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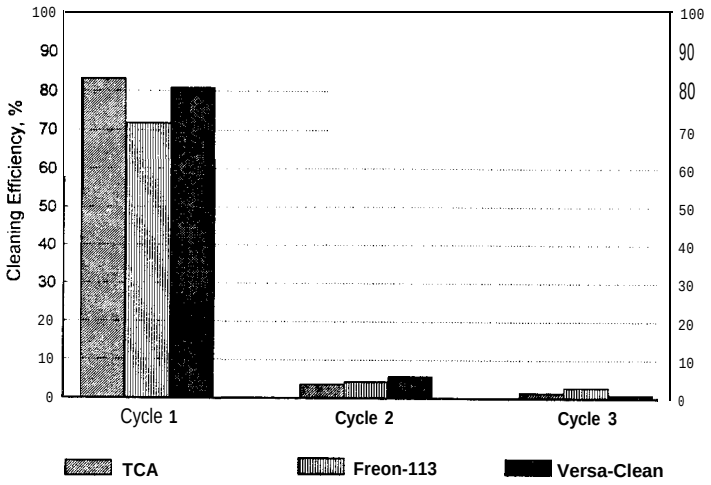

Removal of Silica Particulate

METHODS FOR IMPROVEMENT OF THE STABLE ISOTOPE CLEANING PERFORMANCE EVALUATION PROCEDURE (CPEP)

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The Aerospace Guidance

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Newark Air Force Base

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September 14, 1993

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EXECUTIVE SUMMARY

The Aerospace Guidance and Metrology Center (AGMC) at Newark Air Force Base (NAFB), Ohio, has been using cleaning agents such as 1,1, 1-trichloroethane (TCA) and 1, 1,2-trichloroethane, 1,2,2-trifluoroethane (Freon 113) for repair of inertial guidance equipment. Both of these cleaning agents have been classified as stratospheric ozone layer depleting substance (OLDS). Therefore, AGMC is interested in replacing these with other cleaning agents such as aqueous detergents. In order to assure that reliability and maintainability levels are not degraded when OLDS are phased out, a method is required to validate that the cleaning capability of the suggested alternative is at least as good as that of an existing, proven cleaning agent. The current methods used by AGMC to evaluate cleanliness are not effective when the parts being cleaned are composed of irregular or severe geometries as is the case for precision gyroscopes and accelerometers repaired at AGMC. Therefore, AGMC funded Battelle to develop and demonstrate a suitable cleaning performance evaluation procedure (CPEP) for quantifying cleanliness.

The modified CPEP developed and demonstrated in this project involved two phases. In Phase I, the contaminants which are present in the current cleaning processes were identified to select synthetic inorganic particulate and organic contaminants. In Phase II, unique, stable-isotopes of these contaminants were introduced into the parts foIlowed by cleaning of these parts with various cleaning agents. The amounts of these unique isotopes extracted, as determined by mass spectroscopy (MS) provides a measure of cleaning efficiency. The advantages of this technique are that the analysis is not complicated by introduction or presence of native or airborne contaminants and no special safety precautions needed for work with radioisotopes are necessary. However, the method is complex and requires well-trained staff. The modifications to the original CPEP (developed under Contract Order No. F0960390D2217/Q802) permit the CPEP to be used for a greater variety of devices of interest to AGMC and permit direct determination of the organic compounds in aqueous detergent cleaning residues. The changes recommended to improve the performance of the inorganic particulate contaminant analysis were also implemented and validated in this program.

Silica, obtained for the original program, was retained as the inorganic contaminant for this program. A different aqueous cleaner, Versa-Clean, was used in this program due to problems encountered with Liquid Detergent 2 at AGMC. Versa-Clean was analyzed chemically and contained only 7 ppm silicon. This amount of native silicon did not interfere with the silicon isotopic analysis. Three mass spectrometric techniques were evaluated for the inorganic isotope analyses: glow discharge mass spectrometry (GDMS), spark-source mass spectrometry (SSMS) and secondary ion mass spectrometry (SIMS). GDMS gave the best analysis precision in pretests with organic and aqueous cleaning agents and was used for the method validation tests. The particle size of the contaminant silica was reduced to 3.7µm mass median diameter. The particle size of the calibrant silica was reduced to 4.2µm mass median diameter. These particle sizes compare closely to the average size of contaminant particles observed in AGMC samples, i.e., 4.4µm.

A method for direct analysis of organic compounds in aqueous detergent was developed in this program. A 1ml aliquot of aqueous detergent cleaning residue is diluted in 200ml of distilled water. The dilute detergent solution is then analyzed using the methods developed in the previous program for analysis of the distilled water rinse samples. Because the bulk of the aqueous detergent sample was not used for analysis, the quantity of organic contaminant applied to the test devices was increased. A 20 fold increase (lOµg to 200µg) was used for phenanthrene and dimethyl phthalate.

The octadecanoic acid contaminant level was increased from 100 µg to 3 .6 mg. A greater increase was required for this compound, because the Versa-Clean detergent contained a large quantity of similar fatty acid compounds. Additional octadecanoic acid was thus needed to permit detection of the synthetic compound in the presence of the much larger quantity of native octadecanoic acid present in the detergent. An attempt to analyze a more concentrated detergent solution overloaded the analytical instrument and it is therefore recommended that analysis of more concentrated detergent solutions not be attempted.

A new contaminant doping procedure applicable to small open test devices was also developed. This procedure encloses the part in a Teflon bag during application of the organic contaminant. Use of the bag in conjunction with the dry ice-acetone cold trap used in the original procedure permits collection of the slightly volatile dimethyl phthalate contaminant compound. The dimethyl phthalate that evaporates during evaporation of the organic contaminant carrier liquid is retained in the cold trap as in the original doping procedure. The validation tests in this program were performed using KT 73 gyro hinge and magnet assemblies as test devices. The modified doping method can be easily extended to larger test devices through use of a larger Teflon bag to contain the part.

The procedures developed in this program were validated for three cleaning agents: Freon 113, 1,1, 1-trichloroethane (TCA) and 2% Versa-Clean detergent in distilled water. A 5 minute ultrasonic cleaning cycle in an AGMC ultrasonic cleaner was used for each cleaning cycle. Five test devices were cleaned in each of the three cleaning agents and the cleaning residues were analyzed using the modified CPEP procedures. The cleaning efficiency for removal of the particulate contamination was similar for all of the cleaning agents tested (72 to 83% particulate removal after one cleaning cycle). Cleaning efficiency for the nonpolar phenanthrene was also high and similar for all three cleaners. Cleaning efficiency for dimethyl phthalate was high for both organic cleaners, but significantly lower for the aqueous detergent. Cleaning efficiency for the polar octadecanoic acid contaminant was also similar for both organic cleaners, but the aqueous detergent was much less effective in removing this contaminant. This reduced cleaning efficiency of the polar contaminant in the polar aqueous cleaner is the reverse of the expected behavior of this contaminant. A polar contaminant should be best removed by a polar cleaner. The poor cleaning efficiency in this case is probably due to a chemical reaction between the contaminant and the surface of the test device. Additional effort is needed to determine whether a reaction has occurred. If a reaction is confirmed, modifications to the AGMC cleaning procedures may be required; however, this does not impact the CPEP itself.

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to

THE AEROSPACE GUIDANCE AND METROLOGY CENTER
Newark Air Force Base

September 14, 1993

1.0 BACKGROUND

The Aerospace Guidance and Metrology Center (AGMC), located at the Newark Air Force Base (NAFB), OH, repairs inertial navigation and guidance equipment for the United States Air Force (USAF) and other Department of Defense (DoD) components. The Center repairs thousands of these delicate, sophisticated electromechanical devices each year. The critical tolerances of many of these devices and other considerations mandate extensive precision cleaning during the repair process. The principal solvents used for this cleaning are 1,1,2-trichloroethane, 1,2,2-trifluoroethane (Freon 113) and 1,1, 1-trichloroethane (TCA). These solvents have been classified as stratospheric ozone depleting chemicals under the 1987 international treaty "Montreal Protocol on Substances that Deplete the Ozone Layer". Commonly known as the "Montreal Protocol", the treaty was ratified by the U.S. Senate in December 1988. The Environmental Protection Agency (EPA) has since developed domestic regulations to insure the reduction and eventual elimination of the production and use of various ozone depleting chemicals. AFR 19-15 implements DoD Directive 6050.9 and directs compliance with the Clean Air Act Amendments of 1990 and EPA regulations relating to CFCS, halons, and other ozone depleting chemicals. Based on this direction and a recent supplemental direction to accelerate the timetable for compliance, the Center has initiated a policy to achieve total elimination of CFCs from its industrial cleaning processes by the end of calendar year 1994.

In order to assure that reliability and maintainability of repaired inertial guidance components are not degraded when CFCs are phased out, a validated cleaning method is required that is at least as good as the existing, proven process. The current methods used by AGMC to evaluate cleanliness include, but are not limited to, unaided visual examination, microscopic visual examination, solvent filtering with analysis of filter residue, and deionized water break test. However, these methods are not as effective as desired when the item being cleaned is composed of irregular or severe geometries as is the case in many of the parts and assemblies composing the precision gyroscopes and accelerometers repaired at AGMC.

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to

THE AEROSPACE GUIDANCE AND METROLOGY CENTER
NEWARK AIR FORCE BASE

September 14, 1993

by

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Recent advances in analytical precision, coupled with stable isotope technology, offer a safe and potentially improved approach to measure cleaning effectiveness. By identifying common contaminants, doping components under test with stable isotopes of these contaminants, and then measuring the effectiveness of various cleaning processes to remove these isotopes, a relative measure of cleaning process effectiveness can be established. This cleaning performance evaluation procedure (CPEP) concept for precision cleaning of inertial guidance systems has been demonstrated by Battelle, under a previous contract for AGMC. This report covers additional work performed to increase the usability of CPEP for AGMC operations.

2.0 OBJECTIVE

The objective of this study was to increase the practical value of the stable isotope CPEP for AGMC by further developing and validating procedures for particulate cleaning and for-analysis of organic contamination in detergent solutions.

3.0 CPEP APPROACH, REQUIREMENTS, ADVANTAGES. AND DISADVANTAGES

3.1 CPEP Approach

This CPEP employs a two-phase approach. In Phase I (development phase), the current cleaning processes (CCP) are examined to identify possible contaminants. Samples of cleaning residue at several points in the CCP are analyzed for inorganic particulate and organic compounds. The analytical results are then used to select synthetic contaminants for validation (Phase II) of CPEP.

The synthetic contaminants are not required to be identical to the contaminants found in the samples, but they need to be representative of those contaminants and to respond to the same adherence mechanisms. Some of the possible mechanisms are: surface chemical; magnetic; electrostatic; stickiness (or tendency to leave a coating); and trapping in surface irregularities. For the particulate contaminants, the particle size and chemical form are key considerations because particle removal is strongly dependent on the size of the particles and some particle adherence mechanisms are dependent upon the chemical form of the particles. For the organic compounds, a key characteristic of the synthetic contaminant is the polarity since the cleaning effectiveness for the organic contaminants is strongly dependent upon the volubility of the contaminant in the cleaning agent. Polar contaminates are removed most effectively by a polar cleaning agent, while nonpolar contaminants are best removed with nonpolar cleaning agents.

In Phase II, an extended isotope dilution method is employed for CPEP. This method consists of challenging a test component (part) with a synthetic contaminant which is isotonically different from any native or airborne contaminant. The test component is then cleaned using the cleaning process being evaluated and the cleaning residues are saved. A synthetic calibrant solution containing a different isotope than the synthetic contaminant is then added to the cleaning residue in a

known amount. The resulting mixture containing any native contaminant and the two synthetic isotope forms are then analyzed by mass spectral (MS) and gas chromatographic (GC) techniques to determine the isotopic ratios of the contaminants. The isotope ratios and the amount of calibrant material added are used to determine the quantity of synthetic contaminant (challenge material) removed during the cleaning process. The effectiveness of the cleaning process, e.g., ultrasonic cleaning with TCA, is then calculated based on the amount of contaminant it removed.

3.2 Outline of CPEP

The CPEP involves the 11 generic steps shown in Figure 1. A detailed, step-by-step description of CPEP is provided as Appendix A as a separate, bound volume. The CPEP was modified throughout the development and demonstration stages and the level of written, procedural detail was adjusted to conform to the experience level of AGMC scientists and technicians most likely to use it. The CPEP is written in the style of ASTM procedures and is sufficiently detailed to allow "round-robin" testing and use by researchers outside of AGMC.

3.3 CPEP Requirements

The CPEP is based on an accurate determination of a synthetic contaminant removed from a test component during cleaning since a method for analyzing the residue on the test component is not available. The following three specific requirements must be met for this method of analysis to be successful.

(1) Isotopic contaminants (challenge materials) should not be altered or lost during cleaning process, i.e., the synthetic contaminant should either be in the cleaning extract or as residue on the test component.

(2) Synthetic contaminants as well as the calibrants should be equally well dispersed in the cleaning extract as well as any sampling/analytical aliquots.

(3) The analytical methods for isotope analysis should be accurate and precise (repeatable).

These requirements were tested during prequalifying tests prior to cleaning performance testing in the field.

3.4 CPEP Advantages

The following are the advantages of the CPEP developed in this project:

(1) The special safety precautions required when using radioisotopes are not needed since the CPEP uses stable isotopes.

Figure 1. Cleaning Performance Evaluation Procedure Outline

(1) Examine current cleaning processes (CCP) and identify known and suspected contaminants.

(2) Sample CCP at beginning, end, and in between if possible.

(3) Analyze for organic plus particulate contaminants.

(4) Select candidate isotopic simulants for contaminants.
- Stable isotopes for organics
- >2 stable isotopes for inorganic

(5) Dissolve/suspend synthetic contaminant isotope in volatile organic liquid.

(6) Dope test parts with synthetic contaminant, evaporate liquid carrier, trap exhaust gases for analysis, analyze exhaust gas trap, and calculate contaminant quantity retained in the part.

(7) Clean parts using candidate processes.

(8) Collect samples in suitable containers.

(9) Add second, calibrant isotope.

(lo) Analyze for contaminants by GC/MS.

(11) Conduct data analysis to compare cleaning effectiveness.

(2) The quantity of synthetic contaminant present in a sample of cleaning residue can be accurately determined in the presence of significant amounts of native contamination.

3.5 CPEP Disadvantages

The following are the disadvantages of the CPEP:

(1) The inorganic particulate isotopic materials are expensive and suppliers are limited. The cost is further increased due to the requirements for having two isotonically labeled samples of each contaminant as well as due to the need to use a mass spectrometer to analyze the isotopes.

(2) The procedure is complex and requires well-trained staff.

4.0 RESULTS AND DISCUSSION

The work performed on this program is described in the following sections. The results are discussed in the following sequence: (a) inorganic isotope methods development; (b) method for direct analysis of organics in detergent solution; (c) revised CPEP preparation; and (d) revised CPEP validation.

4.1 Inorganic Isotope Methods Development

In the previous investigation of CPEP by Battelle, it was not possible to prove the CPEP for removal of inorganic particles. While CPEP appeared to work in principle, the errors of measurement were too large to provide a practical method. The primary problems were the difference in mass mean particle size of contaminant and the calibrant stocks and a potential lack of sufficient homogenization of stock suspensions prior to use. Furthermore, in the case of Liquid Detergent 2, an aqueous cleaner, there were additional errors introduced due to a high concentration of native silica in the detergent. For these reasons a number of potential improvements in the the use of alternative isotope materials, were sought as discussed

4.1.1 Alternate Isotope Materials

In order to find a suitable alternative to silica isotopes, that would not interfere with components of cleaning agents, price quotations were obtained from Oak Ridge National Laboratory for isotopes of Mg, Ti, Cr, Ni, Zn and Se. These elements were selected because they possess three or more stable isotopes and are available as water insoluble compounds. After the prices were obtained, a different candidate detergent was selected by AGMC. The aqueous detergent for this study was Versa-Clean in place of the Oakite Liquid Detergent 2 used in the first phase study. The

detergent was changed due to results obtained in another Battelle study. Since the original detergent contained approximately 5 percent sodium metasilicate, the change was beneficial to this program. A sample of undiluted Versa-Clean was analyzed by inductively coupled argon plasma spectroscopy (ICAP) and found to contain only 7 µm silicon. AGMC currently uses a 2 percent Versa-Clean solution. Since the potential for native silicon contamination with the Versa-Clean detergent is much lower than the contamination produced by Liquid Detergent 2, silicon was retained for further studies as the particulate contaminant. A sufficient supply of both the contaminant and calibrant compounds remained from the first phase study that no additional silica was required.

4.1.2 Availability of Alternate Isotope Materials

Due to the change in the detergent which was used in this program and the resulting reduction in the amount of native silicon contamination during the aqueous cleaning tests, additional tests were conducted with the silica materials already on hand.

4.1.3 Particle Size Reduction and Analysis

The results from the first phase (previous) study indicated that it was necessary to reduce the average size of both the contaminant ($^{30}SiO_2$) and calibrant ($^{29}SiO_2$) stock particles in order to improve the accuracy of CPEP for inorganic particles removal. It took two attempts to satisfactorily reduce the particle size. The stock suspensions prepared after the first attempt -- Batch Cent-II (contaminant) and Cal-II (calibrant)-- were used to perform the first set of prequalifying test on silica recovery as well as to compare the precision of three different mass spectrometric (MS) techniques for analysis of the isotopes. This set of prequalifying tests showed that the recovery of the contaminant was below the 85 percent minimum recovery target. To rectify this situation, a second attempt was made to reduce the particle sizes further. These reprocessed stock suspensions -- Batch Cent-III (contaminant) and Cal-III (calibrant) -- were found to be acceptable during a second set of prequalifying tests and therefore retained for CPEP validation.

The stock suspensions for particle size reduction were prepared using the procedures in 6.6.2 of CPEP. The calibrant suspension contained 2.33 mg of $^{29}SiO_2$ in 100 ml of filtered ethanol. The contaminant suspension contained 2.73 mg of $^{30}SiO_2$ in 100 ml of filtered ethanol. Both of the suspensions contained agglomerated particles, which could not be dispersed by placing the containers in an ultrasonic bath. In the first size reduction attempt, the agglomerates were broken apart by touching the agglomerates in the bottom of the container with a cleaned glass stirring rod while the suspensions remained in the ultrasonic bath. In the second size reduction attempt, a stainless steel spatula was used to crush the particles and the crushing procedure was repeated several times with each crushing procedure being followed by a 3 to 5 minute sonication. The combination of light pressure and the ultrasonic agitation succeeded in dispersing the particulate. When the suspensions were allowed to stand, a noticeable quantity of sediment collected on the bottom of the bottles after several minutes. “Resuspension was easily achieved by agitating the bottles. Sedimentation of the particles was expected, since the silica has a specific gravity over 3 times that of ethanol. During the validation tests the suspensions were kept in the ultrasonic bath to ensure complete suspension of the particulate.

The particle size distribution in each suspension, produced after the size reduction procedures, were measured by a coulter counter instrument. The results of the coulter counter analyses are shown in Table 1 (Batches Cent-II, Cent-III, Cal-II, and Cal-III). The results of the coulter counter analyses of the silica suspensions used in the first phase study (Batches Cent-I and Cal-I) are included in the table for comparison. For the new/reprocessed suspensions, retained for CPEP validation, i.e., Batches Cent-III and Cal-III, the mass (volume) statistics are much more similar to each other than found in the previous study. These reprocessed samples also had mass mean diameters (3.65 µm for Cent-III and 4.22 µm for Cal-III) that are similar to those typically found on contaminated parts (i.e., 4.4 pm). Additional particle size distribution data for the new/reprocessed stock suspensions are given in Appendix B.

Table 1. Coulter Counter Determination of Silica Particle Size

Mean Diameter, µm	Inorganic Particles Found in Contaminated Parts	$^{30}SiO_2$ (Contaminant)			$^{29}SiO_2$ (Calibrant)		
		Previous Study (Cent-I)	New (Cent-II)	New/Reprocessed[(a)] (Cent-III)	Previous Study (Cal-1)	New (Cal-11)	New/Reprocessed[(a)] (Cent-III)
Number of particles	ND	9,912	9,791	30,000	9,646	9,775	30,000
Number mean	1.7	1.13	1.10	1.12	1.23	1.18	1.15
Mass (volume) mean	4.4	8.50	5.47	3.65	4.61	5.04	4.22

ND: Not determined.

(a) Overall mean from three measurements of 10,000 particles each.

Proposed Method of Further size Reduction. Despite the efforts made to reduce the size of the silica particles in the suspensions, large particles (> 10µm) remained in the suspensions. Five or six large particles were detected in a typical coulter counter analysis. While the number of these particles was very small, they represented a significant fraction of the silica mass in the suspensions. Using sonication and frequent swirling of the suspensions before each transfer operation, however, a representative sample of the silica particles was obtained. Yet, it is believed that the precision of the CPEP with respect to inorganic particulate removal can be improved by elimination of these oversized particles.

The mean size of the contaminant silica particles can be reduced most simply by sedimentation. (At present there are no commercial suppliers of sized, isotope, particulate material.) By allowing the contaminant silica suspension to stand for several minutes, then pouring the suspension into another container, the large, fast settling particles can be separated from the smaller particles. After the separation has been performed, both the particle size distribution and the silica mass concentration of the fine fraction must be redetermined. The size distribution can be redetermined by another coulter counter analysis. If the size distribution found by the coulter counter analysis is acceptable, the silica mass concentration of the fine particle fraction of the contaminant suspension can be determined by glow-discharge mass spectrometry (GDMS) analysis. Before samples are taken for either coulter counter or GDMS analysis, the suspension must be swirled and sonicated to ensure complete suspension of the particles. The GDMS sample should be prepared by transferring 1 ml aliquots of the contaminant and calibrant suspensions into a clean porcelain crucible containing 50 mg of silver powder and then evaporating the ethanol carrier and submitting the silver powder for GDMS analysis. The isotope ratios measured by GDMS can then be used to calculate the mass concentration of contaminant silica remaining after the separation. This mass concentration is then used to calculate the amount of contaminant silica placed on the test parts during the doping procedure.

4.1.4 Prequalification Silica Recovery Tests and election of Mass Spectrometric Technique

total of three series of prequalifying tests were conducted with the four new batches of silica stock suspensions. The first two series of tests were conducted with Batches Cent-II and Cal-II to determine the recovery of the inorganic contaminant particulate as well as to compare three separate mass spectrometric techniques for isotopic analysis. In the first test series, three bottles of 5 volume percent Versa-Clean detergent in distilled water were doped with O. 136µg/ml of silica contaminant and O. 117µg/ml of silica calibrant. Three 100 ml aliquots of each sample were filtered through Millipore 0.22µm (Type GS) filters. Each filter was handled as described in 7.6.1 and 7.6.2 of CPEP using 50mg of silver powder in 7.6.2.4 in place of the graphite powder for two of the residues from each sample. One sample from each bottle was submitted for spark-source mass spectrographic (SSMS) analysis and the second sample was submitted for glow discharge mass spectrometry (GDMS). The silica residue in the third crucible from each bottle of detergent was transferred to a 3/8 inch square piece of 0.1 mm thick high-purity iridium metal foil. The particle residue was transferred to the foil by pressing the foil against the crucible walls. The particles were imbedded in the soft iridium. The iridium foils were submitted for analysis by secondary ion mass

spectrometry (SIMS). Both SIMS and SSMS analyses were performed at Evans East, while the GDMS analyses were performed at Northern Analytical Laboratory. The results of the mass spectrometric analyses of the aqueous detergent samples are given in Table 2.

Table 2. Percent Recovery of Silica (Batch Cent-H) in Detergent Samples

Test	Analytical Technique		
	SIMS[a]	SsMS([b])	GDMS[c]
D1	79.6	48.2	73.9
D2	61.0	56.3	79.9
D3	87.7	63.3	75.4
Average	76.1	55.9	76.4
Standard Deviation	11.2	6.2	2.5

(a) SIMS: Secondary ion mass spectrometry
(b) SSMS: Spark-source mass spectrometry
(c) GDMS: Glow-discharge mass spectrometry

The second test series used filtered 1,1, 1-trichloroethane (TCA) as the cleaning agent. Three test samples were prepared and doped with the same concentrations of contaminant and calibrant silica as was used for the aqueous detergent samples described above. Three aliquots of each sample, comprising one quarter of each sample, were transferred to precleaned porcelain crucibles and air dried. The crucibles were then fired for 2 hours at 600C. The residue was prepared for isotopic analysis in the same reamer as the residue from the detergent samples. The samples were also submitted for analysis. The results are presented in Table 3.

Table 3. Percent Recovery of Silica (Batch Cent-II) in TCA Samples

Test	Analytical Technique		
	SIMS[a]	SSMS[b]	GDMS[c]
T1	173.4	101.0	61.3
T2	67.0	83.4	64.6
T3	0.2	67.0	67.6
Average	80.2	83.8	64.5
Standard Deviation	71.3	13.9	2.6

(a) SIMS: Secondary ion mass spectrometry
(b) SSMS: Spark-source mass spectrometry
(c) GDMS: Glow-discharge mass spectrometry

Based on these results the GDMS technique was selected because it gave the best agreement between the two cleaning agents and it also gave the best measurement precision, as indicated by the standard deviation of the analyses.

The above series of prequalifying tests also showed that the silica recovery percentage was unacceptably low. The suspected cause of the low recovery was that the mass mean diameters of the contaminant and calibrant were still too high to avoid some uneven settling of the two types of silica particles. Therefore, the stock suspensions were further subjected to a particle size reduction technique discussed in the previous subsection. The resulting suspensions (Cent-III and Cal-III) were used for a third prequalifying test for silica recovery. Duplicate samples of 2 percent Versa-Clean in distilled water and duplicate samples of TCA, were prepared and doped with O. 136µg/ml of silica contaminant and O.117pg/rnl of silica calibrant. One 100ml aliquot of each sample was filtered as described above and submitted for glow-discharge mass spectrometric (GDMS) analysis. The results of the GDMS analyses of the reprocessed samples are shown in Table 4. These results indicate that the contaminant and calibrant silica suspensions can be transferred reproducibly using the techniques described in the CPEP.

Table 4. Percent Recovery of Silica in Reprocessed Samples (Batch Cent-III) as Analyzed by GDMS[a]

Test	Percent Recovery[a]	Std Dev, percent
Versa-Clean-1	95.9	7.50
Versa-Clean-2	94.5	2.79
Average	95.2	--
TCA-1	98.8	1.45
TCA-2	100.0	5.07
Average	99.4	--

(a) Glow-discharge mass spectrometry.

4.1.5 Development Method for Doping Open Parts

AGMC provided 2 KT73 gyro-hinge and magnet assemblies that were used as test parts for this program in place of the A200D accelerometers used in the previous program. These gyro parts are completely open as opposed to the fully-sealable A200D; therefore, a new method for doping was developed. The modified doping method is described in detail in Attachment B of the modified CPEP and described briefly below. The organic doping was conducted in a Teflon® bag to contain the volatile contaminants. The particulate matter can be applied to these parts more easily than to the accelerometers, since the parts can be allowed to air dry without need for the vacuum pump described in CPEP. Each part was placed into a cleaned petri dish. A 2ml aliquot of the contaminant suspension was placed onto the part at several locations. Any contaminant suspension that leaked through the hinge region of the device was collected in the dish. After the ethanol carrier had dried, the part and dish were placed into the Teflon® bag as illustrated in Figure 2 and the open end of the bag was clamped closed. A cold trap and vacuum pump were connected to the bag so that volatile contaminants could be recovered for analysis. The procedure was similar to the original CPEP doping procedure, with the bag serving in place of the A200D accelerometer case. The apparatus connections are show in Figure 3. A 2ml aliquot of organic contaminant was applied to each part and the carrier was evaporated. Following doping, the parts were kept in the bags until the cleaning tests were performed. After the part was removed from the bag, the bag was resealed until the dish and Teflon® bag were washed. The wash was combined with the organic cold trap sample and returned to the lab for analysis.

Since the KT73 gyro-hinge and magnet assembly is not an enclosed part, a test was performed to determine the volatility of the organic contaminants and to evaluate the need for the cold trap used in the CPEP. An aliquot of the contaminant solution was placed on each of four petri dishes and allowed to dry for 5 to 40 minutes. Each dish was washed with dichloromethane and the wash solution was analyzed for dimethyl phthalate-d6 by GCMS. The amount of the contaminant recovered is shown in Table 5.

Table 5. Percent Recovery of Dimethyl Phthalate-d6 vs Drying Time

Drying time (minutes)	% Recovery
5	48
10	40
20	16
40	2

The results in Table 5 demonstrated the need for the cold trap used in the CPEP and indicated that the KT73 parts must be doped in a manner which permits collection of the contaminant compounds during the doping procedure. These results also indicated that the parts must be kept in a sealed enclosure to prevent evaporative losses between the doping and cleaning steps.

A pretest was performed to confirm that the organic contaminants could be recovered from the petri dish, Teflon® bag and cold trap. For these tests the organic doping apparatus was assembled as described in Attachment B, Section 4.0 of CPEP and illustrated in Figure 2, but no part was placed on the petri dish. The organic contaminants were injected onto the petri dish and the carrier liquid was evaporated. After evaporation of the carrier liquid, a 0.5 ml aliquot of calibrant solution was added to the cold trap, the petri dish and the Teflon® bag. Each sample was analyzed separately to determine the location of the major portion of each compound. The results of this pretest are presented in Table 6. These results indicate that both phenanthrene and octadecanoic acid were completely recovered during the doping procedure; however, only 73% of the dimethyl phthalate was recovered during the doping procedure. The remaining dimethyl phthalate was apparently lost by evaporation while the Teflon® bag was open. Given the repeatability of the dimethyl phthalate recovery, the evaporation losses can be accounted for by assuming that 27% of the dimethyl phthalate on the petri dish evaporates during test part doping. This amount of lost dimethyl phthalate is equivalent to about 2.5 minutes of evaporation under the conditions of Table 5. For the validation tests described in Section 5.2, the evaporation loss was corrected by assuming that 73% of the dimethyl phthalate in the composite petri dish, Teflon® bag and cold trap sample was recovered and 27% was lost.

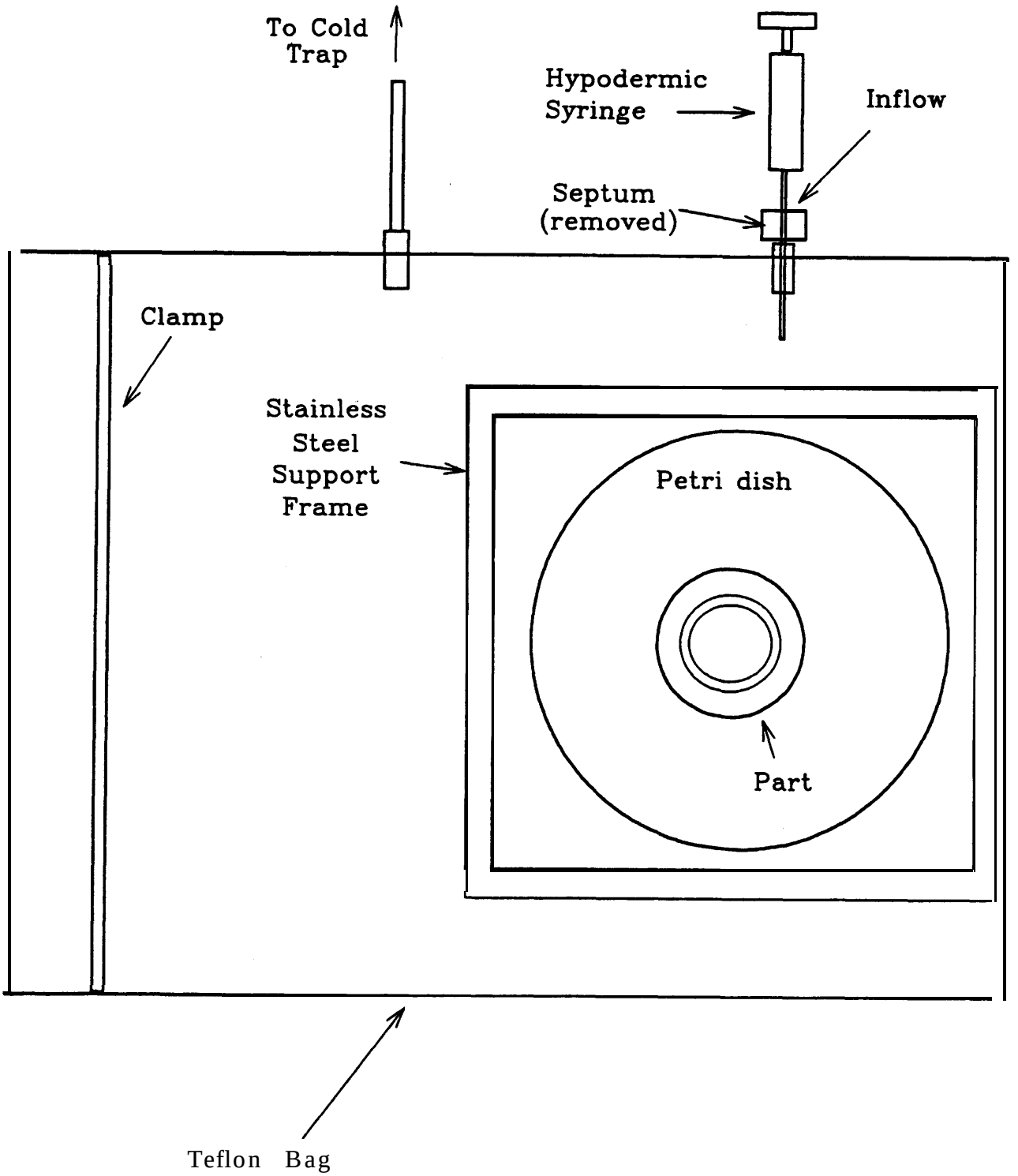

Figure 2. Schematic Diagram of Open Test Part Apparatus

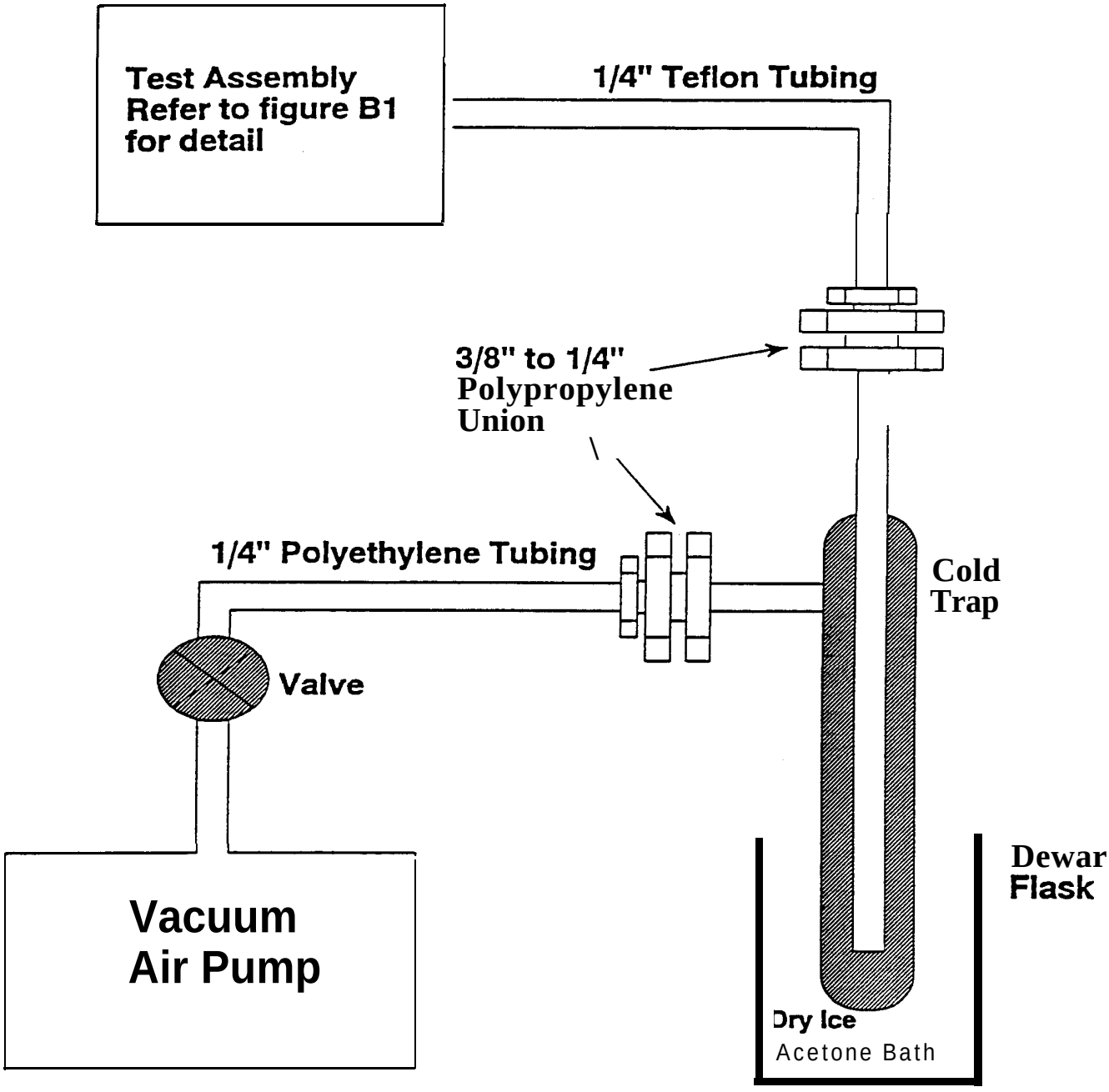

Figure 3. Schematic Diagram of Test Device Organic Doping Interconnections

Table 6. Distribution of Organic Contaminants During the CPEP Doping Procedure

Test	Contaminant Location	Percent Recovery of Contaminant Compound		
		Dimethyl phthalate - d_6	Phenanthrene - d_{10}	Octadecanoic acid
5	Petri dish	36	100	100
6	Petri dish	34	100	100
7	Petri dish	56	100	100
Average	Petri dish	42	100	100
5	Teflon® bag	4	1.3	2.9
6	Teflon® bag	5	0.8	0.2
7	Teflon® bag	5	0.7	0.2
Average	Teflon® bag	4.7	0.9	1.1
5	Cold trap	29	4.6	0.3
6	Cold trap	31	3.1	0.3
7	Cold trap	18	2.4	0.5
Average	Cold trap	26	3.4	0.4
5	Total	69	105.9	103.2
6	Total	70	103.9	100.5
7	Total	79	103.1	100.7
Average	Total	72.7	104.3	101.5

4.2 Development of Method for Direct Analysis of Organics in Detergent Solution

A method which would permit a direct determination of the organic contaminant concentrations was deemed to be beyond the scope of the initial program and was deferred to this follow-on program. This method is based upon the successful analysis of the distilled water rinse sample in the previous program. The rinse water sample contained the same interfering contaminants present in the detergent, but at much lower concentration,. The liquid carryover between cleaning cycles was estimated to be 1 to 2 milliliters. The direct method employs dilution of the detergent to reduce the amount of interfering compounds to a level which permits accurate determination of the concentrations of the contaminant compounds.

The Versa-Clean detergent was analyzed by GC-MS to identify potential interfering components. The GC-MS analysis results indicated that Versa-Clean contains a large quantity of fatty acids similar to the octadecanoic acid synthetic contaminant. In the first experiment, recovery of the synthetic contaminants was tested by spiking a 1 % Versa-Clean solution with the contaminant compounds. A one ml aliquot of 1 % Versa-Clean detergent in distilled water was spiked with 83.3μg of dimethyl phthalate and phenanthrene and with 833µg of octadecanoic acid. The spiked aqueous detergent was acidified with 1ml of 3N hydrochloric acid to reduce the pH to less than 1 and 1g of muffled NaCl was added to the detergent to increase the effectiveness of the extraction. The aqueous detergent was then extracted with three 50 ml aliquots of dichloromethane (DCM). The DCM extracts were combined, then dried over muffled Na_2SO_4 and Kuderna-Danish concentrated to 1ml. The concentrate was analyzed by GC/MS to determine the percent recovery, which is shown in Table 7.

Table 7. Recovery of Contaminants from 1% Versa-Clean Detergent

Compound	% Recovery
Dimethyl Phthalate-d6	34
Phenanthrene-d10	7 0
Octadecanoic Acid-d35	o

The extract from the 1 % detergent overloaded the GC column and required repeated washing to remove the fatty acid compounds from the GC column.

A second experiment using 2% detergent at 200 times dilution was performed next. For this experiment the same amount of the contaminant compounds was spiked into a ten ml aliquot of 2 % Versa-Clean detergent and then diluted by a factor of 200 to 1. The diluted samples were extracted and concentrated as described above. The results of the GC/MS analyses of the concentrates are shown in Table 8. Note that this test was conducted using a 10 ml aliquot of 2 % detergent spiked with 83.3 µg of phenanthrene and dimethyl phthalate and 833 µg of octadecanoic acid. In a cleaning

test using 200 ml of 2 % detergent solution, 20 times more contaminant would be required (1.67 mg and 16.7 mg) to achieve the same concentration as was used in this test. This experiment demonstrates good recovery for all three contaminant compounds. For this experiment, the calibration compound was not added until the concentration step was completed, thus the actual amount of the spiked contaminant recovered from the extraction and concentration processes was measured. In the cleaning performance tests the calibrant is added prior to sample workup to correct for any recovery losses during sample preparation.

Table 8. Percent Recovery of Contaminants from Diluted 2% Versa-Clean Detergent

Test	Dimethyl Phthalate	Phenanthrene	Octadecanoic Acid
1	91	83	102
2	82	80	100
3	86	85	104
Average	86.3	82.7	102

Based upon the results shown in Table 8, dilution of the aqueous detergent reduced the concentration of interfering compounds in the detergent sufficiently so that the three organic compounds of interest could be recovered and determined. Therefore, methods to enhance recovery were not investigated.

4.3 Revised CPEP Preparation

Based on the improvements made in this project, a revised CPEP was prepared (Appendix A). The results of the validation testing are provided in the next section.

4.4 Revised CPEP Validation

4.4.1 Validation Test Plan

To validate the modified methods described in previous sections as well as to determine the precision (reproducibility) of the methods, a test matrix consisting of 15 tests, shown in Table 9, was designed and implemented. All tests were performed at AGMC using KT73 gyro-hinge and magnet assemblies as the test parts. The cleaning efficiency of three cleaning agents, Versa-Clean, TCA and Freon® 113, was compared. The contaminant doping procedures in Attachment B, Section 4.0, of CPEP (Appendix A) were used for these tests. The sample preparation procedures in Attachment B, Section 5.0, Appendix A were used to prepare the samples for organic analysis. For the inorganic

sample preparation, the original CPEP procedures were employed. Silver powder was used as a carrier for the silica particles in place of the graphite powder used in the original program. Silver powder was used to eliminate a possible mass spectral interference between ^{28}Si and $^{12}C^{16}O$ which have the same nominal mass. The GDMS mass spectral technique was employed for all of the inorganic isotopic analyses. The FORTRAN77 program MATRIX, modified for use on IBM PC compatible computers, was used to calculate the quantity of inorganic contaminant removed from the test parts.

Table 9. Test Matrix for Cleaning

Test No.	Part (a)	cleaning Agent(b)	No. of Cleaning cycles(c)	Comments
1,2,3,4,5	1,2,3,4,5	T	3	Tests 2 through 5 are repeats of Test 1
6,7,8,9,10	6,7,8,9,10	W	(d)	Tests 7 through 10 are repeats of Test 6
11,12,13,14,15	11,12,13,14,15	c	3	Test 12 through 15 are repeats of Test 11

(a) KT73 gyro-hinge and magnet assemblies were used for all tests.
(b) T: 1,1, 1-trichloroethane (TCA); C: Freon-1 13; W: aqueous detergent (Versa-Clean).
(c) Each cycle with an equal volume of cleaning agent, with collection and analysis of the cleaning residue from each cycle.
(d) One cycle in aqueous detergent followed by one cycle sonication in deionized water and one cycle in cleaning agent T. The extract from the deionized water rinse and the aqueous detergent residue were analyzed as separate samples.

4.4.2 CPEP Validation Tests

All of the cleaning performance tests were performed at NAFB using a Sonic Systems, Inc. Model 3215 IS ultrasonic cleaner. The ultrasonic generator operating frequency was 40kHz and the full output power setting (600 Watts) was used. Wash tank dimensions were 12 x 14 inches. To couple the ultrasonic energy to the cleaning test containers, approximately 6 inches of water was used in the wash tank. AGMC personnel recommended that the wash tank be used for the tests because the wash tank operated at a higher power density than the rinse tank.

Each cleaning test was performed on a group of 5 test parts. To eliminate the possibility of carryover of the synthetic contaminants between tests, each part was used in only one test. The tests for one cleaning agent were performed on the same day. Five working days elapsed between tests of the different cleaning agents. The time between tests was needed to prepare the cleaning residues for analysis and to reclean the experimental apparatus for the next group of tests.

All of the test devices were treated in the same manner. Inorganic contaminant was applied to the shaft side of the KT73 parts. The contaminant suspension was distributed over the top surface of each part. The hypodermic syringe used to measure and apply the contaminant suspension was rinsed with 1 ml of filtered ethanol and the rinse was placed into the petri dish. Rinse ethanol was not applied to the test part to avoid washing particulate off of the part. After all test parts were doped with inorganic contaminant, the parts were placed under a heat lamp to speed evaporation of the ethanol. For the Freon® 113 cleaning tests the vacuum oven in the AGMC chemistry lab was used to evaporate the ethanol, because the heat lamp was not available. The vacuum oven was set at the normal AGMC operating temperature of 100°C and the vacuum was 30 inches of mercury.

Following evaporation of the ethanol carrier, each test part with its corresponding petri dish, was placed into a Teflon® bag. The bag was connected to the cold trap and air pump as illustrated in Figure 3. The septum seal was removed from the bag, the air pump was started and the cold trap was lowered into the dry ice-acetone cold bath. Two 1 ml aliquots of organic contaminant solution were applied to the part through the septum opening. The part was rocked slowly to spread the liquid on the surface of the part and to speed drying of the carrier liquid. The air pump was stopped and the septum seal was replaced when the last of the carrier liquid had evaporated. The Teflon® bag containing the part was set aside and the contents of the cold trap were transferred to a labeled sample bottle. The cold trap contents were combined with the rinses from the Teflon® bag and the petri dish after the cleaning tests were completed. The contaminant loadings and drying times are given in Table 10.

Concurrently with contaminant doping, AGMC personnel filled the ultrasonic cleaner wash tank with distilled water and adjusted the operating temperature and liquid level. The test parts were cleaned in 250ml glass beakers containing 200 ml of filtered cleaning agent. After each cleaning cycle, the rack holding the beakers was removed from the cleaner, the parts were transferred to a beaker containing fresh cleaning agent, the rack with beakers was returned to the cleaner and the next cleaning cycle was started. When all cleaning cycles were completed, the calibrant suspension and solution were added to each beaker of cleaning agent. The cleaning agent was transferred to labeled sample bottles, the bottle caps were sealed with Teflon® tape, and the samples were returned to Battelle for analysis. Addition of the calibrant was delayed until all cleaning was completed because the 5 minute cleaning cycles used in these tests did not allow sufficient time to add the calibrant and transfer the cleaning residue to the sample bottles during a cleaning cycle.

One milliliter each of inorganic calibrant suspension and organic calibrant solution was placed in the petri dishes. The interior of the Teflon® bags, including the stainless steel support frame, was rinsed with a spray of dichloromethane (DCM). The DCM was then carefully moved over the interior surface of the bag to dissolve any organic contaminant adsorbed on the bag. This DCM rinse was transferred to the petri dish. The rinse was repeated a second time and also transferred to the petri dish. The petri dish - bag rinse solution was then combined with the cold trap sample and returned to Battelle for analysis.

For inorganic particulate analysis, a 100ml aliquot of each cleaning residue sample was filtered through a 0.22µm pore size filter (Millipore Type GS, 25mm diameter). For the petri dish composite sample, a 25ml aliquot was filtered. Each filter was prepared for GDMS analysis as described in Section 4.1.4.

Table 10. Test Device Synthetic Contaminantt Loading (KT73 Gyro-Hinge and Magnet Assembly)

Test	Device ID	Inorganic Contaminant (μg)	Ethanol Rinse (ml)	Organic Contaminant (ml)[a]	Drying Time (min)	Remarks
1[b]	2786	54.6	1.0	2.0	10	
2[b]	2845	54.6	1.0	2.0	5.3	
3[b]	2930	54.6	1.0	2.0	2.3	Tear in Teflon bag.
4[b]	2947	54.6	1.0	2.0	3.2	Device leaked into petri dish.
5[b]	8858	54.6	1.0	2.0	3.2	
6[c]	S 108	54.6	1.0	2.0	2.8	
7[c]	728	54.6	1.0	2.0	2.2	
8[c]	9706	54.6	1.0	2.0	4.6	
9[c]	6839	54.6	1.0	2.0	2.9	
10[c]	149	54.6	1.0	2.0	5.8	Organic calibrant omitted from cold trap sample.
11[d]	2634	54.6	1.0	2.0	4.7	Device leaked into petri dish. Cold trap connected late.
12[d]	1131	54.6	1.0	2.0	10.1	
13[d]	8274	54.6	1.0	2.0	2.6	Device leaked into petri dish.
14[d]	9889	54.6	1.0	2.0	8.3	
15[d]	234	54.6	1.0	2.0	4.6	Device leaked into petri dish.

(a) The organic contaminant solution contained the following compounds dissolved in filtered DCM:
- dimethyl phthalate - d6: 0.1mg/ml
- phenanthrene - 9,10 - $^{13}C_2$: 0.1mg/ml
- octadecanoic acid - 18,18,18 - d3: 1.8mg/ml

(b) Cleaning agent: 1,1, 1-trichloroethane (TCA).

(c) Cleaning agent: 2% Versa-Clean detergent.

(d) Cleaning agent: Freon 113.

For the organic contamination analyses the procedures in Appendix B.5 were employed. Because the ethanol carrier in the inorganic particulate calibrant suspension added to the cleaning agent residues was incompatible with the gas chromatograph column, the nitrogen evaporator technique was used to remove the ethanol contaminated solution. The contaminant compounds were then redissolved in 1ml of filtered dichloromethane. A 1μl aliquot of the redissolved solution was injected into the GC/MS instrument for analysis.

4.4.3 Cleaning Efficiency Calculations and Errors

General Results. The cleaning extract analyses were used to calculate percent cleaning, defined as percent of a contaminant extracted from a contaminated part. The results are tabulated in Tables 11 through 13. The spread of data, means, and 95 percent confidence limits for 4 or 5 replicates, are also shown graphically in Figures 4 through 6. During sample preparation in Test 3, the composite petri dish sample bottle was dropped and the sample was lost. Since the contents of the composite sample were needed to determine the amount of contaminant remaining on the test part, the results from Test 3 were not included in the statistical analysis. Also, the results for organic analyses from Test 10 were not included in statistical analysis since there was no calibrant added due to an operator error.

The standard deviation as a percentage of the mean for the four contaminants and the three cleaning agents are shown in Figure 7. Also shown are standard deviation values from the previous study which utilized sealable (closed) parts for contaminant doping. As shown, the errors from the present study are smaller, except for octadecanoic acid removal by Versa-Clean, than in the previous study even though doping of parts used in the present study is subject to more errors due to leakage into petri dish and due to escaping of some organic contaminant vapors into the bag (see Figure 2). The reason for large variability for octadecanoic acid for detergent solution cleaning is that the mean values are about one-third of values for other contaminants, as discussed later.

Comparison of Cleaning Agents. The three cleaning agents are graphically compared in Figures 8-15 in terms of their cleaning efficiency for the four contaminants. The cleaning efficiency values in these figures are means of 4 to 5 replicates. As seen, most of the cleaning takes place in the first cycle. As expected, the cleaning efficiency in Cycle 3 for any contaminant was lower than in Cycle 2 with the exception of Versa-Clean. This is because the second and third cycles for Versa-Clean used D.I. water and TCA, respectively, as cleaning agents.

A statistical significance analysis of the entire data set showed that there is a statistically significant difference in percent recovery in Cycle 1 across the types of cleaning agents and by the type of contaminant at a 99 percent confidence level.

Table 11. Cumulative Percent Cleaning in 1,1, 1-Trichloroethane (TCA)

Test	Dimethyl Phthalate-d6				Phenanthrene-9,10-$^{13}C_2$				Octadecanoic acid-18,18,18-d3				Inorganic Particulate			
	Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %		
		Cycle 1	Cycle 2	Cycle 3		Cycle 1	Cycle 2	Cycle 3		Cycle 1	Cycle 2	Cycle 3		Cycle 1	Cycle 2	Cycle 2
1	24.5	83.5	84.5	85.4	2.1	94.1	95.3	96.8	3.3	81.8	82.3	84.1	7.1	91.3	95.3	96.5
2	18.9	87.4	88.5	89.0	1.2	93.6	94.4	94.8	0.2	74.9	78.9	79.5	4.8	70.3	72.7	73.8
4	27.7	76.3	77.1	77.7	21.4	90.2	91.6	91.9	6	57.6	60.1	61.8	6.8	85.3	89.6	92.3
5	13.4	96.1	97.3	98.3	5.5	94.4	95.7	98.0	1.1	81.0	81.2	84.5	2.7	85.3	88.8	89.4
Average[a]	21.1	85.8	86.8	87.6	7.6	93.1	94.2	95.4	2.6	73.8	75.6	77.5	5.3	83.1	86.6	88.0
Std Dev[a]	6.3	8.2	8.4	8.5	9.4	1.9	1.8	2.7	2.6	11.2	10.4	10.7	2.0	8.9	9.7	9.9

(a) Device 3 was omitted from the calculation since the composite sample bottle was broken.

Table 12. Cumulative Percent Cleaning in 2% Versa-Clean Detergent

Test	Dimethyl Phthalate-d6				Phenanthrene-9,10-$^{13}C_2$				C Octadecanoic acid-18,18,1843				Inorganic Particulate			
	Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %		
		cycle 1	cycle 2	Cycle 3		Cycle 1	Cycle 2	Cycle 3		Cycle 1	Cycle 2	Cycle 3		Cycle 1	Cycle 2	Cycle 2
6	27.4	66.4	67.6	70.0	6.7	90.7	93.7	98.2	7.1	33.9	35.7	42.8	8.7	57.1	61.2	62.5
7	24.9	69.8	70.7	72.3	14.2	87.6	88.5	89.4	12.7	25.5	26.0	26.8	3.7	76.9	83.7	84.4
8	30.7	65.9	66.2	67.7	15.7	83.3	84.9	85.6	14.3	24.6	25.0	25.3	6.9	78.3	84.9	85.8
9	21.9	63.0	63.9	64.9	20.7	85.8	86.5	87.0	20.7	27.2	27.4	27.6	1.4	85.1	89.9	90.5
10[a]													6.8	106.5	112.1	112.6
Average[a]	26.2	66.3	67.1	68.7	14.3	86.8	88.4	90.1	13.7	27.8	28.5	30.6	5.5	80.8	86.4	87.2
Std Dev[a]	3.7	2.8	2.8	3.2	5.8	3.1	3.8	5.6	5.6	4.2	4.9	8.2	2.9	17.8	18.1	17.9

(a) Device 10 was omitted from calculation for organics since no calibant was added due to operator error.

Table 13. Cumulative Percent Cleaning in Freon-113®

Test	Dimethyl Phthalate-d6				Phenanthrene-9,10-$^{13}C_2$				Octadecanoic acid-18,18,18-d3				Inorganic Particulate			
	Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %			Petri Dish Composite Sample %	Cleaning, %		
		cycle 1	Cycle 2	cycle 3		Cycle 1	Cycle 2	Cycle 3		Cycle 1	Cycle 2	Cycle 3		Cycle 1	Cycle 2	cycle 2
11	16.7	61.8	64.0	66.0	22.7	77.6	80.2	86.7	26.4	70.8	74.3	80.8	10.1	62,2	67,7	72.0
12	16.7	89.1	91.5	92.9	2.81	89.9	91,8	92.6	2.9	75.8	78.0	78.4	5.5	64.5	68.4	71.5
13	21.9	78.1	80.4	81.7	12.1	81.2	82.8	83.5	11.2	82.9	84.6	84.8	8.8	79.4	82.1	84.3
14	11.5	88.1	89.7	90.6	3.6	98.9	101.9	102.1	4.6	98.0	99.2	99.4	1.2	76.0	79.5	81.4
15	25,1	75.9	78.3	79.5	27.6	88.4	90.9	91.4	27.3	113.	115.	115,	4.6	76.9	82.4	84.4
Average	18.4	78.6	80.8	82.1	13.8	87.2	89.5	91.3	14.5	88.1	90.2	91,7	6.0	71.8	76.0	78.7
Std Dev	5.3	11.1	11.0	10.7	11.2	8.3	8.6	7.1	11.7	17.3	16.8	15.4	3.5	7.56	7.36	6.48

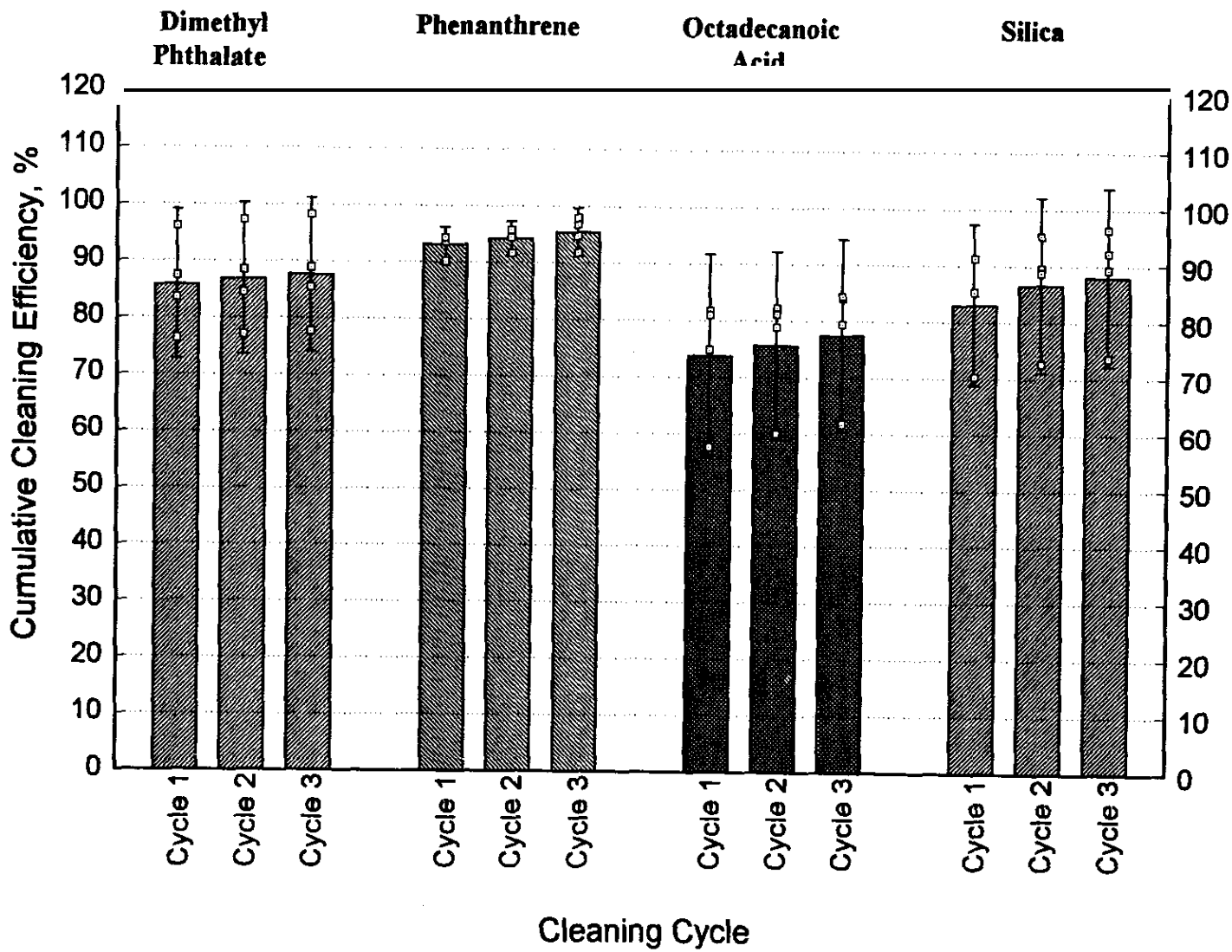

Figure 4. Cumulative cleaning efficiency of TCA. (The bar charts show means for a set of 4 or 5 replicates. The spread of data and 95 percent confidence limits are also shown.)

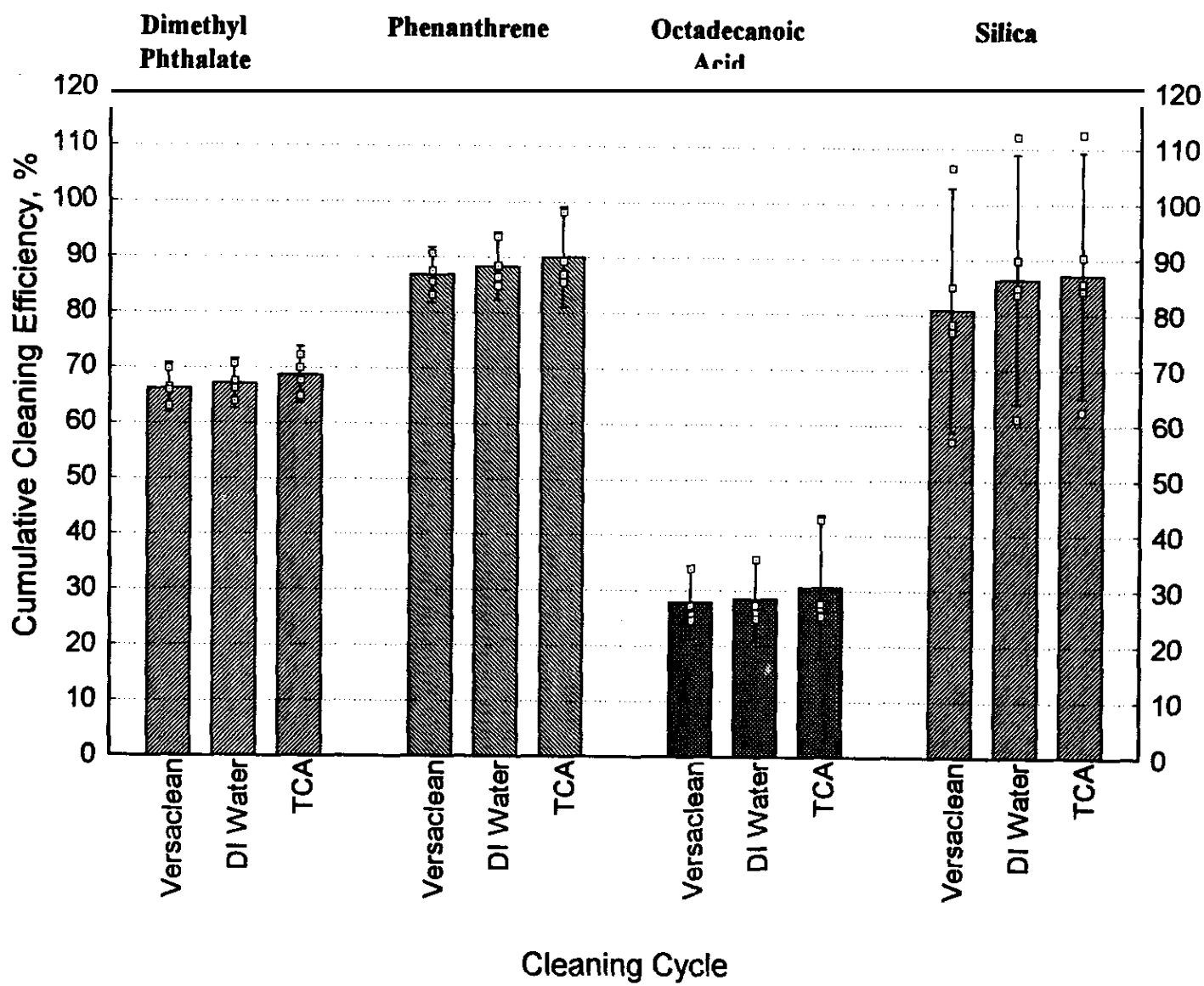

Figure 5. Cumulative cleaning efficiency of 2% Versa-Clean detergent. (The bar charts show means for a set of 4 or 5 replicates. The spread of data and 95 percent confidence limits are also shown.)

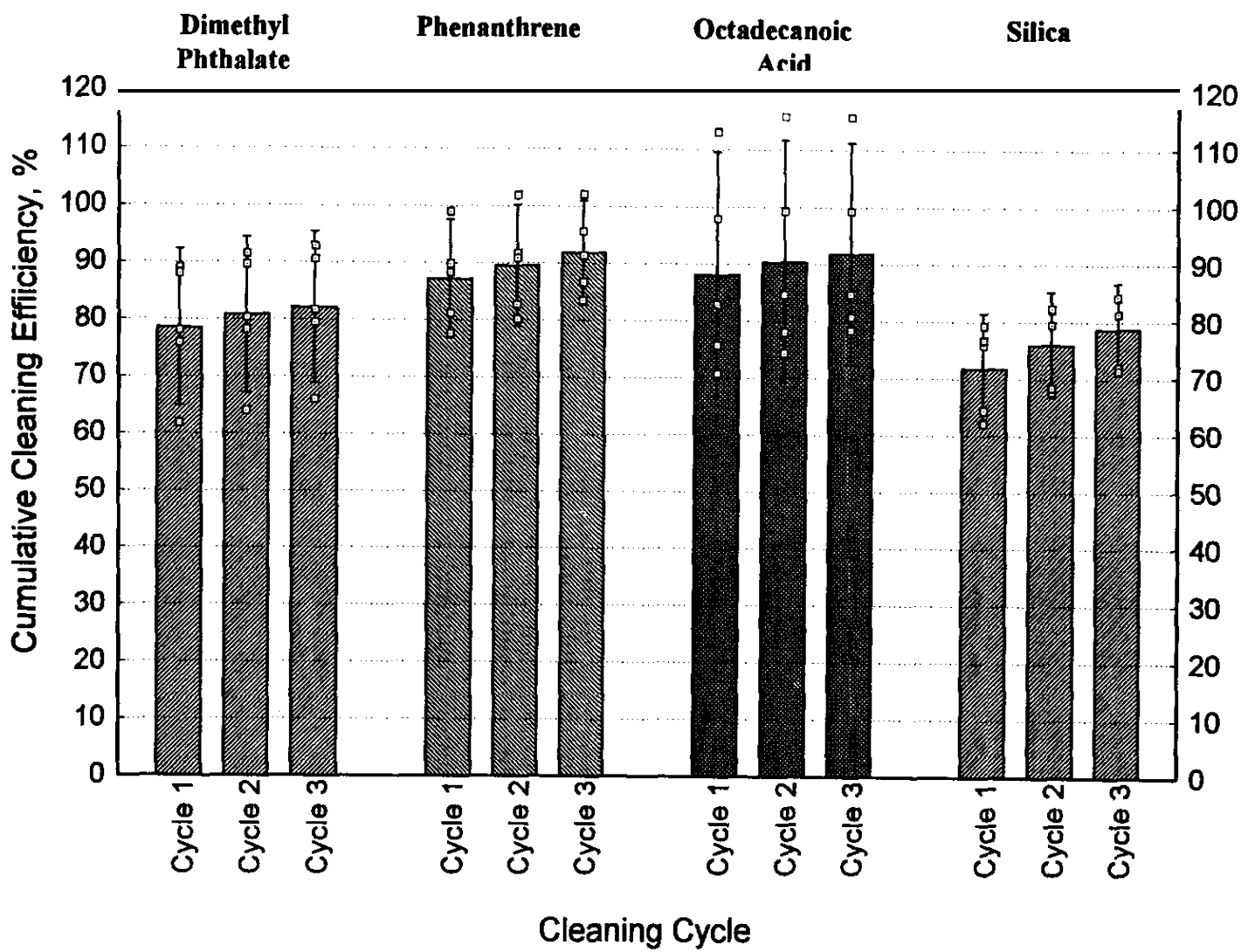

Figure 6. Cumulative cleaning efficiency of Freon 113. (The bar charts show means for a set of 4 or 5 replicates. The spread of data and 95 percent confidence limits are also shown.)

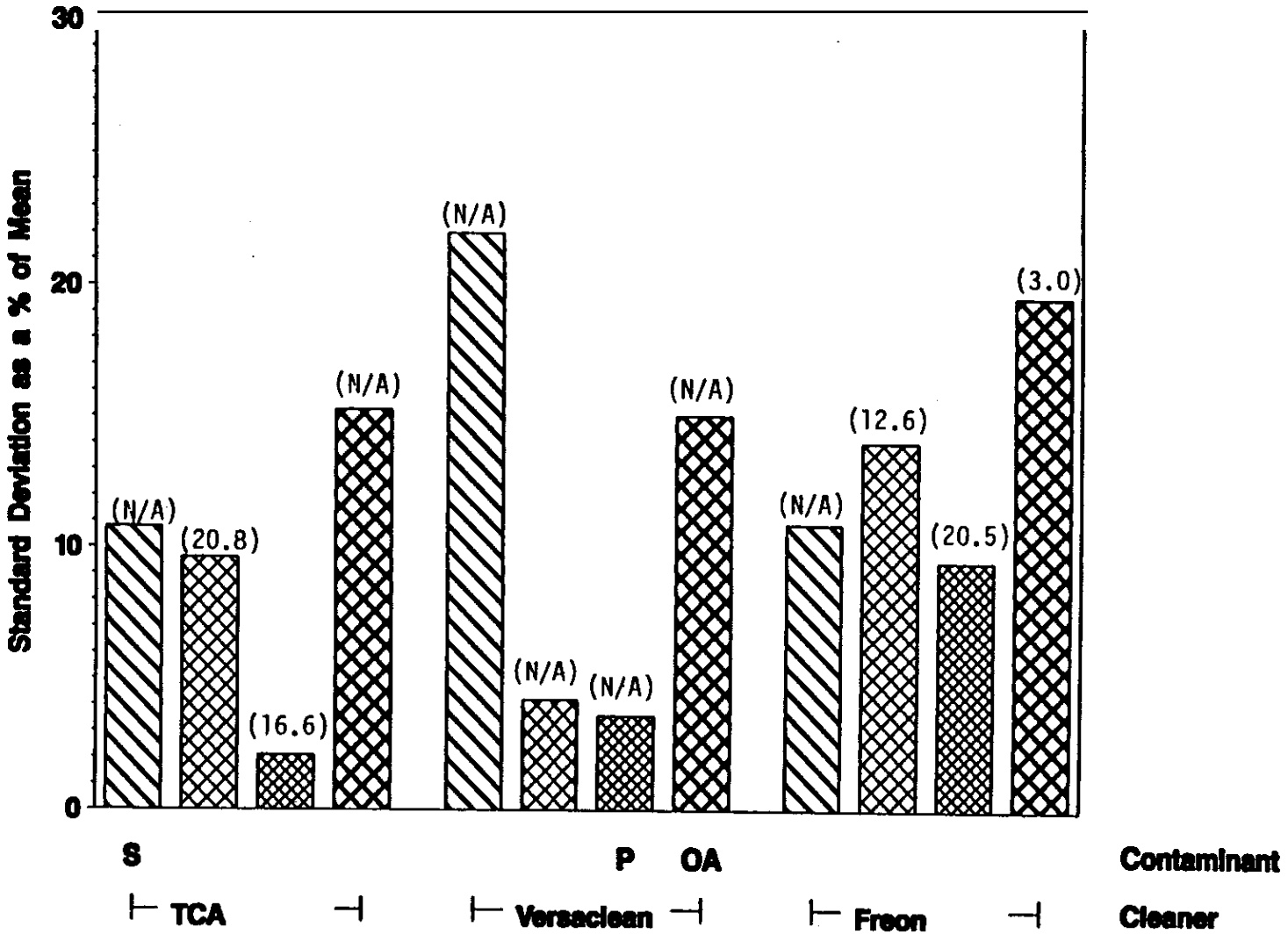

Figure 7. Standard Deviation as a Percentage of Mean for Cycle 1. (The corresponding values, where available, from previous study for sealable parts are shown in parentheses above the bars.)

Legend for contaminants: S = silica; DP = diamethyl phthalate; P = phenanthrene; OA = octadecanoic acid

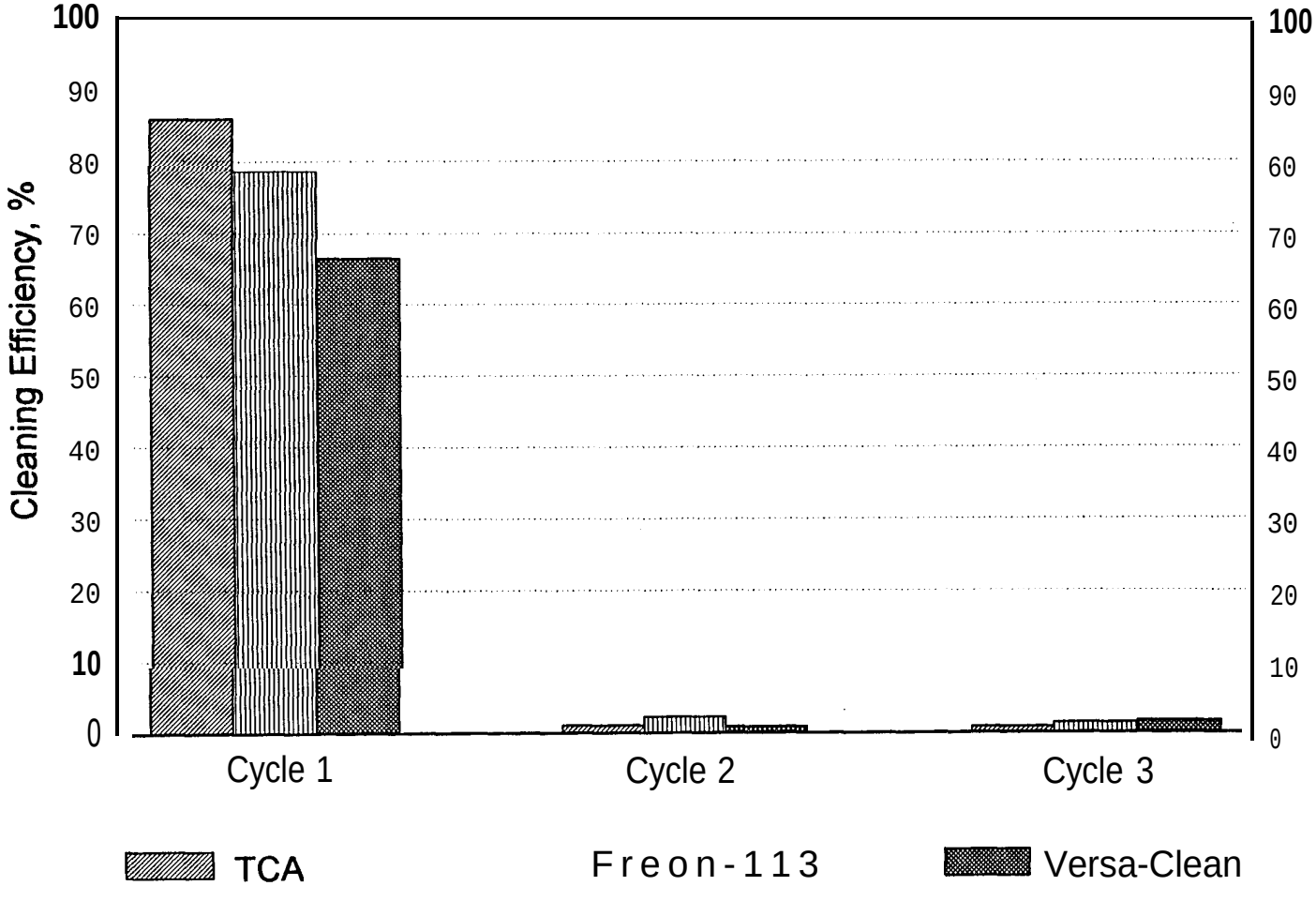

Figure 8. Removal of dimethyl phthalate by three different cleaning agents for three consecutive cleaning cycles (Note: Cycles 2 and 3 for Versa-Clean were with D. I. Water and TCA, respectively.)

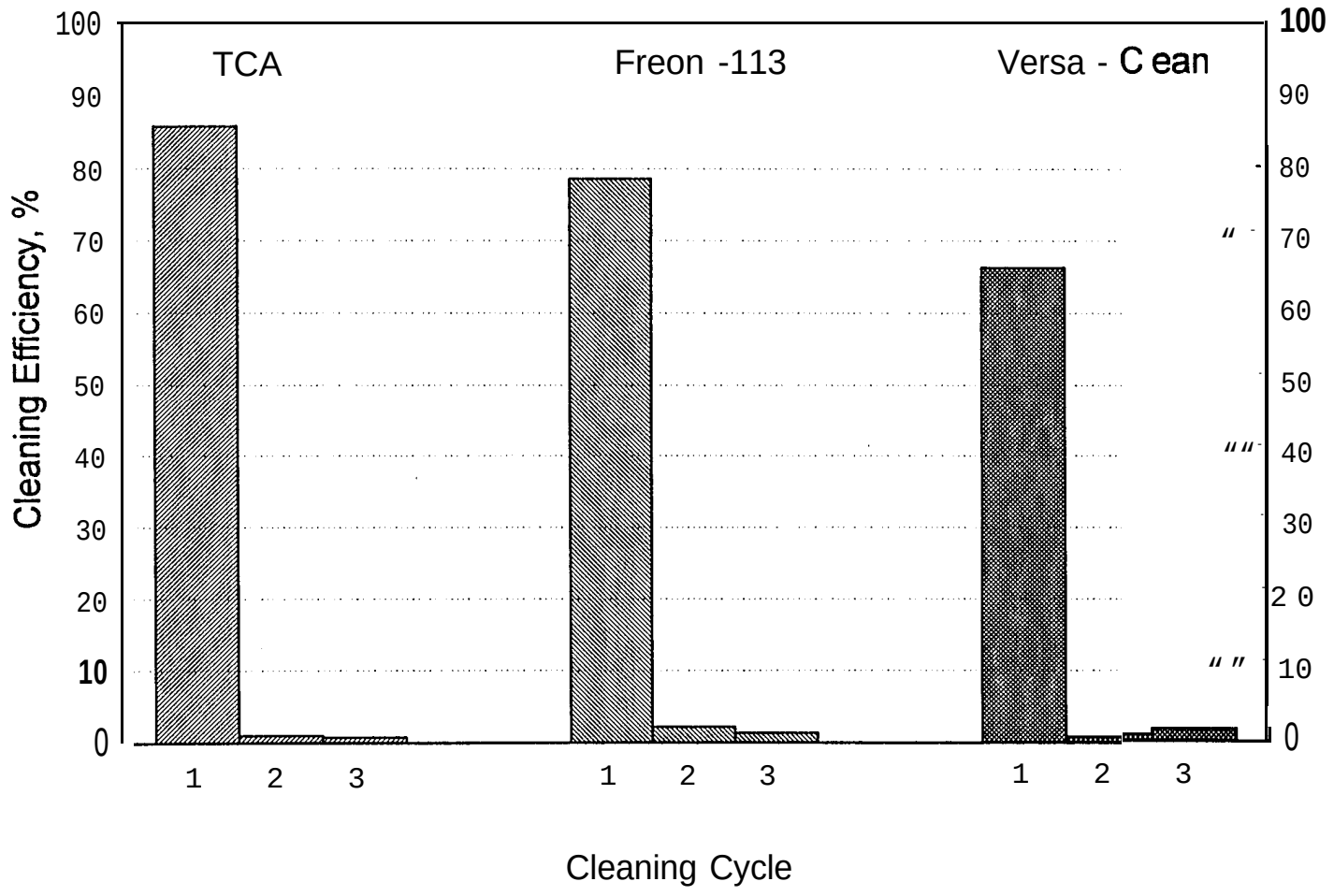

Figure 9. Removal of dimethyl phthalate as a function of cleaning cycle for three cleaning agents (Note: Cycles 2 and 3 for Versa-Clean were with D. I. Water and TCA, respectively.)

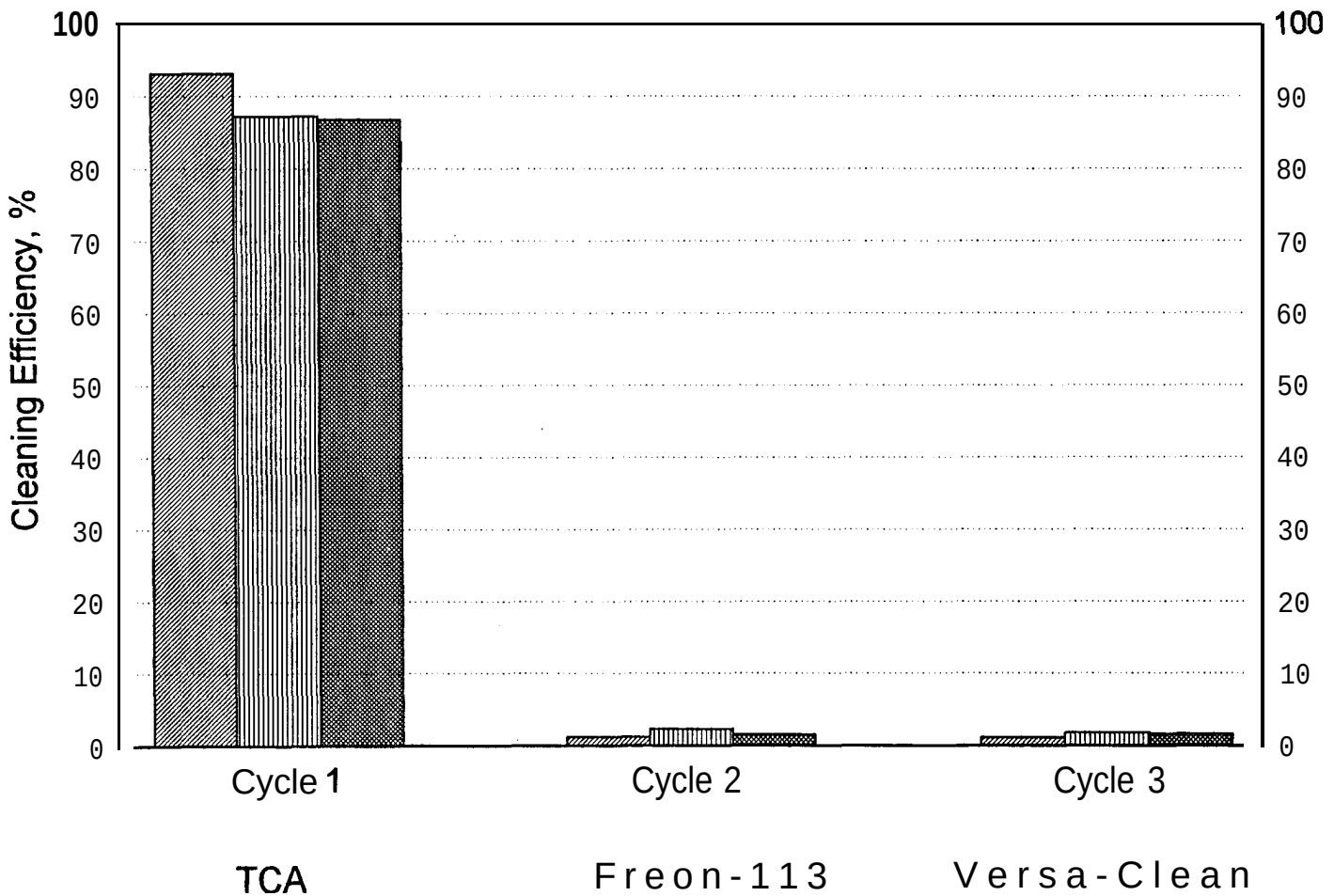

Figure 10. Removal of Phenanthrene by three different cleaning agents for three consecutive cleaning cycles (Note: Cycles 2 and 3 for Versa-Clean were with D. I. Water and TCA, respectively.)

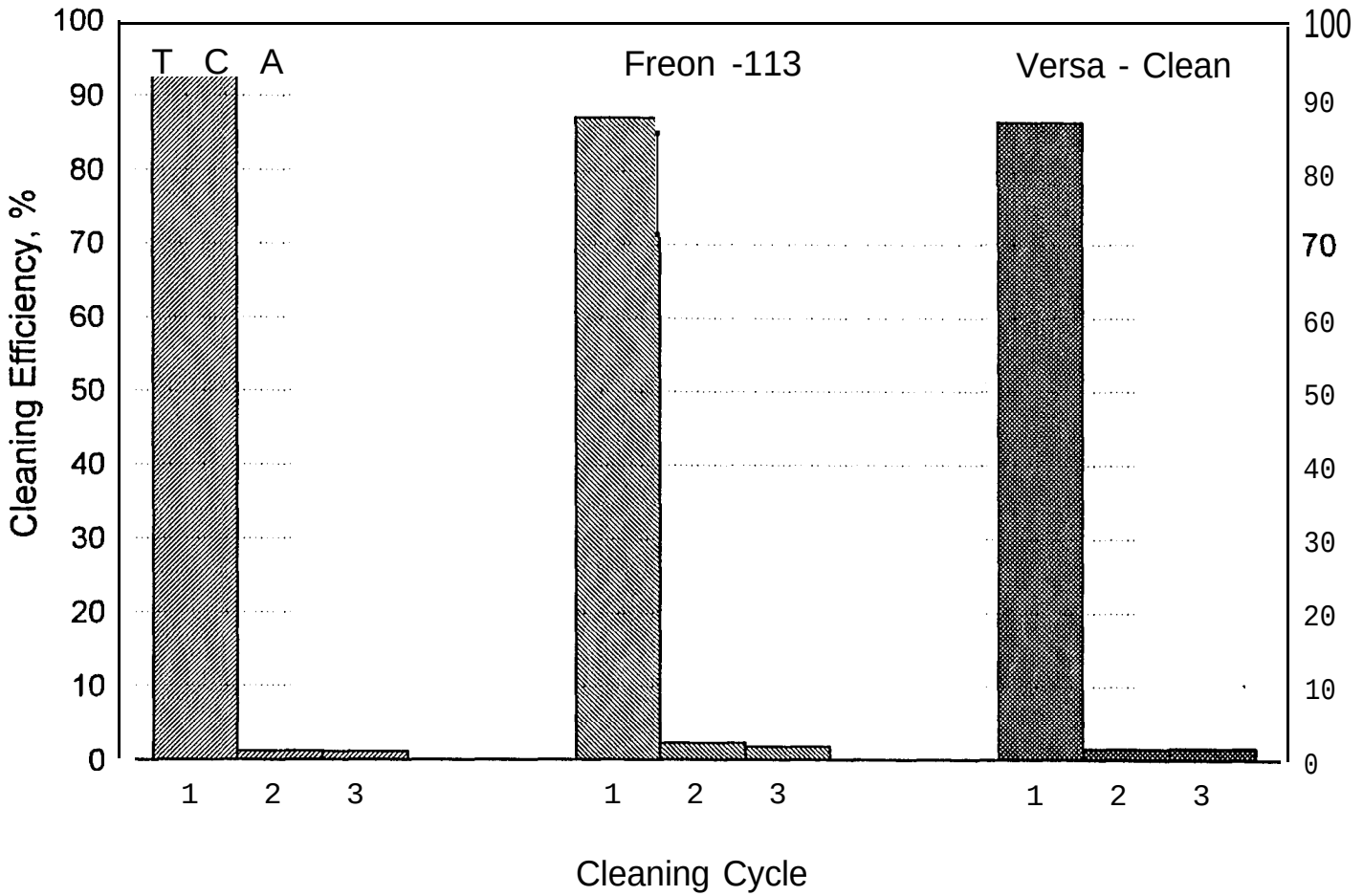

Figure 11. Removal of Phenanthrene as a function of cleaning cycle for three cleaning agents (Note: Cycles 2 and 3 for Versa-Clean were with D. I. Water and TCA, respectively.)

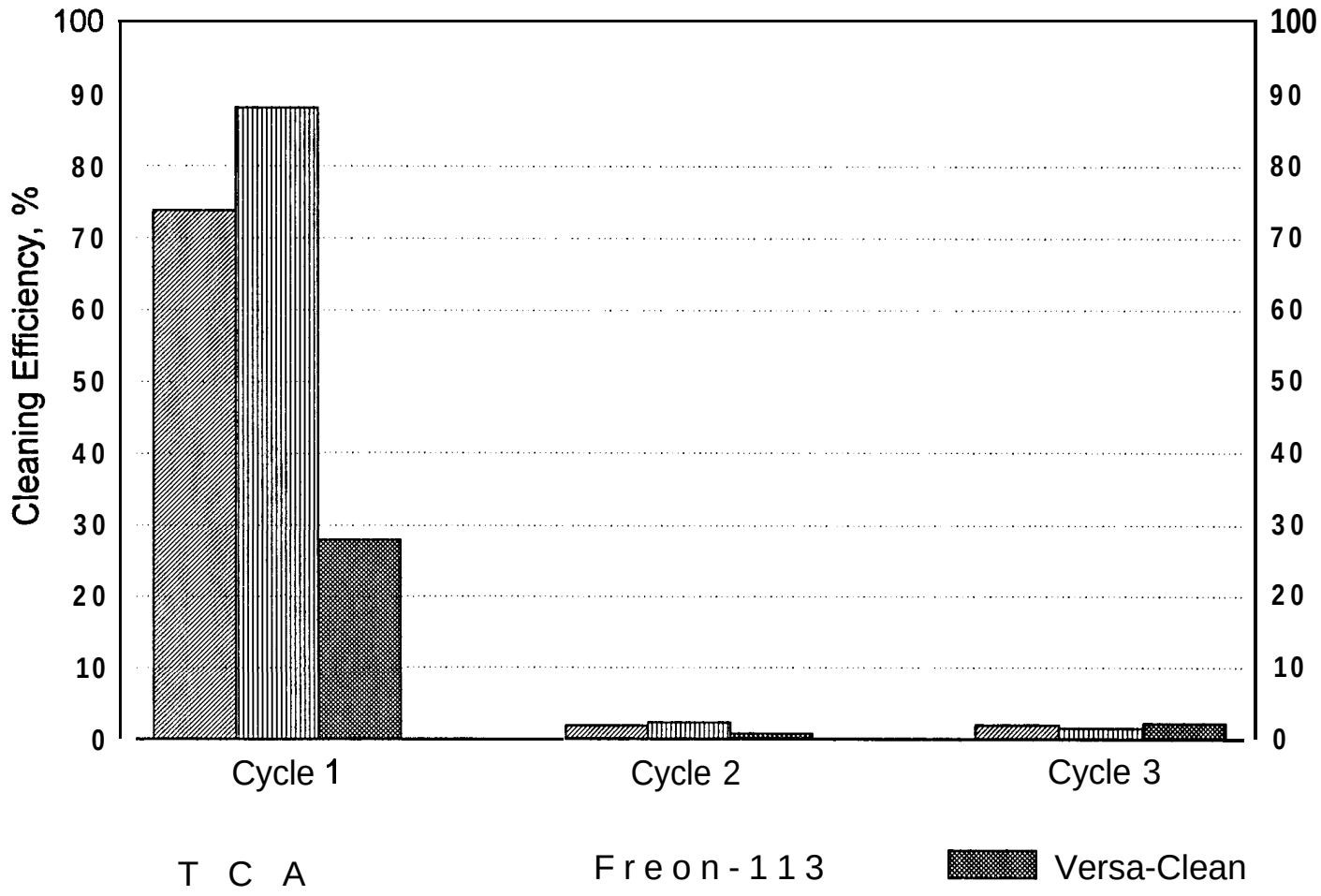

Figure 12. Removal of **octadecanoic** acid **by** three different cleaning agents for three consecutive cleaning cycles (Note: Cycles 2 and 3 for Versa-Clean were with D. I. Water and TCA, respectively.)

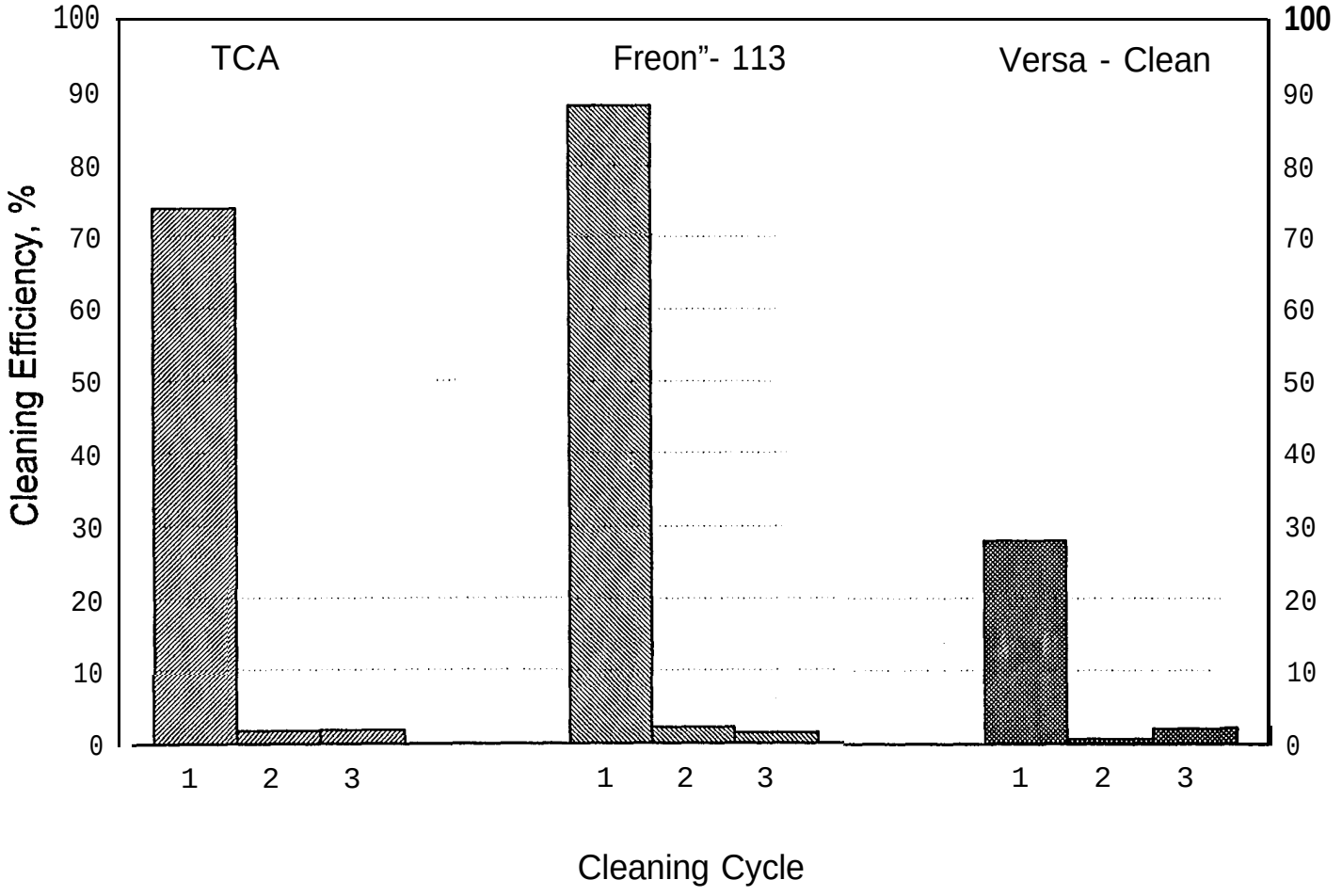

Figure 13. Removal of **octadecanoic** acid as a function of cleaning cycle for three cleaning agents (Note: Cycles 2 and 3 for Versa-Clean were with D. I. Water and TCA, respectively.)

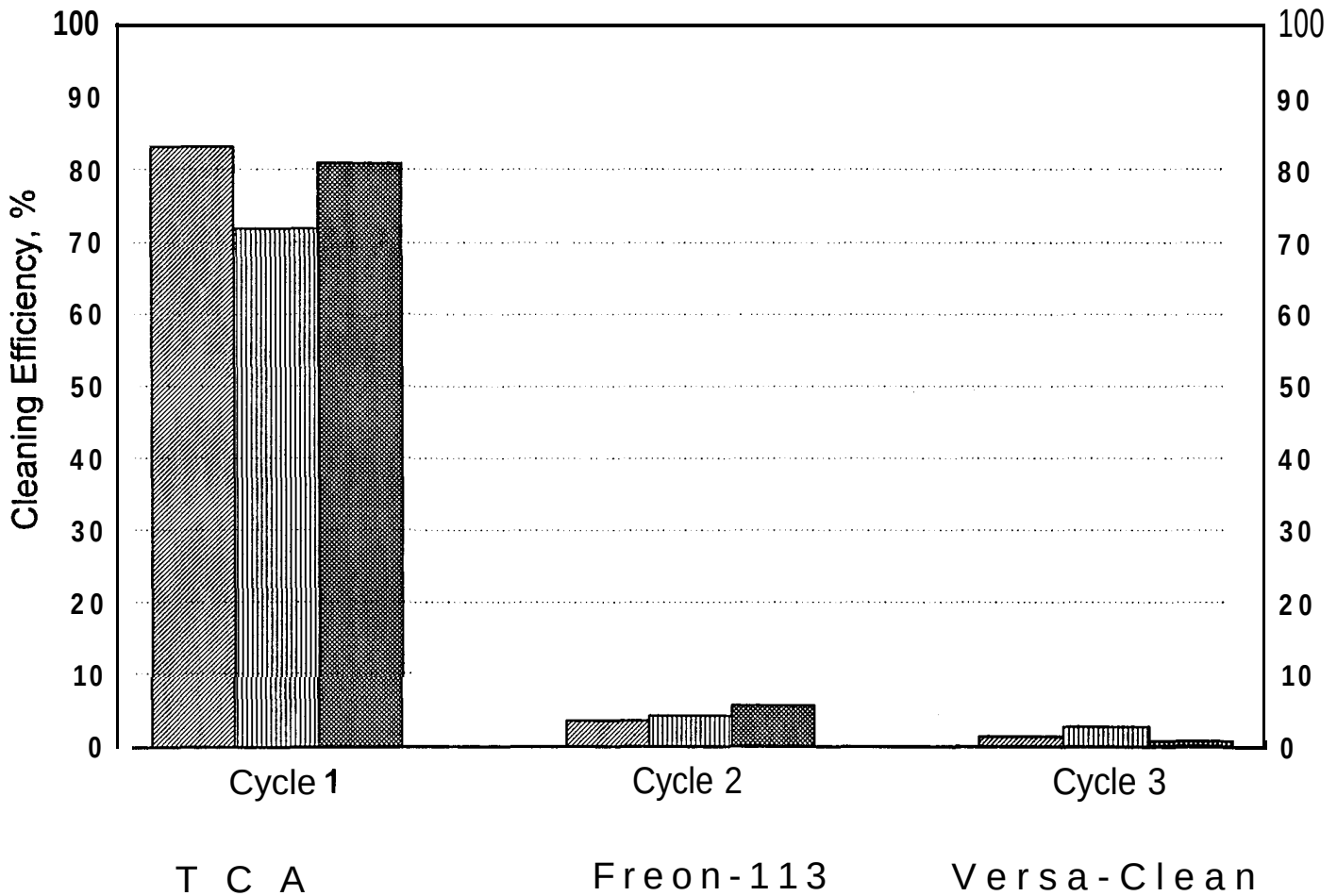

Figure 14. Removal of silica particulate by three different cleaning agents for three consecutive cleaning cycles (Note: Cycles 2 and 3 for Versa-Clean were with D. I. Water and TCA, respectively.)

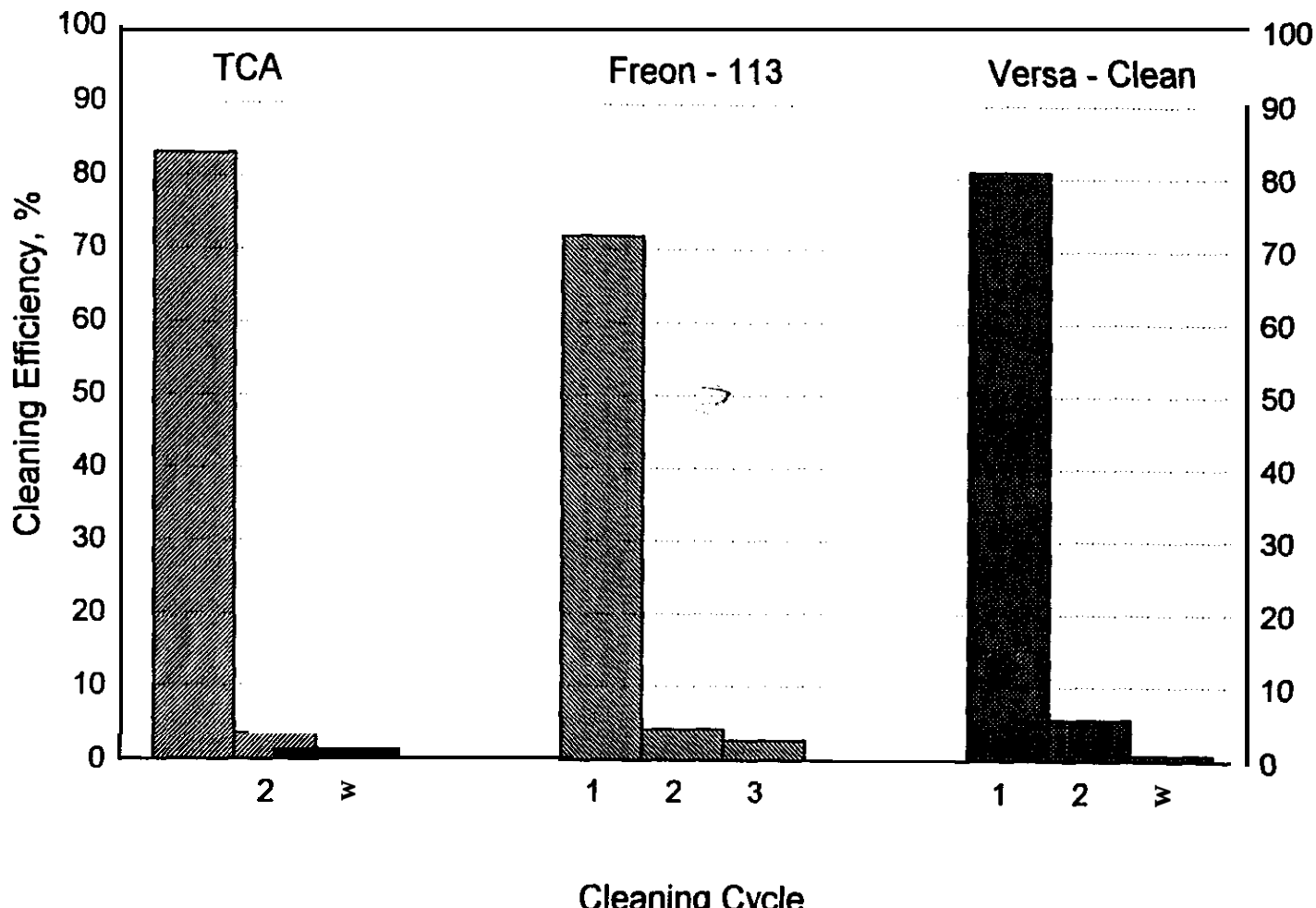

Figure 15. em a function of cleaning cycle for three cleaning agents
(Note: Cycles 2 and 3 for Versa-Clean were with D. I. Water and TCA, respectively.)

Additional statistical analysis results comparing pairs of cleaning agents are given in Table 14. As shown, for cleaning efficiency in the first cycle, TCA is comparable to Freon 113, and both are better than Versa-Clean for dimethyl phthalate and octadecanoic acid removal; all cleaning agents are equally effective in removing phenanthrene and silica. On extending the analysis to three cycles, which was applicable to TCA and Freon 113 only, TCA was better than Freon 113 for removal of dimethyl phthalate and phenanthrene; both TCA and Freon were similar for removal of octadecanoic acid and silica.

Table 14. Statistical Analysis of Differences in Percent Cleaning Among Various Cleaning Agents for the Four Contaminants (95 percent confidence level)

Contaminant	Cycle 1 Only	Cumulative for 3 Cycles[a]
Dimethyl phthalate	TCA = Freon > Versa-Clean	TCA > Freon
Phenanthrene	TCA = Freon = Versa-Clean	TCA > Freon
Octadecanoic acid	TCA = Freon > Versa-Clean	TCA = Freon
Silica	TCA = Freon = Versa-Clean	TCA = Freon

(a) Only one cleaning cycle was used with Versa-Clean, the second and third cycles being with D .1. water and TCA, respectively.

As discussed above, TCA was better than Versa-Clean for removal of dimethyl phthalate, an intermediate polarity organic compound. This was further verified when Cycle 3 for Versa-Clean, which is equivalent to Cycle 2 in the 3-cycle series with TCA, removed 2·4 times more dimethyl phthalate. An examination of Figure 8 shows that the amount of this contaminant remaining after the first cycle with Versa-Clean is roughly 2·4 times that remaining after the first cycle with TCA. This validates the utility of the indirect method of analysis developed in the previous phase for situations where the cleaning performance of a system cannot be directly quantified due to difficulty in collecting the cleaning extract or carrying out chemical analysis.

Octadecanoic Acid Reactivity in Hot 2% Versa-Clean Cleaning Agent. A test was performed to determine whether the octadecanoic acid contaminant compound reacts with the parts being cleaned in hot 2% Versa-Clean cleaning agent. This test was performed because the recovery of octadecanoic acid using the aqueous detergent was much lower than the recovery observed with TCA and Freon-113. The polar aqueous detergent was expected to provide superior removal of the polar fatty acid compared to the nonpolar organic cleaners.

A 2 ml aliquot of organic contaminant solution was air dried in a size 000 porcelain crucible. Because dimethyl phthalate was not of interest for this test, the cold trap and Teflon bag were not used during drying of the solvent. After the contaminant solution had dried completely, the crucible was placed into 200 ml of 2 % Versa-Clean detergent in a 250 ml beaker. The detergent was

preheated to 150°F to approximate the cleaning temperature used at AGMC (145" F). The detergent and crucible were sonicated for 5 minutes in a laboratory ultrasonic cleaning bath. During sonication the detergent temperature decreased to 138 "F. After cleaning, the beaker was allowed to cool for 15 minutes prior to addition of the calibrant solution. The hypodermic needle was placed below the liquid surface during addition of the calibrant solution to reduce evaporative losses of the calibrant compounds. The CPEP procedure was used to prepare the sample for GC/MS analysis.

Measured recovery of the octadecanoic acid was 75%. The recovery of the phenanthrene was 91%. Phenanthrene recovery was similar to the recovery of this compound observed in the cleaning tests performed at AGMC. Octadecanoic acid recovery was approximately 2.5 times greater than was observed in the AGMC tests. This indicates that a fairly large amount of the contaminant was not extractable with Versa-Clean. It is suspected that at the high temperature used with Versa-Clean, there is a significant reaction between fatty acid (background and contaminant) impurities and the metal parts of test devices. Since fatty acids are quite likely to be a contaminant on most parts, a lower temperature for Versa-Clean (or any aqueous cleaner) application may be worth considering. This reaction, however, has no obviously negative implication on CPEP.

5.0 CONCLUSIONS

The results of this study have led to the following conclusions:

(1) The CPEP provides for a valid method for quantifying the efficiency of organic and aqueous cleaning agents for removal of organic as well as inorganic contaminants.

(2) At a 95 percent confidence level, there is a statistically significant difference among TCA, Freon 113, and Versa-Clean detergent cleaning agents as far as removal of organic impurities is concerned, but not for removal of inorganic particulate matter.

(3) The organic contaminant removal by detergent solutions can be determined by a direct GC/MS analysis method, developed in this project.

6.0 RECOMMENDATION

To further increase the value of CPEP for AGMC and other users, the use of di-n-butyl phthalate is recommended (see Appendix C) as a substitute for dimethyl phthalate, especially for examining cleanability of parts that cannot be sealed during contaminant doping.

7.0 DEFINITION OF TERMS

Calibrant	The solution or suspension which contains the calibration isotopes in known concentration.
Contaminant, native	Naturally occurring contaminant material composed of atoms or molecules in the normal abundances.
Contaminant, synthetic	The isotonically altered material placed onto the test devices prior to cleaning. The concentrations of these compounds in the cleaning residues are used to determine cleaning efficiencies.
Doping	Application of a known quantity of synthetic contaminant to the test devices prior to cleaning tests.
Gas Chromatography/ Mass Spectrometer (GC/MS)	A chemical analysis instrument that uses a gas chromatography to separate mixtures of volatile organic

	compounds and a mass spectrometer which identifies the separated compounds.
Glow Discharge Mass Spectrometry (GDMS)	A chemical analysis instrument that uses a glow discharge to ionize atoms at the surface of a nonvolatile sample. GDMS samples a larger surface area than SSMS and is less sensitive to variations in sample electrode composition.
Gravimetric factor	The ratio of the molecular weights of a measured chemical species and a sought species. Gravimetric factors are frequently used to determine the weight of a metal present in an oxide sample.
Kuderna-Danish (K-D) Concentration	A method which concentrates solutions by evaporating the solvent at a temperature below its boiling point. A condenser is used to trap the solute compounds while allowing the solvent to escape slowly.
Overdetermined equation system	A system of linear equations which contains more equations than unknown quantities. In general, such systems of equations have no exact solution; however, various approximate solutions can be found. The approximation which minimizes the sum of the squares of the errors between the given equations and the approximation is called the least squares solution. Program MATRIX finds a least squares solution.
Secondary Ion Mass Spectrometry (SIMS)	A chemical analysis instrument that uses a high-energy ion beam to ionize selected portions of a sample. SIMS can provide isotopic analyses of individual particles, but is not well suited to analysis of bulk samples.
Spark-source mass spectrograph (SSMS)	A chemical analysis instrument that uses a high voltage, radio frequency spark to ionize a nonvolatile sample. The mass spectrum is recorded on an ion sensitive photographic plate.

APPENDIX A

A MODIFIED STABLE ISOTOPE CLEANING PERFORMANCE EVALUATION PROCEDURE (CPEP)

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A Modified Stable Isotope Cleaning Performance Evaluation Procedure (CPEP)

1.0 Scope and General Description

This document* describes a procedure which employs stable isotopes to quantify the effectiveness of a cleaning procedure. The procedure is applied in two phases. In Phase I, the contaminants which are present in the cleaning system are identified and simulants selected. The second phase uses the simulants chosen in Phase I to compare cleaning procedures.

At the beginning of Phase I, the current cleaning process (CCP) is examined to identify possible contaminants. Samples of cleaning residue at several points in the CCP are analyzed for inorganic particulate and organic compounds. The analytical results are used to select synthetic contaminants for Phase II. For the particulate contaminants, the particle size and chemical form are also considered, because particle removal is strongly dependent on the size of the particles and some particle adherence mechanisms are dependent upon the chemical form of the particles.

A synthetic contaminant spike solution is prepared and a known amount of synthetic contaminant is deposited on the test components. The test components are cleaned using the cleaning procedures being evaluated and the cleaning residues are saved. A calibrant solution containing a different isotope than the synthetic contaminant is added to the cleaning residue in a known amount. The cleaning residue containing both isotope forms is analyzed by mass spectral methods to determine the isotopic ratios of the contaminants. The isotope ratios and the amount of calibrant material added are used to determine the quantity of synthetic contaminant removed during the cleaning procedure. The effectiveness of a cleaning procedure is calculated based on the amount of contaminants it removes.

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* This document is Appendix A of the Contract Summary Report, "Methods for Improvement of the Stable Isotope Cleaning Performance Evaluation Procedure".

2.0 Advantages and Disadvantages

2.1 Advantages

This method uses isotonically altered materials assimilated contaminants. Since the isotopes used are stable, the safety precautions required when using radioisotopes are not needed. The stable isotopes uniquely identify the simulated contaminants, even in the presence of significant amounts of native contaminants. The gas chromatography/mass spectroscopy (GC/MS) technique is a commonly available and sensitive method for analysis of trace quantities of organic compounds.

Two isotonically labeled forms of each simulant are employed. One of the isotopic forms is used as the simulated contaminant, applied in a known amount to the test parts before cleaning. The remaining isotopic form is added to the cleaning residue after cleaning. The mass spectral analysis of the cleaning residue is used to determine the quantity of simulated contaminant removed during cleaning.

Phase I need be performed only once for a type of part to be cleaned; however, the Phase II cleaning performance evaluation procedure should be carried every time a cleaning step or procedure, e.g. method for cleaning or cleaning agent, is changed.

Procedures which permit direct analysis of aqueous detergent residues have been developed. These procedures are described in Attachment B.

2.2 Disadvantages

The isotopic materials are expensive and suppliers are limited. To use the method to best effect, two isotonically labeled samples of each simulant are required; this further increases the costs. Mass spectral techniques must be used for analysis, because other chemical analysis techniques cannot distinguish the isotopes.

The procedure is very complex and requires well-trained staff. The selection of synthetic contaminant compounds requires advanced knowledge of chemistry to ensure selection of representative contaminants.

3.0 Limitations

3.1 Inorganic Simulants

For best results, the elements chosen as inorganic simulants should have three or more stable isotopes. Elements with two isotopes can be used by performing a mass spectral analysis before and after addition of the isotonically labeled calibrant but many benefits of the isotope method are lost. Mononuclidic elements, such as, aluminum, beryllium, phosphorous and sodium, cannot be used as simulants. If the simulant element is not available from stock in the desired chemical form or particle size distribution, additional expense will be incurred to alter the chemical form or the particle size distribution.

3.2 Organic Simulants

Each organic simulant must be available in two labeled forms, Since most organic compounds are deuterium labeled and the deuterium atoms can be removed from the molecule by chemical reactions, the organic simulants must be stable under the cleaning conditions or the decomposition products must also be determined.

4.0 Apparatus

Bottles, glass, 2 0z, 4 0z, 16 0z	Beakers, 250 ml, 600 ml, 2000 ml
Balance, analytical	Brush, beaker
Coater, vacuum	Coulter counter
Electron probe microanalyzer	Filter, Anopore, 0.2 µm pore, 25 mm and 37 mm
Filter, cellulose acetate, 0.2 µm pore, 37 mm	Flask, Dewer (3” dia x 6“ high)
Flask, filter, 25 mm, 37 mm	Flask, round bottom
Flask, volumetric, 100 ml	Forceps
Gas chromatography	Image analyzer
Mass spectrometer, inorganic	Mass spectrometer, organic
Pipettes, Eppendorf	Foil, aluminum, heavy duty
Polypropylene nut, 1/4”, 3/8”	Polypropylene union 1/4” to 3/8”
Planchette, carbon, 25 mm	Porcelain crucible
Furnace, muffle, small 600 C	Furnace, muffle, large, 450 C
Nitrogen evaporator	Pump, vacuum, with flow valve
Ring stand with clamp	Flask, Kuderna-Danish
Recliner, Kuderna-Danish	Funnel, separator, 1000 ml
Filter, quartz, 104 mm	Funnel, glass
Spatula	Syringe, hypodermic, 250 µl (2)
Syringe, hypodermic, 1000 µI (3)	Trap, cold, glass
Tape, Teflon	Tubing, 1/4” Teflon
Timer	Tongs
Thermometer, dial	Ultrasonic bath
Snyder distilling column	Vials, glass, 10 dram, 40 dram
Vials, polystyrene, 2 ml	Cap liners, Teflon
Polypropylene Union 1/4” to 1/4”	Scissors

5.0 Reagents

Acetone	Alconox detergent
Dichloromethane, distilled in glass	Dry ice
Ethanol	Hydrochloric acid, 3N
Methanol	Nitric acid
Sodium chloride (muffled 450 C)	Sodium sulfate (muffled 450 C)
Graphite powder (ultracarbon UCP-1)	Water, tap
Water, distilled	

6.0 Phase I Procedure-- Identify Contaminants and Select Isotopes

The apparatus needed for Phase I is listed in Table 1.

Table 1. Apparatus for Phase I Procedures

Brush, beaker	Coater, vacuum
Electron probe microanalyzer	Filter, Anopore, 0.2 μm pore, 25 mm, 37 mm
Flask, filter, 25 mm, 37 mm	Forceps
Flask, Kudema-Danish	Gas chrornatograph
Image analyzer	Furnace, muffle, large, 450 C
Receiver, Kuderna-Danish	Vials, glass, 10 dram, 40 dram
Planchette, carbon, 25 mm	Beakers, 250 ml, 2000 ml
Balance, analytical	Bottles, glass, 4 oz
Snyder distilling column	Ultrasonic bath
Vials, glass, 10 dram, 40 dram	Cap liners, Teflon
Coulter counter	Foil, aluminum, heavy duty
Flask, round bottom	Flask, volumetric, 100 ml
Mass spectrometer, organic	

6.1 Glassware **Cleaning Procedure**

6.1.1 Rinse with 10 percent nitric acid in distilled water.

6.1.2 Rinse with acetone.

6.1.3 Wash with Alconox (1 g/1) in hot tap water.

6.1.4 Rinse with distilled water.

6.1.5 Sonicate 5 minutes in methanol.

6.1.6 Rinse with prefiltered dichloromethane.

6.1.7 Muffle at 450 C for at least 2 hours unless the glassware is volumetric. Dry volumetric glassware at 180 F for at least 1 hour.

6.2 **Examine Current Cleaning Procedure (CCP)**

6.2. Obtain samples of used working fluids from incoming components.

6.2.2 Obtain samples of flushing liquids from cleaned and reassembled components.

6.2.3 Obtain samples of virgin cleaning solutions.

6.2.4 Obtain additional samples from the CCP as appropriate. Possible sample sites include supply taps for cleaning agents, supercleaning sonication tanks and virgin fill fluids.

6.3 **Inorganic Particulate Analysis**

6.3.1 Filter appropriate volume of samples from Section 6.2 through 25 mm, 0.2 µm pore size Anopore filter (1 ml-contaminated samples, 10 ml-clean samples).

6.3.2 Rinse filter with 5 ml prefiltered dichloromethane.

6.3.3 Attach filter to a carbon planchette, vapor deposit a conductive carbon film on the filter surface and load in the electron probe microanalyzer (EPMA).

6.3.4 Acquire multielement X-ray maps for Na, Mg, Si, P, S, Cl, K, Ca, Cr, Fe, Cu, Zn, Al, Sn, C, and O at 400 X with the EPMA (4 fields).

6.3.5 Acquire secondary electron images at 400 X with the EPMA (4 fields).

6.3.6 Identify the most common particle compositions based on the X-ray map results.

6.3.7 Use the image analyzer to determine the particle size distribution. Other methods of particle size analysis such as a coulter counter device can also be used.

6.4 Organic Compound Identification

6.4.1 Dilute samples containing more than 5 percent high boiling point compounds (i.e., above 60 C), such as fill fluids, by 100 times using dichloromethane. Low concentration samples can be run neat.

6.4.2 Inject a 1 µl aliquot of the sample from 6.4.1 into the gas chromatography (GC). The GC operating conditions are given in Table 2.

6.4.3 Perform the GC/MS analysis. MS operating conditions are given in Table 3.

6.4.4 Identify the major types of organic compounds present in the samples.

Table 2. Gas Chromatography Operating Conditions

Column Type	DB-5 fused silica or equivalent
Column Length	30 m
Column Diameter	0.25 mm I.D.
Carrier Gas	Helium
Oven Program	40 C one rnin programmed to 290 C at eight C per min

Table 3. Organic Mass Spectrometer Operating Conditions

Mode	GC/MS
Ionization	70 ev Electron impact
Scan Mode	Full scan
Scan Range	m/z 30 to m/z 650
Scan Start	After elution of solvent peak

6.5 Selection of Simulated Contaminants

6.5.1 Selection of inorganic simulated contaminants.

6.5.1.1 Examine the list of the most common inorganic particulate compositions for the five major elements.

6.5.1.2 Choose the most common element which has three or more stable isotopes to represent the bulk of the particulate.

6.5.1.3 Choose any element which is susceptible to special particle adherence mechanisms (i. e., iron metal--magnetism) of interest, and has three or more stable isotopes.

6.5.1.4 Choose the next most common element which has three or more stable isotopes.

6.5.1.5 Determine the cost and availability of isotopes of the selected elements. The preferred isotopes are those with natural abundances between 0.5 and 10 percent enriched to more than 90 percent. Isotopes with natural abundances above 10 percent yield poorer sensitivity while isotopes below 0.5 percent abundance are very expensive when enriched to high concentrations. Do not use the major isotope. Two enriched isotopes are needed for each element. The isotope with the lowest natural abundance will be used as the simulated contaminant. The second isotope, the calibrant, will be used in the analytical procedure to correct for losses during analysis.

6.5.2 Selection of organic simulated contaminants

6.5.2.1 Examine the list of the most common organic compounds for the different classes of organic compounds (i.e., acids, bases, esters, aliphatic and aromatic hydrocarbons, alcohols, aldehydes, etc.).

6.5.2.2 Select candidate compounds with a range of polarity, since a molecule's polarity has a strong influence on its volubility. A close match between the polarity of a solute and solvent results in good volubility, while a polarity mismatch produces poor volubility.

6.5.2.3 The selected compounds should have low volatility so that they will remain on the parts until the cleaning is performed. Significant fractions of volatile compounds may be lost by evaporation.

6.5.2.4 Determine the cost and availability of the candidate contaminants. Two isotopic forms of each compound are needed, one as the simulated

contaminant and the second as the analytical calibrant. The most commonly available compounds are deuterium labeled; however, ^{13}C labeled compounds can also be used if two deuterium labeled compounds are not available.

6.5.2.5 Since the calibration material is placed in each sample, while the contaminant is placed only on the test part, isotope material costs are minimized by using the less costly isotope material of each pair as the calibrant.

6.6 Preparation of Contaminant and Calibrant

6.6.1 Clean all containers as in 6.1.

6.6.2 Preparation of inorganic suspensions.

6.6.2.1 Both the contaminant and calibrant suspension are prepared in the same manner. The contaminant suspension is prepared using the isotope material chosen to be the contaminant in 6.5.1.5. The calibrant suspension is prepared using the isotope material chosen to be the calibrant in 6.5.1.5.

6.6.2.2 Weigh a known quantity (approximately 2 mg) of each (if more than one) inorganic isotopic material into precleaned labeled 4 oz glass bottles. Add 100 ml of filtered ethanol. Sonicate to disperse the particles. These are stock suspensions.

6.6.2.3 Measure the particle size distribution of the particulate suspension using a Coulter counter. If the average diameter of the contaminant suspension does not match the size distribution determined in 6.3.7 to within a factor of 5, grind or sieve the isotope material to improve the size distribution match. It is especially important to eliminate/ minimize the number of oversized, e.g., about 5 micron-size, particles to assure there is no settling.

6.6.2.4 Prepare a working contaminant suspension using an equal volume of each contaminant suspension prepared in 6.6.2.2. Sonicate the stock suspensions for at least 5 minutes prior to transferring them.

6.6.2.5 Prepare a working calibrant suspension using an equal volume of each calibrant suspension prepared in 6.6.2.2. Sonicate the stock suspensions for at least 5 minutes prior to transferring them.

Note: *Swirl the suspensions immediately prior to transfer. Sonicate the suspensions continuously during the transfer operation.*

6.6.3 Preparation of organic solutions.

6.6.3.1 If direct analysis of aqueous detergent cleaning residues are required, prepare a set of high concentration contaminant and calibrant solutions as described in Attachment B, Section 5.1 (B.5. 1) in addition to the solutions described below.

6.6.3.2 Both the contaminant and calibrant solutions are prepared in the same manner. The contaminant solution is prepared using the most highly deuterated material for each compound selected in 6.5.2.4. The calibrant solution is prepared from the other material.

6.6.3.3 Prepare separate stock solutions of each compound with a concentration of 1 mg/ml in filtered dichloromethane.

6.6.3.4 Determine the relative sensitivities of each organic compound by analysis of 1 µl of each stock solution from 6.6.3.2 in the GC/MS instrument.

6.6.3.5 Prepare 10 ml of a working contaminant solution containing 500 µl of the most easily detected compound stock solution from 6.6.3.2 and proportionately higher concentrations of the remaining contaminant compound stock solutions in filtered dichloromethane.

6.6.3.6 Wrap the labeled container in aluminum foil to protect the compounds from light and store at -20 C or less.

6.6.3.7 Prepare 10 ml of a working calibrant solution containing concentrations of each compound equal to those of the contaminants in 6.6.3.4. Use filtered dichloromethane as the solvent.

6.6.3.8 Wrap the labeled container in aluminum foil to protect the compounds from light and store at -20 C or less.

Note: *Prior to use of the organic solutions, remove them from the freezer and allow them to return to room temperature. Slide the container fiom the aluminum foil wrapper and examine the solution to ensure complete dissolution of the compounds.*

6.7 Organic Compound Stability Test

6.7.1 The stable isotope method assumes that the isotopes will not be altered during the cleaning test. While the inorganic contaminant isotopes cannot be altered by chemical processes, the organic compounds are labeled by substitution of deuterium atoms for hydrogen atoms in the molecules. The stability of the organic compounds under the cleaning conditions must be determined.

6.7.2 Test the stability of the organic compounds by sonication at the standard cleaning power density for the standard cleaning cycle time, at twice the standard power density for the standard time and at twice the standard power density for twice the standard time. If the ultrasonic cleaner does not provide a power adjustment, perform the stability test for the standard sonication time and twice the standard sonication time.

6.7.3 Place 200 μl of the working organic contaminant solution prepared in 6.6.3.4 and 100 ml Freon 113, or a suitable substitute, such as a perfluorocarbon, into each of 8 cleaned 250 ml beakers. Cover the beakers with aluminum foil covers to minimize evaporation losses.

6.7.4 Select the contents of two beakers as control samples. Sonicate the contents of the 6 remaining beakers in duplicate using the conditions of 6.7.2.

6.7.5 Add 200 μl of the working organic calibrant solutions prepared in 6.6.3.6 to the contents of each beaker.

6.7.6 Wash the inside surface of the aluminum foil covers with clean Freon 113. Allow the wash to fall into the beaker.

6.7.7 Transfer the Freon 113 to cleaned, labeled bottles.

6.7.8 Analyze the solutions to determine whether the organic compounds are altered by sonic energy.

7.0 Phase II Procedures -- Cleaning Performance Evaluation

The apparatus needed for Phase II is listed in Table 4.

7.1 Test Matrix

Prepare a test matrix which includes the parts to be cleaned, the cleaning steps and cleaning agents to be evaluated and the number of cleaning cycles required. An example test matrix is shown in Table 5.

7.1.1 A modified method for direct determination of organic contaminants in aqueous detergents is described in Attachment B (B.5.0). 'The two extra steps--rinsing with deionized water and cleaning with an organic cleaning agent for which the cleaning performance versus the extent of cleaning has been established--have been retained to allow a comparison between the direct and indirect analysis methods. The evaluation of cleaning of inorganic contaminants is possible if the detergent does not introduce analytical interferences.

7.1.2 The simplest test plan would be set up to compare the cleaning performance of two cleaning agents - the currently used or baseline cleaning agent and a candidate replacement cleaning agent for one type of test device. A minimum of three test devices should be cleaned in each cleaning agent to permit statistical estimates of the cleaning performance to be made. For cleaning agents in which the contaminant compounds can be determined, three cleaning cycles should be performed on each test part. This will permit a determination of the length of cleaning time needed to achieve a desired level of cleanliness.

7.1.3 Additional candidate cleaning agents can be added to the test matrix by including parts which will be cleaned by that cleaning agent.

7.1.4 If a cleaning agent residue cannot be directly analyzed, an alternate method may be employed. The alternate cleaning method uses three cleaning steps. In the first cleaning step, the test parts are cleaned one time using the candidate cleaning process. The candidate cleaning agent is then rinsed off. For aqueous detergents, rinse with distilled water at the same temperature as the cleaning agent. After rinsing, the test parts are cleaned one time in a baseline cleaning agent for which the cleaning performance, using sonication, as a function of cleaning cycle is known. The amount of contaminant thus removed by the baseline cleaning agent can provide a quantitative assessment of the cleaning effectiveness of the candidate cleaning agent. For example, let us assume that the incremental and cumulative percent contaminant removals are as follows:

Table 4. Apparatus for Phase II Procedures

Beakers, 600 ml, 2000 ml	Bottles, glass, 2 oz, 16 oz.
Brush, beaker	Filter, cellulose acetate, 0.2 μm pore, 37 mm
Flask, Dewer (3" dia x 6" high)	Flask, filter, 37 mm
Flask, Kudema-Danish	Flask, round bottom
Filter, quartz, 104 mm	Funnel, glass
Funnel, separator, 1000 ml	Forceps
Gas chromatography	Mass spectrometer, inorganic
Mass spectrometer, organic	Foil. aluminum
Furnace, muffle, small, 600 C	Furnace, muffle, large, 450 C
Porcelain crucible	Nitrogen evaporator
Pump, vacuum, with flow valve	Ring stand with clamp
Receiver, Kuderna-Danish	Snyder distilling column
Spatula	Syringe, hypodermic, 250 µl (2)
Syringe, hypodermic, 1000 µl (3)	Trap, cold, glass
Tape, Teflon	Tubing, 1/8” Teflon
Tubing, 1/4” Teflon thick wall	Tubing, 1/4” Teflon
Polypropylene nut, 1/4”, 3/8”	Polypropylene union, 1/4” to 3/8”
Timer	Tongs
Thermometer	Ultrasonic bath
Cap liners, Teflon	Vials, glass, 10 dram
Vials, polypropylene, 2 ml	Polypropylene union 1/4” to 1/4”
Scissors	

Table 5. Sample Test Matrix for Cleaning Performance Evaluation

Test No.	Part[a]	Cleaning Agent[b]	No. of Cleaning Cycles[c]	Comments
1,2,3	A1,A2,A3	T	3	Tests 2 and 3 are repeats of Test 1
4,5,6	A4,A5,A6	C	3	Tests 5 and 6 are repeats of Test 4
7,8,9	A7,A8,A9	W	3	Tests 8 and 9 are repeats of Test 7
10,11,12	B1,B2,B3	T	3	Tests 10 and 11 are repeats of Test 9

(a) A: Accelerometer (A-200D); B: Gyroscope (G200/280)

(b) T: 1,1, l-trichloroethane; C: Freon-113; W: aqueous detergent

(c) Each cycle with an equal volume of cleaning agent, with collection and analysis of the cleaning residue from each cycle.

Cycle	TCA Incremental Cleaning, %	TCA Cumulative Cleaning, %
1	60	60
2	20	80
3	10	90
4	5	95
5	3	98

Now, let us assume that after one candidate cleaning agent cycle followed by a quick rinse, a part is recleaned in TCA and the incremental cleaning efficiency is 5 percent. This will mean that one cleaning cycle in the candidate cleaning agent is as effective as three cleaning cycles with TCA.

7.1.5 Additional cleaning steps can be added to the test matrix in the same manner as cleaning agents in 7.1.3. If the cleaning residue cannot be easily collected, an alternate method, similar to 7.1.4 can be employed. In the alternate method, the test part is cleaned through one cycle using the candidate cleaning method, such as liquid spray. The part is then cleaned through one cycle in an ultrasonic bath using a baseline cleaning agent. A calculation similar to the example in 7.1.4 can provide a quantitative assessment of the cleaning effectiveness of the candidate cleaning method.

7.2 Cleaning of Apparatus

7.2.1 Clean all sample containers as described in 6.1.

7.2.2 Form beaker covers from heavy duty aluminum foil. The covers can be formed by wrapping the foil on the outside of a suitably sized round bottom flask, placing the foil and flask over the mouth of the beaker, trimming the foil 1/2 inch to 1 inch beyond the lip of the beaker, then bending the foil down the sides of the beaker to hold it to the beaker.

7.2.3 Wash the foil covers in filtered dichloromethane and muffle as for the glassware.

7.2.4 Wash the inside of the 1/8 inch and 1/4 inch teflon tubing three times with filtered ethanol, then three times with filtered dichloromethane. Air dry the tubes.

7.2.5 Wash the polypropylene fittings using 6.1.3 through 6.1.6. Air dry.

7.2.6 Clean the hypodermic syringes by filling them 5 times with filtered ethanol. After each filling, discard the ethanol. Operate the syringe several times in air. In the same manner, fill the syringe 5 times with filtered dichloromethane. After each filling, discard the dichloromethane.

7.2.7 The filtered ethanol and dichloromethane are prepared by filtering each reagent through a 0.2 µm pore size Anopore filter. Store the reagents in bottles cleaned as in 6.1.

7.3 **Test Part Contaminant Doping**

7.3.1 The contaminant doping procedure will vary depending on the type of test device chosen for the cleaning evaluation. This procedure is designed for A-200D accelerometers; however, a similar procedure would be applicable to other devices where the contaminants can be deposited in a sealed enclosure such as a gyro.

A modified contaminant doping procedure, suitable for small open parts is described in B .4.0. The modified procedure uses a precleaned petri dish to hold the test part.

7.3.2 Prior to contaminant doping, test the seal integrity of a sample test device by injecting several milliliters of ethanol into it through one of the fill tubes. Change the orientation of the part so that the seal regions are below the liquid level inside the part. Examine the seals for leakage. If leakage occurs, steps must be taken to eliminate or minimize it.

7.3.3 Preparation of test parts/devices,

7.3.3.1 Attach two 1/16” copper fill tubes to each test device.

7.3.3.2 Add additional parts to the interior of the device so that it can be sealed.

7.3.3.3 Thoroughly clean the test devices using the current cleaning procedure.

7.3.3.4 Dry the parts after cleaning.

7.3.3.5 Reassemble the cases of the test parts. The case halves should fit well. If a loose fit occurs and several parts are being doped, try to rearrange the halves to obtain good fits for all of the devices.

7.3.4 Preparation of the cold bath.

A dry ice bath is recommended over a liquid nitrogen bath because the liquid nitrogen bath will freeze the dichloromethane and condense atmospheric oxygen in the cold trap. A dry ice + acetone bath produces a temperature of -78 C which is sufficiently low to effective y condense dichloromethane without freezing it.

Caution: Acetone produces volatile, flammable vapors. The cold bath must be set up in a fume hood away from flames and sparks.

7.3.4.1 Fill a small (3 inch diameter x 6 inch tall) Dewar flask half full with dry ice pellets. Slowly and carefully add acetone to within 1 inch of the top of the flask.

7.3.4.2 The cold bath is now ready for use. During the doping, monitor the amount of dry ice remaining in the Dewar flask. Add dry ice pellets as needed.

7.3.4.3 If all of the dry ice sublimes, the temperature of the bath will begin to increase. Add dry ice one pellet at a time until the violent bubbling stops, then add excess pellets. If dry ice is added to an over temperature bath too quickly, the acetone will boil out of the Dewar flask.

7.3.5 Wrap seal regions of the parts with at least three layers of Teflon tape. The tape reduces the probability and amount of leakage at the seals and serves to collect the leaked contaminants. Record a characteristic number on the device for identification.

7.3.6 Attach a length of 1/8" Teflon tubing to one of the fill tubes. Attach the free end of the Teflon tubing, cleaned as in 7.2.4, to a length of 1/4" Teflon tubing using a short (-2 inch) piece of 1/4" thick wall Teflon tubing and a 1/4" polypropylene union and 1/4" polypropylene nuts as an adapter. Attach the free end of the Teflon tubing to a small metal bellows air pump (or equivalent). A valve can be fitted on the pump inlet to permit control of the air flow rate. See Figure 1 for a schematic diagram of the interconnections.

7.3.7 Attach a second length of 1/4" Teflon tubing to the side arm of the cold trap using a 1/4" to 3/8" polypropylene union and 1/4" and 3/8" polypropylene nuts. Attach a length (-2 feet) of 1/4" Teflon tubing to the inlet of the cold trap using a 1/4" to 3/8" polypropylene union and 1/4" and 3/8" polypropylene nuts. Place a 1/4" nut and union on the free end of the 1/4" Teflon tube. See Figure 2 for a schematic diagram of the interconnections. Clamp the cold trap to a ring stand.

7.3.7.1 Remove the organic solutions prepared in 6.6.3.5 and 6.6.3.7 from the freezer and allow it to return to room temperature.

7.3.8 Inorganic contaminant doping.

7.3.8.1 Sonicate the inorganic contaminant suspension for 5 minutes to disperse the particles. The suspension must be sonicated during all transfer operations to insure adequate suspension. Swirl the stock suspension immediately prior to each transfer.

7.3.8.2 Start the vacuum pump and open the flow valve, if present.

7.3.8.3 Inject two 1.0 ml aliquots of the inorganic contaminant suspension through the fill tube using a 1 ml hypodermic syringe.

7.3.8.4 Rinse the fill tube by injecting two 1 ml aliquots of filtered (0.2 µm) ethanol into the device, using the same syringe as in 7.3.8.3.

7.3.8.5 Start a timer to measure the drying time.

Figure 1: Schematic Diagram of Test Device Inorganic Doping Interconnections

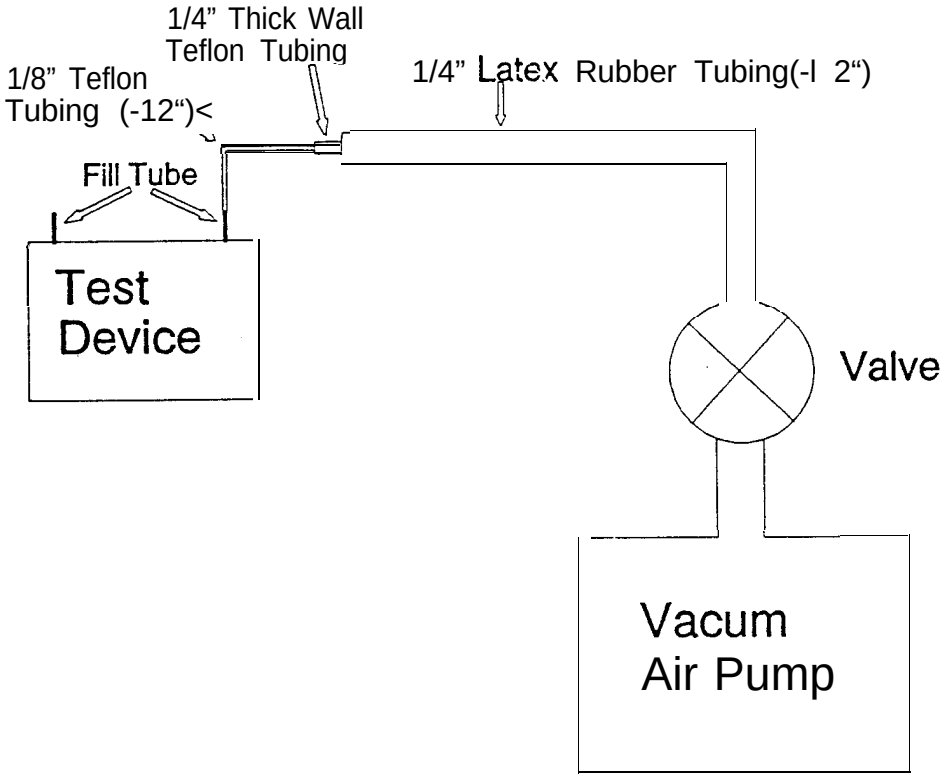
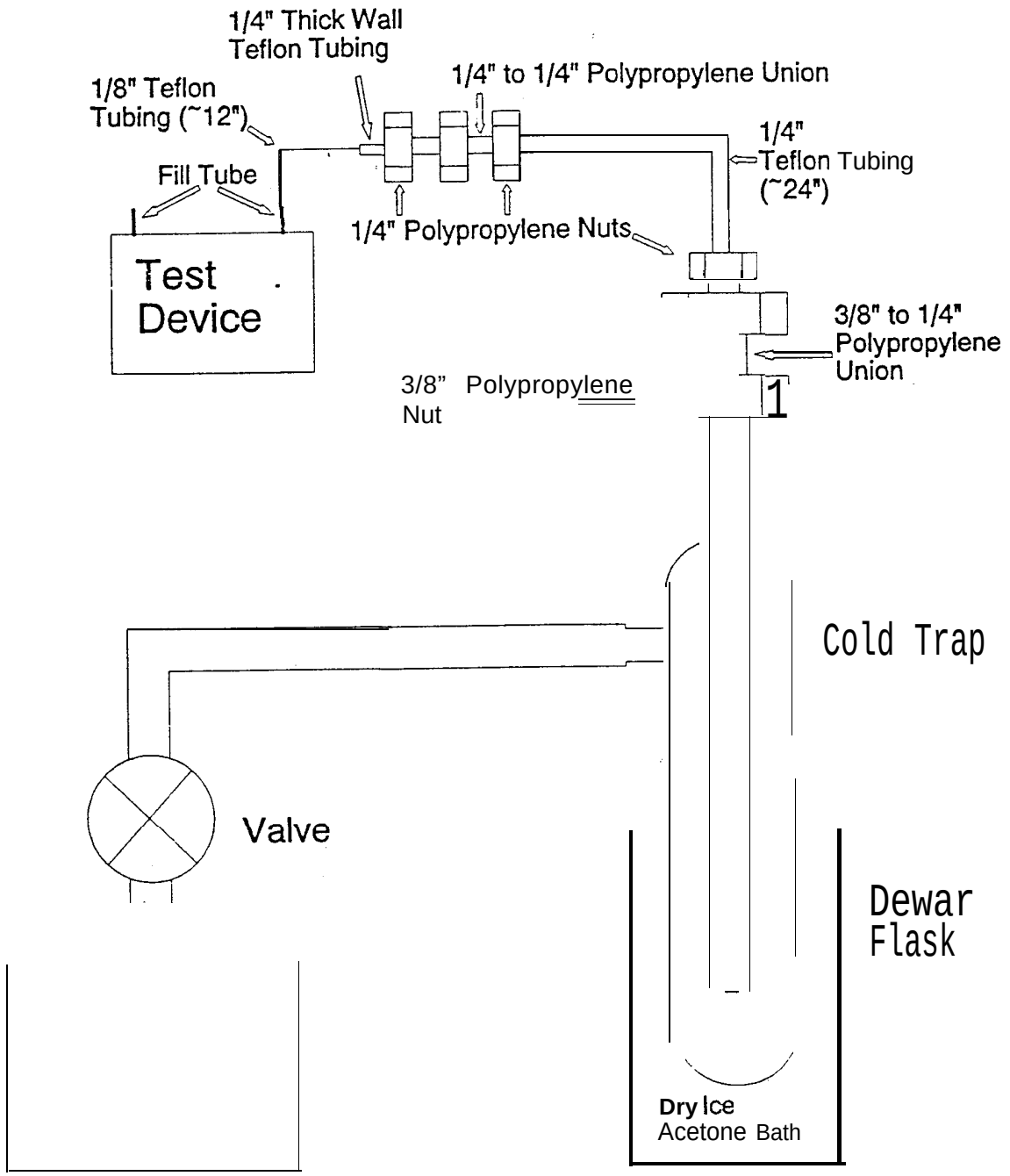


Figure 2: Schematic Diagram of Test Device Organic Doping Interconnections



7.3.8.6 Change the orientation of the part during drying so that the liquid pool inside can wet as much of the internal surfaces as possible. Insure that the liquid does not come close enough to the exit fill tube to be pumped out of the test device. Examine the Teflon tape for evidence of liquid leakage.

7.3.8.7 Hold the device in both hands during the drying step to aid evaporation.

7.3.8.8 The ethanol dries in approximately 15 minutes. Continue the air flow 5 additional minutes to provide a safety factor; no change of orientation of part during this, final drying step is necessary.

7.3.8.9 Stop the vacuum pump leaving the flow valve open, if present.

7.3.9 Check the dry ice-acetone bath for sufficient dry ice. Add dry ice as in 7.3.4.3, if required, and allow bubbling to subside.

7.3.10 Remove the latex tube between the 1/4” Teflon tube adapter and the vacuum pump. Attach the 1/4” Teflon tube adapter to the free end of the 1/4” Teflon tube on the inlet of the cold trap. using a polypropylene 1/4” to 1/4” union and 1/4” nut. Attach the free end of the latex tube on the cold trap to the inlet of the vacuum pump. See Figure 2 for a schematic diagram of the interconnections.

7.3.11 Slowly lower the cold trap into the cold bath.

7.3.12 Organic contaminant doping.

7.3.12.1 Examine the organic solutions for complete dissolution of the organic compounds.

7.3.12.2 Start the vacuum pump.

7.3.12.3 Inject 200 µl of the organic contaminant solution through the fill tube using a 250 µl hypodermic syringe.

7.3.12.4 Rinse the fill tube by injecting two 1 ml aliquots of filtered dichloromethane into the device using a 1 ml hypodermic syringe.

7.3.12.5 Start a timer to measure the drying time.

7.3.12.6 Change the orientation of the part during drying so that the liquid pool inside can wet as much of the internal surface as possible. Insure that the liquid is not pumped out of the test device. Examine the Teflon tape for evidence of liquid leakage.

7.3.12.7 Hold the device in both hands during the drying step to aid evaporation. The device will cool significantly during evaporation of the dichloromethane.

7.3.12.8 The dichloromethane dries in approximately 5 minutes. Continue the air flow 5 additional minutes to provide a safety factor; no change of orientation of part during this, final drying step is necessary.

7.3.12.9 Stop the vacuum pump.

7.3.13 Disconnect the test device from the 1/8" Teflon tube and set the device on a clean surface. Keep the part closed until ready to perform the cleaning.

7.3.14 Remove the cold trap from the cold bath. Check the dry ice level in the cold bath. If additional parts are to be doped, add dry ice as in 7.3.4.3, if required.

7.3.15 Disconnect the latex tube and 1/4" Teflon tube and polypropylene fittings from the cold trap.

7.3.16 Capture cold trap contents for analysis.

7.3.16.1 If liquid leakage was detected during the inorganic contaminant doping, sonicate the calibrant suspension for at least 5 minutes to disperse the particles, then inject 1 ml of the inorganic calibrant suspension into the top of the cold trap using a hypodermic syringe. Wash the syringe with 1 ml of filtered ethanol. Add the wash to the cold trap. Record the addition of the inorganic calibrant for the organic analyst. Inject 200 µl of the organic calibrant solution into the top of the cold trap. Mix the calibrant with the condensed dichloromethane. Wash the center tube with several milliliters of filtered dichloromethane.

7.3,16.2 Transfer the contents of the cold trap to a 2 oz precleaned glass bottle by pouring the contents out the side arm. Pour slowly so liquid does not escape through the top opening in the trap.

7.3.16.3 Wash the trap twice with several milliliter portions of filtered dichloromethane. Add the rinses to the trap's original contents. Label the bottle as the cold trap collection sample. Seal the bottle cap with Teflon tape. Prepare the cold trap sample for analysis as in 7.6.3.4.

7.3.17 Remove the Teflon tape from the test device using a clean forceps. Place the tape in a suitable, labeled container. The Teflon tape will be washed and combined with the cold trap sample as in 7.6.3.4.

7.3.18 The contaminant doping is complete.

7.4 Cleaning Tests

7.4.1 Prepare the cleaning device for operation. Bring the cleaning device to the desired operating temperature. Obtain racks to hold the cleaning containers, as needed.

7.4.2 Mark the cleaning containers with the test identifier and cycle number. Cleaning must be performed in an enclosed container so that all of the cleaning residue can be collected. An aluminum foil cover prepared as in 7.2.2 can be used to close the top of a beaker.

7.4.3 Fill the containers with the proper volume of cleaning agent.

7.4.4 Open the test device and place the test device into the container of cleaning agent using clean tongs. Position the part so that the cleaning agent has good access to the contaminated surfaces.

7.4.5 Place the containers into the cleaning device and perform the cleaning cycle for the desired time.

7.4.6 Label and fill the containers for the next cleaning cycle during the current cycle.

7.4.7 At the end of the cleaning cycle, remove the container from the cleaning device. Using the tongs, transfer the test device to the container as in 7.4.4 for the next cleaning cycle, if appropriate. Repeat steps 7.4.5 to 7.4.7 for each additional cleaning cycle.

7.5 Addition of Calibrant to the Cleaning Residue

7.5.1 The addition of a known quantity of calibrant compounds to the cleaning residue is the basis of the isotope cleaning evaluation method. The calibrant mixture must be placed into the container in which cleaning was performed.

7.5.2 Sonicate the inorganic calibrant suspension from 6.6.2.5 for at least 5 minutes before use. The suspension should be sonicated during all transfer operations to insure uniform distribution of particles. Swirl the suspension immediately before each transfer.

7.5.3 Warm the organic calibrant solution from 6.6.3.7 to room temperature and ensure that the compounds are completely dissolved.

7.5.4 Wash the inside surface of the aluminum foil covers with fresh cleaning agent. Allow the wash to fall into the cleaning residue container.

7.5.5 Inject 1 ml of inorganic calibrant suspension into the cleaning residue. Wash the hypodermic syringe with two 1 ml portions of filtered ethanol.

7.5.6 Add the organic calibrant solution to the cleaning residue.

7.5.6.1 If direct analysis of aqueous detergent cleaning residue will be performed, inject 1.0 ml of high concentration organic calibrant solution prepared in B.5. 1 into the cleaning residue from the first cleaning cycling only.

7.5.6.2 Inject 200 µl of organic calibrant solution prepared in 6.6.3 into all cleaning agent residues where 7.5.6.1 does not apply.

7.5.7 Transfer the cleaning residue into cleaned, labeled sample containers. Wash the container walls with fresh cleaning agent. Add the wash to the cleaning residue.

7.5.8 Return the organic solutions to the freezer after cleaning is completed.

7.6 Analytical Sample Preparation

7.6.1 Separation of inorganic particulate and organic compounds.

7.6.1.1 Clean, as in 6.1, a vacuum filtration apparatus for a 37 mm diameter filter.

7.6.1.2 Filter the entire sample through a 0.2 μm pore size cellulose acetate filter. Agitate the sample bottle before transferring liquid into the filter funnel to resuspend particulate which may have settled to the bottom of the bottle.

7.6.1.3 Wash the interior of the bottle with clean, filtered cleaning agent or distilled water in the case of aqueous cleaning agent. Filter the wash liquid.

7.6.1.4 After filtration is complete, remove the filter from the apparatus and place it into a precleaned porcelain crucible. Return the filtrate to the original sample bottle for organic analysis.

7.6.2 Preparation of inorganic sample for analysis

7.6.2.1 In a fume hood, wet the filter with 3 ml of filtered ethanol. Ignite the ethanol with a flame to char the filter. Allow the ethanol to bum completely.

7.6.2.2 Cover the crucible and place it in a muffle furnace at 200 C. Increase the furnace temperature to 600 C over 1 hour. Hold for 2 hours at 600 C.

7.6.2.3 Remove the crucible from the furnace and cool it to room temperature.

7.6.2.4 Add 10 mg of high-purity graphite powder (ultracarbon UCP-1) or 50 mg of high-purity silver powder to the residue in the crucible.

7.6.2.5 Mix the residue and powder with a noncontaminating spatula. Transfer the mixture to a labeled 2 ml polystyrene vial.

7.6.2.6 The inorganic sample is now ready for submittal to the inorganic mass spectral analytical laboratory.

7.6.3 Preparation of organic sample for analysis

7.6.3.1 Pre-prep of aqueous cleaning agent sample.

This procedure applies to the deionized water rinse sample and to the diluted aqueous detergent residue prepared in B.5.4. If the cleaning agent is nonaqueous, proceed to 7.6.3.2. A special procedure for the cold trap samples is given in 7.6.3.4.

7.6.3.1.1 Add 1 g of muffled (4 hrs, 500 C) NaCl solid crystals to 200 ml aliquot of distilled water rinse or diluted aqueous detergent. Shake, then allow the two layers to separate.

7.6.3.1.2 Transfer a 200 ml aliquot of the distilled water rinse sample to a 500 ml or a 1000 ml separator funnel, and add 1 ml of 3N HCl to adjust the sample's pH value to 2. Add 50 ml of dichloromethane and shake the funnel to extract the organic contaminants into the dichloromethane layer.

7.6.3.1.3 Remove the bottom layer (dichloromethane) into a round bottom flask. Extract the aqueous layer with 50 ml of dichloromethane and repeat the extraction process with another aliquot of 50 ml of dichloromethane. Place all dichloromethane aliquots into the same round bottom flask and process the extract as described in 7.6.3.2.

7.6.3.2 Pre-prep of cloudy organic sample.

If the organic liquid is cloudy, dry the sample over anhydrous Na_2SO_4. If the layer appears clear, go to 7.6.3.3.

7.6.3.2.1 To a 200 ml aliquot of the sample or extract from 7.6.3.1.3 in a round bottomed flask, add ~ 20 g of muffled (4 hrs, 500 C) reagent Na_2SO_4 powder. Stopper the flask and shake the contents to mix the liquid and Na_2SO_4.

7.6.3.2.2 If the liquid layer remains cloudy, indicating that water is still present in the liquid, add more Na_2SO_4 and mix again. Continue adding Na_2SO_4 until the liquid layer clears.

7.6.3.2.3 Place a clean, muffled 104 mm diameter quartz filter into a glass funnel. Wet the filter with dichloromethane, then filter the sample. Wash the round bottom flask and the Na_2SO_4 with dichloromethane to quantitatively transfer the liquid. Discard the filter and Na_2SO_4.

7.6.3.3 Concentrate organic sample for analysis.

7.6.3.3.1 Use Kuderna-Danish (K-D) concentration to reduce the 200 ml liquid volume to approximate 2 ml. Set the water bath temperature to 15 C to 20 C above the boiling point of the organic liquid being concentrated.

7.6.3.3.2 Further concentrate the 2 ml sample extract to 10 μl by nitrogen evaporation then add 1 ml of dichloromethane to the concentrated sample extract. This step is only required while there is ethanol or methanol present in the sample.

7.6.3.3.3 The concentrated sample is ready for GC/MS analysis.

7.6.3.4 Preparation of cold trap sample and Teflon tape.

7.6.3.4.1 Wash the Teflon tape two times with 5 ml of filtered dichloromethane. Combine the wash with the corresponding cold trap sample.

7.6.3.4.2 If inorganic calibrant was added to the cold trap, filter the combined sample as in 7.6.1. Process the resulting filtrate as in 7.6.3.2 except that to further _____ the extract to dryness under nitrogen evaporation, then add 1 ml of filtered dichloromethane to the dry residue.

7.6.3.4.3 If inorganic calibrant was not added to the cold trap, process the combined sample as in 7.6.3.2 with a reduced sample volume.

7.7 Isotope Abundances

The isotope abundances for each element determined by the inorganic analysis form the elements of the column vector **a** used in 9.1.

7.8 Organic Analysis **Peak Utensities**

The organic analysis yields the peak intensity ratio:

$$PIR = \frac{\text{Synthetic contaminant response}}{\text{Analytical calibrant response}}$$

This ratio is used in 9.2.1.

7.9 Cleaning Efficiency

Calculate the percent cleaning efficiency as described in Section 9.3.

7.10 Comparison of Cleaning Efficiencies

Compare the cleaning efficiencies of the candidate cleaning procedures.

8.0 Calibration

8.1 Inorganic Calibration

8.1.1 Measure the isotope abundances for the simulated contaminant and analytical calibrant for each inorganic element selected in 6.5.1.

8.1.2 Normalize the sum of isotope abundances to 1 for each material. Use these abundances and the natural abundances of the elements as the column vectors of a matrix M which has as many rows as the element has stable isotopes and 3 columns. An example matrix for silicon is shown in Table 4.

8.1.3 Calculate the atomic weight of the synthetic contaminant and calibrant materials. The atomic weights can be calculated as follows:

$$\text{Atomic weight} = E\ A_i W_i$$

where

Atomic weight = atomic weight of the isotope mixture

W_i = weight of the isotope in atomic mass units (from a handbook)

A_i = abundance fraction of the isotope in the mixture.

8.1.4 Calculate the gravimetric factor to convert from weight of element to weight of compound. The factor is calculated by taking the reciprocal of the weight fraction of the element in the compound.

For example, to calculate the atomic weight of the synthetic contaminant shown in Table 6:

Table 6. Sample Isotope Abundance Matrix
(M in Equation 1 in Section 9. 1) For Silicon

Isotope	Isotope Weight (amu)	Abundance		
		Natural Element	Analytical Calibrant	Synthetic Contaminant
^{28}Si	27.97693	0.9221	0.0412	0.0440
^{29}Si	28.97649	0.0470	0.9565	0.0032
^{30}Si	29.97376	0.0309	0.0023	0.9528

Atomic weight = 0.0440 * 27.97693 + .0032 * 28.97649 + .9528 * 29.97376
= 29.8827

The corresponding gravimetric factor for conversion from Si to SiO_2 is:

$$G = \frac{29.8827 + 2 * 15.9994}{29.8827}$$

$$= 2.07081$$

8.2 Organic Calibration

8.2.1 Measure the mass spectrum of each organic material selected in 6.5.2.

8.2.2 For each organic compound, prepare a solution which contains a known concentration of each of the synthetic contaminant labeled compounds and the analytical calibration labeled compounds.

8.2.3 Measure the area count of the molecular ion current response for each analyte.

8.2.4 Calculate an instrument response factor, Rf for each organic synthetic contaminant.

$$R f = \frac{\text{Synthetic contaminant area counts}}{\text{Analytical calibrant area counts}} \times \frac{\text{Cone of calibration solution}}{\text{Cone of synthetic contaminantt solution}}$$

Rf corrects for differences in instrument response between each set of synthetic contaminant and analytical calibrant with different isotopic labels.

9.0 Calculations

9.1 Inorganic Data Reduction

9.1.1 The elemental isotope abundances measured by the mass spectrograph form the elements of a column vector **a.**

9.1.2 The vector **a** and the isotope abundance matrix **M** form parts of a matrix equation:

$$\mathbf{M\,c = a} \qquad \text{Eq (1)}$$

The solution of this equation, the column vector c gives the mole fraction of each component, native contaminant, synthetic contaminant and analytical calibrant contributing to produce the observed isotope abundances **a.** The FORTRAN program MATRIX is provided to solve the matrix equation. For example, a mixture of equal mole fractions of natural, analytical calibrant and synthetic contaminant silicon having the isotope abundances shown in Table 6, would contain 33.58 % ^{28}Si, 33.56% ^{29}Si and 32.87% ^{30}Si. Substituting in the matrix equation gives:

Natural	Calibrant	Contaminant	Mole Fraction	Observed
0.9221	0.0412	0.0440	$C_{natural}$	0.3358
0.0470	0.9565	0.0032	C_{cal}	0.3356
0.0309	0.0023	0.9528	$C_{contaminant}$	0.3287

The program MATRIX yields the solution:

$C_{natural}$ = 0.333366
C_{cal} = 0.333366
$C_{contaminant}$ = 0.333367

which is correct to the accuracy of the data supplied.

MATRIX also calculates the quantities of natural and synthetic contaminants in the cleaning residue using the calculated mole fractions and the amount of calibrant added to the residue after cleaning. A description of MATRIX is contained in Appendix A.

9.1.3 Calculate the total moles of each element:

$$T_{element} = S_{cal}/(C_{cal} * G_{cal} * AtWt_{cal}$$

where

$T_{element}$ = total element moles

S_{cal} = the mass of the analytical calibrant added to the sample (µg)

$AtWt_{cal}$ = atomic weight of calibrant element

C_{cal} = the analytical calibrant mole fraction from 9.1.2

G_{cal} = gravimetric factor = molecular weight of calibrant compound/$AtWt_{cal}$

Using the information in Table 6 and the formulas in 8.1.3 and 8.1.4, the atomic weight of the calibrant silicon is 28.9376 and the gravimetric factor is 2.10579. If 10 µg of calibrant silica was added to the cleaning residue whose isotopic analysis and mole fraction are shown in 9.1.2, the total moles of silicon are:

= 0.49227 µmole

$$T_{element} = \frac{10\mu g}{.333366 * 2.10579 * 28.9376\ \mu g/pmole}$$

9.1.4 Calculate the amount of contaminant removed by cleaning:

$$W_{contaminant} = T_{element} * C_{contaminant} * AtWt_{hmirnimmt} * G_{contaminant}$$

where

$W_{contaminant}$ = mass of contaminant removed (µg)

$C_{contaminant}$ = the contaminant mole fraction from 9.1..2

$AtWt_{contaminant}$ = atomic weight of contaminant element

$G_{contaminant}$ = gravimetric factor = molecular weight of contaminate compound/$AtWt_{contaminant}$

Using the results of the preceding example calculations the weight of synthetic contaminant is:

$$W_{contaminant} = .49227\ \mu moles * .333367 * 29.882\ \mu g/pmole * 2.07081 = 10.15\ \mu g$$

9.2 Organic Data Reduction

9.2.1 The Response factor from 8.2.4 and the peak intensity ratio measured for each organic compound by the mass spectrometer in 7.8 are used to calculate the mass of contaminant removed:

$$W_{contaminant} = \frac{PIR * Calibrant}{Rf}$$

where

$W_{contamiant}$ = mass of contaminant removed (µg)

PIR = area intensity ratio between the synthetic contaminant and the analytical calibrant

Calibrant = the mass of the analytical calibrant added to the sample (W)

Rf = the response factor for the synthetic contaminant

For example, assuming that 10 µg of calibrant compound was added to the cleaning residue, the response factor was 0.980 and the measured peak intensity ratio was 0.650, the weight of contaminant in the cleaning residue is:

$$W_{contaminant} = \frac{0.650 * 10\mu g}{0.980} = 6.63\mu g$$

9.3 Cumulative Percent Cleaning Efficiency

9.3.1 Determine the initial contaminant loading:

$$Load_1 = (\text{Injected mass}) - (\text{Lost mass})$$

where

Injected mass = the mass of contaminant put into the test part
Lost mass = the mass of contaminant found in the dry ice cold trap

9.3.2 Calculate the total amount of contaminant removed:

E Clean = the summation of contaminant removed by previous cleaning cycles

9.3.3 Calculate the cumulative percent cleaning efficiency for a given number of cleaning cycles:

$$E\ (\%) = \frac{E\ Clean}{Load_1}$$

10.0 References

Carter, J. A., Franklin, J. C., and Donohue, D. L., Multielement Isotope Dilution Techniques for Traces Analysis, p 299, High Performance Mass Spectrometry: Chemical Applications, Gross, M. L., ed., American Chemical Society, Washington, D .C., 1978.

Isenhour, T. L. and Jurs, P. C., Introduction to Computer Programming for Chemists, Allyn and Bacon, Inc., Boston, MA, 1972.

Ralson, A. and Rabinowitz, P., A First Course in Numerical Analysis, 2nd ed., McGraw-Hill, New York, 1978.

Example Check List for Test Part Contaminant Doping

Test Device; A-200D Accelerometer.

Test seal integrity.

Attach fill tubes.

Attach yoke assembly.

Preclean.

Reassemble case halves-check fit.

Prepare cold bath–Add acetone slowly to control bubbling.

Record device identification.

Wrap part with Teflon tape.

Connect part to vacuum pump.

Set up cold trap and clamp above cold bath.

Remove the organic solutions from the freezer and warm to room temperature.

Start vacuum pump.

Sonicate the inorganic contaminant 5 minutes.

Inject 2.0 ml inorganic contaminant - record volume.

Inject 2 ml filtered ethanol rinse - record volume.

Start timer.

Rock part, check for leakage, keep part warm for 15 minutes.

Dry 5 additional minutes.

Stop pump - record drying time and leakage.

Check the dry ice level in the cold bath - add dry ice if needed.

Insert the cold trap into the vacuum line.

Slowly lower cold trap into cold bath.

Start vacuum pump.

Check organic solutions for complete dissolution.

Inject 200 µl organic contaminant - record volume.

Inject 2 ml filtered dichloromethane - record volume.

Start timer.

Rock part, check for leakage, keep part warm for 5 minutes.

Dry 5 additional minutes.

Stop pump - record drying time and leakage.

Disconnect test device from Teflon tubing - set aside.

Remove cold trap from cold bath.

Disconnect tubing from cold trap.

If leakage occurred during inorganic doping, sonicate the inorganic calibrant 5 minutes, inject 1 ml of inorganic calibrant into cold trap, inject 1 ml of filtered ethanol - record volume and inform organic analyst.

Inject 200 µl organic calibrant into cold trap - record volume.

Rinse with filtered dichloromethane.

Transfer contents of cold trap to labeled bottle.

Rinse cold trap twice with filtered dichloromethane - combine rinses with cold trap's original contents.

Remove Teflon tape from device - place in labeled container.

Doping complete.

Example Check List for Ultrasonic Cleaning

Prepare and clean the cleaning containers and sample bottles, etc.

Prepare the cleaning device for operation.

Bring the cleaning device to the desired operating temperature.

Obtain racks to hold the cleaning containers, as needed.

Mark the containers to identical the test device and cleaning cycle.

Fill the containers with the proper amount of cleaning agent.

Place the test part into the cleaning agent using clean tongs. Position the part for good access by the cleaning agent to the contaminated surfaces.

Place the containers into the cleaning device.

Measure and record the initial temperature.

Begin the first cleaning cycle.

Label and fill containers for the second cleaning cycle during the current cycle.

At the end of the cycle, record the final temperature.

Remove the containers from the cleaning device.

Transfer the test devices to the appropriate Cycle 2 containers for the next cleaning cycle.

Place the containers for the second cycle into the cleaning device.

Measure and record the initial temperature.

Begin the second cleaning cycle.

Wash each container cover from the first cycle with clean cleaning agent. Allow the wash to fall into the corresponding container.

Sonicate the inorganic calibrant for at least 5 minutes before use.

Inject 1.0 ml of inorganic calibrant into the cleaning residue with a hypodermic syringe.

Wash the syringe with two 1 ml portions of filtered ethanol. Add the wash to the cleaning residue.

Inject 200 µl of organic calibrant solution into the cleaning residue.

Transfer the cleaning residue to labeled sample bottles.

Wash the cleaning container with clean cleaning agent. Add the wash to the cleaning residue,

Label and fill containers for the third cleaning cycle during the current cycle.

At the end of the second cycle, record the final temperature.

Remove the containers from the cleaning device.

Transfer the test devices to the appropriate Cycle 3 containers.

Place the containers for the third cycle into the cleaning device.

Measure and record the initial temperature.

Begin the third cleaning cycle.

Wash each container cover with clean cleaning agent. Allow the wash to fall into the corresponding container.

Sonicate the inorganic calibrant at least 5 minutes before use.

Inject 1.0 ml of inorganic calibrant into the cleaning residue with a hypodermic syringe.

Wash the syringe with two 1 ml positions of filtered ethanol. Add the wash to the cleaning residue.

Inject 200 µl of organic calibrant solution into the cleaning residue.

Transfer the cleaning residue to labeled sample bottles.

Wash the cleaning container with clean cleaning agent. Add the wash to the cleaning residue.

At the end of the third cycle, record the final temperature.

Remove the containers from the cleaning device.

Remove the test devices from the containers. Set the test devices aside.

Wash each container cover with clean cleaning agent. Allow the wash to fall into the corresponding container.

Sonicate the inorganic calibrant for at least 5 minutes before use.

Inject 1.0 ml of inorganic calibrant into the cleaning residue with a hypodermic syringe.

Wash the syringe with two 1 ml portions of filtered ethanol. Add the wash to the cleaning residue.

Inject 200 µl of organic calibrant solution into the cleaning residue.

Transfer the cleaning residue to labeled sample bottles.

Wash the cleaning container with clean cleaning agent. Add the wash to the cleaning residue.

Wrap the caps of all sample bottles with Teflon Tape

Submit the samples for isotope analyses.

Attachment

Fortran Program Matrix

Attachment A

Fortran Program Matrix

The program MATRIX is written in FORTRAN77 to solve the matrix equation:

$$M c = a$$

where M = A matrix of coefficients whose columns represent the isotopic abundances of the components of a mixture. The components for this problem are the native and synthetic contaminants and the analytical calibrant.

c = A column solution vector which gives the mole fraction of each component in the mixture.

a = A column vector of isotope abundances measured by the mass spectrometer.

MATRIX uses both keyboard input, which selects the input file and output device, and an input file which provides the input data for the program. The matrix equation, which may be overdeterrnined, is solved using Householder transformation matrices to transform the given matrix to upper triangular form. The upper triangular matrix is solved by back substitution in subroutine OVERD). OVERD functions as a driver routine for the Householder transformation process. It accepts the input information from the main program, initializes array P to a suitably sized identity matrix, then calls the transformation subroutine HOUSEH which replaces array P with the Householder transformation of the original matrix. The right hand vector a is also transformed by multiplying by P to yield an upper triangular matrix equation. The transformed system is solved by back substitution. The Householder transformation procedure is an accepted method for the solution of least squares fit problems, and is more computationally stable than the commonly used least squares normal equations. The Householder transformation approach was chosen because it can solve both 'square' (N equations, N unknowns) and overdetennined (N equations, M unknowns, M< N) systems of equations. An overdetermined system would result when more than three isotopes of an element can be determined by the mass spectrometer while a 'square' system results when three isotopes are used. If only two isotopes are available the system is underdetermined and the program will fail.

MATRIX was modified for use on IBM PC computers or compatibles. The executable file supplied on the program disk is for use under WINDOWS 3.1.

The contents of the input file are described in Table Al below. An example input file is shown in Table A2. All of the numeric input variables are list directed so that the variables on each line may be separated by spaces or a comma. The program has been modified to allow input of multiple sets of isotope abundances. This feature is useful when replicate analyses are available for a sample. Since MATRIX normalizes the isotope abundances so that their sum is one, the isotope abundance data can be input as percent, ppm, etc. and MATRIX will compute and use the normalized isotope abundance fractions.

The program output is comprised of four parts. The first part contains the date and time of the computation, the name of the input file, and the title line from the input file. This information is provided to identify the source of the input data. The second portion of the output gives the solution of the matrix equation. The solution shows the mole fraction of each component comprising the analyzed mixture. The column of the solution corresponds to the identification of the columns in matrix M. The third portion of the output shows the residuals of the right hand vector A not accounted for by the least squares solution of the matrix equation. The residuals are nonzero only for the overdetermined matrices and zero for square matrices. The last output section gives the mass of the contaminant species, native and synthetic, present in the sample, based on the mass of calibrant added to the sample after cleaning. The units are the same as the units of the input variable CALWT. The mass of element and compound are given. The compound weight is calculated from the element weight and the user supplied gravimetric factors.

The program output produced using the input data given in Table A2 is shown in Table A3 .

The program source code is contained in the file MATRIX4.FOR on the 5-1/2” floppy disk included with this procedure. The sample input data is on file SAMPLE.DAT.

Table A-1. Matrix Program Input Variables

Line	Variable	Type	Description
1	TITLE	Character *8O	Descriptive identifier for the problem
2	NR	Integer	Number of rows in the matrix
2	NC	Integer	Number of columns in the matrix
3	A(l,NC)	Real*8	First row of the coefficient matrix
4	A(2,NC)	Real*8	Second row of the coefficient matrix
2+NR	A(NR,NC)	Real*8	Last row of the coefficient matrix
3+NR	ATOMWT(NC)	Real*8	Atomic weight for each mixture component. Use the column order of the coefficient matrix.
4+NR	GRAVP(NC)	Real*8	Gravimetric factor for conversion from element to compound for each mixture component. Use the column order of the coefficient matrix.
5+NR	NCAL	Integer	Column in the coefficient matrix corresponding to the calibrant component of the mixture
5+NR	CALWT	Real*8	Weight of the calibrant compound added to the sample. The output weights will be in the same units (i.e., µg).
6+ NR[a]	B(NR)	Real*8	Measured isotope abundances determined by mass Spectrometric analysis in 9.1.1. Use the row order of the coefficient matrix.

(a) Additional sets of isotope abundance data from replicate mass spectral analyses can be included in the calculations. Put each set of abundance data on a separate line.

Table A-2. Program Matrix Sample Input

```
Silicon isotope analysis - SAMPLE INPUT
3 3
.9221   .0412.0440
.0470   .9565.0032
.0309   .0023.9528
28.08628.937629.8827
2.139322.105792.07081
223.3
397.565294.039547.271
286.316292.983547.759
267.109252.884461.443
248.787249.508443.468
221.277180.513365.758
```

Table A-3.

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FILE - b: sample. OUT

Silicon isotope analysis - SAMPLE INPUT

COLUMN	SOLUTION
1	3.16086E-01
2	2.31091E-O1
3	4.52823E-01

ROW	RESIDUALS
1	0.00000E+00
2	0.00000E+00
3	0. OOOOOE+OO

COLUMN	ELEMENT	COMPOUND
1	14.69	31.42
3	22.39	46.36
1	9.98	21.35
3	22.19	45.95
1	10.98	23.49
3	21.71	44.95
1	10.27	21.98
3	21.09	43.67
1	12.99	27.80
3	24.31	50.35

PROGRAM MATRIX

```
C     USES THE HOUSEHOLDER TRANSFORMATION MATRIX METHOD TO SOLVE A
c     SYSTEM OF EQUATIONS. THE SYSTEM MAY BE OVERDETERMINED.

      PARAMETER (NS = 100,NCC= 13)
      IMPLICIT REAL* 8(A-H,0-Z)
      CHARACTER TITLE* 80, NAMEV*7,NAMEF*9, NAMEEX*4,FILENM* 19
      COMMON /STORE/ A(NS,NCC),B(NS* NCC),C(NS,NCC), P(NS,NS),R(NS),
     1               U(NS),W(NS),GRAVF(NCC), ATOMWT(NCC)
      DATA LFILE,LUNIT/5,6/
c
      NCOL= NCC
 10   WRITE(*,500) ' VOLUME NAME? '
 500  FORMAT(A)
      READ(*,500) NAMEV
      WRITE(*,500) ' FILE NAME? '
      READ(*,500) NAMEF
      WRITE(*,500) ' EXTENSION NAME? '
      READ(*,500) NAMEEX
      LENV=INDEX(NAMEV, ' ')-1
      LENF=INDEX(NAMEF, ' ')-1
      LENEX =INDEX(NAMEEX, ' ')-1
      FILENM =NAMEV(1:LENV)//':'//NAMEF(1:LENF)//'.'//NAMEEX(1:LENEX)
      LENFIL=LENV + LENF +LENEX + 2
      OPEN(LFILE,FILE = FILENM(1:LENFIL),STATUS = 'OLD' ,
     1     IOSTAT=IERR,ERR= 1000)
C     OPEN OUTPUT FILE
      FILENM = NAMEV(1:LENV)//':'//NAMEF(1:LENF)//'.OUT'
      LENFIL= LENV + LENF + 5
      OPEN(LUNIT,FILE =FILENM(1:LENFIL),STATUS = 'NEW' ,
     1     IOSTAT=IERR,ERR= 1000)
C
C     INPUT MATRIX VALUES
C
      READ(LFILE,500) TITLE
      READ(LFILE,*) NR,NC
C
      CALL INPUT(LFILE,NC,NR,NP,A,B,GRAVF,ATOMWT,NCAL,CALWT)
C
      WRITE(*,*) 'SOLVING.. '
      CALL OVERD(NC,NR,A,B, P, U,W,R)
C
C     ouTPuT Results
C
      CALL PDATE(LUNIT)
      WRITE(LUNIT,590) FILENM(1:LENFIL)
 590  FORMAT(' FILE - ' ,A/)
      WRITE(LUNIT,600) TITLE
```

```
 600   FORMAT(lX,A//3X,'COLUMN',3X,'SOLUTION'/)
c
      DO 11 I=1,NC
 11     WRITE(LUNIT,61O)  I,W(I)
 610  FORMAT(4X,15,5X,1  PE14.5)
      PAUSE  'CONTINUE?'
      WRITE(LUNIT,620)
 620  FORMAT(//1X,5X,'ROW',5 X,'RESIDUALS'/)
      DO 22 I=1,NR
 22     WRITE(LUNIT,61O)  I,R(I)
      WRITE(LUNIT,630)
 630  FORMAT(//1X,2X,'COLUMN',5X,'ELEMENT',5X,  'COMPOUND'/)
c
      DO 44 II=1,NP
c
      IF(II.GT. 1) CALL TRANSB(NC,NR,A, B((II-l)*NR+ l), P, U,W,R)
c
c      CALCULATE THE AMOUNTS OF NATIVE AND SYNTHETIC CONTAMINANTS
C
      CMOLE =CALWT/(GRAVF(NCAL)  *ATOMWT(NCAL))
      TMOLE =CMOLE/W(NCAL)

      DO 33 I=1,NC
        IF(I.NE.NCAL) THEN
          CONWT  =TMOLE*W(I)*ATOMWT(I)
          WRITE(LUNIT,640)  I,  CONWT,CONWT*GRAVF(I)
 640        FORMAT(1X,17,2(6X, F6.2))
        ENDIF
 33   CONTINUE
 44   CONTINUE

      STOP  'DONE'
c
 1000 WRITE(*, 1010) FILENM(1:LENFIL),IERR
 1010 FORMAT(' CAN"T OPEN ', A,' - ERROR ',15/
     1        ' TRY ANOTHER FILE NAME?')
      READ(*,500)  FILENM
      IF(FILENM(1 : 1). NE. 'N') GO TO 10
      STOP
      END

*****************
      SUBROUTINE  PDATE(LUN)
c      WRITES CURRENT DATE TO LUN
      INTEGER*2 YR,MO,DY,HR,MIN,SEC,FRAC
c
      CALL   GETDAT(YR,MO,DY)
      CALL GETTIM(HR,MIN,SEC, FRAC)
```

```
      YR=MOD(YR, 100)
      WRITE(LUN,600) MO, DY,YR,HR,MIN,SEC
 600  FORMAT(lX,2(12,'/'),12,5X,2(12,': '),12/)
      RETURN
      END
***************************
      SUBROUTINE INPUT(LIN,NC,NR, NP,A,B ,GRAVF,ATOMWT,NCAL, CALWT)
      IMPLICIT REAL* 8(A-H,0-Z)
      DIMENSION A(NR,NC),B(NR*1OO) ,GRAVF(NC),ATOMWT(NC)
C
      DO 11 I=1,NR
 11     READ(LIN,*)(A(I,J),J = 1,NC)
c
      READ(LIN,*)(ATOMWT(I),I=l, NC)
      READ(LIN,*)(GRAVF(I),I = 1,NC)
      READ(LIN,*) NCAL,CALWT
      J=O
 20     READ(LIN,*,END =30) (B(J*NR+I),I=1,NR)
       J=J+1
      GO TO 20
 30   NP=J
c
c     NORMALIZE ISOTOPE FRACTIONS
      DO 44 J=1,NP
      SUM=O.
      JJ=J-1
      DO 33 I=1,NR
 33     SUM= SUM + B(JJ*NR+I)
      DO 44 I=1,NR
 44     B(JJ*NR+I) =B(JJ*NR+I)/SUM
      RETURN
      END

***********************
      SUBROUTINE OVERD(NC,NR,A,B, P, U,X,Y)
C     DRIVER ROUTINE FOR SOLUTION OF OVERDETERMINED SYSTEMS OF
C     EQUATIONS USING HOUSEHOLDER TRANSFORMATIONS
C     SEE DISCUSSION OF OVERDETERMINED SYSTEMS IN RALSTON &
C     RABINOWITZ (SECTION 9.9)
C
C     INPUTS :
C
C     NC       - NUMBER OF COLUMNS IN A
C     NR       - NUMBER OF ROWS IN A AND B
C     A(NR,NC) - COEFFICIENT MATRIX
C     B(NR)    - VECTOR OF RIGHT HAND SIDES
C     U(NR)    - WORKING STORAGE
C
```

```
C     OUTPUTS:
C
C     A(NR,NC) - TRANSFORMED COEFFICIENT MATRIX (P*A)
C     P(NR,NR) - HOUSEHOLDER TRANSFORMATION MATRIX
C     X(NC)    - SOLUTION VECTOR
C     Y(NR)    - VECTOR OF RESIDUALS
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NR,NC),P(NR,NR), B(NR),U(NR),X(NR), Y(NR)
C
C     INITIALIZE P TO I MATRIX
      DO 11 J=1,NR
        DO 11 I=1,NR
          IF(I.EQ.J) THEN
            P(I,J)=1.
          ELSE
            P(I,J) =0.
          ENDIF
 11   CONTINUE
c     GENERATE HOUSEHOLDER TRANSFORMATION MATRIX
      CALL HOUSEH(NC,NR,A, P, U,X,Y)
      ENTRY TRANSB(NC,NR,A, B, P, U,X,Y)
c     TRANSFORM B
      I=1
      CALL MMULT(NR,NR,I,P, B,X)
c
c     PERFORM BACK SUBSTITUTION
      X(NC) =X(NC)/A(NC,NC)
      DO 33 K= NC-1,1,-1
        DO 22 J=K+1,NC
 22       X(K) =X(K) - A(K,J)*X(J)
        IF(ABS(A(K,K)).GT. 1.E-10) THEN
          X(K) =X(K)/A(K,K)
        ELSE
          X(K) =0.
        ENDIF
 33     CONTINUE
c     CALCULATE RESIDUALS
      DO 55 I=1,NR
        IF(I.LE.NC) THEN
          U(I) =0.
        ELSE
          U(I) = X(I)
        ENDIF
 55   CONTINUE
c     MULTIPLY BY P TRANSPOSE FOR RESIDUALS
      DO 66 I=1,NR
        Y(I) =0.
```

```
      DO 66 J=1,NR
 66     Y(I) =Y(I) + P(J,I)*U(J)
      RETURN
      END
c**********************
      SUBROUTINE HOUSEH(NC,NR,A, P, U,X,Y)
C     GENERATE HOUSEHOLDER TRANSFORMATION MATRIX TO TRIANGULARIZE A
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NR,NC),P(NR,NR) ,U(NR),X(NR),Y(NR)
C
C     FIND THE HOUSEHOLDER MATRIX FOR EACH COLUMN OF A
      DO 111 K=1,NC
       DO 11 I=1,NR
 11      X(I) =A(I,K)
c     DETERMINE U VECTOR
       CALL UFIND(NR,K,U,X,D)
c     CALCULATE UT*P
       DO 22 I=1,NR
 22      X(I)=0.
       DO 33 J=1,NR
        DO 33 I=1,NR
 33       X(J) =X(J) + U(I)*P(I,J)
c     COMPLETE CALCULATION OF P-D* U*UT*P
      DO 55 I=1,NR
       UU=U(I)
       IF(UU.NE.0.) THEN
        DO 44 J=1,NR
 44       P(I,J)=P(I,J) - D* UU*X(J)
       ENDIF
 55   CONTINUE
c     CALCULATE UT*A
       DO 66 I=1,NR
 66      X(I) =0.
C** NR Changed to NC to MATCH A Array Bounds 7/6/90 **
       DO 77 J=1,NC
        DO 77 I=1,NR
 77       X(J) =X(J) + U(I)* A(I,J)
c     COMPLETE CALCULATION OF A-D* U*UT*A
      DO 99 I=1,NR
       UU=U(I)
       IF(UU.NE.0.) THEN
C ** NR CHANGED TO NC TO MATCH A ARRAY BOUNDS 7/6/90 **
        DO 88 J=1,NC
 88       A(I,J)=A(I,J) - D*UU*X(J)
       ENDIF
 99  CONTINUE
 111 CONTINUE
      R E T U R N
```

```
      END
c**********************
      SUBROUTINE MMULT(N1 ,N2,N3,A,B,C)
c      MATRIX MULTIPLICATION
      IMPLICIT REAL* 8(A-H,0-Z)
      DIMENSION A(N1 ,N2),B(N2,N3),C(N1 ,N3)
c
      DO 11 I=1,N1
        DO 11 J=1,N3
          C(I,J) =0.
          DO 11 K=1,N2
 11         C(I,J)=C(I,J) + A(I,K)*B(K,J)
      RETURN
      END
c**********************
      SUBROUTINE UFIND(NR,K,U,X,D)
C      DEVELOPTHEVECTOR UFORTHE HOUSEHOLDER TRANSFORMATION GIVEN
C      THECOLUMNVECTOR X. D=2/UT*U
      IMPLICIT REAL* 8 (A-H,O-Z)
      D I M E N S I O N ,X(NR)
C
      SUM1 =0.
      SUM2=SUM1
      SA = X(K)
      DO 11 I=1,NR
        XX= X(1)*X(I)
        SUM1=SUM1 + XX
        IF(I.LT.K) THEN
          U(I)=0.
          SUM2=SUM2 + xx
        ELSE
          U(I) =X(I)
        ENDIF
 11    CONTINUE
c      CHOOSE SIGN = MINUS SIGN OF X(K)
      IF(SA.LT.0.) THEN
        SA=1.
      ELSE
        SA=-1.
      ENDIF
      U(K) =X(K) - SQRT(SUM1-SUM2)*SA
      SUM1=0.
      DO 22 I=1,NR
 22     SUM1 =SUM1 + U(I)*U(I)
      D=2./SUM1
      RETURN
      END
```

Attachment B

Modified Procedures for Doping of Open Test Devices and for Direct Analysis of Aqueous Detergent Cleaning Residues

Attachment B

Modified Procedures for Doping of Open Test Devices and for Direct Analysis of Aqueous Detergent Cleaning Residues

B.1.0 Scope and General Description

These modified procedures were developed to address two limitations of the original CPEP:

(1) The inability to test open parts

(2) The inability to perform organic analyses of aqueous detergent cleaning residues.

The modified procedures provide a means to extend the CPEP to both of these situations.

B.2.0 Limitations

B.2.1 Test Part Size

The test part doping procedure described here has been validated for parts approximately 2 x 4 x 4 inches or smaller. Larger parts, such as circuit boards would require a larger bag to enclose the part and probably a large pan to retain any contaminant material which drips off the test device during doping. Correspondingly, larger cleaning agent volumes would also be required.

B.2.2 Organic Contaminants in Aqueous Detergent

The modified procedure for direct analysis of the aqueous detergent residue employs a 200-fold dilution of the residue to reduce total organic compound loading which is presented to the GC/MS instrument. Since the GC/MS instrument detection limit for octadecanoic acid is about 8 ng, the total quantity of contaminant and calibrant must be increased to ensure that a sufficient amount of both

calibrant and contaminant are present in the cleaning residues. To retain comparability among the candidate cleaning agents, the same contaminant loadings must be used for all tests.

B.3.0 Apparatus for Doping of Open Test Parts

This apparatus is in addition to the equipment listed in Table 4 of CPEP:

Teflon bag, with septum seal and hose bib (Altech 41224) 8“ x 12”	4“ petri dish
Heat lamp or vacuum oven	Stainless steel support frame for petri dish
12” length of 1/4” Teflon tube	Clipboard

B.4.0 Modified Contaminant Doping Procedure for Open Test Parts

This test part contaminant doping procedure is suitable for small (up to 2“ x 4“ x 4“) parts of irregular geometry which do not include a sealable enclosure as is required for the CPEP doping procedure. The procedure is applicable to larger parts, but the size of the containers and liquid volumes specified in this procedure would need to be increased. If both sides of the device are to be doped, apply half of contaminant suspension to each side of the device. Allow the ethanol carrier to dry before doping the second side.

B.4.1 Preparation of Test Parts/Devices

B.4.1.1 Thoroughly clean the test devices using the current cleaning procedure.

B.4.1.2 Dry the parts after the precleaning operation.

B.4.1.3 Preclean a glass petri dish for each test part using the cleaning procedure in 6.1. The petri dishes will be used to collect contaminant material which does not dry on the test part surface. Record the identification of each part and place them in petri dishes.

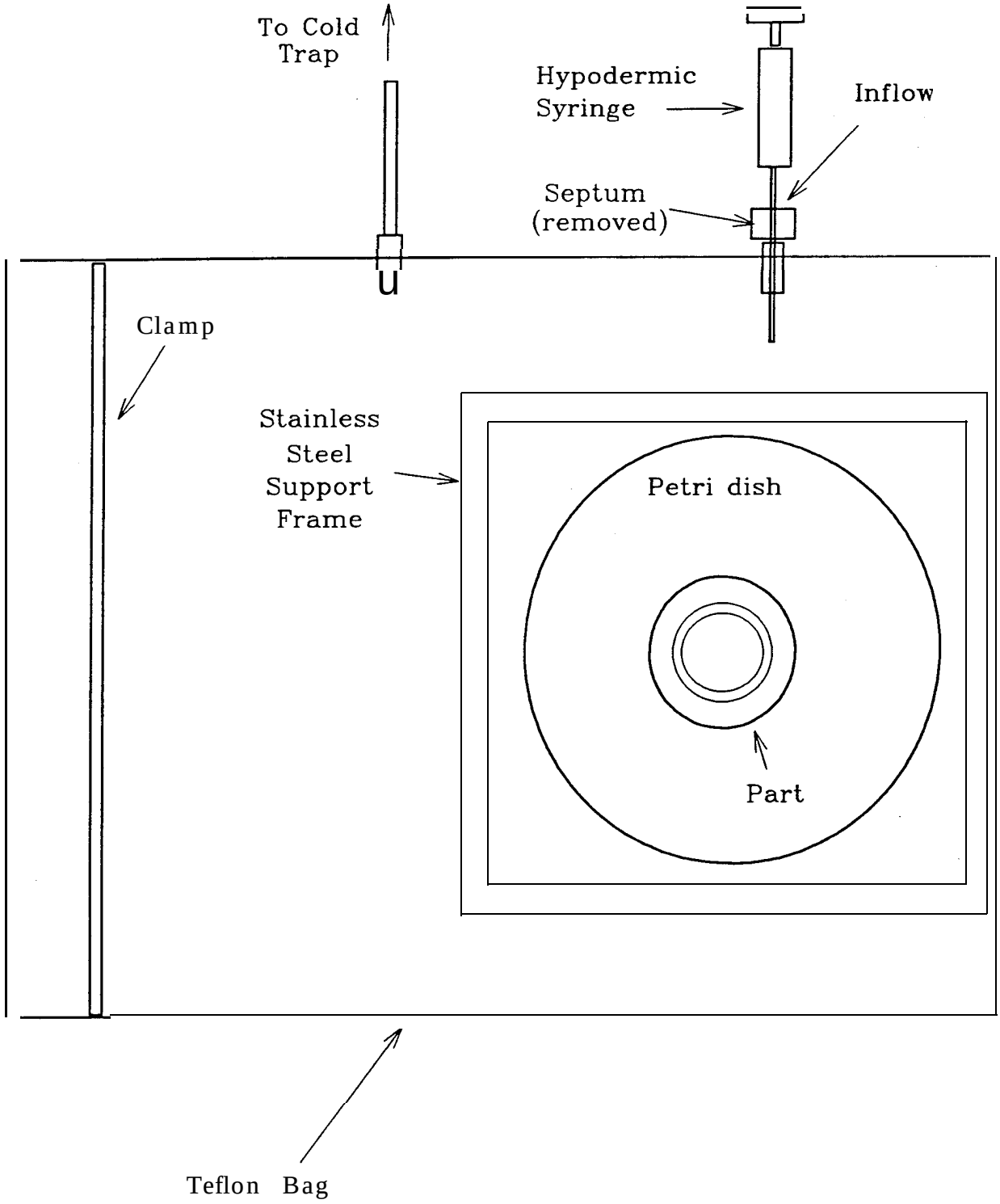

Figure B-1. Schematic Diagram of Open Test Part Apparatus

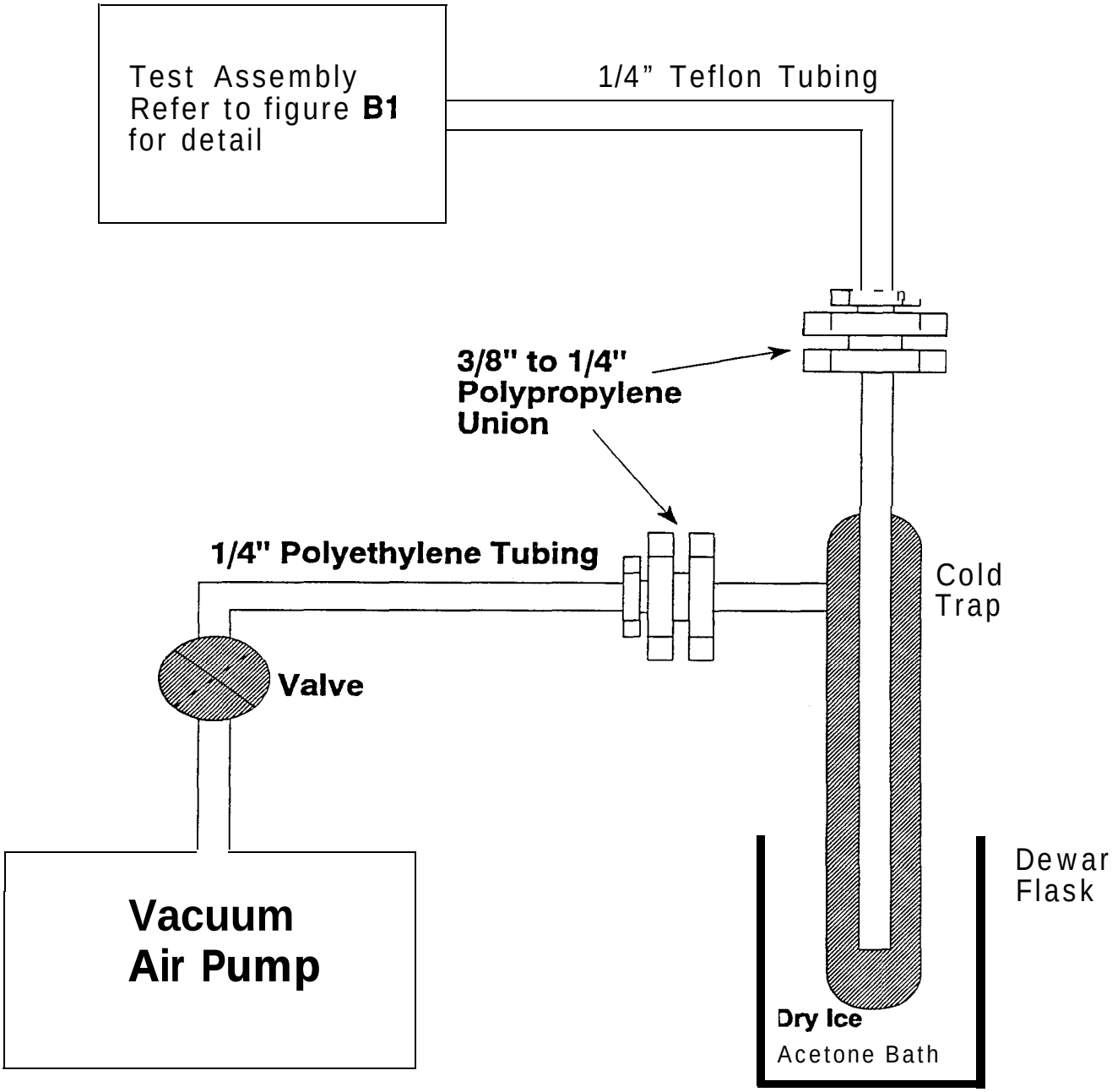

Figure B-2. Schematic Diagram of Test Device Organic Doping Interconnections

B.4.11.2 Close the valve between the cold trap and the vacuum pump.

B.4.11.3 Start the vacuum pump. Increase the flow slowly by opening the vacuum pump valve until the bag begins to collapse, then reduce the flow until collapse stops. This will provide maximum air flow without collapse of the Teflon bag and thus minimize drying times.

B.4.11.4 Apply organic contaminant solution to the part.

B.4.11.4.1 If the cleaning tests will include direct analysis of aqueous cleaning agent residues (B.5. 0), inject two 1.0 ml aliquots of the high concentration organic contaminant solution prepared in B.5. 1 onto the part through the septum seal opening using a 1.0 ml hypodermic syringe. The Teflon bag provides sufficient flexibility to allow application of the contaminant solution to selected regions of the part.

B.4.11.4.2 If the cleaning tests will not include direct analysis of aqueous cleaning agent residues (B.5. 0), inject 200µPI of the organic contaminant solution prepared in 6.6.3.

B.4.11.5 Observe the evaporation of the dichloromethane carrier on the part and in the petri dish, if any. Close the Teflon bag valve when evaporation is complete.

B.4.11.6 Stop the vacuum pump, replace the septum seal, and record the drying time.

B.4.11.7 Set the clipboard, bag and enclosed part aside.

B.4.11.8 Capture the cold trap contents for analysis.

B.4.11 .8.1 Remove the cold trap from the cold bath. Check the dry ice level in the cold bath. If additional parts are to be doped, add dry ice as in 7.3.4.3, if required.

B.4.11 .8.2 Remove the fittings from the cold trap. Add several milliliters of filtered dichloromethane to the trap while still cold. Warm the trap to room temperature.

B.4.11.8.3 Wash the center tube of the cold trap with several milliliters of filtered dichloromethane.

B.4.11 .8.4 Transfer the contents of the cold trap to a 2 oz precleaned glass bottle by pouring the contents out the side arm. Pour slowly so liquid does not escape through the top opening of the trap.

B.4.11.8.5 Wash the trap twice with several milliliter portions of filtered dichloromethane. Add the rinses to the trap's original contents.

B.4.11.9 The contaminant doping operation is complete. Keep all doped parts in the sealed Teflon bags until needed for the cleaning tests. This minimizes evaporative losses of volatile compounds.

B.4.11.1O Perform the cleaning tests according to 7.4. As each test part is removed from the Teflon bag, place it into the cleaning agent, then reseal the bag.

B.4.11.11 After each cleaning cycle add the inorganic and organic calibrant materials to each cleaning residue as in 7.5.

B.4.11.12 Capture the petri dish and Teflon bag contents for analysis.

B.4. 11.12.1 carefully remove the petri dish from the Teflon bag. Reseal the bag.

B .4.11 .12.2 Cover the bottom of the petri dish with filtered dichloromethane. This liquid will reduce evaporation of volatile contaminant compounds.

B.4. 11.12.3 Inject 1.0 ml of inorganic calibrant suspension into the petri dish using a 1 ml hypodermic syringe. Wash the syringe with 1 ml of filtered ethanol. Add the wash to the petri dish.

B .4.11 .12.4 Add the organic calibrant solution to the petri dish sample.

B.4.11 .12.4.1 If direct analysis of aqueous detergent residues will be performed, inject 1.0 ml of high concentration organic calibrant solution prepared in B. 5.1 into the combined sample.

B.4.11.12.4.2 If direct analysis of aqueous detergent residues will not be performed, inject 200 µl of organic calibrant solution prepared in 6.6.3.

B.4. 11.12.5 Wash the interior of the Teflon bag and support frame twice with several milliliter aliquots of filtered dichloromethane. Do not allow the dichloromethane to contact the septum. Combine each wash with the petri dish.

B.4. 11.12.6 Combine the contents of the petri dish and teflon bag rinse with the corresponding cold trap sample.

B.4. 11.12.7 Wash the petri dish twice with several milliliters of filtered dichloromethane. Combine each wash with the corresponding cold trap sample. Set the petri dish aside.

B.4. 11.12.8 Seal the sample bottle cap with Teflon tape.

B.4.11.13 This completes the modified procedure for doping of open test parts.

B.5.0 Modified Organic Analysis Procedure for Aqueous Detergent Residues

B.5.1 Preparation of high concentration organic contaminant and calibrant solution. These high concentration solutions are used to apply contaminant to the test parts during doping and as the calibrant solution which is added to the cold trap sample and the cleaning agent residue from the first cleaning cycle. Use hese solutions for all cleaning tests in which cleaning efficiency comparisons with aqueous detergents are made.

B.5.1.1 Both the contaminant and calibrant solutions are prepared in the same manner. The contaminant solution is prepared using the most expensive isotopic material of each compound pair. The other compound of the pair will be used in the calibrant solution. The less expensive compound is used a the calibrant, because more calibrant is used during testing.

B.5.1.2 Prepare separate stock solutions for each compound.

B.5.1.2.1 Test the compatibility of dichloromethane and the aqueous detergent.

B.5.1.2.1.1 Add 25 ml of dichloromethane to 100 ml of aqueous detergent in a 500 ml separator funnel.

B.5.1.2.1.2 Mix the liquids in the funnel and allow to stand.

B.5.1.2.1.3 The detergent and dichloromethane are compatible if the liquid layers separate completely.

B.5.1.2.1.4 If the liquid layers do not separate, dichloromethane is not compatible with the aqueous detergent.

B.5.1.2.2 If dichloromethane is not compatible with the aqueous detergent, repeat the test in B.5. 1.2.1 substituting methanol for dichloromethane.

B.5.1.2.3 Prepare stock solutions of the contaminant compounds in filtered dichloromethane. Dichloromethane can be used for the contaminant solutions, because it will be evaporated from the parts prior to cleaning. Use a solution concentration of 2 mg/rd for the most easily detected compound and proportionately higher concentrations of the remaining compounds.

B.5. 1.2.4 Prepare stock solutions of the calibration compounds. Use a solution concentration of 2 mg/ml for the most easily detected compound and proportionately higher concentrations of the remaining compounds. Use a solvent that is compatible with the aqueous detergent as determined in B.5. 1.2.1. Dichloromethane may be used as a solvent for calibrant compounds which comprise 10 percent or less of the calibrant solution.

B.5.1.3 Prepare 50 ml of a working contaminant solution.

B.5.1.4 Prepare 100 ml of a working calibrant solution.

B.5.1.5 Wrap the labeled contaminant and calibrant solution containers in aluminum foil to protect the compounds from light and store at -20 C or less.

Note: *Prior to use of the organic solutions, remove them from the freezer and allow them to return to room temperature. Slide the containers from the aluminum foil wrapper and examine the solution to ensure complete dissolution of the compounds.*

B.5.2 Apply the contaminant compounds to the test device. Use the procedure in 7.3 if the test devices have a sealable case. To apply the contaminant to open parts, use the modified procedure in B .4.0. Use the high concentration solutions prepared in B.5. 1.

B.5.3 Perform the cleaning tests described in 7.4 and the calibrant addition in 7.5 Use the high concentration calibrant solution in each cleaning cycle residue. To maintain consistency among the cleaning tests, use the high concentration calibrant for organic and aqueous cleaning agents.

B.5.4 Reduce the concentration of the interfering organic compounds in the aqueous detergent cleaning residue by diluting a 1 ml aliquot of the residue to 200 ml with distilled water.

B.5.5 Prepare the dilute aqueous detergent residue as described in 7.6.3. Use the standard procedure for the remainder of the sample preparation.

APPENDIX B

PARTICLE SIZE DISTRIBUTIONS

APPENDIX B

Particle Size Distributions

The mass and number distributions by particle size for the two stock suspensions used in this study for CPEP validation are shown in Tables B-1 (contaminant suspension) and B-2 (calibrant suspension). For each suspension, three sets of measurements were made; the analysis for each set is given in the tables. The mean values for each set of three measurements are given in Table 1, Section 4.1.3.

For comparison, the particle size distribution, based on an image analysis technique, for typical, contaminated parts is shown in Figure B-1.

Table B-1. Size Distribution of Contaminant ($^{30}SiO_2$) Particles (Batch Cont-III)

% Smaller than Indicated, Diameter	Volume Distribution Particle Diameter (µm)			Number Distribution Particle Diameter (µm)		
	Runl	Run2	Run3	Run 1	Run 2	Run 3
10	1.126	1.149	1.125	0.779	0.773	0.777
25	1.669	1.721	1.722	0.858	0.848	0.850
50	3.052	3.169	3.471	1.038	1.028	1.015
75	6.656	10.34	10.09	1.341	1.355	1.311
90	11.46	17.79	13.40	1.827	1.812	1.778

Table B-2. Size Distribution of Calibrant ($^{29}SiO_2$) Particles (Batch Cal III)

% Smaller than Indicated Diameter	Volume Distribution Particle Diameter µm)			Number Distribution Particle Diameter (pm)		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
10	1.175	1.230	1.319	0.779	0.785	0.774
25	1.753	1.857	2.235	0.862	0.876	0.852
50	3.067	3.765	5.709	1.049	1.074	1.032
75	6.793	7.556	16.83	1.393	1.415	1.369
90	11.79	11.68	18.10	1.906	1.907	1.889

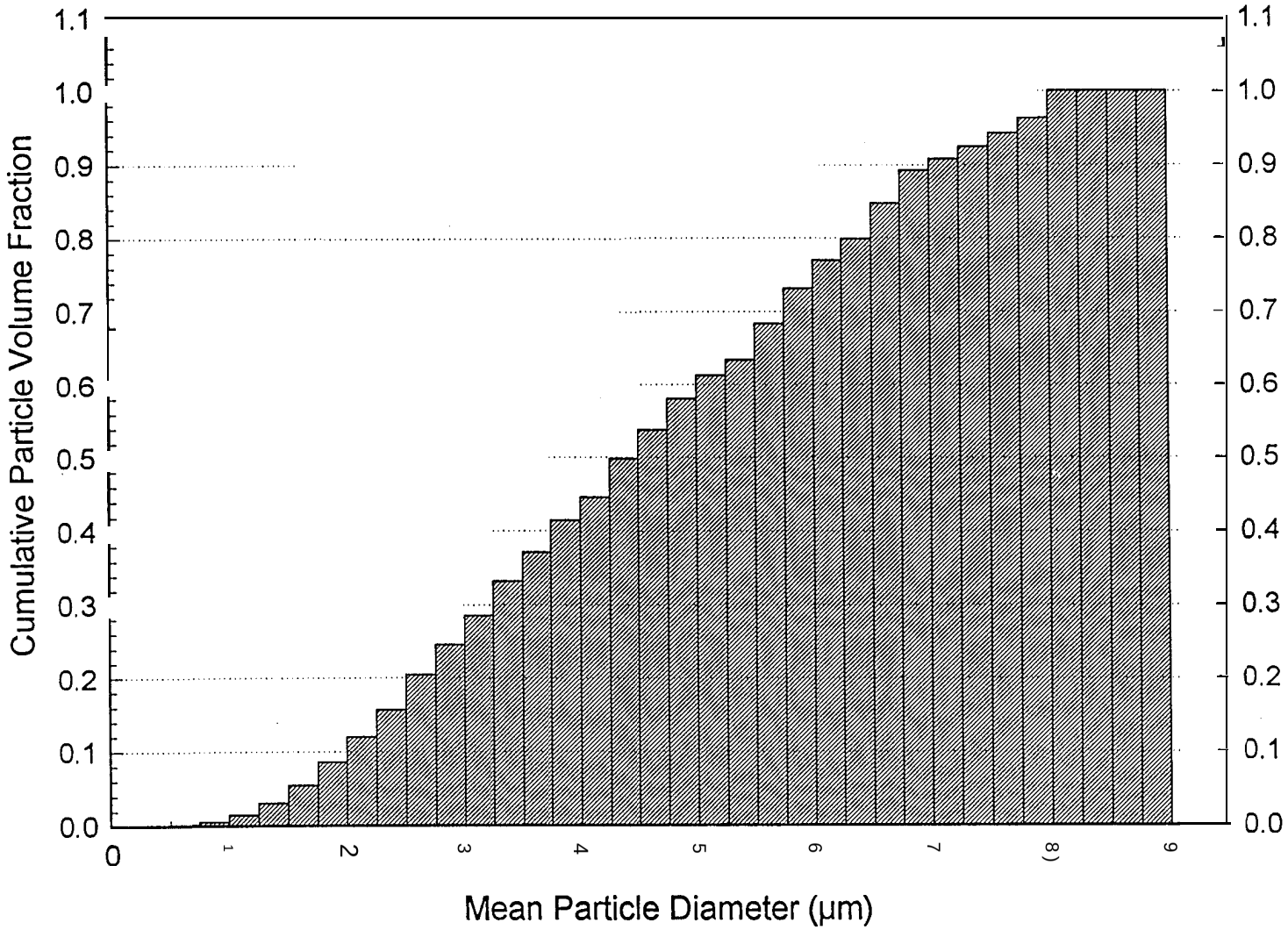

Figure B-1. Particle Size Distribution in G300 Gyro Fill Fluid

APPENDIX C

ALTERNATE ORGANIC CONTAMINANT COMPOUNDS