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Decontamination by Cleaning with Fluorocarbon Surfactant Solutions

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Chemical Technology Division

DECONTAMINATION BY CLEANING WITH FLUOROCARBON
SURFACTANT SOLUTIONS

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ABSTRACT

In the nuclear industry, facilities and their components inevitably become contaminated with radioactive materials. This report documents the application of a novel particle-removal process developed by Entropic Systems, Inc. (ESI), to decontaminate critical instruments and parts that are contaminated with small radioactive particles that adhere to equipment surfaces. The tests were performed as a cooperative effort between ESI and the Chemical Technology Division of the Oak Ridge National Laboratory (ORNL).

ESI developed a new, environmentally compatible process to remove small particles from solid surfaces that is more effective than spraying or sonicating with CFC-113. This process uses inert perfluorinated liquids as working media; the liquids have zero ozone-depleting potential, are nontoxic and nonflammable, and are generally recognized as nonhazardous materials.

In the ESI process, parts to be cleaned are first sprayed or sonicated with a dilute solution of a high-molecular-weight fluorocarbon surfactant in an inert perfluorinated liquid to effect particle removal. The parts are then rinsed with the perfluorinated liquid to remove the fluorocarbon surfactant applied in the first step, and the residual rinse liquid is then evaporated from the parts into an air or nitrogen stream from which it is recovered.

Nuclear contamination is inherently a surface phenomenon. The presence of radioactive particles is responsible for all "smearable" contamination and, if the radioactive particles are small enough, for some of the fixed contamination. Because radioactivity does not influence the physical chemistry of particle adhesion, the ESI process should be just as effective in removing radioactive particles as it is in removing nonradioactive particles.

The concept here was to use the ESI process to remove radioactive particles from large contaminated objects. The suspended radioactive particles were then removed from the process liquid by filtration to allow liquid recycle and disposal of the filter and particles as waste. The perceived advantage is that this process greatly reduces the volume of radioactive waste requiring disposal and allows valuable equipment to be salvaged.

The main goals of the experiments performed at ORNL were to (1) demonstrate that the ESI process removes a variety of radioactive particulates from complex parts; (2) demonstrate that these complex mechanical parts can be decontaminated to "green tag" tolerances by this process; (3) compare the rate and completeness of decontamination using a perfluorinated liquid with no additives with that of a perfluorinated liquid containing a perfluorinated surfactant; and (4) demonstrate that any radioactive materials present in the used perfluorinated liquid could be removed by simple physical means, such as filtration or decantation, to allow solvent recycle.

This report discusses the fluorocarbon surfactant solutions and presents a summary of radiological and other data compiled during the demonstrations.

1. INTRODUCTION

This report documents the application of a novel particle-removal process that was developed by Entropic Systems, Inc. (ESI), to decontaminate critical instruments and parts of small radioactive particles that adhere to the surfaces of equipment. The tests were performed in a cooperative effort between ESI and the Chemical Technology Division (CTD) of the Oak Ridge National Laboratory (ORNL).

In the nuclear industry, facilities and their components inevitably become contaminated with radioactive materials. While contamination may result from chemical reactions between radioactive process materials and the materials used in the construction of these facilities and components, contamination is most often caused by the deposition of thin films of fine adherent radioactive particles, especially in the case of accidental discharge, that are not chemically bonded to the substrates.

Design and operational procedures contribute to minimize these effects, but decontamination is a necessary process in reducing radiation levels in the working environment. Whereas facilities are occasionally cleaned either for reuse or decommissioning, components from active areas commonly require decontamination for reuse or maintenance operations on a much more frequent schedule.

Decontamination has been defined as "the removal of unwanted radionuclides from surfaces" (Ayres, 1970). Decontamination processes are similar to traditional surface-cleaning processes that remove unwanted nonradioactive surface contaminants—except for the types of contaminants and, to a certain extent, the degree of removal. Nuclear decontamination requires an essentially complete level of contaminant removal—a high level of cleaning that is required by only select manufacturing operations that are very sensitive to foreign contaminants, such as the semiconductor industry. As a result, most of the decontamination processes now used in the

nuclear industry involve abrasive mechanical operations or aggressive cleaning solutions (Ayres, 1970; Rankin and McGlynn, 1989). The mechanical methods are destructive because to attain the required degree of decontamination, the external surface layer of the object being decontaminated is removed along with the contaminating radionuclides. Most cleaning solutions are water based and may contain detergents, sequestering agents, acids or bases, inhibitors, etc. These solutions are usually applied under conditions of high shear with apparatuses that range from agitated tanks to high-pressure jets.

With the exception of chlorinated solvents such as trichloroethylene (TRIC) and chlorofluorocarbons (CFCs) such as trichlorotrifluoroethane (CFC-113), organic liquids have been used to a very limited extent as cleaning media in the nuclear industry because of safety concerns, particularly flammability. CFC-113 base liquids have been of particular interest to the nuclear industry because they can be used to clean electrical components without damage and to clean product-contaminated material without the risk of criticality (Bond and Keasey, 1984). High-pressure spraying of CFC-113 has been found to be a particularly effective means of removing radioactive particulate contamination from devices, including electrical equipment and hardware (Ashley, 1984).

Decontamination processes based on CFCs are now obsolete. Because of new evidence that the earth's atmospheric ozone shield may be weakening faster than previously thought, President Bush announced in early 1992 that under the provisions of the Clean Air Act of 1990, the production of all chemicals known to be sources of atmospheric chlorine, including CFC-113 and TRIC, will be banned after December 31, 1995. As a consequence, after that date no viable method of reclaiming radioactively contaminated electronic and other sensitive, high-value equipment will be available to the nuclear industry.

ESI has developed a new, environmentally compatible process to remove small particles from solid surfaces that is more effective than spraying or sonicating with CFC-113. The process uses inert perfluorinated liquids as working media; the liquids have zero ozone-depletion potential, are nontoxic and nonflammable, and are generally recognized as nonhazardous materials. These liquids are compatible with delicate electronic and electromechanical equipment.

In the ESI process, the parts to be cleaned are first sprayed or sonicated with a dilute solution of a high-molecular-weight fluorocarbon surfactant in an inert perfluorinated liquid to effect particle removal. The parts are then rinsed with the perfluorinated liquid to remove the fluorocarbon surfactant applied in the first step, and the residual rinse liquid is then evaporated from the parts into an air or a nitrogen stream from which it is subsequently recovered.

Phasex Corporation of Lawrence, Massachusetts, and ESI recently completed Phase I of an Air Force-sponsored Small Business Innovative Research program (AF 91-186) to develop new processes to replace existing CFC-113 for cleaning operations of precision parts. The approach taken was to remove oils by supercritical fluid (Phasex) and to remove particles with fluorocarbon surfactant solutions (Gallagher, Krukonis, and Kaiser, 1992). Phasex and ESI were awarded a Phase-II program, which started in June 1992.

One order of magnitude increase in the rate and extent of particle removal was observed when inertial guidance instrument parts were ultrasonically cleaned in a dilute solution of a Krytox™ surfactant, a carboxylic acid-terminated oligomer of hexafluoropropyleneoxide (HFPO carboxylic acid), in a perfluorinated liquid instead of CFC-113. It has also been demonstrated that adsorbed HFPO carboxylic acid can be removed from metal washers and from instrument parts by simple extraction with a surfactant-free fluorinated liquid.

Nuclear contamination is inherently a surface phenomenon. Much nuclear waste is the result of the deposition of radioactive particles onto nonradioactive substrates. The presence of

radioactive particles is responsible for all "smearable" contamination and, if the radioactive particles are small enough, for some of the fixed contamination. Because radioactivity does not influence the physical chemistry of particle adhesion, the ESI process should be just as effective in removing radioactive particles as it is in removing nonradioactive particles.

The concept is to use the ESI process to remove radioactive particles from large and, therefore, costly-to-dispose-of contaminated objects of high inherent value. The suspended radioactive particles are then removed from the process liquid by filtration so that the liquid can be reused. The radioactive particles from the decontaminated parts accumulate on the filter. The filter and the captured particles are periodically disposed of as radioactive waste. The perceived advantage of the proposed process is that it greatly reduces the volume of the radioactive waste requiring disposal and allows valuable equipment to be salvaged.

The feasibility of using the ESI process for nuclear decontamination was demonstrated in a recently completed U.S. Nuclear Regulatory Commission study (Kaiser and Harling, 1993). The major results of this study are as follows:

1. The fluorocarbon surfactant solutions used as working media in the ESI process survived exposure of up to 10-Mrad doses of gamma rays with only minor changes; thus they are considered sufficiently radiation resistant.
2. Ultrasonic cleaning in perfluorinated surfactant solutions was found to be an effective method of removing radioactive iron (^{59}Fe) oxide particles from test pieces contaminated by immersion in a suspension of radioactive iron oxide powders in a carrier liquid.
3. The suspended radioactive particles could be quantitatively removed from the process liquids by filtration through a 0.1- μm membrane filter.

The major limitation of the previous study was that it examined only the removal of radioactive iron oxide from parts artificially contaminated by immersion in a suspension of this powder.

ORNL is a multipurpose research and development (R&D) facility operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy. Since its establishment in the early 1940s, ORNL has operated numerous facilities that have generated radioactively contaminated materials as a by-product of other activities. The contamination originates in facilities such as research reactors, radiochemical pilot plants, radioisotope production facilities, and numerous R&D laboratories. A major mission of Energy Systems during the 1990s is environmental cleanup and compliance to health and safety requirements. In pursuit of this mission, numerous remediation projects are under way, and many others are being planned. These projects present an opportunity for ORNL to restore its facilities to a much cleaner condition and to use its expertise in addressing other national environmental problems. In response to the growing need for efficient decontamination techniques and equipment to conduct remediation projects, the Radiochemical Technology Section of CTD formed a group whose primary mission is decontamination technology development (DTD). The objective of the group is to design new equipment, to identify new applications of existing technology for decontamination activities, and to evaluate equipment capabilities through decontamination demonstrations.

To further these objectives, DTD coordinated a cooperative endeavor between ESI of Winchester, Massachusetts, and CTD to test whether ESI's patented process for removing common particulates from surfaces was effective also for removing radioactive particulates. ESI directed the tests at ORNL. Personnel in CTD provided laboratory space, contaminated samples, analytical services, and technical support personnel for performing the tests.

The research addressed the application of ESI's particle-removal process to the nondestructive decontamination of nuclear equipment. The cleaning medium used in this process is a solution of a high-molecular-weight fluorocarbon surfactant which in an inert perfluorinated

liquid results in enhanced particle removal. The perfluorinated liquids of interest, which are recycled in the process, are nontoxic, nonflammable, and environmentally compatible because they do not present a hazard to the ozone layer.

The main goals of the experiments performed at ORNL were as follows:

1. To demonstrate that the ESI process can remove a variety of radioactive particulate contaminants from complex parts, not just radioactive iron oxide powders.
2. To demonstrate that complex mechanical parts that are contaminated only with radioactive particles can be decontaminated to "green-tag" tolerances by this process. For parts that have a combination of radioactive particulates and chemically bonded (fixed) radioactivity, the purpose is to demonstrate that the items can be cleaned to meet "green-tag" tolerances, that is, to remove the particulate matter.
3. To compare the rate and completeness of decontamination using a perfluorinated liquid with no additives with that of a perfluorinated liquid containing a perfluorinated surfactant.
4. To demonstrate that any radioactive materials present in the used perfluorinated liquids were removed by simple physical means, such as decantation, filtration, or distillation, so that the solvents may be recycled.

This report discusses the fluorocarbon surfactant solutions and presents a summary of radiological and other data compiled during the demonstrations.

2. PROCEDURES

2.1 DESCRIPTION OF THE TEST SEQUENCES

In the first two runs, the part was cleaned in a series of cycles using rinse solution [pure perfluoroheptane (PF-5070)] followed by a series of cleaning cycles using the wash solution (a 1% solution of a HFPO carboxylic acid surfactant in PF-5070), followed again by a final rinse to remove any adsorbed surfactant from the part. In Run 3, the initial cleaning was with the wash solution, followed by the rinse; the initial washing and rinsing were then followed by more washes and ended with a manual rinse.

2.2 PROCEDURE FOR THE CLEANING PROCESS

Each part was placed in a clean, dry 600-mL stainless steel beaker. Between 150 and 500 mL of liquid was preheated to about 60°C and degassed for at least 5 min under ultrasonic agitation and added so that the liquid surface was at least 2 cm above the top of the part. The beaker was covered with a petrie dish to prevent bath water from splashing into the beaker. The dry part was allowed to soak in the cleaning liquid for 20 min the first time it was cleaned before the ultrasonic power was turned on. (A waiting period of 5 min between adding the preheated liquid to the part for subsequent cleaning cycles and initiating the ultrasonic agitation was used as a standardized equilibration period.)

After sonification, the part was removed from the beaker with a pair of tongs, thus allowing any liquid adhering to the part to drain back into the beaker. Then the part was placed in a bottle and was rinsed with a fresh solution of the type used in the previous cleaning cycle using a wash bottle. The wash liquid was collected in a used solvent container.

The washed part was placed in a clean plastic bag and counted on a portable "pancake" beta-gamma probe. At selected intervals, the bagged part was analyzed using a NOMAD gamma ray counter. (Details are given in Sect. 2.7.) The solution left in the beaker was sampled after an additional 1 min of ultrasonic agitation to resuspend any particulate matter and homogenize the solution.

The beaker was then removed from the ultrasonic bath, and the residual liquid was filtered by gravity through either a 0.1- or a 0.2- μ m filter membrane. While filtering, the solution was checked for any sign of turbidity or settled layers. (A part that is oily may release the oil to the solution where it will eventually settle out as a separate layer because perfluorinated liquids are notoriously poor solvents for oils or most other liquids. A settled layer may be either on top of or under¹ the perfluorinated liquid.)

This completed a typical cleaning cycle in a decontamination test run.

The previous process was repeated for further cycles until the radioactivity of the part became constant—as implied by successive beta-gamma probe results showing little change in residual activity.

After all the cleaning cycles were completed, the cleaned part was washed with fresh (surfactant-free) perfluorinated liquid to remove any residual surfactant chemicals. The cleaned part, the liquid samples, and the filters were collected for analysis.

2.3 PROCEDURE FOR PREPARING RINSE AND WASH SOLUTIONS

2.3.1 Rinse Solution (PF-5070)

Perfluoroheptane (PF-5070 by 3M Corporation) from the shipping container was used as the rinse solvent and as the diluent for the wash solution described below.

¹The density of the perfluorinated liquids is very high. Most liquids will float in them.

2.3.2 Wash Solution [PF-5070 — 1 wt % K157FS(M) or K157FS(L)]

Taking a known quantity of diluent (described in Sect. 2.3.1), sufficient Krytox 157FS(M) or Krytox 157FS(L)² was used to make a 1-wt % solution. The results for a sample sent for analysis by uv indicated that its concentration was 0.95 wt %, using the standard curve provided by ESI. (See Sect. 2.7 and the Appendix for details.)

2.4 PREPARATION OF CONTAMINATED TEST PIECES

2.4.1 Washer Test Assemblies (WTAs)

WTAs have been used in other tests at ESI and are considered a standardized test material. They consist of two or more washers separated by three to five 0.002-in. stainless steel spacer washers and held together by a 0.25-in. stainless steel bolt and nut. The test washers may be made of stainless steel, mild steel, or copper. One assembly of stainless steel washers (WTA-6) and one assembly of mild steel washers (WTA-3) were used in this series of tests. The overall dimensions are about 1.25 in. OD by about 0.75 in. tall.

2.4.2 Mechanical Components

Components from CRL Model 8 manipulator hands were obtained from the ORNL Plant and Equipment Division manipulator repair shop. The hands had been surveyed and packaged on November 7, 1991. A wrist assembly housing and gear (WL) were chosen for cleaning.

2.4.3 Contamination of Test Assemblies and Manipulator Parts

The WTAs were placed in Cell C (a beta-gamma hot cell) in Building 3047 on March 1, 1993. They were moistened with water and placed on a contaminated high-efficiency particulate air filter in the cell. Periodically, they were moved about and rubbed on the filter. On March 11,

²Both surfactants are commercial mixtures of HFPO carboxylic acids made by the DuPont Company. The "L" version has a lower molecular weight (2400 daltons) than the "M" (3900 daltons).

1993, the WTAs were placed in a stainless steel tray and moistened with water. On April 6, 1993, cloth wiping rags, moistened with a commercial cleaner (Formula 409™) and used to decontaminate other objects, and thus contaminated with ¹⁹²Ir and ¹⁹¹Os, were inadvertently placed on top of the WTAs. On April 15, 1993, the WTAs were removed from the cell and placed in clean plastic bags for later use.

The manipulator hands and parts were contaminated in service. They had been partially decontaminated in 1991 with an ultrasonic treatment in water to remove alpha contamination and some beta-gamma contamination.

2.5 PROCEDURE FOR DETERMINING THE LEVEL OF ULTRASONIC AGITATION

The Branson 1200 ultrasonic cleaner has only one level of agitation. A piece of aluminum foil in water was essentially unchanged after 1 min of ultrasonic agitation. This unit was used only for preheating and degassing the rinse and wash solutions before each cleaning cycle.

The Crest unit has a dial to adjust the sweep frequency, with settings from about 0 to 9. In 1 min at the highest setting (9), the test piece of aluminum foil was severely eroded and had developed many perforations of about 0.5 mm in size. This phenomenon indicates that the protective surface oxide film was being removed. At the 0 setting, a small amount of surface change was seen after 1 min, but no perforations occurred. Intermediate values gave intermediate results in what appeared to be an orderly changing fashion. This unit was used for the cleaning cycles. In the early tests, a value of 5 was used, which was raised to 9 in later experiments.

2.6 FILTRATION TESTS AND FLUID RECOVERY

The residual liquid in the beakers after sonification and sampling was passed through a filter of either 0.1- or 0.2- μ m pore size by gravity flow. The filtration rate was slow enough such that it

was necessary to have more than one filtering unit in process at one time. Consequently, the designations of F1, F2, etc., are more for identifying them for analytical purposes than for placing them in the sequence of the cleaning tests.

2.7 ANALYTICAL PROCEDURES

2.7.1 Radioactivity of Parts

A semiquantitative measurement of initial and residual activity was made at the beginning and after each cleaning cycle using a Bicron "pancake" probe. The part was placed at the center of the probe face in about the same orientation for each measurement. The parts were analyzed using the automatic cycle, and counts were collected for 1 min.

Initially and at selected times during each series of cleaning steps, the test piece was removed and nondestructively reanalyzed using the ORTEC NOMAD germanium gamma detector system to estimate the amounts of activity remaining. Lack of full control of geometry³ and the effects of self-shielding limited the accuracy and precision of the results; however, it is believed that these measurements provided reasonable estimates of the total radioactivity (fixed and smearable) on the test pieces.

Standard smear techniques were used for determining the residual, transferrable contamination on the parts after selected cleaning cycles and at the end.

2.7.2 Surfactant Concentration

The analytical method of choice for determining surfactant concentration is uv analysis between about 200 and 220 nm. The diluent is clear in this region. The spectra determined at ORNL are presented in Figs. A.1 and A.2, in the Appendix, along with a standardization curve

³The parts were large in comparison to the detector and were relatively close, as well, so that the "point source" assumption could not be used.

provided by ESI for Krytox 157FS(M) (Fig. A.3). The surfactant has an active carboxyl group ($-\text{COOH}$), which absorbs around 210 nm. Krytox 157FS(L) has a lower molecular weight, yielding a higher concentration of ($-\text{COOH}$) groups; therefore, the absorbance is higher for a 1-wt % solution (Fig. A.2).

2.7.3 Used or Recycled Diluent or Rinse Solution

The radioactivity per volume of used, filtered liquid was estimated by impregnating two Whatman analytical filters, one with a 5-mL sample of composited filtered rinse and the other with a 5-mL sample of composited filtered wash solution, and allowing the volatile materials to evaporate. The dried filter papers were counted in a standard smear counter. Each had the same counting rate as background. A longer term count (1000 s) of both filters at one time in the NOMAD germanium detector gave no evidence of any peaks above the counter background.

A more precise measurement of residual activity after filtration was made by ORNL Analytical Chemistry Division personnel using procedure EPA-901.1.

2.7.4 Filters

The recovered filters were analyzed by a beta-gamma probe and by gamma scans.

3. EXPERIMENTAL EQUIPMENT

3.1 ULTRASONIC BATHS

The following ultrasonic baths were used:

- Branson ultrasonic cleaner; model B-1200R-4, 5.5 in. long \times 6 in. wide \times 4 in. high, 0.5-gal capacity, 80-W sonification power, 150-W heater, and digital control of temperature and sonification time.
- Crest model 4HT-710-3 ultrasonic bath having a fluid capacity of 3 gal and a cavity of 7 \times 10 \times 10 in., and a 500-W heater. The ultrasonic power was provided by a model 4G-250-3 ultrasonic generator, delivering 250-W ultrasonic power at 40 kHz. The power supply has the capability of changing the sweep frequency by 10% using dial readings of 0 to 9.

3.2 FILTRATION EQUIPMENT

The following filters and filter holders were used:

- Nylaflow filter membrane, 0.2- μ m pore size
- Durapore Type VV filter membrane, 0.1- μ m pore size
- Nalgene 250-mL filter holder with 500-mL receiver, model 300-4000
- Nalgene 500-mL filter holder with 1000-mL receiver, model 300-4100
- Nalgene 500-mL filter holder with funnel, model 310-4050

3.3 ANALYTICAL MEASURING EQUIPMENT

The following detectors and probes were used:

- Bicron Probe with Scaler, model Surveyor M, Geiger-Müller type, pancake gamma probe.

- EG&G Ortec NOMAD, a portable gamma spectroscopy system, model 92X-P with a high-purity germanium detector, model GEM-15190-P. It has a useful gamma-energy-detection capability of 40 keV to 10 MeV. OMNIGAM(63) I3.02.27 software was used.

3.4 OTHER EQUIPMENT

Standard laboratory glassware (e.g., graduated cylinders, pipettes, and burettes) and equipment (e.g., laboratory balance) were used.

4. RESULTS

4.1 RUN 1, WTA-6

The first run used a low-level contaminated washer test assembly, WTA-6 (made completely of stainless steel). As a low-activity sample, it was ideal for testing the procedures and the cleaning system while performing an actual set of cleaning cycles. It measured a net 2162 counts per minute (cpm) on the pancake beta-gamma probe (see Table 1). The run consisted of four cleaning cycles with rinse liquid, which were followed by three cleaning cycles using wash solution and then by a final cleaning cycle with rinse liquid.

The first four cycles of cleaning were performed with 150-mL batches of preheated, degassed rinse liquid (PF-5070). After each cycle, the rinsed part was counted through a plastic petrie dish cover, using the pancake beta-gamma probe. After the fourth cleaning cycle, the part was taken to the NOMAD system for analysis, and the beta-gamma probe was moved from the hood to a far corner of the room to lower the background (see Table A.1, Appendix). After the fifth cleaning cycle using wash solution (1% Krytox), it was discovered that significant blocking of the radiation⁴ was occurring in the relatively thick plastic petrie dish; therefore, future readings were made through thin plastic bags (Table A.2, Appendix). At this time, it was also discovered that the WTA had a higher probe reading when the bolt head was down (facing the probe surface) than when the screw end was down (lying at an angle on the probe surface); therefore, the orientation of the WTA was controlled for subsequent cleanings and measurements. In addition, several measurements were made and averaged for the results presented in the data-run tables (Table A.3, Appendix).

⁴The radiation that was blocked was assumed to be low-energy radiation.

Table 1. Run data for WTA-6

Date: April 19, 20, 1993

Run number: 1 (WTA-6)

Test sample: WTA-6

Purpose of test: Procedure validation and training;
measure removal with rinse and wash solutions

Scan determined by E. S. Meyers

Process step	cycle number							
	1	2	3	4	5	6	7	8
Liquid, R/W ^a	R	R	R	R	W	W	W	R
Volume, mL	150	150	150	150	150	150	150	150
Degas								
Time, min	5	5	5	5	5	6	5	5
Temperature, °C	40	-	-	-	54	41	56	58
Presoak								
Time, min	5	5	5	5	5	5	5	5
Temperature, °C	56	-	-	-	-	50	50	50
Sweep								
Frequency	5	5	5	5	5	6.5	6.5	6.5
Time, min	3	3	3	3	3	3	3	3
Temperature, °C	56	-	-	-	-	50	50	50
Net activity, cpm, hd ^b	104	-	-	85	1069	225	407	278
pancake probe, sd ^c	HD?	28	11	42	226	149	-	37
Ge detector				SURF ^d	SURF		SURF	SURF
Scan ID.SPC				64	65		67	68
Isotope, Bq					286			
¹⁹¹ Os				285	<i>e</i>		136	145
¹⁹² Ir				35			<i>e</i>	<i>e</i>
Liquid sample no.	6-1	6-2	6-5	6-4/ SURF	6-5	6-6	6-7	6-8
Volume, mL	5	5	5	6L14	5	5	5	5
Net activity, cpm (pancake probe)	nd	nd	nd	5\450 nd\nd	nd ^f	nd	nd	nd
Filter no.				6F1		6F2		6F3
Net activity, cpm				459		167		114
Isotope, Bq				SURF		SURF		SURF
¹⁹¹ Os				6F1		6F2		6F2
				68		<i>e</i>		<i>e</i>

Note: Cycles 1-4 were counted in petrie dish; cycles 5-8 were counted in plastic, not petrie dish.

^aR = rinse; W = wash.

^bhd = head down.

^csd = screw down.

^dSURF = surfactant.

^eValues are presented as "less than" numbers.

^fnd = not detected.

WTA-6 was counted in the plastic bag after four cleanings with rinse liquid and one cleaning with wash solution. It measured a net 1109 cpm on the pancake beta-gamma probe, indicating a decrease to about half the original count rate. Three additional cleaning cycles were provided — two with wash solution and the final one with rinse liquid — to remove the Krytox. After these three treatments, the readings on the pancake beta-gamma probe had decreased to an average of about 300 cpm for the three cycles.

The decrease in the residual activity, as measured by the probe, is presented in Fig. 1. The very low activity levels penetrating the plastic petrie dish are also shown. The only activities present in sufficient quantities to be measured by the germanium detector system were ^{191}Os and ^{192}Ir . The decreases in their activities are presented in Fig. 2 and Table 2.

The smear results for WTA-6 after cycle 8 were 90 disintegrations per minute (dpm) on the bolt end, 250 dpm between the washers, and 10 dpm on the nut end.

About 450 mL of filtered, used rinse solution in a glass bottle (SURF6L14) was analyzed by the NOMAD system; no peaks above background were found.

4.2 RUN 2, WTA-3

The second run used the highest level of the contaminated WTA-3 (with large washers of mild steel). The first part of Run 2 followed the pattern of four cleaning cycles with rinse liquid, followed by three cleaning cycles of wash liquid, and a final rinse cycle. WTA-6 was disassembled and given two more cleaning cycles, one with wash and one with rinse liquid.

WTA-3 had two mild steel washers, and all the other components were stainless steel. Its initial reading was a net 20,467 cpm on the pancake beta-gamma probe with the bolt head down (facing the probe surface), and 7072 cpm, up (lying at an angle on the probe surface) through the plastic bag. The run data for WTA-3 are presented in Table 3.

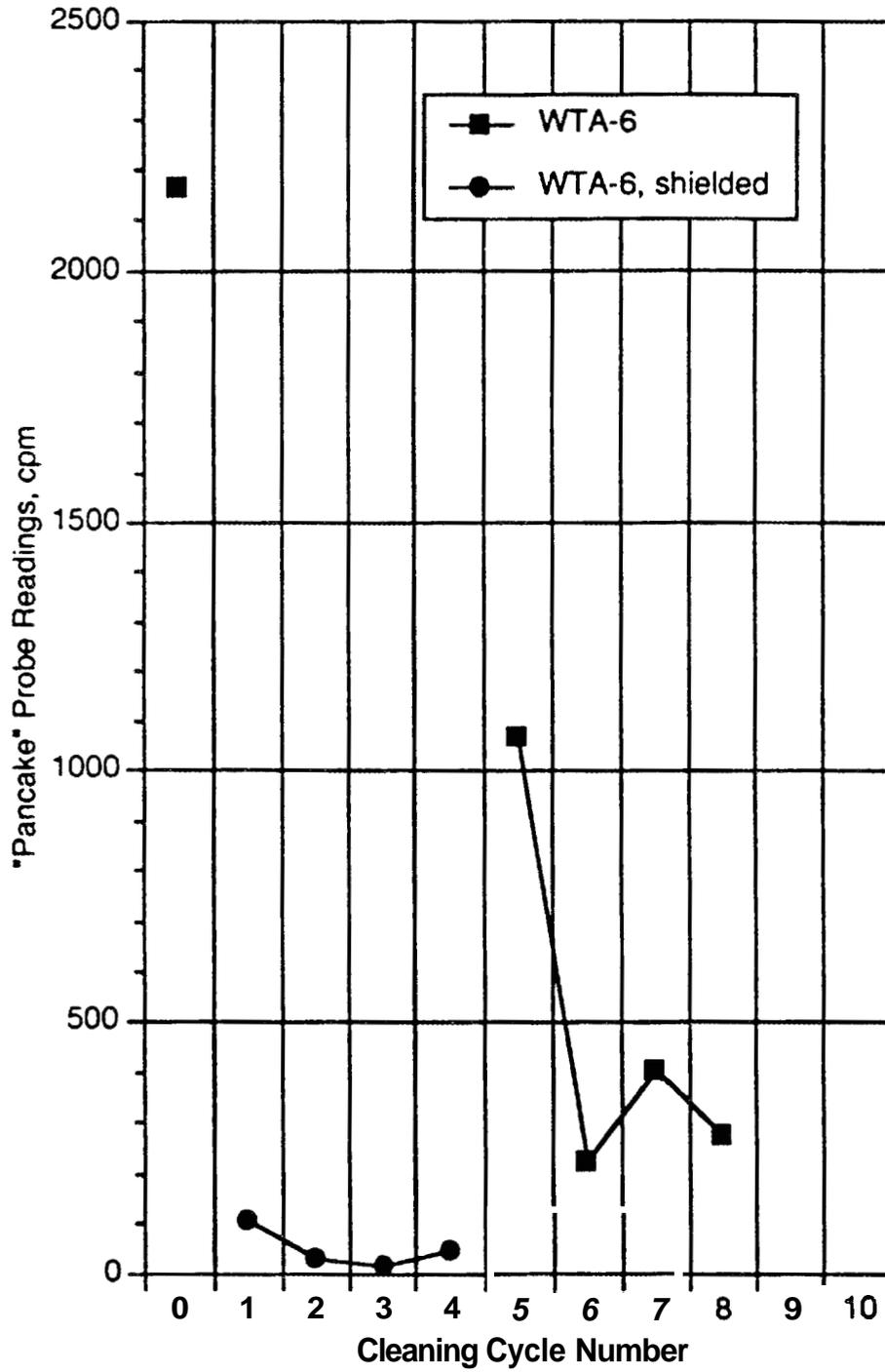


Fig. 1. Decontaminating WTA-6 (pancake probe readings).

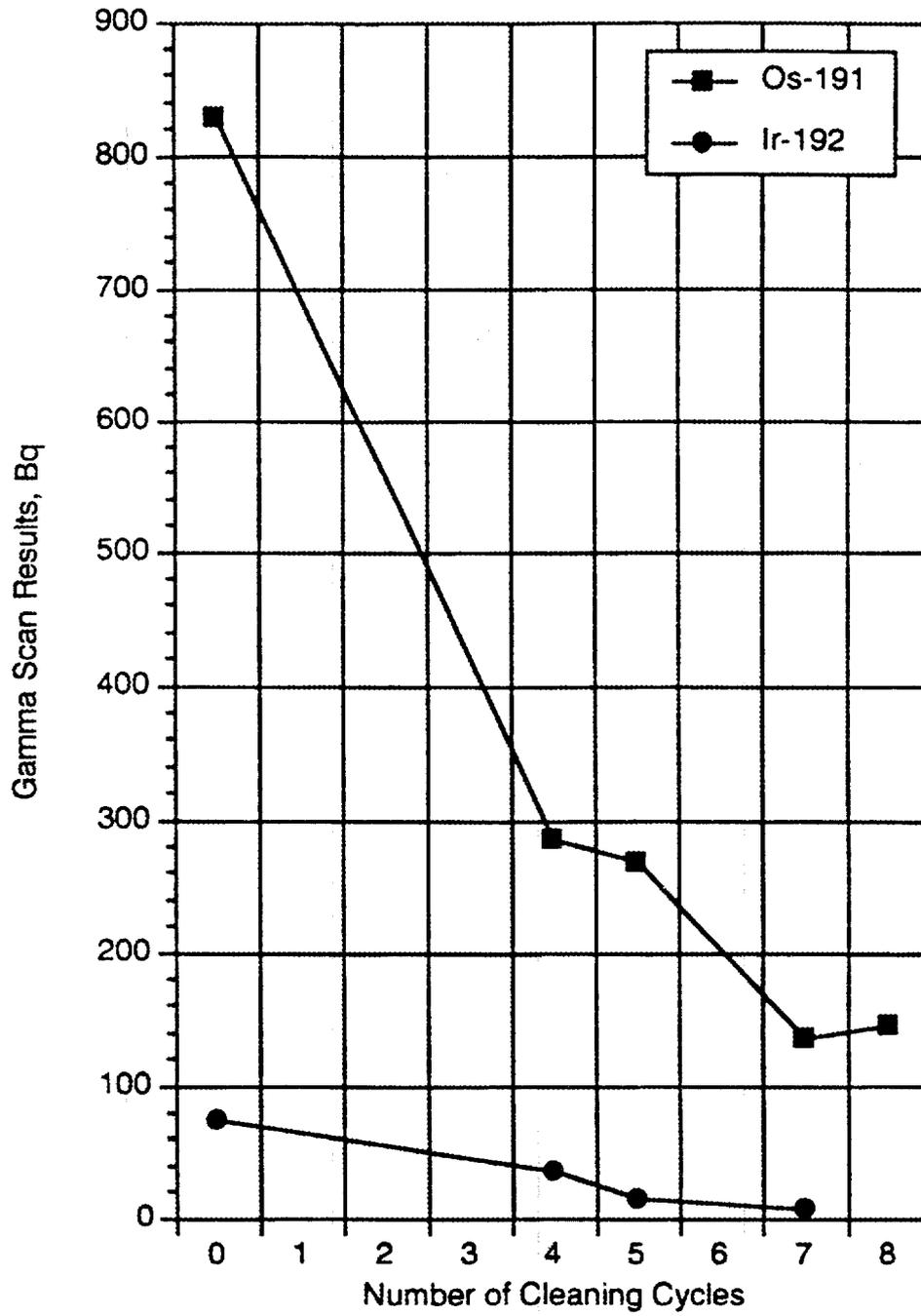


Fig. 2. Decontamination of WTA-6.

Table 2. Gamma scan data for WTA-6

Sample ID specimens	Description	Probe data (cpm)		Germanium detector data ^a (Bq)					
		Beta-gamma head down	Beta-gamma screw down	⁶⁰ Co	¹³⁷ Cs	¹⁵² Eu	¹⁵⁴ Eu	¹⁹¹ Os	¹⁹² Ir
Probed through a plastic bag									
SURF6.SPC	Initial scan WTA-6	2162	orientation ?	<115	<47	<64	<107	829	74
Probed through a petrie dish									
	After cycle 1	104							
	After cycle 2	28							
	After cycle 3		11						
	After cycle 4	85							
SURF64.SPC	After cycles 1-4	85	42	<78	<10	<88	<53	285	35
SURF65.SPC	After cycle 5	84	32	<7	<6	<70	<32	268	<15
Probed through a plastic bag									
	After cycle 5	1109	225						
	After cycle 6	225	149						
SURF67.SPC	After cycle 7	366		<9	<2	<44	<94	136	<7
SURF68.SPC	After cycle 8	278	37	<10	<21	<41	<36	145	<62
SURF6F1.SPC	Filter after cycles 1-4	459		<10	<9	<57	<20	68	<7
SURF6F2.SPC	Filter after cycles 5-6	167		<38	<7	<45	<26	<29	<80
SURF6F3.SPC	Filter after cycles 7-8	114		<41	<24	<20	<13	<10	<34
SURF6L12.SPC	Filtrate from cycles 1-4	(450) not detected		<11	<2	<54	<94	<12	<3
SURF61.SPC	Sample cycle 1 liquid (5 mL)	not detected		<16	<8	<7	<10	<18	<5

^aAll gamma scans made through plastic bag.

Table 3. Run data for WTA-3

Process step	Cycle number									
	1	2	3	4	5	6	7	8	9 ^a	10 ^a
Liquid (R/W) ^b	R	R	R	R	W	W	W	R	W	R
Volume, mL	150	150	150	150	150	150	150	150	200	200
Degas										
Time, min.	5	5	>15	5	5	5	5	5	7	5
Temperature, °C	62	62	60	62	62	61	61	58	60	60
Presoak										
Time, min.	5	5	5	5	22	5	5	5	20	5
Temperature, °C	50	50	-	-	50	50	50	50	-	-
Sweep										
Frequency	5	5	5	5	5	5	5	5	5	5
Time, min.	3	5	3	3	3	3	3	3	3	3
Temperature, °C	50	50	50	50	50	50	50	50	-	-
Net activity, cpm, hd ^c	2934	2402	2799	2835	1916	2071	1800	1635	-	820
Pancake probe, sd ^d	1312	1211	1078	1050	825	-	552	444	-	362
Ge detector										
Scan ID.SFC				SURF ^e 34			SURF 37	SURF 38		SURF 310
Isotopes, Bq										
⁶⁰ Co				107			f	f		f
¹³⁷ Cs				f			f	f		f
¹⁵² Eu				f			f	f		f
¹⁵⁴ Eu				f			f	f		f
¹⁹¹ Os				f			f	f		f
¹⁹² Ir				f			f	f		f
Liquid sample no.	3-1	3-2	3-3	3-4	3-5	3-6	3-7	3-8	3-9	3-10
Volume, mL	5	5	5	5	5	5	5	5	5	5
Net activity, cpm	68	nd ^g	nd	nd	nd	nd	nd	nd	nd	nd
Filter no.				3F1		3F2 here?		3F3 here?		3F4
Net activity, cpm				4909		957		91		603
Isotope, Bq										
⁶⁰ Co				704		182		f		238

^aSeparated.^bR = rinse; W = wash.^chd = head down.^dsd = screw down.^eSURF = surfactant.^fValues are given as "less than" numbers.^gnd = not detected.

The first four cleaning cycles were performed with rinse liquid. The cleaning was continued using wash solution for cycles 5 through 7. Because the beta-gamma probe of radiation levels remained relatively high, WTA-3 was disassembled, and the parts were hung on wires in the beaker. One additional cycle of cleaning and one cycle of rinse were performed using 200 mL of solution — in each case further reducing the residual radioactivity.

Because of the relatively slow filtration by gravity, it was occasionally necessary to add the used cleaning liquid to an empty filter housing while a previous one was emptying. Thus, the placement of the filters in Tables 2 and 3 is somewhat misleading — the filters are identified for sampling purposes rather than for sequence in the run cycles. The final two batches of liquids were passed through the final filter, 3F4.

A steep drop in the probe reading was found for the first cycle, followed by a nearly constant residual readings for the remaining three cycles of rinse liquid. A steady drop in residual activity was observed for the subsequent steps (Fig. 3). Run 1 data are superimposed on the graph. Although the values for cycles 2, 3, and 4 are not plotted because of the shielding of the petrie dish in Run 1, there is qualitative similarity in the later cycles. Gamma scan results for Run 2 are presented in Fig. 4 and Table 4.

The smear results for WTA-3 were 340 dpm for the bolt end, 70 dpm between the washers, and 80 dpm at the nut end.

4.3 RUN 3, MANIPULATOR WRIST HOUSING (WL)

The third run used a contaminated wrist housing assembly from the slave end (in-cell part) of a manipulator hand. It consisted of three cleaning cycles with wash solution, followed by a cleaning cycle with rinse liquid. It was disassembled and given a longer cleaning cycle (in three stages) in wash solution; washing was followed by manual rinsing.

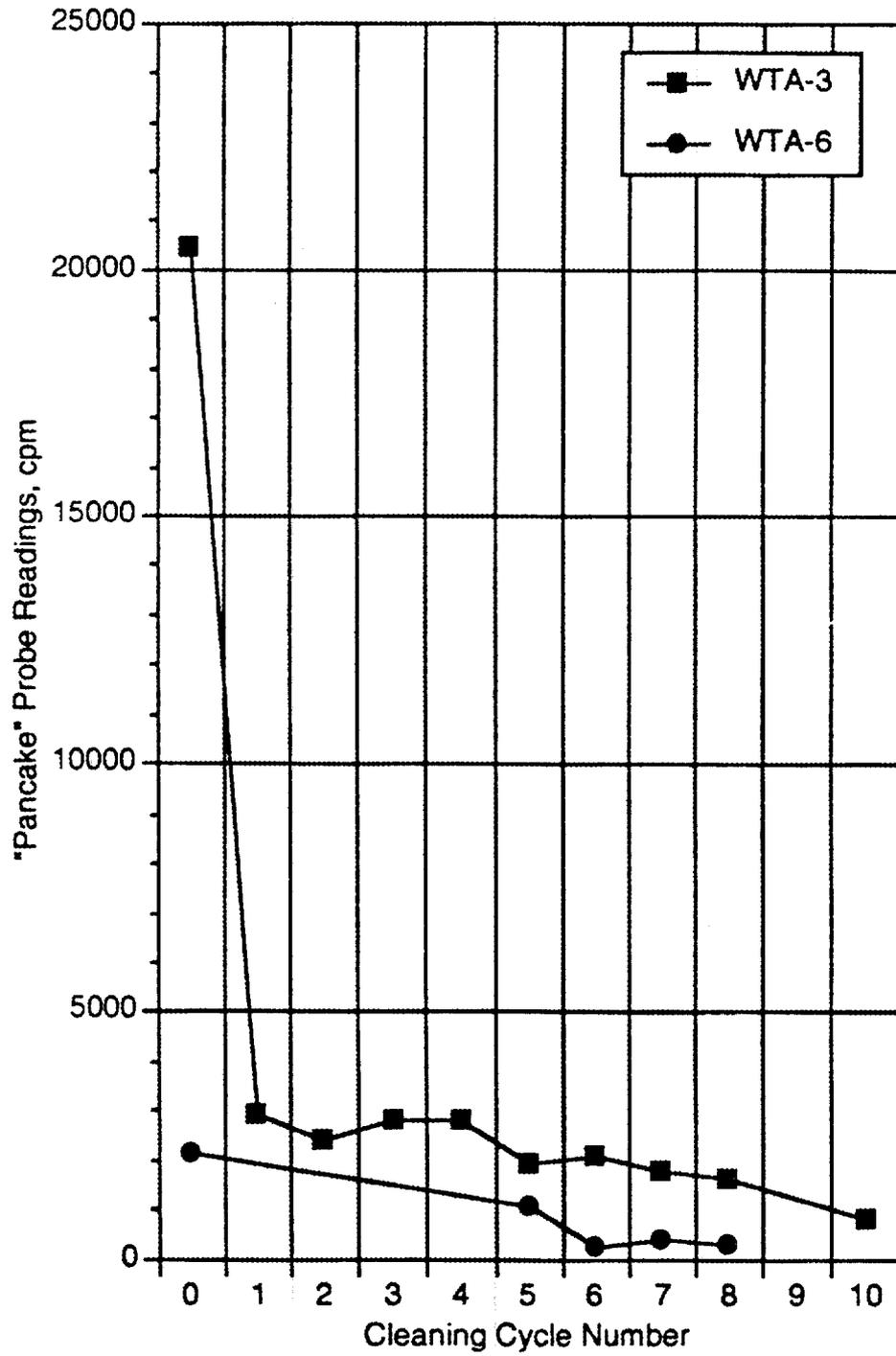


Fig. 3. Decontaminating WTAs 3 and 6 (pancake probe readings).

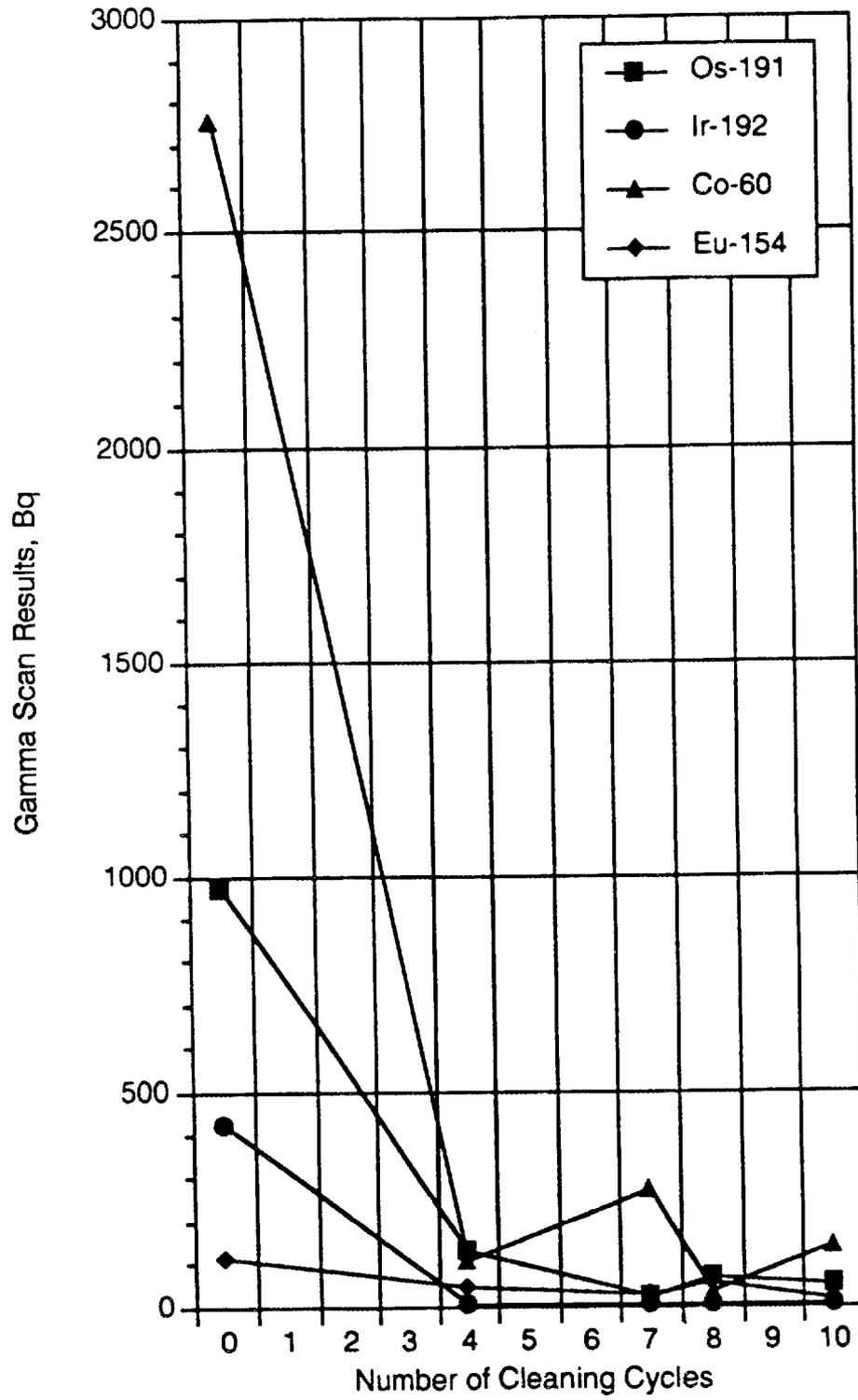


Fig. 4. Cleaning of WTA-3.

Table 4. Gamma scan data for WTA-3

Sample ID specimens	Description	Probe data (cpm)		Germanium detector data (Bq)					
		Beta-gamma head down	Beta-gamma screw down	⁶⁰ Co	¹³⁷ Cs	¹⁵² Eu	¹⁵⁴ Eu	¹⁹¹ Os	¹⁹² Ir
SURF 3	WTA-3 initial scan	20,467	7,037	2,754	<65	<338	110	970	<425
SURF 34	Scan after cycle 4	2,835	1,050	107	<14	<209	<46	<128	<4
SURF 37	Scan after cycle 7	1,800	552	<276	<2	<140	<27	<21	<3
SURF 38	Scan after cycle 8	1,635	444	<31	<4	<91	<57	<69	<2
SURF 310	Scan after cycle 10	820	362	<141	<17	<94	<15	<5	<2
SURF 3F1	Filter from cycles 1-4	4,909	NA ^a	704	<61	<293	<151	<168	<62
SURF 3F2	Filter from cycles 5-7	957	NA	182	<3	<28	<70	<86	<26
SURF 3F3	Filter from cycle 8	91	NA	<43	<42	<20	<14	<4	<11
SURF 3F4	Filter from cycles 9-10	603	NA	238	<103	<70	<74	<74	<14

^aNA = not applicable.

The left half⁵ of a manipulator wrist housing chosen for Run 3 was a dull black color on the outside, a color typical of anodized aluminum. On the inside, it was a dull aluminum color. The inner side of the wrist assembly had a circular bearing race (without bearing) containing some black "crud"—probably leftover lubricant.⁶ Near this place was a gear and a washer affixed to the housing by a screw coming from the outside. The gear had some "crud" near it also, and it turned relatively stiffly. It loosened up after cleaning. The master end of the housing had two "ears" attached with screws. The radiation levels were quite high relative to the WTA parts, reading over 62,000 cpm on the pancake beta-gamma probe, and were at maximum levels on the outside surface in the vicinity of the screw holding the gear.⁷ Because the housing assembly was too long for the 600-mL beaker, each cleaning cycle was done in two steps. The part was inverted between steps.

The run data for WL are presented in Table 5.

After the first cycle, the wash solution on the filter looked somewhat turbid, and small flakes of "paint" were seen floating in it. In the first half-cycle of the second wash, the sweep frequency level was raised to 6 (from 5); and in the second half-cycle, to 7. The "crud" did not seem to be removed from the bearing circle. After the second cycle with wash solution, the part was smeared. One smear (No. 1, 21,820 dpm) caught some of the black "crud"; the other (No. 2, 5330 dpm) was "crud" free. The sweep frequency level was raised to 9, the highest value, for the third cycle with wash solution. The fourth cycle was performed with rinse solution. After the fourth

⁵Determined by facing the manipulator hand from the front.

⁶The manipulator shop identified their radiation-resistant lubricant as Chevron NRRG 235.

⁷While the initial part was smeared before it was placed in the hood, the smear results were not recorded. However, the health physicist recalled that the smear read 2400 dpm on the smear counter. It was not known if that smear had "crud" on it.

Table 5. Run data for manipulatory wrist housing (WL)

Process step	Cycle number						After disassembly (housing only)
	1	2	3	4	5	6	
Liquid (R/W) ^a	W	W	W	R	W	W	
Volume, mL	300	350	350	350	500	500	
Degas							
Time, min	>5	5	5	5	15	>5	
Temperature, °C	min 60	60	60	62	60	60	
Presoak							
Time, min	20/20	3/4.5	5/5	1/1	3	20	
Temperature, °C	55	50	50	50	50	50	
Sweep							
Frequency	5	6/7	9	9	5-9	9	
Time, min	3/3	3/3	3/3	3/3	3	10	
Temperature, °C	52	50	50	50	50	50	
Net activity, cpm	52,868	61,465	59,956	60,414	60,572	48,738	56,036
pancake probe	12,799	11,342	9,892	8,717	8,738	7,855	9,604
Smear activity, cpm							
Outside (black)	-	-	-	220	470	590	
Inside (shiny)	-	-	-	5,130	3,660	710	
Ge detector scan		SURFWL2 ^b		SURFWL4	SURFWL5	SURFWL6	
Isotope, Bq							
⁶⁰ Co		49,805		39,860	47,994	45,074	
^{152,154} Eu		55,865		47,539	31,591	30,364	
Liquid sample no.	LW-1	LW-2	LW-3	LW-4	LW-5	LW-6	
Volume, mL	5	5	5	5	5	5	
Filter no.			WLF-1		WLF-2	WLF-3	
Net activity, cpm			8,673		18,155	2,199	
Isotopic activity, Bq			SURFWLF1		SURFWLF	SURFWLF	
⁶⁰ Co			126		2	3	
¹⁵² Eu, ¹⁵⁴ Eu			850		2,466	304	
					3,751	699	

^aR = rinse; W = wash.^bSURF = surfactant.

cycle, the aluminum looked brighter, and it appeared that the "crud" might have been loosened. The gear rotated freely. The housing was smeared inside (5130 dpm), outside (220 dpm), and gear and hole (0 dpm). Cycle 5 used a combination of 300 mL of original wash solution and 200 mL of freshly prepared Krytox 157FS(L) solution (33.80 g/1760 mL total liquid). The part was removed from the beaker, rinsed with a wash solution, rinsed again by rinse solution, and bagged for storage overnight.

The wrist housing assembly was taken apart prior to cycle 6. The "ears" were removed and counted with the screws (net 4897 cpm with the outside and 1251 cpm with the inside facing the probe). The gear and split (C) retainer ring were removed. The gear mounting post and matching area on the housing, which became exposed when the gear mounting post was removed, showed an uneven corrosion and a yellowish-whitish discoloration. The radiation readings of the gear mounting post and nut were a net 5207 cpm outside and 3314 cpm inside. The wrist housing, without the removable parts, read about 56,180 cpm outside and about 9600 cpm inside.

The nut, gear, and ears were threaded on a wire for cleaning. The housing rested on the bottom of the beaker. Enough wash solution was added to make 500 mL, an amount sufficient to cover the parts. The 3-min sonification seemed to be raising bubbles from the housing (shiny side) but not from the other parts or the outside surfaces.⁸ The housing was inverted, and all parts were given another 3-min treatment, followed by another 4-min treatment. The parts were removed, and each was given a manual rinse before packaging in plastic bags. The wrist housing read about 48,740 cpm outside and about 7860 cpm inside on the pancake beta-gamma probe.

The progress of the decontamination is shown in Fig. 5. The probe results showed very little change until the wrist assembly was disassembled; then decontamination proceeded. The gamma

⁸After cleaning, the inside was bright and shiny. It looked as if the cleaning treatment at a sweep frequency level of 9 had roughened the surface. There were several small, aluminum-colored filings in the bottom of the beaker. The anodized side did not appear to change during the treatment, although some flakes of "paint" were seen on the filter.

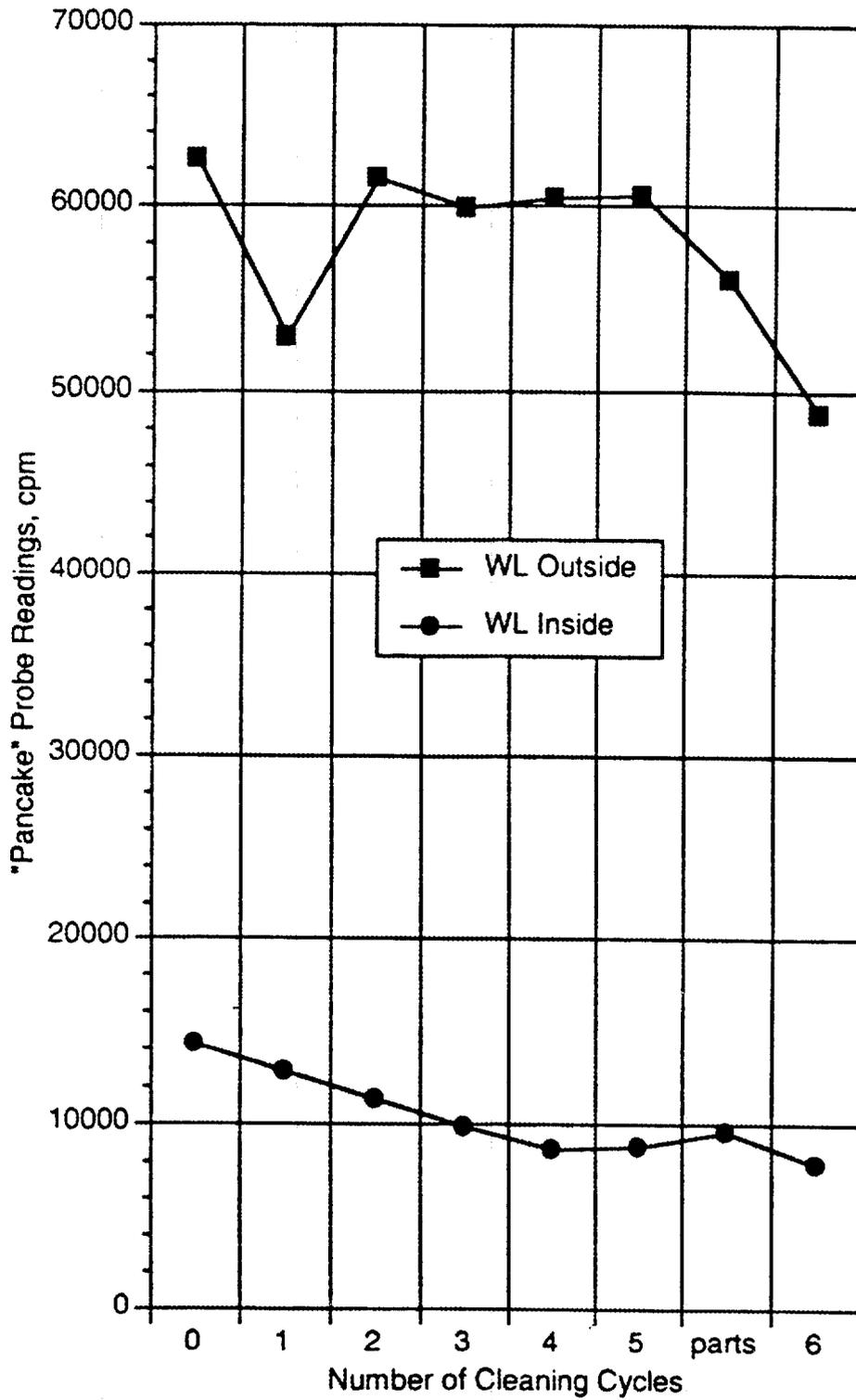


Fig. 5. Decontaminating a manipulator wrist housing (WL) pancake probe readings. Note: The initial points (0 cycles) are maxima, not averages.

scans showed steady decreases of ^{60}Co and $^{152,154}\text{Eu}$ ⁹ (Fig. 6 and Table 6). The smear data for WL are presented in Table 7. This more complex piece was smeared after cleaning steps 2, 4, 5, and 6. Between steps 5 and 6, the WL was taken apart. A smear of all surfaces, including the "crud" in the holes, read nearly 22,000 dpm after two cycles of cleaning. The data from the smears taken after cycle 6 range from about 590 to 710 dpm — if the "crud" is omitted.

A 100-mL sample of wash filtrate from test specimen WL, which was filtered through a 0.2- μm filter by gravity, was analyzed by the ORNL Low-Level Radiochemical Analysis Laboratory. The results were $33 \pm 5 \text{ Bq/L } ^{60}\text{Co}$, $43 \pm 22 \text{ Bq/L } ^{152}\text{Eu}$, $40 \pm 11 \text{ Bq/L } ^{154}\text{Eu}$, and $0.3 \pm 2.0 \text{ Bq/L } ^{191}\text{Os}$. These values are about three orders of magnitude lower¹⁰ than specified in the ORNL Health Physics Manual for reuse of liquids not intended for human consumption.

⁹The peaks for ^{152}Eu and ^{154}Eu were very close together, and the NOMAD system had difficulty distinguishing them. On the advice of E. S. Meyers, they were added together to get the values in the table and plotted in this figure.

¹⁰The values given are 18 Bq/mL for ^{60}Co , 22 Bq/mL for ^{152}Eu , 74 Bq/mL for ^{191}Os , and 15 Bq/mL for ^{192}Ir .

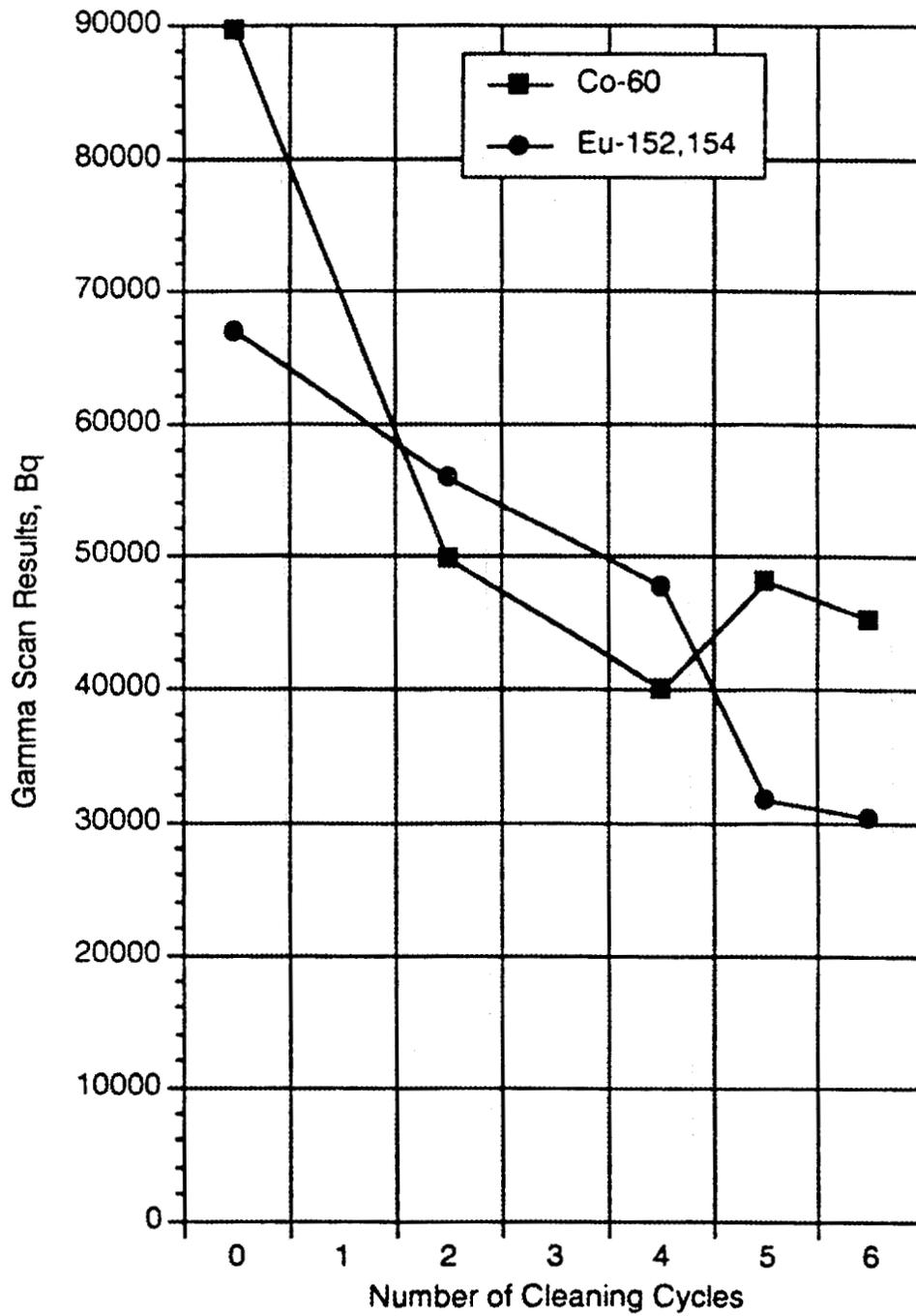


Fig. 6. Decontamination of a manipulator wrist housing. Note: Housing disassembled after cycle 5. All ^{60}Co peaks had bad shape for cycle 5.

Table 6. Gamma scan data manipulator wrist housing (WL)

Sample ID specimens	Description	Probe data (cpm)		Germanium data detector (Bq)				
		Beta-gamma outside	Beta-gamma inside	⁶⁰ Co	¹³⁷ Cs	¹⁵² Eu, ¹⁵⁴ Eu	¹⁹¹ Os	¹⁹² Ir
		Outside is black anodized Inside is aluminum colored						
SURFWL	WL, initial scan	62,567	14,333	89,544	<571	66,916	<395	<459
SURFWL2	Scan after cycle 2	61,465	11,342	49,805	<1,150	55,865	<218	<165
SURFWL4	Scan after cycle 4	60,414	8,717	39,860	<844	47,539	<409	<34
SURFWL5	Scan after cycle 5	60,572	8,738	47,994	<1,320	31,591	<326	<600
SURFWL6	Scan after cycle 6	55,376	9,604	45,074	<551	30,364	<218	<216
SURFWL2	Smear from cycle 2			319	<66	386	<32	<6
SURFWLF1	Filter from cycles 1 and 2	8,673		126	<10	850	<67	<64
SURFWLF2	Filter from cycles 3 and 4	18,155		2,466	<165	3,751	<103	<36
SURFWLF3	Filter from cycles 5 and 6	2,199		304	<7	699	<12	<13

Table 7. Smear data for the disassembled manipulator housing (WL),
Run 3 (in disintegrations per minute per 100 cm²)

Part smeared after cycle	Cycle			
	2	4	5	6
All surfaces	21,820			
Without holes	5,330			
Black side		220	470	590
Shiny side		5,130	3,660	710
Gear and hole		50		
Crud			3,730	2,380
Nut			37,440	
Gear			200	

5. DISCUSSION

The procedure for contaminating the WTAs allowed for the possible formation of fixed contamination in addition to particulates. The exposure of the WTAs to Cell 3 atmosphere and rubbing around on the used filters in the cell provided surface contamination by particulates containing radioactive species. However, the periodic wetting of the samples may have caused some of the radioactive materials to go into solution on the surface, perhaps reacting with the surfaces or drying out in nonparticulate forms. Furthermore, the unintended placement of wipes contaminated with Os, Ir, and U and containing unknown amounts of water and "409" cleaning agents may also have led to contamination of surfaces by nonparticulate species.

The consequences of these events should provide a more challenging cleaning environment, but they may also have taken the tests outside of regions where the ESI process is known to be effective.

5.1 RUN 1, WTA-6

WTA-6, which was chosen for the first experiment as a low activity sample, proved to be ideal to test our procedures and system while performing an actual set of cleaning cycles. The low activity levels provided some assurance that any unforeseen events would have minor consequences. The data, however, provided some initial information. For example, the beta-gamma probe, which was initially located in the same hood where the experiments were performed, suffered from too high a background (213 ± 16 cpm) to be useful as a qualitative estimate of cleaning effectiveness, and it was moved to a far corner of the decontamination room for the subsequent runs. Likewise, the effects of shielding by the plastic petrie dish and the importance of the placement and orientation of the sample on the beta-gamma probe were discovered.

Referring to the decrease in residual activity, presented graphically in Fig. 1, it was found that the probe readings decreased after the first treatment with rinse liquid and stayed low for the next three treatments. The plastic petrie dish absorbed essentially all the beta and any very low energy gamma components,¹¹ rendering the initial series of four measurements difficult to interpret as absolute measures of total cleaning effectiveness. Qualitatively, however, there seemed to be little net change with subsequent treatments using the rinse liquid (PF-5070), thus indicating that the bulk of any cleaning action had been performed in the first cleaning cycle. Taking the probe reading prior to cycle 5 (counted in a plastic bag), one calculates that about 50% of the initial activity was removed in the four washings in rinse liquid. The removal increased to $\geq 85\%$ after the additional three cycles of wash solution (1% Krytox in PF-5070) followed by a final rinse.

Many of the specific radioactive isotopes measured by the NOMAD system and presented in Table 2 are shown as "less than" numbers, implying that these are, at best, upper limits. All the reported values were plotted in Fig. 2, showing the decrease in residual amounts of specific isotopes. Except for ^{191}Os and ^{192}Ir , the curves shown represent upper limits for the stated isotopes and do not represent accurate measurements. Using ^{191}Os as the tracer, the decontamination was $\geq 60\%$ in the first four cycles and rose to $\geq 80\%$ at the end. Using ^{192}Ir , the decontamination achieved in the first four treatments was $\geq 50\%$, but the rest of the values were below the detection sensitivity. The results of the scans in measuring the decontamination are consistent with those based on the probe data. This degree of decontamination was accomplished in about 24 min of total treatment time.

¹¹A crude estimate of shielding was made by ratio of the probe readings through the petrie dish and through the plastic bag. Two samples had been measured both ways; one gave a ratio of 12.7:1.0, the other 7.1:1.0. If one strikes a simple average, that is, a ratio of 10:1, then some 90% of the radiation was absorbed by the thicker plastic.

The results of smear analysis showed that all smears were ≤ 250 dpm. Because the washer test assemblies are very small, they do not have enough surface area (100 cm^2) for a standard green-tag test.

The 450-mL sample of used rinse solution did not have measurable radioactivity when counted in the NOMAD gamma-scanning system. In other words, no gamma-emitting radioactive species were detected in the filtered solvent. However, the effects of self-shielding by the liquid and of shielding by the glass bottle were not measured, and the amounts of beta emitters present, if any, could not be determined by this method.

5.2 RUN 2, WTA-3

WTA-6, chosen for the second run, had the highest activity of the WTAs exposed to the atmosphere and filters in Cell 3, Building 3047. The decrease in total activity, as measured by the pancake beta-gamma probe, with cleaning cycle is presented in Table 3 and Fig. 3. For comparison purposes, the unshielded probe results for WTA-3 are also presented in the figure. A much larger effect of the first cleaning cycle is evident for the hotter sample. The largest change occurred in the first cycle (down to about 14% of the starting value) and was followed by a plateau. A second decrease was noted when the Krytox wash solution was used, and a steady decrease in residual activity was noted with increasing cycles (terminating with about 8% left). The WTA was disassembled for the last two cycles. After disassembly and one further cleaning cycle and one rinse cycle, the final probe reading reached 820 cpm, approximately 4% of the starting value. The total cleaning time was about 30 min.

The results of the gamma-scan analyses, which are presented in Table 4 and Fig. 4, indicate that the first four cleaning cycles reduced the ^{60}Co to about 4% of its original value. All other isotopes were "less than" numbers, and two upper limit values were all that could be calculated

($\leq 42\%$ remaining for ^{154}Eu and $\leq 13\%$ remaining for ^{191}Os) for the first four cleaning cycles. The curves plotted in Fig. 4 are all upper limit curves, indicating that the decontamination may have been better than shown.

The results of smear analysis showed all smears were ≤ 340 dpm. Because the WTAs are very small, they do not have enough surface area (100 cm^2) for a standard green-tag test.

5.3 SUMMARY OF THE WTA RESULTS

The two runs with the WTAs followed similar patterns. A significant amount of activity was removed in the first cleaning cycle with pure PF 5070, but three further treatments resulted in little additional decontamination. The use of wash solution resulted in a steady decrease in residual activity with three additional cycles of wash followed by a rinse cycle. Disassembly of WTA-3 and two further cycles of cleaning (one wash solution, one rinse) resulted in further removal of radioactive species. The smear-test results indicated good removal of loose particulates, but they cannot be related to standard green-tag tolerances because of the small size of the WTAs.

5.4 RUN 3, MANIPULATOR WRIST HOUSING (WL)

A used and previously decontaminated wrist housing from the slave end of a manipulator was used for the third run. This provided a good test of whether additional cleaning using the ESI process was possible. The run consisted of three cycles of cleaning with wash solution, followed first by a rinse cycle and then another wash cycle.

The results showed some additional cleaning took place, but it was selective (Table 5 and Fig. 5). The probe readings were relatively constant until the wrist assembly was taken apart and the parts cleaned by another wash cycle. This constancy could imply that the isotopes responsible

for the bulk probe readings were not removed by this process; however, it is known that beta emitters are prone to self-shielding and that such readings are not proportional to the quantities present when they are present in "thick" layers. If the beta emitters were diffused into the outer surface of the housing, decontamination might not greatly reduce the probe readings. The probe readings decreased after disassembly. Because the geometry also changed on disassembly, the probe data are ambiguous.

The gamma scans, however, made after the second, fourth, fifth, and sixth cycles, showed significant decontamination was taking place. As seen in Table 6 and Fig. 6, decontamination from ^{60}Co and $^{152,154}\text{Eu}$ was continuous throughout the procedure.¹² After three cycles of wash and one of rinse, about 50% of the ^{60}Co had been removed, and about 30% of the combined europium isotopes had been removed.¹³ After disassembly (with one cleaning cycle before and one after disassembly), the results for ^{60}Co appeared to be essentially unchanged, while the decontamination of the $^{152,154}\text{Eu}$ isotopes continued until about 55% was removed. The treatment did not remove the "crud" efficiently, which was a complicating factor.

The final, extended cleaning cycle with wash solution after disassembly did not appear to cause any significant changes in the quantities of ^{60}Co and $^{152,154}\text{Eu}$. The corrosion found when the parts were removed from the wrist housing assembly provided two explanations for the relatively low cleaning efficiencies noted. The first observation is that some of the contamination was trapped in such a way that the cleaning liquids could not get to it. The second observation is that the ESI process does not claim to remove fixed contamination from surfaces — it is useful

¹²According to the gamma scan information, the NOMAD system could not reliably distinguish between the two europium isotopes, and the values reported for them were summed for this analysis.

¹³All of the other isotopes were reported as "less than" values.

mainly for adherent particulates. (A third explanation is, of course, that the previous cleaning cycles with wet chemicals had "fixed" some of the contamination to the surface.)

The change in appearance of the inner surface of the housing (it looked brighter and slightly rougher) and the presence of a few metallic shards in the used cleaning liquids after sonification were noted without further analysis or consideration.

The results of smear analyses, which are given in Table 7, showed that smears of the disassembled housing decreased to ≤ 710 dpm after six cycles of cleaning and disassembly. Some of the separated parts and "crud" samples were more highly contaminated. The disassembled nut had high levels of smearable contamination (37,440 dpm) on it after cycle 5. It was not smeared after cycle 6. The smear containing "crud" read 2380 dpm. The probe results were above green-tag tolerance.

The analysis of a 100-mL sample of wash solution filtered by gravity through a 0.2- μm filter showed that the filtration removed the radioactive materials to levels well below those permitted for reuse or disposal.¹⁴

¹⁴These levels might be reduced even further by filtration through a finer filter (0.1 μm), if desired.

6. CONCLUSIONS

1. The tests of the ESI process with a variety of radioactive isotopes and forms of contamination show that ultrasonic agitation in these fluorocarbon liquids can remove the radioactive contamination.
2. The effectiveness of the removal is increased by using a surfactant in the fluorocarbon liquid.
3. Decontamination was still occurring when the tests were terminated, and additional time would have increased the effectiveness.
4. To be effective, the contamination must be "available" to wetting by the cleaning agents and not chemically bound to the surface.
5. These preliminary experiments indicate that filtration should be an effective method for removing radioactive materials from the process streams, allowing them to be recycled for further use.

7. RECOMMENDATIONS FOR FUTURE WORK

1. Perform larger scale tests using a continuous process with circulating liquids and in-line filters on a wider variety of contaminated items (i.e., electronic and electrical).
2. Optimize the ESI process.

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APPENDIX A

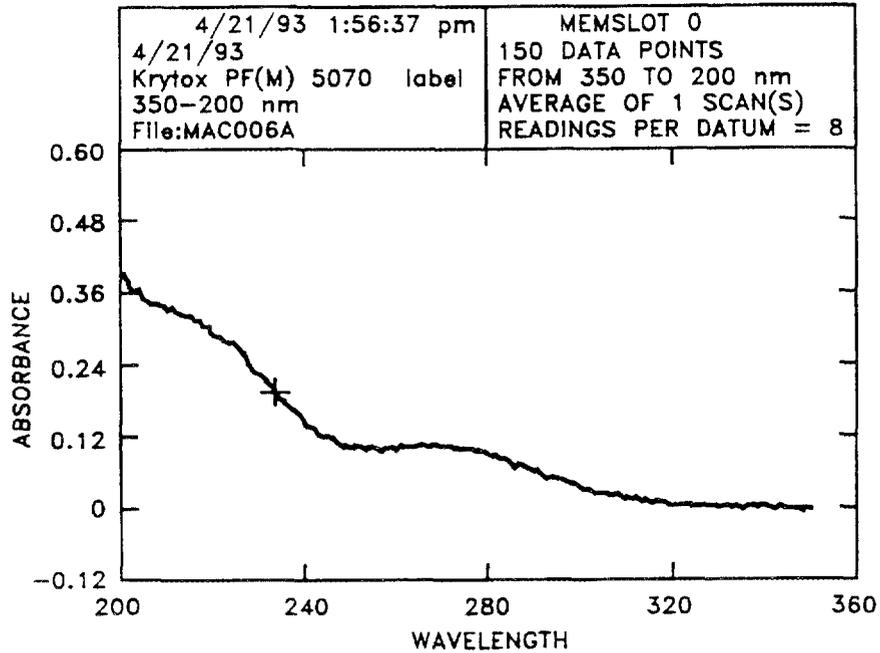


Fig. A.1. Absorbance of wash solution for Krytox(M) in PF-5070.

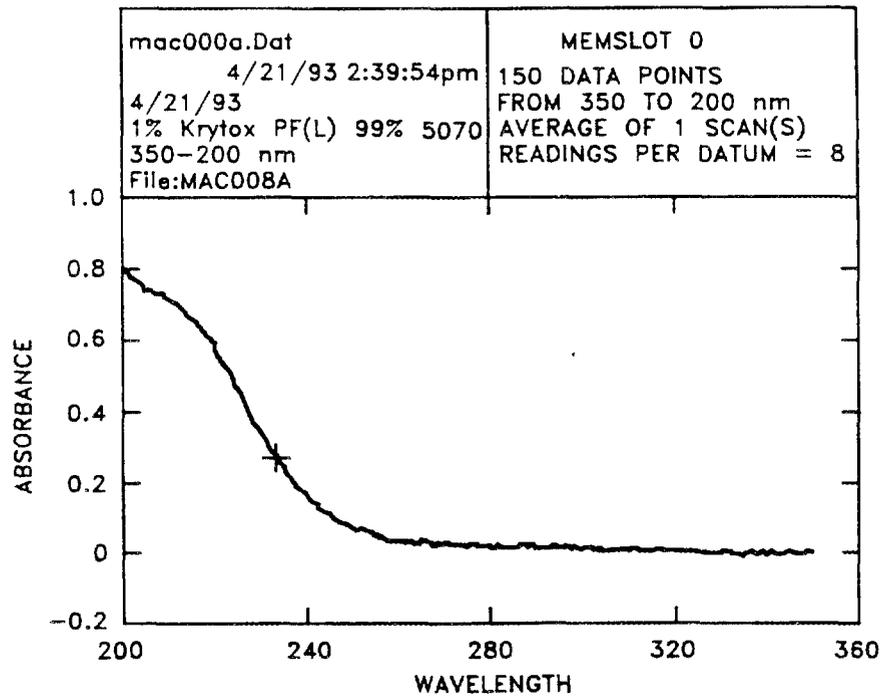


Fig. A.2. Absorbance of wash solution for Krytox(L) in PF-5070.

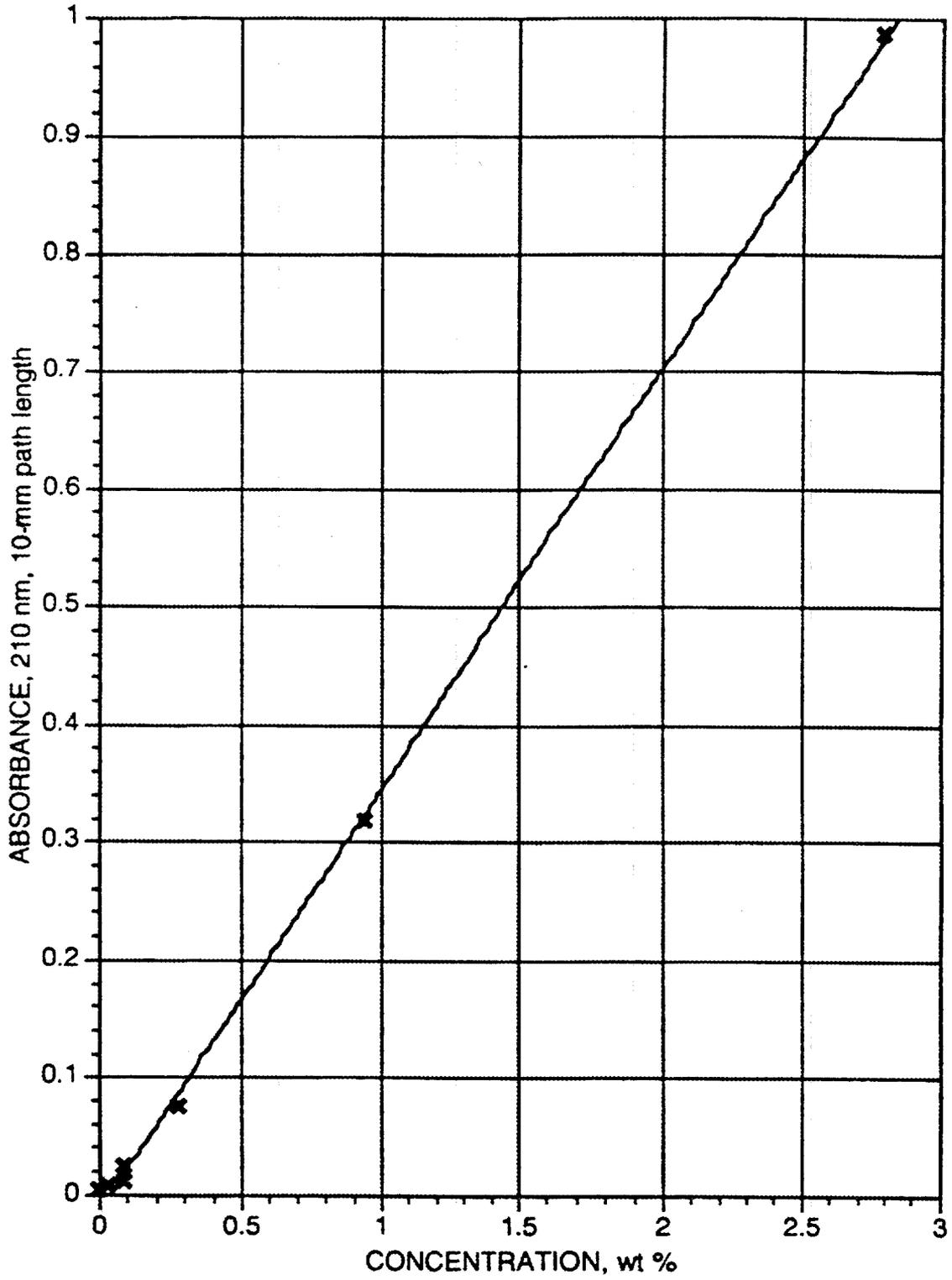


Fig. A.3. Standard curve for Krytox 157FS(M) in PF-5070.

Table A.1. Background counts on the probe

Run 1, WTA-6			Run 2, WTA-3			Run 3, WL		
Date	cpm	Time	Date	cpm	Time	Date	cpm	Time
4/19/93	196	12:45	4/20/93	142	15:15	4/22/93	178 ^a	8:15
	201	13:22		135	15:40		158 ^a	8:21
	225	13:39		145	16:00		181	8:21
	213	13:43		158	16:15		136	8:35
	207	13:56	4/21/93	171 ^a	7:20		139	8:55
	238	Time?		143	8:05		137	9:13
Average	213.3			154	8:07		138	9:16
std. dev.	15.7			142	8:30		169	9:52
				144	8:40		139	9:53
4/20/93	150	Time?		140	10:12		153	10:05
	148	9:30		133	10:15		149	10:14
	154	10:06	Average	146.1			152	12:30
			std. dev.	11.0			165	14:11
	121	10:28					141	14:13
	142	10:39					120	14:45
	167	13:30					129	14:47
	147	14:15					130	15:45
	150	Time?						
	136	Time?				Avg.	147.88	Std. dev.
	310	Omitted						
Average	146.1							
std. dev.	12.7							

^aInstrument has not stabilized (still cold).

Table A.2. Probe data and averages: ESI Runs 1 through 3

Cycle ID	Orientation	Count (cpm)				Average	Net
		1	2	3	4		
Run No. 1							
6-init		2,375				2,375	2,162
6-5	hd ^a	1,175	1,255			1,215	1,069
	sd ^b	398	345			372	226
6F1	fd ^c	605				605	459
	fu ^d	402				402	256
6-6	hd	371				371	225
	sd	295				295	149
6-7	hd	602	631	500	477	553	407
	sd						
6-8	hd	429	422	421		424	278
	sd	183				183	37
6F2	fd	313				313	167
6F3	fd	285	235			260	114
Run No. 2							
3-init	hd	17,048	22,851	21,940		20,613	20,467
	sd	6,798	7,285	7,573		7,219	7,073
3-1	hd	3,020	3,139			3,080	2,934
	sd	1,483	1,433			1,458	1,312
3-2	hd	2,583	2,530	2,531		2,548	2,402
	sd	1,241	1,342	1,487		1,357	1,211
3-3	hd	2,873	3,004	2,959		2,945	2,799
	sd	1,288	1,160			1,224	1,078
3-4	hd	2,996	2,958	2,989		2,981	2,835
	sd	1,243	1,148			1,196	1,050
3F1		5,202	5,199	4,892	5,074	5,055	4,909
3-5	hd	2,088	2,072	2,025		2,062	1,916
	sd	973	968			971	825
3-6	hd	2,198	2,221	2,231		2,217	2,071
	sd						
3-7	hd	1,859	2,024	1,909	1,991	1,946	1,800
	sd	624	617	852		698	552
3-8	hd	1,688	1,810	1,844		1,781	1,635
	sd	604	575			590	444
3-10	hd	966				966	820
	sd	508				508	362
3F2	fd	1,103				1,103	957
3F3	fd	237				237	91
3F4	fd	768	729			479	603
Run No. 3							
WL-init	gear						
	up	62,567	51,242			56,905	56,759
WL-1	dn	11,235	11,815	14,479	11,288	12,204	12,058
	up	53,014				53,014	52,868
WL-2	dn	12,945				12,945	12,799
	up	61,611				61,611	61,465
WL-3	dn	11,488				11,488	11,342
	up	60,102				60,102	59,956
WL-4	dn	10,038				10,038	9,892
	up	60,560				60,560	60,414
WL-5	dn	8,863				8,863	8,717
	up	57,356	60,688	61,304	63,522	60,718	60,572
WLF-1	dn	8,884				8,884	8,738
	fd	8,749	8,950	8,757		8,819	8,673
Disassembled WLHOUSING	up	56,282	53,456	58,808		56,182	56,036
	dn	9,750				9,750	9,604
WLF-2	fd	18,084	18,144	18,676		18,301	18,155
WL-6	up	45,576	48,366	52,710		48,884	48,738
	dn	8,797	7,204			8,001	7,855
WLF-3	fd	2,345				2,345	2,199

^ahd = head down.^bsd = screw down.^cfd = face down.^dfu = face up.

Table A.3. Comparison of probe readings for sample WTA-6
through a plastic bag and through a petrie dish

Specimen ID	Net probe reading (cpm)		Orientation	Ratio	Ratio approximation
	Through bag	Through petrie dish			
6-1		104	Not known		
6-2		28	Screw down		
6-3		11	Screw down		
6-4		85	Head down		
6-4		42	Screw down		
6-5	1069	84	Head down	12.7:1.0	10:1
6-5	226	32	Screw down	7.1:1.0	10:1
3F1-1	4928	1312	Face down	3.8:1.0	4:1
3-7	1733	478	Head down	3.6:1.0	4:1

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