

## AQUEOUS CLEANING AND VALIDATION FOR SPACE SHUTTLE PROPULSION HARDWARE AT THE WHITE SANDS TEST FACILITY

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### INTRODUCTION

The NASA White Sands Test Facility (WSTF) has developed an entirely aqueous final cleaning and verification process to replace the current chlorofluorocarbon (CFC) 113 based process. This process has been accepted for final cleaning and cleanliness verification of WSTF ground support equipment. The aqueous process relies on ultrapure\*\* water at 50 °C (323 K) and ultrasonic agitation for removal of organic compounds and particulate. The cleanliness is verified by determining the total organic carbon (TOC) content and filtration with particulate counting. The effectiveness of the aqueous methods for detecting hydrocarbon contamination and particulate was compared to the accepted CFC 113 sampling procedures. Testing with known contaminants, such as hydraulic fluid and cutting and lubricating oils, to establish a correlation between aqueous TOC and CFC 113 nonvolatile residue (NVR) was performed. Particulate sampling on cleaned batches of hardware that were randomly separated and sampled by the two methods was performed.

This paper presents the approach and results, and discusses the issues in establishing the equivalence of aqueous sampling to CFC 113 sampling, while describing the approach for implementing aqueous techniques on Space Shuttle Propulsion hardware.

### BACKGROUND

The application of aqueous cleanliness verification is based on a Kennedy Space Center developed procedure, which has been adopted as ASTM method 131-96,<sup>1</sup> and the method for sampling for residual organics is based on ASTM method G-144-96.<sup>2</sup> In the cleaning verification procedure, parts are sampled in 50 °C (323 K) ultrapure water using a 25-kHz, 1000-W ultrasonic bath. The organic content of this water is then determined using a high temperature, catalytic combustion TOC analyzer. The particulate is determined by filtration and counting the particulate on the filter as a function of size.

Cleaning operations at WSTF encompass support for materials, components, propulsion test systems, and a large Shuttle depot activity. As part of these operations, components and piece parts are cleaned for a variety of services including oxygen, hydrogen, hydrazines, and nitrogen tetroxide. The majority of the parts is constructed of stainless steel and is resistant to corrosion in aqueous media. Cleanliness levels to 50A are required for high pressure oxygen service. For precision cleaned parts, the standard cleaning process consists of two major elements: precleaning and final cleaning, and cleanliness verification. The precleaning process is shown in Fig. 1. Parts are first inspected, and any gross contamination is removed. For stainless steel parts, the cleaning consists of an alkaline cleaner with ultrasonic agitation, rinse, a phosphoric acid cleaner with ultrasonic agitation, rinse, and then drying in a HEPA-filtered oven. Following drying, the parts are visually inspected, and if passed, are transferred to the Class 100 clean room. The accepted CFC-based final cleaning, shown in Fig. 2, is a CFC 113 rinse, followed by a final rinse of 100 mL per 0.1 m<sup>2</sup> (1 ft<sup>2</sup>) of surface. The rinse is then collected for filtering and NVR. The results

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\*\* Ultrapure water defined having resistivity of 12.5 to 18 MOhm.

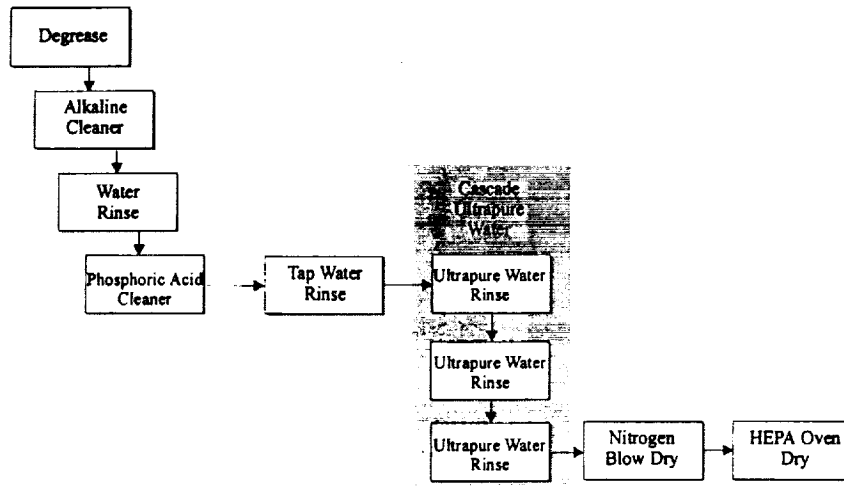


Fig. 1. Standard Precleaning Process

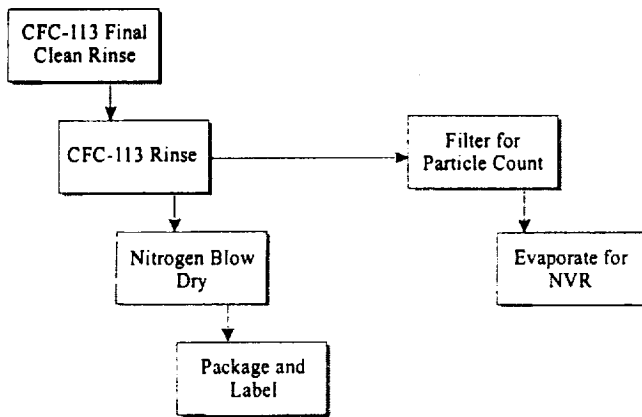


Fig. 2. CFC Final Cleaning and Verification Process

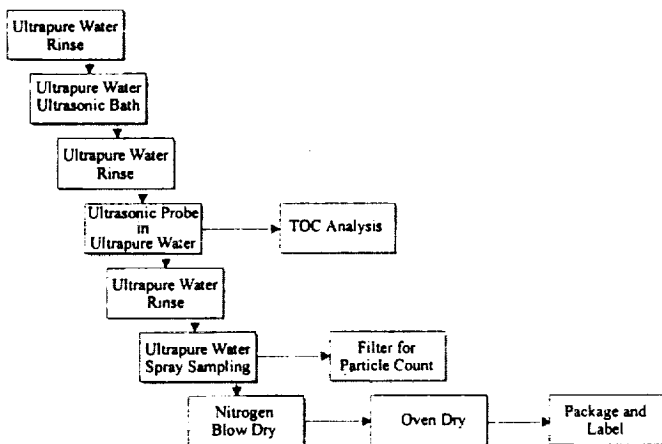


Fig. 3. Aqueous Final Cleaning and Verification Process

of the NVR and particulate sampling are expressed in *passing levels* defined in the cleaning specifications, such as JHB 5322.<sup>3</sup> For NVR, the levels are <1, <2, <3, and <4 mg/ft<sup>2</sup> of sampled surface area and are designated A, B, C, and D, respectively. Particulate levels are usually defined by the largest particle acceptable, 50, 100, 200, 300, and 400 $\mu$  per 0.1 m<sup>2</sup> (1 ft<sup>2</sup>) of sampled surface area. The proposed aqueous final cleaning and verification process is shown in Fig. 3. The final cleaning procedure consists of a rinse with filtered hot ultrapure water, agitation with ultrapure water in a 1000-W ultrasonic bath, followed by final rinse. Cleanliness verification consists of a 1.27-cm (0.5-in.) tip ultrasonic probe delivering approximately 600 W of power into the sampling container for a total of 30 seconds. A small aliquot of the solution is then removed for sampling by TOC, and the remainder of the water is filtered for the particle count. The use of the ultrasonic probe allows a higher ultrasonic energy density in the sampling container. This aqueous process is directed at piece parts which are not corrosion or ultrasonic sensitive, and do not have small passages or entrapment spaces.

## APPROACH

The testing used to certify the aqueous alternative to CFC 113 sampling was divided into three phases: development, batch parts sampling, and process validation. In the development phase, equipment and procedures were tested to determine the most promising method of aqueous cleanliness verification. Development testing was also performed to determine that there was a relationship between the contaminant levels and the sampling response. The batch parts sampling was aimed at assessing the efficiency of contaminant removal, both organic and particulate, compared to CFC 113. More extensive batch parts sampling tests were then conducted to compare the efficiency of removal of contaminants. The batch parts sampling was performed only to establish the efficiency of the cleanliness verification and did not include the final cleaning step. CFC 113 was used as the standard against which the results were compared. Process validation was performed to determine the reliability of the process.

### ORGANIC CARBON METHODS

In the development testing, numbered stainless-steel and -aluminum plates, 5 X 7.6 cm (2 X 3 in.) were used. These plates were fabricated according to ASTM-G121.<sup>4</sup> A representative plate is shown in Fig. 4. A tare weight on each plate was obtained and either single contaminants or contaminant mixtures in a CFC 113 carrier contaminated the plate. These contaminants were representative of the types of contaminants encountered in WSTF cleaning operations. The plates were re-weighed; to determine the contaminant loading, then sampled using the aqueous process. The results of the TOC analysis were compared with the original contaminant loading to determine percent recovery for each of the contaminants. These tests were performed over a range of contaminant loading, and a slope of the fitted data determined the efficiency of recovery.

In batch sampling, representative batches of fittings numbering between 10 and 30 parts were contaminated by a mixture of compounds in CFC 113, allowed to dry, then divided into two groups at random. An example of these fittings is shown in Fig. 5. One group was sampled by the aqueous method and the other using CFC 113. In both cases, a final cleaning or rinse did not precede the sampling, as is usually the case with CFC 113 cleanliness verification. The TOC response was compared to the CFC 113 NVR. Results were tabulated in the form of JHB-5322 passing levels. Because Krytox<sup>®</sup> is often used as a thread lubricant in the assembly of systems, it was treated separately from the other contaminants.

### PARTICULATE COUNTING METHODS

Because of the difficulty of uniformly contaminating plates or a batch of parts at a low enough particulate level, cleaned batches of parts were used for the particulate studies. The particulate contamination on these parts was due to residual particles that were not removed during the cleaning process.

The development testing and the batch sampling for the particulate consisted of cleaning batches of fittings numbering between 10-30 parts and separating them into two groups at random. One group was sampled by the aqueous method and was followed by filtering to collect the particles. The other group used CFC 113 with the standard filtering technique. In both cases, a final cleaning or rinse did not precede the sampling, as is usually the case with CFC 113 cleanliness verification. The total number of particles on the filter was counted according to size. The passing levels for the aqueous and CFC 113 sample pairs were tabulated using JHB-5322 passing levels.

### ORGANIC AND PARTICULATE PROCESS TESTING

Process testing was performed on actual hardware. The aqueous method, which included an aqueous ultrasonic final cleaning step, was followed by the accepted CFC 113 method. Particulate and NVR passing levels were recorded for each batch. This sequential sampling was performed to assess the possibility of obtaining a passing level with the aqueous method followed by a failure with the CFC 113 method. The viability of this technique in a production environment was also evaluated in terms of throughput and recleaning required due to excessive failures. A wider variety of parts were sampled in this testing and included disassembled valves and filters as well as fittings and short lengths of tubing. An example of a disassembled filter assembly is shown in Fig. 6.

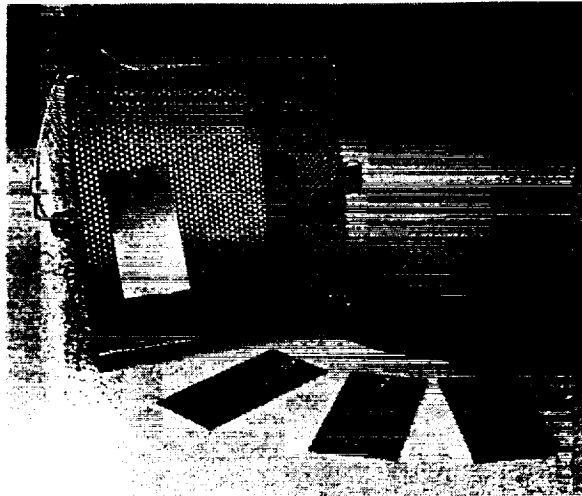


Fig. 4. Representative Plates

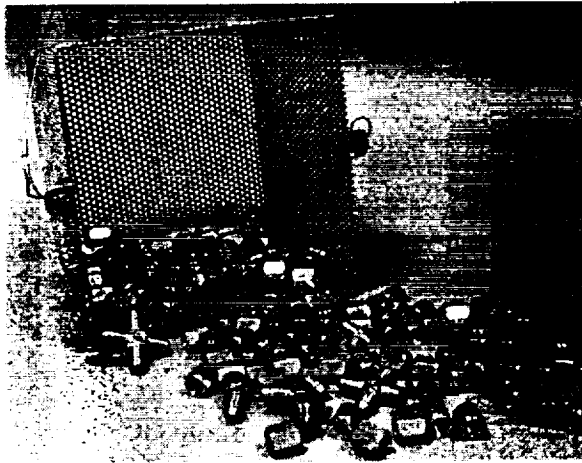


Fig. 5. Example of Fittings

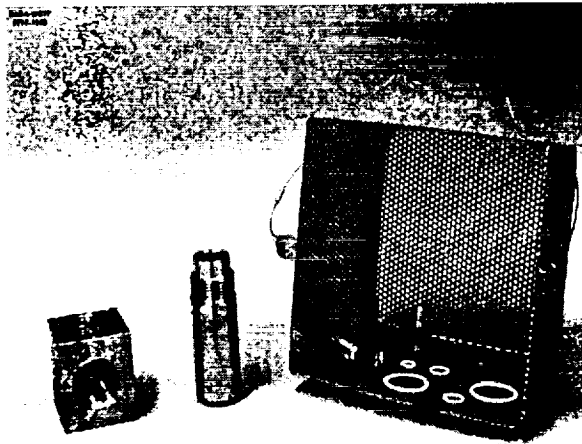


Fig. 6. Disassembled Filter Element

## RESULTS

### ORGANIC CARBON METHODS - DEVELOPMENT TESTING

Tare weights were obtained on numbered stainless-steel plates 5 by 7.6 cm (2 by 3 in.). A contaminant mixture consisting of 0.5 grams of each contaminant, including hydraulic, vacuum pump, lubricating, and cutting oil were dispersed in 200 mL of CFC 113. Approximately 0.25 mL of this contaminant mixture was placed on each plate and allowed to air dry. The mass of the plate plus the contaminant was determined. For higher contaminant levels, this procedure was repeated several times. Before each sampling, the TOC was determined on the water to serve as a blank or reference.

The coupon was placed in a 600-mL beaker and covered with 400 mL of ultrapure water at 50 °C (323 K). The coupon was agitated ultrasonically for 1 minute with 0.3-second pulses for a total ultrasonic exposure time of 30 seconds. A gastight syringe was used to remove 250 µL of the water, which was injected into the TOC analyzer. From the measured concentration, the mass removed by this technique was calculated. The results of this testing is represented by a graph in Fig. 7. This initial testing showed a good correlation with a slope of approximately 0.65. This slope indicates there is a linear increase in the TOC response with the contaminant mass.

To assess the recovery of Krytox<sup>®</sup> by the aqueous method, approximately 2 mg was deposited on the coupon directly from the tube and sampled as previously described. No TOC response could be found in this case. However, Krytox<sup>®</sup> was detected in the form of particles when the water was filtered. Further work on the sampling for Krytox<sup>®</sup> was done from this particle count data. An example of Krytox<sup>®</sup> particles detected by aqueous ultrasonic sampling is shown in Fig. 8.

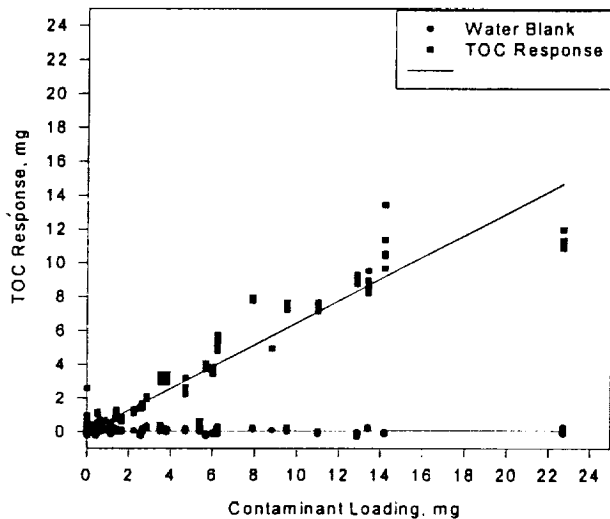


Fig. 7. Recovery of Organic Contaminants

### ORGANIC BATCH TESTING

The batches of parts, primarily fittings, numbering at least 10-30 pieces were contaminated using the same solution as in the development testing. These were then dried, and the batch was split into two groups at random. One group was added to a 600-mL beaker, covered with 400 mL of 50 °C (323 K) ultrapure water and ultrasonicated for 60 seconds. 250 µL was then removed for TOC analysis. The second group was sampled using the standard CFC 113 rinse with 100 mL from which the nonvolatile residue was obtained in mg. The equivalent TOC was calculated from the concentration obtained from the TOC by the following equation:

$$\text{Equivalent TOC (mg)} = C(\text{ppm}) * V(L)/S(\text{mg CFC/mg TOC}) \quad (1)$$

where

- C = the concentration obtained from the TOC
- V = the volume of ultrapure water used in liters, and
- S = the experimentally determined sensitivity factor

The sensitivity factor was obtained in this case by plotting the milligram response (ppm by volume) of the TOC versus the results obtained from the NVR to determine the slope of the line.

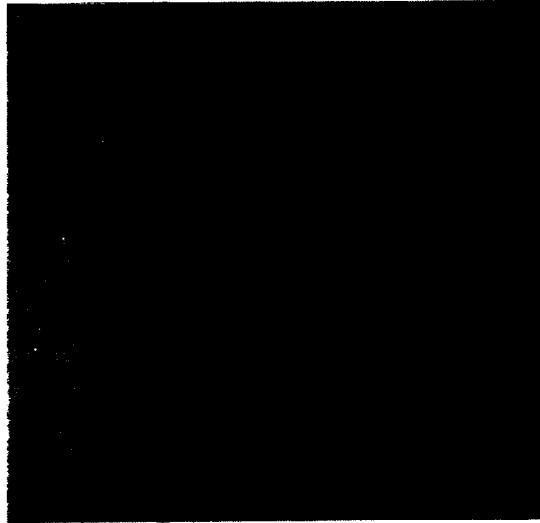


Fig. 8. Example of Krytox<sup>®</sup> Particles

From the batch testing, a sensitivity factor of 0.4 was determined and applied in all subsequent tests. To compare the NVR and TOC sampling methods, the results were distributed into the discreet, integer passing levels used in the cleaning specifications. For example, a result of 1.4 mg would pass a 2 mg or *B* level; a result of 0.8 mg would pass a 1 mg or *A* level. A *figure of merit*,  $\Delta W$ , which expresses the relative efficiency of the two sampling techniques was also calculated by subtracting the CFC 113 passing level from the aqueous passing level. When  $\Delta W$  is zero, the results of the two sampling techniques are equal. When  $\Delta W$  is negative, the CFC 113 showed more contamination on the parts. When  $\Delta W$  is positive, the aqueous method showed more contamination on the parts.

The number of observations of each result was then tabulated to give a distribution of the number of observations for each value of  $\Delta W$ . In Fig. 9,  $\Delta W$  is plotted versus number of observations. The mean or average passing level is 1.2  $\Delta W$ , and is on the side of the distribution where the aqueous technique is more effective. The mode, or most likely occurring value of  $\Delta W$  is zero, where the two techniques yield equal results. The median  $\Delta W$ , the value with equal numbers of observations above and below, is 1, is also on the side of the distribution where the aqueous technique is more effective. From this set of data, the aqueous ultrasonic sampling is equal to or more effective than CFC 113 and samples 91 percent of the time in detecting residual contamination.

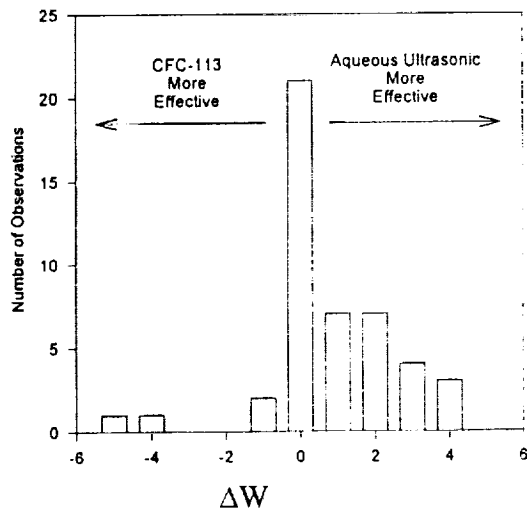


Fig. 9. Distribution of  $\Delta W$  for Organic Passing Levels on Batch Parts

### PARTICULATE BATCH TESTING

The batches of parts (primarily of at least 10-30 pieces or fittings) were precleaned and transferred to the Class 100 clean room where the batch was split into two groups at random. One group was then added to a 600-mL beaker, covered with 400 mL of 50 °C (323 K) ultrapure water, and ultrasonicated for 60 seconds. All of the 400 mL was filtered, and the total number of particles on the filter was counted. The second group was sampled using a rinse of 100 mL of CFC 113, which was then filtered. The total number of particles on the filter was counted as a function of size. Using the passing levels from the cleanliness specification, the aqueous and CFC 113 particle counts were then assigned the appropriate passing level.

A *figure of merit*,  $\Delta P$ , which expresses the relative efficiency of the two sampling techniques was also calculated by subtracting the CFC 113 passing level from the aqueous passing level. When  $\Delta P$  is 0, the results of the two sampling techniques are equal. When  $\Delta P$  is negative, the CFC 113 detected a higher particulate level on the parts. When  $\Delta P$  is positive, the aqueous method detected a higher particulate level on the parts. The number of observations of each result was then tabulated to give a distribution of the number of observations for each value of  $\Delta P$ . In Fig. 10,  $\Delta P$  is plotted versus number of observations. The average  $\Delta P$  is 53 and is on the side of the distribution where the aqueous technique is more effective. The mode, or most likely occurring value of  $\Delta P$  is zero, where the two techniques yield equal results, and the median  $\Delta P$  with equal numbers of observations above and below is also 0. From the tabulated data, the aqueous sampling for particulate is equal to or more effective than the CFC 113 and samples 73 percent of the time.

### KRYTOX® BATCH TESTING

The studies and experience gained at WSTF indicate through the CFC 113 cleanliness verification and the aqueous ultrasonic sampling that Krytox® is detected in the particulate count rather than the NVR. To assess the effectiveness of the aqueous technique in detecting Krytox® by particle count, six batches of four threaded fittings were contaminated by a heavy application and distribution of Krytox® grease over the threads. These batches were cleaned using the precleaning process. Following precleaning and inspection, three batches were sampled aqueously without the final cleaning step; and CFC 113, without the final cleaning step, sampled three batches. Out of the three batches, aqueous sampling detected Krytox® in one batch of fittings, and CFC 113 detected Krytox® in two batches of fittings. The CFC 113 sampled batches all passed a level A, or 1.0 mg NVR. To relate this particulate detection of Krytox® to a comparable number for NVR, a calculation was performed to determine the mass, which would result from a particulate passing level if all the allowed particulate were Krytox®. As shown in Table 1, a sample passing the 200 level with the maximum allowable number of Krytox® particles would have less than 0.90 mg of Krytox® present. This represents the *worst case* NVR equivalent of a Krytox® particle count.

#### Process Testing

In this phase of testing, batches of hardware were final cleaned and sampled using aqueous methods, and then final cleaned and sampled using CFC 113 methods. To accomplish this, the glass beakers for the ultrasonic sampling were replaced with a metal container along with an internal basket. The metal container and basket generated particulate during the ultrasonic exposure.

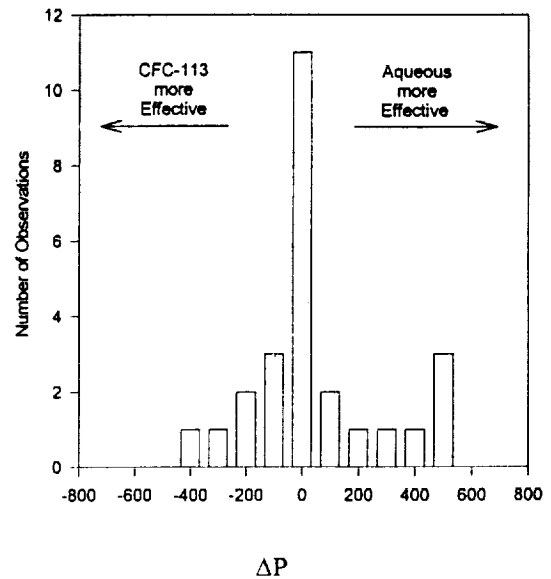


Fig. 10. Distribution of  $\Delta P$  for Particulate Passing Levels on Batch Parts

Table 1. Worst Case NVR Equivalent

Specification Passing Level	Mass Equivalent as Krytox® (mg)
300	1.62
200	0.90
100	0.10
50	0.01

The process was changed to use a rinse of 50 °C (323 K) water for the particulate sampling. The sampling for organics was unchanged from that used for the batch testing. The passing levels were compared for both particulate and organic recovery. Out of a total of 300 trials, the aqueous ultrasonic with TOC detection registered five failures and CFC 113 NVR gave no failures at the A passing level. For particulate counts, the figure of merit  $\Delta P$ , was applied to 92 sampling runs. The results are tabulated in Fig. 11 where  $\Delta P$  is plotted versus number of observations of each value of  $\Delta P$ . The mode, or most likely occurring value of  $\Delta P$  is 0, where the two techniques yield equal results. The average  $\Delta P$  is 32, and the median value of  $\Delta P$  with equal numbers of observations above and below is zero. Based on this testing, this process has been accepted for final cleaning and cleanliness verification of WSTF ground support equipment.

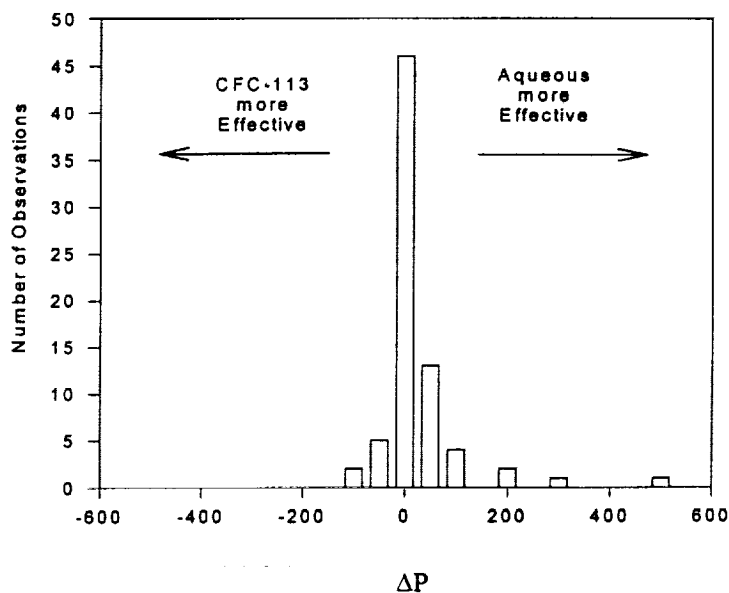


Fig. 11. Distribution of  $\Delta P$  for Particulate Process Testing

#### AQUEOUS CLEANING FOR PROPULSION HARDWARE

CFC replacement is a critical issue for Space Shuttle Propulsion hardware. Adaptation of a new process required a clear technical approach to the selection of alternative verification methods. This technical approach consisted of a part-by-part analysis with consideration given to configuration, materials, and types of contaminants.

Part configurations were considered critical, especially evaluating any potential entrapment areas where drying processes may not be effective. Since most of the flight hardware repair work involves total unit disassembly, down to its piece-part level, the part configurations during cleaning are generally very simple. Therefore, piece-part configurations were perfect candidates for using the water-verification process. In addition, where there were potential ultrasonic damage concerns, either testing was performed to verify that there were no harmful effects or the configuration in question was deemed to be suitable for a solvent verification. Examples of this include filter assemblies and anodized parts.

The part material was also a consideration. All soft goods were cleanliness verified using solvents. Although many soft goods could have been cleaned and verified aqueously, many have questionable aqueous verification applications. The aqueous verification method was also discarded where there were corrosion concerns, specifically when drying methods were in question. Materials such as 400-series stainless or titanium are specific examples of materials that will not be verified aqueously.

The final evaluation criteria dealt with the types of contaminants likely to be found on the Shuttle. Most of the flight hardware requiring cleaning at WSTF is exposed to nitrogen tetroxide or monomethylhydrazine propellants or their combustion products. All of these contaminants are soluble in water, and therefore the water cleaning and verification method is effective. The other main types of contaminants are assembly lubricants, such as fluorocarbon grease. The WSTF data indicate that aqueous verification methods are effective at verifying the presence of this class of contaminants.



## CONCLUSIONS

These results apply to piece parts which were primarily stainless steel and resistant to corrosion in aqueous media. Contaminants used in this study were representative of those encountered at WSTF. The following conclusions are made:

- Aqueous ultrasonic cleanliness verification does not increase the risk of passing a contaminated part over the current CFC 113 cleanliness verification technique.
- The use of the aqueous ultrasonic sampling with TOC detection as a substitute for the CFC 113 NVR is effective and was found to be more conservative than CFC 113.
- The use of aqueous ultrasonic sampling followed by rinse sampling for particulate is effective and was shown to be equivalent to CFC 113 particulate sampling.
- Detection of Krytox<sup>®</sup> is by particulate count and is conservative for particulate levels below level 200.
- Aqueous methods are applicable to propulsion type hardware, although, rigorous engineering evaluations including configuration, material, and contaminant reviews, must be thoroughly documented especially when changing certified processes.

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