

MEMORANDUM

To: AIR QUALITY CONSULTANTS

From: John Sliwinski
OSB Lab

Re: OSB LAB Calibration and Quality
Assurance/Control
VOC-ATD-GC-MSD

Date: 03.07.17

SURROGATE PREPARATION

Primary Surrogate Bag

A gas bag is prepared containing four surrogates (Tetrafluoroethane, Difluorobenzene, D8-Toluene and either Hexachlorobutadiene or D26-Dodecane if required by type of sample) approximately every four to six weeks based on the monitoring of the degeneration of instrument response of the surrogates. A Tedlar bag is filled with 10L Zero air and 1000uL of gaseous 1,1,1,2-Tetrafluoroethane, 5.0uL of liquid 1,4-Difluorobenzene, 5.0uL of liquid D8-Toluene and 2.5uL of liquid 1,1,2,3,4,4-Hexachloro-1,3-butadiene or 5.0uL of liquid D26-Dodecane are then added. The Tedlar bag is labeled with the date then heated for 15 minutes at 50°C to volatilize and disperse the added surrogates. This bag is used for the spiking of all samples and standards, in the preparation of QUALITY CONTROL CHARTS on a LOTUS spreadsheet, and in generating LIBRARY SEARCH REPORTS using HP-Agilent software. Concentrations of surrogates are calculated based on the actual volume of Zero air in the gas bag, which is determined by a calibrated airflow over a period of time using a manual or electronic bubble meter. The relative standard deviation of 10 consecutive flow measurements should not exceed 0.25%.

Secondary Surrogate Bags

Additional surrogate bags are prepared in similar fashion as dictated by analytical requirements.

<u>Surrogate</u>	<u>Amount Injected (uL)</u>	<u>Gas Bag Volume (L)</u>
1,1-Difluoroethane	50.0 (gas)	1
Fluorobenzene	3.0 (liquid)	5
D10-p-Xylene	10.0 (liquid)	1

Secondary Surrogates Bags can also be prepared by combining two or three of these surrogates as required. Other surrogates that are available for use are D-Chloroform, 1-Bromo-4-

Fluorobenzene, D6-Benzene and D8-Naphthalene.

QUALITY CONTROL CHARTS

Surrogate QC Template and Database

An initial daily conditioning run of a 250uL portion of the Surrogate Bag is analyzed on either an HP5972 or HP5973 MSD. At least one additional 250uL portion of the Surrogate Bag is analyzed (called Performance Run) to verify that the peak area ratios for the total ion chromatogram (TIC) versus selected ions (multiplication factors (MF)) for all four surrogates, when entered onto the SURROGATE QC template, fall within the upper and lower warning limits (± 2 STD) of the previous five Performance Runs. If any of the calculated multiplication factors of the latest Performance Run are flagged because they fall outside the current limits, corrective action must be taken either by overriding the flag, if the limits are too narrow, or by running more Performance Runs to establish new multiplication factors that represent the current stability of surrogate instrument response. The SURROGATE QC database for each instrument is updated with all Performance Runs, as a record to demonstrate consistency and reproducibility. The four surrogates with their different volatilities and elution times were chosen to cover the entire chromatogram period.

SURFORM QC TEMPLATE and DATABASE

MB, SS, VOST Tubes

Standard procedure stipulates a 250uL aliquot from the Surrogate Bag to be spiked onto the MB, SS or VOST sorbent tube used to collect the sample. Using an external tube desorber and fractionator, the collected sample is transferred in a ratio of approximately 1:1 at 280°C using a stream of dry Helium onto two multisorbent C tubes. Samples known to have low concentrations can be transferred directly without splitting while overloaded samples may be split using a higher dilution ratio with critical capillary orifices or split several times to avoid saturating the MSD. The ratio that the sample is transferred onto two C tubes is the split factor (SFT) and is determined by flow measurements using a bubble meter.

Gas Bags

An appropriate amount of sample (determined from an estimate of the expected level of unknowns in the sample) is transferred onto a multisorbent C tube in preparation of analytical determination and a 250uL aliquot from the Surrogate Bag is then added.

After analysis by GC-MSD, selected ions for the four surrogates are integrated manually and entered into SURFORM QC template along with details pertaining to the running of the sample or standards (Sample Run, Tube ID, SFT, Volume (L)). Formulas in the SURFORM QC template calculate (using MFs based on the previous five SURROGATE QC Performance Runs) the D8-Toluene Response Factor (D8-RF). The D8-RF for each sample or standard normalizes the responses of all the peaks (area counts) in that chromatogram's LIBRARY

SEARCH REPORT in order that effective comparisons can be made among all the other samples or standards for a particular project. Response Factors (RFs) for the other surrogates are used to verify that instrument response has remained stable for the entire chromatogram period and to verify D8-RF integrity (accuracy, bias, precision and reliability)

<u>Surrogate</u>	<u>Selected Ions</u>	<u>CAS#</u>
1,1,1,2-Tetrafluoroethane	33, 69, 83	811-97-2
1,4-Difluorobenzene	63, 88, 114	540-36-3
D8-Toluene	98, 100	2037-26-5
1,1,2,3,4,4-Hexachloro-1,3-butadiene	223, 225, 227	87-68-3
D26-Dodecane	46, 50, 66	16416-30-1
1,1-Difluoroethane	51, 65	75-37-6
Fluorobenzene	70, 96	462-06-6
D10-p-Xylene	98, 116	41051-88-1

LIBRARY SEARCH REPORT

For report preparation, all the relevant peaks in the chromatogram have to be identified and quantified. A LIBRARY SEARCH REPORT is generated by an HP-Agilent macro based on either automated or manually set integration parameters that produces the best ion fragmentation match for each integrated peak from the latest NIST mass spectral library using an HP-Agilent probability-based matching (PBM) algorithm that compares the fragmentation pattern of the peak with those in the NIST library. The HP-Agilent macro has been modified by OSB LAB to convert the integrated peak areas into relative concentrations as D8-Toluene by inputting into the computer the sample split factor (SFT), the volume of sample collected in the case of SS, MB or VOST tubes, or volume of sub-sample for a gas bag and the D8-Toluene Response Factor calculated for that sample.

STANDARD CALIBRATION

SCAN

Relative concentrations of the identified peaks have to be converted to actual chemical concentrations. Standards are prepared on an as needed basis for compounds of interest and analyzed the same way as samples at a suitable range of concentrations with surrogates. Linear or quadratic calibration curves are constructed from the TIC for each compound and are converted to dependent variable relationships with D8-Toluene, which are called chemical D8-Toluene Response Factors (TRFs) for linear curves. The relative concentration of each identified sample peak is multiplied by the TRF of that compound to obtain the actual concentration. Calibration is also performed traditionally using quadratic equations.

In cases where identification and integration of the peaks in a sample is difficult because of

interfering peak co-elution, calibration curves are constructed from the integrated area of a selected ion of the compound of interest in the standards. Chemical D8-Toluene Response Factors are then determined for the chosen ion for that compound. The same ion is identified in the sample chromatogram at the standard compound retention time, manually integrated, and actual concentrations calculated using the ion TRF or quadratic equations.

TIVA(Target Ion Verification Analysis) is a semi-automated method developed by OSB Lab utilizing existing HP-Agilent software. Target ions for compounds from a suitable range of concentrations of standards are identified and used to establish retention time windows for each elution program. The standard parameters are then used to set up a search method in instrument data analysis to process sample chromatograms semi-automatically. The same target ions in a sample chromatogram are identified within the same retention time windows, integrated automatically or manually if necessary, and actual concentrations are calculated based on SFT, sample Volume(L), TRFs or quadratic equations.

SIM

In situations where enhanced sensitivity is required to achieve lower detection limits or only specific target chemicals sought, Selective Ion Monitoring is utilized. Data collection methods are set up to narrow the number or range of ions that are counted. In full scan mode, the data collection function of the HP-Agilent software rapidly measures the response of all the ions from approximately 26 to 500 m/z in each scan for the duration of the full chromatogram. In SIM mode, the HP-Agilent data acquisition software allows more time (dwell time) to count the electronic signals of a single target ion and one or two qualifying ions for a particular compound during each scan within a retention time window (Group) resulting in much higher target area counts, enhancing the sensitivity and resulting in the ability to detect much lower quantities of the compound. The flexibility of SIM mode allows data for up to 30 individual ions to be collected in each window up to 50 Groups. Unfortunately, all data for unprogrammed chemicals would not be captured and the sample information lost.

STANDARDS

Calibration to obtain accuracy with respect to a true reference point is achieved using commercially prepared certified standard gas high pressure cylinders or achieved using in-house preparation of Tedlar gas bag standards. These are prepared in two forms: the addition of one or more individual chemicals into a gas bag or the preparation of neat mixtures of up to 30 chemicals and injecting such a mixture into a gas bag termed a standard campaign.