LAGUS APPLIED TECHNOLOGY, INCORPORATED

August 11, 2009

Clerk of the Board
California Air Resources Board
1001 I Street
Sacramento, CA 95814

Cc: Dr. Jon Herner, Manager Greenhouse Gas Technology, jherner@arb.ca.gov
Elizabeth Scheehle, Greenhouse Gas Technology, escheele@arb.ca.gov

Re: Comments on the PROPOSED 15-DAY MODIFICATIONS issued July 27, 2009 for the "Regulation to Reduce Sulfur Hexafluoride Emissions in Non-Semiconductor and Non-Utility Applications"

As stated in initial comment letter issued in February 2009 our company, Lagus Applied Technology, Inc. (LAT), is located in Escondido, CA and has been in business for almost 19 years. Primarily LAT generates quantitative data using tracer gas technology to understand the behavior of complex flow systems existing in of residential, industrial, commercial and government facilities. LAT also manufactures a line of very sensitive measurement-specific gas analyzers that are optimized for the measurement of SF6 when used as a tracer. While the majority of our work utilizes SF6 as the tracer gas we also have extensive experience in using perfluorocarbon tracers (PFCs) in many of our tests for the previous 10+ years. Having used both SF6 and PFCs we understand the advantages and limitations of both types of tracers.

It appears that the Board did not feel that some of the concerns outlined in our February letter merited a change in the proposed regulation. Since no justification will be given for this decision until the Final Statement of Reasons is issued we felt these concerns should be reiterated in this letter. Also, we will attempt to shed some light on the limitations of the PFCs so that the Board will understand these problems before we have to submit applications for exemptions of this rule for certain tests.

LAT would like to thank the Board for responding to our concern regarding the storage of cylinders containing dilute mixtures of SF6 in nitrogen or air at our Escondido, CA office for use at out-of-state testing locations. This change in the regulation may allow LAT to retain its primary office in California.

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The following points were detailed in the February letter but were not addressed in the Proposed 15-Day Modifications:

There are no published TLVs or PELs for PFCs

The absence of a TLV/PEL for any of the PFCs does not imply that the chemical/substance is unsafe. PFCs do not possess listed TLVs/PELs since little to no toxicological data exist with which to support publishing a TLV or PEL value. SF6 exhibits the highest TLV/PEL value (1000 ppm) attached to any man-made chemical. Many toxicological studies as well as the extensive use of SF6 in certain medical and veterinary procedures have shown that there are no known adverse health effects. Often clients desiring a tracer gas test may be legally or ethically bound to use a tracer that has a published PEL/TLV.

One should also note that the ASTM standard for tracer gas ventilation testing (E741) specifically cautions against using any gas *for which no OSHA PEL exists*.

SF6 purity is 99.99+% while purity of PFCs is approximately 95%

This difference in purity produces a substantial increase in measurement uncertainty when using a PFC due to the compounding of concentration uncertainties in both the source gas mixture(s) and in analyzer calibration gas mixtures. This will be elaborated in an appendix to this letter

***De minimus* quantities**

Small release quantities coupled with a carbon offset tax would encourage the use of PFCs whenever their use is technically feasible. It should be noted that allowance of a single-event fume hood test using SF6 per the ASHRAE 110 Standard releases a considerably greater quantity of SF6 than any single ventilation or flow rate test using SF6 tracer gas.

Parenthetically it should be noted that during a meeting of the Working Group a staff member of the University of California system stated (via telephone) that he had approximately 1500 fume hoods that required testing. Based on this alone, since each ASHRAE test utilizes approximately 2/3 Kg (1.5 pounds) of SF6, it is difficult to understand the Board's apparent unwillingness to allow *de minimus* releases of SF6 in other applications.

Addition to section 95341(a) adding an exemption for research purposes

The thrust of this section is that only government laboratories or universities can conduct acceptable research using tracer gases. This ignores that fact that large, well respected private

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companies have been capable in the past of undertaking serious research using tracer gases. This section precludes participation by the private sector in appropriate research.

To cite a few examples, in the 1980s, Aerovironment Corporation and Meteorology Research Incorporated performed significant research into using tracer gases for meteorological and pollution studies. The S-Cubed Division of Maxwell Laboratories, Incorporated developed the basic techniques which are used in both the nuclear power industry and the semiconductor fabrication industry under contract for the Army Toxic and Hazardous Materials Agency. A blanket preclusion of appropriate private sector firms does not seem appropriate given the history of this subject.

In an attached appendix LAT has attempted to clarify issues regarding the use of SF6 as a tracer that directly affect its continuing business in three particular areas. These include flow rate measurements, ventilation performance measurements for energy conservation, indoor air quality hazardous containment integrity testing within the semiconductor industry, and safe haven testing. In particular, the inability to continue providing flow rate calibration of in-situ flow measurement stations will directly lead to a loss of between 10% and 15% in yearly revenues. It is difficult to estimate the effect on other business segments of the loss of SF6 measurement capability in California since measurement service demands can be variable from year to year.

In summary, Lagus Applied Technology, Inc. is committed to reducing SF6 emissions specifically by utilizing the extraordinary sensitivity of the LAT tracer gas analyzers to allow measurements to be undertaken at very low initial gas concentrations. In the future LAT will expand the use of PFCs where technically feasible. However, LAT staff truly believes that there are both technical and potential health/safety issues that make a complete ban on SF6 tracer use an unwise decision. LAT hopes that this letter and the attached appendix has allowed the board become more knowledgeable on the entire SF6 usage issue so they can make an informed decision during this rulemaking process.

Sincerely,

Lagus Applied Technology, Inc.

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Appendix to CARB response letter dated August 11, 2009

In this appendix we attempt to provide a brief description of the major test types that LAT routinely provides for clients both in California and throughout the US.

Tracer Gas Flow Rate Testing

In a tracer gas flow rate test, a tracer gas of known concentration (usually a mixture of SF6 diluted in nitrogen) is continuously injected into a flowing stream at a known (measured) and constant rate. The resulting concentration downstream of the injection point may be used in conjunction with a conservation of mass equation to calculate the flow rate of the stream.

Tracer gas flow rate testing is an approved alternate method for the Southern California Air Quality Management District (AQMD) when performing a Relative Accuracy Test Audit (RATA). It is based on ASTM Standard E2029 "Standard Test Method for Volumetric and Mass Flow Rate Measurement in a Duct Using Tracer Gas Dilution".

A RATA is done to verify and certify the environmental emissions monitoring that occurs in industrial facilities. In certain situations traditional flow rate measurements (i.e. pitot tube, thermo-anemometer, annubar) of stack flow are not technically feasible. For a Southern California refinery client, LAT performs tracer gas tests to provide periodic in-situ calibrations of the facility fuel flow meters. Flow rate measurements of fuel gas feeding an individual heater that induces flow in a particular stack are then used to indirectly measure stack flow. These stack flow values in turn are provided to the AQMD to demonstrate compliance with a variety of environmental permits. Typically LAT performs approximately 30 of these fuel flow meter calibration tests per year. Each test is run for approximately 10 hours and uses roughly 10 grams of SF6. This implies a total use on the order of 300 grams/year.

Switching the tracer gas to a PFC raises the following three issues:

Quantitative measurement a PFC in a fuel gas stream onsite may not be technically feasible

SF6 measurement is typically accomplished using a measurement specific gas chromatograph optimized for the detection of very low concentrations of SF6. This analyzer can be configured to respond to many of the PFCs. However, refinery fuel gas streams contain numerous compounds that can interfere with a chromatograph output signal. Fortuitously the SF6 signal arrives in a quiescent part of the chromatograph output. It is known that PFC signals do not arrive in a correspondingly quiescent part of the chromatograph response output. In a chromatograph it is possible for two gaseous components to provide output signals that partially

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or completely overlap in time. In such a case it is not possible to assign a quantitative value to the PFC output.

The accuracy of the PFC measurement WILL be less than for a comparable SF6 measurement

SF6 is commercially available at 99.99% purity while the purity of PFCs is typically 95%. This decrease in purity creates a larger measurement uncertainty for PFC injection gases and calibration gases than for corresponding SF6 gas mixtures. Table 1 provides the measurement uncertainty for various SF6 and PFC injection and calibration gases. For a calculation of total measurement bias (systematic uncertainty) the uncertainty of the injection gas concentration is added to the uncertainty of the calibration gases (as a root sum square). Using the values in Table 1, the bias portion of the measurement uncertainty attributed to injection/calibration gases for PFCs would be 7.1% but only 2.2% if SF6 is used. Such a large measurement uncertainty may eliminate the potential value to the client of in-situ flow meter calibration using a PFC tracer.

The measurement of high fuel gas flow rates will not be possible

PFCs are liquids at normal temperature and pressure (NTP) while SF6 is a gas. As stated above, test gas injection mixtures consist of diluted tracer in nitrogen. Since SF6 is a gas at NTP it can be mixed with nitrogen in higher concentrations than any PFC. Per our gas mixture supplier, SF6 can be prepared to concentrations of approximately 8.8% SF6 in N2, while resulting PFC concentrations vary (due to the chemical’s vapor pressure) from approximately 0.0075%- to 0.36% (75 ppm to 3600 ppm).

Note that higher flow rates create a greater dilution. From Table 1 it is clear that PFCs exhibit between 25 to 1200 times less measurement range based upon injection gases alone. Table 1 also lists the maximum measureable flow rate for each tracer gas under typical conditions for a fuel gas flow rate RATA.

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Table 1

Tracer Gas Type	Injection Gas Max. Conc.	Uncert.	Calibration Gas Concentration Uncertainty ppm** range	1-999 ppb**	100-999 ppt**	<100 ppt	Max. meas. flow rate (scfm)***
SF6	8.8%*	1%	1%	2%	2%	5%	155000
PDCB	3600 ppm	5%	5%	5%	10%	up to 50%	6300
PMCP	324 ppm	5%	5%	5%	10%	up to 50%	570
PmCH	80 ppm	5%	5%	5%	10%	up to 50%	140
PDCH	75 ppm	5%	5%	5%	10-20%	up to 50%	130

* 8.8% is equal to 88000 ppm

** ppm is parts per million, ppb is parts per billion, ppt is part per trillion (10^{-12})

** *Assumes 5 slpm injection rate and 100 ppb downstream concentration (typical operating values for AQMD fuel flow rate tests)

Semiconductor Fabrication Equipment Containment Test

Within the semiconductor industry many hazardous compounds are used in chip fabrication. SEMI Standard F15 SEMI F15 "Test Method for Enclosures using Sulfur Hexafluoride Tracer Gas and Gas Chromatography" is used to evaluate the ability of an exhausted chip fabrication tool enclosure to contain a worst case leak of a potentially hazardous gas or vapor. (Note that the test methodology of this standard has recently been incorporated into a more comprehensive testing standard denoted SEMI S6 "EHS Guidelines for Exhaust Ventilation of Semiconductor Manufacturing Equipment".)

This test releases a known flow rate (typically 28.3 SLPM of 1 CFM) of diluted tracer gas within the enclosure at potential failure points. The periphery is sampled for the existence or absence of tracer gas. The measured concentration of tracer gas is used along with the potential concentration of internal process gas to calculate an equivalent release (external to the enclosure) concentration of hazardous gas. A companion SEMI standard (SEMI S2) dictates that outside a successful enclosure no more than 25% of the TLV/PEL concentration of the most hazardous gas/vapor used within the enclosure will be measured.

For many of the gases or vapors used in the semiconductor industry this criterion can be satisfactorily sensed using any one of several of the PFCs. However three compounds used within the semiconductor chip fabrication industry possess low TLV/PEL values. These are listed in Table 2 along with their corresponding health safety limits.

Because the PFCs are liquids at NTP, they must be diluted in nitrogen or air to allow a realistic release within the enclosure. Table 2 also provides the allowable maximum external concentration under SEMI S2. Using a PFC source these equivalent concentration values are

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extremely difficult to reliably measure for Germane and DiBorane. These difficulties are related to the chromatographic separation of the constituent and the ultimate sensitivity of the gas detector. The required detection limit is *not* attainable for Arsine using a PFC source.

Table 2

Semiconductor Fabrication Compounds Health and Safety Limits

Compound	TLV/PEL	Typical Source Gas Concentration	Allowable External Concentration
Arsine-AsH3	5 ppb	10%	0.1 ppb
DiBorane-B2H6	100 ppb	1%	0.25 ppb
Germane-GeH4	200 ppb	1%	0.5 ppb

Note also that in some semiconductor facilities the lack of a published health and safety limit resulted in the denial of permission to use a PFC tracer within the facility.

Ventilation Testing

Ventilation testing using tracer gas is most often undertaken using ASTM Standard E741 "Standard Test Method for Determining Air Change Rate in a Single Zone by means of a Tracer Dilution". This test methodology is commonly used in structures to measure the quantity of fresh air delivered.

Originally the standard was developed in response to the energy crisis of the 1970s as an aid in energy conservation programs. The technique measures fresh air infiltration which can be a significant component of the total heating and cooling load of a building.

Later the technique was adopted for use in Indoor Air Quality Studies and Health Safety studies within the petrochemical and chemical process industries. The US military has used the technique to study energy conservation issues as well as CBW habitability and protection issues. The nuclear power generation industry has adopted the standard as a reliable means to demonstrate the safety and integrity of Control Room ventilation systems.

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Since 9-11 the method has found wide applicability in consequence analysis of potential CBW attacks on occupied structures.

Although there is no “standard” tracer gas, Table X1.1 of the ASTM E714 standard provides a list of some of the compounds that have been used as tracer gases under the standard. It is instructive to calculate the likely global warming consequences of some of the gases in this table if each is used to measure the infiltration.

The following Table 3 provides a comparison of the amount of tracer gas to achieve at least 10 times the detection level (as defined by the ASTM standard) in order to perform an air infiltration measurement for a modest office building having a volume of 2831 m^3 (100,000 ft^3). In the case of CO2 the injection amount is set to approximately 5 times the background level in the atmosphere so as to not exceed the TLV.

Table 3

Gas Quantities Required for Infiltration Measurements using ASTM E741

Tracer	GWP	Initial Concentration	Injection Amount (cm^3)	Injection Amount (gm)	Mass Ratio of Selected Tracers to CO2
SF6	22,800	1 ppb	2.8	0.0174	3.69×10^{-6}
PFC-318	10,300	500 ppb	1415	7.22	1.53×10^{-3}
N2O	298	25 ppm	70792	132.4	0.028
Halon 1301	7140	10 ppb	28.3	0.0879	1.87×10^{-5}
CO2	1	2500 ppm	7.08×10^{6}	4712.4	1

As is apparent from the above table, even though SF6 exhibits a large GWP, on a mass basis SF6 contributes a lesser total to warming than any of the other gases listed for a typical ventilation test using the ASTM standard.

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