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March 22, 2010

Clerk of the Boards

South Coast Air Quality Management District

21865 Copley Drive

Diamond Bar, California 91765-4178

***Re: Proposed Amendments to Rule 1144 – Metalworking Fluids and
Direct Contact Lubricants***

The Independent Lubricant Manufacturers Association (“ILMA”) submits the following comments on the South Coast Air Quality Management District’s (“AQMD”) Proposed Amendments of Rule 1144 — Metalworking Fluids and Direct-Contact Lubricants (“PAR 1144”). ILMA’s comments also address the Draft Staff Report (“DSR”) that accompanies PAR 1144. ILMA and its representatives have met regularly over the past year with AQMD staff and other interested parties to develop appropriate amendments to Rule 1144 regarding test methods, recordkeeping requirements, and emissions limitations.

Subject to the comments below, ILMA supports PAR 1144. AQMD staff and interested parties, including ILMA and its member companies, have worked tirelessly to develop sound data to support the rulemaking. ILMA’s primary concerns with PAR 1144 are:

1. ILMA Supports the Inclusion of the TGA Method for Determining VOC Content

ILMA appreciates that AQMD has agreed and has included in PAR 1144 that VOC content should be determined by thermogravimetric analysis (“TGA”) at 81 °C for 110 minutes.¹ The TGA method proposed for inclusion in PAR 1144 satisfies the AQMD Governing Board’s March 6, 2009 Resolution that this method be validated using ASTM Method E691, Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.

ILMA recommended and AQMD staff included in PAR 1144 at Section (h)(1) (A) that the actual reference to the TGA method in the final rule be ASTM Method E1868 -10, Standard Test Method for Loss-On-Drying by Thermogravimetry. ASTM Method E1868 is being revised to incorporate the results of the just-completed inter-laboratory study coordinated by ILMA. A round-robin study was conducted to develop precision and bias data for E1868 Method A. Eight laboratories participated in the study, and each of the labs was asked to report five replicate test results for five different liquid lubricant sample materials. The results of this study yielded results of acceptable repeatability and reproducibility in accordance with ASTM Method E691

400 N. Columbus Street
Suite 201
Alexandria, VA 22314
phone: 703/684-5574
fax: 703/836-8503
email: ilma@ilma.org
web: www.ilma.org

1. At the same time, PAR 1144 would delete all references to EPA Method 24 from Rule 1144. ILMA concurs with AQMD’s statement in the preliminary draft of the staff report that EPA Method 24 “is unreliable for semi-volatile materials typically found in lubricants and metal working fluids.”

ASTM currently is in the process of balloting the consensus revision of ASTM Method E1868 at the specified time, temperature and other conditions. ILMA initially expected that the ASTM balloting would have been completed prior to the presentation of PAR 1144 to the AQMD Governing Board on April 2, 2010.² However, ILMA learned early last week – and notified AQMD staff -- that the final publication of ASTM Method E1868-10 will be delayed from the end of this month until the beginning of May 2010. There was a several weeks delay in getting the proposed revisions out to the ASTM committee for ballot.

In addition, one substantive comment received during the ASTM balloting may result in moving specifics from ASTM Method E1868-10's Test Method A (i.e., those things that were specific to the semi-volatile lubricant samples tested, such as gas flow rates, sample volume and pan characteristics) into a document which is called a "Research Report." This document contains all of the statistical calculations that were part of the Inter-Laboratory ("ILS") Study 500. The effect of this change simply is that regulated parties now will need to obtain two documents from ASTM — that is, E1868-10 and the ILS500 Research Report.

Because ASTM Method E1868-10 will not be finalized until after the Governing Board's scheduled adoption of PAR 1144 on April 2, 2010, ILMA understands that the timing presents an administrative issue for AQMD. ILMA proposes two possible "fixes" to address this timing issue.

First, because it is likely that ASTM Method E1868-10 will be subject to revision in future years, ILMA proposes the following language be used to describe the test method in Section (h)(1)(A):

The latest, approved edition of ASTM E1868, Method A, using the parameters and the repeatability and reproducibility numbers specified in the ASTM Research Report for ILS 500.³

The use of this suggested language will avoid the need for AQMD to go back and amend Rule 1144 in another 45 to 60 days after ASTM Method E1868-10 is finalized.

Second, and as an alternative, the Governing Board simply can postpone consideration of PAR 1144 until shortly after ASTM Method E1868-10 is approved. ILMA appreciates that AQMD staff is sensitive to industry concerns that sufficient time is needed for compliance purposes. However, most metalworking fluid formulators are aware of AQMD's rulemaking and the TGA method. Even though the ASTM will not finalize Method E1868-10 until early May, regulated parties know enough about the time, temperature and other parameters in what will become ASTM Method E1868-10 that they can proceed with their compliance activities during the short, envisioned rulemaking delay.

ILMA opposes interim efforts by AQMD staff to take ASTM Method E1868-10 and copy it into a new AQMD Method 319. As an initial matter, ASTM Methods are protected intellectual property, and AQMD likely would be violating ASTM International's copyright(s). To the extent that AQMD lab staff adds QA/QC components and/or other changes to the test method, such actions violate the spirit of the Governing Board's March 6, 2009 resolution that any test method developed for Rule 1144 undergo validation using ASTM Method E691. Further, AQMD Method 319 is being inserted into the Rule at the "Midnight hour" without any opportunity for public review and comment. ILMA and its members have incurred in excess of \$200,000 in testing costs alone over the past year, generating literally thousands of TGA data points. It is only appropriate for the Governing Board to delay the rulemaking for 45 to 60 days in order for ASTM E1868-10 to be finalized.

2. With the TGA test method in place, further testing of water dilutable fluids indicate that almost every fluid tested with a water content of 90% or more would be "super compliant." Thus, there is no need to include water dilutable fluids in final Rule 1144, because there would be no VOC reductions while all parties would incur substantial compliance costs.

3. ILMA assumes that AQMD staff, if necessary, can appropriately style the reference to the most recently-approved edition of ASTM Method E1868.

2. The Annual Quantity and Emission Inventory Report Should be as Narrow as Possible

Under Section (f)(3) of PAR 1144, manufacturers and distributors will be required to provide AQMD with an annual quantity and emission report, documenting sales volume and volatile organic content of metalworking fluids and direct-contact lubricants sold in the District for calendar years 2011 through 2013. ILMA understands that AQMD staff is drafting a Governing Board resolution that will direct staff to work with interested stakeholders in developing reasonable content and format requirements for the annual report that are protective of “confidential business information” to the extent allowable under AQMD’s Public Records Act Guidelines. ILMA wants to participate in this activity and agrees that the annual report form can be completed by September 30, 2010.

However, ILMA requests that the Governing Board’s Resolution make it explicit to the staff that content requirements of the reporting form should be drawn as narrowly as possible. The reporting form should respect that the lubricants marketplace is highly competitive and that it is not to be used as a “back door” way for AQMD staff to develop regulatory and enforcement information.

3. AQMD Should not Propose Another Test Method as an Alternate to the TGA Test Method

AQMD should terminate further work on the development of SCAQMD Method 313L –Determination of VOC Hydrocarbon Compounds in Lubricants. The TGA test method included in PAR 1144 is the cost-effective manner to determine compliance with Rule 1144. The AQMD’s prior fruitless effort to validate Method 313L has actually interfered with and delayed the successful effort to validate the TGA test. The AQMD’s continued effort to validate Method 313L will result in the imprudent expenditure of limited resources by the AQMD and the interested parties who will have to monitor and participate in this effort. AQMD has purchased and has brought into use TGA equipment in its laboratory. It is time for AQMD to terminate further efforts to develop Method 313L as an alternative to the TGA test method.

ILMA previously has shared with AQMD staff detailed concerns with Method 313L. AQMD staff’s response to those comments is included in the DSR. The AQMD staff’s response has done nothing to allay ILMA’s concerns with Method 313L. Accordingly, ILMA submits the following reply to the AQMD staff’s response to ILMA’s comments:

ILMA Comment #1:

Running the method as written requires a minimum of 10 hours of instrument time for just one sample. Each additional sample adds at least 90 minutes of additional analysis time. This does not account for the lab hours required to prepare the seven standards, sample duplicates, blanks, and matrix spikes.

AQMD Staff Response:

The estimate of “10 hours of instrument time” is overestimated. The reality is that Method 313L currently takes less time per sample than TGA: 105 minutes versus 140 minutes (including between-sample GC cleanup and TGA cool-down). Although Method 313-L requires more quality control, the ability to run GC autosamplers overnight more than compensates for the additional injections.

ILMA Reply:

Method 313L requires the analysis of seven external standards, a blank, a matrix spike standard, and matrix spike standard duplicate at a minimum for each batch of metalworking fluids analyzed. Additionally, the column must be “baked out” in-between sample runs to minimize sample carry-over. As each run is approximately 45 minutes, and assuming one sample is analyzed in duplicate, this works out to 13 runs x 45 minutes = 9.75 hours. Good analytical practice demands that all standards are run for

every batch of samples tested. The assumption that all labs have autosampler capability is dubious.

The “10 hour” number could also be an under-estimate of the method set-up time, as the 10- hour estimate assumes the preparation goes as planned. TGA analysis does not require the extensive preparation steps/standards that GC/FID analysis requires.

ILMA Comment #2:

Following the method as written, final calculations require at least 10 mathematical steps to arrive at an answer. Calculations require the generation of a statistics package and the use of linear regression. Results may be affected by how the analyst chooses to perform the regression (dropping the y-intercept or forcing the equation through zero).

AQMD Staff Response:

These kinds of calculations should be within the capacity of GC laboratories experienced with ASTM simulated distillation and similar methods. The calculation of linear regressions, for example, is a routine part of GC analysis and can be accomplished either using standard chromatography software or functions built into modern spreadsheets. In any case, if the participating laboratory does not want to develop its own spreadsheets, the AQMD will supply them.

ILMA Reply:

Relative to the TGA method (ASTM E1868-10), the calculations required to arrive at an answer for Method 313L are clearly more complex and subject to more opportunities for error. The fact that AQMD staff has to help individual labs to perform calculations by creating spreadsheets is self-evidence of the highly complex nature of the method.

AQMD lab staff has revised the VOC calculations several times because of inconsistent instrument response. AQMD lab staff also has attempted to apply correction factors to data generated by outside labs in order to obtain the results they desired to see. These calculations involve operator judgment, which is always a problem for standardized methods.

ILMA Comment #3:

The method calls for ramped flow rates, which require electronic flow control (EFC). Many older or entry level GC's in use today do not have this capability, and thus, some labs will be forced to alter the method to suit available hardware. This has been shown to lead to large discrepancies in the retention times of the marker compound (methyl palmitate). During the initial Method 313L robustness testing, retention times for methyl palmitate among the participating labs ranged from 25–42 minutes, which is an enormous spread in GC terms.

AQMD Staff Response:

Most GC methods (including this one) assume uneven instrument capabilities. This is why most GC methods (including ASTM GC methods) either “recommend” or list “typical” instrument parameters rather than “require” them; and focus instead on performance check standards to validate final results. Retention time markers are a common form of quality control which specifically allow for variations in flow, temperature, column performance etc. (deliberate or otherwise) without disturbing the final result. Whether the observed retention time spread is “too large” to generate a reproducible result is one purpose of the interlaboratory study, and should not be assumed in advance. So far, results do not support concerns about the range of methyl palmitate retention times. However, staff is also continuing to evaluate other Method 313-L endpoints to address other issues.

ILMA Reply:

There is a large difference between “uneven instrument capabilities” resulting in fluctuations of retention times by 1 – 5 % among labs, and the results observed for the inter-lab study, in which retention times were found to differ by as much as 30 – 40 %. The method, as written, assumes advanced GC capabilities that all labs do not have, and the results of the initial inter-lab study clearly reflect this.

The variations considered acceptable by the AQMD lab staff may be okay for analysis of organic compounds of a similar chemical nature (hydrocarbons, carboxylic acids, carboxylic esters, amines, and fatty alcohols), but they become unacceptable when analyzing a complex mixture of organic compounds.

ILMA Comment #4:

Under Method 313L parameters, the signal/ noise (S/N) ratio for 60 and 100 second oils is relatively low. Additionally, natural oils do not elute as sharp, clean peaks, but as broad unresolved “humps”. In practice, this means that such oils are difficult to clearly distinguish from the electrical noise generated by the instrument (a.k.a. column “bleed”). This results in ambiguity as to how to properly place the baseline for oil-based samples, and thus how to correctly integrate the chromatogram. Baseline placement has a profound effect on the final calculated results for oil based samples, as evidenced by data generated during the robustness testing.

AQMD Staff Response:

There are several issues folded into one comment. Signal/ noise: AQMD has noted that some laboratories appear to have higher baseline signals and less sample response. The current Method 313L method has been modified to increase the sample amount. Part of this problem may have resulted from suboptimal injection port liners, which have been more exactly specified.

ILMA Reply:

This does not address the fundamental issue that natural oils are extremely difficult to handle quantitatively and reproducibly by GC/FID. Specifying injection liner type is good practice, though the type of liner chosen will have little to no effect on overall difficult to handle peak shape generated by natural oils.

Further AQMD Staff Response:

Column bleed: inter-sample solvent injection has eliminated carryover; some laboratories appear to have a baseline rise of unknown origin, which the AQMD is working to understand and eliminate. In any case, the current version of Method 313L does not include the area of baseline rise.

ILMA Reply:

Inter-sample solvent injection may reduce carry-over, but its elimination cannot be guaranteed. The baseline will rise some finite amount with increasing oven temperature, no matter what is injected. For samples of low signal/noise ratio, accidental inclusion of this column bleed or electrical noise by inexperienced outside laboratories is a real concern that should not be overlooked by AQMD lab staff. Such practice would lead to artificially high calculated VOC values.

Further AQMD Staff Response:

Baseline placement: The appropriate placement of the baseline is unambiguous- It is the blank baseline at the beginning of the run. In this regard, both the baseline difficulties and the baseline placement in Method 313L are similar to ASTM simulated distillation methods and other GC methods of natural products. These difficulties have been successfully negotiated by many laboratories performing similar methods.

ILMA Reply:

Upon close inspection of the solvent blank baseline, an S-shaped curve may be observed. Placement of the baseline at the lower or higher end of the curve will affect the final results for samples of low signal/noise ratio. There is no provision to account for this in the method as written, and thus is considered ambiguous.

The attempt at baseline manipulation does not consider sample influence on the FID detector response. The FID is a flame, anything which disrupts the flame impacts the signal response.

ILMA Comment #5:

Column (DB-624) is classified as mid-polar, and is thus not suitable for performing a simulated distillation, in which compounds are separated strictly by boiling point. The use of a column such as DB-624 introduces a secondary retention mechanism into the chromatography (dipole-dipole interactions). The analysis of MWFs, which contain polar compounds, will result in a separation that is influenced by both chemical structure (dipole moment) and boiling point.

AQMD Staff Response:

The column was not intended to perform simulated distillation. The specified column helps resolve exempt compounds from VOC compounds, allowing more accurate analysis. In addition, there is no reason to assume that a “boiling point” column is more reflective of real-life evaporation. In fact, since real-life evaporation involves chemical structure (dipole-dipole interactions), an argument could be made that DB-624 is more reflective of real-life conditions. (ASTM D7398, Standard Test Method for FAME Boiling Point Range by GC). From further work with the method, we have found that this column can, in fact, reproduce both Method 24 and TGA evaporative methods reasonably well.

ILMA Reply:

The method as written clearly does not reproduce the approved TGA method (which has been demonstrated to reflect long term evaporation in an oven), as evidenced by the artificially high VOC values obtained for semi-volatile oils.

The statement “The column was not intended to perform simulated distillation” indicates an improper understanding of GC instrumentation. The column is actually being used to replicate and perform simulated distillation, with chemical adsorption/desorption interactions also being involved. The use of a marker compound to differentiate a VOC from a non-VOC compound, with the stipulation that ALL compounds that elute prior to the marker compound are VOC in nature, replicates distillation. The adsorption/desorption characteristics of the column stationary phase are not the same as the dipole-dipole interactions of air atmosphere chemical volatilization.

ILMA Comment #6:

Methyl palmitate is a poor choice of marker compound, for the secondary interaction reasons given above, and its choice has never been clearly explained. In essence, methyl palmitate (being a polarizable compound) is retained for a longer time period (due to secondary column interactions) than a hydrocarbon of comparable molecular weight (C19H40). The end result is an artificially large “retention window” in which VOC is calculated, that is not representative of a true boiling point separation.

AQMD Staff Response:

Again, since the column was not chosen for boiling point determination, neither was the endpoint. The endpoint was determined as the closest approximation of EPA Method 24 results. Staff is currently evaluating alternative endpoints to assess if greater conformity with VOC results, as determined by evaporation rate studies and TGA, is achievable.

ILMA Reply:

The behavior of methyl palmitate under the conditions of EPA 24 and on a semi-polar GC column of arbitrary temperature conditions has a tenuous correlation, if any. It is clear from the initial inter-lab studies that using methyl palmitate as the key retention time marker results in calculated VOC values for semi-volatile oils that are significantly higher than results obtained by the Dodge evaporation study or by the approved TGA method. Investigation of alternative marker compounds would certainly improve the method, though would likely require months of additional research and data generation.

ILMA Comment #7:

Detector response factors for non-hydrocarbons are mentioned, but never clearly addressed. Given the vast amount of volatile/semi-volatile raw materials that could conceivably be present in a given MWF, the chance for erroneous results appears to be high. These errors could be compounding with more complex fluids.

AQMD Staff Response:

The errors, if there are any, will be biased low, in favor of metalworking fluids, since the presence of heteroatoms (oxygen, nitrogen, sulfur, and chlorine) reduces sample response. However, in typical metalworking fluid compounds, these heteroatoms are expected to have only a small negative effect. ("Modern Practice of Gas Chromatography" Robert Lee Grob, Eugene F. Barry p.303, "Effect of Molecular Structure Upon the Response of the Flame Ionization Detector", M Kallai, J. Balla, Chromatographia 2002).

ILMA Reply:

The unpredictable GC response of the thousands of possible compounds that might be present in a given MWF adds yet another layer of uncertainty to the method, and introduces additional sources of error to Method 313-L. As many labs would be performing the analysis on fluids of unknown composition, there is no practical way to account for such error during routine testing.

FID detector response is a very real problem, not all compounds produce linear FID response. ILMA is concerned with the generalized opinions expressed in the AQMD response, and the assumptions being made.

ILMA Comment #8:

Split injection technique does not address the possibility of split discrimination in the injector. Discrimination is a phenomenon that can occur for wide boiling point mixtures in which the entire vaporized sample is not swept onto the column homogeneously.

AQMD Staff Response:

AQMD has noted that some laboratories appear to have had injection irreproducibility and some discrimination. To obviate any potential problems, the method has been modified to specify a double-tapered, glass-wool filled, passivated injection port liner. This is very much like specifying the type of pan required for TGA analysis. However, embedded quality control in Method 313L will indicate whether injection port discrimination is taking place. Therefore, the GC method is both self-reporting and self-correcting.

ILMA Reply:

Split discrimination is a function of the injection technique itself, not the type of liner used. Discrimination (by definition) is an indeterminate source of error that could also be a function of injection technique. Normalizing liner type is good practice, but cannot eliminate split discrimination, particularly for wide boiling point mixtures. The notion that the GC method is self-reporting and self-correcting is debatable, at best.

In order to properly determine VOC content by GC analysis, a split injection should not be utilized. ALL the volatile compounds should pass through the column for detection/analysis. A split injection technique could discriminate and “lose” some highly volatile compounds, thus skewing the results.

ILMA Comment #9:

Thick fill columns (1.00 μm) are prone to bleed more than the more common 0.25 μm columns. This effect increases over time as the column ages and the temperature is repeatedly cycled. This will exacerbate baseline placement issues discussed above.

AQMD Staff Response:

The column in the AQMD laboratory has been in use for two years, analyzing lubricants and paints and coatings, and has not deteriorated in performance or developed column bleed. Analysis blanks further address the issue of baseline drift and is therefore added to Method 313L protocol.

ILMA Reply:

The degradation of GC columns over time with repeated use and temperature cycling is an accepted fact. Injection of real-world samples that may contain more aggressive compounds (inorganic acids/bases) than have been studied in the AQMD labs will exacerbate degradation, and may lead to baseline and/or column problems that staff has thus far not anticipated.

Column degradation is a very real concern, especially when the cost per column is rather high. One cannot extrapolate column life expectancy based upon analysis of simple organic mixtures.

ILMA Comment #10:

When real samples are analyzed, many high molecular weight components (surfactants, polymers, polyol esters, sulfonates, etc.) will not elute from the column and remain trapped in the inlet liner or at the head of the column. This may lead to “ghost peaks” in subsequent runs, which in effect is the appearance of compounds not present in sample proper, but slow volatilization of the “leftovers.” Single inter-run “bakeouts” may not fully address this issue.

AQMD Staff Response:

The current method requires an inter-sample solvent injection, which eliminates carryover in a normally clean system. However, as with any analysis of complex samples, the injection port liner should be replaced and possibly the first loop of column trimmed. AQMD does replace injection port liners about once every six months, but has not yet had to either trim or replace a column. Laboratories are also encouraged to perform periodic maintenance which may include and overnight bakeout to clean out contamination.

ILMA Reply:

Again, inter-sample solvent injection is helpful, but cannot guarantee elimination of sample carry-over. This “hope for the best” approach, particularly when dealing with contract laboratories unfamiliar with lubricant/MWF formulations, may lead to chromatography problems and artificially high calculated VOC values that will not be immediately obvious to the inexperienced analyst.

Sample carry-over is one problem, another problem is reactive interference. Reactive interference occurs when the residue left in the injection liner from one sample adversely reacts with the compounds of a different sample when the new sample is injected for analysis.

ILMA Comment #11:

Automated integration performed by a given chromatography software program will have a difficult time handling the complex baseline placement issues for natural oils described above. The notion that any and all contract analytical labs will successfully navigate this issue (via manual integration) is hopefully optimistic, at best.

AQMD Staff Response:

Method 313L contains sufficient quality control to determine whether integrations have been performed properly. In summary, Method 313L is at least as efficient as TGA in terms of output. But Method 313L includes quality control procedures which reveal whether the final results are accurate. In addition, the Method 313L shows greater potential for analyzing water-based samples more accurately than the TGA method, which depends on a secondary water analysis which has not been validated for metalworking fluids. Proposed changes to the Method 313L protocol are expected to mitigate many of the concerns listed above. This protocol will be revised prior to initiating another round robin, and staff will share any changes with ILMA and other stakeholders.

ILMA Reply:

Method 313L, when performed as written with good analytical practice, is clearly not as efficient as the TGA method. The embedded quality control procedures in Method 313L are useful in detecting abnormalities in individual injections, but do not account for proper integration of oil-based unknowns, the most critical issue at stake in the analysis. Proposed changes to Method 313L will require months of additional study/research to determine their effectiveness at mitigating the myriad problems with the method staff has admitted to. This is an unnecessary expense of time and money, when a rapid, reproducible, and accurate TGA method has already been developed and validated.

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ILMA appreciates this opportunity to submit these comments on PAR 1144 and the DSR. ILMA remains available to answer any questions these comments may generate.

Sincerely,



Celeste M. Powers, CAE
Executive Director

cc: ILMA Board of Directors
ILMA SHERA Committee
Charles F. Timms, Esq.
Jeffrey L. Leiter, Esq.
Adam B. Cramer, Esq.