

Standard Operation Procedure (SOP) for the Extraction and Instrument Analysis of Siloxanes from Cartridges

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1.0 Scope and Application

This method covers the extraction and instrument analysis of siloxanes in air sampled onto cartridges. This method was developed specifically for extracting and analyzing higher concentrations of D5 in controlled laboratory experiments but can be adapted for more siloxane compounds and lower concentrations. The samples are extracted using hexane directly into GC vials, spiked with internal standard, and analyzed using gas chromatography with mass spectrometry (GC-MS).

The method is adapted from Yucuis, R.A.; Stanier, C.O.; and Hornbuckle, K.C. 2013. "Cyclic siloxanes in air, including identification of high levels in Chicago and distinct diurnal variation" *Chemosphere*, 92, 905-910.

2.0 Quality Assurance and Control (QA/QC)

2.1 Method blanks

Interferences from glassware, cartridge, and solvents are monitored by analyzing method blanks. The method blank is run through the extraction process in parallel with the samples. The method blank consists of a cleaned sample cartridge. The D5 in the method blanks is quantified and used to calculate the limit of quantification (LOQ) equal to the average plus three times the standard deviation (the upper level of the 99% confidence interval).

2.2 Field blanks

Contamination during deployment and handling in the field is monitored by analyzing field blanks. The field blank is a clean cartridge identical to a sample cartridge but that is not connected to the sampling system. The field blank is instead unwrapped from its foil and set next to the sampling system during sample collection, then re-wrapped in its foil and returned to its clean amber jar. The field blanks are run through the extraction process in parallel with the samples.

2.3 Instrument blanks

An instrument blank consisting of hexane is run before and after the calibration standard and at the end of the sequence to check for interferences. Samples are sequenced from lowest to highest expected concentrations to limit potential carryover between injections.

2.4 Duplicates

Duplicate method blanks, field blanks, and samples are collected and analyzed together.

2.5 Cleaning glassware and supplies

All glassware including test tubes, caps, aluminum foil, amber glass jars with Teflon lined caps, Pasteur pipets, GC vials, and GC vial caps are triple rinsed with methanol, acetone, and hexane immediately prior to use.

2.6 Cleaning sampling cartridges

Cartridges are cleaned by soaking in hexane in triple-rinsed amber jars overnight. Then they are washed through with DCM 3x and hexane 3x. Lastly they are wrapped in triple-rinsed aluminum foil and placed in triple-rinsed amber jars with triple-rinsed Teflon caps and kept in the cleaned media fridge until deployment.

2.7 Sample Handling

Samples are re-wrapped in their triple-rinsed aluminum foil, returned to their triple-rinsed amber jars with triple-rinsed Teflon caps, and kept in the freezer until extraction.

2.8 Recovery

Before starting sample extraction in a project, two recovery experiments are performed.

2.4.1 Spike Test

Three GC vials (triplicates) are spiked with the target compound D5 and the internal standard PCB30. The three vials are run on the GC and the quantified D5 is compared with the known amount spiked.

2.4.2 Blank and Blank Spike Test

Three cleaned sample cartridges (blank spike triplicates) are spiked with the target compound D5 and eluted with hexane alongside three cleaned, unspiked sample cartridges (method blank triplicates). The D5 in the blank spike triplicates is quantified and compared to the known amount spiked. The D5 in the method blanks is quantified and used to calculate a preliminary limit of quantification (LOQ) equal to the average plus three times the standard deviation (the upper level of the 99% confidence interval).

2.9 Cartridge Breakthrough

Before starting sample extraction, a cartridge breakthrough test is performed. Using highest anticipated flow and concentration sampling conditions, a backup cartridge is connected immediately following the primary cartridge in the sampling setup. Samples are otherwise collected, extracted, and analyzed as usual. Mass on the backup cartridge should be negligible compared to the primary cartridge.

2.10 Elution Volume

Before starting sample extraction, a test on the volume used to elute the sample cartridges is performed. Following the highest anticipated concentration sampling conditions, a second elution of the same solvent volume should be collected from the sampling cartridge into a separate GC vial and analyzed on the instrument in the same sequence as the first elution. Mass on the second elution should be negligible compared to the primary elution.

3.0 Safety

All personnel conducting experiments in the EES labs are required to pass several lab safety courses before working in the lab - see the lab manager for information on which courses required and how to complete them.

D5 is a common ingredient in personal care products. PCBs are known carcinogens, endocrine disruptors, and neurotoxins.

Personal protective equipment (PPE) are worn when handling samples and solvents used in this method: pants, closed-toe shoes, nitrile gloves, lab goggles, and lab coat. Extraction and standard spiking take place in a fume hood. Heavy rubber gloves are worn over nitrile gloves for extra protection when triple rinsing with solvents.

4.0 Glassware and Supplies

- SPE cartridges, 10 mg isolute ENV+ with 1 mL capacity, Biotage AB
- Pasture pipettes, borosilicate & non-sterile, 5 ¾", Fisher 13-678-20B
- Pyrex test tubes, 16x125 mm with Teflon-lined screw caps
- GC sample vials, 2mL capacity, amber, large ID, crimp, Fisher 03-391-6
- Teflon aluminum crimp caps with Teflon septa, SUN-Sri 200 100 TFE/RUB 11MM seal
- Volumetric flask
- Amber glass jars with Teflon-lined screw caps
- Aluminum foil
- 100 uL syringe for spiking IS, Hamilton 81075 gas tight syringe model 1710w/ cemented 22s gauge needle, point style 3 (blunt tip), 2 in

5.0 Chemicals and Solvents

- Hexanes, pesticide grade, H300-4, Fisher Scientific
- Methylene Chloride, pesticide grade, D142-4, Fisher Scientific
- Methanol, pesticide grade, Fisher Scientific

- Acetone, pesticide grade, Fisher Scientific

6.0 Standards

6.1 Internal Standard (IS)

2,4,6-trichlorobiphenyl (PCB 30), Cambridge Isotope Labs
~5000 ng/mL prepared gravimetrically from ~1mL of 35 ug/mL standard.

6.2 Calibration standard

2,4,6-trichlorobiphenyl (PCB 30) Cambridge Isotope Labs
Decamethylcyclopentasiloxane (D5) Moravek Biochemicals

~500 ng/mL prepared gravimetrically from combining and diluting stock of ~5000 ng/mL each of PCB 30 and D5. D5 stock was prepared from 5 mg neat standard into 10 mL volumetric flask.

7.0 Extraction Procedure

Samples are eluted with ~1.5 mL hexane into GC vials, taking care that the solvent doesn't leak out of the GC vials as the columns are eluting. Large ID GC vials are important to extraction success.

8.0 Spiking with Internal Standard

Clean syringe 3x with DCM and rinse the outside of the syringe with DCM, then clean 3x with hexane and rinse the outside of the syringe with hexane. Spike 100 uL of ~500 ng/mL IS into GC vials. Repeat syringe cleaning.

9.0 Instrumental Analysis

An HP 6890 Series GC coupled with an HP 5973 MSD equipped with an Agilent DB-5 column (30 m × 0.25 mm ID, and 1.0 µm film thickness) is used in select ion monitoring (SIM) mode.

9.1 GC parameters

9.1.1 Injector

3 washes in DCM, 3 washes in hexane pre and post injection
3 sample pumps
Fast plunger speed
Injection volume 2 uL with a 10 uL syringe

9.1.2 Oven program

Initial temp 60 °C, hold for 2 min, rate 20 °C/min to final temp 250 °C, hold 5 min for total run time of 16.5 min
Flow 0.8 mL/min

9.1.3 Inlet

Helium carrier gas
Back inlet in splitless mode, temp 200 °C, pressure 5.3 psi, purge flow 50 mL/min, purge time 1 min, total flow 53.6 mL/min, gas saver 20 mL/min, saver time 2 min
3 min solvent delay

9.1.4 Transfer line (thermal aux 2)

Temperature 280 °C

9.1.5 Post Run

5 min at 60 °C

9.2 MS parameters

SIM mode Ions monitored: 355 (D5) and 258 (PCB 30)
MS source temp 250 °C, MS quad temp 150 °C