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**Investigation of Cleanliness Verification Techniques for Rocket Engine Hardware**

By

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**Abstract**

Oxidizer propellant systems for liquid-fueled rocket engines must meet stringent cleanliness requirements for particulate and nonvolatile residue. These requirements were established to limit residual contaminants which could block small orifices or ignite in the oxidizer system during engine operation. Limiting organic residues in high pressure oxygen systems is particularly important. The current method of cleanliness verification used by Rocketdyne requires an organic solvent flush of the critical hardware surfaces. The solvent is filtered and analyzed for particulate matter, followed by gravimetric determination of the nonvolatile residue (NVR) content of the filtered solvent. The organic solvents currently specified for use (1,1,1-trichloroethane and CFC-113) are ozone-depleting chemicals slated for elimination by December 1995.

A test program is in progress to evaluate alternative methods for cleanliness verification that do not require the use of ozone-depleting chemicals and that minimize or eliminate the use of solvents regulated as hazardous air pollutants or smog precursors. Initial results from the laboratory test program to evaluate aqueous-based methods and organic solvent flush methods for NVR verification are provided and compared with results obtained using the current method. Evaluation of the alternative methods was conducted using a range of contaminants encountered in the manufacture of rocket engine hardware.

**Introduction**

Background

Stringent particulate and nonvolatile residue (NVR) cleanliness requirements for liquid rocket engine hardware, including fuel, oxidizer and pneumatic systems, are imposed by customer specifications. The current method for cleanliness verification involves a final flush of the hardware surfaces immediately following the vapor degrease or solvent flush precision cleaning operation. A sample of the final flush solvent is collected, filtered for particulate matter analysis and tested for nonvolatile residue by a gravimetric technique. The specified cleanliness requirement is less than 1 mg of NVR per square foot of significant surface area. Significant surfaces are defined as those hardware surfaces that may contact the propellants or pneumatic gases during engine operation.

A variety of hardware configurations, material substrates and contaminants are encountered during the final cleaning and verification process. The hardware includes simple detail parts such as seals, bearings, nuts and bolts; complex detail parts such as lines, pump and valve housings, and pump volutes and impellers; moderate size subassemblies such as valves, flex joints and turbopumps; and large complex subassemblies such as flexible propellant ducts, powerheads, nozzles and main combustion chambers. Material substrates include nickel, iron and cobalt-base superalloys; stainless and low alloy steels; aluminum alloys; copper alloys; nickel, silver, gold and copper plating; polychlorotrifluoroethylene, polytetrafluoroethylene, polyimide and polyethylene terephthalate plastics; various elastomers; carbon; and dry film lubricants. Typical contaminants include machine coolants; machining, cutting and tapping fluids; hydraulic fluids; inks; dye penetrants and other fluids to support NDT operations; hydrocarbon, fluorinated and silicone greases; paraffin waxes; detergent residues; tape adhesive residues; and fingerprints.

The solvent predominantly utilized by Rocketdyne for precision cleaning and cleanliness verification is 1,1,1-trichloroethane (TCA). TCA is an ozone-depleting substance and will be banned from

manufacture as of December 1995. Rocketdyne has an environmental task to evaluate and implement alternative methods of cleanliness verification that do not require the use of ozone-depleting chemicals and that minimize or eliminate the use of other regulated solvents. In general, the alternative technique(s) must be capable of detecting a variety of contaminants, be suitable for use on a variety of surface finishes, be capable of sampling internal cavities where the residue is most likely to be entrapped, not recontaminate the hardware, yield quantitative results that can be correlated to the current technique, be compatible with hardware materials, be applicable in a production environment and at the same time meet environmental and safety constraints.

### Approach

The overall task proceeds from laboratory evaluation of the candidate techniques to hardware-scale demonstration to final production implementation. The status of the laboratory-scale evaluation of the aqueous and the organic solvent techniques will be discussed.

NASA-KSC has developed an aqueous verification technique in which the cleaned part is ultrasonically agitated in heated deionized (DI) water to remove any residual organic contaminants from the surfaces.<sup>(1)</sup> The contaminant concentration in the water is then determined by total organic carbon (TOC) analysis. Based upon the promising results obtained by NASA-KSC, the technique is under evaluation using the contaminants, substrates and configurations specific to Rocketdyne. However, as the technique is applicable to hardware of a limited size and some items (i.e., dry film lubricated parts and fragile instrumentation) are damaged by the ultrasonics, additional techniques will also be required. Organic solvents, other than the ozone-depleting chemicals, are under evaluation for these applications.

To evaluate the aqueous technique developed by KSC, the effectiveness of ultrasonic agitation for removing contaminants from surfaces was determined and the method of TOC analysis for determining the contaminant concentration in an aqueous medium was investigated. The effectiveness of ultrasonics was initially determined on small, flat coupons. Investigation of the TOC technique included determination of sample preparation techniques, construction of correlation curves and determination of the limits of detection. Finally, the entire verification process, ultrasonic removal and TOC analysis, was performed on coupons with a known level of contamination and the results verified gravimetrically. Additional testing will be conducted using complex test samples and small hardware.

The evaluation of alternative organic solvents will proceed along the same path as the investigation of the aqueous method except greater emphasis will be placed on solubility characteristics rather than on mechanical agitation techniques to remove the contaminant from a surface. The candidate fluids were identified, physical and chemical properties tabulated, and a review performed by Rocketdyne's Health, Safety & Fire Engineering and Environmental Protection departments. Downselected candidates were tested for residue and contaminant removal effectiveness. Once the final candidates have been identified, they will be tested for rinsability and material compatibility. Removal testing on complex coupons and small hardware will then proceed as with the aqueous method.

### **Procedure**

#### Ultrasonic Contaminant Removal Tests

Initial testing to determine the effectiveness of ultrasonic agitation with heated water to remove contaminants from flat coupons was evaluated. Small (1" x 1") flat Alloy 718 coupons were initially prepared by ultrasonic cleaning in tetrachloroethylene, drying, ultrasonic cleaning in heated DI water and drying. The coupon weights were monitored after each drying step to verify cleanliness. The cleaning cycle was repeated until no weight change was noted. Upon verification of cleanliness, each coupon was contaminated by spreading approximately 2 mg of the contaminant over one surface. The coupons were then heated for 1 hour at 95°C, allowed to cool and reweighed to determine the amount of contaminant remaining. The heating step eliminated any highly volatile species and more closely simulated the nature of a contaminant residue as it is present on actual hardware. Each coupon was then immersed in 100 mL of deionized water heated to 52°C and ultrasonically agitated for 10 minutes. The coupons were dried for 0.5 hour at 95°C, allowed to cool and reweighed to determine the residual contaminant remaining on the coupon. The percentage contaminant removed from each coupon was calculated from the weight data.

Testing was conducted using a 0.75-gallon, 47-kHz ultrasonic tank with a 150-watt power level and a 5-gallon, 25-kHz ultrasonic tank with a 600-watt power level. All tests were performed in triplicate using the contaminants listed in Table 1.

Test Contaminant	Description
Cool Tool, Monroe Fluid Tech.	Hand-applied cutting and tapping fluid containing paraffinic oil
MIL-H-83282 Micronic 882, Bray Oil Co.	Synthetic hydrocarbon hydraulic fluid containing triphenyl phosphate
MIL-H-5606	Hydraulic fluid containing naphthenic distillate with polymer additives and triphenyl phosphate
Rust Foil L-492 Preservative Oil, Franklin Oil Co.	Solvent-dispersed corrosion preventive compound containing aliphatic hydrocarbons and mineral oil
Krytox 240 AC, DuPont	Perfluoroalkylether grease with TFE filler used as a lubricant for oxygen systems and for pressure testing
CIMSTAR 3700, Cincinnati Milacron	Semi-synthetic water-soluble metal working fluid containing mineral oil, di- and tri-ethanolamines, aminomethylpropanol and a synthetic lubricant
DTE 24, Mobil Oil	Petroleum distillate oil
Lapping Compound 38-1200, USP	Ultra fine grit lapping compound containing aluminum oxide
CRC 3-36, CRC Ind.	Petroleum distillate and paraffinic oil containing lubricant and rust inhibitor
Centerpoint Lube, Chicago Manuf. & Dist.	High viscosity, grease-like extreme pressure machining lubricant containing petroleum oil, wax, and rosin ester
Bio-Pen P6R, Ardrex Inc.	Detergent-based visible, solvent-removable dye penetrant
Bio-Pen P6F-4, Ardrex, Inc.	Fluorescent, water-washable dye penetrant
Bio-Pen NQ-1 Developer, Ardrex Inc.	IPA and silica containing spray developer for penetrant inspection
Turco 3878 LF-NC, Turco Products	Aqueous emulsion cleaner containing sodium tripolyphosphate, glycol ether, and proprietary salts of anionic surfactants
Braycote 236, Castrol Inc.	Petrolatum used to lubricate o-rings during pressure test
Paraffin Wax	Low-melting-point, 107°F, wax used as machining maskant
Vacuum Grease, Dow Corning	Silicone vacuum grease used during pressure test
China Marker 165-T, Empire Berol Corp.	Red water-resistant marking pencil
Hydro Marker 665-T, Empire Berol Corp.	Red water-soluble marking pencil

Table 1. Test Contaminants

#### TOC / Contaminant Concentration Correlation Curves

To relate the TOC value of a sample to the actual contaminant concentration, a series of correlation curves were generated using prepared standards. Standard solutions of 20.5 ppm, 50.5 ppm and 80.3 ppm of Cool Tool; 19.5 ppm, 50.8 ppm and 93.3 ppm of MIL-H-5606 hydraulic fluid; 24.0 ppm, 52.3 ppm and 81.0 ppm of CRC 3-36; and 20.3 ppm, 59.3 ppm and 88.0 ppm of Centerpoint Lube each in 400 mL of DI water were prepared. To emulsify the contaminant, each solution was agitated by manual shaking for 30 seconds and then immersed in a 25-kHz ultrasonic bath at 52°C and agitated for 10 minutes after thermal equilibrium had been obtained. Each solution was then analyzed in triplicate for TOC content using a Rosemount Analytical Model DC-190 High Temperature TOC Analyzer. A sample of DI water was also analyzed to obtain a blank value.

### TOC Analysis of Water from Coupon Tests

A quick assessment of the feasibility of the ultrasonic agitation/TOC analysis for cleanliness verification was performed using the small Alloy 718 coupons. The coupons were cleaned, verified and contaminated as in the ultrasonic removal tests, except varying levels of initial contaminant were applied. The target contamination levels were 1 mg, 2 mg and 5 mg. Two contaminants were tested, Cool Tool and Centerpoint Lube. Each sample was ultrasonically agitated in 100 mL of heated DI water as described previously. The water sample was then analyzed for TOC content. From the correlation curves, the contaminant concentration in the water was calculated and the total amount of contaminant removed from the coupon was calculated using Equation 1.

$$\text{Contaminant Removed (mg)} = \frac{\text{TOC} - \text{B}}{\text{M}} \times \text{V} \quad (1)$$

TOC	=	TOC value in ppm or mg/liter
B	=	the y-intercept of the correlation curve, i.e., the TOC of the DI water blank in ppm or mg/liter
M	=	slope of line of correlation curve in ppm TOC / ppm contaminant concentration or (mg/liter) / (mg/liter)
V	=	volume of water used for ultrasonic extraction in liters

For comparison, the amount of contaminant removed was also calculated by the change in coupon weight after ultrasonic immersion.

### Complex Coupon Tests

Test coupons with configurational complexities (Figure 1) were utilized to further test the aqueous verification technique. The coupons were precleaned by ultrasonic agitation in TCA for 10 minutes. Cleanliness was then verified by ultrasonically agitating each coupon in 500 mL of TCA and performing a gravimetric NVR on the TCA. Each sample was immersed in 500 mL of 52°C DI water and ultrasonically agitated for 10 minutes. The water sample was analyzed for TOC to provide a "blank" value. The samples were dried and 5 to 10 mg of Cool Tool applied to each coupon. Each sample was then immersed in 500 mL of 52°C deionized water and ultrasonically agitated for 10 minutes. The water sample was subsequently analyzed for TOC. Each coupon was reverified clean by ultrasonic agitation in TCA followed by gravimetric NVR. A sample that had been contaminated, but not aqueously verified, was solvent verified as a control.

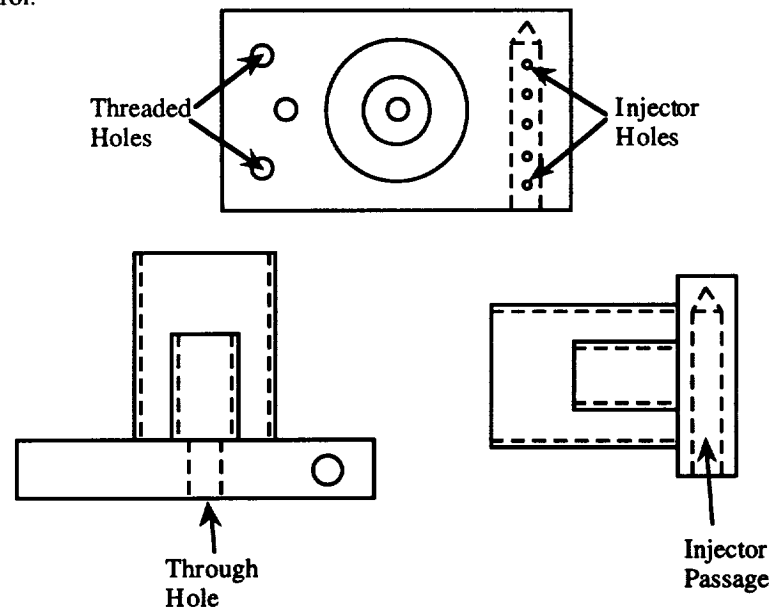


Figure 1. Alloy 718 Complex Test Coupon Configuration

### Organic Solvent Evaluation

A list of candidate alternative solvents was compiled from a literature search, published data bases and supplier information. The categories of solvents considered included chlorinated solvents, hydrochlorofluorocarbons (HCFCs), perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), fluoroiodocarbons (FICs), alcohols, terpenes, ketones, aliphatic and alicyclic hydrocarbons, ethers, glycol ethers, esters, amines, aromatic hydrocarbons, methyl siloxanes and parachlorobenzotrifluoride. An abbreviated list of candidates was compiled using the following criteria:

#### Essential characteristics:

- Moderate to high volatility to promote evaporation from complex hardware and ease of performing a gravimetric NVR
- Comparable solubility to trichloroethane for a range of contaminants used at Rocketdyne
- Available in high purity and leaves little or no residue upon evaporation
- Existing or near-term availability
- Non-ozone depleting

#### Desirable characteristics:

- Not currently listed nor proposed to be listed on California Proposition 65, AB2588 or classified as a HAP (hazardous air pollutant)
- Does not contribute to global warming
- Not classified as a VOC (volatile organic compound)
- Permissible exposure level greater than 100 ppm
- Nonflammable
- Inoffensive odor

Contaminant removal tests were then performed to assess the effectiveness of the candidate solvents relative to TCA. Approximately 10 to 30 mg of contaminant were applied to the bottom of a clean, tared aluminum weighing pan. The contaminated pan was heated for 1 hour at 95°C, allowed to cool to room temperature and reweighed to determine the amount of contaminant remaining. The dish was then sequentially filled and drained with the filtered test solvent until a total of 100 mL had been used. The pan was dried for 1 hour at 108°C to evaporate any residual solvent, allowed to cool to room temperature and reweighed. The percentage of the initial contaminant removed was calculated using the weight data. A gravimetric NVR was also performed on each solvent sample and a percentage of contaminant removed was calculated. Tests were performed in triplicate with the contaminants listed in Table 1.

## **Results and Discussion**

### Ultrasonic Contaminant Removal Tests

The results from the removal tests for the seventeen contaminants tested using both the 47-kHz ultrasonic bath and the 25-kHz bath are shown graphically in Figure 2. In general, the 25-kHz bath was slightly more effective than the 47-kHz bath. The average removal of all of the contaminants was 83% for the 47-kHz bath and 85% for the 25-kHz bath. For the majority of the contaminants, ultrasonic agitation in water was greater than 90% effective in removing the contaminant residues. The Krytox grease, silicone vacuum grease, paraffin wax and China marker were the most difficult contaminants to remove as shown by their 10 to 80% removal. Not surprisingly, these contaminants are also the most difficult to remove using organic solvents.

Because of the simple configuration of the test coupons used, the removal efficiencies may not translate directly to more complex geometries. The coupons were selected so the contaminant removed could be determined by simple gravimetric means with relatively little error. For example, the accuracy of the percentage removal data is approximately  $\pm 5\%$  with the error derived from the limitations of the balance. To fully evaluate the effectiveness of the ultrasonics, more complex test coupons and hardware will be tested and an organic solvent verification method used to assess the results.

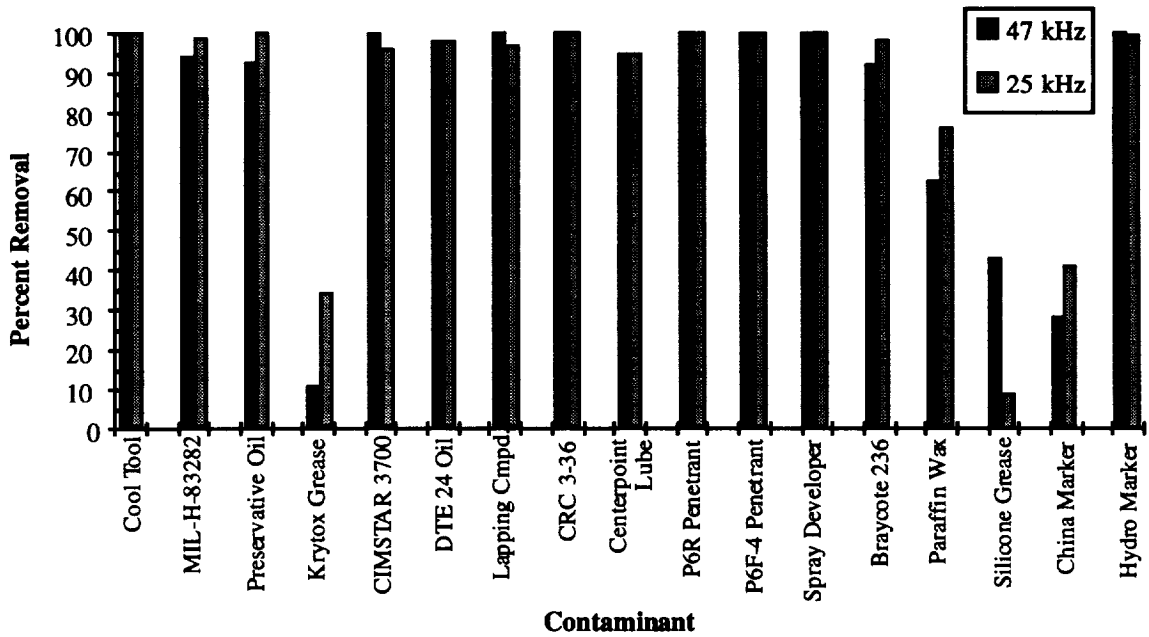


Figure 2. Contaminant Removal Effectiveness by 10-Minute Immersion in 52°C DI Water with Ultrasonic Agitation

TOC / Contaminant Concentration Correlation Curves

In order to relate the measured TOC value to the actual concentration of the contaminant in water, correlation curves were generated. The curves for four contaminants, Cool Tool, Centerpoint Lube, CRC 3-36 and MIL-H-5606 hydraulic fluid are shown in Figure 3. The average measured TOC value for each of the standard solutions prepared was plotted and a best fit line determined by the method of least squares. As shown, for the concentration ranges tested, the linear fit of the data is excellent. Testing is continuing to generate correlation curves for the other contaminants of interest.

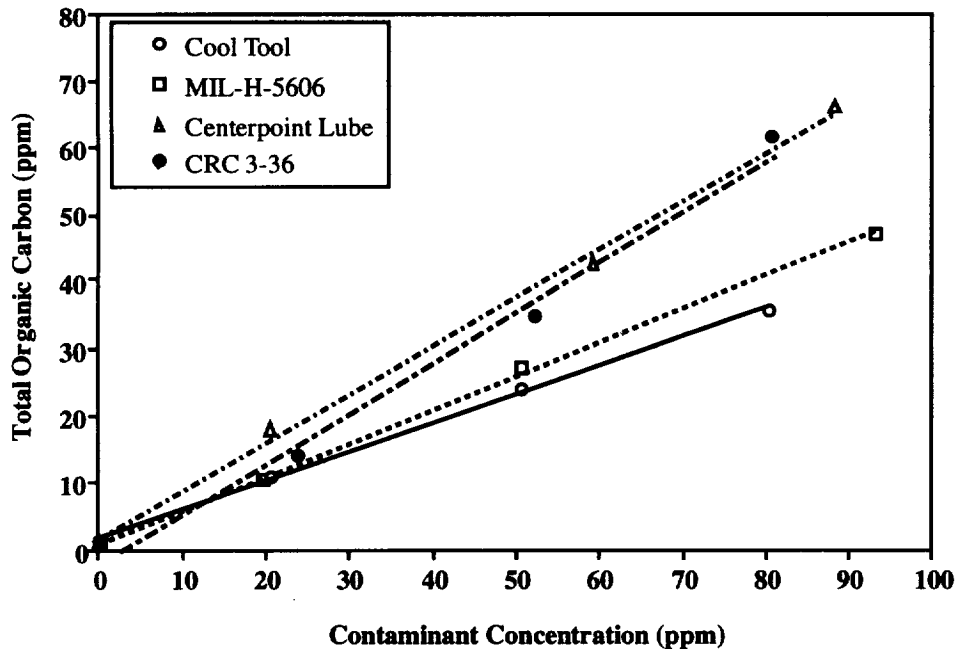


Figure 3. Correlation of Contaminant Concentration with TOC

### TOC Analysis of Water from Coupon Tests

Testing was performed using the small coupons to verify the ability of the TOC analysis to accurately measure the amount of contaminant removed after ultrasonic agitation. The contaminant removed was calculated both gravimetrically and by TOC analysis. These coupons were used because cleanliness assessment could be made gravimetrically rather than by the more time consuming solvent verification method. As shown in Figures 4 and 5, contaminant removal results determined by the TOC method compare favorably to those obtained by the gravimetric method. The favorable results indicate that the aqueous verification technique is viable, at least for simple geometries and the contaminants tested to date. Based upon these successful results, testing was initiated with more complex geometries.

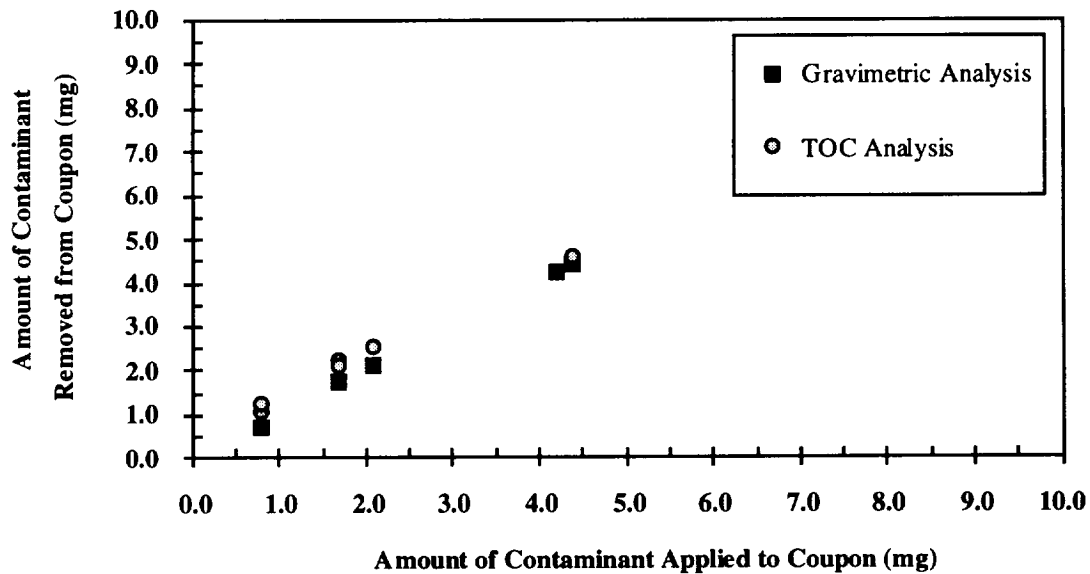


Figure 4. Comparison of Aqueous Verification with Gravimetric Results for Determining Cool Tool Residue on Alloy 718 Coupons

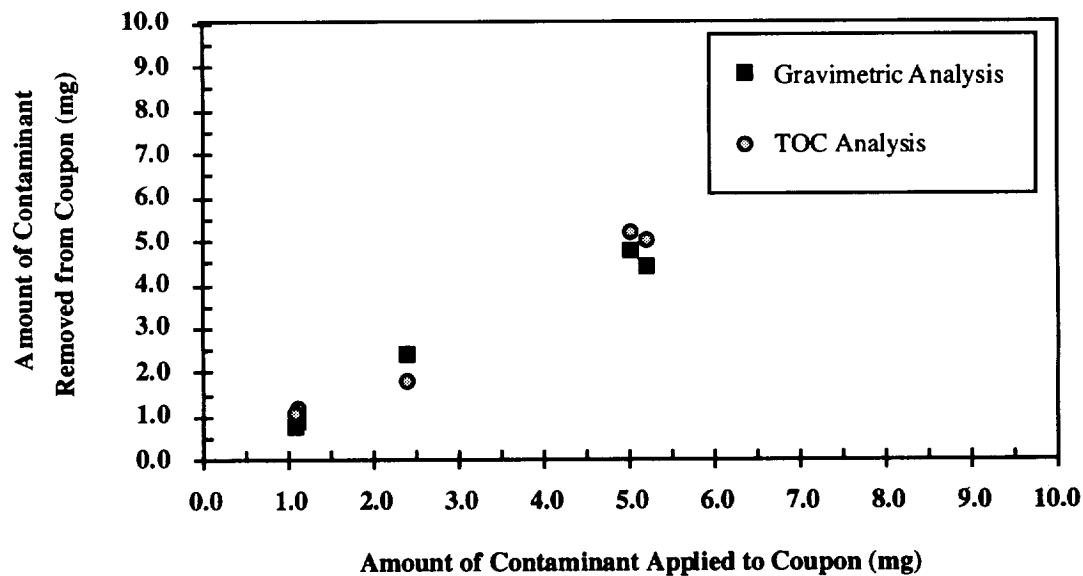


Figure 5. Comparison of Aqueous Verification with Gravimetric Results for Determining Centerpoint Lube Residue on Alloy 718 Coupons

### Complex Coupon Tests

The first series of tests performed with the more complex test coupons involved placing a controlled amount of contamination on a relatively exposed surface of the Alloy 718 coupon and performing the aqueous verification technique. The TOC results were converted to amount of contaminant removed from the test piece by use of the correlation curve and the results are shown in Table 2 along with the results from the subsequent NVR analysis. As shown by the TOC results and by the low NVR results, the aqueous technique was successful in detecting the contaminant on the test pieces. The control coupon which was contaminated and then verified with TCA shows that not even the standard solvent verification method is precise in determining the entire amount of contaminant on a surface. This may be due either to incomplete removal by the solvent or to slight evaporation of the Cool Tool during the gravimetric analysis. Testing is now being extended to include additional contaminants and to contaminate more inaccessible regions on the test sample, such as the threaded holes and the through holes. If required, the process parameters will be adjusted to maximize the contaminant removal.

Contaminant	Amt. Applied (mg)	Verification Results	
		By TOC (mg)	By TCA NVR (mg)
Cool Tool	10.98	8.40	0.1
	13.70	13.87	0
	5.18	Not Performed	4.4

Table 2. Aqueous Verification Results on Complex Test Coupons

### Organic Solvent Alternatives

Candidate organic solvents under initial consideration as alternatives to TCA include isopropyl alcohol (IPA), acetone, cyclohexane, ethyl acetate, a 33% IPA - 67% cyclohexane azeotrope, HCFC 225 and an HFC. Of these, IPA, acetone, cyclohexane, ethyl acetate, and the azeotrope have been subjected to solubility testing. These solvents were selected for initial evaluation based upon promising results obtained by other companies that require alternative verification methods. Testing was also conducted using TCA for comparison.

A comparison of the percentage of contaminant removed as determined by coupon weight data and by solvent NVR was conducted to assess the accuracy of the current gravimetric technique. Testing was performed for all of the contaminants using TCA, IPA, cyclohexane and ethyl acetate; however, only the TCA results are shown. From Figure 6, it can be seen that for those contaminants readily removed by the solvent, the NVR results are typically 85 to 100% of the results obtained gravimetrically, except for the MIL-H-5606 and the DTE 24. The difference between the NVR and the gravimetric results is primarily attributed to the volatility of the contaminant, i.e., some of the contaminant is evaporated along with the solvent during the evaporation phase of the NVR procedure. This is particularly apparent with the light hydrocarbon contaminants, such as the MIL-H-5606 hydraulic fluid and the DTE 24. Previous testing in which the contaminant was not initially dried resulted in an even greater difference between the NVR and weight data. Drying the contaminant prior to testing aids in reducing the difference but does not entirely eliminate the effect.

The effectiveness of each solvent for removing the selected contaminants is presented as a percentage removal in Figures 7 and 8. The results are based upon the gravimetric data rather than the NVR values and are shown with the TCA results for comparison. As shown, isopropyl alcohol and acetone are less effective than TCA for the contaminants tested, whereas cyclohexane, ethyl acetate and IPA/cyclohexane are nearly as effective as TCA for the majority of the contaminants. As shown, even the TCA only partially removed the lapping compound, the Centerpoint Lube and the Turco 3878. Furthermore, the TCA is relatively ineffective in removing the Krytox grease, the silicone vacuum grease, and the markers. For these contaminants, it was noted that any removal at all was primarily the result of



mechanical action rather than dissolution in any of the solvents. Of the solvents tested to date, cyclohexane showed the most promise as an alternative to TCA. However, testing is still in progress with some of the other candidates.

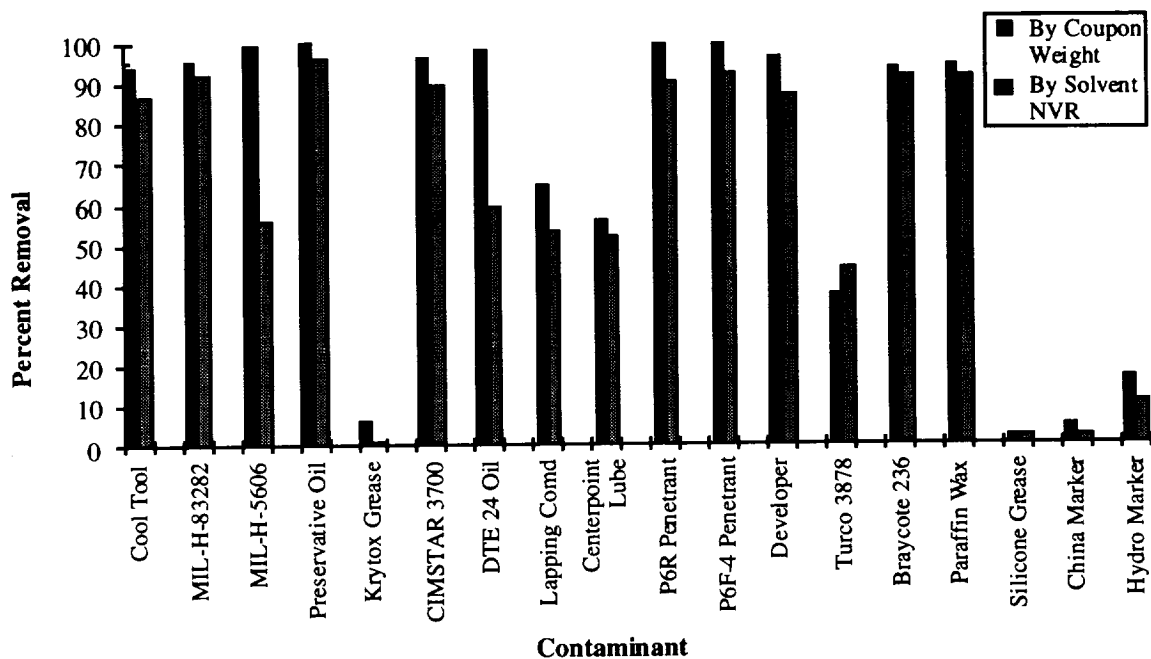


Figure 6. Contaminant Removal Tests with Ambient Temperature TCA

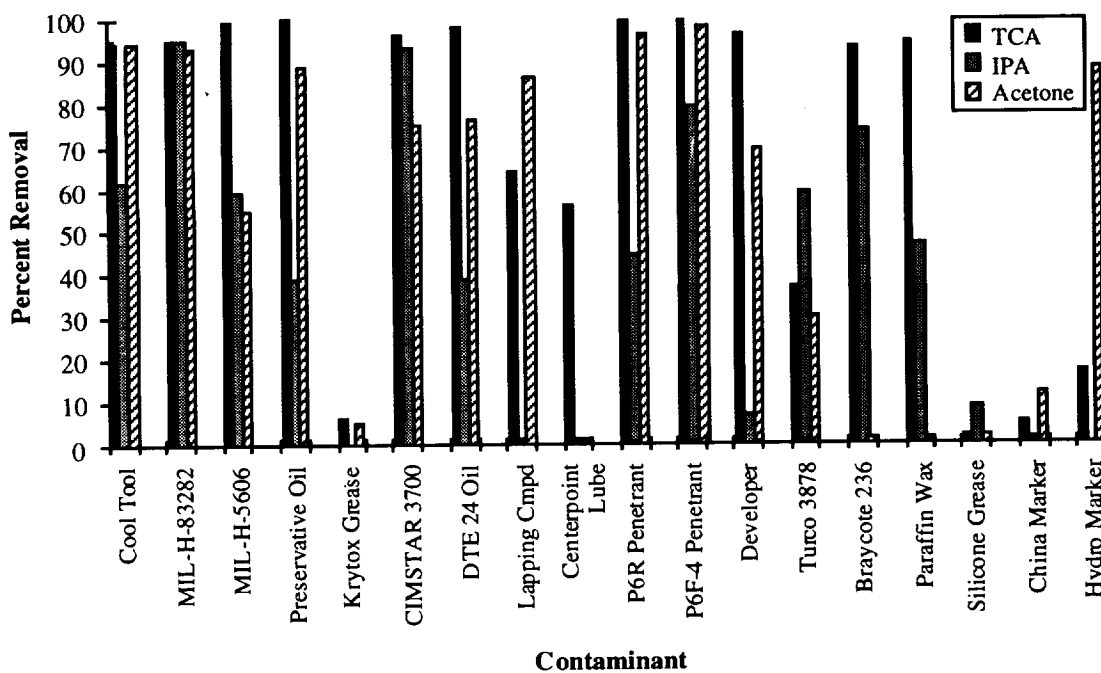


Figure 7. Contaminant Removal Tests with Ambient Temperature 1,1,1 Trichloroethane, Isopropyl Alcohol and Acetone

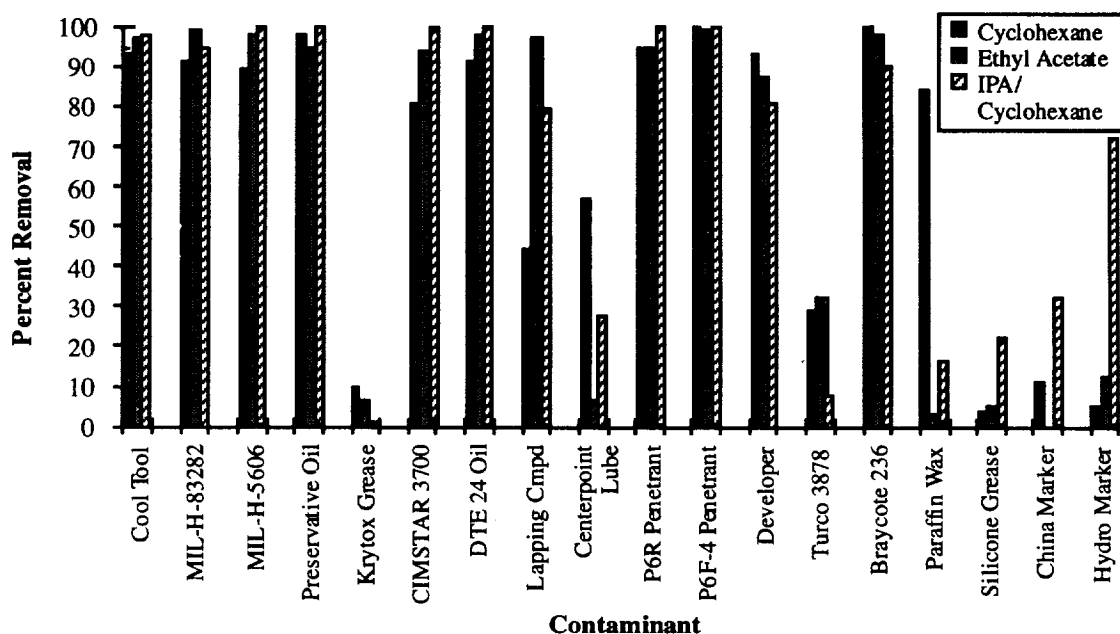


Figure 8. Contaminant Removal Tests with Ambient Temperature Cyclohexane, Ethyl Acetate and IPA/Cyclohexane

## Conclusions

Based upon limited laboratory testing, the aqueous verification technique developed by NASA-KSC has been shown to be feasible for some Rocketdyne applications. Use of 25-kHz ultrasonic agitation is slightly more effective than 47-kHz ultrasonic agitation for removing the majority of the test contaminants with heated DI water. Through the use of correlation curves, TOC analysis of the water used during the ultrasonic cleaning is accurate in determining the amount of contaminant removed from the surface. Testing, however, was very limited and must be extended to the more difficult to remove contaminants and more complex geometries.

The majority of the organic solvents that can be considered as alternatives to TCA have disadvantages such as toxicity, flammability, or classification as VOCs (volatile organic compounds) or HAPs (hazardous air pollutants). From the limited testing performed to date, cyclohexane is nearly equivalent to TCA in contaminant removal. However, cyclohexane is a VOC and has a low flash point. Furthermore, as with the majority of the solvents, cyclohexane is not compatible with oxygen and must be completely removed from any oxidizer hardware. Testing will continue to evaluate other alternatives with final technique validation performed on full-scale hardware.

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## Reference

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