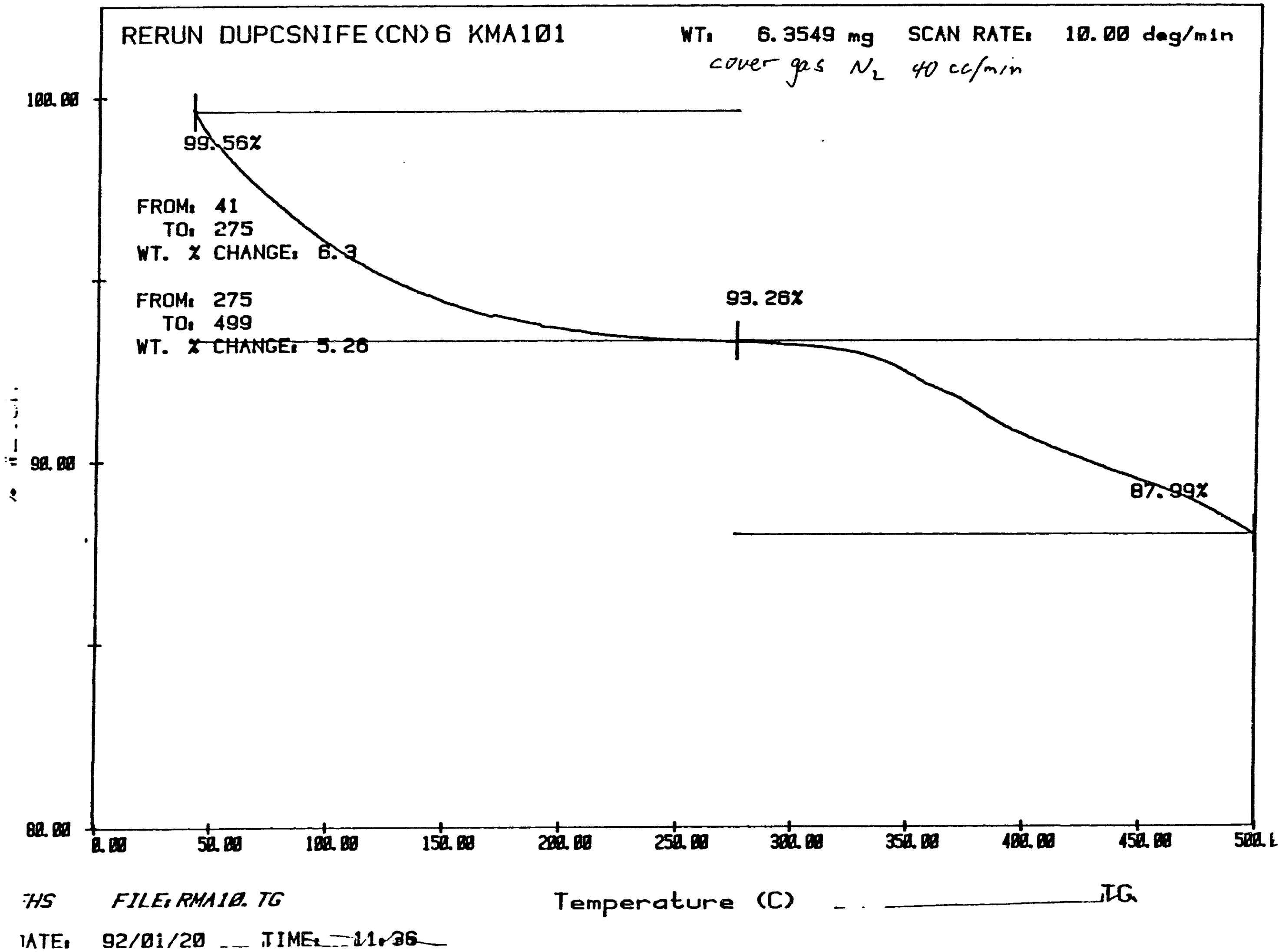
PEAK FROM: 332
TO: 446
ONSET: 394.08
CAL/GRAM: 24.97

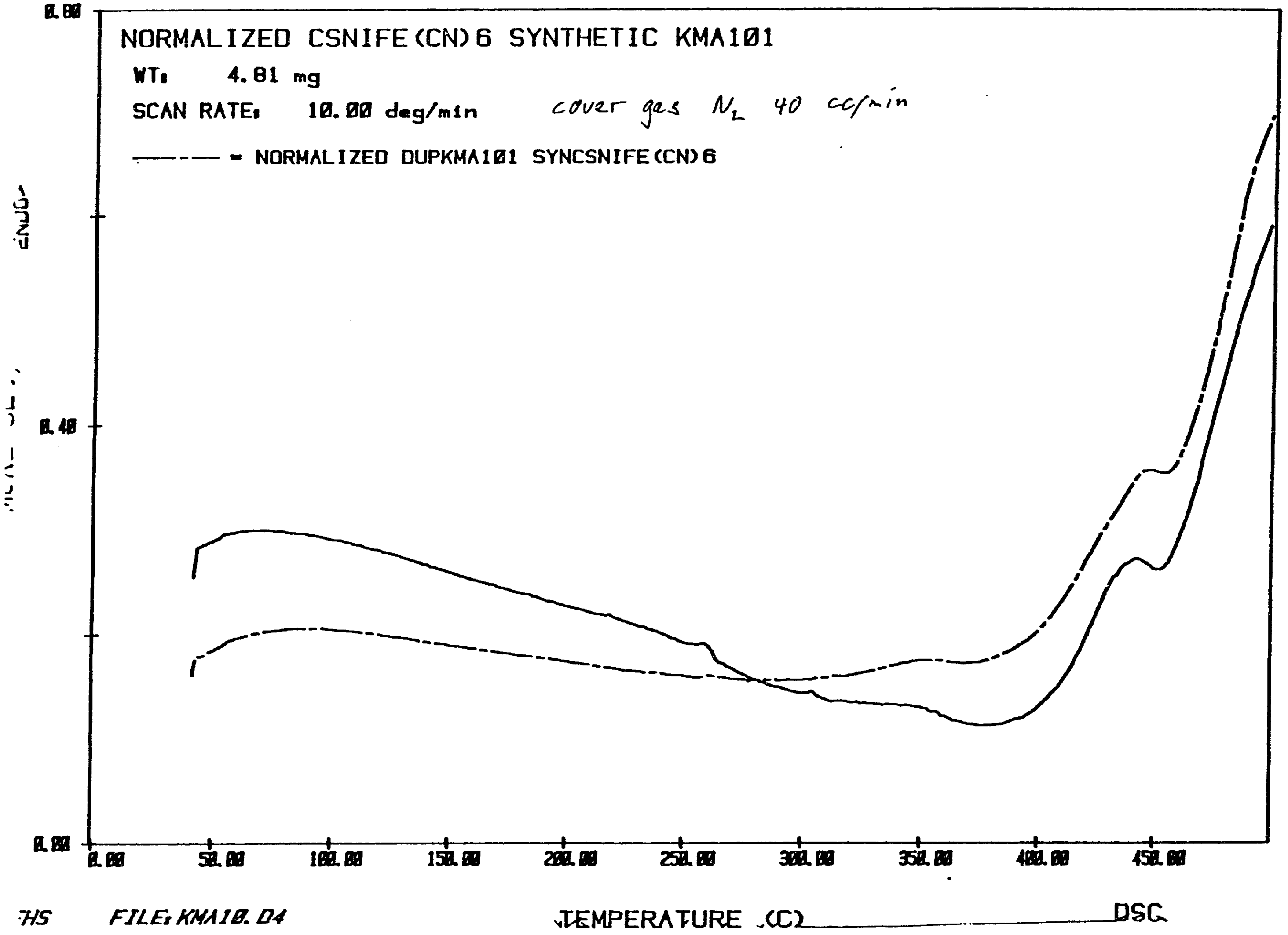
-HS FILE: 30310.04

IATE: 92/02/05 TIME: 14:00


NORMALIZED 31XC0310 103TY H20LEACHDRIED
WT: 8.00 mg
cover gas: N₂ 40 cc/min
SCAN RATE: 10.00 deg/min
PEAK FROM: 44
TO: 220
ONSET: 47.37
CAL/GRAM: 56.08
PEAK FROM: 240
TO: 305
ONSET: 251.81
CAL/GRAM: 6.8
PEAK FROM: 340
TO: 433
ONSET: 387.82
CAL/GRAM: 20.36
MAX: 117.09
MAX: 271.4
MAX: 421.39
ENDO->
0.50
0.25
0.00
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
TEMPERATURE (C)
DSC
FHS
FILE: 31310.D4
DATE: 92/02/05
TIME: 09:52


CSNIFE(CN)6 SYNTHETIC
WT: 5.2735 mg
SCAN RATE: 10.00 deg/min
cover gas N2 40 cc/min
98.37%
FROM: 41
TO: 275
WT. % CHANGE: 5.31
FROM: 275
TO: 499
WT. % CHANGE: 3.9
93.06%
89.15%
100.00
92.50
85.00
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
Temperature (C)
TG
FHS
FILE: KMA10.TG
DATE: 92/01/17
TIME: 08:24
% WEIGHT


RERUN DUPCSNIFE(CN)6 KMA101
WT: 6.3549 mg
SCAN RATE: 10.00 deg/min
cover gas N2 40 cc/min
100.00
90.00
80.00
99.56%
FROM: 41
TO: 275
WT. % CHANGE: 6.3
FROM: 275
TO: 499
WT. % CHANGE: 5.26
93.26%
87.99%
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.
Temperature (C)
TG
HS
FILE: RMA10. TG
ATE: 92/01/20
TIME: 11:36



HS FILE: KMA10.D4

DATE: 92/02/05 ~~TIME: 15.00~~

APPENDIX E

PERCENT WATER AND PERCENT SOLUBILITY DATA

FeCN ARCHIVE SAMPLE -- % INSOLUBLES (WATER LEACH)

Sample No./Description: 51XC0000/101-TY ARCHIVE SAMPLE

Date NOV 8, 1991

INPUT DATA

All weights given in grams

Tare Weight (W1) =	113.48878		
Tare + Sample (W2) =	114.50237		
Filter Jar Tare (W6) =	120.48767	Blank (W6) =	119.10969
Smpl, Fltr, Jar (W7) =	120.94104	Blank (W7) =	119.12451

COMMENTS

Original sample into ultrasonic at 9:40 am/11-6-91

Remove from ultrasonic at 10:40 am/11-6-91

Filter sample at 8:15 am/11-7-91

Dry filter/residue 11-8-91

RESULTS

Net Smpl Wgt (W5) =	1.01359		
Gross Ppt Weight =	0.45337	Net Filter Wgt (W8)	0.01482
Net Residue Weight =	0.43855		
Wgt % Insolubles =	43.27%		

Net Wgt = W2 - W1 = W5

Gross Ppt Wgt = W7 - W6

Residue Wgt = W7 - W6 - W8

Wgt % Insolubles = ((W7-W6-W8)/W5)*100

FeCN ARCHIVE SAMPLE -- % INSOLUBLES (WATER LEACH)

Sample No./Description: 31XC0000/103-TY ARCHIVE SAMPLE

Date: NOV 8, 1991

INPUT DATA

All weights given in grams

Tare Weight (W1) =	113.35190		
Tare + Sample (W2) =	114.37935		
Filter Jar Tare (W6) =	118.93218	Blank (W6) =	122.32187
Smpl, Fltr, Jar (W7) =	119.37777	Blank (W7) =	122.33657

COMMENTS

Original sample into ultrasonic at 9:40 am/11-6-91

Remove from ultrasonic at 10:40 am/11-6-91

Filter sample at 8:15 am/11-7-91

Dry filter/residue 11-8-91

RESULTS

Net Smpl Wgt (W5) =	1.02745		
Gross Ppt Weight =	0.44559	Net Filter Wgt (W8)	0.01470
Net Residue Weight =	0.43089		
Wgt % Insolubles =	41.94%		

Net Wgt = W2 - W1 = W5

Gross Ppt Wgt = W7 - W6

Residue Wgt = W7 - W6 - W8

Wgt % Insolubles =

((W7-W6-W8)/W5)*100

FeCN ARCHIVE SAMPLE – % WATER ANALYSIS

Sample No./Description: 51XC0000/101-TY ARCHIVE SAMPLE

Date: OCT 31, 1991

INPUT DATA	Aliquot A	Aliquot B	COMMENTS
	All weights given in grams		
Tare Weight (W1) =	16.89260	16.94841	Original sample into oven at 2:50 pm/10-31-91
Tare + Sample (W2) =	19.26426	18.95620	
Dry Weight (W3) =	19.12197	18.84105	Remove from oven at 10:15 am/11-1-91
Dry Weight 2 (W4) =	19.11568	18.83548	Complete re-heat at 1:20 pm/11-1-91

RESULTS

Net Sample Weight =	2.37166	2.00779
Weight Loss =	0.14229	0.11515
Net Residue Weight =	2.22308	1.88707
Weight % H2O Loss =	5.99960	5.73516
% Difference =	0.033	0.030

Net Wgt = W2 - W1
Wgt Loss = W2 - W3
Residue Wgt = W4 - W1
Wgt %H2O Loss = ((W2 - W3)/(W2 - W1)) * 100
% Diff = ((W3 - W4)/W4) * 100
Std. Dev = Range/(sqrt(2))

5.87 = Average % H2O Loss
0.19 = Std Dev

FeCN ARCHIVE SAMPLE -- % WATER ANALYSIS

Sample No./Description: 31XC0000/103-TY ARCHIVE SAMPLE

Date: OCT 31, 1991

All weights given in grams

INPUT DATA	Aliquot A	Aliquot B	COMMENTS
Tare Weight (W1) =	16.84161	16.88581	Original sample into oven at 3:10 pm/10-31-91
Tare + Sample (W2) =	19.69567	19.42461	
Dry Weight (W3) =	19.56057	19.30208	Remove from oven at 10:15 am/11-1-91
Dry Weight 2 (W4) =	19.54924	19.29282	Complete re-heat at 1:20 pm/11-1-91

RESULTS

Net Sample Weight =	2.85406	2.53880
Weight Loss =	0.13510	0.12253
Net Residue Weight =	2.70763	2.40701
Weight % H2O Loss =	4.73361	4.82630
% Difference =	0.058	0.048

Net Wgt = W2 - W1

Wgt Loss = W2 - W3

Residue Wgt = W4 - W1

Wgt %H2O Loss = ((W2 - W3)/(W2 - W1)) * 100

% Diff = ((W3 - W4)/W4) * 100

Std. Dev = Range/(Sqrt(2))

4.78 = Average % H2O Loss

0.07 = Std Dev

APPENDIX F

PROCEDURE FOR PREPARING A MIXTURE OF $Cs_2NiFe(CN)_6$ AND $NaNO_2/NaNO_3$

6-$\overset{27}{\cancel{28}}$-91 Procedure for preparing a mixture of $Cs_2NiFe(CN)_6$ and $NaNO_2/NaNO_3$

Began water-washing $Cs_2NiFe(CN)_6$ prepared by D. Hart as described by the following procedure.

Procedure for preparing a mixture of $Cs_2NiFe(CN)_6$ and $NaNO_2/NaNO_3$

1. Begin by water-washing $Cs_2NiFe(CN)_6$.

   a. Add about 30 ml water to the sample in a 50 cc centrifuge cone and shake the mixture. (Not vigorously, but enough to mix.)

   b. Centrifuge the mixture and decant water from precipitate.

   c. Repeat water-washing at least two more times.

2. Prepare a sample of $Cs_2NiFe(CN)_6$ for the oven. Place 16 g on a watchglass and set ia a oven preheated to 110°C. Dry until a constant weight is obtained.

3. $Cs_2NiFe(CN)_6$ will need to be ground into a fine powder using the mortar and pestle method. If the $Cs_2NiFe(CN)_6$ mixture is too hard to break up, place in triple-lined bag and pound with a hammer until pieces are broken up enough to grind.

4. The total amount of mixture needed is 20 g. A ratio of 2.2 $Cs_2NiFe(CN)_6$ to 1 $NaNO_2/NaNO_3$ is desired so combine 6.25 g of a 50% by mole mixture of $NaNO_2/NaNO_3$ to a 13.75 g mixture of $Cs_2NiFe(CN)_6$.

   a. (HAZARD)---
   The mixture required has a slight potential for ignition so do not slide pestle in the mortar. Instead, rock the pedestal in the mortar to grind the $Cs_2NiFe(CN)_6$.

   b. Stir the mixture with a spatula to ensure that the material is thoroughly homogenized.

See changes p. 46 - 8-16-91 K. L. Lookabill

- While mixing H_2O w/ the $Cs_2NiFe(CN)_6$ I used a stirring bar to stir because the bottom would not release the $Cs_2NiFe(CN)_6$. I then centrifuged the mixture for 5 minutes. Repeated procedure two more times. On the third run the ~~pecep~~ ppt didn't completely settle out, so I ran it for two more minutes. The ppt still hadn't settled, so I ran it again for another 5 minutes.

The ppt still hadn't settled out, so I decided to let it centrifuge for another hour over lunch. The ppt settled and the H_2O was virtually clear, so I proceeded along to the next step.

To dry the $Cs_2NiFe(CN)_6$ I used a petrie dish and left it at 2:45 pm. Will stop drying tomorrow morning.

-K. L. Lookabill (6-27-91)

6-28-91 Procedure for $Cs_2NiFe(CN)_6$ and $NaNO_2/NaNO_3$ cont.

I removed the $Cs_2NiFe(CN)_6$ from the oven at 7:30 a.m. and placed in dessicator.

Weight (petrie dish + watch glass + $Cs_2NiFe(CN)_6$)

1st trial	124.30 g	4th trial	124.27 g
2nd trial	124.26 g		
3rd trial	124.30 g		

Kelly Lookabill 7-1-91 2nd trial - placed in oven ~~for~~ at 9:35 a.m. took out $Cs_2NiFe(CN)_6$ and placed in dessicator ~~[illegible]~~ at 11:30 a.m.

3rd trial - placed in oven at 1:30 p.m. placed $Cs_2NiFe(CN)_6$ in dessicator at 3:30 p.m. ann left overnight.

7-1-91 4th trial - placed in oven at 7:35 a.m. at 9:30 a.m. placed $Cs_2NiFe(CN)_6$ in dessicator.

after the fourth trial the $Cs_2NiFe(CN)_6$ had obtained a nearly constant weight so I ground it up into a powder. ~~9.49~~ 9.567 g was obtained.

I was hoping to obtain at least 14 g of $Cs_2NiFe(CN)_6$, but more water evaporated than I had expected. The following ratios ~~provides~~ ~~an~~ ~~alot~~ state the allotment of $NaNO_2/NaNO_3$ required to obtain a 2.2 ratio.

$$\frac{6.25\,g\ NaNO_2/NaNO_3}{13.75\,g\ Cs_2NiFe(CN)_6} = \frac{X\,g\ NaNO_2/NaNO_3}{9.57} \longrightarrow X = 4.35\,g\ NaNO_2/NaNO_3$$

To obtain a total of 20 g, I will repeat procedure for preparing the $Cs_2NiFe(CN)_6 : NaNO_2/NaNO_3$ mixture. I placed the already ground mixture (13.92 g) in a labelled bottle with the date and my name. Will begin the rest tomorrow.

7-1-91
K. L. Lookabill

$Cs_2NiFe(CN)_6$ procedure

7-3-91 - I started water washing the $Cs_2NiFe(CN)_6$ for more mixture. I'm centrifuging about 40 cc's, so there should be plenty. The same procedure for water washing was used today as on the 27th of June.

I placed 2 petrie dishes of $Cs_2NiFe(CN)_6$ in the oven at 12:00 (NOON).

One of the $Cs_2NiFe(CN)_6$ mixtures has a white horizontal stripe seperating two of the layers, so I kept the mixtures seperate. The potentially contaminated $Cs_2NiFe(CN)_6$ is the petrie dish with the straight glass rod. (#2)

At 3:00 I moved the petrie dishes to the dessicator. The $Cs_2NiFe(CN)_6$ with the potential contamination is green-grey instead of blue-grey, so I assume contamination has occured. I will now ask Dave about it.

Dave said not to worry about it because in all probability it is just that the mixtures might ~~contain~~ be at different levels of hydration. If it doesn't assume the same color once a constant weight is obtained, then worry

7-3-91 K. L. Lookabill

7-8-91 Procedure for preparing a mixture of $Cs_2NiFe(CN)_6$ and $NaNO_2/NaNO_3$

~~1st trial~~	weight 1	weight 2
~~2nd trial~~ 1st trial	130.675 g	126.583 g
~~3rd trial~~ 2nd trial	130.399 g	126.503 g
3rd trial	130.383 g	126.524 g
4th trial	130.228 g	126.425 g
5th trial	130.231 g	126.449 g

Removed the $Cs_2NiFe(CN)_6$ from the dessicator at 8:00 a.m. and weighed it for the first trial at 8:07 a.m. I placed $Cs_2NiFe(CN)_6$ in the 40°C oven.

At 10:00 I placed the 2 mixtures of $Cs_2NiFe(CN)_6$ into the dessicator.

At 11:50 I weighed the cyanide mixture a second time and placed it again in the oven.

At 1:40 p.m. I placed the $Cs_2NiFe(CN)_6$ in the dessicator.

At 3:25 p.m. I weighed the $Cs_2NiFe(CN)_6$ mixture for the third time and placed them in the oven. (Note: NO. 2 watchglass has more dried mixture on it)

K.L. Lockabill
7-9-91

7-9-91 $Cs_2NiFe(CN)_6$ mixture cont.

at 7:30 a.m. I placed the cesium mixture in the dessicator.

at 9:30 a.m I weighed the Cesium mixture a 4th time, then placed back in oven.

at 11:25 a.m. I placed the Cesium mixture in the dessicator.

at 1:30 p.m. I weighed the Cesium mixture for the fifth time. I finally obtained a constant weight. I then ground the Cesium mixture and placed them in bottles marked ~~1A~~ and 2.

Kelly Lockabill 7-10-91

7-10-91 Cesium and $NaNO_2/NaNO_3$ mixtures cont.

I called Sargent Welch's the other day so I can order the sieves today. These are needed for the Cesium mixture and the $NaNO_2/NaNO_3$.

- The sieves are ordered and they are due to arrive about the 15th of August.

7-31-91 Kelly Lockabill

7/12/91 Review pg. 40 to here.

1) Don't forget to sign and date entry

7-31-91 ~~$Cs_2NiFe(CN)_6$~~ [illegible] sludge / H_2O_2 Reaction [illegible]

Procedure for mixing ~~$Cs_2NiFe(CN)_6$~~ [illegible] sludge with H_2O_2 — See changes on pg. 44 8-5-91 [illegible]

1. Contact standards lab for a mixture of 20% H_2O_2 in H_2O for use in this procedure.
2. Add 1cc ~~$Cs_2NiFe(CN)_6$~~ [illegible] sludge to a centrifuge cone, then add 1cc H_2O_2 and observe for 1 hour. Contact Cindy Jorgensen for excess sludge.

8

$NiCs_2Fe(CN)_6$ Synthesis - Denise J. Hert

10-12-90 The oxident added to the fuel is a mixture of

47.5 % $NaNO_3$
47.5 % $NaNO_2$
5.0 % EDTA

	(g/mol)	x (mol %)	= g needed	Adjusted to make 40g
$NaNO_2$	69.00	47.5	32.78	21.63 g
$NaNO_3$	84.99	47.5	40.37	26.64 g
EDTA	372.24	5	18.61	12.28 g
			91.76	60.55 g

did a scale down run to determine what would happen when $NaNO_3$ + $NaNO_2$ were mixed & melted. Two grams of each were finely ground with a mortar & pestle, put in a Pt/Rh crucible, & placed in a muffle furnace heated to about 300°c.

The crucible turned blue. This is probably due to a run with the fumes. There were no other suprises. The salts melted & solidified with no problems. Regrinding the salts w/ a mortar - pestle are difficult.

10-15-90 A mixture of 14.75 g $NaNO_2$ + 18.17 g $NaNO_3$ ~~was~~ ground finely & melted. The crucible placed in a hood & allowed to cool. As it cooled dirt looking powder found its way into the crucible & was solidified into the surface of the salts.

A second mixture of 21.63 g $NaNO_2$ + 26.64 g $NaNO_3$ were melted together at 300°F. Approximately 15 min was required for meltdown. A scum of dark particles was floating on the top. This must be due to impurities & not from dust in an unclean hood as suspected before. The mixture cooled on the counter & then easily slid out of the crucible. Lee reported he ground this up in a crucible (this is hard to believe.) I put in in a plastic sack (tripled) & busted the salts with a hammer.

0-6-90 The crunching up of the oxident continued using the mortar & pestle. Ground to a fine powder.

The fuel was washed with water several times. The solid is dark grey blue. Lee reported a gray green ppt. I forgot to wash the ppt. 10-12-90 so I did it today. No chemical changes are expected, however, because of a different color than reported by Lee, we decided to make another batch. Upon drying the fuel was dark grey. Undried solutes are labled DH-8a

Denise J Hert
10-9-90

$NiCs_2Fe(CN)_6$ Synthesis - D.J. Hect

Another batch of $NiCs_2Fe(CN)_6$ is made as described under trial #3 on page 7

$K_4Fe(CN)_6$ soln added to CsCl soln, both at 65°C
$NiSO_4$ soln (65°C) added to the above. Pale green ppt. Agitated 10 min + washed w/ D water
Sample was washed 3X (until yellow color gone)
Centrifuged in between washings.
Ppt spread on a watchglass + dried at 110°C.

10-17-90 Ppt ground using a mortar + pestle. Ppt = dark grey/brown. Turns blacker when water from air hits at the ground (fine). $Cs_2NiFe(CN)_6$ pkged into a plastic vial + sealed lid w/ tape. 50 g packaged. About 2 g set aside for Dave Bechtold TGA/DSC analyses.

66 g of the $NaNO_3/NaNO_2$ were put in a plastic vial + taped shut. About 10 g was set aside for Dave's analysis.

10-19-90 Two pkgs were shipped to Fauske. One containing 1 jar 20 g $Na_4EDTA \cdot 2H_2O$; 1 bottle ~~another~~ 66 g of the oxidizer. Pkged in styrofoam bubbles. Sent by air.

Another pkg has 50 g $NiCs_2Fe(CN)_6$ in a sealed plastic vial. Pkged in styrofoam bubbles. Sent 10-19-90

11-19-90 Adiabatic Calorimetry Results from Fauske & Associates Inc

Test #	Fuel/Oxident Ratio	Propagation Rxn begins at
1	4	260°C
2	2	230°C
3	1	222°C

Had Arrhenius type rxns up to:

Test #	Fuel/Oxident Ratio	Arrhenius rxn
1	4	210°C
2	2	190°C
3	1	185°C

10-30-90

11-21-90 DSC tests of $Cs_2NiFe(CN)_6$

Dave Bechtold is going to do 6 experiments varying the amount (ratios) of fuel/oxident. The fuel is $Cs_2NiFe(CN)_6$. The oxident is a sodium salt mixture ($NaNO_3/NaNO_2$) as prepared on page 8 under 10-15-90. The prep. of the $Cs_2NiFe(CN)_6$ is on pages 8+9.

The following ratios will be prepared to make 0.2 DJH ~~m~~g portions.

Test No.	$Cs_2NiFe(CN)_6$ (g)	Oxident (g)	EDTA (g)	Fuel/Oxident Ratio
1	0.05104	0.11598	0.03300	1
2	0.01844	0.14136	0.04020	2/3
3	0.10318	0.07536	0.02144	2
4	0.14306	0.04432	0.01262	4
5	~~0.2000~~ DJH 0	0.15570	0.04430	10/19
6	0.2000	0	0	

The EDTA used was tetrasodium dihydrate.

Each sample was ground with a mortar + pestle to assure thorough mixing. The samples (Test 1 thru 6) were put in dram vials + labeled Test #1, Test #2...

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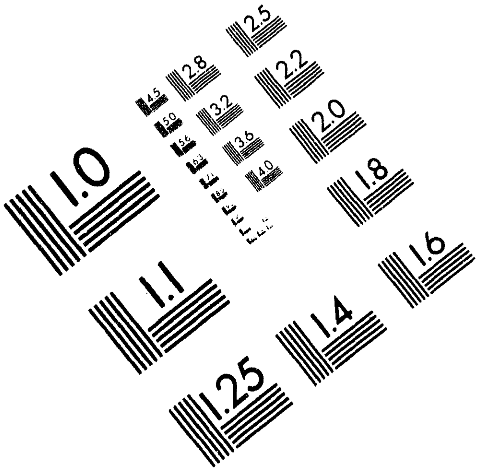

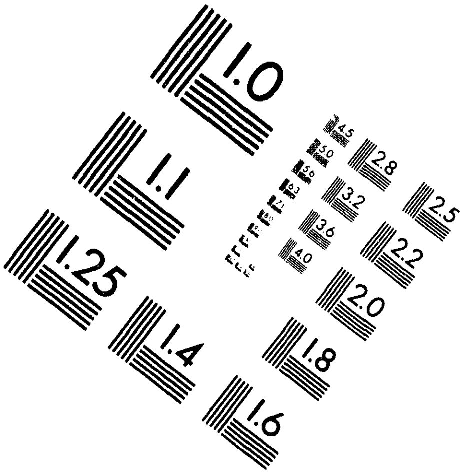

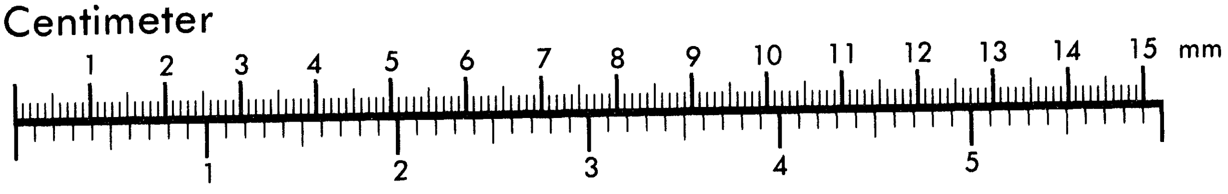

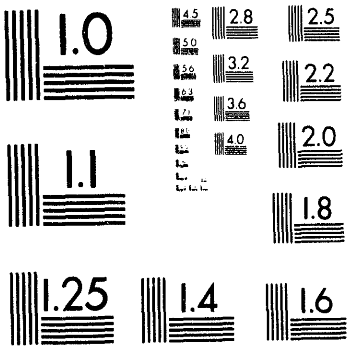

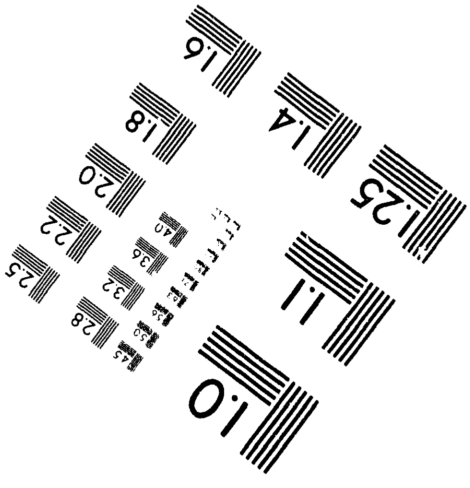

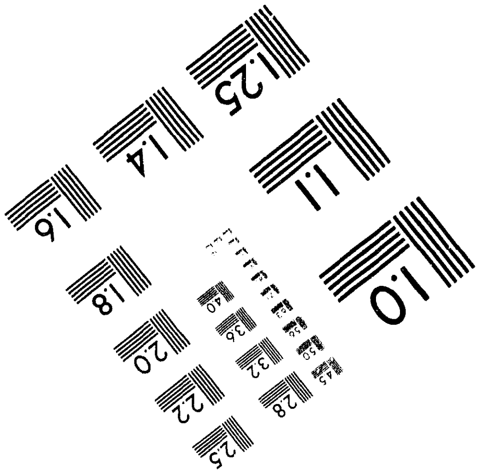

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