ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

ATTACHMENT C

1.0 PURPOSE:

1.1 To describe the setup, calibration and procedure for analyzing soil and sludge for the presence of 1,4-dioxane by purge and trap gas chromatography, mass spectrometry.

2.0 SCOPE:

2.1 This method is used for the quantitative determination of 1,4-dioxane in soil and sludge.

2.2 This method is a purge and trap gas chromatographic/mass spectrometer(GC/MS) method using an ion trap detector.

2.3 The method detection limit is 10ug/kg for 1,4-dioxane, based on a 5g sample size.

2.4 This method is restricted to use by or under the supervision of analysts experienced in the use and operation of purge and trap and GC/MS systems and in the interpretation of mass spectra.

3.0 PROCEDURE:

3.1 Apparatus and Materials

3.1.1 4oz clear wide mouth jars with Teflon lined caps.

3.1.2 Purge and trap device. Must consist of a 25ml purge vessel, needle sparge, volatiles trap, and a desorber.

3.1.3 GC/MS system:

3.1.3.1 Temperature programmable Gas Chromatograph with a split/splitless injector.

3.1.3.2 JW DB-WAX 30M by .25mm ID column with a .5um film, or equivalent.

3.1.3.3 Mass Spectrometer capable of scanning from 20 to 260 amu full scan electron impact ionization mode and capable of meeting tune criteria for 4-bromofluorobenzene (see tune criteria for BFB in SW-846, volume 1B, method 8240)

3.1.4 Syringes

3.1.4.1 25ml syringe with luer lock tip and 2 way luer lock valves.

3.1.4.2 micro syringes ranging from 10ul to 1000ul.

3.1.5 Analytical balance which can weigh accurately to 0.0001g.

3.1.6 Ultra high purity helium for carrier gas supply and purge gas.

3.1.7 Crucibles

3.2 Reagents

3.2.1 Reagent water (water which does not contain interferences at the MDL of the parameter of interest, i.e. carbon filtered tap water).

3.2.2 Methanol-pesticide quality or equivalent

3.2.3 Pure standard materials or certified solutions of 4-bromofluorobenzene, 1,4-dioxane and deuterated 1,4-dioxane (1,4-dioxane-d_8)

3.2.4 Stock standard solutions-a stock standard solution of 1,4-dioxane can be prepared from assayed material in methanol.

3.2.4.1 Place 9.8ml of pesticide grade methanol into a 10ml ground glass stoppered volumetric flask. Let stand

unstoppered for a few minutes to allow the wetted surfaces to dry.

3.2.4.2 Add the assayed reference material using a 50uL syringe. Add approximataly 0.02g by letting 2 or more drops fall directly into the alcohol without contacting the sides of the flask.

3.2.4.3 Reweigh, dilute to volume, stopper and invert three times to mix the solution. Calculate the concentration in ug/L by the net gain in weight.

3.2.4.4 Transfer the material to a clean glass, Teflon sealed screw cap vial. Store at -10 to -20 °C and protect from light.

3.2.4.5 Prepare a fresh standard every two months or when comparison with a check standard indicates a problem.

3.2.4.6 Prepare an internal standard of 1,4-dioxane-d8 in the same manner by following steps 3.2.4.1 through 3.2.4.5.

3.2.4.7 Prepare a solution of 4-bromofluorobenzene in methanol in the same manner as above.

3.2.5 Secondary dilution standards-using the stock standard solutions, prepare secondary dilution standards in the following manner;

3.2.5.1 Prepare a standard of 1,4-dioxane by adding a calculated volume of stock standard material to 5ml of reagent water for a final concentration of 10 ug/ml.

3.2.5.2 Prepare a secondary dilution standard of 1,4-dioxane-d8 (internal standard) by adding a calculated volume of stock standard material to 5ml

of reagent water for a final concentration of 30 ug/ml.

3.2.5.3 Prepare a secondary dilution standard of BFB by adding a calculated volume of stock standard material to 5ml of pesticide grade methanol for a final concentration of 25ug/ml.

3.3 Sample handling, preservation and storage.

3.3.1 Collect all samples in 4oz clear wide mouth jars with teflon lined lids.

3.3.2 The samples must be kept at 4°C from the time of collection until analysis.

3.3.3 Samples should be analyzed within 14 days of collection.

3.4 Daily GC/MS Performance evaluation

3.4.1 At the beginning of each day the GC/MS must be checked to assure that proper identification of ions is achieved and acceptable performance criteria is met for BFB. The performance tests must be passed before calibration standards, blanks, and samples can be run.

3.4.2 Inject 2uL of the BFB secondary dilution standard directly onto the column or, add 30uL to 15ml reagent water (50ppb final concentration) and purge the sample according to the procedure described in (3.5.1)

3.4.3 Obtain a background corrected mass spectra of BFB and confirm that all m/z ratios described in section 3.1.3.2 are met. If these criteria are not met retune the instrument until proper ratios are obtained.

3.5 Calibration

3.5.1 The purge and trap system and the GC/MS can be run under the following typical conditions;

3.5.1.1 LSC 2000/ALS 2016 with Supelco #1 trap.

purge flow	50ml/min
prepurge	0 min
preheat	4 min
sample temp	70°C
purge	10 min
dry purge	2 min
desorb preheat	175°C
desorb	180 for 4 min
bake	220°C for 10 min
autodrain	off
BGB	on at 0 sec delay
valve temp	LSC 2000 at 180°C
valve temp	ALS 2016 at 170°C
line temp	LSC 2000 at 180°C
line temp	ALS 2016 at 170°C
mount temp	ALS 2016 at 170°C
runs/sample	1

3.5.1.2 Gas Chromatograph

head pressure	16psi
flow velocity	20cm/sec
initial temp	40°C hold for 2 min
ramp and hold	8°C/min to 90°C, hold for 3 min
ramp and hold	25°C/min to 220°C for 2 min
relay	on (1) for the entire run

3.5.1.3 Mass Spectrometer

open split	1ml/min
mass range	50-250
sec/scan	6uScans/sec (analyst discretion)
acquire time	analyst discretion
Xfer temp	220°C
peak threshold	2
fil/mul delay	200 sec
mass defect	49
AGC on	mass 45
scan mode	full

3.5.2 Determine the response factor (RF) for 1,4-dioxane. (Prepare calibration standards by using the secondary dilution standard and the internal standard 1,4-dioxane-d8.)

3.5.2.1 Fill the 25ml syringe with reagent water and adjust to 15ml. Be sure no air bubbles are present.

3.5.2.2 With a 50ul micro syringe, add 25ul of the 30ug/ml internal standard. This will give a final concentration of 50ug/L.

3.5.2.3 Add a volume of the 1,4-dioxane standard which would result in a final concentration at or just above the MDL (1ug/L).

3.5.2.4 Transfer the calibration sample to a 25ml purge vessel through the sample introduction port on the ALS 2016.

3.5.2.5 Analyze the calibration standard according to the parameters set up in section 3.5.1.

3.5.2.6 Tabulate the area response of m/z 88 for 1,4-dioxane to that of the internal standard m/z 96 and calculate the response factor according to Equation 1.

Equation 1.

$$RF = (A_s)(C_{is})/(A_{is})(C_s)$$

where:

A_s = Area of the characteristic primary m/z for the standard.

A_{is} = Area of the characteristic primary m/z for the internal standard 1,4-dioxane-d8 (96). The secondary m/z is 62.

C_s = Concentration of the standard.

C_{is} = Concentration of the internal standard 1,4-dioxane-d8.

3.5.2.7 Repeat steps 3.5.2.1 through 3.5.2.6 by adding volumes of 1,4-dioxane standard which cover the working range of the instrument or, which cover the range of concantrations of the samples which will be run.

3.5.2.8 If the RF values over the range have a relative standard deviation (RSD) <35%, the average RF can be used for the calculations. If the variance is >35%, rerun the calibration standard which is out of range. Repeat this procedure until a average RF is obtained.

3.6 Sample analysis for concantrations below 0.1mg/kg. For sample concentrations expected to exceed 0.1mg/kg use a 1.0g sample size.

3.6.1 Let the sample come to room temperature.

3.6.2 Weigh approximately 5.0g of sample directly into a 25ml purge vessel. Connect the vessel to the ALS.

3.6.3 Fill a 25ml syringe with reagent water.

3.6.4 Insert the plunger and adjust the volume to 15ml and close the luer lock. Be sure no air bubbles are present in the water.

3.6.5 Open the luer lock valve and inject a volume of internal standard which will result in a final concentration of 50ug/L (ppb) in the water.

3.6.6 Introduce the water to the vessel containing the sample through the sample introduction valve.

3.6.7 Analyze the sample under the conditions described in section 3.5.

3.6.8 Tabulate the area responses of the primary m/z for 1,4-dioxane and the internal standard. Calculate the concentration of 1,4-dioxane in the sample using Equation 2:

Equation 2:

$$Conc\ (ug/kg) = (A_s)(C_{is})(V_{dil})/(A_{is})(RF)(W_{samp})$$

Where:

A_s = Area of the characteristic primary m/z for the compound.

A_{is} = Area of the characteristic primary m/z for the internal standard 1,4-dioxane-d8 (96). The secondary m/z is 62.

C_{is} = Concentration of the internal standard 1,4-dioxane-d8 (ug/L).

RF = The response factor for the compound calculated in Equation 1.

W_{samp} = sample size (kg)

V_{dil} = volume (L) of I.S. spiked reagent water used for dilution (0.015L used in this method).

3.6.9 Determine the dry wieght basis of the sample.

3.6.9.1 Weigh 5-10g of sample into a tared crucible and record the weight to the nearest 0.1mg.

3.6.9.2 Place the sample into an oven at 105°C over night.

3.6.9.3 Remove the sample from the oven and place in a desiccator until it reaches room temperature.

3.6.9.4 Reweigh the sample and record to the nearest 0.1mg.

3.6.9.5 Calculate the percent moisture following equation 3.

Equation 3:

$$\%moisture = [(Wt_{sam} - Wt_{dry\,sam}) * 100] / Wt_{sam}$$

Wt_{sam} = grams of sample

$Wt_{dry\,sam}$ = grams of dry sample

3.6.10 Report concentration of 1,4-dioxane and percent moisture.

3.7 Daily Quality control

3.7.1 BFB tune criteria must be met before analysis of blanks, standards or samples may begin.

3.7.2 Analyze system blanks of reagent grade water spiked with internal standard to determine system background.

3.7.3 Calibration check standard.

3.7.3.1 A daily check of the calibration curve must be performed before sample analysis can begin. This is accomplished by analyzing a calibration standard at a midpoint concentration.

3.7.3.2 The check standard must fall within $\pm$%25 error. If this cannot be accomplished the instrument must be recalibrated.

3.7.4 Analysis of sample spikes and duplicates.

3.7.4.1 Daily analysis or a minimum of %15 of all samples must be analyzed in duplicate and spiked with a known concentration of 1,4-dioxane standard to establish precision and percent recovery data.

3.7.5 File all QC data with the raw data from each sample lot.

4.0 MISCELLANEOUS:

4.1 If the analyst is unsure of the concentration range of the sample it is a good idea to screen the sample before analysis. High concentrations of analytes (>0.100mg/kg) in a sample can cause memory in the system or carryover into the next sample run.

4.2 If analyte sample concentrations exceed 0.100mg/kg, analyze a reagent blank to ensure there is no system carryover.

5.0 REFERENCE DOCUMENTATION:

5.1 Test Methods for Evaluating Solid Waste, SW-846 Third Edition, Volume 1B, method 8240.