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Evaluation of Aqueous Cleaners as Alternatives to Vapor Degreasing

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Stephen J. Martin, George Moore

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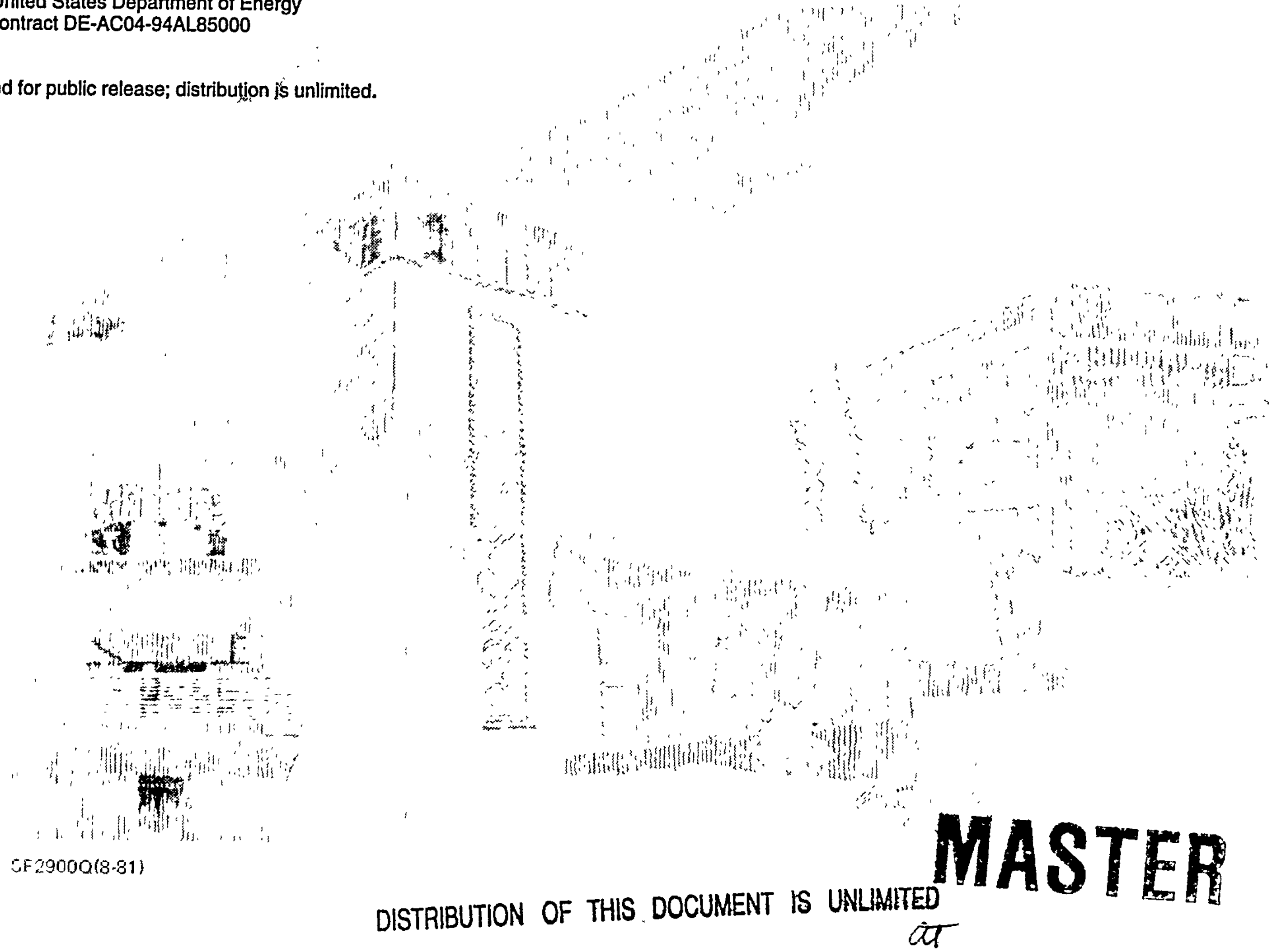

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Evaluation of Aqueous Cleaners as Alternatives to Vapor Degreasing

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Abstract

As part of the preparation process during assembly of thermally activated batteries, the stainless steel piece parts are normally cleaned by vapor degreasing with trichloroethylene. Severe restrictions on the use of chlorinated and fluorinated hydrocarbons in recent years prompted the evaluation of a number of aqueous cleaners as a replacement technology for this application. A total of seven commercial aqueous degreasers was evaluated in this study at several dilution ratios and temperatures. One organic cleaner was also examined under ambient conditions. The effectiveness of the cleaner was determined by the use of x-ray photoelectron spectroscopy (XPS), which is a surface analytical technique that is very sensitive to low levels of surface contaminants. A quartz-crystal microbalance (QCM) that is immersed in the cleaning bath was evaluated as a tool for monitoring the bath cleanliness. The best overall cleaning results were obtained with Micro, Impro-Clean 3800, and Sonicor cleaners.

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Evaluation of Aqueous Cleaners as Alternatives to Vapor Degreasing

Introduction

As part of the preparation process during assembly of thermally activated batteries, a number of stainless steel piece parts require thorough cleaning to remove films of oil, grease, and wax. These metal parts include the battery case, current collectors, blank end plates, and headers which are metal plates containing glass-to-metal feedthroughs. In the past, these were normally cleaned by vapor degreasing with trichloroethylene, since this provided excellent results. However, severe restrictions as a result of the Montreal Protocol have been imposed on the use of chlorinated and fluorinated hydrocarbons in recent years. These materials have been linked with destruction of the protective ozone layer in the upper atmosphere. The Department of Energy (DOE) has mandated that these halogenated organic cleaners can no longer be used at any of the facilities within the nuclear-weapon complex, which includes Sandia National Laboratories and, until last year, Martin-Marietta Specialty Components, Inc. (Largo, FL).

A number of alternatives were considered. One possibility involved the use of non-halogenated organic solvents. This option would be difficult to implement because of costs and concerns involving environmental safety and health (ES&H) issues at Sandia and the DOE. The flammability and toxicity of such solvents would make them unacceptable.

A second alternative considered was supercritical extraction with CO_2. This was deemed too costly and time-consuming for a production environment. In addition, the high pressures and large tanks required were ES&H concerns.

A third option was the use of aqueous cleaners. On first examination, there did not appear to be any serious ES&H issues with this technology. It is relatively easy to use and the cost should be reasonable. There are a fair number of commercial aqueous cleaners on the market, with a wide variety of active ingredients. Some of the aqueous cleaners are terpene based, while others contain various proprietary alcohols, activators, and surfactants. Inhibitors are usually added to prevent corrosion of metal parts during cleaning. (Compatibility of the cleaner with the parts to be cleaned can be an important issue for some materials.) Many have little or no volatile organic compounds (VOCs), which increases safety by minimizing flammability and personnel-exposure concerns. Many are biodegradable, which facilitates waste disposal. Consequently, they are considered environmentally benign.

We decided to pursue the last option, as it appeared to be the most viable one for implementation at Sandia and for the DOE in the long run to address cleaning needs, based on preliminary work at Sandia, Martin-Marietta, and Allied Signal, Kansas City, MO. A total of seven commercial aqueous degreasers was evaluated in our study. A commercial organic solvent was added later in the study, for comparative purposes, fully realizing that it was unlikely to be used.

To be practical, it was envisioned that parts would be cleaned in a batch mode, rather than using a once-through technique. Since the contaminants would continue to accrue with repeated use, some means of monitoring the bath would be necessary. The bath could be monitored either directly for the contaminants or indirectly for the concentration of the active cleaning ingredients. This information would be necessary for deciding when to replace the bath. Ideally, it was desirable to be able to monitor the bath in real time, to gauge the rate of cleaning.

One analytical technique that was considered for solution monitoring was Fourier transform infrared spectroscopy (FTIR). There are a number of difficulties associated with such a technique for aqueous cleaners. First, the bath is composed of many ingredients that would be active in the IR region. The nature of the organic contaminant that is to be removed is not always known and can vary, depending on the sample history; i.e., the component for which an IR signature could be tracked during cleaning was undefined. What is more important, the small of amount of organic contaminant would be lost in the noise of the large IR signal that would be generated by the active organic ingredients in the aqueous cleaners. Similar problems would result with related spectroscopic techniques.

What was desired was a measurement technique that was not contaminant specific. A possibility that showed very good promise was the quartz-crystal microbalance (QCM). Earlier work at Sandia had shown that this technique to be a viable option. The use of an immersed QCM was explored as a potential monitoring device in this study.

The effectiveness of the cleaner was determined by x-ray photoelectron spectroscopy (XPS), which is an analytical technique that is very sensitive to low levels of surface contaminants. For our applications, the main element of interest was carbon. The atomic ratio of Fe/C or the atomic concentration of carbon on the surface provided by XPS were used as metrics for quantifying the level of cleanliness.

This paper presents the results of the evaluation of select commercial aqueous cleaners as well as the initial results of the use of the QCM for monitoring bath cleanliness.

Experimental Procedures

Cleaners

The cleaners that were evaluated in the study are listed in Table 1.

TABLE 1. Cleaners Examined in Cleaning Study.

Cleaner	Type	Company
Micro	Aqueous	International Products Corp., Burlington, NJ
Inpro-Clean 3800	Aqueous	Oakite Products, Inc., Berkeley Heights, NJ
Citridet	Aqueous	Oakite Products, Inc., Berkeley Heights, NJ
RB Degreaser	Aqueous	Etus, Inc., Sanford, FL
Sonicor	Aqueous	Sonicor Instruments Corp., Copiague, NY
Uniclean VII	Aqueous	Uniclean Products, Inc.
d-limonene	Pure	Florida Chemical Co., Inc., Lake Alfred, FL
D-Greeze 500	Organic	Solvent Kleene, Peabody, MA

Cleaning Procedure

The test coupons were 304L stainless steel discs, 3.18 cm (1.25") in diameter by 0.0254 cm (0.010") thick. These were dipped into vacuum pump oil (Sargent Welch DuoSeal) and the excess allowed to drain away onto a paper towel. This resulted in a thin film of oil remaining afterwards. The test coupons were then cleaned under the various test conditions.

The cleaners were evaluated at ambient temperature (~25°C) and under hot conditions (55°-60°C) at dilutions of 1:5 and 1:10 by volume, as well as at full strength. Typically, the cleaning process involved ultrasonic agitation for 10-15 min at room temperature or 60°C in the cleaning solution, followed by a dip rinse with clean, hot (50°-60°C) deionized (DI) water. The dip rinse was finished with a rinse of hot DI water from a squeeze bottle. The excess water was allowed to drain onto a clean absorbent towel and the parts were then dried in an oven at 100°C. Not all the cleaners were exposed to the full range of test conditions, however, due to time constraints. For comparison, a number of oil-contaminated stainless steel discs were cleaned by normal vapor degreasing with trichloroethylene (TCE) or by cleaning in liquid (boiling) trichloroethane.

In the case of the single organic solvent that was evaluated, the solvent was agitated by blowing a stream of air through it while the part to be cleaned was suspended in it. After removal from the solvent, the part was blown dry with a stream of clean dry air or nitrogen, as recommended by the manufacturer.

XPS Analysis

The XPS spectra were taken with a Model 5400LS x-ray photoelectron spectroscope (Physical Electronics), using a monochromatic Al x-ray source and position-sensitive detector.

Quartz Crystal Microbalance

The 1" AT-cut QCM used in this study had a nominal fundamental frequency of 5 MHz and was purchased from Maxteck (Torrance, CA). The electrodes were fabricated by first vapor depositing 15-nm-thick chromium film to act as an adhesion layer for a 160-nm-thick gold film. The electrode which served as the ground of the QCM was modified to simulate a stainless steel surface by coating the gold with an addition 15-nm-thick chromium film. This was to provide a more-valid basis for comparison of the cleaning efficacy of the various systems with the stainless-steel piece parts. The electrode surface exposed to the liquid cleaner was 0.66 cm in diameter (0.34 cm^2). The electrode surface on the reverse side of the crystal was 1.29 cm in diameter. The output signal from an oscillator running at 5 MHz was connected across the quartz crystal to maintain it at its resonance frequency.

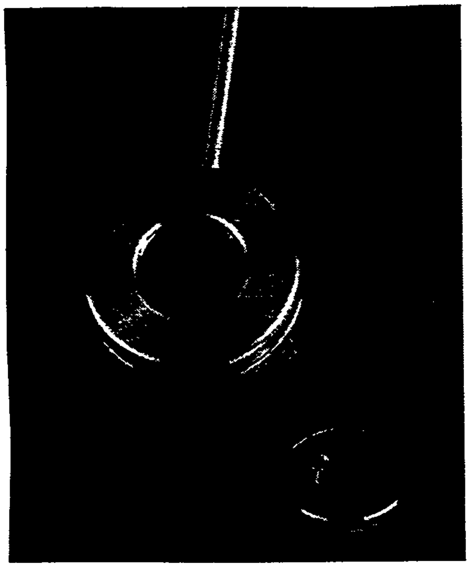

Figure 1. Photo of Assembled Immersible QCM Test Fixture.

Immersible QCM Test Fixture

A photo of the immersible fixture that incorporates the QCM is shown in Figure 1. The fixture is shown schematically in an exploded view in Figure 2. (Details regarding the construction can be found in reference 1.) These electrodes were connected to an oscillator circuit board that was an integral part of the fixture. The oscillator board was built in house and was designed to allow the use of the QCM in liquids with viscosities of up to 200 cP; excessive signal dampening occurs with viscosities higher than this. Power and sensing leads to the sensor were contained in a stainless steel tube attached to the sensor housing.

The response of the QCM was obtained from two output signals from the oscillator board. One signal provided the peak resonance frequency, indicating any shift in the natural resonance frequency of 5 MHz as a result of addition or removal of contaminant films. A voltage signal was also obtained which was directly proportional to the magnitude of the damped resonance signal. The resonant frequency was measured with an HP5384A frequency counter and the voltage was measured with an HP3478A digital multimeter. Together, these responses provide good metrics on the QCM performance.

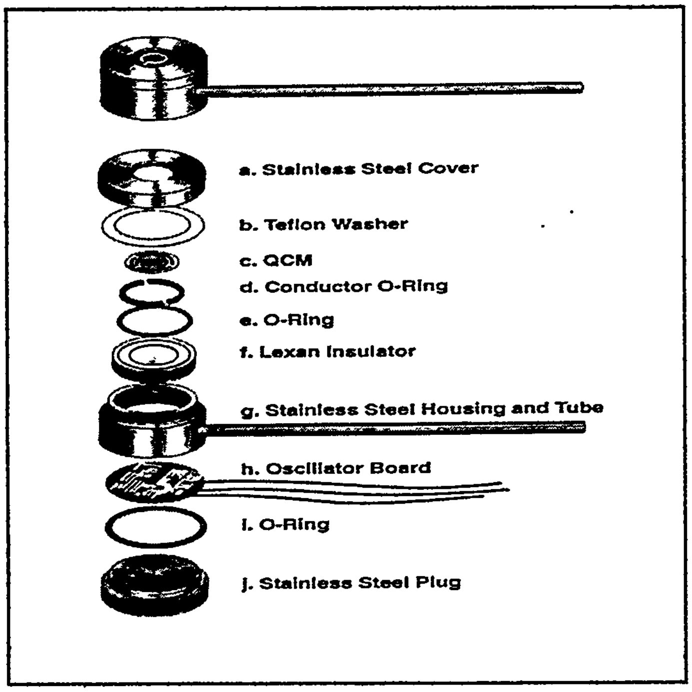

Figure 2. Exploded View of Immersible QCM Test Fixture.

Results and Discussion

XPS Examination

Preliminary Experiments

In earlier preliminary work, a citrus-based solvent containing pure *d*-limonene (a terpene) was evaluated as a replacement for Freon®113 for cleaning soldering flux from printed-circuit boards.[2]. The results showed that *d*-limonene was more effective than Freon®113 as a solvent at room temperature.

Based on these encouraging results, further work was undertaken to evaluate aqueous solutions of Citridet, which contains *d*-limonene as the active cleaning ingredient. Ceramic parts and stainless steel bolts were first contaminated with vacuum-pump oil (Sanovac), paraffin wax, and silicone oil (Dow-Corning 705). The contaminated parts were then cleaned in 50% and 100% Citridet solutions at room temperature and at 60°C, as before. For control purposes, similar samples were also cleaned in boiling trichloroethane.

The samples were examined by XPS for surface cleanliness. Tests results are shown in Table 2 for the atomic concentration of carbon on the surface. (The lower the carbon value, the cleaner the surface.) The values for trichloroethane were taken as reference points. The relative effectiveness of the aqueous cleaning solutions varied depending on the contaminant involved. The pump oil was the most difficult material to remove, followed by the silicone oil.

The 50% Citridet solution showed improved cleaning at the higher temperature for all contaminants. The temperature effect was not as pronounced for the 100% Citridet, however. For the paraffin, both Citridet solutions were better or equal to trichloroethane in cleaning efficiency at 60°C. For the pump oil, the best results were obtained using 100% Citridet hot. For the silicone oil, better results were obtained with 100% Citridet.

Tabler 2. Results of Preliminary Cleaning Experiments with Stainless Steel Discs Coated with Vacuum-Pump Oil and Cleaned with Citridet Solutions.

Treatment	Surface Carbon Concentration, Atomic Percent		
	Paraffin	Pump Oil	Silicone Oil
None (contaminated)	52.2	70.3	73.6
Trichloroethane, boiling	29.0	48.1	49.4
100% Citridet, 25°C	22.3	50.3	42.7
100% Citridet, 60°C	27.0	45.3	43.0
50% Citridet, 25°C	30.8	56.3	53.3
50% Citridet, 60°C	26.2	51.2	44.8

By proper selection of parameters, the parts could be more effectively cleaned with the aqueous cleaner than with trichloroethane.

Follow-up Citridet Tests

The very promising results from the initial cleaning tests with Citridet (Table 2) made this material–or materials based on *d*-limonene–very attractive candidates for replacement of the TCE vapor-degreasing process that we were currently using. In addition, the ES&H issues were minimal with these materials. This encouraged us to do further tests but with the actual stainless steel discs (current collectors) used in thermal batteries. These were coated with a film of vacuum-pump oil (see Cleaning Procedures) and cleaned in a similar manner as those in the initial tests with 100% Citridet and *d*-limonene, but at room temperature. (It was desirable to avoid heating the samples, if possible, to reduce the overall cleaning time.) As before, XPS was used to check for surface cleanliness. In this series of experiments, samples that had been vapor degreased with TCE were also included as controls.

A typical XPS spectrum is shown in Figure 3 for a stainless steel disc after contamination with vacuum-pump oil. The corresponding spectrum for the sample after vapor degreasing with TCE is shown in Figure 4 and that after cleaning with Citridet is shown in Figure 5. (The XPS spectrum for the sample cleaned with *d*-limonene was very similar to that cleaned in Citridet.) The carbon contamination was readily followed by monitoring the intensity of the C1s peak, located at an energy of ~290 eV. This peak was considerably reduced after the sample was vapor degreased (Figure 4) and when it was cleaned with the Citridet (Figure 5). The Fe 2p3 peak was used to monitor the Fe concentration.

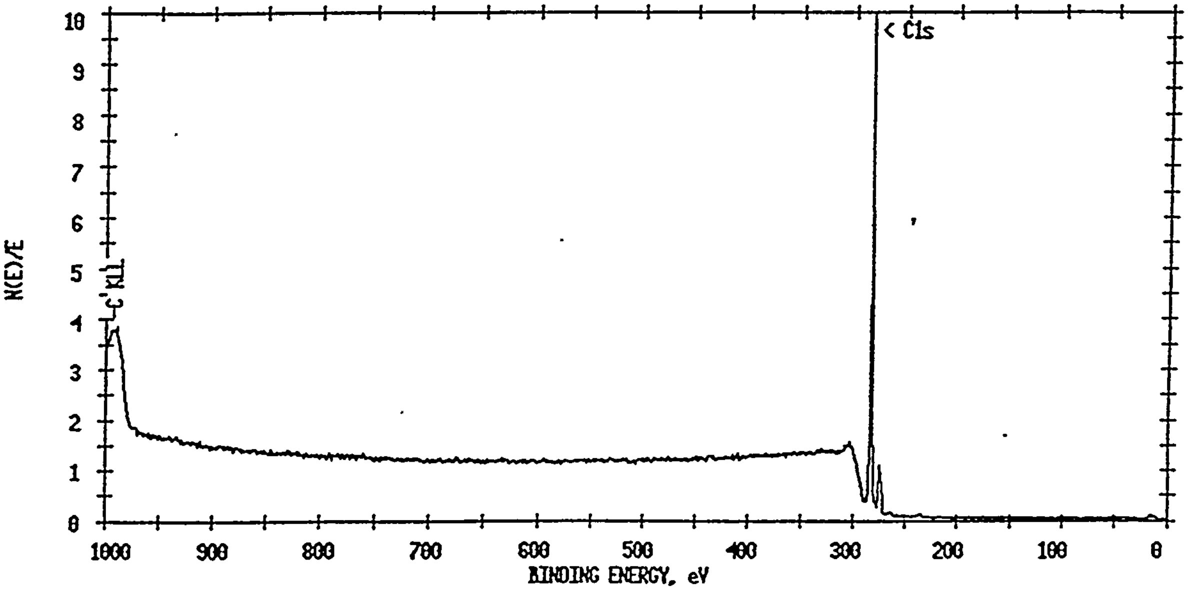

Figure 3. XPS Spectrum for Untreated, Stainless Steel Disc Coated with an Oil Film.

The measured surface-carbon concentrations are summarized in Table 3 for the various samples before and after cleaning. Pure *d*-limonene was not as effective as vapor degreasing with TCE. The sample with the lowest carbon level (i.e., the cleanest) was the one cleaned with the Citridet solution, which contains *d*-limonene along with surfactants.

Because the effectiveness of Citridet had been demonstrated, we began using it at full strength for our cleaning needs, as we were no longer able to use vapor degreasing with TCE. While no obvious problems were encountered after using the bath for six months or more, there was an increasing concern with the projected lifetime for the bath. The bath tended to darken with use, which was indicative of some chemical breakdown occurring with time–the most likely being oxidation of the *d*-limonene component. Lacking any

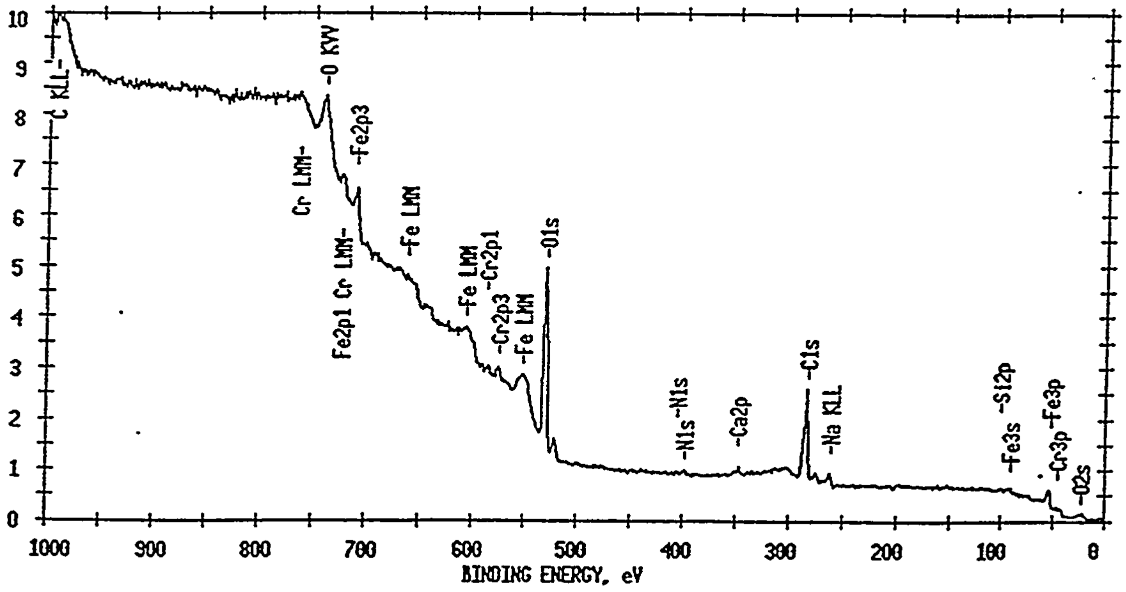

Figure 4. XPS Spectrum for Oil-Contaminated Stainless Steel Disc After Cleaning by Vapor Degreasing with TCE.

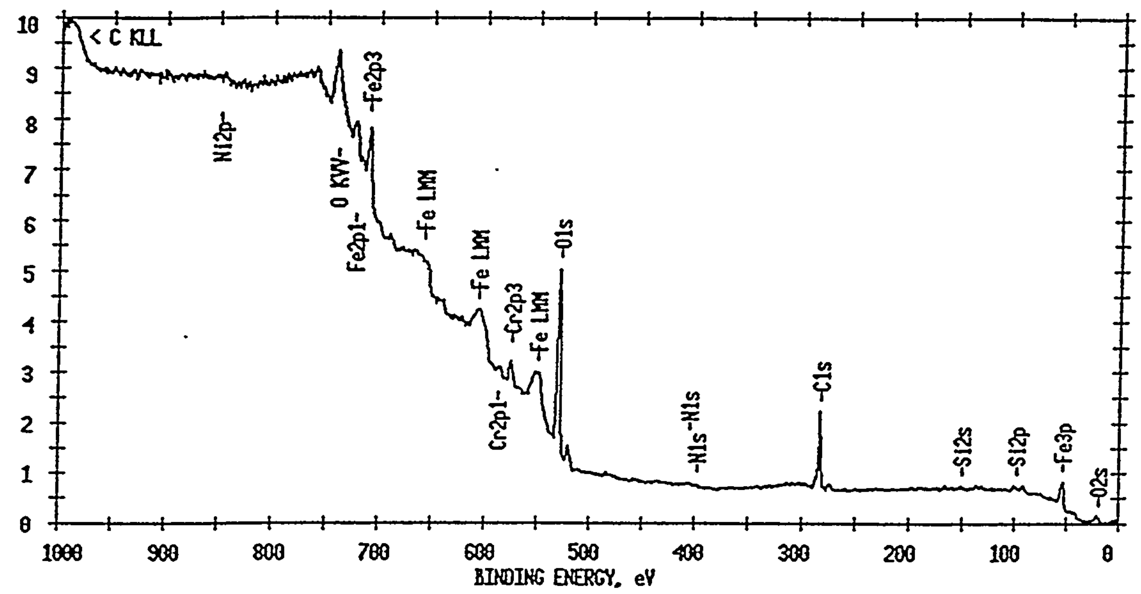

Figure 5. XPS Spectrum for Oil-Contaminated Stainless Steel Disc After Cleaning with 100% Citridet at Room Temperature.

Table 3. Results of Additional Cleaning Experiments with Citridet and *d*-Limonene at 25°C.

Treatment	Surface Carbon Concentration, Atomic Percent
None (contaminated)	100[a]
Trichloroethylene	45.5
100% Citridet	33.8
d-limonene	49.8

[a] Data are normalized to 100% C for the oil-contaminated sample

suitable monitoring technique at the time, we were forced to consider replacing the bath at some periodic interval, which could become costly. (The monitoring issue will be discussed in detail in the following section on the QCM.). This, coupled with the fact that some of the bath operators found the strong citrus smell objectionable, encouraged us to consider alternate aqueous cleaners.

Alternate Cleaner Survey

In surveying the market, we became aware of other aqueous cleaners that could be suitable for our purposes. These could be diluted by up to 10:1 in some cases, which would make their use economical if we were forced to replace the cleaning bath on a regular basis. The additional cleaners that we examined included Micro, Impro-Clean 3800, RB Degreaser, and Uniclean VII. We also examined D-Greeze 500 which was a nonaqueous, organic-solvent cleaner. We tested these alternate cleaners with our oil-coated stainless steel discs at 25°C and 60°C at full strength and diluted to 10% and 20%. The results of the XPS analyses of these cleaning tests are summarized in Table 4 in the form of the measured Fe/C atomic ratios.

The best overall results were obtained with Micro. It was ineffective at full strength, but worked as well at a concentration of 10% and 20%. The cleaning efficiency of Micro decreased when it was used at the higher temperature. The best conditions for using Micro are at room temperature and a concentration of 10%.

The next best cleaners were Sonicor and Impro-Clean 3800. The cleaning efficiency of Inpro-Clean 3800 was better at elevated temperature. There was little effect of concentration evident over the range of 10%-20%. The limited data for Sonicor indicate it was comparable to Inpro-Clean 3800 when used at 20% concentration at 60°C. (No data at room temperature were generated with Sonicor.)

Citridet at full strength was a reasonable good cleaner, although not as good as Micro, Sonicor, and Inpro-Clean 3800. When diluted to 20%, however, Citridet performed poorly as a cleaner. Its efficiency also dropped when it was used at room

Table 4. Summary of XPS Data for Stainless Steel Discs Contaminated with Vacuum-Pump Oil and Cleaned with Various Cleaners.

Sample	Concentration, %	Temperature, °C	Fe/C, a/a
Micro	100	25	0.087
	20	25	0.58
	10	25	0.59
	100	60	0.043
	20	60	0.45
	10	60	0.35
Impro-Clean 3800	20	25	0.31
	10	25	0.33
	100	60	0.091
	20	60	0.39
	10	60	0.36
RB Degreaser	20	60	0.191
	10	60	0.208
Citridet	20	25	0.0174
	20	60	0.060
	100	60	>0.228
Sonicor	20	55	0.374
Uniclean VII	33	25	0.082
	10	25	0.014
D-Greeze 500	100	25	0.30
Trichloroethane	100	114	N.A.[a]

[a] Not available.

temperature. The inability to use Citridet at other than full strength makes it more expensive to use than the other aqueous cleaners. This, coupled with its strong odor, and need to be used at elevated temperatures to be effective in cleaning, makes it unattractive for our use.

When diluted to 10%-20%, RB Degreaser at 60°C was comparable to Citridet at the same temperature. (No room-temperature data were generated for this cleaner.) The cleaning power was not dependent upon concentration over this range, which is similar to what was observed with Micro and Impro-Clean 3800. It was still inferior to these latter two cleaners, however.

The least effective aqueous cleaner was Uniclean VII. It was ineffective at room temperature and its cleaning efficiency was degraded when it was diluted. It would be totally unacceptable for our cleaning applications.

The D-Greeze 500 organic-solvent cleaner was comparable to Inpro-Clean 3800 in cleaning power which could make it a reasonable candidate for our needs. As indicated earlier, however, its flammability would make it unsuitable for our use, because of the ES&H concerns that would have to be addressed–concerns that wouldn't exist with the use of aqueous cleaners that are equal or better in their cleaning effectiveness.

Based on the results of the XPS analyses, the cleaners evaluated in this study are ranked in Table 5 in the order of their effectiveness. Micro had excellent cleaning capabilities at room temperature at relatively low concentration. This, coupled with its environmental friendliness, makes it a good candidate for cleaning stainless steel parts for thermal batteries as a replacement for vapor degreasing with TCE.

Table 5. Optimum Cleaning Conditions for Various Cleaners Evaluated in This Study in Order of Decreasing Effectiveness Based on XPS Analyses.

Cleaner	Temperature, °C	Concentration, %
Micro	25	10
Inpro-Clean 3800	60	20
Sonicor	55	20
D-Greeze 500	25	100
Citridet	60	100
RB-Degreaser	60	10
Uniclean VII	25	33

It should be noted here that the lifetime of baths made with any of the aqueous cleaners has not been addressed at this time; i.e., the relative effectiveness with continued use is unknown. This is an area where bath monitoring with the QCM would be ideally suited.

QCM Evaluation

Theory

The resonance frequency of the QCM will be affected by any changes to its surface, such as the addition of a thin oil film or contaminant. The deposition of a film of oil, for example, will cause the oscillation frequency to be damped, resulting in a shift to a lower resonance frequency. At the same time, the voltage signal from the oscillator circuit incorporated into the immersible QCM text fixture will increase.

The shift in frequency of the QCM in the case of an oil film has been measured and compared to that calculated using the Sauerbrey equation.[1,3] The Sauerbrey equation can be reduced to the following:

$$\Delta f = -C_f \Delta m \qquad (1)$$

where $-C_f$ is the sensitivity factor and is equal to 56.6 Hz-cm^2/μg at 5 MHz and Δm is the change in the film mass.[3] For oil film thicknesses up to 1.15 μm, the calculated shift in resonance frequency was in good agreement with that calculated with the Sauerbrey equation. That is, the shift in frequency was found to be fairly linear for oil film thicknesses up to 1.15 μm. Above about 3 μm, the frequency response levels off and the acoustic signal becomes completely damped by the film.

When the immersible QCM fixture is immersed in a liquid, such as an aqueous cleaning bath, a considerable negative shift in resonance frequency of the QCM to lower values will take place. In the case of a QCM that has a film of oil being cleaned off the surface, an offsetting shift to higher frequency will occur–along with a corresponding decay in the voltage of the oscillator circuit–while the film of oil is being removed during aqueous cleaning. Though this shift is small, the oscillator circuit incorporated into the test fixture is sensitive enough to detect this offset. As an example, for a film of oil 1.5 μm thick and a sensitivity factor of 56.6 Hz-cm^2/μg, the corresponding shift in the QCM frequency will be 6,500 Hz.

Thus, if the QCM is coated with a thin film of the expected contaminant–oil, in the case of the stainless steel current collectors for thermal batteries–the response of the QCM during aqueous cleaning can be used to determine when all of the oil has been removed.

The rate of decay of the damping voltage from the oscillator output circuit can be used to obtain kinetic data about the cleaning process. Generally, the decay can be fitted to an exponential function of the type:

$$f(t) = f_0 \exp((t-t_0)/\tau)) \qquad (2)$$

The time constant for the cleaning process, τ, can be extracted by fitting the voltage decay to Equation 2. The smaller that τ is, the faster the surface of the QCM is being cleaned. This provides a means of comparing different cleaners under various cleaning conditions.

Results of Cleaning Tests

The suitability of the QCM for monitoring of aqueous cleaning baths was examined with several of the cleaning solvents. The tests conducted with Micro at concentrations of 2%, 10%, and 20% at 23°C and 50°C will be reported along with similar data for Impro-Clean 3800. Similar tests were conducted with DI water for control purposes.

Bath Temperature of 23°C - The frequency and voltage response of the QCM when it was covered with a thin film of oil and then immersed into a bath of DI water at 23°C are shown in Figures 6a and 6b, respectively. The figures are partitioned into five distinct regions for ease of discussion.

In region I, a thin film of oil is applied to the QCM surface in air. This causes a rapid damping of the resonance frequency by ~3,400 Hz and a corresponding increase in oscillator voltage of ~ 0.5 V. The change continues as the film redistributes itself across the surface of the QCM. Surface sorption of moisture may also be occurring at the same time.

In region II, the QCM is inserted into the DI water. The final steady-state resonance frequency will reflect the loading of the signal damping by the water and any offsets (increases) caused by oil removal.

In region III, the QCM is removed from the bath and physically cleaned by repeated spraying with aqueous cleaning solution followed by rinses with DI water. The erratic signal during this external cleaning process is due to the rapid changes taking place on the surface of the QCM as the surface is alternately wet and then dry.

Region IV shows the response of a clean QCM when immersed in clean DI water. The difference in the steady-state frequency in region IV with that in region II allows the amount of oil remaining to be determined. When all the oil has been removed by the cleaning process, the two values will be identical. The poor removal of oil that would be expected for DI water is reflected in the large difference in the steady-state frequency values for these two regions.

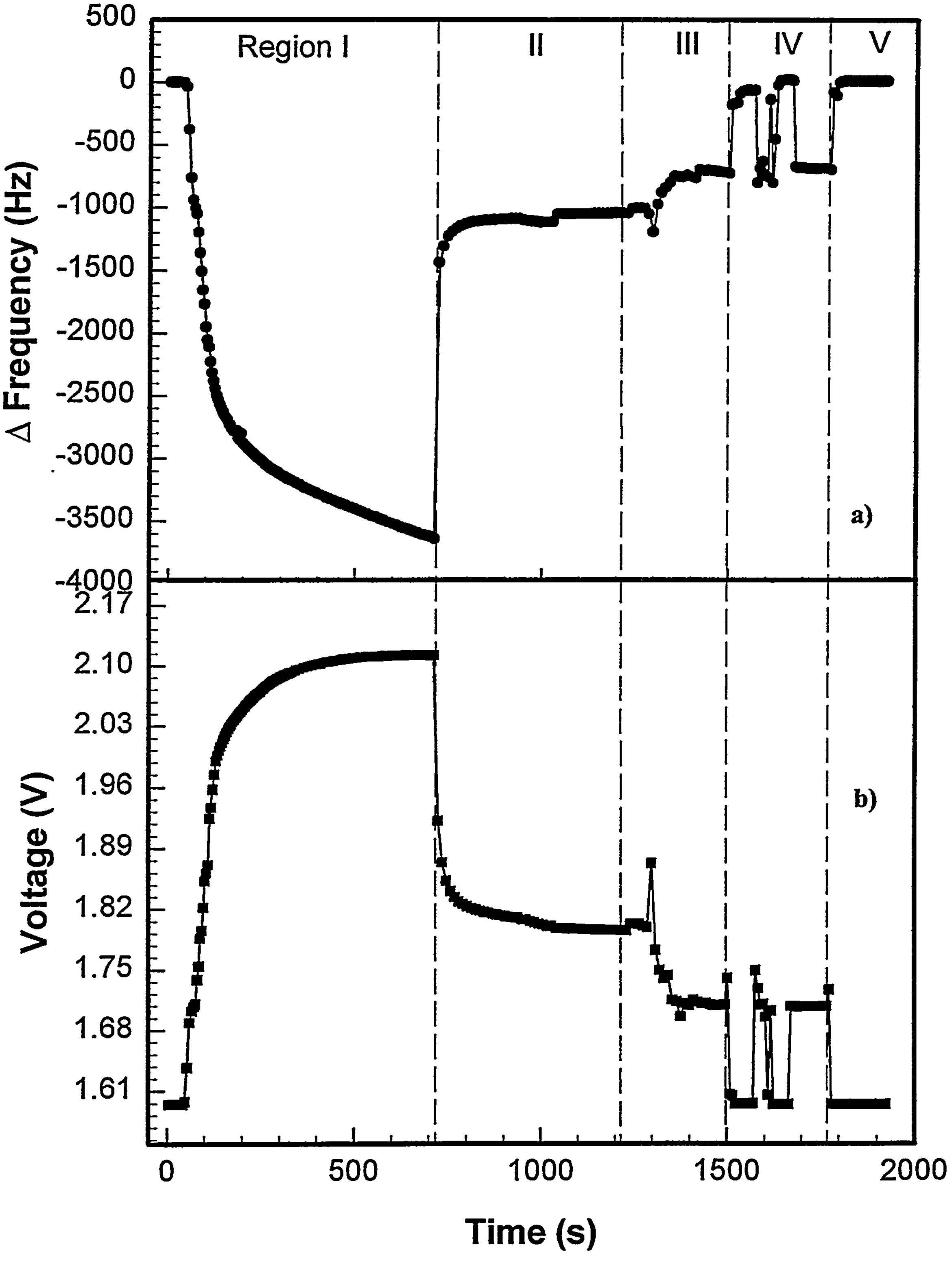

Figure 6. Cleaning Experiment at 23°C with DI Water. a) Oscillator Frequency Response. b) Damping Voltage Resonse.

Region V shows the response of the QCM after removal from the bath, cleaning, and drying. The accuracy of the test results are verified if the response in region V is identical to that for region I. This serves as a check on instrumentation and the experimental procedure.

The response of the QCM during coating with a thin film of oil and subsequent cleaning at room temperature in 10% Micro is shown in Figures 7a and 7b. Note that the steady-state frequency in region II during cleaning is very close to that in region IV as a result of effective oil removal. The relative response with 20% Micro as well as solutions of Inpro-Clean 3800 was very similar to that of 10% Micro.

Bath Temperature of 50°C - The response of the QCM when immersed in a DI water at 50°C is shown in Figures 8a and 8b. The application of the initial oil film at room temperature is shown in region I. The QCM fixture was then immersed in the hot bath of DI water. The stability of the frequency signal was not as good as at room temperature because of thermal effects. This resulted in the large overshoot in the frequency response. A similar overshoot (spike) is evident in the voltage response. Still, when the QCM was thermally equilibrated at room temperature, (regions III and V), the frequency and voltage responses returned to the original values.

The response of the QCM when immersed in a bath of 10% Micro at 50°C is shown in Figures 9a and 9b. The overshoot in the frequency and voltage is similar to that observed with the DI water under the same conditions. The data in region IV indicate that the sensor may not have reached thermal equilibrium during this test. The similar offsets in frequency in regions II and IV indicate effective removal of the oil.

As discussed previously, analysis of the voltage response during the cleaning process provided information of the kinetics of the cleaning process. The effect of Micro concentration on the rate of cleaning at room temperature is shown in Figure 10 for three different concentrations. This same information is presented in tabular form in Table 6 as part of the summary of the cleaning tests. As can be seen, the cleaning rate was much faster (lower τ) in 10% Micro than in 2% Micro, with only a slight increase in going to 20% Micro.

The results of the QCM experiments indicate that cleaning effectiveness increased with increase in concentration for both cleaners at both temperatures. The cleaning rate constant, τ, decreased with increasing concentration for both Micro and Inpro-Clean 3800 at 23°C, which reflects the enhanced kinetics at higher concentrations. The values of τ at 50°C were much lower than their counterparts at 23°C which shows that higher temperatures also improved the cleaning rate. The effect of concentration at 50°C upon τ was similar to that at 23°C for Inpro-Clean 3800 but was reversed for Micro. This may be due to degradation of the active cleaner in Micro at elevated temperatures.

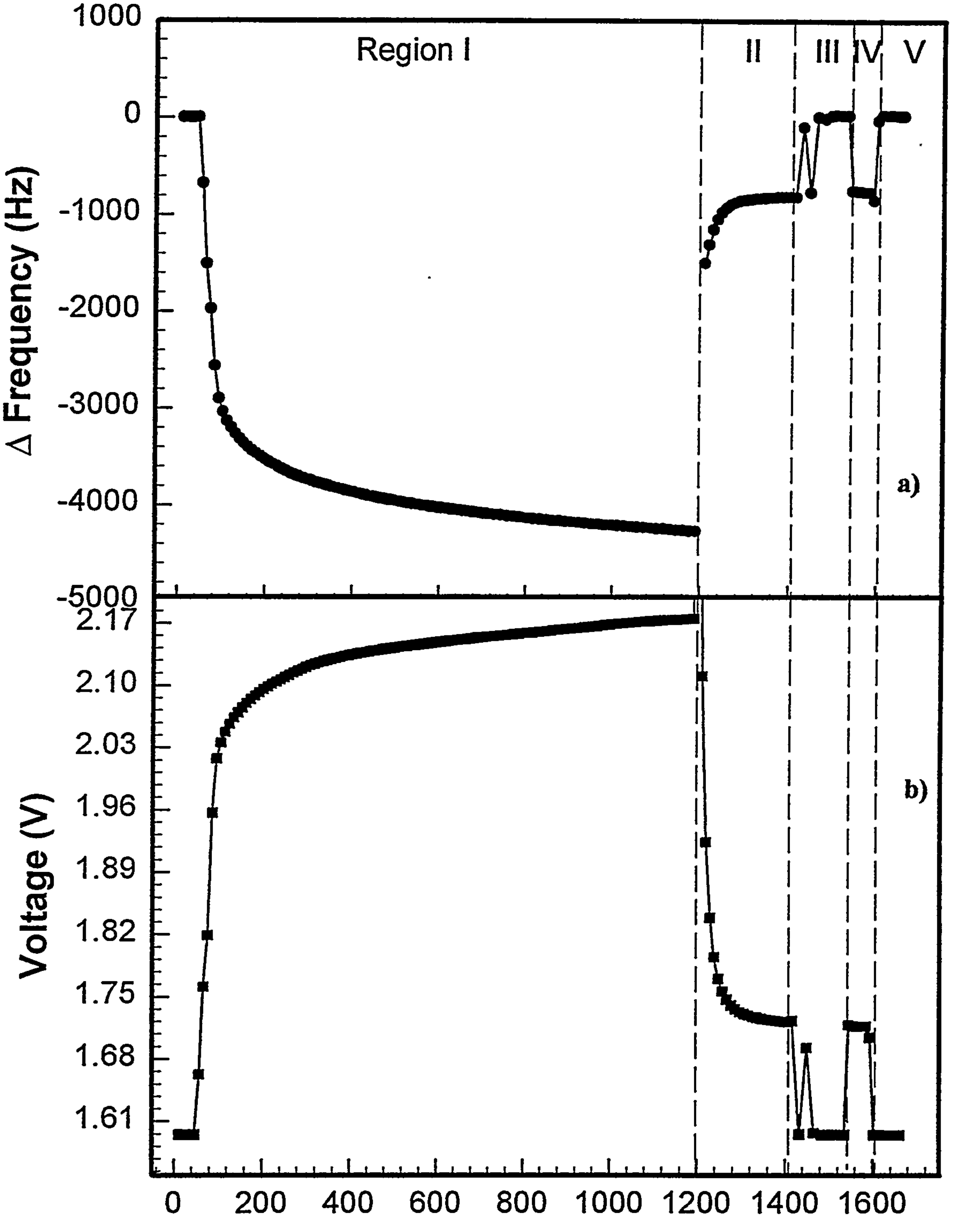

Figure 7. Cleaning Experiment at 23°C with 10% Micro. a) Oscillator Frequency Response. b) Damping Voltage Resonse.

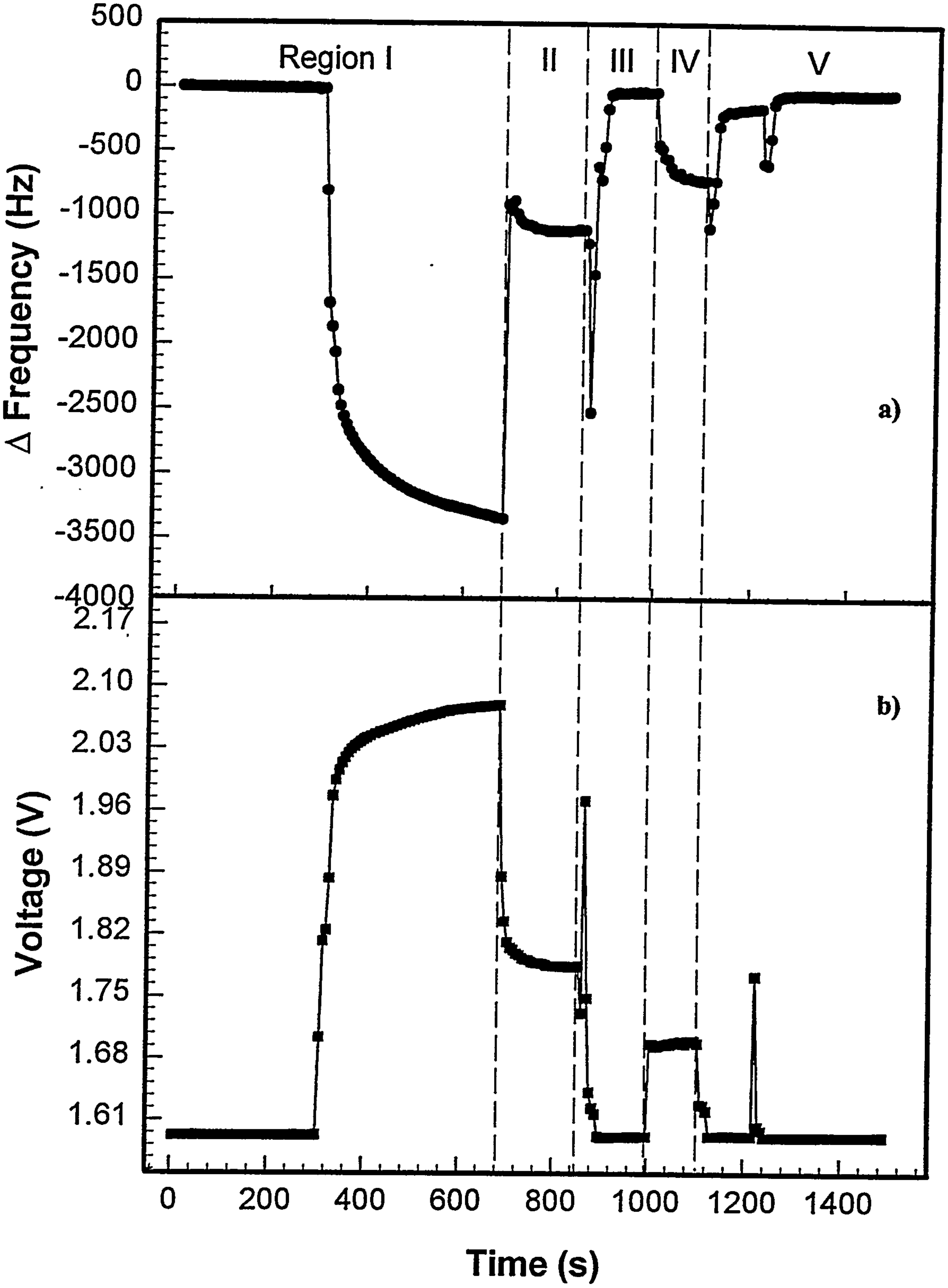

Figure 8. Cleaning Experiment at 50°C with DI Water. a) Oscillator Frequency Response. b) Damping Voltage Resonse.

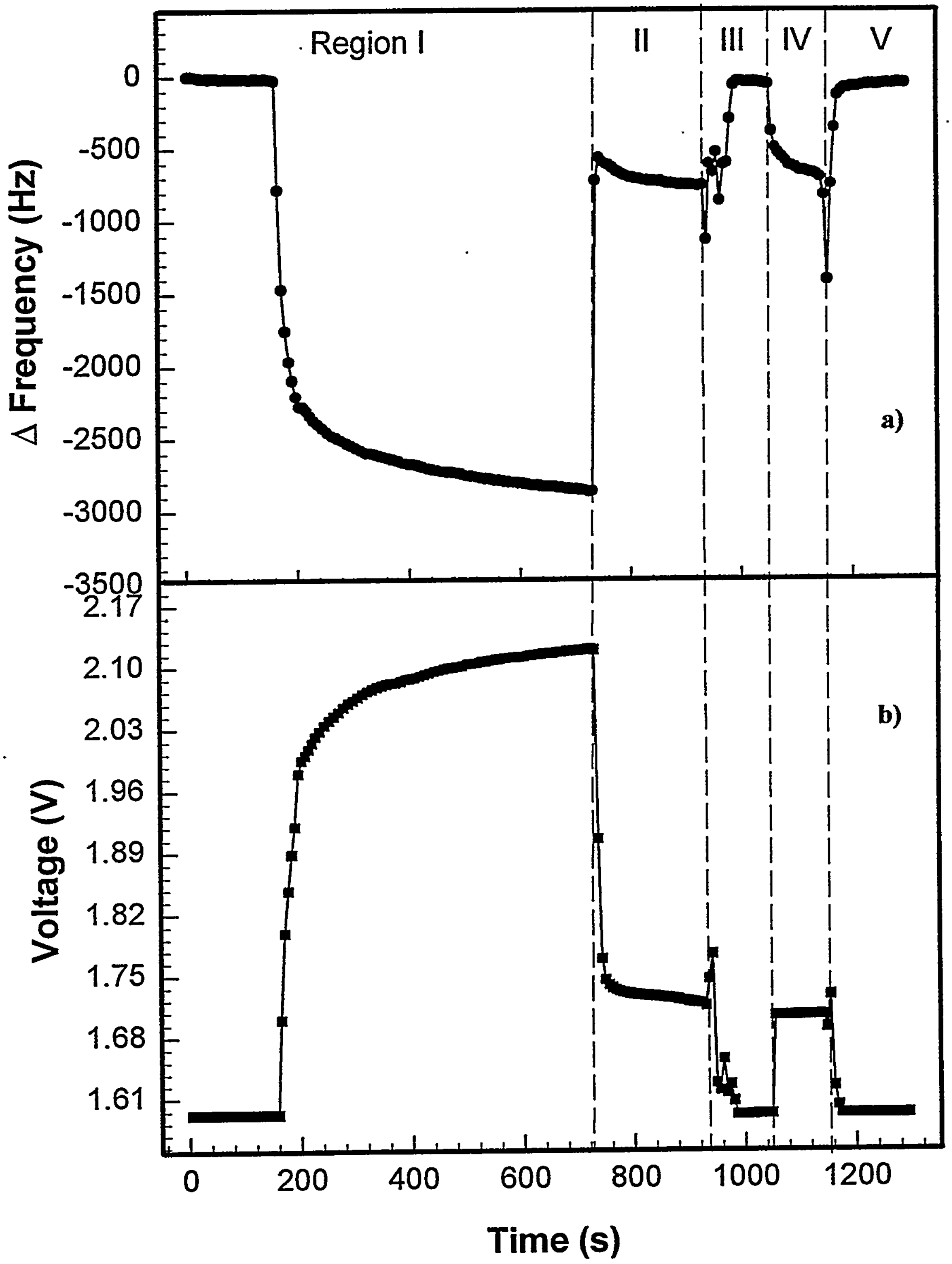

Figure 9. Cleaning Experiment at 50°C with 10% Micro. a) Oscillator Frequency Response. b) Damping Voltage Resonse.

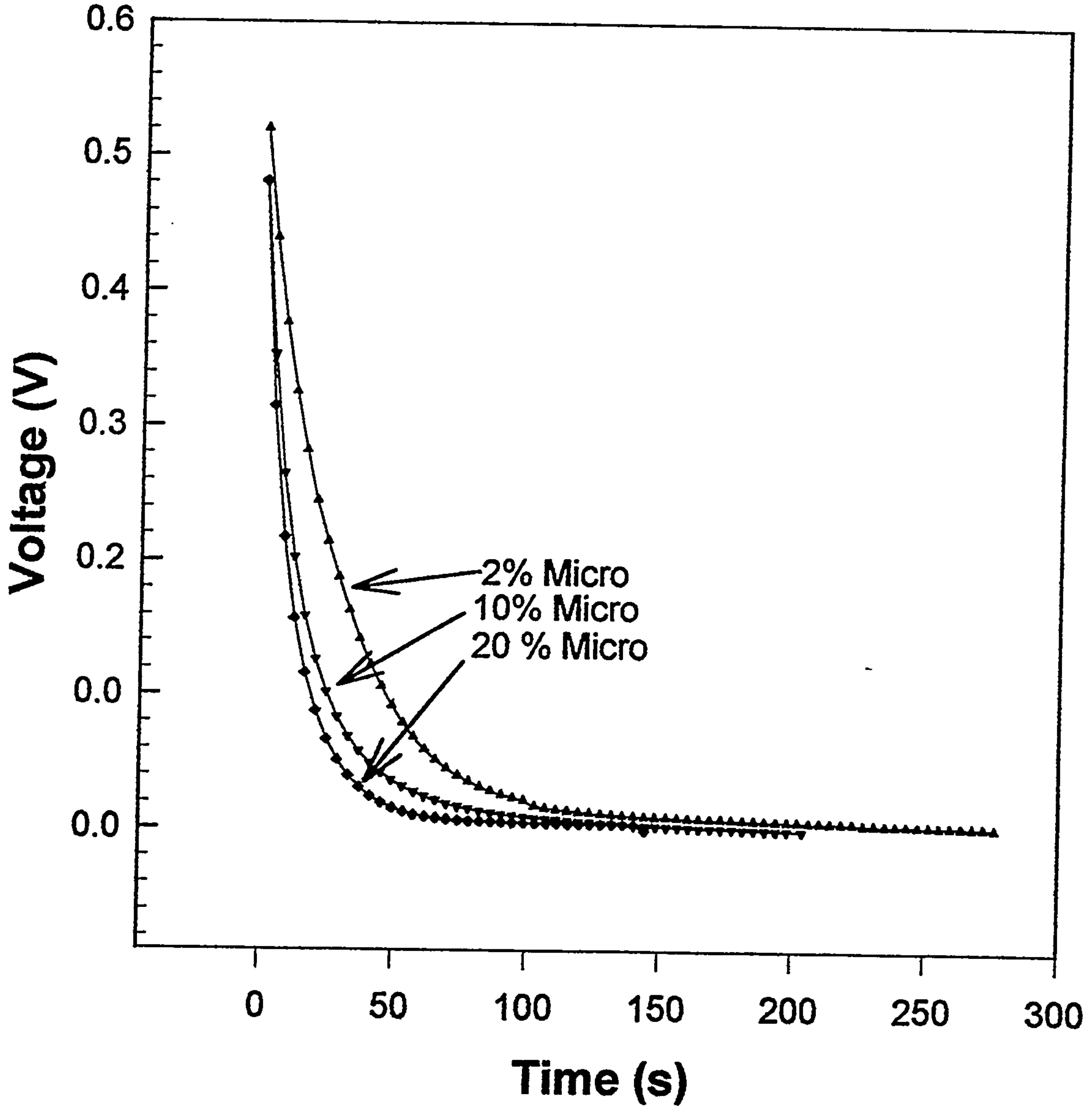

Figure 10. Damping Voltage Resonse of Oscillator at 23°C for 2%, 10%, and 20% Micro.

The data in Table 6 show that the relative amount of oil removed at 23°C was enhanced with increase in cleaner concentration for both cleaners. The amount removed was greater for the 10% and 20% Micro solutions compared to the corresponding Inpro-Clean 3800 solutions. This is consistent with the XPS data (Table 4). At 50°C, however, oil removal was more complete with the Inpro-Clean 3800 and the efficiency of Micro decreased. Again, this is in generally good agreement with the results of XPS analyses, when the

Table 6. Summary of Results of Cleaning Tests with QCM in DI Water and Micro Solutions

Solution	Temperature, °C	Amount of Oil Removed, %	Cleaning Constant (τ), s
DI Water	23	86.0	42
2% Micro	23	98.4	29
10% Micro	23	98.9	16
20% Micro	23	100	12
10% Inpro-Clean	23	94.7	6.5
20% Inpro-Clean	23	97.1	6.1
DI Water	50	88.0	4.9
2% Micro	50	94.3	3.9
10% Micro	50	97.3	4.5
20% Micro	50	100	7.0
10% Inpro-Clean	50	100	1.4
20% Inpro-Clean	50	100	0.7

experimental error is considered. Inpro-Clean 3800 was faster in cleaning oil from the QCM but it was not as complete as Micro unless elevated temperatures were used.

The repeatability and sensitivity of the QCM have been shown to be exceptional. The noise associated with the frequency response of the QCM in a liquid medium amounts to only 1 Hz. This translates to a mass change of only 20 ng/cm^2. What is more important, this change can be measured in real time during cleaning. Experiments performed during which the QCM was repeatedly wet and dried to remove liquid effects have shown a reproducibility of 0.6 Hz. This is equivalent to a mass change of 12 ng/cm^2. The sensitivity of the QCM is great enough to detect less than a monolayer of contaminant.[4]

Simplified QCM Instrumentation

The experimental setup used for monitoring the response of the QCM for this study would be more complicated than desired for routine bath surveillance, in terms of instrumentation required. A prototype comparator circuit has been developed that would not require added instrumentation. The circuit was designed to use the damping voltage to follow the cleaning process. A calibration is necessary to determine the voltage thresholds for "dirty", "clean", and "dry" states of the QCM. Once the threshold calibrations have been done, simple LED readouts on the control panel are used to follow the cleaning process.

Such a circuit would be more than adequate for our cleaning purpose and would provide instant visual indication to the operator when to remove the parts from the cleaning bath. This would not require the training that operation of the more-complicated system entails.

Future Work

Additional work is necessary to correlate the results of the XPS measurements with those made with the QCM. Initially, experiments were planned where the immersible QCM would be placed in the cleaning bath along with the oil-coated stainless steel discs during cleaning. The results of the XPS analyses could then be directly compared to the cleaning data from the QCM. This would allow a one-to-one comparison of data generated under the same conditions.

Another area that merits further work is the incorporation of a thermistor (or similar temperature-dependent device) and associated circuitry into the QCM test fixture to automatically compensate the response parameters of the sensor for temperature. This should provide greater signal stability over varying temperatures.

Conclusions

XPS is a sensitive tool for monitoring the cleanliness of metal parts after being subjected to various cleaning processes. The XPS data show that aqueous cleaners perform as well as or even better than conventional vapor degreasing with trichloroethylene or solution cleaning with trichloroethane. A number of commercial aqueous cleaners can be considered as cleaning alternatives. Comparable cleaning can be attained depending on the temperature and concentrations used. For room-temperature applications at a reasonable cost, a 10% Micro solution provides excellent cleaning. This material is environmentally friendly, which makes it attractive for cleaning applications within the DOE nuclear-weapon complex.

The QCM was shown to be a viable, sensitive, and accurate technique for monitoring the cleanliness of an aqueous cleaning bath. The prototype developed at Sandia provides both a frequency and voltage output that allow the cleaning process to be monitored in real time. The voltage relaxation during cleaning provides a means of monitoring the kinetics of the cleaning process. Inpro-Clean 3800 is faster than Micro in cleaning but is not as thorough. The QCM data were in generally good agreement with the results of the XPS analyses. More work is needed to obtain a one-to-one comparison for the two types of data for ultimate validation.

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