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DATE: April 9, 1956

SUBJECT: HRP-CP: Analytical Requirements for
the HRT Chemical Processing Plant

TO: M. T. Bailey

FROM: W. L. Carter

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OAK RIDGE NATIONAL LABORATORY

April 9, 1956

TO: M. T. Kelley

FROM: W. L. Carter

SUBJECT: HRP-CP: Analytical Requirements for the HRT Chemical Processing Plant

In recent discussions with the Design Review Committee, the question of analytical requirements for the HRT chemical processing plant was introduced. An initial study of these requirements was made and reviewed with members of the Design Review Committee, Analytical Chemistry Division, and Process Design Section. This memorandum presents the results of these discussions and tabulates the proposed analytical requirements.

Since the HRT chemical processing plant is an experimental facility, it is thought that its operation should include plans for obtaining as much information as possible on performance of all pieces of equipment, rate of corrosion, behavior and solubilities of fission and corrosion products, material balance data and enriched fuel losses. With this in mind, an analysis schedule has been prepared which is intended to be all inclusive in giving this information. The preponderance of this information will be furnished by analyses of the hydroclone overflow and hydroclone underflow samples (Tables I and II), and it may be expected that a regular schedule of submission of these samples will be maintained. However, since the chemical plant operates on a two-day per week cycle, this does not constitute a large analytical load. Also a favorable factor is that the heavy analytical load occasioned by reactor start-up will have been alleviated before the chemical plant begins operation. The reactor will have been operating about one month before start-up of the chemical plant.

Tables I and II describe the analyses of samples taken during and immediately following hydroclone operation. These samples are green fuel solution and will be taken from streams that have aged only a few minutes or at most a couple of hours. The analyses of these samples can be categorized as quantitative chemical measurements, quantitative spectrographic measurements, activity measurements and physical measurements, i.e., weight and volume. The analytical schedule should be arranged so that as much of this information as possible can be obtained in the five-day interim between the completion of one chemical plant run and the start of another. The data would be valuable information to the operator for setting the conditions of the subsequent run. However, it should be pointed out that for best results the radio-chemical analyses should be performed on a sample that has aged at least one week. The aging allows the short lived nuclides to decay and thus permits more accurate measurements on the longer lived components.

Table III contains a list of samples that will be taken occasionally or less frequently than the hydroclone samples. The activity of these samples should be relatively low and require only the usual care in handling. The information from these analyses pertains to such data as enriched fuel losses from leaks or spills, heavy water loss from inefficient recombination and activity discharges to the stack and settling basin.

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Analytical Chemistry Division personnel were very helpful in establishing the limits of analytical accuracy or precision and estimating analytical time. The figures quoted for analytical time and accuracy on fuel and corrosion component analyses refer to numbers that have been obtained in bench-top assays with bench-top shielding. The samples from the chemical plant will be much more radioactive than any tested before, and handling these samples in the new hot analytical facility may introduce complicating factors which may have a bearing upon the time or accuracy. A similar statement may be made about the spectrographic analyses for the rare earths. In this instance, previous tests have been made in connection with rare earth determinations in thorium metal on cold samples; stringent handling requirements on the very hot HRE chemical plant samples may influence analytical time and accuracy but probably not the precision. The principal factor entering into these analyses is the remote separations chemistry to obtain the rare earth group free of atoms that have interfering spectra. Because of no previous experience in this separation, it is not known what process losses may be encountered. Unknown process losses will affect the accuracy of the result but not the precision with which the test was made. Likewise, it may be stated for the radiochemical analyses that lack of experience with extremely hot and green samples dictates conservatism in estimating time and precision figures. In some cases, the activities of certain nuclides has never been measured, e.g., technitium, and the figures given are only a rough estimate.

Of due concern to the analyst is the condition of the sample when it is received by the laboratory. A sample from which all liquid had been evaporated by radioactive decay energy could present a processing problem. Only the hydroclone samples (Tables I and II) need to be considered in this respect. It has been calculated these samples will lose heat fast enough to the surroundings at the condition of maximum radioactivity to preclude evaporation to dryness. Also in substantiation it has been pointed out that HRE samples did not evaporate to dryness. Since the activity of the sample is decreasing - one-half of the activity is lost in 10 hours - it might be concluded that the chemical plant samples will remain liquid.

William L. Carter

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Process Design Section
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TABLE I

HYDROCLONE OVERFLOW ANALYSIS

Sample volume = 5 ml
 Calculated sample activity when taken = 143 curies (1.27 watts)
 Calculated sample activity after 10 hours = 72 curies (0.63 watts)
 Sample frequency = 2 - 6 per week

FUEL COMPONENTS

<u>Component</u>	<u>Approximate conc. in sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
U	10.4	Quantitative U for check on reactor fuel concentration	2 - 3	± 1	Some U might be coprecipitated with solids therefore will need separate analyses of both supernate and solids for U.
CuSO ₄	0.2	Quantitative Cu for check on reactor fuel concentration	0.5	± 5	CuSO ₄ might be coprecipitated with solids therefore need analysis of both supernate and solids for CuSO ₄ .
H ₂ SO ₄	2.3	Quantitative H ₂ SO ₄ for check on reactor fuel concentration	1 - 2	± 1	Wash solids well to remove adhering acid. Acid conc. might be ± 50% of estimated value.
pH		Acidity	1	0.1 of pH unit	Analysis would be required only if heater H-3 is being used. Would indicate change in pH due to hydrolysis.

CORROSION COMPONENTS

<u>Component</u>	<u>Approximate conc. in sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
Fe ₂ O ₃	0.0005 - 0.28	Quantitative Fe to check separability in hydroclone	1	± 3 at 50 µg/ml ± 10 at 10 µg/ml ± 50 at 1 µg/ml	Analyze for total Fe - precipitated and dissolved. Need not analyze supernate and precipitate separately.
ZrO ₂	0.001 - 0.30	Quantitative Zr to check separability in hydroclone	2 - 3	± 3 at 50 µg/ml ± 10 at 10 µg/ml ± 50 at 1 µg/ml	Analyze for total Zr - precipitated and dissolved. Need not analyze supernate and precipitate separately.
Cr ₂ O ₃	0.0005 - 0.08	Quantitative Cr to check separability in hydroclone	3	± 2 at 1 µg/ml	Analyze for total Cr - precipitated and dissolved. Need not analyze supernate and precipitate separately.

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CORROSION COMPONENTS, continued

<u>Component</u>	<u>Approximate conc. in sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
NiO ₂	0.06	Quantitative Ni to check stainless steel corrosion	4	± 3 at 25 - 50 µg/ml	Analyze for total Ni; should be no Ni precipitate unless coprecipitated with solids.
Sn	0.006	Quantitative Sn to check core tank corrosion	Unknown	Unknown	All Sn should be soluble; might be some coprecipitated in solids.

FISSION COMPONENTS

<u>Component</u>	<u>Approximate conc. in sample, mg/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical precision, %</u>	<u>Remarks</u>
Ce	12 - 30	Quantitative amounts and activities of each R. E., rate of removal and separability by hydroclone, and solubility information; the general behavior in the system and material balance information.	25 Hrs. total for all spectrographic analyses; 20 Hrs. total for all radiochemical analyses	± 3 on spectrographic duplicate and triplicate samples; ± 10 for radiochemical analyses	Quantitative analysis is by spectrograph. About 75% of analytical time is used in chemically preparing sample for analysis; i.e., separating R. E. group from U and crud to eliminate interfering lines. Sample concentration is about 100 times sensitivity level of spectrograph. Spectrograph lab can handle only 2 - 3 samples per week. If R. E. activity measurements on individual atoms are to be made, they can best be made on unused portion of sample prepared for spectrographic analysis because this preparation removes foreign atoms. Overflow sample should be taken at same time as reactor sample to get concentration factor across hydroclone by radiochemical analyses.
La					
Pr					
Nd					
Pm					
Y					
Total R.E.	1200	Activity measurement only	2.5 - 3	± 10	Total R.E. and Ce activity is a compromise for individual R.E. activities. This is an easy, cheap and quick way to get a measurement of total hazard.
Ce		Activity measurement only	2.5	± 5	

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FISSION COMPONENTS, continued

Component	Approximate conc. in sample, mg/kg D ₂ O	Information sought
Zr	75	Activity of each F.P. to determine behavior in system. Information to determine if there is a concentration of any of the F.P.'s in the underflow receiver or possibly on the system heater. Also to obtain solubility information and material balance data. Most important are data on quantity of biologically hazardous material being removed from reactor.
Nb		
Ru		
I		
²³⁷ Np and ²³⁹ Np		
Pu		
Cs		
Te		
Tc		
Sr		
Ba		

FUEL, CORROSION AND FISSION COMPONENTS

Component	Approximate conc. in sample gm/kg D ₂ O	Information sought
Liquid	Bulk of sample	Volumes and weights of liquid portion and solid portion of sample to determine overall solids concentration in reactor fuel
Solid	0.0005 - 0.30	

TABLE I (continued)

Estimated time for analysis, Hrs.	Probable analytical precision, %	Remarks
3.5	± 5	Overflow sample should be taken at same time as reactor sample in order to get ratio of F. P. activity in reactor to F. P. activity in overflow of hydroclone. Absolute disintegration rates will not be necessary because only comparison between various points of sampling required. For best results, samples should be cooled about one week to allow short lived activity to decay. Precision of iodine measurement is unknown due to unknown losses in processing sample. Technitium activity cannot be measured until reactor has been running several months because of low yield and long half line.
3.5	± 5	
2.5	± 5	
2.5	Unknown	
3	± 10	
2.5 - 3	± 5	
2.5	± 5	
4	± 10	
Unknown	± 20	
2.5	± 5	
2.5	± 5	

Estimated time for analysis, Hrs.	Probable analytical accuracy, %	Remarks
2 - 3	± 2 on volume	Analysis would be centrifugation to get volumes and by weighing to get masses. Overflow sample might contain so few solids that getting a volumetric reading will be difficult.
	± 1 on weight	

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TABLE II

HYDROCLONE UNDERFLOW ANALYSIS

Sample volume = 5 ml
 Calculated sample activity when taken = 109 curies (0.97 watts)
 Calculated sample activity after 10 hours = 54 curies (0.49 watts)
 Sample frequency = 1 per week

FUEL COMPONENTS

<u>Component</u>	<u>Approximate conc. in sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analyses, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
U	10.4	Quantitative U for check on reactor fuel concentration and U coprecipitated with solids	2 - 3	± 1	Some U might be coprecipitated with solids therefore will need separate analyses of both supernate and solids
CuSO ₄	0.2	Quantitative Cu for check on reactor fuel concentration and Cu coprecipitated with solids	0.5	± 5	CuSO ₄ might be coprecipitated with solids therefore will need separate analyses of both supernate and solids
H ₂ SO ₄	2.3	Quantitative H ₂ SO ₄ for check on reactor fuel concentration	1 - 2	± 1	Wash solids well to remove adhering acid. Acid conc. might be ± 50% of this value.
pH		Acidity	0.5		Analysis would be required only if heater H-3 were being used. Would indicate change in pH due to hydrolysis

CORROSION COMPONENTS

<u>Component</u>	<u>Approximate conc. in sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
Fe ₂ O ₃	18	Quantitative Fe to determine stainless steel corrosion rate and separability in hydroclones	1	± 3 at 50 µg/ml ± 10 at 10 µg/ml ± 50 at 1 µg/ml	Analyze for total Fe - precipitated and dissolved; need not analyze supernate and precipitate separately
ZrO ₂	20	Quantitative Zr to determine core tank corrosion rate and separability in hydroclones	2 - 3	± 3 at 50 µg/ml ± 10 at 10 µg/ml ± 50 at 1 µg/ml	Analyze for total Zr - precipitated and dissolved; need not analyze supernate and precipitate separately
Cr ₂ O ₃	5.7	Quantitative Cr to determine stainless steel corrosion rate and separability in hydroclone	3	± 2 at 1 µg/ml	Analyze for total Cr - precipitated and dissolved; need not analyze supernate and precipitate separately

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CORROSION COMPONENTS, continued

<u>Component</u>	<u>Approximate conc. in sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
NiO ₂	0.06	Quantitative Ni to check stainless steel corrosion	4	± 3 at 25 - 50 µg/ml	Analyse for total Ni; should be no Ni precipitate unless coprecipitated with solids
Sn	0.006	Quantitative Sn to check core tank corrosion	Unknown	Unknown	All Sn should be soluble; some could be coprecipitated with solids

FISSION COMPONENTS

<u>Component</u>	<u>Approximate conc. in sample, mg/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical precision, %</u>	<u>Remarks</u>
Ce	1200	Quantitative amounts and activities of each R.E., rate of removal and separability in hydroclone, solubility data, general behavior in the system and material balance information	25 hours total for all spectrographic analyses; 20 hours total for all radiochemical analyses	± 3 on spectrographic duplicate and triplicate samples; ± 10 for radiochemical analyses	Quantitative analysis is by spectrograph. About 75% of analytical time is used in chemically preparing sample for analysis, i.e., separating R.E. group from U and crud to eliminate interfering lines. Sample concentration is > 100 times sensitivity level of spectrograph. Spectrograph lab can handle only 2 - 3 samples per week. If R.E. activity measurements on individual atoms are to be made, they can best be made on unused portion of sample prepared for spectrographic analysis because this preparation removes foreign atoms.
La					
Pr					
Nd					
Pm					
Y					
Total R.E.	1200	Activity measurement only	2.5 - 3	± 10	Total R.E. and Ce activity is a compromise for individual R.E. activities. This is an easy, cheap and quick way to get a measurement of total hazard.
Ce		Activity measurement only	2.5	± 5	
Zr	75	Activity of each F.P. to determine behavior in system. Information to determine if there is a concentration of any of the F.P.'s in the underflow receiver or possibly on the system heater. Also to obtain solubility information and material balance data. Most important are data on quantity of biologically hazardous atoms being removed from reactor.	3.5	± 5	Absolute disintegration rates will not be necessary because only comparison between various points of sampling required. For best results samples should be cooled about one week to allow short lived activity to decay. Precision of iodine measurement is unknown due to unknown losses in processing sample. Technitium activity cannot be measured until reactor has operated several months because of low yield and long half life.
Nb			3.5	± 5	
Ru			2.5	± 5	
I			2.5	Unknown	
Np ²³⁷ and Np ²³⁹			3	± 10	
Pu			2.5 - 3	± 5	
Cs			2.5	± 5	
Te			4	± 10	
Tc			Unknown	± 20	
Sr			2.5	± 5	
Ba			2.5	± 5	

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FUEL, CORROSION AND FISSION COMPONENTS

<u>Component</u>	<u>Approximate conc. in sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
Liquid	Bulk of sample	Volumes and weights of liquid portion and solid	} 2 - 3	± 2 on volume	Analysis would be by centrifugation
Solid	5 - 20	portion of sample to determine overall solids concentration in hydroclone underflow		± 1 on weight	

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TABLE III

MISCELLANEOUS CHEMICAL PLANT SAMPLESOFF GAS BEFORE AND AFTER CARBON BED

Sample volume = 200 - 300 ml
 Sample pressure = 1 atm
 Sample activity = Unknown (probably low)
 Sample frequency = 4 per month (2 before bed + 2 after bed)

<u>Component</u>	<u>Approximate Concentration</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical precision, %</u>	<u>Remarks</u>
Xe	trace	Activity to determine effectiveness of carbon bed and quantity of activity being exhausted to stack	2	Unknown; at best ± 5	Measurement would be for ^{133}Xe , short lived Xe and Kr should be allowed to decay before measurement is made. Kr need not be measured because it is not an important biological hazard. Should be no iodine in sample at exit of carbon bed.
I	trace				
D ₂	ultra trace	Quantitative D ₂ to determine efficiency of recombiner	1	± 5	
N ₂ + O ₂	Bulk of gas				

CELL C SUMP

Sample volume = 5 ml
 Sample activity = 50 - 100 curies
 Sample frequency = occasional

<u>Component</u>	<u>Approximate conc. of sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
U	< 10	Quantitative U to determine fuel losses from process equipment	2 - 3	± 1	Analysis would only be called for when a spill or leak in process equipment is suspected

SHIELD WATER

Sample volume = 200 - 300 ml
 Sample activity = Unknown (probably low)
 Sample frequency = Occasional

<u>Component</u>	<u>Approximate conc. in sample</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
Gross β	Unknown	Activity to determine contamination of settling basin	0.4	± 5	Sample might be submitted each time cell is flooded
Gross γ	Unknown		0.5	± 10	
U	Small to trace	Quantitative U to determine loss in shield water		Unknown	

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FRESH FUEL MAKE-UP

Sample volume = 5 ml
Sample activity = non-radioactive
Sample frequency = 1 (or less) per week

<u>Component</u>	<u>Approximate conc. in sample, gm/kg D₂O</u>	<u>Information sought</u>	<u>Estimated time for analysis, Hrs.</u>	<u>Probable analytical accuracy, %</u>	<u>Remarks</u>
U	500	Quantitative U to determine fresh fuel make-up	2 - 3	± 1	It might be that fresh fuel solution will be made up in large batches from which the small weekly additions will be measured gravimetrically. In this case, it will be necessary to analyze only the large batch.
CuSO ₄	6.78	Quantitative Cu to determine fresh fuel make-up	0.5	± 5	
H ₂ SO ₄	72.7	Quantitative H ₂ SO ₄ to determine fresh fuel make-up	1 - 2	± 1	

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