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Richland, Washington
June 26, 1950

To: H.I. Analytical Advisory Committee

From: R. C. Thorburn

This Document consists of

9 Pages No.

Serial

A REVIEW OF PAST EXPERIENCES WITH H.I. SURVEY PROBLEMS

Introduction

Because of the type of operations at Hanford Works, many potential sources of radioactive contamination exist. In addition to known locales, such as the 100 and 200 Area off gas stacks, the effluent water lines, accidental spills during maintenance work etc., experience has shown contamination from unexpected trace elements activated in the pile and cross contamination from other sites.

It is proposed to discuss herein the handling of the routine samples of contamination submitted by the H.I. Operational Group and to give a brief review of some of the samples mentioned above.

Historical

The H.I. Methods and Development Group first started analyzing samples routinely early 1947. Since then approximately six hundred samples have been submitted ranging in requests from total beta determinations to the analysis of a spot of contamination found in a railroad car from an unknown depot. During this

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period, the personnel available for this type of work ranged from a minimum of less than one full time to three. The average cost/analysis was between 10 and 20 dollars.

Discussion

Since samples from the three types of areas fall into very general classifications the paper will be divided into three parts: (1) samples from the 300 Area (2) samples from the 200 Areas, and (3) samples from the 100 Areas.

300 Areas

There are two main operating divisions in the 300 Area: the Technical Department Laboratories and the operating area used for slug preparation and U chip recovery.

Samples of contamination from the laboratories submitted by the H.I. Survey Group are primarily air samples, taken on CWS type 6 filters, and submitted for Pu determinations. These samples are analyzed by digestion in nitric acid, ashing to remove organic materials, leaching of the alpha activity with hot nitric acid followed by respective alpha emitters determinations. Total alpha emitters are usually determined in two ways: direct plating of aliquots, drying, and counting, and by the ether extraction process. Pu determinations are made by preferably a TTA analysis or by counting a LaF_3 precipitation. Uranium analyses are made on these sample solutions by fluorophotometer or by the difference between total alpha activity and the activity due to Pu.

It should be noted that these methods have shown acceptable recoveries on spiked filters and good recoveries on samples from 300 Area filters. The recoveries on 300 Area filters are based on a direct count of the filter assuming a 65% counting efficiency. Filters from 234-5 are not adaptable to these procedures however. This is probably due to the predominance of the insoluble plutonium fluoride particles in that area.

These filters generally show an activity range from zero to 100-200 d/m with the activity from Pu usually being 10 d/m or less.

Other samples from the laboratories of the 300 Area have consisted of smears,

samples of exhaust from oil, trap liquids, etc. In general the method outlined above for filters was applied.

A sample of note was a vial of mercury from a pipette cleaner, some of which had accidentally been swallowed, making an accurate analysis essential. The method of treatment was to remove the Hg by evacuation over heat leaving any non-volatile Pu behind. This residue was then digested in 2N HNO_3 and analyzed for Pu with a TTA extraction.

Very few samples have been submitted for a beta emitter analysis from the 300 Area probably due to the fact that work done in the labs is with specific beta emitters and the source of any beta contamination is known.

A sample worth note submitted for beta emitter analysis from these laboratories was a sample of graphite ends or papooses (small pieces of graphite exposed in the pile). The samples were burned in a micro combustion furnace and the resulting gases collected in a $\text{Ba}(\text{OH})_2$ trap. The precipitate of $\text{Ba}(\text{CO}_3)_3$ was mounted in a series of weighed plates and counted. The salts remaining in the combustion boat were then analyzed in the standard quantitative manner. Two other radioelements, Fe and Ca, were found.

Other than air samples, in which total alpha activity is desired, only one sample has originated in the operations area in the 300 Area. This sample, consisting of some orange-colored salts had a high beta activity as measured with a C.P. meter, but no alpha as checked with a zeuto. The sample originated from the recovery operation, in which U chips from the slug preparation are melted in a pressure of only a few microns. Subsequent analysis showed the salts to consist of UX_1 and UX_2 . (Thorium analysis and absorption curve compared favorably to U chip). Apparently under the conditions outlined above UX_1 and UX_2 distill to the top of the melt pot and were scattered as the top was removed.

200 Areas

The 200 areas are the separations areas; theoretically all beta contamination

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should be fission products and the alpha contamination should primarily be due to Pu, since even in the dissolver solution, the amount of alpha activity due to Pu is 20 times as great as that due to U. The fission products found are primarily long-lived because of the long cooling time. I^{131} (8.0 day) and Xe^{135} (5.4 day), two short-lived F.P.s, are given off from the off-gas stacks however.

The physical forms of the samples have varied considerably; inorganic and organic solutions, smears, dust, air filters, small particles, rocks, vegetation, wood chips, and paint are some of the many forms that have been submitted.

The general analytical method is to digest the sample in sodium hydroxide, run I^{131} determinations on aliquots of this solution, combine the original sample residue with this solution, acidify with HNO_3 and further digest to solubilize the fission products. The residue is then centrifuged off, dried, and counted to check for completeness of removal of the activity. If contamination still exists, the residue is further treated by HF and H_2SO_4 to remove silica, followed by fusion with carbonate to effect the solution. The fused mass is then leached with H_2O , and the residue dissolved in acid. Aliquots of these solutions are plated to determine the activity. Usually the activity is in the acid solution which may be combined with the original supernate. The water solution may not be combined with the acid since the original precipitate will probably reform. Aliquots of these two solutions, the acid digestate and the water leach are then analyzed for Sr, Ru, Ce, Y, and R.E., Cs and Zr by standard fission product analyses.

The importance of absorption and decay studies should be stressed for use in confirmation of all chemical results. In addition, if the absorption curves of the two above mentioned solutions are similar an analysis of only one solution is usually sufficient.

Yields are usually reported in %/sample for total beta activity and as percent of total activity for each fission product. Total beta activity is obtained by plating aliquots with 20 mg of Ce carrier $[as Co(OH)_3]$ drying and counting.

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Analyses for alpha emitters are run on aliquots of the digested sample in the manner outlined for 300 Area samples.

A general schematic diagram is given below:

OUTLINE OF ANALYTICAL METHOD FOR

300 AREA PROBLEMS

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A general correlation between sample source and type of activity has been found to exist. These data are summarized in the table below:

TABLE 1

<u>Sample Location</u>	<u>Type of Expected Activity</u>
Canyon air samples near dissolver	30-50% Ce ¹⁴¹ - 20-40% Y ⁹⁰ 10-15% Sr 10% Zr, < 5% Co, < 5% I ¹³¹ Trace of α Emitters
Canyon air samples near GR to 19 L	50 to 100% Ru, 10-20% Ce, < 10% all other F.P.s. Trace of α Emitters
Operating gallery air samples	50 to 100% Ru - 50% to 100% I ¹³¹ < 10% all other F.P.s. No trace of α Emitters
Particles	30 - 50% Ce, 20-40% Y, 10-15% Sr, < 10% Zr, < 5% Co, < 5% I ¹³¹
Dried droplets from outside scraped off wood or cement	30-50% Ce, 20-40% Y, 10-15% Sr, < 10% Zr, < 5% Co, < 5% I ¹³¹
Soil from Geology wells	If wells are distant from source Ru, Co and Zr predominate. If wells are close to source Rare Earths and Sr predominate.
Smears from inside buildings	Similar to air samples except usually higher in I ¹³¹ .
Dust from cells	Oxidation cells usually predominate in Ru - reduction cells have mixtures. Ce and Zr are hardest to separate and carry farther down the process. These F.P.s predominate at lower end of canyon.
Dust from air inlet and outlet pads T and B Plants.	30-50% Co, 20-40% Y, 10-15% Sr, < 10% Zr, < 5% Ce, < 5% I ¹³¹ , Trace of α Emitters
Laundry contamination	No general type of contamination noticed.
Samples from 234, 232, 234-5	Traces of F.P.s, high α > 9% Pu

A few other generalizations should be noted: (1) The Pu to U activity ratio in the dissolver is 20 to 1 and the ratio gets higher as the separations proceed. (2) Cs is easily removed from Pu, is not volatile, and therefore is rarely found in other than waste samples. (3) I¹³¹ is not removed to any great extent by untreated CWS type 6 filter papers. (4) Ru forms a volatile RuO₄ during oxidation steps and spreads easily.

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It should be stressed that these guides are extremely qualitative. For illustration the following non-typical samples are mentioned. Some black metallic chips, found on the shoes of a laundry employee, were submitted for an analysis of alpha and beta emitters. Results indicated the contamination was uranium chips. Further investigation showed the employee had been in the 313-14 Area earlier and probably had picked them up there; some contaminated droplets from the hand rail of the steps near 291-T when analyzed for F.P.s showed the activity due entirely to Sr^{90} - Y^{90} . A complete suit of clothes, including wallet and shoes, from a visitor and thought to have been contaminated at 231 was submitted for alpha identification. Results indicated that the activity was due to actinium, not U or Pu. Further investigation disclosed that the visitor was working with Ac at another site. A similar incident occurred at the T plant: the roof of an AEC truck was contaminated with an alpha emitter. Chemical investigation showed the contamination to be Po and a historical tracer showed the truck had apparently become contaminated at another site. There have been many other incidents of cross contamination challenging the analyst of 200 Area survey samples.

100 Areas

Contamination from the 100 Areas poses the most difficult problems for identification. The high neutron fluxes in the pile activate almost any element exposed to it thru entrance via the cooling water, the He gas, trace impurities in the construction materials and impurities on the slugs. Occasionally, breakdowns or required repairs allow the atmosphere to seep into the pile adding a new source of isotopes. The possibility of any isotope should never be ruled out because impurities much too small to be detected by any standard means may show up, after activation in the pile, in seriously high amounts when considered from the radio hazard view point.

In general, unknown samples from the 100 Areas are divided into two parts. One part being analyzed for the anions, the other for the cations. Anion analyses usually

include S^{35} , P^{32} , Cl^{36} . The sample, if organic, is muffled, the off gases analyzed for Cl^{36} by trapping in a $Ba(OH)_2$ trap, regenerating the $Cl^{36}O_2$ with HCl and H_2O_2 and again trapping in $Ba(OH)_2$, centrifuging and mounting the precipitate for counting. The by-product precipitate $Ba(SO_4)$ is also counted to confirm that no S^{35} was given off as SO_2 . The salts from the muffling are digested in acid to effect solution and aliquots analyzed for the other anions. In solubilizing the sample for cation analysis care must be exercised to avoid loss through volatility. Use of hydrochloric acid should be avoided for this reason and if used, digestion should be effected with a reflux condensor and the off gases trapped in a $NaOH$ trap. The customary practice has been to digest the sample with HNO_3 , mount any insoluble residue for counting and if activity is still present remove silica with HF and H_2SO_4 , digest salts in HNO_3 again, mount for counting and if activity is present, fuse. Frequently a clear solution can be obtained by cooling the HNO_3 - sample mixture, adding a gram or two of hydroxylamine hydrochloride and warming to $\sim 40^\circ C$. Following solution, standard quantitative procedures are applied to the sample; group separations, counting the precipitates to determine which group contains the activity, followed by subsequent separations of these groups.

All chemical results should be confirmed with absorption curves and when possible with decay curves. Absorption and decay studies are also used to guide the analytical work. A value for half-life and energy will eliminate many isotopes and thus limit the chemical work.

There are a few locations, as in the 200 areas, where type of contamination is more or less consistent. These locations and types are listed in Table II below:

Table II

Sample Location	Type of Expected Long-lived Activity
No drier condensate	100% S^{35} as SO_4
Neoprene seals	~ 80 to 100% SO_4

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Gas stream

Argon if now sample, C^{14} , S^{35} possibly

metal carbonyls. Ni

Crud from rear face

Activity primarily Po

Beta activity. Po^{59} , Ca^{45} , As^{76} , Ti^{51} , PO_4 , Rare Earths, Zr

Rust from control rods and thimbles

 Po^{59} , Ti^{51} with traces of Ca^{45}

Effluent water

 PO_4 , Rare Earths, Fe, Ca, traces of
the Cu-As group.

Table II is even less quantitative than is Table I for the 200 Areas. Samples of crud from the rear face have been found with Cn^{45} as the only contaminant. The contaminant in another sample from the loading pad was found to be radio silver. The radio chemical results of this sample were viewed with suspicion, since radio silver had never been encountered before. Absorption studies limited the number of isotope tending to confirm the chemical results. An observed half-life of 224 days, compared to 220 days for Ag, positively proved the presence of radio silver. Another unusual sample of salts was submitted for an alpha emitter determination. Subsequent analysis showed the activity to be Ra and its daughters. The historical investigation indicated the Ra contamination had been picked up at another site. Many other incidences of unexpected isotopes and cross contamination could be cited.

SUMMARY

In general, samples from the 300 Area are contaminated with U, traces of Pu and known beta emitters; samples from the 200 Areas contain Pu with traces of U and long-lived fission products; while samples from the 100 Areas may contain practically all known isotopes.

Many problems still exist for the analytical chemist on these samples. The conversion to micro techniques, the possibility of separation, at least group wise, by ion columns, improved mounting techniques, and some immediate possibilities suggested for investigation.

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