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Investigative Report

Improved Detection Technique For Solvent Rinse Cleanliness Verification

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Amflo® is a registered trademark of Schrader-Bridgeport International, Inc., Muskogie, OK.

DC 190® is a registered trademark of Dow Corning, Midland, MI.

Duo Seal® is a registered trademark of Welch Vacuum Technology, Inc., Skokie, IL.

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1.0 Introduction

The NASA White Sands Test Facility (WSTF) has an ongoing effort to reduce or eliminate usage of cleaning solvents such as CFC-113 and its replacements. These solvents are used in the final clean and cleanliness verification processes for flight and ground support hardware, especially for oxygen systems where organic contaminants can pose an ignition hazard. For the final cleanliness verification in the standard process, the equivalent of one square foot of surface area of parts is rinsed with the solvent, and the final 100 mL of the rinse is captured. The amount of nonvolatile residue (NVR) in the solvent is determined by weight after the evaporation of the solvent. An improved process of sampling this rinse, developed at WSTF, requires evaporation of less than 2 mL of the solvent to make the cleanliness verification. Small amounts of the solvent are evaporated in a clean stainless steel cup, and the cleanliness of the stainless steel cup is measured using a commercially available surface quality monitor.

The effectiveness of this new cleanliness verification technique was compared to the accepted NVR sampling procedures. Testing with known contaminants in solution, such as hydraulic fluid, fluorinated lubricants, and cutting and lubricating oils, was performed to establish a correlation between amount in solution and the process response. This report presents the approach and results and discusses the issues in establishing the surface quality monitor-based cleanliness verification.

2.0 Background

Cleaning operations at WSTF encompass support for materials, components, propulsion test systems, and a sizeable 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. Most of these parts are constructed of stainless steel and are resistant to corrosion in aqueous media. For precision cleaned parts, the standard cleaning process consists of two major elements: an aqueous precleaning process and a solvent-based final cleaning and cleanliness verification. Cleanlinesss levels are specified by a number that has an associated number of particles at this maximum size in micrometers followed by a letter to specify the maximum residue allowed on 1 ft^2 of surface area. The letters A, B, C, and D refer to 1, 2, 3, and 4 mg of residue, respectively. Cleanliness levels to 50A are required for high-pressure oxygen service. Following the aqueous precleaning, the parts are dried, visually inspected, and if passed, are transferred to the Class 100 clean room. The accepted process for solvent-based final cleaning are rinsed with HFE 7100 in the vapor degreaser followed immediately by a sampling rinse of approximately 100 mL/ft^2 of component surface area. This rinse is then filtered for a particulate count and then submitted for NVR determination. The components are then blown dry with nitrogen, packaged, and labeled for use.

Figure 2 shows the steps in obtaining the NVR from the solvent rinse. First the solvent is transferred to a boiling flask, and the volume of the solvent is reduced to 10 to 15 mL by distillation. The solvent trapped in the distillation by a condenser is recycled the remaining 10 to 15 mL is transferred to a tared weighing pan and placed in a 100° C oven for 30 min. to complete the drying. The weighing pan is allowed to cool in a desiccator before weighing again to determine the NVR. For HFE 7100, the process takes approximately 40 min. It should also be noted that some of the more volatile contaminants could be volatilized, especially during the 30 min drying in the oven. Light hydrocarbons can show 40% per NVR recovery or less from spiked solvent samples.

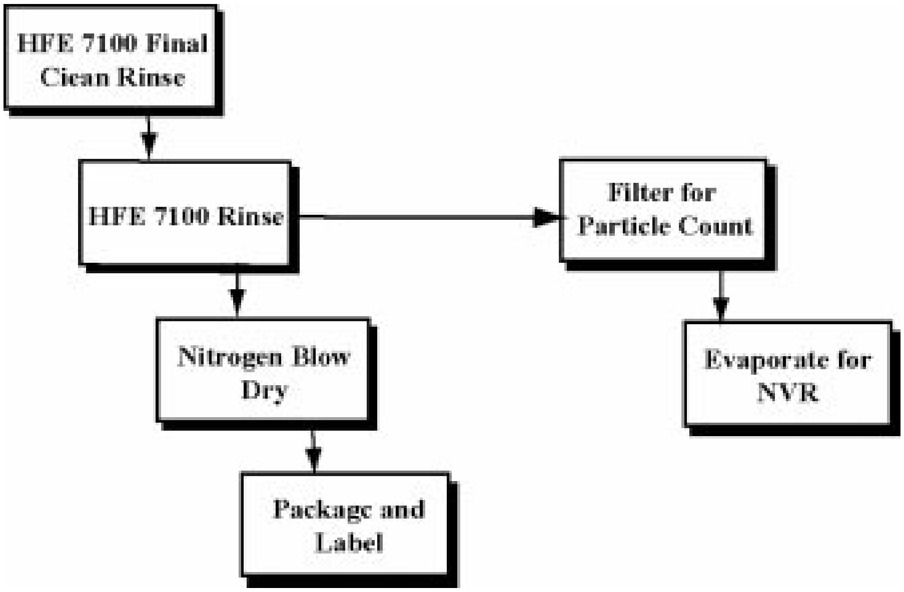


Figure 1
Solvent Final Cleaning and Verification Process

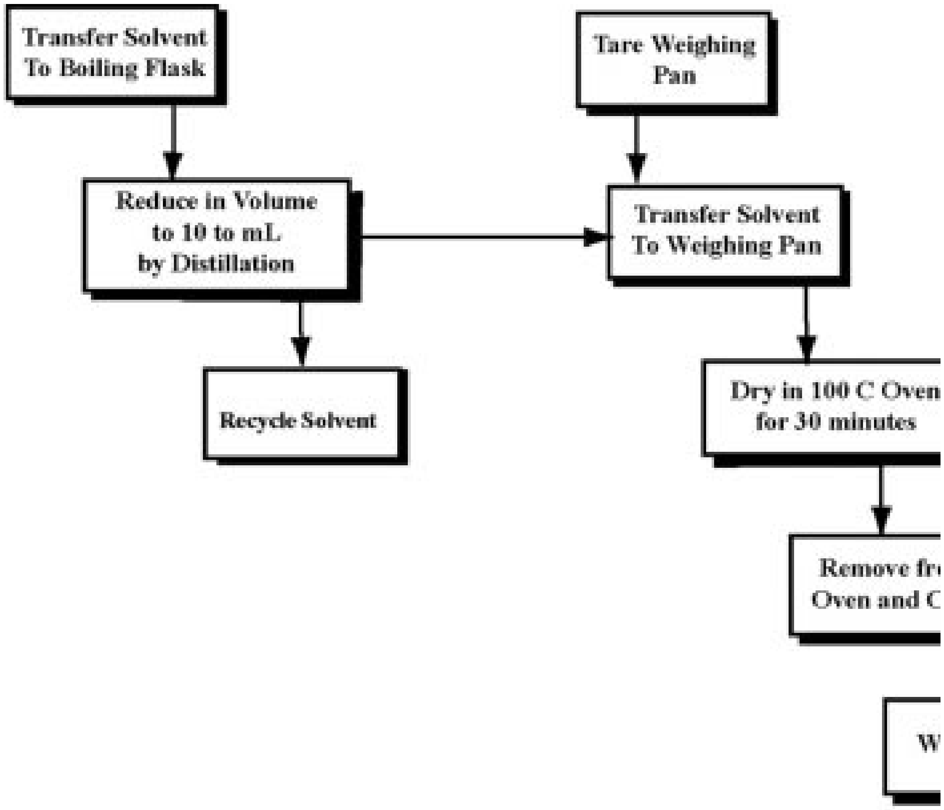


Figure 2
NVR Process for Cleanliness Verification

An improved cleanliness verification process that replaced the current NVR procedure makes use of a commercially available surface quality monitor. This monitor measures the photocurrent produced from a sample when it is exposed to ultraviolet light. The photocurrent magnitude depends on surface characteristics. A clean metal surface will give a high photocurrent while an organic compound will give a much lower photocurrent or photoelectron yield. For example, a clean stainless steel surface will give up to 10 times the photocurrent of an organic compound. And because photoelectrons can escape from only the top few atomic layers, this measurement technique is very sensitive to thin layers of organic contaminants on metals. A photograph of the surface quality monitor (SQM) is shown in Figure 3.

3.0 Approach

The testing used to certify the SQM cleanliness verification process was divided into two phases: proof-of-concept testing and process validation. In the proof-of-concept phase, the feasibility of the technique was evaluated, and variables such as aliquot size, evaporation temperature, and distance from the probe were investigated to determine the optimum setting for a production test. Several different contaminants were also tested with concentrations ranging from 0.5 to 2 mg per 100 mL of solvent to determine the sensitivity and detection limit of the technique. These 100 mL solutions are analogous to the 100mL solvent verification rinse, and it is assumed that all contaminant on a surface would be taken into solution by the solvent rinse. These solutions were mixed well upon preparation and were assumed to be a true solution rather than an emulsion. No homogenization of the solution was made before sampling with the SQM.

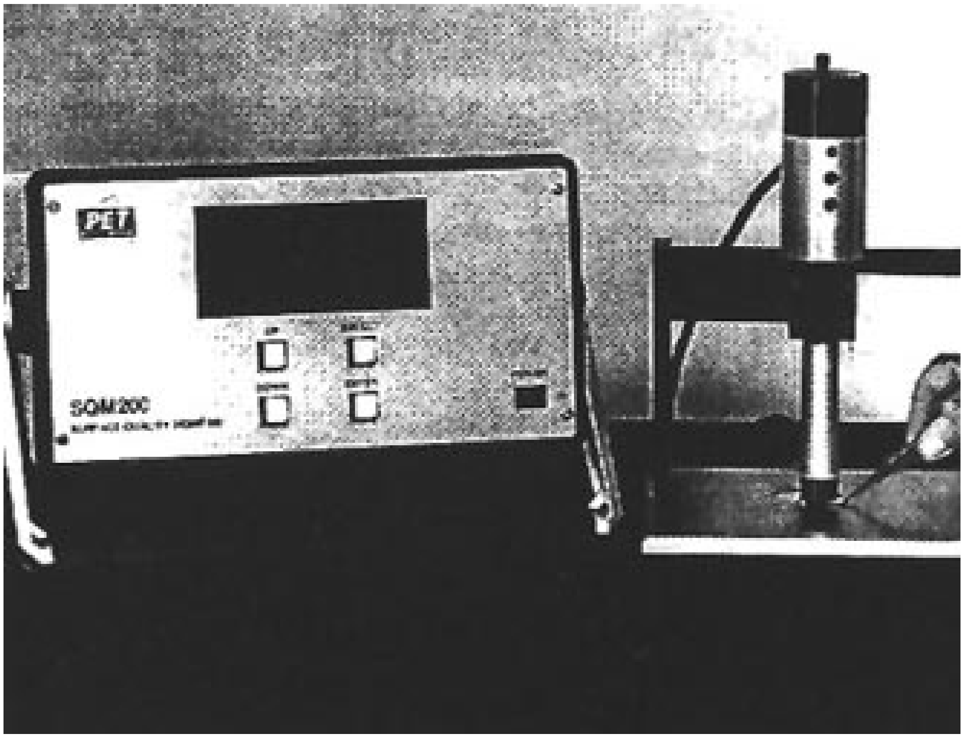


Figure 3
SQM 200 Surface Quality Monitor

Process validation was performed to determine the reliability of the process on a production scale and the frequency of false pass or false failure as compared with the standard HFE 7100 NVR. Sampling was performed on actual cleanliness verification rinses from WSTF cleaning processes. In this parallel sampling, 2.2 mL of the 100 mL for the standard HFE 7100 NVR was removed for testing with the SQM-based technique, and the remainder was evaporated by the standard NVR technique. In addition, 40 samples of HFE 7100, spiked with selected contaminants at concentrations ranging from 0.25 to 2.0 mg/100mL, were submitted for parallel sampling. Results from the SQM-based cleanliness verification were compared with the results from the standard NVR method.

3.1 Proof-of-Concept Testing

Proof-of-concept testing was performed to determine the response of the technique to varying levels of contaminants dissolved in HFE 7100. Test solutions were prepared by dissolving 2 mg of Krytox 240 AC or Duo Seal oil contaminant in 100 mL of HFE 7100. At least 10 tests were performed for each contaminant and concentration. First, the photocurrent was measured from clean cup; a reading of at least 400 was required before the test could proceed. Using the same cup, a 0.3 mL aliquot of the contaminated solvent was placed in the cup. The cup was then heated to 40° C on a hot plate until the solvent evaporated, approximately 1 min. After the cup was allowed to cool for 3 to 5 s, another measurement was taken. This process was repeated for a total 5 doses of the contaminated HFE 7100. An illustrated procedure is shown in Appendix A.

3.2 Process Validation

Process validation was performed in parallel with the standard HFE 7100 NVR technique. The parallel sampling included 74 work orders sampled over a period of two months. When solvent rinses were submitted for the NVR determination, four doses of 0.5 mL were removed for sampling by the SQM method. The remainder of the solvent was processed by the standard NVR method.

In order to obtain a statistically significant number of samplings that produce an NVR in the measurable range, it was necessary to submit solvent samples spiked with contaminants. This was accomplished by spiking the submitted NVR with 5 mL of solvent containing 0.5 mg of a five-component contaminant mix consisting of equal amounts of Krytox, Sebacate, DC 190 silicone oil, hydraulic fluid, and Tap Magic. These were processed in the same way as the other NVR samples.

4.0 Equipment Reagents

The following equipment and reagents were used in this study. Trademark holders are listed on the trademarks page at the front of this document.

- Photoemission Technology, Inc., Model SQM 200 with 0.25-in aperture

- Stainless steel sample cup, 1.9 cm diameter (0.75 in.) with 0.6 cm (0.25 in.) indentation

- 3M Brand HFE 7100

- Contaminants: Tap Magic, DC 190 silicone oil, Duo Seal pump oil, hydraulic fluid, Amflo lubricating oil, Krytox 240AC, and di-2-ethylhexyl sebacate calibration fluid.

5.0 Results and Discussion

5.1 Proof-of-Concept Testing

When HFE 7100 containing Krytox 240 AC at a concentration of 2 mg in 100 mL is used in this process, the plot shown in figure 4 results. This is a Tukey box plot in which the box represents the range of the 25th to 75th percentiles of the data and the 10th and 90th percentiles as error bars. The mean is shown as a horizontal line in the box. The photocurrent values reported are the direct readout from the instrument and are dependent on the gain settings in the instrument. This plot of photocurrent as a function of solvent dosage shows a large initial drop followed by sequentially smaller drops in the photocurrent for a leveling off effect. This is attributed to the coverage of the clean metal surface by the contaminant, which has a lower photoelectron yield than the clean metal. As additional doses of contaminant are added, the photocurrent drops from the high values for clean stainless steel and approaches the photocurrent for a thick film of the contaminant. Table 1 give the measured photocurrent for the very thick films of the contaminants applied to the stainless steel cups. These contaminants have much lower photoelectron yields than does clean stainless steel, making it advantageous for the detection of small amounts of these. Also the photoelectron yields of the contaminants are all of the same order of magnitude, making the technique relatively insensitive to contaminant makeup. Regardless of the contaminant, the photocurrent will follow the same relationship. Figures 5 and 6 show a similar photocurrent versus dose curve for DuoSeal oil and DC 190 silicone oil.

For comparison, results of a set of tests using clean HFE 7100 are shown in Figure 7. This figure shows that the photocurrent drops with each sequential addition of HFE 7100. The means of the distributions show a nearly linear drop in photocurrent with successive solvent doses. This drop is still readily differentiated from those for HFE 7100 containing a contaminant. The mechanism of the photocurrent reduction by the clean solvent is unknown and will require further study.

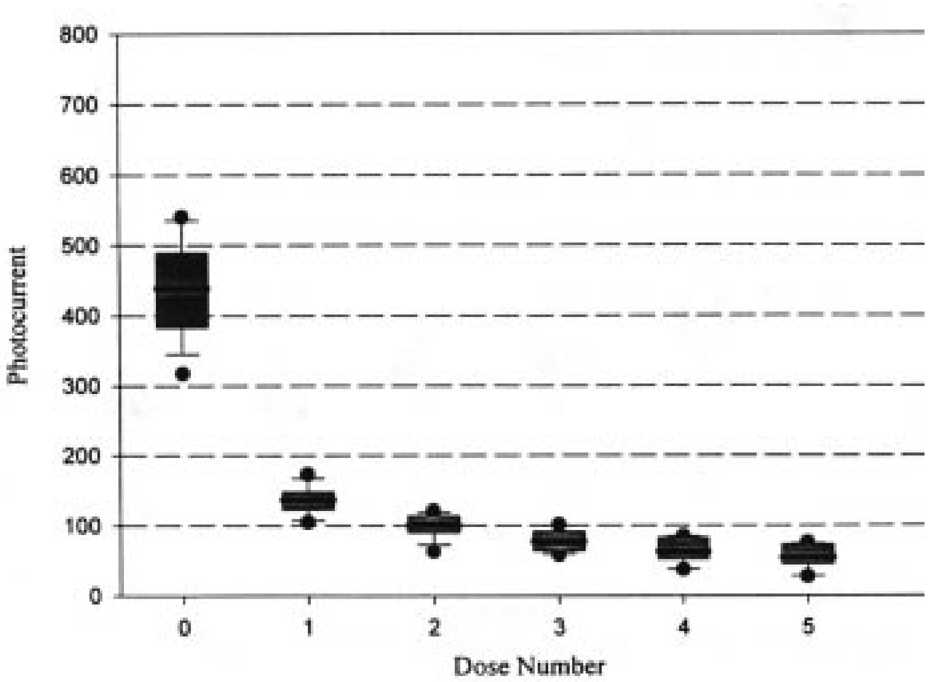


Figure 4
Photocurrent as a Function of Dose with HFE 7100 Containing 2 mg Krytox® in 100 mL

Table 1
Measured Photocurrent for Thick Films

Material	Photocurrent

WSTF Cleaned Stainless Steel 304	>500
Duo Seal®	80
Amflo® Oil	105
DC 190® Silicone Oil	40
Hydraulic Fluid	100
Houghto Draw®	40
Tap Magic®	100
Krytox® 240 AC	60

NOTE: Instrument gain set at 1, probe gain set at 7

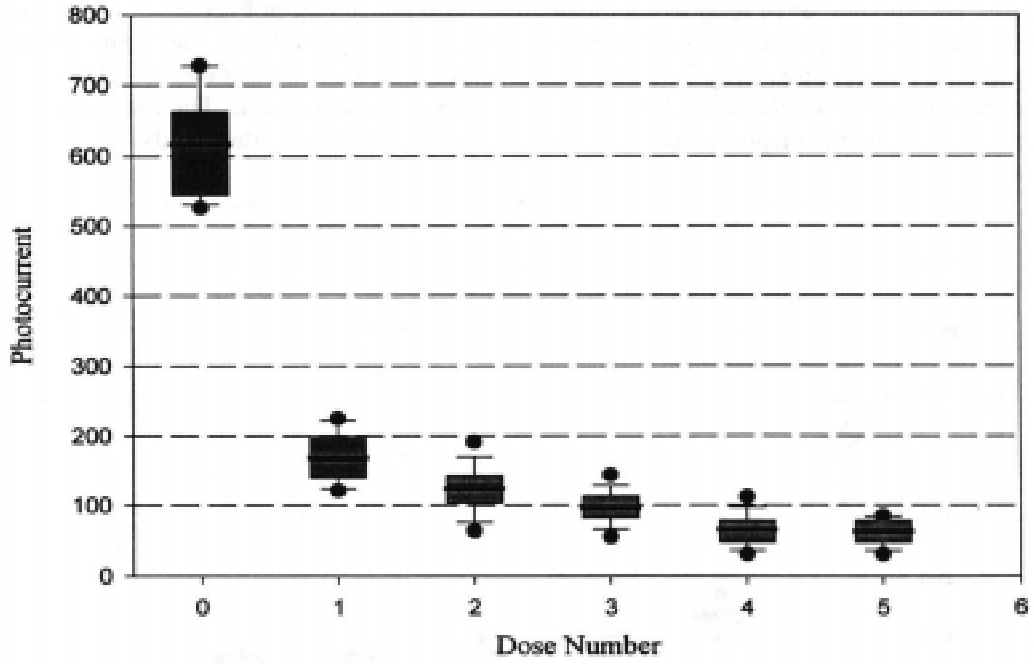


Figure 5
Photocurrent as a Function of dose with HFE 7100 Containing 2 mg Duo Seal® in 100 mL

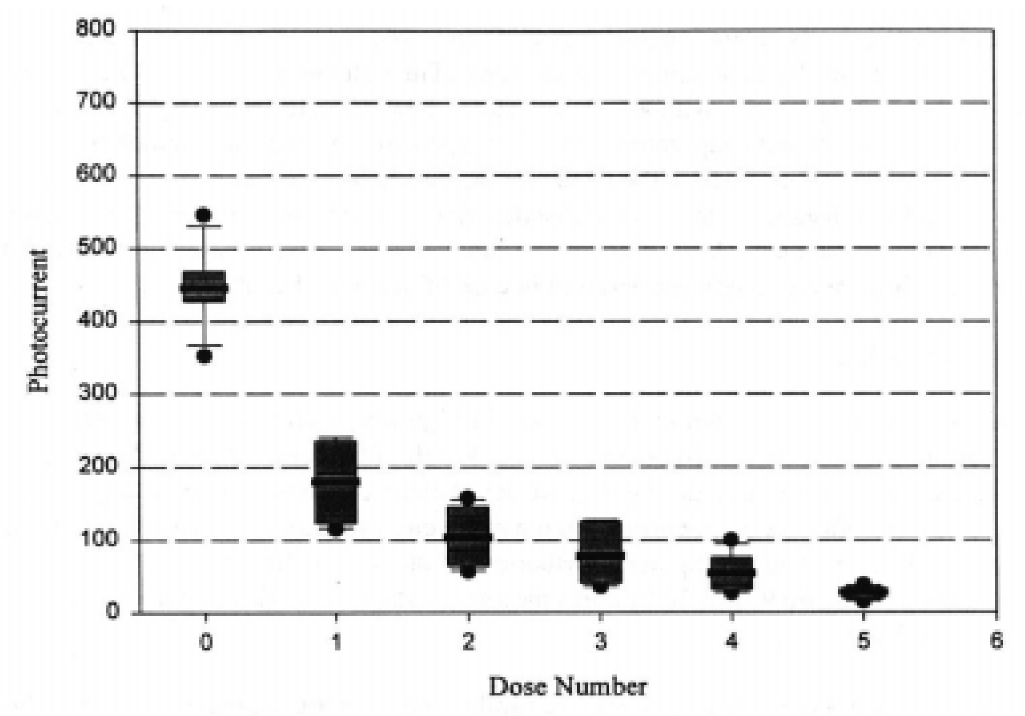


Figure 6
Photocurrent as a Function of Dose for HFE 7100
Containing 1 mg DC 190® Silicone Oil in 100 mL

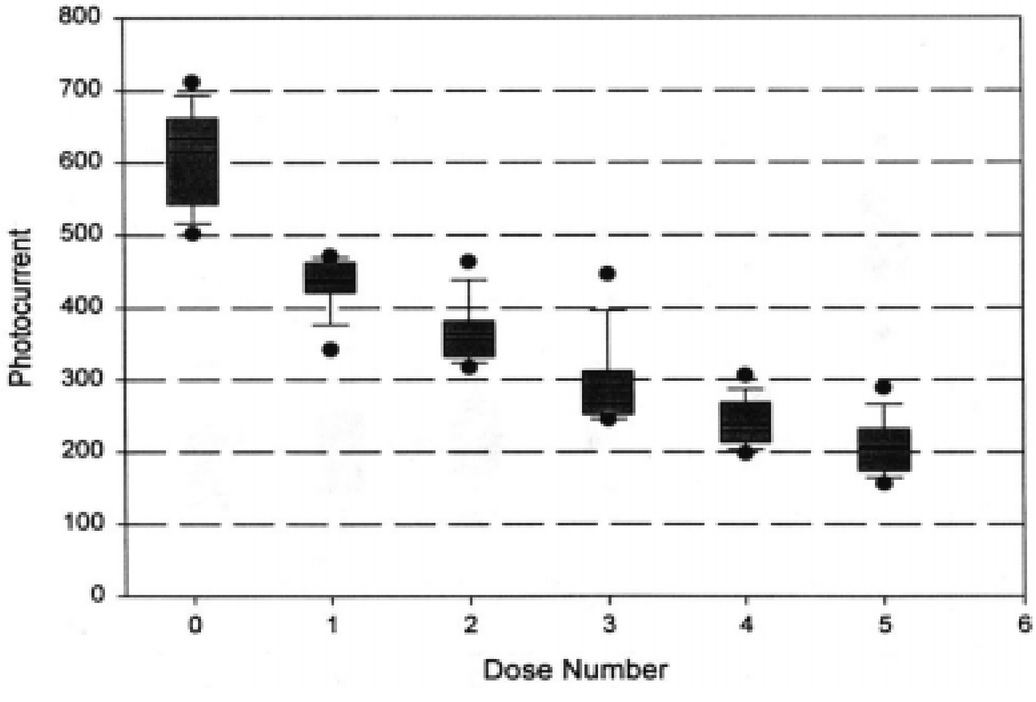


Figure 7
Photocurrent as a Function of Dose with Clean HFE 7100

Using Krytox and Duo Seal oils, operational parameters were optimized to produce the maximum change in signal between the clean cup and the initial dose. The volume and shape of the stainless steel cup was adjusted to hold 0.5 mL with a 0.25 in. central depression to concentrate the solution at the center of the cup as the solvent evaporates. A 0.25 in. aperture was chosen to match the central depression in the stainless steel cup where the contaminant should be concentrated upon solvent evaporation. The working distance is the closest distance that can be achieved given the variation in the height from one cup to the next. A hot plate temperature of 40° C gave acceptable drying times, minimal contaminant loss, and is a safe temperature in case of accidental contact by the operator.

5.2 Process Validation

The process validation results are shown in the box plot in Figure 8. It shows the same behavior as in the Figure 7 results from the proof-of-concept testing. Much of the range (spread, distribution) in the data is due to the variability in photocurrent in the set of clean coupons. For each cup tested, a ratio was obtained by dividing the photocurrent from a clean cup by the photocurrent from the same cup after each dose. This resulted in a tighter distribution of data for the first three doses. The resulting plot is shown in Figure 9. All 74 samples passed the standard NVR cleanliness verification with a residue of less than 0.2 mg.

The results as photocurrent and photocurrent ratio for spiked samples are shown in Figures 10 and 11. Comparing Figures 9 and 11, it is possible to distinguish between clean and spiked solvent with no overlap in the distributions by the second dose of solvent. Based on the need for no more than three doses of solvent to detect contaminants, the improved cleanliness verification process is shown is Figure 12.

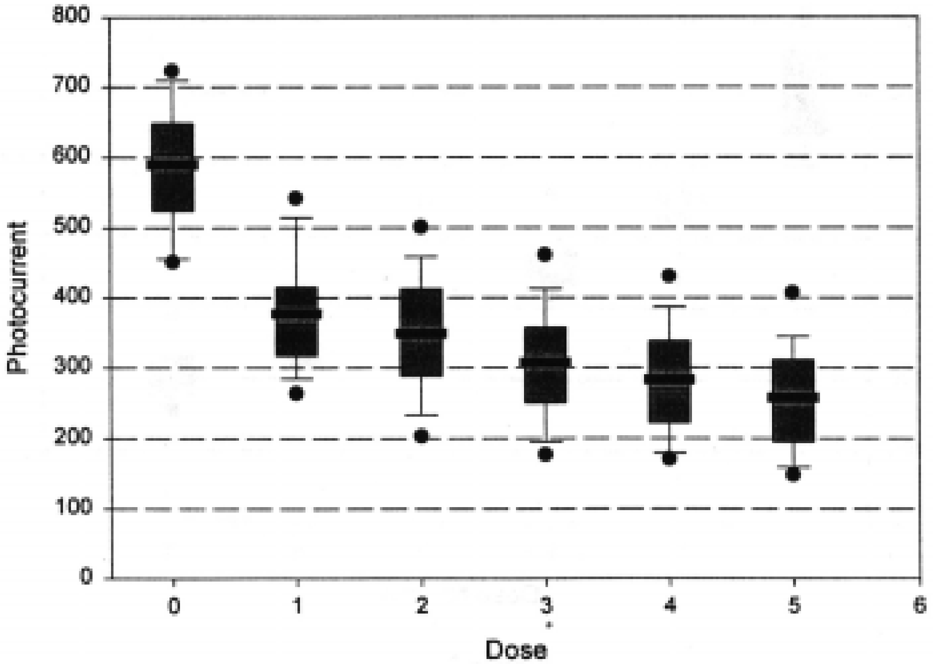


Figure 8
Photocurrent as a Function of dose for Parallel sample Work Orders

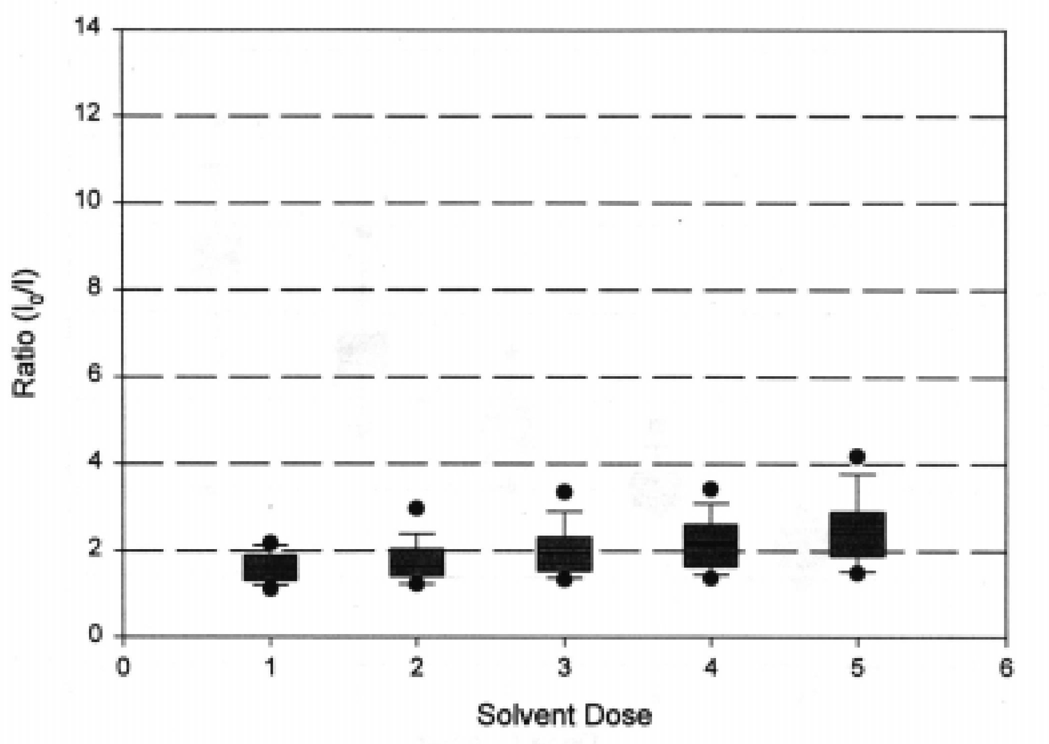


Figure 9
Photocurrent Ratio as a Function of Dose Number for Parallel Sampled Work Orders

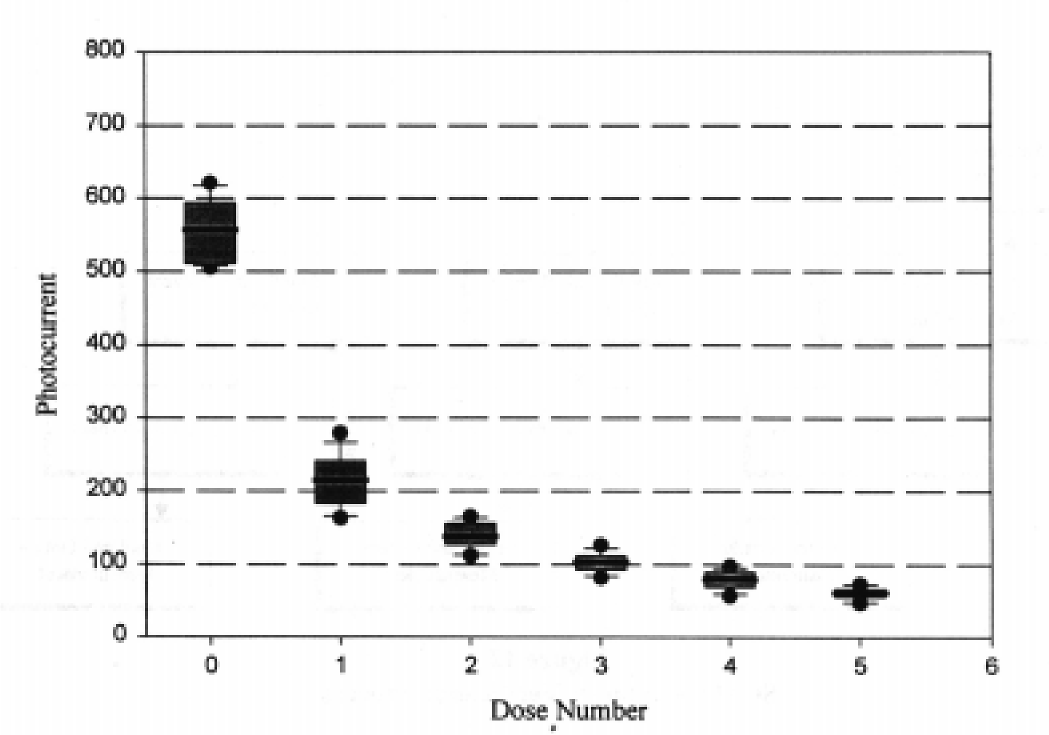


Figure 10
Photocurrent as a Function of Dose Number for HFE 7100 Samples spiked with
0.5 mg Five-Component Mix

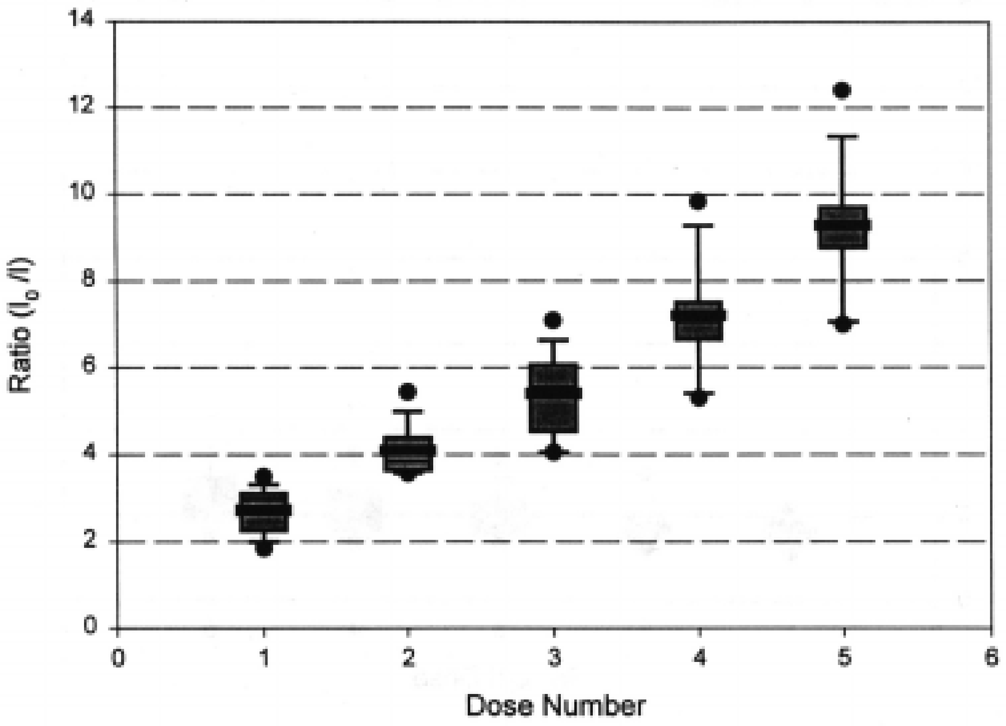


Figure 11
Photocurrent Ratio as a Function of Dose Number for HFE 7100 Samples spiked with 0.5 mg Five-Component Mix

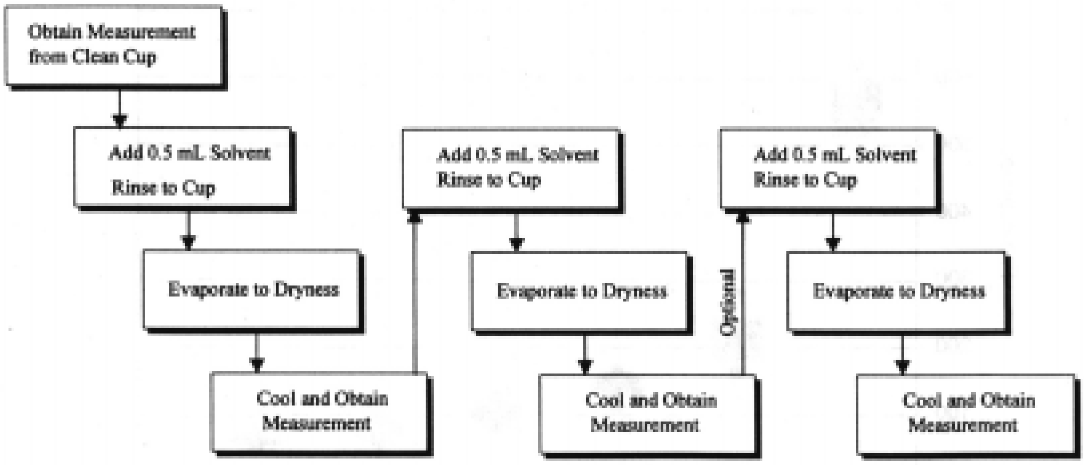


Figure 12
SQM Cleanliness Verification Process

In operation, the SQM is connected to a computer for data logging and computation. First a baseline photocurrent measurement is taken from a clean cup. The signal is averaged for 10 s. From the 100 mL rinse acquired for the NVR, a 0.5 mL aliquot is placed in the cup. The cup is then heated to 40° C until the solvent evaporates, approximately 1 min. After the cup is allowed to cool, another measurement is taken. Using the same cup, a second sample of the HFE 7100 rinse is then processed in the same way. An optional third evaporation and measurement of the solvent can be taken if further confirmation is required.

5.3 Setting the Pass-Fail Threshold

A set of response curves fro three doses of clean HFE 7100 and HFE 7100 contaminated with 0.25, 0.5, 1.0, and 1.5, and 2.0 mg of the five-component mix was generated from the average of 10 replicate samplings at each concentration. These response curves are shown in Figure 13 where the average photocurrent and linear regressions are plotted for the first three doses. Figure 14 is a plot of the photocurrent ratio as a function of dose number from the same data set. These curves can be used to set a pass-fail threshold for a particular cleanliness requirement. The data may also be used to construct a calibration curve for each dose from which the contaminant amount can be determined for a given photocurrent or photocurrent ratio.

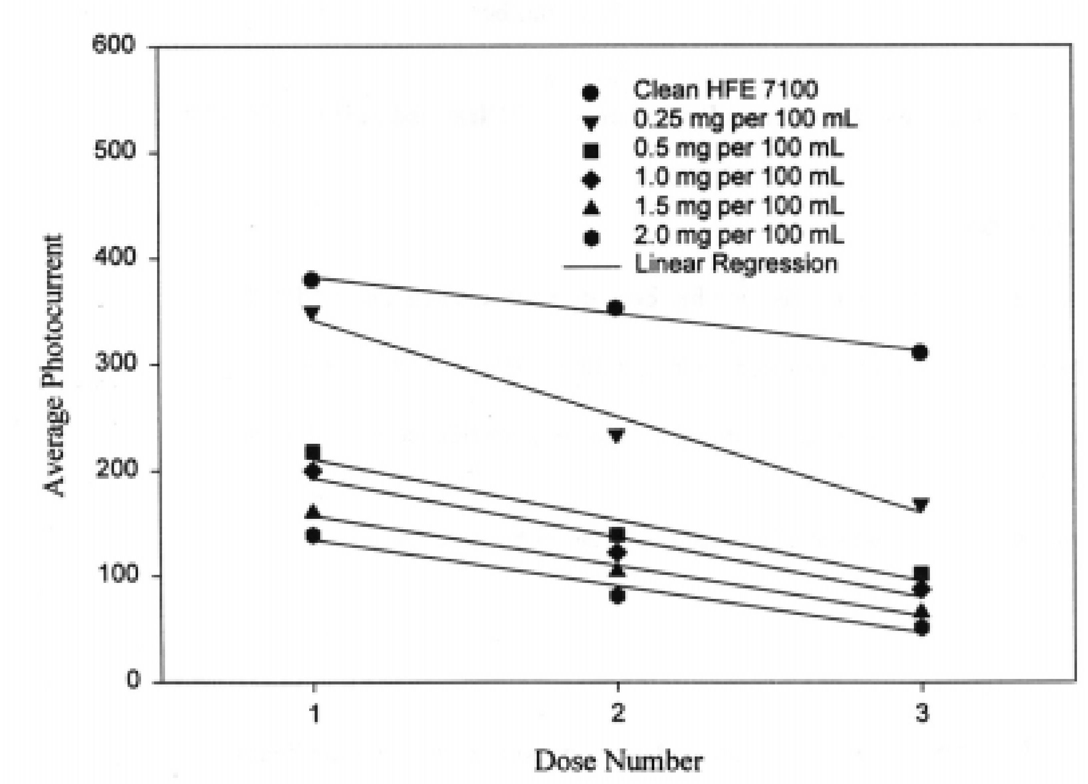


Figure 13
Average Photocurrent versus Dose Number for Clean and Spiked HFE 7100

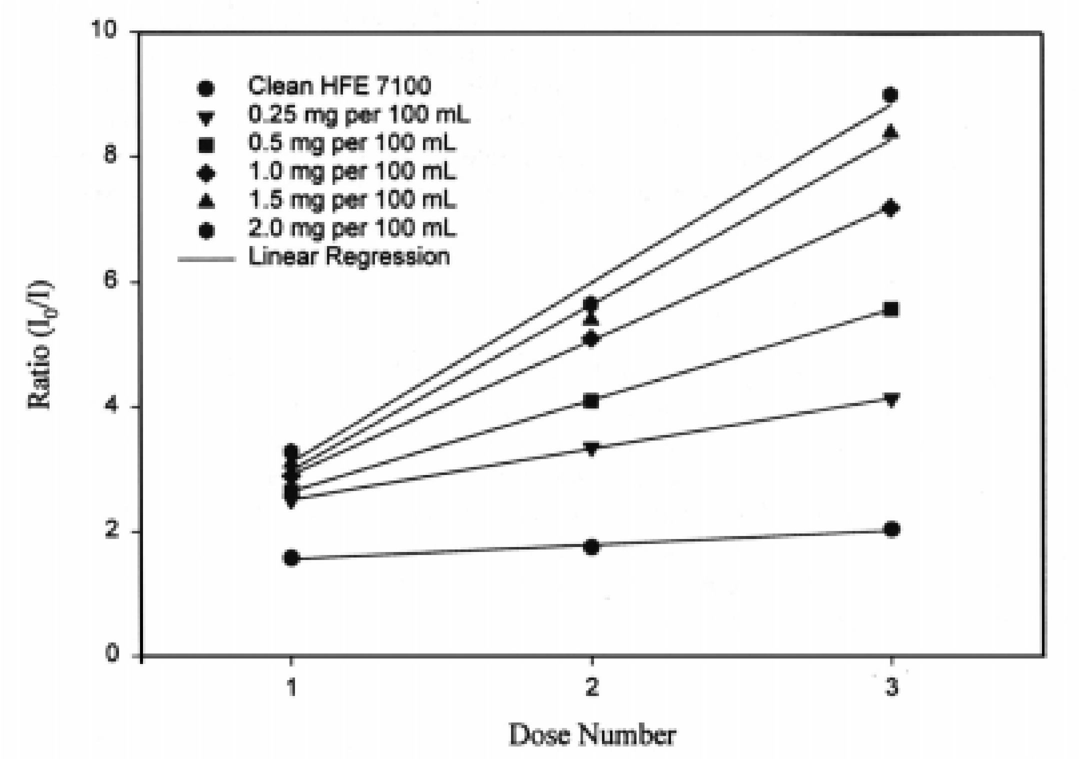


Figure 14
Photocurrent Ratio versus Dose Number for Clean and Spiked HFE 7100

6.0 Summary

A method for cleanliness verification has been developed using the SQM 200.

A number of contaminant responses were measured and the responses were very nearly equal.

By sampling the rinse solvent two or more times, the confidence in the measurements is increased.

Because of the small amount of solvent used, retests are possible.

7.0 Conclusions

The SQM and NVR methods are equivalent in measuring surface cleanliness.

The SQM offers significant savings in the time required to process the NVR.

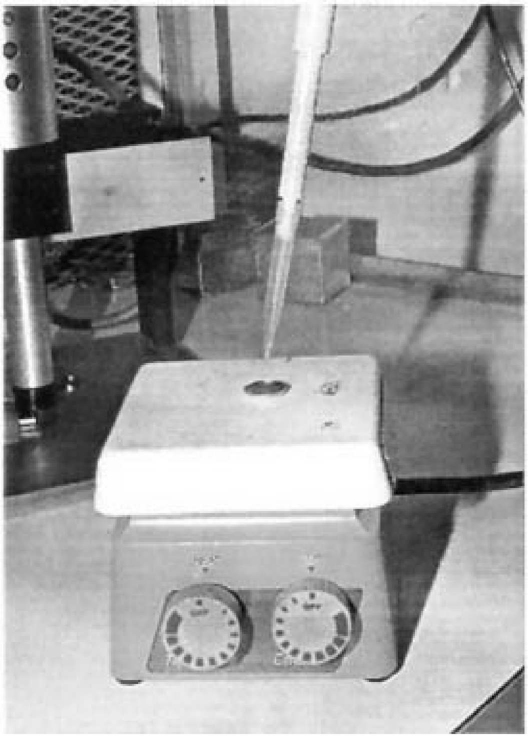
In handling and evaporating less solvent, significant solvent savings can be realized.

Reference

NASA. *Contamination Control Requirements Manual.* JHB 5322, Revision C, NASA Johnson Space Center, Houston, TX (February 1994 or latest revision).

Appendix A

Description of SQM Technique



A

To begin the measurement, a clean cup is placed under the probe of the SQM 200. A guide is used to ensure repeatable positioning. A reading on the SQM 200 is taken after allowing 10 seconds for the signal to stabilize. A minimum photocurrent reading for the clean cup must be achieved; otherwise, the cup is set aside for recleaning and another clean cup is selected.

The cup is then placed on a hot plate at a nominal temperature of 40ºC, and 0.5 mL of the solvent is added to the cup using a dispensing pipette. Evaporation of 0.5 mL of HFE 7100 is complete in less than one minute. Immediately after evaporation, the cup is removed from the hot plate and allowed to cool. Depending on the mass of the cup, cooling my take a few seconds or longer.

B

C

After the cup has cooled, it is replaced under the probe and a reading taken in the same manner as previously described. The dosing, evaporation, cooling, and measurement steps may be repeated up to five times to build up any contaminants present in the solvent to obtain the required confidence in the cleanliness measurements.