

Determining Cleanliness Levels Along
The Neutron Tube Manufacturing LineE. P. Lopez and M. G. Montoya
Sandia National Laboratories
Albuquerque, New Mexico

RECEIVED

JAN 31 1997

OSTI

MASTER

Abstract

A study is underway to identify a rapid, easy method for determining cleanliness levels during the manufacture of neutron tubes. Due to high reliability concerns associated with neutron tubes, cleanliness levels of metal and ceramic piece parts are critical. Sandia has traditionally used quantitative surface analytical methods, such as Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy for determining cleanliness levels. A critical disadvantage of these techniques is the time required to perform them. More rapid, reliable methods are needed for in-line testing of neutron tube assemblies. Several methods including contact angle, MESERAN, Fourier Transform Infrared Spectroscopy, and Optically Stimulated Electron Emission measurements are being evaluated as potential candidates. Cleanliness levels for each of these methods have been compared to Auger Electron Spectroscopy results, after processing samples through similar test conditions. An attempt was made to correlate the results from the alternative methods to those of Auger Electron Spectroscopy. Test results are presented.

Introduction

Full production of neutron tubes at Sandia National Laboratories (Sandia) will require a quick and accurate method for determining cleanliness levels along the manufacturing line. Historically, quantitative surface analytical methods, such as Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy, have been used.¹ While these methods are suitable, several alternative methods are being studied as potential replacements to provide quicker analytical results. The methods include: contact angle/goniometer, an evaporative rate analysis technique, a.k.a., MESERAN, Fourier Transform Infrared Spectroscopy (FTIR), and Optically Stimulated Electron Emission (OSEE). Each of these methods are sensitive to organic contaminants typically found in neutron tubes.

Due to reliability concerns, cleanliness levels of materials fabricated at Sandia and/or from incoming materials, prior to subsequent processing operations are of vital importance. In the reported case study, mineral oil is the primary contaminant. It is used as a lubricant during the forming of the neutron tube targets. The oil is applied to various metals and ceramic and then cleaned with either of two aqueous alkaline cleaning processes or with methylene chloride (MC). After cleaning, data obtained from each of the alternative methods was compared to AES data to determine the level of cleanliness.

Experimental Procedure/Coupon Study

Materials common to the neutron tube were evaluated. Four metals, including molybdenum, AISI stainless steel type 304, KovarTM, Triclad (KovarTM-Copper-KovarTM), and one ceramic (94% alumina) substrate were evaluated. In most cases, five substrates for each condition were tested. The substrates used for AES analysis were nominally 0.75" square. The substrates for MESERAN, contact angle and FTIR were 1.125" square. The ceramic substrates were 0.5" in diameter. To provide an initial uniform surface for analysis, each substrate was precleaned by vapor degreasing in trichloroethylene (TCE) for 2 minutes and rinsed in isopropyl alcohol (IPA)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

8

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

for an additional 2 minutes. The substrates were contaminated with a known amount (~ 0.3 ml for the 1.125" square coupons, ~ 0.2 ml for the 0.75" square coupons, and ~ 0.1-0.15 ml for the 0.5" diameter alumina discs) of mineral oil. To simulate a machining process, the substrates were heated on a hot plate, for approximately 5 minutes at 150°F. This procedure was derived after consulting an experienced machinist. After heating, the substrates were allowed to sit for approximately one hour before being cleaned.

Cleaning of substrates was performed with one of three different cleaning processes. The first process was the baseline cleaning process, using MC. Cleaning with MC was performed by ultrasonically cleaning for 5 minutes at ambient temperature, using a 40 KHz NEY ProSONIK ultrasonic cleaner. After cleaning, the substrates were ultrasonically rinsed in ambient IPA for 2 minutes and then blown dry with filtered dry nitrogen. The aqueous cleaning processes utilized aqueous alkaline cleaners Brulin 815GD and Oakite Citridet. Each cleaner was used in a 10% by volume cleaner/90% by volume deionized water (DIW) solution. Substrates were: 1) ultrasonically cleaned for 5 minutes in the specified aqueous alkaline cleaner at 135°F ±5°, 2) rinsed with ambient DIW for 2-3 minutes using spray nozzles and a hand spray, 3) rinsed with 120°F DIW for 5 minutes in the first of two cascading rinse stations, 4) rinsed with 120°F DIW for 5 minutes in the second of two cascading rinse stations, 5) ultrasonically rinsed in ambient IPA for 30-60 seconds (to expedite drying), and 6) blown dry with filtered dry nitrogen.

Cleanliness Evaluation Methods

Four alternative methods for determining cleanliness levels were studied as potential replacements for AES. The alternative methods included contact angle, MESERAN, FTIR and OSEE analyses. The following section discusses each of these methods, including AES in greater detail.

Residual surface contamination on metals and ceramics was measured by sputter depth profiling using a Physical Electronics Scanning Auger instrument. The analysis was done using a 5 keV accelerating voltage and approximately 500 nanoamps beam current. Sputtering was done using a rastered 3 keV Xenon ion beam, producing a sputter rate of approximately 140 ±10 Å/minute on a standard SiO₂ specimen. The sputter depth on the depth profile data can be approximated using this rate, but there is variation of sputter rate on the different materials, so the thickness measurements should only be used for comparative purposes. Before profiling each specimen, an AES survey was obtained from the area selected to identify the contaminants present. These elements were selected for depth profiling.

The attached depth profile data is displayed in tabulated and graphed form. The atomic concentrations were determined using tabulated sensitivity values supplied by the instrument manufacturer. These values cannot be considered accurate in absolute value, but can be used for direct comparison of each data set. The AES data for the plots includes noise levels, which explains why the contamination level does not go to zero percent after sputtering for some of the reported results. Either the contaminant was completely removed or present only below the detectability limits of the AES technique. The detection limit was nominally defined as approximately 1%, although it could be as low as 0.1% for Cl, which the AES technique is very sensitive to. The limit may be much higher in cases where AES peak overlaps occur. The data shown in the tables were normalized to a total of 100% at each sputter step. In some cases, the values for the contamination may not go to zero percent due to poor removal during sputtering caused by the surface roughness of the part being analyzed. Carbon can go to zero even though oxygen is still detected. This can occur because the AES technique is more sensitive (> 2.0) to oxygen than carbon.

A Ramé Hart Model 100/Contact Angle Goniometer was used to determine surface wettability. The goniometer test measures the contact (tangent) angle that is formed between a drop of water

and its supporting surface. In general, the cleaner and less oxidized the surface, the lower the contact angle measurement. The method is a qualitative measurement of surface wettability.

A MESERAN Surface Analyzer provided another analytical method for determining quantitative measurement of microorganic residues to nanogram levels using a slope technique. The MESERAN is one of the few non-destructive methods available for in-process organic contamination detection and measurement.² Its operation is based on the technology of Evaporative Rate Analysis. The technique measures the rate of evaporation of a carbon-14 tagged radioactive chemical with a Geiger counter. The carbon-14 labeled radiochemical used in the process is "Exempt" from United States Nuclear Regulatory Commission licensing requirements. The optimal slope of the log count versus time evaporation curve, expressed as a positive integer, is a valid inverse measure of the amount of residue, i.e., the higher the slope the less the residue.³

A third analytical method studied was FTIR. FTIR is a non-destructive method that is generally used by organic chemists to obtain useful structural information by referencing characteristic spectral bands to chemical functional groups.⁴ In this study, it was used to detect the presence of surface contaminants. Data was captured using a BioRad FTS-7 spectrometer with a specular reflectance attachment in the reflectance mode. This method detects light reflected off shiny metal surfaces. The larger the magnitude of reflectance - the cleaner the surface. The smaller the magnitude of reflectance - the more contaminated the surface. The latter is caused by organic compounds absorbing the directed light. The spectra frequency were run from 3998.4 to 401.38 cm^{-1} . The reflectance was summed over a large range to allow for differentiation between nearly identical spectra. The higher the reflectance totals, the shinier the surface. It should be noted that total reflectance numbers can only be compared within a single surface type in order to correlate degree of "shininess" to cleanliness. For example, stainless steel did not reflect as much light as Kovar™, even after the initial preclean step. Each different type of substrate will have a unique characteristic spectra.

An OSEE method was also evaluated as a potential replacement for AES. This method can detect both organic and inorganic contamination. Its principal of operation is as follows; a surface is illuminated with an ultraviolet light having a wavelength of 185 nanometers (6.7 electron volts), whereupon electrons are emitted from the surface. Emission of electrons is the key to the test method. Conductivity, porosity, or reflectivity of the material should have no effect on the outcome of the test. The electrons are collected and measured as a current, which is then converted into voltage. Depending on a particular contaminant's photoemission characteristics, the contaminant can either enhance or attenuate the inherent emission from the clean surface. A clean surface is a current generator and a contaminant acts as a resistance. In general, the thicker the contaminant, the higher the resistance and, consequently, the greater the decrease in measured signal.⁵

Auger Electron Spectroscopy Results and Discussion

AES data is presented for the various materials in tabular and graphical form. In general, both aqueous alkaline cleaners performed as well as the MC baseline cleaning process. Concentration values are reported in atomic %. Contamination thicknesses were determined by estimating the inflection point of the curve from the depth profiles. The inflection point was defined as the half-way point of the slope of the interface. The time (in minutes) to the inflection point was then determined from these curves and multiplied by the sputter rate to arrive at a thickness. It should be noted that this is a subjective method for determining thicknesses and the results are approximations. Yet, it is clear that the results of the data indicate that all samples analyzed with AES are relatively clean per the reference standards. Representative samples of molybdenum cleaned with the different cleaners are shown in Tables 1-4 and Figures 1-4.

Table 1 and Figure 1 show the results for molybdenum precleaned with TCE and IPA. Carbon was measured to be approximately 14 Å and oxygen was estimated to be approximately 70 Å. After contaminating with mineral oil and cleaning with MC, (Table 2 and Figure 2), approximately 14 Å residual carbon and 84 Å oxygen were measured. As seen in Table 3 and Figure 3, residual carbon after contamination and cleaning with Brulin 815GD was 27 Å and oxygen was 22 Å. The coupon contaminated with mineral oil and cleaned with Oakite Citridet (Table 4 and Figure 4), had approximately 38 Å of carbon and 17 Å of oxygen. For molybdenum, the MC cleaning process reflected the carbon level of the original preclean state and the oxygen levels were approximately the same. Brulin 815GD and Oakite Citridet indicate higher carbon levels, but less oxides as indicated by the lower oxygen levels.

For the representative stainless steel coupon, the residual carbon after the preclean condition was approximately 16 Å and the oxygen level was approximately 38 Å. After contamination and cleaning with MC, the carbon level was approximately 20 Å and the oxygen level was 43 Å. Trace levels of calcium and sulfur were also detected. Coupons contaminated and cleaned with Brulin 815GD measured approximately 13 Å of carbon and 54 Å of oxygen. In addition to carbon and oxygen, approximately 26 Å of silicon was detected as well as a trace level of sulfur. Coupons contaminated and cleaned with Oakite Citridet measured approximately 16 Å of carbon and 54 Å of oxygen, with trace levels of sulfur. The residual silicon and sulfur could have either come from the bulk metal alloy or from residual cleaner from the cleaning process. Regardless of the source, the levels detected are considered insignificant. In this case, it appears that all three cleaners cleaned stainless steel 304 equally well.

The representative Kovar™ coupon after precleaning exhibited approximately 13 Å residual carbon and approximately 22 Å oxygen. After contaminating and cleaning with MC, residual carbon was approximated at 14 Å for both carbon and oxygen and 32 Å for silicon. The Kovar™ coupon that was contaminated and cleaned with Brulin 815GD had approximately 17 Å of carbon, 22 Å of oxygen, 13 Å of silicon and a trace amount of sulfur. The contaminated coupon cleaned with Oakite Citridet exhibited approximately 11 Å of residual carbon and 22 Å of oxygen. Again, AES demonstrates that MC, Brulin 815GD and Oakite Citridet cleaned Kovar™ approximately the same.

Due to surface charging problems associated with the ceramic substrate, the AES method was not pursued. Some preliminary cleaning studies were performed using x-ray photoelectron spectroscopy, but the results are not presented in this paper.

Goniometer/Contact Angle Test Results and Discussion

For statistical purposes, five samples per condition were tested. Measurements were taken after the preclean process, and after contaminating with mineral oil and cleaning with either Brulin 815GD, Oakite Citridet or MC. Test results are summarized in Table 5. The average contamination level detected on molybdenum after the preclean process was $13^{\circ} \pm 3^{\circ}$. After contamination with mineral oil, cleaning with Brulin 815GD recorded values of $9^{\circ} \pm 0.8^{\circ}$, while cleaning with Oakite Citridet recorded values of $9^{\circ} \pm 2^{\circ}$ and MC recorded values of $14^{\circ} \pm 3^{\circ}$. Each of the three cleaners returned the molybdenum surface back to its original preclean state and it appears that both aqueous cleaners may have cleaned slightly better. It appears that molybdenum is polished when it comes into contact with water i.e., when cleaning with the aqueous alkaline cleaners as well as when performing contact angle measurements after cleaning with TCE/IPA and MC.

The preclean average value of $55^{\circ} \pm 2^{\circ}$ for stainless steel 304 was much higher than the preclean value recorded for molybdenum. After contaminating with mineral oil, cleaning with Brulin 815GD recorded an average value of $10^{\circ} \pm 1^{\circ}$, while Oakite Citridet recorded an average value of

33° ±2° and MC recorded an average value of 59° ±6°. It is clear in this case, that the aqueous cleaners performed significantly better than MC, with Brulin 815GD cleaning the best. On the other hand, the decrease in angle could be an effect of the cleaner modifying the surface energy.

The same general trend can be seen for Kovar™ and aluminum oxide, whereby Brulin 815GD and Oakite Citridet cleaned significantly better than MC, with Brulin 815GD cleaning the best. In addition to removing organic contaminants from the surface, it is possible that the aqueous cleaners are polishing the surface.¹ In most cases, the standard deviation was very small.

MESERAN Test Results And Discussion

As with the goniometer measurements, five samples per condition were tested. The tests were performed after the samples were precleaned with TCE and IPA, contaminated with mineral oil, and then cleaned with Brulin 815GD, Oakite Citridet, or MC. Unless specifically stated, the slope values are the average of a particular group of five. The preclean slope values for molybdenum and stainless steel are an average of three samples. The results are listed in Table 6.

The MESERAN slope after TCE/IPA preclean for molybdenum was 2356 with a standard deviation of 850. Sample number 1 of this group of three exhibited a slope of 1378. Samples 2 and 3, having significantly higher slope values, were more representative of a clean surface. If slope 1 is deleted, the average slope then becomes 2848 with a standard deviation of 94. The slope for molybdenum cleaned with Brulin 815GD was 2750 with a standard deviation of 178. The slope after cleaning with Oakite Citridet was 2449 with a standard deviation of 294, and the slope after cleaning with MC was 2455 with a standard deviation of 494. One sample in the MC molybdenum group had a slope value of 1627, significantly lower than each of the other four. There are two possible explanations why significantly lower slopes occurred within a group: 1) the sample might not have been cleaned as well as the others in the group, or 2) there might be a slight difference in its surface characteristics, such as microcracks in the surface or other surface irregularities that could retain the radiochemical longer, resulting in the lower slope value. It appears that Brulin 815GD cleaned the mineral oil off molybdenum better and more consistently than Oakite Citridet or MC, but did not display a slope as high as the original preclean state. Based upon MESERAN calibrations for similar contaminants, the slopes obtained for this grouping are indicative of approximately 0.1 nanograms/cm² for Brulin 815GD and approximately 1 nanogram/cm² for Oakite Citridet and MC. Based on these values, the preclean condition was probably < 0.1 nanograms/cm².

The slope value after TCE preclean for stainless steel type 304 was 3043 with a standard deviation of 273. The slope for stainless steel 304 cleaned with Brulin 815GD was 3200 with a standard deviation of 131. The slope for samples cleaned with Oakite Citridet was 3180 with a standard deviation of 220, and the slope after cleaning with MC was 2554 with a standard deviation of 203. For the stainless steel 304 group, Brulin 815GD cleaned the mineral oil better and more consistently than MC and slightly better than Oakite Citridet. Both Brulin 815GD and Oakite Citridet had higher slopes than the original preclean state. Based upon MESERAN calibrations for similar contaminants, the slopes obtained for this grouping are indicative of < 0.1 nanograms/cm² for the TCE/IPA preclean, Brulin 815GD and Oakite Citridet cleaning processes. The MC samples are indicative of approximately 1 nanogram/cm². For comparison purposes, a representative calibration curve for sunquench oil on glass cones is shown in Figure 5. Sunquench oil and mineral oil have similar carbon chain lengths. Calibration curves for mineral oil still need to be determined.

The slope for Kovar™ after TCE preclean was 2012 with a standard deviation of 402. The slope for Kovar™ cleaned with Brulin 815GD was 2218 with a standard deviation of 142. The slope for

samples cleaned with Oakite Citridet was 1862 with a standard deviation of 196 and the slope after cleaning with MC was 2231 with a standard deviation of 504. As in the case of the MC molybdenum group, one sample in the MC Kovar™ group had a low slope value of 1474. The same reasoning mentioned above for low slopes within a particular group applies. The MC and Brulin 815GD cleaning processes removed the mineral oil from the Kovar™ comparably, and better than the Oakite Citridet, but the Brulin 815GD standard deviation was significantly lower than that of MC, 142 compared to 504. Both the Brulin 815GD and the Oakite Citridet had higher slope values than the preclean group. In this case, actual contamination levels could not be determined for the Kovar™ group because the MESERAN calibration curve for mineral oil on Kovar™ has yet to be determined. However, if the calibration curve on Kovar™ is similar to other metals and contaminants already defined, the slope values obtained indicate that the Kovar™ was not as clean as the molybdenum and stainless steel samples, regardless of which cleaning process was used.

The slope after TCE preclean for alumina was 863 with a standard deviation of 232. The slope for alumina cleaned with Brulin 815GD was 803 with a standard deviation of 423. The slope for samples cleaned with Oakite Citridet was 1224 with a standard deviation of 655, and the slope after cleaning with MC was 1534 with a standard deviation of 437. The variance was relatively high for all cleaning methods on alumina. In this case, MC cleaned the alumina samples better than the TCE/IPA preclean, Brulin 815GD, and Oakite Citridet cleaning processes. It should be noted that the manufacturer of the MESERAN Micro Organic Residue Analyzer does not recommend utilizing the MESERAN test method to directly analyze cleanliness levels of ceramic materials. The surfaces of these materials are considered too porous to obtain accurate data. Instead, the substrate can be extracted with a solvent and the extract can then be deposited onto a clean reference surface for MESERAN analysis.

As with the other test methods, it is important to note, that different substrates and contaminants may produce different MESERAN results. One cannot compare results of one material type with another. Comparisons must be made within the test group of the same material.

FTIR Results And Discussion

Statistical methods were used to decide whether the performance of one cleaner was different from another cleaner. Two points of interest were evaluated: 1) How well the cleaners performed (including MC) in returning the surface to the precleaned condition, and 2) how well Brulin 815GD and Oakite Citridet cleaned compared to MC.

In the first case, the null hypothesis (H_0) is: alternate cleaner cleans the same as TCE/IPA. In the second case, H_0 is : alternate cleaner cleans the same as MC. The rejection region is two tailed and is based on a t-distribution using (n_1+n_2-2) as the pooled degrees of freedom. A 95% confidence interval ($\alpha = 0.05$) was also used. The rejection region is: $t < -t_{\alpha/2}$ or $t > t_{\alpha/2}$.

In Table 7, the column titled "Conclusions: Alternate Cleaners vs. Trichloroethylene," the data was worked using the null hypothesis: Alternate cleaner cleans the same as TCE. Looking at the data for molybdenum, the average total reflectance for MC on molybdenum with mineral oil (2841) was very close in number to Brulin 815GD on molybdenum with mineral oil (2903). For the molybdenum set, there were 6 pooled degrees of freedom, so for $\alpha = 0.05$, the hypothesis would be rejected if $t < -2.447$ or $t > 2.447$ for all molybdenum samples. For molybdenum contaminated with mineral oil and cleaned with MC, t was calculated to be 3.07, resulting in a null hypothesis rejection. Therefore, MC did not clean molybdenum as well the TCE/IPA preclean.

In the case of molybdenum contaminated with mineral oil and cleaned with Brulin 815GD, t was calculated to be 2.19. Therefore, H_0 is accepted, which means that the alternative cleaner cleaned the same as TCE. If H_0 is rejected, then either the alternative cleaner cleaned better or worse than TCE. To determine if the cleaning efficacy was better or worse, the average total reflectance was consulted for both the alternative cleaner in question and TCE. If the average total reflectance is greater than that of TCE, then the alternative cleaner is said to have "cleaned better than TCE." If the average total reflectance is less than TCE, then the alternative cleaner is said to have "cleaned worse than TCE."

The same rationale was followed for the other column titled, "Conclusions: Alternate Cleaner vs. Methylene Chloride." The other data sets, stainless steel and Kovar™ both had a pooled degree of freedom equal to 8. This means that the t calculated for these sets is rejected if it falls outside the following: $t < -2.306$ or $t > 2.306$. Results for this scenario can also be seen in Table 7.

OSEE Results And Discussion

A total of thirty five samples were sent to Photo Emission Technology Inc. for analysis by OSEE. The materials included Kovar™, alumina and Triclad. Due to lack of resources and time, not all the different types of materials were tested. Two samples per surface condition were analyzed, except for Kovar™ cleaned with Citridet, which only had one sample. In general, the higher the voltage reading, the cleaner the surface. Because there was no clean standard to reference, it was assumed that the highest value obtained within a material group was 100% clean. All other values within a group were then compared to the highest value. Results are shown in Table 8.

The results for Kovar™ indicate that the samples cleaned with Brulin 815GD along the manufacturing line had the highest reading of 8.24 volts and, therefore, the cleanest surface. If one assumes that this value is 100% clean, then the samples cleaned with Brulin 815GD in a laboratory situation, which had the next highest reading of 6.39 volts were the next cleanest at 87.9%. This was calculated by taking the natural log of each number, dividing the smaller number by the larger number and then multiplying by 100 to obtain a relative percent. The rest of the cleanliness percentages were determined in a similar manner and are: 1) Oakite Citridet at 6.27 volts in a laboratory situation recorded 87.0% clean, followed by 2) Oakite Citridet along the manufacturing line at 4.30 volts or 69.2% clean, and 3) 2.62 volts or 45.7% clean when cleaned with MC. The as-received samples were considered the dirtiest at < 1% clean. For Kovar™, Brulin 815GD appears to clean the best, regardless of whether it was cleaned along the manufacturing line or in a laboratory situation.

The results for alumina indicate that the Oakite Citridet cleaning process along the manufacturing line exhibited the highest value of 6.21 volts and therefore 100% clean. This was followed closely by MC cleaning with 5.39 volts or 92.2% clean, followed by Oakite Citridet cleaning in a laboratory situation with 4.83 volts or 86.2% clean. Brulin 815GD cleaning in a manufacturing line was next with 4.38 volts or 80.9% clean, followed by the as-received condition at 2.73 volts or 55.0% clean and Brulin 815GD in a laboratory situation with the lowest reading of 1.03 volts or 1.6% clean. It is difficult to ascertain why the alumina samples cleaned with Brulin 815GD were dirtier than the as-received samples. In general, Oakite Citridet appeared to clean the alumina substrate better than either Brulin 815GD or MC.

For Triclad, samples cleaned with Brulin 815GD along the manufacturing line appear to be significantly cleaner (11.85 volts or 100% clean) than any of the other cleaning processes. Oakite Citridet cleaning in a laboratory situation recorded the next highest value of 7.24 volts or 80.1% clean, followed by Brulin 815GD in a laboratory situation with 4.70 volts or 62.6% clean,

followed by Oakite Citridet along the manufacturing line with 3.65 volts or 52.4% clean, followed by MC cleaning with 1.36 volts or 12.4% clean and finally the as-received condition with 1.02 volts or 0.8% clean.

With the exception of the alumina samples cleaned with MC, it appears that the aqueous alkaline cleaners cleaned better than the MC baseline cleaning process. On the other hand, there does not appear to be any real consistency in the data obtained so far, possibly because of the lack of replicates.

Correlation's Between Different Methods of Analysis

A subjective inflection point method was used to estimate cleanliness levels after AES analysis. This method of analysis yielded results that were difficult to distinguish for stainless steel and Kovar™. However, there were distinguishable differences in oxygen and carbon levels for molybdenum. Although the method may be subjective, it is clear from the data that the samples analyzed using AES are clean per the reference standards. As a result, it is difficult to directly correlate the results of the other methods to AES. Furthermore, some of the alternative methods studied exhibited relatively high scatter in data and it would appear that more replicates are required before any direct correlation's can be made.

Contact angle measurements appear to have the smallest standard deviations of all the methods and it appears that the aqueous alkaline cleaners cleaned better than the MC and preclean cleaning processes. For example, for stainless steel, Brulin 815GD cleaned much better (10°) than either the preclean average of 55° or the MC clean average of 59°. No direct correlation's can be made to AES because as noted above. The MESERAN method provides slope values for the various substrates that define cleanliness levels down to the nanogram/cm² level. FTIR provides a statistical method that compares the difference between two population means for determining whether a cleaner is acceptable or not. OSEE provides information in volts that can be used to determine contamination thicknesses. Again, distinctions in cleanliness levels can be made with MESERAN, FTIR and OSEE but they cannot be directly correlated to AES.

Summary

Several analytical methods for determining cleanliness levels along the manufacturing line were studied as potential replacements for AES. The methods included, goniometer/contact angle measurements, MESERAN, FTIR and OSEE. An attempt was made to correlate the results of each of these methods back to AES. Each of the methods selected for this study are sensitive to organic contamination to varying degrees; i.e. the goniometer or contact angle measurement is considered qualitative because it gives an indication of how clean a surface is via a tangent angle, the MESERAN method is considered quantitative because it provides information of how much contamination there is on a surface per square area, FTIR is considered quantitative because it provides structural information about the surface contaminants of interest, and OSEE is considered quantitative because it provides information that can be correlated to contamination thicknesses within a range up to 300 Å. While some comparisons can be made between these methods and AES, there does not appear to be a direct correlation to AES under the investigated test conditions. Each of the methods studied is unique and provides useful information about the cleanliness levels of a surface. Further studies including more test replicates, and the development of calibration curves for each technique are required before a final determination can be made on which method is most suitable.

Acknowledgments

The authors would like to acknowledge Ginger De Marquis, Ed O'Toole and Wayne Buttry of Sandia National Laboratories, and Mark Benkovich of Allied Signal Kansas City, Federal Manufacturing Technology, for interpretation of results and for assisting in the writing of this report. The manuscript was reviewed by Mike Hosking of Sandia.

References

1. E. P. Lopez, J. A. Ohlhausen, D. E. Peebles, and M. G. Benkovich, "Environmentally Conscious Manufacturing Solvent Substitution Program/Switch Tube Assemblies Final Report," (Technical Report SAND95-1205, Sandia National Laboratories, 1995).
2. L. C. Jackson, "Contaminant Cleaning For Critical Electrical Assembly Areas", (Final Report), Unclassified, Allied Signal Inc., Kansas City Division: BDX-613-1695, February, 1978.
3. John L. Anderson and Mark G. Benkovich, "Quantification of Microorganic Residues To Low Nanogram Levels", Precision Cleaning 96 Conference Proceedings, May 15-16, 1996.
4. Ginger De Marquis, Ed O'Toole, and Carl Robinson, "Evaluation of FTIR Technique for Measuring Cleaning Efficacy", October 16, 1996.
5. Mantosh K. Chawla, "How Clean Is Clean?, A Quantitative Answer, Presented at Surface/Finish '90, Boston, Massachusetts, July 10, 1990.

*This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

Table 1 - AES Analysis of Molybdenum After Preclean

Sputter Time (min)	Mo at%	O at%	C at%	N at%
0.0	29	39	16	16
0.2	45	39	6	11
0.4	58	30	4	8
0.6	68	23	4	5
0.8	74	19	3	4
1.0	78	15	3	4
1.2	82	13	3	3
1.4	84	11	3	2
1.6	86	9	2	2
1.8	88	8	3	1
2.0	90	7	2	1
2.2	89	7	3	2
2.4	90	6	2	2
2.6	91	6	2	1
2.8	92	5	2	1
3.0	93	4	1	1
3.2	93	4	2	1
3.4	94	4	2	1
3.6	94	3	2	1
3.8	94	3	2	1
4.0	94	3	2	1
4.2	95	3	2	1
4.4	96	3	1	1
4.6	95	3	2	1
4.8	95	3	2	1
5.0	96	2	2	0

Figure 1 - AES Analysis of Molybdenum After Preclean

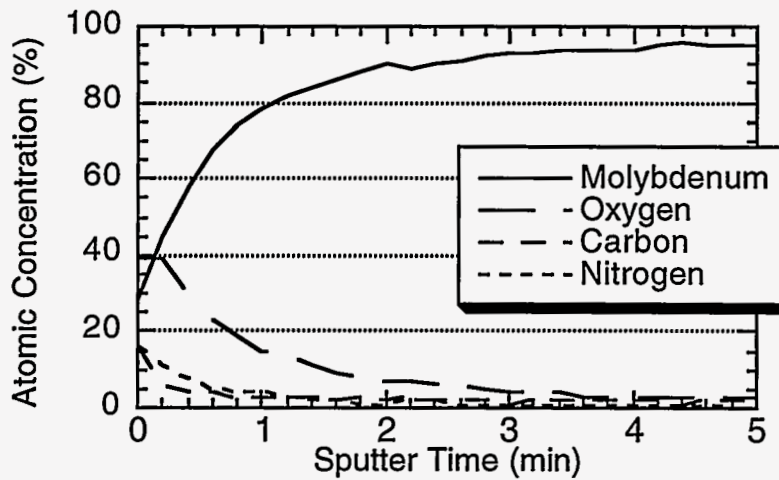


Table 2 - AES Analysis of Molybdenum After Methylene Chloride Clean

Sputter Time (min)	Mo at%	O at%	C at%	N at%	Ca at%
0.0	24	40	19	13	4
0.2	25	39	19	14	3
0.4	34	42	8	11	5
0.6	45	36	6	8	5
0.8	61	25	5	5	3
1.0	74	16	5	3	2
1.2	80	11	4	2	3
1.4	84	8	4	2	3
1.6	87	7	3	1	2
1.8	88	6	3	1	2
2.0	88	5	4	1	2
2.2	88	5	3	1	2
2.4	91	4	3	1	1
2.6	90	4	3	1	2
2.8	93	3	2	0	2
3.0	90	4	3	1	1
3.2	92	3	3	0	2
3.4	92	3	3	0	2
3.6	93	3	3	1	1
3.8	92	3	3	1	1
4.0	93	3	2	1	1
4.2	94	2	2	0	2
4.4	93	3	3	1	1
4.6	94	2	2	0	2
4.8	94	2	2	0	1
5.0	96	1	1	0	1

Figure 2 - AES Analysis of Molybdenum After Methylene Chloride Clean

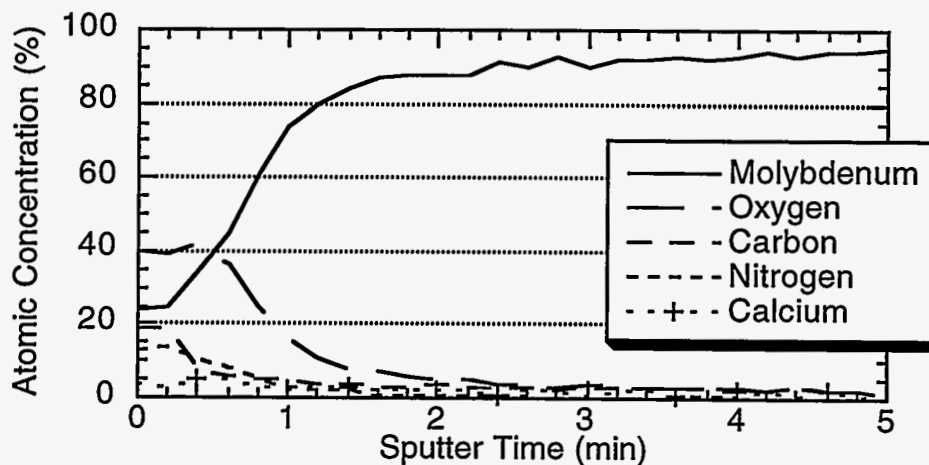


Table 3 - AES Analysis of Molybdenum After Brulin 815GD Clean

Sputter Time (min)	Mo at%	O at%	C at%	N at%
0.0	50	13	34	3
0.2	81	5	13	1
0.4	89	3	8	0
0.6	93	2	6	0
0.8	94	1	4	1
1.0	95	2	4	0
1.2	94	1	4	1
1.4	95	2	3	0
1.6	95	1	3	1
1.8	96	1	2	0
2.0	96	1	2	1
2.2	96	1	3	1
2.4	95	1	4	1
2.6	96	1	3	1
2.8	96	1	3	0
3.0	96	1	3	0
3.2	96	1	3	0
3.4	96	1	2	0
3.6	96	1	3	1
3.8	97	1	2	0
4.0	96	1	3	0
4.2	96	1	2	1
4.4	96	1	3	0
4.6	95	1	3	1
4.8	96	1	2	0
5.0	96	1	3	0

Figure 3 - AES Analysis of Molybdenum After Brulin 815GD Clean

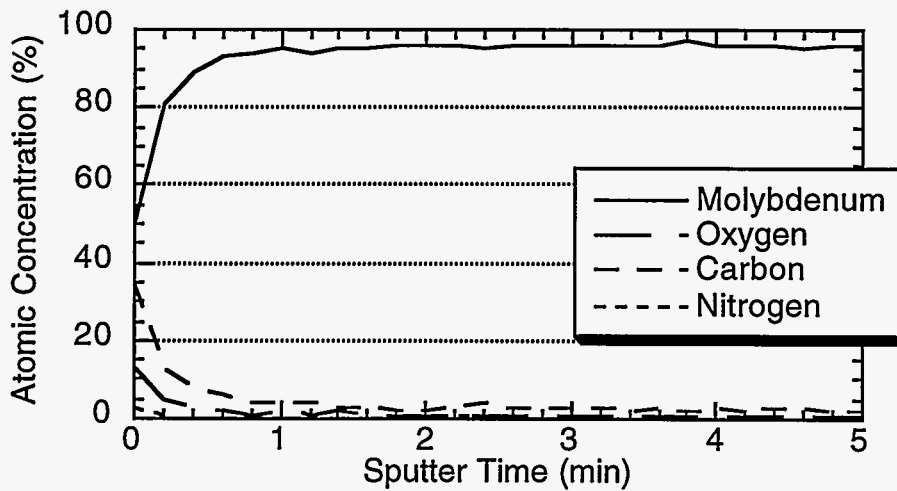


Table 4 - AES Analysis of Molybdenum After Oakite Citridet Clean

Sputter Time (min)	Mo at%	O at%	C at%	N at%
0.0	37	13	47	3
0.2	69	4	26	1
0.4	84	2	13	1
0.6	89	1	10	1
0.8	91	1	7	1
1.0	91	1	7	1
1.2	91	1	7	1
1.4	93	1	5	1
1.6	94	1	5	1
1.8	94	1	4	1
2.0	95	1	4	1
2.2	95	1	4	0
2.4	96	1	3	0
2.6	96	1	3	0
2.8	96	1	3	0
3.0	96	1	3	1
3.2	95	1	4	0
3.4	95	1	3	1
3.6	97	1	2	0
3.8	95	1	3	0
4.0	96	1	2	1
4.2	96	0	3	0
4.4	97	0	2	1
4.6	96	1	3	0
4.8	98	1	2	0
5.0	97	0	2	1

Figure - 4 AES Analysis of Molybdenum After Oakite Citridet Clean

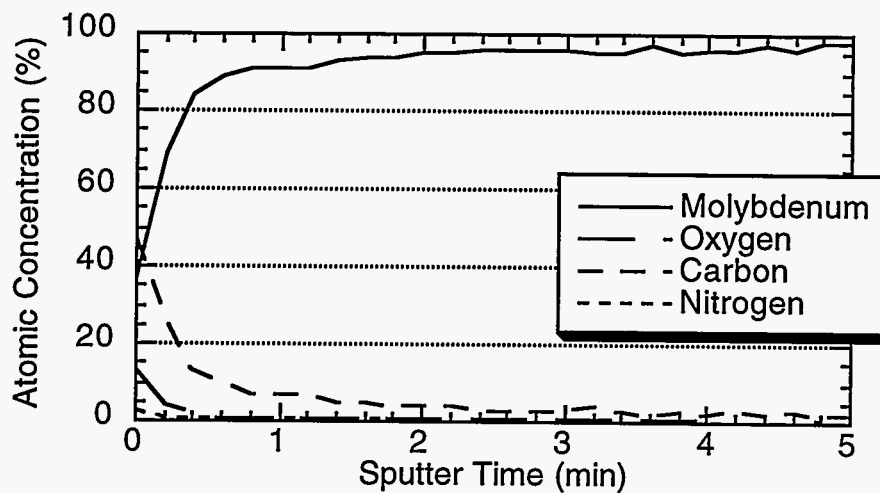


Figure 5
Calibration Curve For
Sunquench Oil On Glass Cones
(Ln Smoothed MESERAN Slope Values)

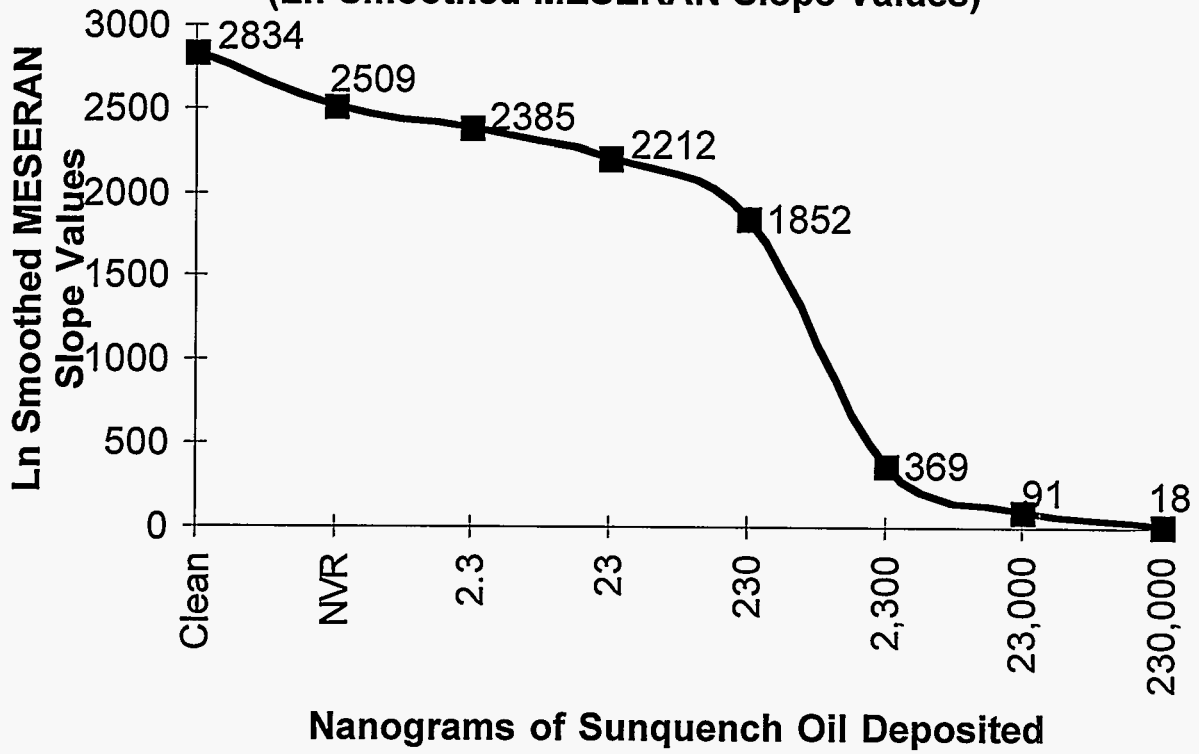


Table 5 - Contact Angle Test Results

	Material: Molybdenum		Contaminant: Mineral Oil	
	<u>Preclean</u>	<u>10% Brulin 815GD</u>	<u>10% Oakite Citridet</u>	<u>Methylene Chloride</u>
Sample #1	15°	9°	10°	15°
Sample #2	10°	10°	12°	12°
Sample #3	15°	8°	8°	11°
Sample #4	10°	10°	6°	14°
Sample #5	9°	9°	9°	18°
AVG	13.3°	*9.2°	*9°	*14°
STD	2.9	0.8	2.2	2.7

	Material: Stainless Steel 304		Contaminant: Mineral Oil	
	<u>Preclean</u>	<u>10% Brulin 815GD</u>	<u>10% Oakite Citridet</u>	<u>Methylene Chloride</u>
Sample #1	57°	10°	33°	50°
Sample #2	53°	9°	30°	59°
Sample #3	55°	11°	34°	62°
Sample #4	-	10°	33°	63°
Sample #5	-	12°	36°	
AVG	55°	10.4°	33.2°	58.5°
STD	2.0	1.1	2.2	5.9

	Material: Aluminum Oxide		Contaminant: Mineral Oil	
	<u>Preclean</u>	<u>10% Brulin 815GD</u>	<u>10% Oakite Citridet</u>	<u>Methylene Chloride</u>
Sample #1	67°	16°	51°	54°
Sample #2	62°	21°	34°	50°
Sample #3	61°	15°	36°	50°
Sample #4	-	21°	36°	53°
Sample #5	-	18°	42°	65°
AVG	63.3°	18.2°	39.8°	54.4°
STD	3.2	2.8	6.9	6.2

	Material: Kovar		Contaminant: Mineral Oil	
	<u>Preclean</u>	<u>10% Brulin 815GD</u>	<u>10% Oakite Citridet</u>	<u>Methylene Chloride</u>
Sample #1	54°	10°	24°	59°
Sample #2	50°	7°	26°	61°
Sample #3	54°	9°	28°	58°
Sample #4	44°	7°	30°	54°
Sample #5	57°	8°	30°	61°
AVG	51.8°	8.2°	27.6°	58.6°
STD	5.0	1.3	2.6	2.9

Note: An asterik (*) indicates the water drop administered for the contact angle measurement reacted severly with the molybdenum substrate. The water appeared to polish the surface upon contact and therefore continue to spread on the surface while the angle was being read.

Table 6 - MESERAN Test Results

	Material: Molybdenum		Contaminant: Mineral Oil	
	<u>Preclean</u>	<u>10% Brulin 815GD</u>	<u>10% Oakite Citridet</u>	<u>Methylene Chloride</u>
	Slope	Slope	Slope	Slope
Sample #1	1378	2718	2252	2603
Sample #2	2779	2517	2114	2933
Sample #3	2912	3018	2517	1627
Sample #4		2738	2884	2455
Sample #5		2758	2479	2655
AVG	2356	2750	2449	2455
STD	850	178	294	494

	Material: Stainless Steel 304		Contaminant: Mineral Oil	
	<u>Preclean</u>	<u>10% Brulin 815GD</u>	<u>10% Oakite Citridet</u>	<u>Methylene Chloride</u>
	Slope	Slope	Slope	Slope
Sample #1	2978	3117	2845	2396
Sample #2	3343	3200	3171	2665
Sample #3	2808	3411	3260	2299
Sample #4		3201	3452	2796
Sample #5		3070	3170	2613
AVG	3043	3200	3180	2554
STD	273	131	220	203

	Material: Aluminum Oxide		Contaminant: Mineral Oil	
	<u>Preclean</u>	<u>10% Brulin 815GD</u>	<u>10% Oakite Citridet</u>	<u>Methylene Chloride</u>
	Slope	Slope	Slope	Slope
Sample #1	1147	392	1312	1366
Sample #2	941	858	2279	1042
Sample #3	935	912	686	1627
Sample #4	767	1427	672	1415
Sample #5	525	426	1170	2220
AVG	863	803	1224	1534
STD	232	423	655	437

	Material: Kovar™		Contaminant: Mineral Oil	
	<u>Preclean</u>	<u>10% Brulin 815GD</u>	<u>10% Oakite Citridet</u>	<u>Methylene Chloride</u>
	Slope	Slope	Slope	Slope
Sample #1	1575	2333	1728	2287
Sample #2	1815	2153	2017	2086
Sample #3	1804	2000	2126	1474
Sample #4	2532	2333	1747	2482
Sample #5	2335	2272	1692	2828
AVG	2012	2218	1862	2231
STD	402	142	196	504

**Table 7 - Cleaning Efficacy Measured Using FTIR
Using Specular Reflectance**

Reflectance was measured over the range of 3998.4 to 401.38
cm⁻¹. Summing the reflectance over a large range allows the
differentiation between very subtle differences between spectra.

Substrate Condition	Ave Total Reflect ance	%CV	t	Conclusions: Alternate Cleaner vs. trichloroethylene (TCE)	t	Conclusions: Alternate Cleaner vs. Methylene Chloride (MC)
TCE on Moly (Pre-Clean)	3226	3.3		(trichloroethylene)	-3.07	TCE cleaned better than MC
MC on Moly w/min oil	2841	6.9	3.07	MC cleaned worse than TCE		(Methylene Chloride)
Burlin on Moly w/min oil	2903	8.1	2.19	Burlin cleaned the same as TCE	-0.45	Burlin cleaned the same as MC
Citridet on Moly w/min oil	3240	3.2	-0.19	Citridet cleaned the same as TCE	-4.02	Citridet cleaned better than MC
TCE on SS (Pre-Clean)	2413	3.8		(trichloroethylene)	1.18	TCE cleaned the same as MC
MC on SS w/min oil	2469	2.1	-1.18	MC cleaned the same as TCE		(Methylene Chloride)
Burlin on SS w/min oil	2552	2.6	-2.75	Burlin cleaned better than TCE	-2.22	Burlin cleaned the same as MC
Burlin on SS w/min oil	2582	1.6	-3.71	Burlin cleaned better than TCE	-3.73	Burlin cleaned better than MC
Citridet on SS w/min oil	2489	1.2	-1.73	Citridet cleaned the same as TCE	-0.70	Citridet cleaned the same as MC
TCE on Kovar (Pre-Clean)	3201	2.2		(trichloroethylene)	3.69	TCE cleaned worse than MC
TCE on Kovar (Pre-Clean)	3284	3.8	-1.29	N/A	0.84	TCE cleaned the same as MC
MC on Kovar w/min oil	3334	1.2	-3.69	MC cleaned better than TCE		(Methylene Chloride)
Burlin on Kovar w/min oil	3443	1.9	-5.64	Burlin cleaned better than TCE	-3.19	Burlin cleaned better than MC
Citridet on Kovar w/min oil	3288	3.4	-1.46	Citridet cleaned the same as TCE	0.85	Citridet cleaned the same as MC

Table 8 - OSEE Results

Sample Condition	Alumina Mean (Volts)	Kovar TM Mean (Volts)	Triclad Mean (Volts)
As Received	2.73	0.86	1.02
Methylene Chloride	5.39	2.62	1.36
*Brulin 815GD	1.03	6.39	4.70
*Oakite Citridet	4.83	6.27	7.24
**Brulin 815GD	4.38	8.24	11.85
**Oakite Citridet	6.21	4.30	3.65

Note: Samples designated with one asterik () are samples cleaned in a laboratory situation. Samples designated with two asteriks (**) are samples cleaned on the manufacturing line.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
