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M. G. Benkovich

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# IMPROVED METHOD FOR QUANTIFYING NONVOLATILE RESIDUES ON SURFACES AND IN LIQUIDS

M. G. Benkovich

Published March 2004

Final Report on CRADA No. 98KCP1053
M. G. Benkovich, Project Leader

# Improved Method for Quantifying Nonvolatile Residues on Surfaces and in Liquids

## Project Accomplishments Summary

## CRADA Number 98KCP1053

Date: 9/30/03
Revision:

**A. Parties**

The project is a relationship between

Honeywell International Inc.
2000 E 95th Street
PO Box 419159
Kansas City, MO 64141-6159

ERA Systems, Inc.
The MESERAN Company
50 North Crest Road
Chattanooga, TN 37404-1828

Astro Pak Corporation
12201 Pangborn Ave.
Downey, CA 90241

Lockheed Martin Corporation
1111 Lockheed Martin Way
Sunnyvale, CA 94088-3504

## B. Background

Nonvolatile residue (NVR) measurements are an integral function for companies that must clean parts to a required level. The gravimetric method primarily used for measuring NVR is time-consuming, is not environmentally conscious, and is not very accurate (particularly at lower part-per-million NVR levels or below a few hundred nanograms). An alternative method was sought that would be faster and more accurate at low contamination levels.

Honeywell Federal Manufacturing & Technologies is a prime contractor for the U.S. Department of Energy. The primary mission at FM&T is to assemble and manufacture a wide array of nonnuclear mechanical, electronic, and engineered material components for our nation’s nuclear weapons stockpile. FM&T supports nearly 40 technically demanding product families, including arming devices, microcircuits, plastics, radars, and polymers. It also supports 80 advanced technologies, including failure analysis, machining, optics, laminates, and software engineering. In addition, FM&T is at the forefront of cleaning technology and cleanliness measurement. FM&T is the leading expert in the world for using the MESERAN Analyzers for detecting and quantifying organic residues. This technology has been in use at FM&T for over 25 years to evaluate cleaning process effectiveness and part cleanliness and has been involved in the development of new data analysis methods which enhance detection capabilities to subnanogram levels. FM&T has the knowledge, experience, cleaning equipment, solvents, analytical equipment, and trained personnel to clean substrates, perform gravimetric NVR analysis, evaluate the MicroSolventEvaporator, and perform MESERAN Analysis and other analytical analyses as required. FM&T is interested in developing this technique for use in determining NVRs for incoming inspection of solvents and for quantifying cleanliness levels on parts.

ERA Systems Inc., The MESERAN Company, manufactures the MESERAN Analyzers, which detect and measure organic residues down to levels less than 1 nanogram/cm$^2$. They have shown that it is possible to quantify organic contamination levels down to and below 1 nanogram/cm$^2$ by depositing as little as 10 microliters of solvent containing a known amount of contamination on a clean substrate, allowing it to evaporate, and measuring the evaporated residue with the MESERAN Analyzer. The MESERAN Company also has the expertise to provide the radiochemical solutions used with the MESERAN Analyzers, very pure solvent, and calibration solutions of known contaminants. They also developed the idea and initial design for the MicroSolventEvaporator.

Astro Pak is a precision chemical cleaning contractor. Astro Pak performs precision chemical cleaning of various surfaces and determines the nonvolatile residue levels on the surface pre- and post-cleaning via the traditional gravimetric method. Astro Pak has all of the necessary laboratory equipment (rotary evaporator, Labconco Rapidvap vortex evaporator, Mettler analytical balances, vacuum oven), purified solvents (CFC-113, IPA), and trained laboratory personnel to carry out traditional gravimetric NVR analysis. Astro Pak can determine NVR levels on reference surfaces for comparison to the new improved method. NVR determination is a routine component of their business and they are interested in finding a cheaper and faster way to quantify NVRs and a better way to quantify NVRs at low contamination levels.

Lockheed-Martin is a large aerospace corporation. Lockheed-Martin has several labs, some that routinely process wipers used for taking NVR samples. The wipers are extracted with a solvent and the solvent extract is then measured for NVR via the traditional gravimetric method. Lockheed-Martin also performs NVR measurements using solvent extraction on aluminum foils that are hung in manufacturing areas. Lockheed-Martin routinely has to sample satellites and launch vehicle components to detect NVR at less than 1 $mg/ft^2$. Lockheed-Martin can determine NVR levels on reference surfaces for comparison to the new improved method. NVR determination is a routine component of their business, and they are interested in finding a cheaper and faster way to quantify NVRs and a better way to quantify NVRs at low contamination levels.

## C. Description

The objective of the project was to develop an improved method to quantify nonvolatile residues on surfaces and in liquids.

Kansas City Plant (KCP) personnel organized and led the CRADA. KCP developed and evaluated various cleaning processes to clean the reference substrates to acceptable levels. KCP developed numerous calibrations of various organic contaminants on the reference substrates so that quantitative data could be obtained. KCP also tested and evaluated the MicroSolventEvaporator in conjunction with the MESERAN Analyzer to prove-in the process and compared the data to NVRs obtained gravimetrically. In addition, KCP personnel traveled to the partner facilities to install MicroSolventEvaporators and MESERAN Analyzers and provided training on the use of the equipment.

ERA Systems, Inc., The MESERAN Company, designed, developed, built, evaluated, tested, and delivered an initial prototype MicroSolventEvaporator to the KCP for automatically depositing and evaporating successive small quantities (~5-10 microliters) of solvents onto clean reference surfaces. They also provided a MESERAN Analyzer and radiochemical solutions used by the MESERAN Analyzer to evaluate the microorganic residues on the surfaces (for the calibrations performed and residues evaluated after depositions with the MicroSolventEvaporator). The MESERAN Company provided calibration solutions of the various organic contaminants to KCP so that calibrations could be performed on the reference surfaces. The MESERAN Company also provided various stainless steel disks with machined grooves to be used as reference substrates. In addition, The MESERAN Company built two additional MicroSolventEvaporators and provided them to Astro Pak and Lockheed Martin Missiles and Space along with MESERAN Analyzers for evaluations at their facilities.
Dr. Anderson traveled to the partner facilities to install the MicroSolventEvaporators and MESERAN Analyzers and provide training on the use of the equipment.

Astro Pak Corporation and Lockheed Martin Missiles and Space entered the CRADA for the purpose of assisting with the evaluation of the MESERAN/MicroSolventEvaporator technique as a possible replacement for, or complement to, gravimetric techniques used in the determination of cleanliness with regard to residues. Their role was to compare the gravimetric technique side-by-side with the MESERAN/MicroSolventEvaporator technique and report the correlated data to KCP personnel. The value of the collaborative effort, from their point of view, is found in the possibility that a replacement for the time-consuming gravimetric NVR technique may be found as a result of the CRADA that will be faster, cheaper, and more reliable (especially at low contamination levels). Also, there is an intangible benefit for all involved in that information is transferred to one another as a natural result of performing collaborative research. Such information transfer can be expected to provide benefit to all entities involved.

The project accomplishments are summarized below:

- ERA Systems, Inc., The MESERAN Company has designed, developed, built, evaluated, tested, and delivered MicroSolventEvaporator systems to KCP, Astro Pak, and Lockheed Martin, that automatically deposit and evaporate successive small quantities (5-10 microliters) of solvents onto clean reference surfaces.
- ERA Systems, Inc., The MESERAN Company, and KCP have designed, procured, and evaluated stainless steel disks with specific machined grooves to be used as reference surfaces with the MicroSolventEvaporator and MESERAN Analyzers.
- KCP evaluated various cleaning processes to easily clean the reference surfaces to acceptable levels. Even though some methods (or a combination of methods) may have worked better than others, an easy method that most companies could use to acceptably clean the disks was desired. Aqueous ultrasonic cleaning with Dirl Lum 603 (30 g per liter concentration) followed by flowing DI water and ultrasonic DI water rinses, nitrogen blow drying, and baking in a HEPA filtered oven at 220°F for 30 minutes proved to be a relatively simple method that most companies could use.
- KCP developed calibrations of several contaminants on the chosen reference substrates so the MESERAN data could be converted into quantifiable amounts of contamination.
- KCP performed a prove-in of the MicroSolventEvaporator in conjunction with the MESERAN Analyzer and compared the results to gravimetric data. The method worked and was able to provide data at low contamination levels that can not be reliably obtained gravimetrically.
- Astro Pak and Lockheed Martin have done limited testing at their facilities. The MESERAN Company has agreed to let them keep the units for awhile so they can continue to perform tests to prove-in the process at their facilities even after the CRADA is completed.

### D. Expected Economic Impact

Lockheed Martin Missiles and Space believe that they may be able to use the MESERAN Analyzer to perform direct tests on witness panels. This would eliminate the need to perform the laborious and time-consuming extractions on aluminum foils followed by gravimetric analysis. If they can test witness panels using the MESERAN Analyzer (something KCP does regularly), they would not even need the MicroSolventEvaporator. This would significantly reduce their costs for performing NVR measurements on the aluminum foils. They could still use the MicroSolventEvaporator and MESERAN Analyzer for samples of parts that needed to be extracted.

Astro Pak will continue to evaluate the MicroSolventEvaporator and MESERAN Analyzer to see if it is applicable to their operations.

### E. Benefits to DOE

The partnership was of great value for the Kansas City Plant. A good working relationship with The MESERAN Company was strengthened with this project. The project also enabled KCP to make contacts with Astro Pak and Lockheed Martin to learn about the cleaning needs of companies that work with DOD and commercial firms. KCP will definitely purchase a MicroSolventEvaporator and MESERAN Analyzer to perform NVR evaluations for KCP product and support the rest of the Nuclear Weapons Complex desiring this testing. Astro Pak and Lockheed Martin were able to learn about the use of MESERAN technology for quantifying organic contamination.

The partnership between KCP and The MESERAN Company (along with KCP's intimate knowledge of MESERAN technology) enabled the discovery of a problem with the radiochemicals supplied to The MESERAN Company from their supplier. In the future, greater care will be taken by the supplier to ensure that the radiochemicals are consistently pure.

The technology developed in this project has already been deployed to support KCP as follows:

- Obtain new business for testing NVRs for Lawrence Livermore National Laboratory (LLNL) on the NIF project
- Evaluate KCP's ability to clean PEPC LRU NIF hardware for LLNL in support of a $1.2 million reimbursable order
- Evaluate contamination levels on LAC Shells
- Evaluate contamination for LED Bond Analysis project in Telemetry
- Evaluate contamination levels on MSAD Detector Hook Assembly
- SMRI support for Department 92 ultrasonic cleaning equipment
- Evaluate cleaning ability of various atmospheric plasma equipment for production ADAPT and Department 833 ADAPT projects

Additional work currently scheduled for use with MicroSolventEvaporator and MESERAN Analyzer include:

- Production cleaning evaluations performed for Sandia National Laboratory/New Mexico and Pantex to evaluate alternate wiping solvents.
- Evaluate the ability of plasma cleaning to remove contamination from pits for Los Alamos.

As a result of this project, the software for analyzing MESERAN data has been improved and will be installed in new units.

## F. Industry Area

Many industries (automotive, aerospace, electronics, microchip manufacturing, medical, chemistry, biochemistry, etc.) should benefit from this technology. The principle used in the MicroSolventEvaporator (which results in the highly protected evaporation process) will prove of great importance in almost all chemical and biochemical laboratory processes which now use manual deposition of chemicals from syringes. In addition, any industry requiring the validation of cleanliness with regard to residues, or the quantification of low levels of residues, will benefit. Microelectronic manufacturing, specifically microchip manufacturing, is one such area. High-power laser facilities such as LLNL's NIF project could benefit as well. The precision cleaning industry would also benefit from a properly calibrated and validated technique such as MESERAN.

## G. Project Status

The project was completed in most aspects; however, unforeseen problems with the radiochemicals and reference substrates were encountered that required considerable time to solve. Working to solve these problems depleted the hours and money KCP had budgeted for the project. Therefore, the number of contaminants that were calibrated on acceptable substrates had to be reduced. This also reduced the amount of time KCP had for performing evaluations of actual NVR samples. Finally, this significantly reduced the time that Astro Pak and Lockheed Martin Missiles and Space had to evaluate the MicroSolventEvaporator and MESERAN Analyzer prior to the end of the project. Even though KCP does not have any more money to continue with the project, ERA Systems, Inc., The MESERAN Company, is going to let Astro Pak and Lockheed Martin Missiles and Space keep the MicroSolventEvaporators and MESERAN Analyzers at their facilities so they can continue to evaluate them.

## H. Point of Contact for Project Information

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Kansas City, MO 64141-6159
Telephone: (816) 997-3529
Fax: (816) 997-2049

## I. Company Size and Point of Contact

ERA Systems, Inc., The MESERAN Company
Annual Sales: Varies from $60,000 - $200,000
Number of Employees: 3
Responsible employee: Dr. John (Jack) L. Anderson, Owner
Telephone: (423) 266-0400
Fax: (423) 698-2633
Feedback employee: Dr. John (Jack) L. Anderson, Owner

Astro Pak Corporation
Annual sales: $15,000,000
Number of employees: 103
Responsible employee: Dr. Brent J. Ekstrand, Director of Training & Safety
Telephone: (800) 743-5444 ext. 105

Fax:  (562) 803-3870
Feedback employee:  Dr. Brent J. Ekstrand, Director of Training & Safety

Lockheed Martin Corporation
Annual sales:  $26.6 billion
Number of employees:  125,000
Responsible employee:  Francis Seidl, Manager – Chemistry and Contamination Control Engineering & Labs
Telephone:  (408) 742-9133
Fax:  (408) 742-0290
Feedback employee:  Francis Seidl, Manager – Chemistry and Contamination Control Engineering & Labs

### J. Project Examples

A paper entitled “The MESERAN Method: Rapid Quantification of Non-Volatile Organic Residue (NVOR)” is shown in Appendix A. This paper, presented at the CleanTech 2002 Conference, details some of the evaluations performed on this project using the MESERAN Analyzer and MicroSolvent Evaporator.

Figure 1 shows the MicroSolventEvaporator that was designed, developed, built, and evaluated for automatically depositing and evaporating successive small quantities
(~5-10 microliters) of solvents onto clean reference surfaces.

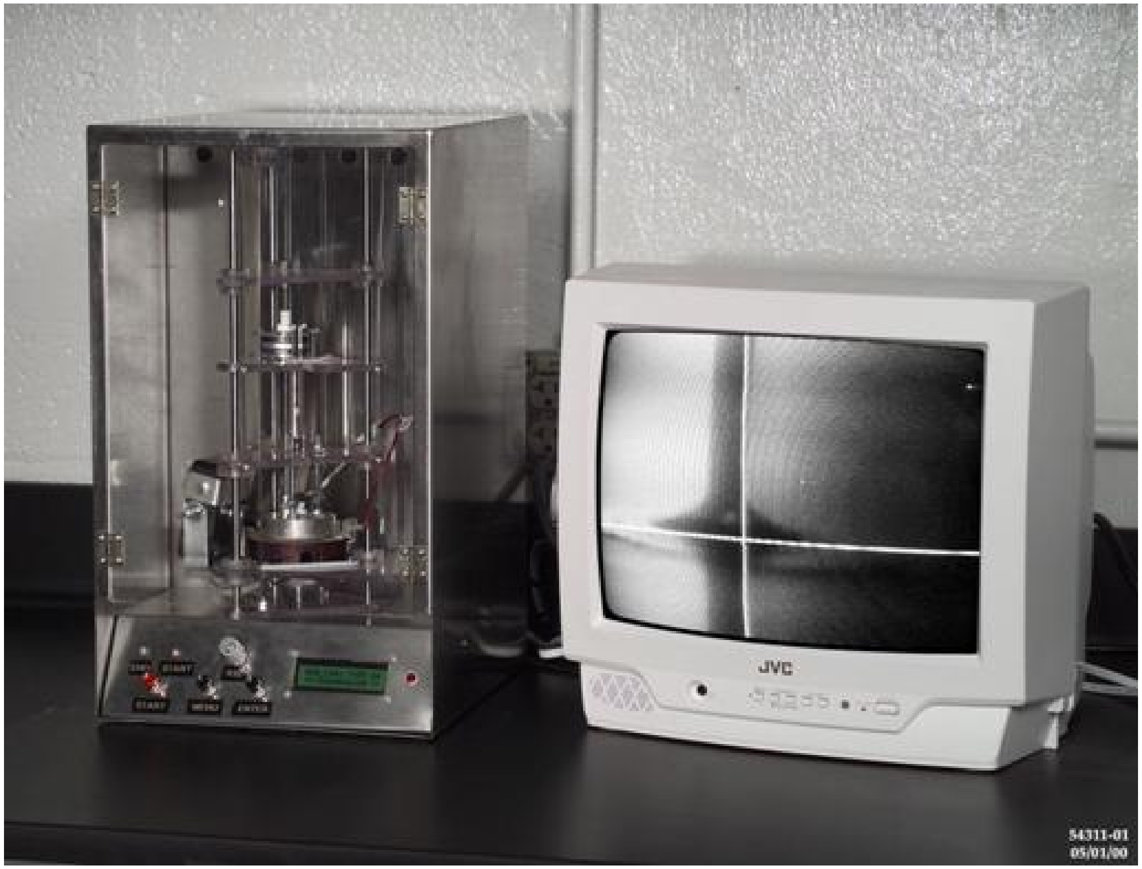

Figure 1.  MicroSolventEvaporator

Figure 2 shows the 250-microliter syringe and stainless steel reference disk used in the MicroSolventEvaporator.

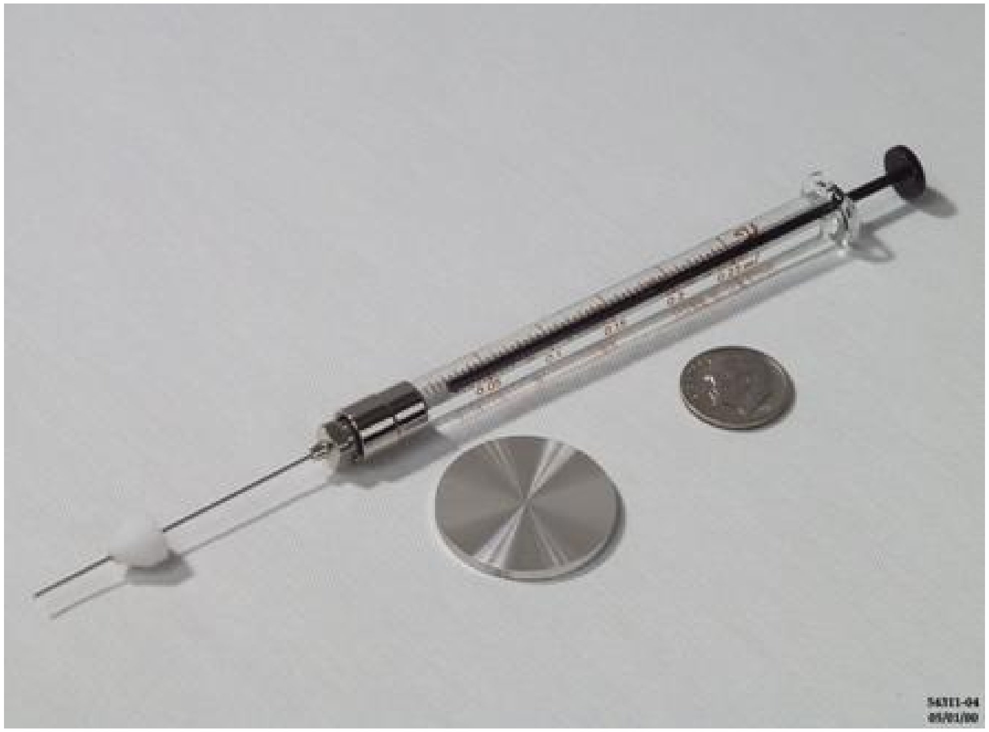

Figure 2.  250-Microliter Syringe and SS Disk

### K.  Technology Commercialization

ERA Systems Inc., The MESERAN Company, already manufactures the MESERAN Analyzers that detect and measure organic residues down to levels less than
1 nanogram/cm$^2$.  They applied for a U S Patent Application in late April of 1998 in relation to the MicroSolventEvaporator.  With substantial additional legal advice, a revised patent application was approved and has been issued on September 15, 2003, to E R A Systems, Inc.  This patent covers broadly the technology of the MESERAN MicroSolventEvaporator.  Without that technology much of the work carried out in this project would have proved virtually impossible.  The MESERAN Company plans to explore a wide application of this technology.

They believe that many industries (automotive, aerospace, electronics, microchip manufacturing, medical, chemistry, biochemistry, etc.) should benefit from this technology.  The principle used in the MicroSolventEvaporator (which results in the highly protected evaporation process) will prove of great importance in almost all chemical and biochemical laboratory processes which now use manual deposition of chemicals from syringes.  In initial limited sales contacts, almost everyone contacted in these fields felt the process employed would be of great benefit to prevent inadvertent contamination.  Actual sales in these fields have been temporarily postponed pending issuance of the patent previously discussed and further development of improved techniques.

## L. Release of Information

I have reviewed the attached Project Accomplishment Summary prepared by Honeywell International Inc. and agree that the information about our CRADA may be released for external distribution.

Original signed by John L. (Jack) Anderson

---

Name:
Organization: ERA Systems, Inc. (A Tennessee Corp.)
Title: President

---

Date: 10/13/03

## L. Release of Information

I have reviewed the attached Project Accomplishment Summary prepared by Honeywell International Inc. and agree that the information about our CRADA may be released for external distribution.

Original signed by Brent J. Ekstrand

---

Name:
Organization: Astro Pak Corporation
Title: Director of Training & Safety

---

Date: 10/16/03

## L. Release of Information

I have reviewed the attached Project Accomplishment Summary prepared by Honeywell International Inc. and agree that the information about our CRADA may be released for external distribution.

Original signed by F. J. Seidl

---

Name:
Organization: Lockheed Martin Space Systems Company, Sunnyvale

Title: Manager, Chemistry and Contamination Control Engineering and Labs, Material and Process Engineering, L450, B195B

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Date: 15 October 2003

# The MESERAN Method:
# Rapid Quantification of Non-Volatile Organic Residue (NVOR)

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## ABSTRACT

The precision analytical technique known as MESERAN Analysis permits quantitative measurement of the level of preexisting nonvolatile organic residue (NVOR) on a substrate from <1 nanogram (ng)/cm$^2$ to > 100 micrograms (μg)/cm$^2$ in 2 minutes. MESERAN Analysis is also applicable to determining NVOR in solvents and solvent extracts. The MESERAN method is able to quantify organic contamination levels down to and below 1 ng by depositing as little as 10 microliters (μL) of solvent containing a known amount of contamination on a clean substrate, allowing it to evaporate, and measuring the evaporated residue. The method will be described in detail and NVOR measurements determined from MESERAN data will be presented.

## DEFINITIONS

In this paper a number of abbreviations, special words, and trademarks are employed:

(1) μ*Ci* means *microCurie*, a unit of radiation which corresponds to 3.7 E 4 (37,000) disintegrations per second.
(2) *Carbon-14 ( C-14)* refers to the radioactive isotope of the element Carbon, an isotope which emits only soft or low energy beta particles; most C-14 beta particles are stopped by a sheet of paper.
(3) USNRC *EXEMPT* means the very low level of Carbon-14 that is not regulated by the U. S Nuclear Regulatory Commission. No license is required for

possession or use. Only USNRC licensed companies are permitted to distribute EXEMPT quantities not to exceed ten 100 μCi of C14 (or combinations of smaller quantities that added up to 100 μCi of C14) at one time. Multiple quantities may be stored by the user. Shipments may be made to anyone in the US. Foreign shipments under IATA regulations must conform to the regulations of the country of final destination.

(4) *ng* means *nanogram* (1 E - 9 grams); μ*g* means *microgram* (1 E - 6 grams)

(5) μ*L* means *microliter* (1 E - 6 liter).

(6) GM detector refers to a thin end-window Geiger Mueller detector tube which detects the C-14 beta emissions which penetrate through the 1.4 - 2.0 mg/cm$^2$ mica window.

(7) One nanomole (*nmole*) is 1 E - 9 moles which equals approximately. 6 E 14 molecules (from Avogadro's ~ 6 E 23 molecules per gram mole).

(8) 1 square centimeter (sq cm) with a roughness factor of 3 is equal to 3 E 16 square Angstroms.

(9) M*onolayer* refers to the number of molecules of a material which covers 1 sq cm in a conventional non-closepacked configuration. For example, each molecule of n-tridecane occupies about 50 sq Angstroms -- which equates to ~ 6 E 14 molecules per sq cm (with a roughness factor of 3)--*i.e. one nanomole*.

(10) *NVR* means *non-volatile residue*; *NVOR means non-volatile organic residue.*

(11) *MESERAN* is an acronym for *Measurement* and *Evaluation* of *Surfaces* by *Evaporative Rate ANalysis*.

(12) *MESERAN*, *MicroSolventEvaporator (MSE)*, *MicroOrganicResidue*, and *MOR* are trademarks licensed to ERA Systems, Inc.

*Operated for the United States Department of Energy under prime contract DE-AC04-01AL66850

## MESERAN METHOD OF ANALYSIS FOR NON-VOLATILE ORGANIC RESIDUE (NVOR) DETECTION[1-6]

The standard microcomputer-based MESERAN technology involves deposition, using a “clean” precision microsyringe, onto a flat or concave surface of 18 μL of a test solution consisting of a low boiling solvent or solvent combination (for these evaluations - cyclopentane) and a high-boiling-but-volatile Carbon-14 labeled compound (in a ratio of approximately 60,000:1). Figure 1 shows the application of test solution. For example, the amount of tridecane-C14 radiochemical per single test (< 0.06 μCi) corresponds to approximately 6 E 14 molecules which equates to *one nanomole*, the *equivalent* of approximately one molecular layer over one square centimeter. Metered air or nitrogen gas is permitted to flow across the surface and between the surface and a Geiger Mueller detector positioned directly above the surface. The evaporation of the low boiling solvent and then the radiochemical is observed as a function of time by recording the detected emissions per second arising from the radiochemical molecules remaining on, or retained by, the surface--the vapor-phase, already-evaporated molecules having been swept out from under the detector by the metered gas (see Figure 2).

Figure 1. Application of Test Solution

Figure 2. Measurement of Emissions

Each test takes less than 3 minutes and the amount of radiochemical employed is EXEMPT from U S Nuclear Regulatory Commission and/or 'Agreement State' licensing regulations due to the very low level of C-14 involved.

Applied to the measurement of microorganic residues, the MESERAN method may be used:

(1) Directly on a flat or concave surface and any microorganic residue thereon which is chemically compatible with the particular radiochemical employed or

(2) Indirectly using an extracting solvent followed by depositing and evaporating an aliquot amount onto a “clean” reference surface. Subsequent deposition and evaporation of the radiochemical solution permits measurement of the amount of deposited residue by comparing the results with previously obtained standards similarly deposited from volumetric dilutions.

For non-polar and/or hydrocarbon type residues, tridecane-C14 in cyclopentane (designated BK) is employed. For more polar residues, tetrabromoethane-C14 in cyclopentane (designated AK) is used. In order to provide a high number of detected emissions for the minimal amount of radiochemical deposited, the tridecane-C14 has a specific activity of approximately 57 µCi/µmole (one carbon atom is essentially pure C14 isotope) while the tetrabromoethane has both carbon atoms labeled (approximately 114 µCi/µmole). Approximately 200 nanograms of radiochemical is deposited in each test with similar levels of radioactivity.

The ERA method assumes that the particular radiochemical employed is chemically compatible with the residue, that the test solution droplet covers all of the residue, and that the test solution solvent substantially dissolves the residue within the time period of the solvent evaporation. *Attention to the avoidance of inadvertent contamination and the maintenance of reasonably constant temperature and pressure are required for optimal reproducibility from test to test.*

## MECHANISM OF THE MESERAN METHOD FOR QUANTIFYING NVOR[1-6]

When a homogeneous chemical is permitted to evaporate, the classical mechanism of the process (normally measured by monitoring the already evaporated portion) follows first order kinetics - the plot of log concentration vs. time is a straight line. This mechanism applies to pure materials as well as to solutions of chemicals in which the components are chemically compatible and in which the second component is non-volatile under the conditions of the process. In the presence of the second component, the rate of evaporation is slowed.

In the MESERAN technology, however, the amount of radiochemical retained by the surface system as a function of time is measured by counting the emissions arising from the radiochemical molecules remaining on the surface. In this discussion the factors of temperature and pressure are assumed constant and the concentration of already evaporated molecules in the adjacent gaseous phase approaches zero due to the flowing air or nitrogen referred to above. The molecular weight of each evaporating molecule and the intermolecular forces among the molecular near-neighbors are thus the primary factors in determining the tendency of each molecule to remain in solution or conversely to escape from the liquid portion of the air/liquid (or semisolid) interface. As applied in MESERAN technology, which employs only a monolayer *equivalent* of the radiochemical, the observed rate of evaporation is thus a function of the residual concentration of the non-evaporated molecules of the Carbon-14 radiochemical. Figure 3 illustrates the typical evaporation of the radiochemical solution from a clean surface. The A-B line represents the evaporation of the low boiling solvent (e.g., cyclopentane). The rationale for the initial increase in counts/second is that the C-14 soft beta emissions are partially absorbed by the solvent molecules. B represents the point at which substantially all of the low boiling solvent has evaporated and the maximal amount of residual radiation reaches the GM detector. The B-C line represents the evaporation of the radiochemical from the surface under the conditions of the test. C represents a level where the GM detector can no longer adequately differentiate the residual radiation from background.

A solution of the high-boiling-but-volatile tridecane-C14 in higher boiling hydrocarbons (i.e., contamination) follows a similar but slower path than does the evaporation of the labeled tridecane itself since the non-volatile “residue” molecules occupy increasing portions of the liquid (or semi-solid) interface. The rate at which the solvent evaporates is slowed somewhat and the rate at which the radiochemical evaporates is slowed considerably with the observed rate of evaporation being a function of the amount of residue on the surface. The observed rate of evaporation of the radiochemical (*the slope expressed as a positive integer*) thus is an inverse measure of the amount of non-evaporating residue. The lower the slope, the more the residue and vice versa. Figure 4 illustrates typical evaporations of the radiochemical solution with increasing amounts of residue. ABC is repeated from Figure 3 and illustrates a typical evaporation of the radiochemical solution with no interactions from residue (i.e., a clean substrate). A*B*C* illustrates a typical evaporation of the radiochemical solution with some contamination present. A**B**C** illustrates a typical evaporation of the radiochemical solution with a larger amount of contamination present.

## METHODS OF ANALYZING MESERAN DATA[1-6]

There are two general methods for analyzing the MESERAN data:  (1) Total Counts (total area under each curve based on counts minus background) and (2) Slope of the evaporation of radiochemical (the post-peak portion of the curve).  Based upon raw data minus background, Figure 5 illustrates three typical experimentally derived curves of Ln counts per second minus background vs. time in seconds.  Figure 5 is similar to Figure 4 except raw data from actual tests are shown.

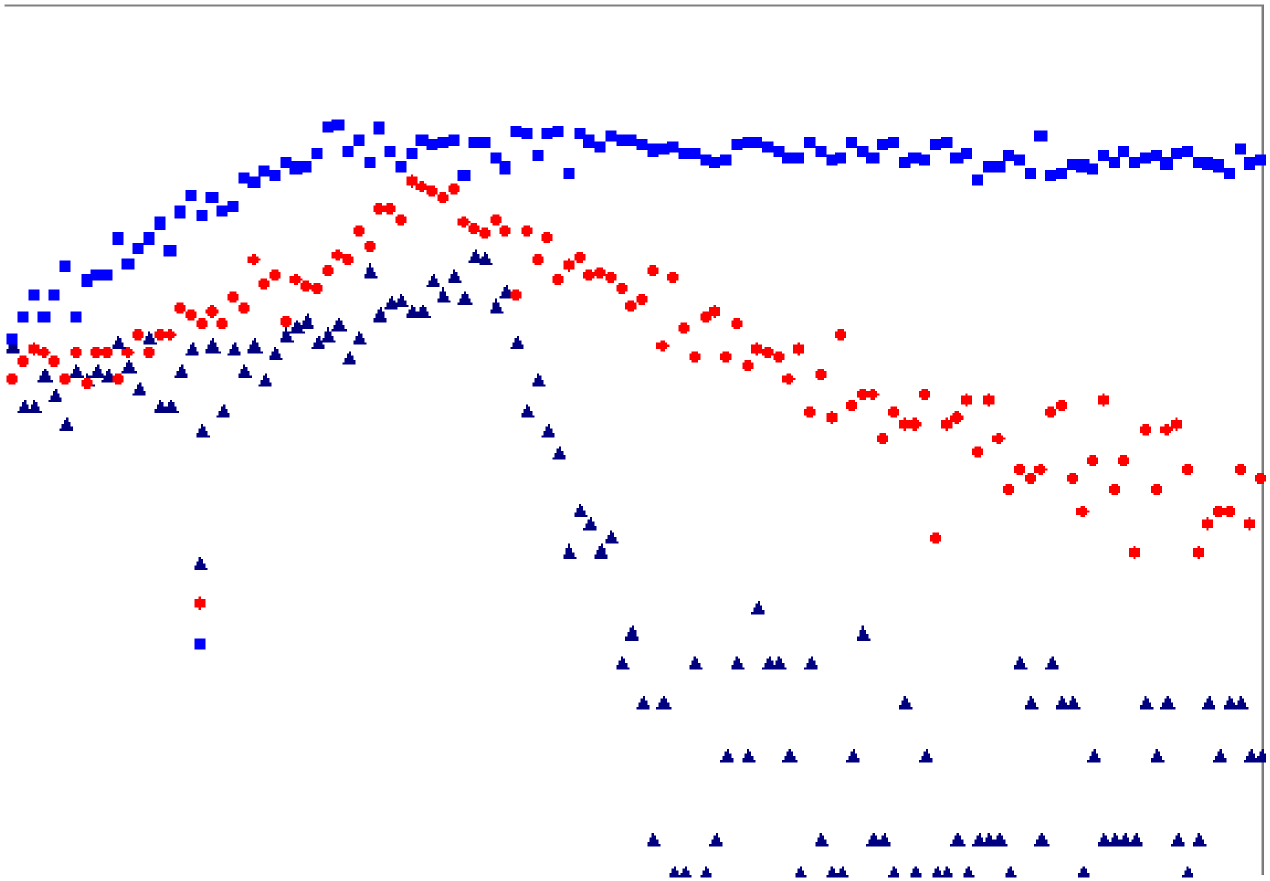
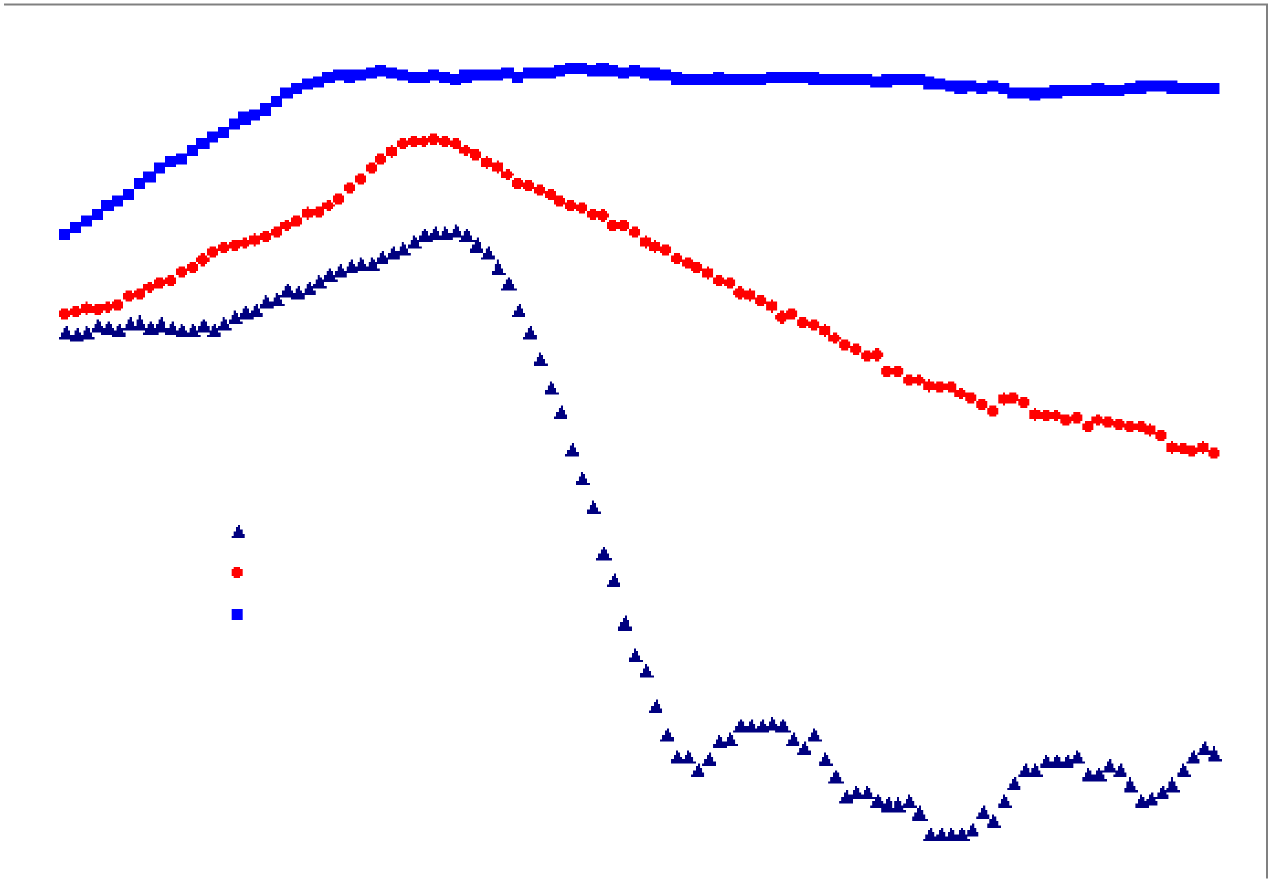


Figure 5. Plot of Raw Data Showing Low, Medium, and High Levels of Organic Contamination

The upper curve represents a high level of organic residue, the middle curve represents a medium level of organic residue, and the lower curve represents a low level of organic residue. The scatter particularly at the lower values is due to the inherent randomness of radiation (the Poisson distribution in which the square root of each count total is the best estimate of one standard deviation). The slope method is more sensitive, especially at low levels of contamination. For measuring microorganic residues, the total count method of analysis (i.e., the area under each overall curve based on actual counts) is valid from somewhat less than 200 ng to approximately 100,000 ng (100 µg). Higher total counts are indicative of higher organic residue levels and vice versa. The slope method of data analysis, normally based on statistically smoothed data and based on the log count vs. time relationship, increases the sensitivity of the lower limit markedly (to less than 1 ng) since the total counts method (the total area under each curve) approaches statistical insignificance somewhat below 200 ng. Expressed as a positive integer, the higher (or steeper) the slope, the cleaner the surface and conversely, the lower (or more flat) the slope, the greater the residue. Figure 6 represents the same data that is in Figure 5 except that the data in Figure 6 is logarithmically smoothed to increase the reliability of the individual points.

Figure 6. Plot of Logarithmically Smoothed Data Showing Low, Medium, and High Levels of Organic Contamination



Both the total counts and slope methods of analysis can be used qualitatively or quantitatively. The total count method has been used for over 30 years by testing a surface with the MESERAN Analyzer and comparing the results to those obtained from known clean standards for that particular surface. The total counts of the clean standard are subtracted from the total counts obtained on the surface being tested to give a net total counts representing the contamination amount. This result can be compared to previously performed calibrations of contamination to obtain a quantitative result for the contamination amount. Similarly, the slope method can be used to compare the slope obtained on the surface being tested to the slope obtained from known clean standards for that particular surface. The slope can also be compared to previously performed calibrations of contamination to obtain a quantitative result for the contamination amount.

In many cases, quantitative data is not needed. For instance, if one is performing process control work to determine if the cleaning process is performing as it is designed, quantitative data on the actual amount of contamination may not be necessary. It may have been established that as long as the parts being cleaned are less than a certain amount of contamination, then they are clean enough. Therefore, one only has to establish the MESERAN total counts or MESERAN slopes that correspond to that level of contamination and relate the tests as being in compliance or not in compliance. Honeywell Federal Manufacturing & Technologies (FM&T), Kansas City Plant (KCP), has used this technique for years to control cleanliness and compare the abilities of different cleaners and cleaning processes to remove various contaminants. Net total count values were established that corresponded to electrical failures and catastrophic adhesive failures. As long as the MESERAN net total counts were below these levels, no cleaning related failures occurred.

In recent years, KCP has been incorporating the use of the slope technique to give more quantifiable data for lower amounts of contamination. Calibrations of various contaminants have been performed by KCP to develop calibration curves for these contaminants on substrates of interest. MESERAN slope results obtained can now be compared to the calibration curves to determine quantitative amounts of contamination detected.

These calibrations were performed in the following manner. A master calibration solution was prepared in a 10-milliliter (mL) volumetric flask by dissolving 100 milligrams (mg) of the organic contaminant in 10 mL of solvent (e.g., cyclopentane, methylene chloride, or hexane that has been double distilled in an all-glass still with no grease in the joints – NVOR of these solvents are approximately 10 ppb). Volumetric dilutions were used to make contamination solutions for depositing known amounts of the organic contaminant on reference substrates (e.g., aluminum panels, stainless steel disks, glass cones, etc.). The master calibration solution was thoroughly mixed and 1 mL of this solution was placed in another 10-mL volumetric flask. The second volumetric flask was then diluted with the double distilled solvent until the solution level was at 10 mL and this solution was thoroughly mixed. Subsequent dilutions were carried out in a similar fashion. Ten microliters (µL) of each calibration solution was deposited on the precleaned substrates and allowed to evaporate. This resulted in the following amounts of contamination on the substrates: 1 ng, 10 ng, 100 ng, 1 µg, 10 µg, and 100 µg. Some intermediate levels were obtained by depositing 3 µL and 5 µL of the calibration solutions. The volumetric dilution process for making calibration solutions is shown in Figure 7.

Figure 7. Volumetric Dilution Process for Formulating Calibration Solutions

The substrates that were contaminated were then tested using the MESERAN Analyzer to develop a calibration curve of the contaminant. For example, calibrations curves for Dioctyl Phthalate (DOP) using radiochemical test solution AK (tetrabromoethane-C14 in cyclopentane) on aluminum panels are shown in Figures 8 and 9. Figure 8 shows the calibration curve for DOP using the total count method of analysis. Figure 9 shows the calibration curve for DOP using the slope method of analysis. As can be seen from examining Figure 8, the total count method of analysis loses its ability to differentiate contamination amounts (i.e., loses its statistical significance) below a few hundred nanograms of contamination (approximately a monolayer). However, the slope method of analysis shown in Figure 9 is able to differentiate contamination amounts down to 1 nanogram. In general practice, total counts can be used to quantify contamination amounts greater than a monolayer (a few hundred nanograms) up towards the 100 microgram range. The slope method can be used to quantify contamination levels well below the monolayer (down to a nanogram) as well as up to approximately 100 micrograms.

Whenever possible it is advantageous to develop calibration curves for the contaminants of interest. KCP has developed calibration curves for numerous contaminants typically encountered in KCP operations such as oils, greases, mold releases, solder fluxes, resins, etc. However, since one does not always know all of the contaminants that may be present on a part, KCP developed a general calibration curve to use for unknown samples based upon hydrocarbon residues. Thus far, most hydrocarbon residues tested have similar calibration curves for the various amounts of residue.

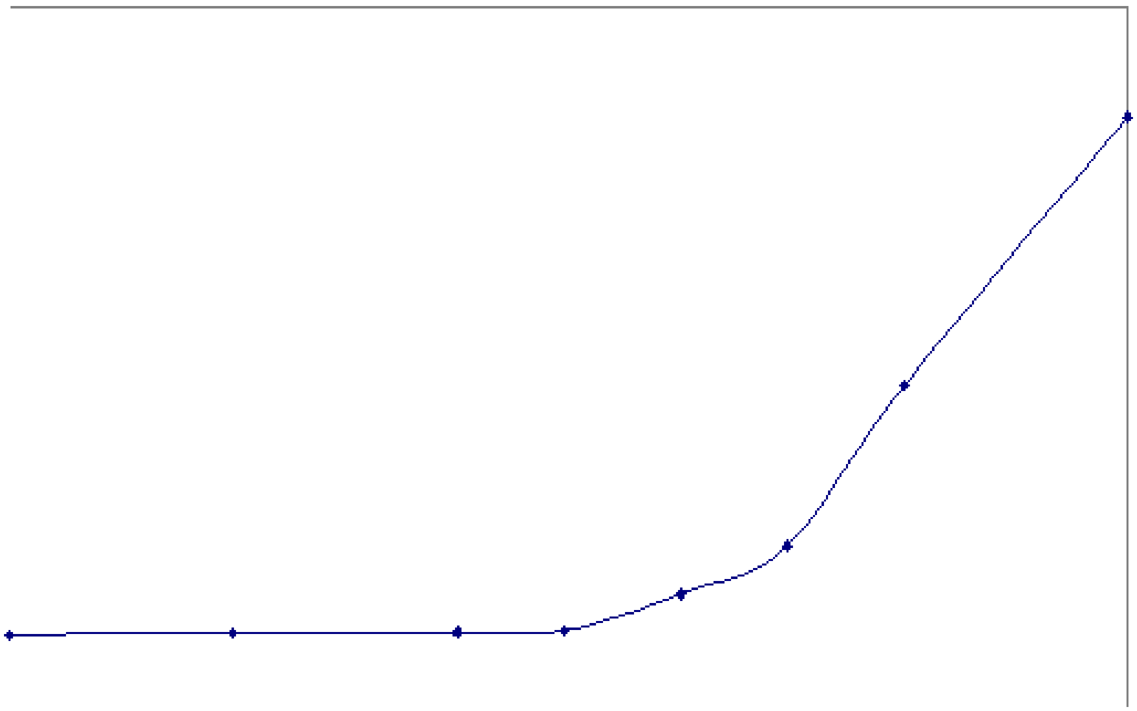


Figure 8. Calibration Curve of DOP on Aluminum Panels Using MESERAN Total Counts

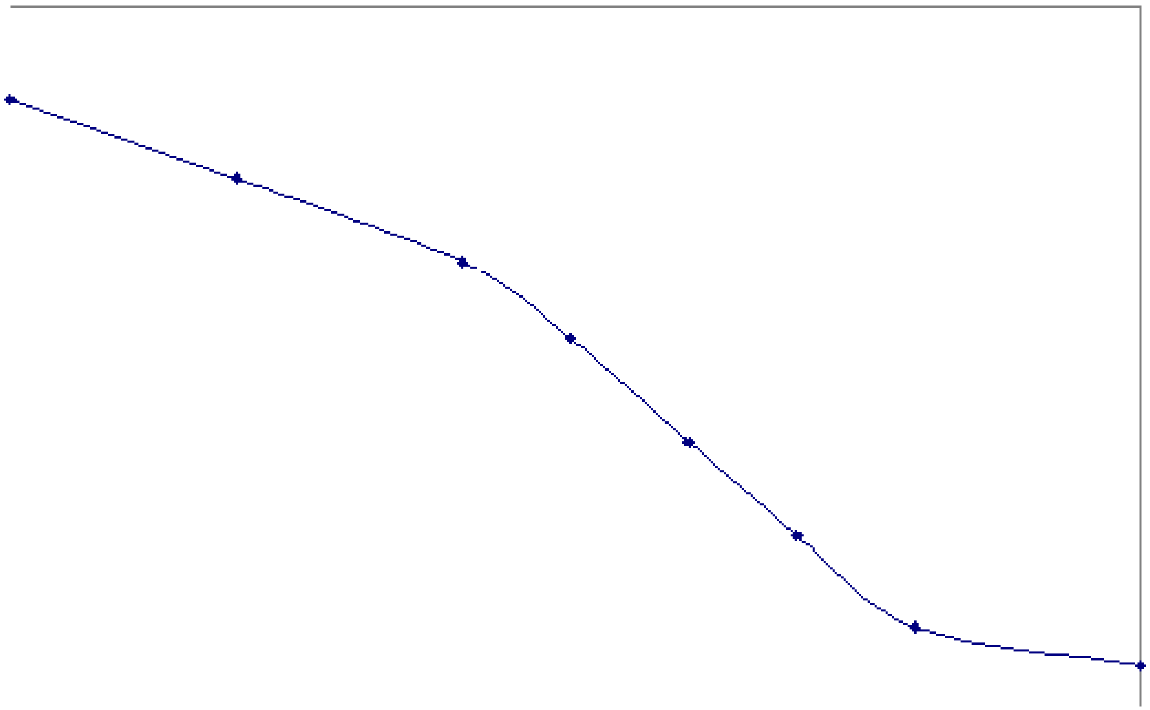


Figure 9. Calibration Curve of DOP on Aluminum Panels Using MESERAN Low Variance Slopes

## CASE STUDIES

### Background

KCP has been using MESERAN Analyzers for about 30 years to detect organic contamination and evaluate cleaning processes. In recent years, KCP has been working on several projects with The MESERAN Company to improve data analysis and develop new methods for using the MESERAN technology. One area that has been concentrated on is the evaluation of NVR in solvents and solvent extracts.

Solvent NVR is comprised of molecular contamination (or non-volatile organic residue – NVOR) which represents the majority of the NVR and particulate contamination which normally represents a small fraction of the NVR. KCP is primarily interested in NVOR. Suitable filtration of the solvent followed by weighing, particle size analysis or other determination provides a reasonably satisfactory solution for determining particulate contamination. Molecular contamination or NVOR consists primarily of hydrocarbons (probably the most prevalent), vegetable and/or animal oils, silicone oils and greases, detergents and soaps, and polyfluorinated oils and greases.

The following are some reasons that solvent NVR tests are performed:

- Measuring NVR levels of incoming solvents for acceptance tests,
- Determining part cleanliness by rinsing a part with a solvent to extract residue from the parts and analyze the solvent to determine the NVR extracted,
- Determining contaminant loading in a solvent cleaning process.

Several case studies detailing the use of MESERAN technology to perform these kinds of tests are discussed below.

## NVOR Determinations of Solvents[5]

The calibration curves of typical contaminants developed at KCP showed that the MESERAN Analyzer can detect as little as 1 ng of organic contamination in 10 μL of solvent after it is evaporated on a clean substrate. Typical gravimetric NVR evaluations at KCP require the evaporation of at least 1 liter of solvent to be able to detect ppm levels of NVR in solvents to make sure that the solvents meet specification requirements. Since the MESERAN Analyzer is very sensitive to measuring organic contamination, it was decided to determine if this system could be used to quantify the NVR of solvents by evaporating smaller quantities on clean reference surfaces and then testing them with the MESERAN Analyzer. The following shows examples of solvents that have been evaluated.

Aluminum panels were precleaned using a trichloroethylene vapor degreasing and ultrasonic cleaning process. The panels were then plasma cleaned in oxygen for 1 hour at 100 watts and 0.8 torr. After cleaning (and allowing the panels to sit for 24 hours so the activity dissipated), the panels were tested with the MESERAN Analyzer to make sure they were clean. MESERAN slope values and their corresponding contamination amounts (based upon previously performed calibrations of hydrocarbon contaminants) for the clean aluminum panels are shown in Table 1. All of the panels tested were extremely clean with contamination amounts <1 ng/cm$^2$. (Note – the radiochemical droplet covers approximately 1 cm$^2$ on the aluminum panels)

| Panel Number | MESERAN Slope | Contamination (ng/cm$^2$) |
|---|---|---|
| 1 | 2889 | <1 |
| 2 | 2923 | <1 |
| 3 | 3103 | <1 |
| 4 | 2846 | <1 |

Table 1. MESERAN Slopes and Contamination Amounts on Clean Aluminum Panels

Three solvents (hexane, toluene, and methylene chloride) were evaluated for NVR using the MESERAN technique and compared to the values stated on the manufacturer's label. Specific information about the solvents is as follows:

- Hexane (Burdick & Jackson 216-4 from Van Waters & Rogers, stated evaporative residue: none, <1 mg/L ),
- Toluene (Fisher Scientific, stated evaporative residue = 0.0004% or 4 ppm),
- Methylene Chloride (Fisher Scientific, Optima Grade, stated evaporative residue = 1 ppm).

These solvents were deposited on clean aluminum panels 10 μL at a time using a clean microsyringe and allowed to evaporate until the total quantity being analyzed had been deposited. The depositions were carried out in this manner to make sure that the evaporative residue would be encompassed by the 18 μL droplet of radiochemical test solution. These depositions and evaporations were carried out at room temperature. The hexane and toluene evaluations were conducted on 50 μL aliquots and the methylene chloride evaluations were conducted on 100 μL aliquots. The MESERAN slope values and their corresponding contamination amounts (based upon previously performed calibrations of hydrocarbon contaminants) for the solvents being analyzed are shown in Table 2.

| | **50 μL of Hexane** | | **50 μL of Toluene** | | **100 μL of Methylene Chloride** | |
|---|---|---|---|---|---|---|
| | MESERAN Slope | Contamination | MESERAN Slope | Contamination | MESERAN Slope | Contamination |

| Test Number | | (ng) | | (ng) | | (ng) |
|---|---|---|---|---|---|---|
| 1 | 2106 | 26 | 1630 | 244 | 2078 | 31 |
| 2 | 2111 | 25 | 1668 | 215 | 2051 | 37 |
| 3 | 2156 | 19 | 1622 | 251 | 2148 | 20 |
| 4 | 2318 | 6 | | | | |
| **AVG** | | **19** | | **236.67** | | **29.33** |

Table 2. MESERAN Slopes and Contamination Amounts for Hexane, Toluene, and Methylene Chloride

The average contamination amount in 50 µL of hexane was 19 ng or 0.38 ng/µL. This is equivalent to 0.38 mg/L. Therefore, by depositing only 50 µL of hexane on a clean substrate, allowing it to evaporate, and then testing it with the MESERAN Analyzer, it was confirmed that the NVR of the hexane was indeed <1 mg/L and was quantified to be 0.38 mg/L. The average contamination amount in 50 µL of toluene was 236.67 ng or 4.73 ng/µL. For a solvent density of 1 g/mL (i.e., water), 1 mg/L = 1 ng/µL = 1 ppm. For other solvent densities, one must divide the contamination amount in ng/µL by the solvent density to determine actual ppm levels. The density of toluene at 20°C is 0.86696 g/mL. Therefore, 4.73 ng/µL divided by 0.86696 g/mL = 5.46 ppm. The MESERAN Analyzer was able to quantify the contamination in 50 µL of toluene to be 4.73 ng/µL or 5.46 ppm. The average contamination amount in 100 µL of methylene chloride was 29.33 ng or 0.2933 ng/µL. The density of methylene chloride at 20°C is 1.3256 g/mL. Therefore, 0.2933 ng/µL divided by 1.3256 g/mL = 0.22 ppm. The MESERAN Analyzer was able to quantify the contamination in 100 µL of methylene chloride to be 0.2933 ng/µL or 0.22 ppm.

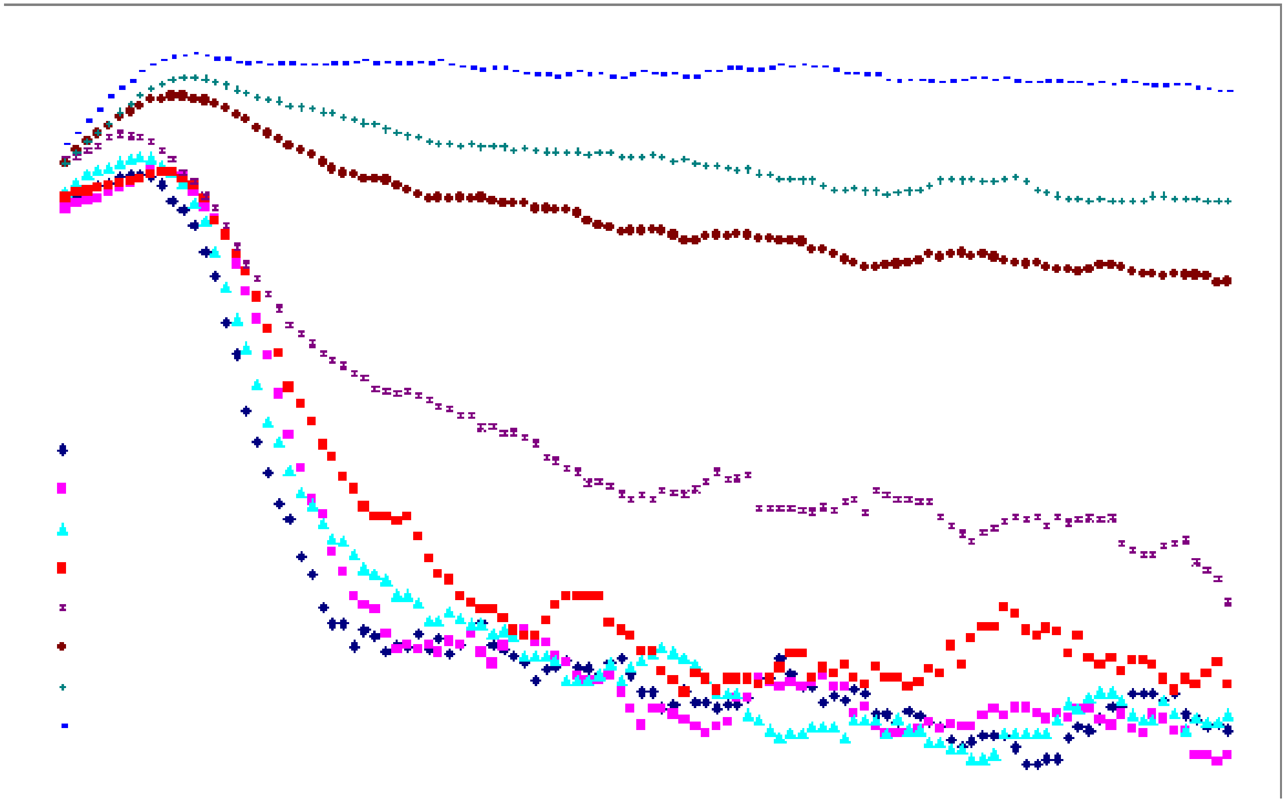
The hexane and methylene chloride samples that were tested in these examples came from unopened bottles while the toluene came from a previously opened bottle (about half-full). The MESERAN results indicate that the NVR of the solvents in unopened bottles did indeed meet or exceed the specified NVR limit on the label; however, the previously opened bottle of toluene did not meet the specified NVR limit on the label. As one would expect, after bottles are opened, the solvents in them can become contaminated through exposure to the environment or misuse. It should be mentioned that the NVR amounts shown on the labels were probably determined gravimetrically by evaporating large quantities of the solvent; therefore, these weight measurements would also contain the contribution of particles. MESERAN Analysis will only quantify the amount of organic residue (NVOR) in the solvents (which is exactly the information of interest to KCP). This work on evaluating the NVOR in solvents indicates that the MESERAN Analyzer can be used to quantify solvent NVOR down to the ppm and higher ppb ranges. Obviously greater sensitivity (i.e., lower levels) can be achieved by evaporating larger quantities of solvents.

## Residue Quantification for Electrical Assembly Cleaning Development

### Background and Problem Description

A customer specifically requested MESERAN testing to quantify the cleaning effectiveness of trichloroethylene (TCE), isopropyl alcohol (IPA) and d-limonene for removing solder flux paste from a particular electrical assembly. The baseline cleaning process was cold spray cleaning with TCE using a paint spray type of system at approximately 40 psig. IPA and d-limonene were also evaluated using the same spray cleaning process. Numerous samples (3/8 inch diameter copper) were prepared to simulate the actual electrical assembly. However the samples were too small for direct testing with the MESERAN Analyzer. It was proposed to extract contamination from the samples with TCE, use the newly developed MicroSolventEvaporator to evaporate aliquots of the extract solution onto clean reference substrates, and then test the contaminated substrates with the MESERAN Analyzer to quantify the residue extracted from the samples.

### Calibration of Solder Flux Paste



Since this particular solder flux paste (EFD 6-411) was different than most of the solder fluxes that have previously been calibrated at KCP, a calibration curve was developed for this material. A master calibration solution was prepared in a 10 mL volumetric flask by dissolving 100 mg of the dried flux in 10 mL of TCE. Volumetric dilutions were then performed to make calibration solutions contaminated with known amounts of the flux (as was described previously and shown in Figure 7). Ten (10) µL of each calibration solution was deposited on clean stainless steel (SS) disks and allowed to evaporate, resulting in the following amounts of contamination: 1 ng, 10 ng, 100 ng, 1 µg, 10 µg, and 100 µg. Five (5) µL of two of the solutions were also deposited on clean SS disks, resulting in 500 ng and 5 µg of contamination to enhance the calibration curve in the areas that were deemed likely for the contamination results of the actual parts. The SS Disks were then tested with the MESERAN Analyzer using radiochemical BK to develop a calibration curve of the EFD 6-411 solder flux paste. Figure 10 shows the plot of various amounts of EFD 6-411 solder flux paste on the SS disks using the logarithmically smoothed MESERAN data.

Figure 10. Plot of Various Amounts of EFD 6-411 Solder Flux Paste on SS Disks Using Logarithmically Smoothed MESERAN Data (Tested with Radiochemical BK)

A minimum of five replicates was run at each contamination level. Table 3 shows the calibration data obtained for the average slopes determined from the evaluation of the MESERAN curves for the various amounts of EFD 6-411 solder flux paste on SS disks using logarithmically smoothed MESERAN data. The calibration curve developed from this data is shown in Figure 11. As can be seen from the data and the calibration curve, radiochemical BK loses sensitivity for detecting the EFD 6-411 solder flux paste on the SS disks below 10 ng. In addition, the slope values at 100,000 ng (100 µg) are probably also in question. Good sensitivity is shown between 10 ng and 10,000 ng (10 µg). Normally radiochemical AK would have been used for detecting the EFD 6-411 solder flux paste because it is more sensitive to detecting polar residues; however, there was not any in stock at KCP when these evaluations were required. Therefore, radiochemical BK was used since it was postulated that it would have the required sensitivity in the contamination region of interest. Based upon previous evaluations of rosin fluxes, it is assumed that radiochemical AK would have increased sensitivity below 10 ng.

| **Contamination (ng)** | **Log of Contamination** | **Low Variance Slope Average** | **Standard Deviation** | **Coefficient of Variation** |
|---|---|---|---|---|
| 1 | 0 | 2972 | 152.7 | 5.14% |
| 10 | 1 | 2941 | 144.3 | 4.91% |
| 100 | 2 | 2475 | 223.1 | 9.01% |
| 500 | 2.699 | 1818 | 182.8 | 10.06% |
| 1000 | 3 | 1291 | 117.8 | 9.12% |
| 5000 | 3.699 | 476 | 72.9 | 15.32% |
| 10000 | 4 | 276 | 32.5 | 11.78% |
| 100000 | 5 | 93 | 32.0 | 34.41% |

Table 3. Calibration Data for MESERAN Low Variance Slopes of EFD 6-411 Solder Flux Paste on SS Disks Tested with Radiochemical BK

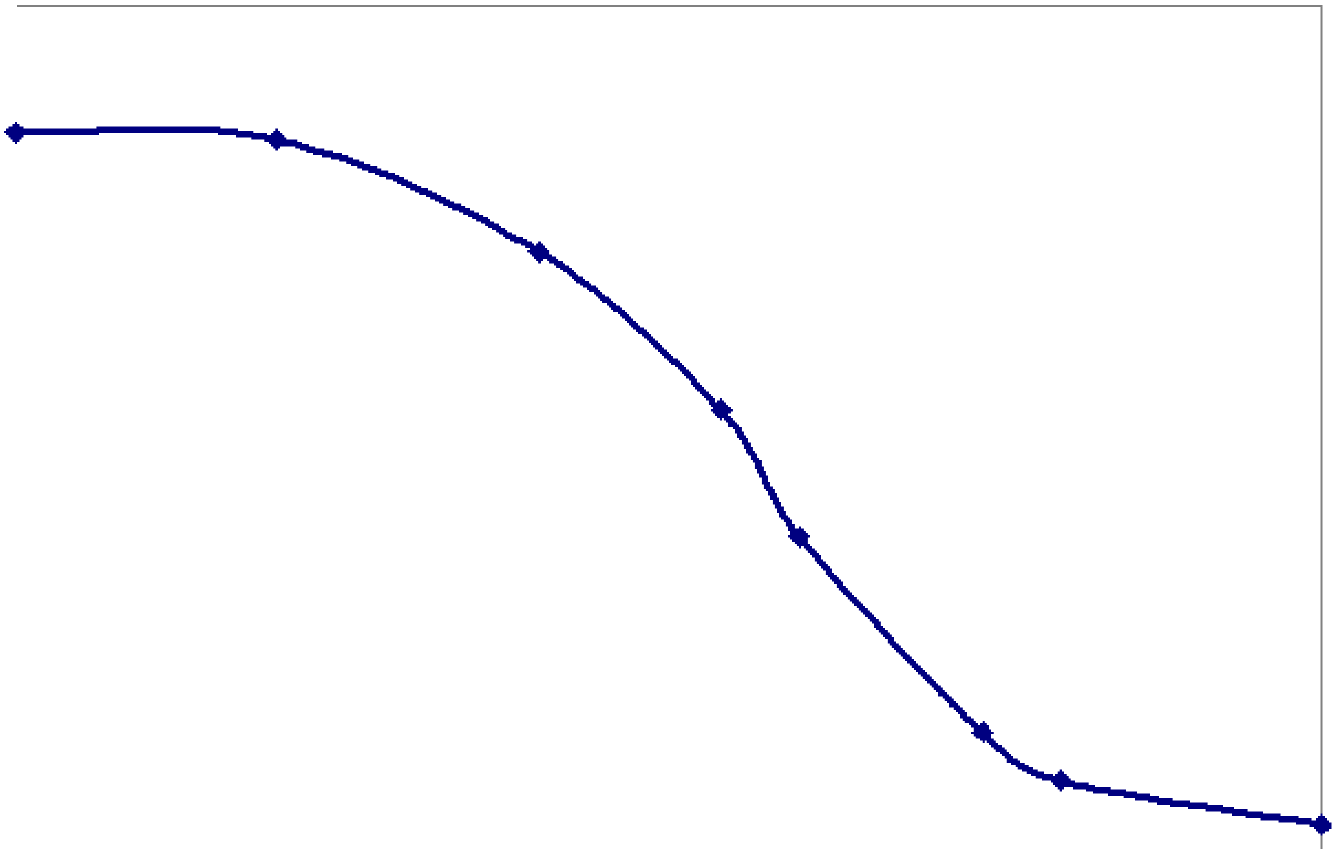


Figure 11. Calibration Data for MESERAN Low Variance Slopes of EFD 6-411 Solder Flux Paste on SS Disks Tested with Radiochemical BK

## Evaluation of Samples for EFD 6-411 Solder Flux Paste Residue Quantification

The samples were prepared in two different groups, supposedly made the same way but at different times. The 3/8 inch diameter copper samples being evaluated were too small for direct testing with the MESERAN Analyzer. Therefore an extraction procedure was developed using TCE to extract the EFD 6-411 solder flux paste from the samples. Approximately 10 copper samples were placed in a clean 50 mL flask. Twenty (20) mL of TCE was added to the flask to extract the residue. The flask containing the copper samples and the TCE was agitated in an 40 kHz ultrasonic cleaner for 5 minutes to aid in the extraction process and thoroughly mixed the solution. A clean microsyringe was used to take 250 μL aliquots from the flasks containing the 20 mL of TCE and the extracted flux residue. The newly developed MicroSolventEvaporator was used to evaporate the 250 μL aliquots onto clean SS disks. The SS disks were then tested with the MESERAN Analyzer. A minimum of five replicates were run for each condition tested. Figure 12 shows a picture of the microsyringe and one of the SS disks used in the evaluation. Figure 13 shows a picture of the MicroSolventEvaporator system used to evaporate the 250 μL aliquots onto the SS disks. The MicroSolventEvaporator was used to automatically deposit and evaporate small quantities of the extract solution (~5-10 microliters at a time) until the 250 μL aliquots of the extract solution were completely evaporated on the SS disks. This reproducible and time-saving method of preparing these samples allowed many replicates to be run so that statistically valid results could be obtained.

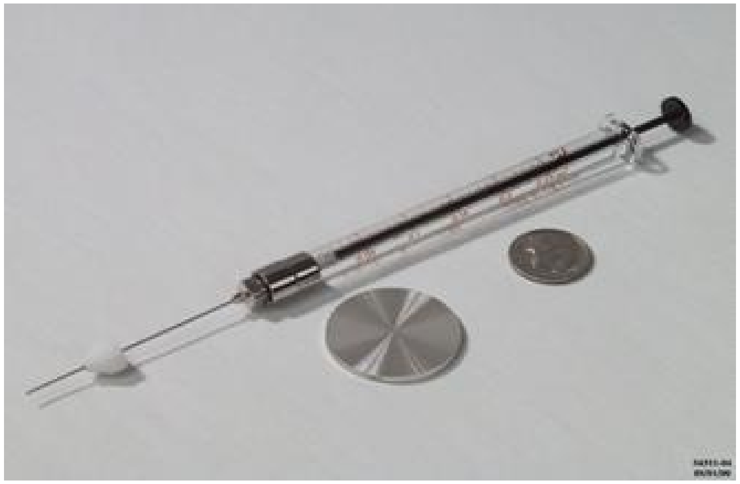


Figure 12. Microsyringe and SS Disk

Figure 13. MicroSolventEvaporator

The SS disks with the evaporated residues from the 250 µL aliquots were then tested with the MESERAN Analyzer using radiochemical BK to quantify the contamination from each aliquot. The average low variance MESERAN slope results of these tests are shown in Table 4.

| | | | |
|---|---|---|---|
| **Group 1** | | | |
| **Sample** | **Average Slope** | **Standard Deviation** | **Coefficient of Variation** |
| TCE Used for Extractions | 2614 | 116.7 | 4.5% |
| No Clean | 338 | 40.8 | 12.1% |
| TCE Clean | 1820 | 142.7 | 7.8% |
| d-Limonene Clean | 2020 | 180.5 | 8.9% |
| IPA Clean | 1785 | 26.9 | 1.5% |
| | | | |
| **Group 2** | | | |
| **Sample** | **Average Slope** | **Standard Deviation** | **Coefficient of Variation** |
| TCE Used for Extractions | 2614 | 116.7 | 4.5% |
| No Clean | 98 | 31 | 32.0% |
| TCE Clean | 1615 | 74.7 | 4.6% |
| d-Limonene Clean | 1765 | 60.3 | 3.4% |
| IPA Clean | 1746 | 189.2 | 10.8% |

Table 4. MESERAN Slope Results for 250 µL Aliquots of 20 mL Extract Solutions

The slope results were compared to those obtained from the calibration of EFD 6-411 solder flux paste shown previously in Figure 11. A linear-log interpolation using the values from the calibration in Figure 11 was performed to calculate the contamination amounts. The contamination results calculated for the 250 µL aliquots are shown in Table 5.

| **Group 1** | | |
|---|---|---|
| | **Average** | **Equivalent** |
| **Sample** | **Slope** | **Contamination (ng)** |
| TCE Used for Extractions | 2614 | 50 |
| No Clean | 338 | 8066 |
| TCE Clean | 1820 | 498 |
| d-Limonene Clean | 2020 | 305 |
| IPA Clean | 1785 | 522 |
| | | |
| **Group 2** | | |
| | **Average** | **Equivalent** |
| **Sample** | **Slope** | **Contamination (ng)** |
| TCE Used for Extractions | 2614 | 50 |
| No Clean | 98 | >100,000 |
| TCE Clean | 1615 | 653 |
| d-Limonene Clean | 1765 | 536 |
| IPA Clean | 1746 | 550 |

Table 5. EFD 6-411 Solder Flux Paste Contamination Amounts Calculated for the 250 µL Aliquots Evaluated

The TCE used in the extractions was determined to contain 50 ng of contamination in 250 µL. Therefore, 50 ng was subtracted from the results for the other samples to determine the quantity of contamination extracted from the samples in each 250 µL aliquot. Then these contamination results for the 250 µL aliquots had to be factored up to account for the total contamination in the 20 mL extract solutions. Next, the contamination amounts were converted from ng to µg. Finally, the contamination amounts in µg were divided by the total area (in$^2$) of the samples evaluated for each condition to achieve a contamination per unit area (µg/ in$^2$). Table 6 shows the final contamination amounts calculated for each condition.

| **Group 1 Samples** | **Equivalent Contam. (ng)** | **Equivalent Contam. – TCE NVR (ng)** | **Total Contam. in 20 mL (ng)** | **Total Contam. in 20 mL (µg)** | **Number of Samples Extracted** | **Area per Sample** | **Contam./ Unit Area (µg/ in$^2$)** |
|---|---|---|---|---|---|---|---|
| TCE NVR | 50 | 0 | N/A | N/A | N/A | N/A | N/A |
| No Clean | 8,066 | 8,016 | 641,280 | 641.28 | 10 | 0.221 | 290.17 |
| TCE Clean | 498 | 448 | 35,840 | 35.84 | 10 | 0.221 | 16.22 |
| d-Limonene Clean | 305 | 255 | 20,400 | 20.4 | 10 | 0.221 | 9.23 |
| IPA Clean | 522 | 472 | 37,760 | 37.76 | 9 | 0.221 | 18.98 |
| | | | | | | | |
| **Group 2 Samples** | **Equivalent Contam. (ng)** | **Equivalent Contam. – TCE NVR (ng)** | **Total Contam. in 20 mL (ng)** | **Total Contam. in 20 mL (µg)** | **Number of Samples Extracted** | **Area per Sample** | **Contam./ Unit Area (µg/ in$^2$)** |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| TCE NVR | 50 | 0 | N/A | N/A | N/A | N/A | N/A |
| No Clean | >100,000 | >100,000 | >8,000,000 | >8,000 | 10 | 0.221 | >3,620 |
| TCE Clean | 653 | 603 | 48,240 | 48.24 | 12 | 0.221 | 18.19 |
| d-Limonene Clean | 536 | 486 | 38,880 | 38.88 | 10 | 0.221 | 17.59 |
| IPA Clean | 550 | 500 | 40,000 | 40.00 | 10 | 0.221 | 18.10 |

Table 6. EFD 6-411 Solder Flux Paste Final Contamination Amounts Calculated for Each Condition Evaluated

Figure 14 shows a graphical representation of all of the contamination amounts calculated in Table 6 and Figure 15 shows a graphical representation of the contamination amounts calculated in Table 6 for the cleaned samples only.

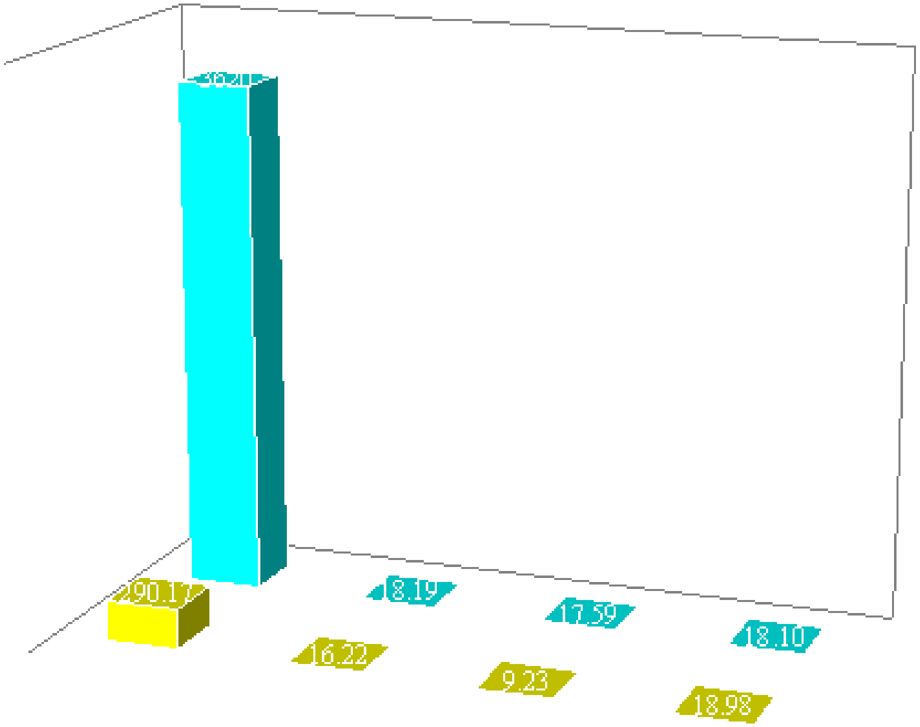


Figure 14. EFD 6-411 Solder Flux Paste Contamination Determined by MESERAN Analysis on All Samples (Contaminated and Cleaned)

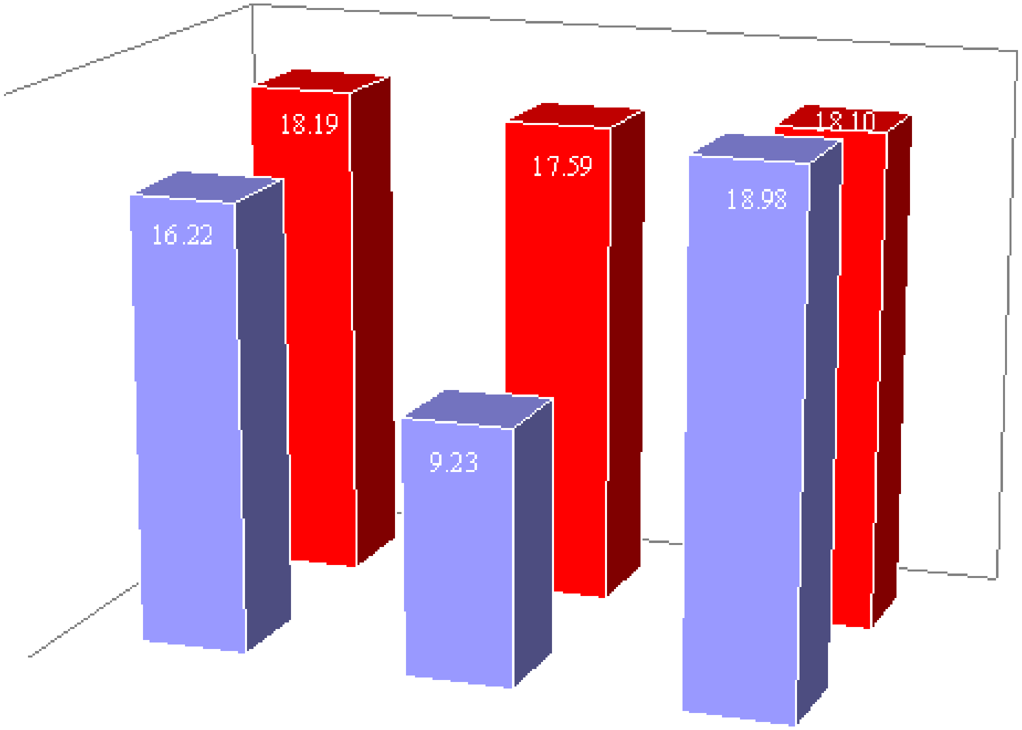


Figure 15. EFD 6-411 Solder Flux Paste Contamination Determined by MESERAN Analysis on Cleaned Samples

As can be seen from the data in Table 6 and Figure 14, the Group 2 “no clean” samples were significantly more contaminated than the “no clean” samples from Group 1. However, as can be seen in Figure 15, regardless of the amount of contamination on the samples before cleaning, all of the samples from both groups were able to be cleaned to approximately the same levels with each of the respective solvents. For the Group 1 samples, d-limonene removed the EFD 6-411 solder flux paste better than either TCE or IPA. For the Group 2 samples, all of the solvents were able to remove the EFD 6-411 solder flux paste to similar levels.

## Conclusion

Based upon these results, it was decided that d-limonene could be used to replace TCE for cleaning these particular electronic parts. This marked the first time that the newly developed MicroSolventEvaporator/MESERAN Analysis method had been used to quantify cleanliness on parts for production applications at KCP.

## NVOR Determinations on Aluminum and Stainless Steel Parts[6]

### Purpose

KCP conducted a cleanliness evaluation to determine the non-volatile residue (NVR) amounts on aluminum and stainless steel panels which were made using KCP machining fluids and cleaning processes chosen for production of hardware for an outside customer. This case study describes how KCP used recent advances in MESERAN technology to determine the NVR amounts on four stainless steel panels and four aluminum panels (31 $in^2$ each, excluding edges) by extracting the panels with methylene chloride and quantifying the extracted residues in $mg/ft^2$. The virgin methylene chloride solvent was also evaluated so that its contribution could be subtracted from the solvent extracts.

## Sample Details

For the NVR evaluations, four each aluminum and stainless steel samples (10 cm x 10 cm x 0.7 cm) were machined at KCP using particular machining fluids and associated machining methods. The four KCP machining fluids evaluated were a hydrocarbon blend (mixture of 70% Pennex N 47 and 30% Hangsterfer's Hard Cut # 511) and three aqueous-based coolants (Cimtech 200, Trimsol, and Cimstar 3700). Two of the stainless steel samples were improperly labeled; therefore, the contaminant for these two panels is not known for sure. They were either contaminated with the hydrocarbon blend or Cimtech 200 and are described as such in Tables 2, 3, and 4. All of the stainless steel samples were passivated by KCP plating group. This evaluation was conducted on these eight small samples to allow cleanliness verifications to be performed at KCP prior to cleaning large samples (25.4 cm x 25.4 cm x 1.3 cm) that would be sent to the customer for cleanliness verification.

## Cleaning Process

The aluminum and stainless steel panels tested in this evaluation were cleaned using the following process: (1) ultrasonic cleaned in Dirl Lum 603 (30g per liter concentration) for 5 minutes at 140°F, (2) rinsed in flowing DI water for 15 – 30 seconds, (3) DI water rinsed in ultrasonic cascade rinse station with 3 tanks (30 seconds in each tank) at 110 – 115°F, (4) blown dry with filtered nitrogen, (5) baked for 30 minutes minimum at 220°F in a HEPA filtered convection oven with nitrogen flowing into the oven. The panels were then packaged in nylon bags and heat sealed.

## Customer Cleanliness Requirements and Associated Problems

The customer has cleanliness level requirements for this hardware which can be extremely difficult to measure. The desired cleanliness of the hardware is $<0.1\ mg/ft^2$. Cleanliness measurements performed by the customer for these parts are typically generated using a gravimetric NVR procedure. The part being measured is rinsed with a known volume of a "clean" solvent (methylene chloride) to extract contamination from the part. The solvent and extracted residues are caught in a clean receptacle and evaporated in a precleaned and preweighed dish. After all of the solvent extract has evaporated, the dish is reweighed to obtain a weight of the dish plus the residue. The dish weight is subtracted from the dish plus residue weight to determine the level of the contamination extracted from the part. Similar evaluations are performed on the virgin solvent to determine the residue in the solvent itself. This residue amount is then subtracted from the extracted residue amount to give a final result for the residue extracted.

Gravimetric analysis can be difficult to consistently measure low levels of contamination (<1 mg) because many things can affect these small weight measurements. Customer cleanliness criteria of $<0.1\ mg/ft^2$ definitely complicates matters. Error is prone to being introduced during sample collection and sample processing. Every piece of laboratory equipment (such as glassware, weighing trays, funnels, etc.) that comes in contact with the solvent will contribute a small but variable amount of NVR to the solvent. The magnitude of this contribution is not constant due to fluctuations in contact time, surface temperature, and other variables. These variables are controlled as well as possible, but still contribute some level of error to the reported results. At the low levels of contamination being discussed, this error may be significant. In addition, gravimetric analysis is typically performed after rinsing a 1 $ft^2$ (144 $in^2$) sample area while the samples used in this evaluation were significantly smaller (31 $in^2$).

## KCP Proposed Method of Evaluating NVR Levels

Due to the problems discussed above, KCP proposed the following: (1) Extract the contamination from the panels with methylene chloride just as would be done in the gravimetric procedure, (2) use the newly developed MicroSolventEvaporator to evaporate 250-microliter aliquots of the methylene chloride extract onto clean reference substrates, (3) test the evaporated residues using the MESERAN Analyzer to quantify the NVR levels extracted from the samples, and (4) perform gravimetric analysis on the remaining extract to determine if there is enough residue to weigh on a balance.

## KCP Machining Fluid Information

The ingredients for the machining fluids (as obtained from their Material Safety Data Sheets) are as follows:

Hydrocarbon Blend
Pennex N 47 - petroleum distillates (~78%) and proprietary additives (~22%).
Hangsterfer's Hard Cut #511 – petroleum oil, chlorinated paraffin, and triglycerides.

Cimtech 200
Ethanolamine (10% max), caprylic acid ( 10% max), triethanolamine (10% max), isononanoic acid (10% max), and the balance is water.

Trim Sol
Petroleum oil (30-40%), petroleum sulfonate (20-30%), chlorinated alkene polymer (20-30%), nonionic surfactant (1-10%), aromatic alcohol (1-10%), propylene glycol ether (1-10%), propylene glycol (<1%), substituted indole (<1%), blue-green dye (<1%), silicone defoamer (<1%), and the balance is water.

Cimstar 3700
Mineral Oil (10% max), diethanolamine (10% max), triethanolamine, (10% max), aminomethylpropanol (10% max), and the balance is water.

A quick evaluation was made to determine the volatility of the machining fluids. The fluids were weighed out in a weighing dish, allowed to air dry at room temperature for 20 hours, and reweighed. The results are shown in Table 7. As would be expected from looking at their ingredients, the hydrocarbon blend is the least volatile and the aqueous machining fluids are the most volatile. Therefore, theoretically, there should be larger quantities of the hydrocarbon blend that must be cleaned off the samples than the aqueous cutting oils. This should make it much easier to clean the aqueous machining fluids to acceptable levels since their residue amount is relatively low even if they are not removed.

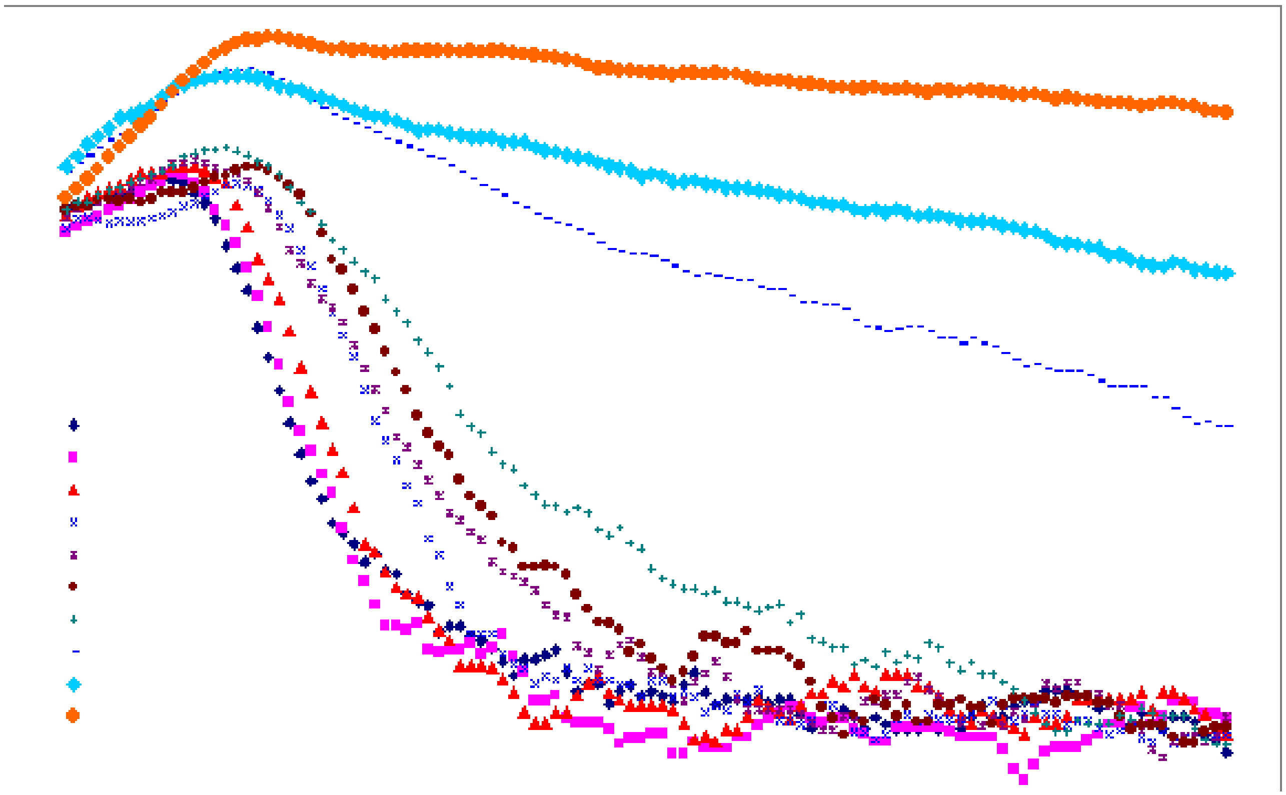
| **Cutting Oil** | **Initial Weight (g)** | **Weight After 20 Hour Air Dry (g)** | **% Volatile** |
|---|---|---|---|
| Hydrocarbon Blend | 0.11322 | 0.11292 | 0.26 |
| Cimtech 200 | 0.10790 | 0.00290 | 97.31 |
| Trim Sol | 0.17500 | 0.01100 | 93.71 |
| Cimstar 3700 | 0.11665 | 0.00400 | 96.57 |

Table 7. Volatility of KCP Machining Fluids

## Calibration of Hydrocarbon Blend

Based upon the volatility evaluation and since petroleum oils are the most likely contaminant from the machining fluids being evaluated, it was decided to develop a calibration curve using MESERAN Analysis for the hydrocarbon blend as a reference for future cleanliness evaluations.

A master calibration solution was prepared in a 10 mL volumetric flask by dissolving 100 mg of the hydrocarbon blend in 10 mL of hexane (NVR<1mg/L). Volumetric dilutions were used to make contamination solutions for depositing known amounts of the hydrocarbon blend on stainless steel disks. The master calibration solution was thoroughly mixed and 1 mL of this solution was placed in another 10-mL volumetric flask. The second volumetric flask was then diluted with hexane until the solution level was at 10 mL and this solution was thoroughly mixed. Subsequent dilutions were carried out in a similar fashion. Ten microliters (μL) of each calibration solution was deposited on the precleaned stainless steel disks and allowed to evaporate. This resulted in the following amounts of contamination on the stainless steel disks: 1 ng, 10 ng, 100 ng, 1 μg, 10 μg, and 100 μg. Some intermediate levels were obtained by depositing 3 μL and 5 μL of the calibration solutions.



The stainless steel disks that were contaminated were then tested using the MESERAN Analyzer to develop a calibration curve of the hydrocarbon blend. Example plots of the MESERAN data for these calibrations at various contamination levels is shown in Figure 16. A minimum of five replicates were run at each contamination level. The calibration curve of the low variance slopes for the hydrocarbon blend on these stainless steel disks is shown in Figure 17.

Figure 16. Plot of Various Amounts of Hydrocarbon Blend (70% Pennex N 47 and Hangsterfer's Hard Cut #511) on Stainless Steel Disks Using Logarithmically Smoothed MESERAN Data (Tested with Radiochemical BK)

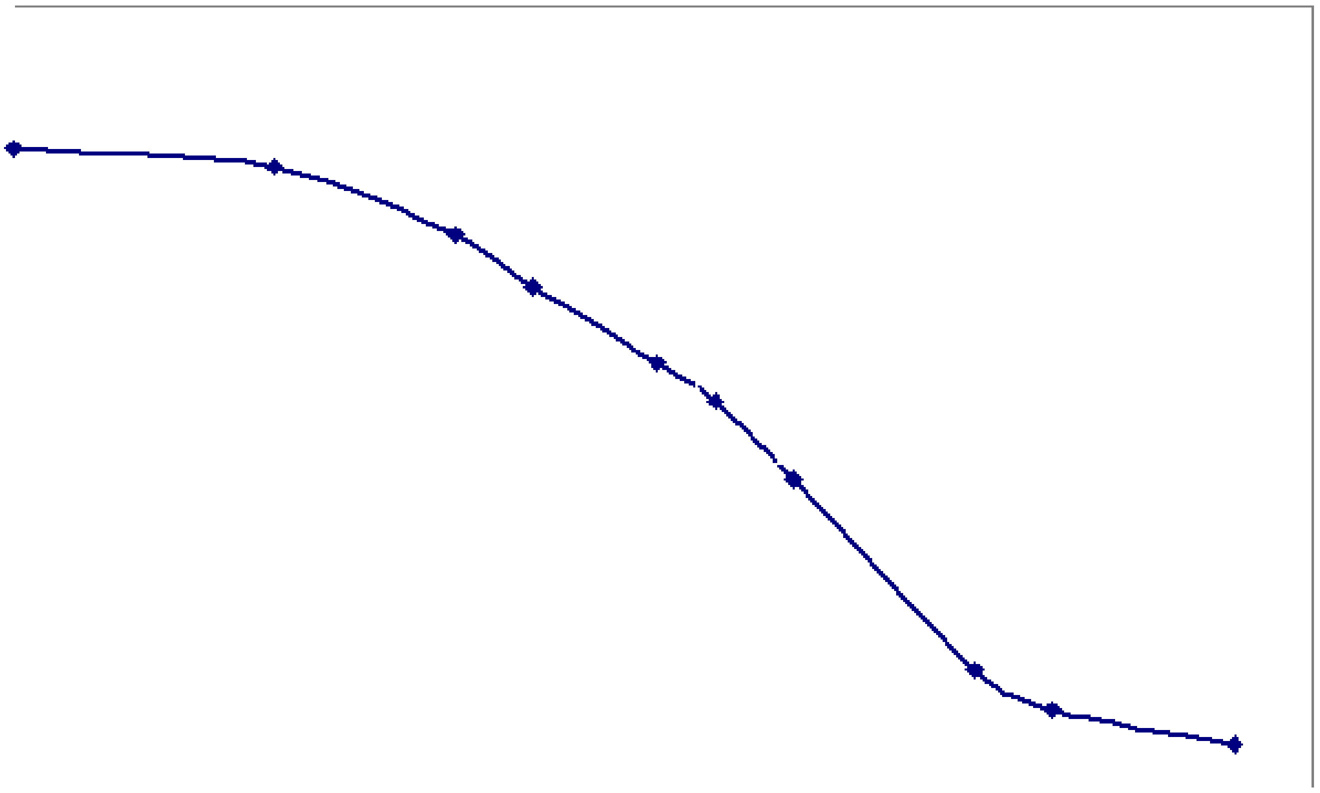


Figure 17. Calibration Curve of Hydrocarbon Blend (70% Pennex N 47 and Hangsterfer's Hard Cut #511) on Stainless Steel Disks Using Logarithmically Smoothed MESERAN Data (Tested with Radiochemical BK)

## Extraction and Overview of NVR Measurement Processes

One-hundred (100) mL of methylene chloride (Optima Grade, stated residue after evaporation is 1ppm) was used to extract both sides of the cleaned aluminum and passivated and cleaned stainless steel panels. The panels were 10 cm x 10 cm x 0.7 cm for a total of 31 square inches (200 square cm) of surface area (discounting the edges). The samples were placed (one at a time) in a large cleaned stainless steel funnel. One-hundred (100) mL of methylene chloride was measured and poured into a precleaned Teflon squeeze bottle. Each side of the panel was rinsed with the solvent to extract contamination. The methylene chloride extract was drained from the funnel into precleaned glass bottles that were then capped. The caps had Teflon inserts and were screwed onto the bottles.

The funnel was aqueous ultrasonic cleaned in Dirl Lum 603, ultrasonic rinsed in cascading DI water, blown dry with nitrogen, dried in a HEPA filtered oven, and rinsed with virgin methylene chloride after each extraction before being used for the next sample. All glassware (bottles, graduated cylinders, etc.) was also cleaned with the same process before being used.

The methylene chloride extracts were thoroughly mixed using an ultrasonic cleaner and vigorous shaking of the bottle prior to taking aliquots for analysis. Using the MicroSolventEvaporator and clean microsyringes, 250 microliters of the extracts were deposited onto cleaned stainless steel reference substrates. The methylene chloride evaporation process using the MicroSolventEvaporator takes 10-20 minutes per 250 microliter sample when performed at 30°C. The evaporated residue was then tested with the MESERAN Analyzer. A minimum of 5 replicates was run for each condition tested. The data was compared to calibrations performed using the KCP hydrocarbon blend cutting oil (mixture of 70% Pennex N 47 and 30% Hangsterfer's Hard Cut # 511) deposited on those same stainless steel substrates (see Figure 17). Linear-log interpolations between the calibration points were performed to determine how much residue was in the extract. This amount was then factored up to determine the quantity of residue in the entire amount of extract that was obtained from each panel. The amount of extract obtained from each sample was measured so this calculation could be performed. Recovery of 70-80% of the 100-mL of methylene chloride solvent was typical. The NVR of the methylene chloride was analyzed in a similar fashion to generate a baseline value for the solvent. Ultimately, the NVR of the methylene chloride was subtracted to determine the amount of residue actually extracted from the sample panels. This result was then converted to an amount per square foot for comparison with the customer's specification.

### MESERAN Analysis of Virgin Methylene Chloride and Methylene Chloride Extracts

The newly developed MicroSolventEvaporator (a prototype designed and developed by The MESERAN Company) was used to deposit and evaporate the methylene chloride onto precleaned stainless steel disks. This system was used to evaporate 250 µL of the methylene chloride onto the stainless steel surfaces in sequential small quantities (~5-10 µL increments) to concentrate the residue in a small area so that it could be tested with the MESERAN Analyzer. The evaporations were carried out at 30°C to slightly speed up the process. The MicroSolventEvaporator allowed the evaporations to be carried out in a reproducible fashion to help reduce the error associated by evaporating the quantities manually. In addition, these stainless steel disks have grooves machined in them which act as a self-centering mechanism so that the solvent evaporates in a confined space and does not migrate elsewhere.

After the methylene chloride was evaporated onto the stainless steel disks, the disks were tested with the MESERAN Analyzer using radiochemical BK (best suited for detecting nonpolar residues). The average low variance MESERAN slope results for the 250-µL depositions from the methylene chloride extracts are shown in Table 8.

The results were compared to those obtained previously from the calibration of known amounts of the KCP hydrocarbon blend machining fluid (mixture of 70% Pennex N 47 and 30% Hangsterfer's Hard Cut # 511) on these same substrates, which was shown previously in Figure 17. The average low variance slope obtained for the methylene chloride blanks was 2412. A linear-log interpolation using the values from the calibration in Figure 17 was performed to calculate the contamination level. The slope of 2412 corresponds to a contamination level of 3 ng (or 0.000003 mg) for the 250 µL of methylene chloride evaporated on the stainless steel disks. Therefore, the NVR of the 100-mL methylene chloride blanks would be 1.2 µg (or 0.0012 mg) as calculated below:

$$(3 \text{ ng} / 250 \,\mu\text{L}) \times (1000\mu\text{L} / 1 \text{ mL}) \times (100 \text{ mL}) \times (1 \,\mu\text{g} / 1000 \text{ ng}) = 1.2 \,\mu\text{g} \text{ (or } 0.0012 \text{ mg)}$$

| **Description of Sample Tested** | **Average MESERAN Low Variance Slope** | **Standard Deviation** | **Coefficient of Variation** |
|---|---|---|---|
| Methylene Chloride (Straight from Bottle) | 2412 | 111.71 | 4.63% |
| Hydrocarbon Blend on Aluminum | 2392 | 186.34 | 7.79% |
| Hydrocarbon Blend or Cimtech 200 on Stainless Steel | 2319 | 196.57 | 8.48% |
| Hydrocarbon Blend or Cimtech 200 on Stainless Steel | 2324 | 176.14 | 7.58% |

| | | | |
|---|---|---|---|
| Cimtech 200 on Aluminum | 2049 | 45.35 | 2.21% |
| Trim Sol on Aluminum | 2205 | 351.69 | 15.95% |
| Trim Sol on Stainless Steel | 2399 | 55.25 | 2.30% |
| Cimstar 3700 on Stainless Steel | 2208 | 46.33 | 2.10% |
| Cimstar 3700 on Aluminum | 2385 | 141.25 | 5.92% |

Table 8. MESERAN Slope Results for 250-μL Depositions from Methylene Chloride Extractions

The contamination results obtained from the MESERAN Analysis for the methylene chloride extracts from the panels tested are shown in Table 9. The average low variance slopes obtained for the samples were converted into equivalent contamination amounts (in nanograms) for the 250 microliters of extract evaporated by performing a linear-log interpolation using the values from the calibration in Figure 17. Then the amount of contamination in all of the extract collected for each sample was calculated (shown in micrograms) using similar equations as is shown previously for the methylene chloride blanks. Next, the methylene chloride NVR was subtracted from the contamination amount in all of the extract collected to determine the NVR amount extracted from each sample (this result is shown as μg/31 in$^2$). Finally, this contamination was converted to an amount per square foot to compare to the customer requirement of <0.1 mg/ft$^2$. All of the samples tested were less than the <0.1 mg/ft$^2$ requirement and most of them were significantly lower.

| **Description of Sample Tested** | **Panel Size (in$^2$)** | **Average MESERAN Low Variance Slope** | **Equivalent Contam. in 250 μL of Extract (ng)** | **Extract Amount Collected (mL)** | **Calculated Contam. in All of Extract (μg)** | **Calculated Contam. in All of Extract - Methylene Chloride NVR (μg/31 in$^2$)** | **Calculated Contam. in All of Extract - Methylene Chloride NVR (mg/ft$^2$)** |
|---|---|---|---|---|---|---|---|
| Methylene Chloride (Straight from Bottle) | N/A | 2411 | 3 | 100 | 1.200 | N/A | **N/A** |
| Hydrocarbon Blend on Aluminum | 31 | 2392 | 7 | 86 | 2.408 | 1.208 | **0.0056** |
| Hydrocarbon Blend or Cimtech 200 on Stainless Steel | 31 | 2319 | 15 | 85.5 | 5.130 | 3.930 | **0.01826** |
| Hydrocarbon Blend or Cimtech 200 on Stainless Steel | 31 | 2324 | 14 | 78.5 | 4.396 | 3.196 | **0.01485** |
| Cimtech 200 on Aluminum | 31 | 2049 | 64 | 79 | 20.224 | 19.024 | **0.08837** |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Trimsol<br>on Aluminum | 31 | 2205 | 29 | 81.75 | 9.483 | 8.283 | **0.03848** |
| Trimsol<br>on Stainless Steel | 31 | 2399 | 5 | 79 | 1.580 | 0.380 | **0.00177** |
| Cimstar 3700<br>on Stainless Steel | 31 | 2208 | 29 | 75.5 | 8.758 | 7.558 | **0.03511** |
| Cimstar 3700<br>on Aluminum | 31 | 2385 | 8 | 81 | 2.592 | 1.392 | **0.00647** |

Table 9. MESERAN Analysis of Methylene Chloride Extractions of Aluminum and Stainless Steel Panels

## KCP Gravimetric Analysis Discussion

After the MESERAN Analysis was conducted, the remaining solvent extracts were sent to KCP's Analytical Sciences to completely evaporate the remaining solvent extracts and attempt to quantify the resulting residue gravimetrically. A Mettler AE163 balance was used to make the weight measurements. The calibration sticker on the balance indicates the performance specification is +/- 0.005% of reading + 0.1 mg. The weights were measured to the nearest 0.00001g (or 0.01 mg). There is definitely greater error associated with weighing to these small amounts. KCP Analytical Sciences personnel indicated that the residue values determined gravimetrically are good only to approximately +/- 0.00003 g (+/- 0.03 mg) at best.

The virgin methylene chloride and the methylene chloride extracts were processed as follows:

1. Weighing trays were baked in an oven for 1 hour @ 105°C.
2. The weighing trays were taken from the oven and placed in a desiccator and allowed to cool.
3. The weighing trays were placed on an analytical balance and massed to the nearest 0.01 mg.
4. The methylene chloride and methylene chloride extracts were poured into individual weighing trays and allowed to evaporate. This process continued until all of the solvent evaporated for each sample.
5. The weighing trays were placed in an oven for 1 hour @ 105°C.
6. The weighing trays were removed from the oven and placed in a desiccator to cool.
7. The weighing trays were placed on an analytical balance and massed to the nearest 0.01 mg.
8. The NVR of the methylene chloride was calculated by subtracting the result of step 3 from the result of step 7.

Two samples of virgin methylene chloride were evaluated using this procedure. One sample was 100 mL of methylene chloride taken straight from the original bottle, measured in a clean graduated cylinder, poured into a precleaned glass bottle, and sealed with caps containing Teflon inserts. The second methylene chloride NVR sample was obtained using the following procedure: (1) 100 mL of methylene chloride from the original bottle was measured in a clean graduated cylinder, (2) the methylene chloride was poured into a precleaned Teflon squeeze bottle, (3) the precleaned stainless steel funnel that was used to hold the samples that were extracted was rinsed with 100 mL of methylene chloride, (4) the methylene chloride drained through the funnel and was captured in a precleaned glass bottle, and (5) the glass bottle was sealed with caps containing Teflon inserts. This process captured 89 mL of methylene chloride for analysis.

After aliquots from the extracts were analyzed using the MicroSolventEvaporator and MESERAN Analyzer, the remainder of each of the extracts was poured into clean graduated cylinders to measure the amount of solvent left for gravimetric analysis. The extracts were then poured back into their respective bottles and sent to be evaporated and measured gravimetrically.

The results obtained in the gravimetric analysis for the methylene chloride blanks and the methylene chloride extracts are shown in Table 10. Since the extract amount analyzed gravimetrically was less than the original extract amount (due to aliquots being taken for MESERAN Analysis), the gravimetrically determined NVRs were factored up to account for the lost contamination. In all cases except two, the contamination determined gravimetrically was less than the gravimetrically determined methylene chloride NVR which by definition makes the extracted residue less than the customer limit of <0.1 mg/ft$^2$. One of the hydrocarbon blend or Cimtech 200 samples on stainless steel had a positive result after the methylene chloride NVR was subtracted. After factoring up the contamination to account for the area per square foot, the contamination determined is higher than the customer limit of <0.1 mg/ft$^2$. The Cimstar 3700 on stainless steel sample also had a positive result after the methylene chloride NVR was subtracted; however, the resulting contamination was still less than the customer limit of <0.1 mg/ft$^2$. The error associated with measuring these small amounts of contamination makes all of these gravimetric results in doubt and it is recommended that they be dismissed.

| **Description of Sample Tested** | **Panel Size (in$^2$)** | **Original Extract Amount Collected (mL)** | **Extract Amount Analyzed Gravimetrically (mL)** | **Contamination in Gravimetrically Analyzed Extract (mg)** | **Calculated Contamination in All of Extract (mg)** | **Calculated Contamination in All of Extract - Methylene Chloride NVR (mg/31 in$^2$)** | **Extracted NVR (mg/ft$^2$)** |
|---|---|---|---|---|---|---|---|
| Methylene Chloride (Straight from Bottle) | N/A | 100 | 100 | 0.09 | 0.09 | 0 | **N/A** |
| Methylene Chloride (Poured Thru Funnel) | N/A | 100 | 89 | 0.09 | 0.09 | 0 | **N/A** |
| Hydrocarbon Blend on Aluminum | 31 | 86 | 82 | 0.06 | 0.063 | 0 | **0** |
| Hydrocarbon Blend or Cimtech 200 on Stainless Steel | 31 | 85.5 | 81 | 0.05 | 0.053 | 0 | **0** |
| Hydrocarbon Blend or Cimtech 200 on Stainless Steel | 31 | 78.5 | 74.5 | 0.12 | 0.126 | 0.0364 | **0.1693** |
| Cimtech 200 on Aluminum | 31 | 79 | 75 | 0.05 | 0.053 | 0 | **0** |
| Trimsol on Aluminum | 31 | 81.75 | 77.75 | 0.08 | 0.084 | 0 | **0** |
| Trimsol on Stainless Steel | 31 | 79 | 71 | 0.06 | 0.067 | 0 | **0** |
| Cimstar 3700 on Stainless Steel | 31 | 75.5 | 71.5 | 0.01 | 0.011 | 0 | **0** |
| Cimstar 3700 on Aluminum | 31 | 81 | 73 | 0.09 | 0.100 | 0.0099 | **0.0458** |

Table 10. KCP Gravimetric Analysis of Methylene Chloride Extractions of Aluminum and Stainless Steel Panels

## Gravimetric NVR Evaluations of Large Panels by Customer

Based upon the MESERAN results obtained for the small panels (31 in$^2$), KCP was convinced that its existing capabilities could be used to clean the large panels to acceptable levels for the customer. Therefore, large panels were manufactured with the same machining fluids, cleaned, and sent to the customer for evaluation. The customer evaluated the samples using their extraction and gravimetric NVR procedure described below.

The analytical procedure involves three steps: 1) rinsing the surface to be tested with solvent and collecting the rinse solvent; 2) concentrating the solvent to near dryness by evaporation with a clean gas; and 3) weighing the dry residue to determine the NVR. In the first step, the organic material is rinsed from the metal surface with methylene chloride, which must be completely captured in the sample container. The concentration stage consists of evaporating the solvent first by bubbling with clean gas (helium or nitrogen) and then by blow-down after transferring the residual solvent with the NVR into progressively smaller containers to minimize the container surface area and potential loss of NVR. All transfer steps must be quantitative and will require small aliquots of methylene chloride to rinse the containers. The final step is to transfer the remaining solvent containing the NVR into a tared weighing boat and weigh to a constant weight after all of the solvent is allowed to evaporate.

The gravimetric NVR results obtained by the customer on the large aluminum and stainless steel panels (100 in$^2$) machined, cleaned, and packaged at KCP are shown in Table 11. The customer determined that 100 mL of virgin methylene chloride had a NVR of 0.004 mg. They did not subtract this amount from the final results of the extracts when they reported their results. All of the panels evaluated were less than the <0.1 mg/ft$^2$ customer requirement.

| **Description of Sample Tested** | **NVR Level (mg/ft$^2$)** |
|---|---|
| Hydrocarbon Blend on Aluminum | 0.03 |
| Hydrocarbon Blend on Stainless Steel | 0.04 |
| Cimtech 200 on Aluminum | 0.07 |
| Cimtech 200 on Stainless Steel | 0.04 |
| Trimsol on Aluminum | 0.04 |
| Trimsol on Stainless Steel | 0.02 |
| Cimstar 3700 on Aluminum | 0.02 |
| Cimstar 3700 on Stainless Steel | 0.06 |

Table 11. Gravimetric Analysis of Methylene Chloride Extractions of 100 in$^2$ Aluminum and Stainless Steel Panels Performed by the Customer

## Conclusions

Analysis of the solvent extracts with the MicroSolventEvaporator and MESERAN Analyzer indicate that all of the samples tested were less than the <0.1 mg/ft$^2$ customer requirement and most of them were significantly lower. The cleaning process being used sufficiently cleaned the cutting oils from the panels tested.

Basically, the amounts of contamination being determined are too small to accurately measure them gravimetrically for the small samples extracted (31 in$^2$). The error associated with these measurements is extremely high at these levels. These results provide further proof that for gravimetric NVRs to be accurate, it is best to extract at least a one square foot area so there is plenty of contamination in the extract to measure. Therefore, when quantifying extremely small residues from solvent extracts of small parts, the only viable method currently available is the MicroSolventEvaporator/MESERAN Analysis method.

The large panels (100 in$^2$) evaluated gravimetrically by the customer indicated that all of the panels were cleaned to acceptable levels (less than the <0.1 mg/ft$^2$ customer requirement). Even though the panels the customer evaluated were significantly larger than the ones evaluated by KCP and different methods were used for determining the NVR levels, the results obtained were remarkably consistent.

The NVR data determined by KCP with the MicroSolventEvaporator and MESERAN technique and the NVR data determined gravimetrically by the customer follow a similar pattern. Tables 9 and 11 indicate that the results of both test methods exhibited the same cleanliness level relationship between the aluminum and stainless steel panels for each specific contaminant evaluated. Hydrocarbon blend-contaminated samples had more contamination after cleaning on the stainless steel panels than the aluminum panels.

Cimtech 200-contaminated samples had more contamination after cleaning on the aluminum panels than the stainless steel panels. Trimsol-contaminated samples had more contamination after cleaning on the aluminum panels than the stainless steel panels. Cimstar 3700-contaminated samples had more contamination after cleaning on the stainless steel panels than the aluminum panels.

## NVOR Determinations on Lightning Arrester Connector (LAC) Shells

### Background

It was believed that there might be contaminants/residue on the surface of some LAC shells which appeared to inhibit thermal oxidation of the 304L stainless steel. The shells are intentionally subjected to a controlled oxidation schedule prior to glass sealing and some of the parts develop a non-uniform or spotty appearance. A request was made to detect and identify the substance responsible on parts that had not yet been exposed to the high temperature (~1000°C) oxidation process. Six 26-pin LAC shells were received to evaluate contamination on the shells after various cleaning process conditions performed at the vendor.

The 26-pin LAC shells have a surface area of 12.955 $in^2$. These shells were cleaned at the vendor, packaged in polyethylene bags, and shipped to KCP for analysis. Two shells were processed at the vendor in each of the following conditions:

| Shell Evaluated | Processing Condition |
|---|---|
| 0124-20-1 and 0124-20-2 | Passivated and No Cleaning |
| 0124-21-1 and 0124-21-2 | Passivated and Line Cleaned with Oakite Inpro-Clean 3800 |
| 0124-22-1 and 0124-22-2 | As Machined and Line Cleaned with Oakite Inpro-Clean 3800 |

Oakite Inpro-Clean 3800 is a mildly alkaline liquid aqueous cleaner for immersion and ultrasonic cleaning applications. The normal working concentrations are 5-20% by volume of water, the normal working temperatures are 40-120°F (but can be ambient to 160°F), and the pH at working conditions is 11.0 to 11.8. The Material Safety Data Sheet lists its chemical composition as a blend of silicates and surfactants. Specific ingredients are listed as sodium metasilicate (5-10%), Trade Secret Registry 735517 (1-5%), sodium xylenesulfonate (1-5%), and non-hazardous ingredients (balance).

### Extraction and Overview of Non-Volatile Residue (NVR) Measurement Processes

The 26-pin LAC shells were extracted (one at a time) by submerging them in a clean beaker with 85 mL of methylene chloride (Optima Grade, stated residue after evaporation is 1 ppm) and ultrasonically cleaning them for 5 minutes to aid in the removal of any contamination. Aliquots of the solvent extract (250 microliters) were then deposited on clean SS disks using the MicroSolventEvaporator. After the solvent extracts were evaporated onto the SS disks, the SS disks were tested with the MESERAN MicroOrganic Residue Analyzer to quantify the evaporated residue. The data obtained by the MESERAN Analyzer was then compared to calibrations performed previously on a hydrocarbon machining fluid (mixture of 70% Pennex N 47 and 30% Hangsterfer's Hard Cut # 511) used at KCP. Interpolations between the calibration points were performed to determine how much residue was in each 250 microliter extract aliquot. This amount was then factored up to determine the quantity of residue in the entire amount of extract (85 mL). The NVR of the methylene chloride was analyzed in a similar fashion to generate a baseline value for the solvent. Ultimately the NVR of the methylene chloride was subtracted to determine the amount of residue actually extracted from the shells. This amount was then converted to an amount per unit area to compare to typical cleanliness information for metal parts.

### MESERAN Analysis of Virgin Methylene Chloride and Methylene Chloride Extracts

The newly developed MicroSolventEvaporator (a prototype designed and developed by The MESERAN Company) was used to deposit and evaporate the methylene chloride onto precleaned stainless steel disks. This system was used to evaporate 250 µL of the methylene chloride onto the stainless steel surfaces in sequential small quantities (~5-10 µL increments) to concentrate the residue in a small area so that it could be tested with the MESERAN Analyzer. The evaporations were carried out at 30°C to slightly speed up the process. The MicroSolventEvaporator allowed the evaporations to be carried out in a reproducible fashion to help reduce the error associated by evaporating the quantities manually. In addition, these stainless steel disks have grooves machined in them which act as a self-centering mechanism so that the solvent evaporates in a confined space and does not migrate elsewhere.

After the methylene chloride was evaporated onto the stainless steel disks, they were tested with the MESERAN Analyzer using radiochemical BK (best suited for detecting nonpolar residues). The results were compared to those obtained previously from a calibration of known amounts of the KCP hydrocarbon blend cutting oil (mixture of 70% Pennex N 47 and 30% Hangsterfer's Hard Cut # 511) on these same substrates. The calibration curve of the low variance slopes for the hydrocarbon blend on these stainless steel disks was shown previously in Figure 17.

The average low variance slope obtained for the methylene chloride blanks was 2411. A linear-log interpolation using the values from the calibration in Figure 17 was performed to calculate the contamination level. The slope of 2411 corresponds to a contamination level of 4 nanograms (ng) for the 250 µL of methylene chloride evaporated on the stainless steel disks. Therefore, the NVR of the 85 mL methylene chloride blanks would be 1.36 µg as calculated below:

$$(4 \text{ ng} / 250\ \mu\text{L}) \times (1000\ \mu\text{L} / 1 \text{ mL}) \times (85 \text{ mL}) \times (1\ \mu\text{g} / 1000 \text{ ng}) = 1.36\ \mu\text{g}$$

The contamination results obtained from the MESERAN Analysis for the methylene chloride extracts from the 26-pin LAC shells tested are shown in Table 12. The average low variance slopes obtained for the samples were converted into equivalent contamination amounts (in nanograms) for the 250 microliters of extract evaporated by performing a linear-log interpolation using the values from the calibration in Figure 17. Then the amount of contamination in all of the extract collected for each sample was calculated (shown in micrograms) using similar equations as is shown above for the methylene chloride blanks. Next, the methylene chloride NVR was subtracted from the contamination amount in all of the extract collected to determine the NVR amount extracted from each sample. This amount was then divided by the surface area to show the contamination in µg/in$^2$ and µg/cm$^2$.

| **Description of Sample Evaluated** | **Average MESERAN Low Variance Slope** | **Equivalent Contam. in 250 µl of Extract (ng)** | **Extract Amount (mL)** | **Calculated Contam. in All of Extract (µg)** | **Calculated Contam. in All of Extract - Methylene Chloride NVR (µg)** | **Calculated Contam. in All of Extract - Methylene Chloride NVR (µg/in$^2$)** | **Calculated Contam. in All of Extract - Methylene Chloride NVR (µg/cm$^2$)** |
|---|---|---|---|---|---|---|---|
| **Methylene Chloride**<br>(Straight from Bottle) | 2411 | 4 | 85 | 1.36 | 0.0 | N/A | **N/A** |
| **Shell 0124-20-1**<br>Passivated and No Cleaning | 1211 | 937 | 85 | 318.58 | 317.22 | 21.27 | **3.30** |
| **Shell 0124-20-2**<br>Passivated and No Cleaning | 1182 | 1002 | 85 | 340.68 | 339.32 | 22.75 | **3.53** |
| **Shell 0124-21-1**<br>Passivated and Line Cleaned with Oakite Inpro-Clean 3800 | 1348 | 681 | 85 | 231.54 | 230.18 | 15.43 | **2.39** |
| **Shell 0124-21-2**<br>Passivated and Line Cleaned with Oakite Inpro-Clean 3800 | 1483 | 497 | 85 | 168.98 | 167.62 | 11.24 | **1.74** |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Shell 0124-22-1** As Machined and Line Cleaned with Oakite Inpro-Clean 3800 | 1367 | 652 | 85 | 221.68 | 220.32 | 14.77 | **2.29** |
| **Shell 0124-22-2** As Machined and Line Cleaned with Oakite Inpro-Clean 3800 | 1308 | 748 | 85 | 254.32 | 252.96 | 16.96 | **2.63** |

Table 12. MESERAN Analysis of Methylene Chloride Extracts From 26-Pin LAC Shells (Surface Area – 12.955 in$^2$)

The 26-pin shells that were passivated but not cleaned had contamination amounts of 3.30 μg/cm$^2$ and 3.53 μg/cm$^2$. The shells that were passivated and standard line cleaned with Oakite Inpro-Clean 3800 had contamination amounts of 2.39 μg/cm$^2$ and 1.74 μg/cm$^2$. The shells that were as machined (not passivated) and standard line cleaned with Oakite Inpro-Clean 3800 had contamination amounts of 2.29 μg/cm$^2$ and 2.63 μg/cm$^2$.

The LAC shells do not have any particular cleanliness levels called out as a requirement. Most aerospace companies typically call out a cleanliness level of 1 μg/cm$^2$ for their metal cleaning applications. However, there are some applications where they call out lower levels, even as low as 0.1 μg/cm$^2$ (or 100 ng/cm$^2$). Recent work has shown that KCP has the capability to clean stainless steel and aluminum panels to levels <0.1 μg/cm$^2$ (actual levels ranged from 0.0019 to 0.0884 μg/cm$^2$) using an aqueous ultrasonic cleaning and rinsing process. Based upon typical Aerospace industry standards for metal parts (<1 μg/cm$^2$) and KCP's proven ability to clean aluminum and stainless steel panels to levels <0.1 μg/cm$^2$, the LAC shells evaluated appear to have a significant amount of contamination.

KCP personnel evaluated the extract solutions using Mass Spectrometry to identify the contamination. The majority of the contamination found was Erucamide (the slip agent from the polyethylene bags the shells were packaged in) with a little DOP (dioctyl phthalate). In addition, handling oils were detected on the uncleaned samples.

### Conclusion of 26 Pin LAC Shell Evaluations

The solvent extraction/MicroSolventEvaporator/MESERAN technique was definitely able to detect contamination on the 26-pin LAC shells. Even though there are not any specific cleanliness requirements for these parts, based upon cleanliness requirements typical of aerospace industry standards for metal parts (<1 μg/cm$^2$) and KCP's proven ability to clean aluminum and stainless steel panels to levels <0.1 μg/cm$^2$, these shells appear to have too much contamination. However, the majority of what was extracted was the Erucamide from the packaging material. Therefore, a true picture of the cleaning process used at the vendor was not obtained (unless they normally package the shells in polyethylene bags after they are cleaned). This work underscores the importance of proper packaging of parts to maintain cleanliness as well as for samples that are going to be analyzed for cleanliness.

### Recommendations Related to 26-Pin LAC Shell Evaluations

It was recommended that KCP send Nylon clean room bags to the vendor so future LAC shells could be packaged appropriately and sent to KCP for additional evaluations.

### Postscript

Subsequent evaluations on additional LAC shells cleaned and packaged in nylon clean room bags indicated contamination amounts of ~2 μg/cm$^2$. After the contamination amount was quantified, the evaporated extract solutions were evaluated using Mass Spectrometry and the contamination was identified as stearic acid, hydrocarbons, and inorganic residues and particles. The evaporated residue was also evaluated using Scanning Electron Microscopy (SEM) and determined that the inorganic residues and particles were stainless steel, silicon dioxide, fibers and trash (as sodium, chlorine, potassium, calcium, magnesium and sulfur). Possible sources of the organic contamination are as follows: stearic acid - gloves and lubricants, hydrocarbons - machining fluids used to manufacture the shells, handling oils – workers.

Changes have been incorporated at the vendor which appear to have eliminated the problem with improper oxidation of the 304L stainless steel. One such change was to reduce the amount of time between cleaning and the oxidation operation. The shells must now be cleaned within 48 hours prior to oxidation or they must be re-cleaned. In addition, it was determined that the passivation procedure had been performed using ambient temperature nitric acid instead of heated nitric acid as was called out in the specification. The passivation process was changed to use heated (120 – 140°F) nitric acid. Besides providing passivation, the use of heated nitric acid should significantly increase the cleanliness of the shells because the heated nitric acid also cleans the shells by oxidizing any organic contamination.

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## NOTE

All data prepared, analyzed and presented has been developed in a specific context of work and was prepared for internal evaluation and use pursuant to that work authorized under the referenced contract. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof or Honeywell Federal Manufacturing & Technologies, LLC.

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