

Sample Preparation and GC Analysis of Organo Tin Compounds

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Organo tin compounds are of environmental interest because of their addition to several lists of endocrine disrupters,¹ and the attribution of shellfish growth abnormalities to the use of tributyl tin as a marine antifouling agent. Although this interest primarily has been focused on the butyl tin series to date, concern has expanded to include other organo tin compounds, such as triphenyl tin, a crop pesticide. The US Environmental Protection Agency (EPA) has not adopted methods for the preparation and analysis of tributyl tin and its breakdown products (dibutyl tin and monobutyl tin), and the analysis presents the laboratory with several challenges. Difficulties arise in preparing sample matrices, ranging from water and seawater to soil and biota. Also, the tin compounds exhibit ligand exchange and are unstable when mixed in solution, which accounts for the short shelf-life of multi-component standards. Finally, these compounds are used and recovered as chlorides. This presents a wide range of polarities and creates difficulty in gas chromatographic (GC) separation—the most common technique used in environmental testing.

Because an “EPA accepted” method does not exist for this analysis, most laboratories do not accept requests, or they subcontract the analysis to one of the few laboratories that do perform it. Many chemists are under the impression that the analysis will require complex techniques and considerable capital expenditure. However, this does not have to be the case. In fact, most laboratories could perform this analysis using the equipment they already have.

Generally, laboratories must achieve a minimum detection limit of 50pg/L in water, sometimes lower. The addition of organo tin compounds to the list of endocrine disrupters may lower that limit to 1 or 2pg/L. This latter detection requirement entails either a large-volume injection, further concentration of the extract, or the use of a more sensitive detector. The steps presented in this note take all of these factors into account, while allowing adaptation for a commercial laboratory.

Sample Extraction Methods

Water Samples

1. Measure 1000mL of sample into 2L separatory funnel.
2. Adjust sample pH to below pH 2, using HCl.
3. Add surrogate and/or matrix spike compounds.
4. Extract using three serial additions of 0.1% tropolone in hexane, 60mL each.*
5. Collect extract into Kuderna-Danish (KD) concentrator, passing through granular sodium sulfate, 10-60 mesh.
6. Rinse concentrator with additional extraction solvent.
7. Concentrate extract to approximately 5mL and transfer to 20mL vial.

Biota

Follow the procedure for soils, but use a homogenizer (tissuemizer) to prepare the material and, if necessary, reserve a sample for percent lipids determination.

*Extraction solvent is made by dissolving 4g tropolone in 4L hexane. Tributyl (trialkyl) tin can be extracted with methylene chloride, but di and mono butyl tin require the addition of a chelating agent.

Soil Samples

1. Measure 30g of sample into a 400mL beaker.
2. Add 10mL 1:1 HCl:DI water.
3. Add surrogate and/or matrix spike compounds.
4. Extract using three serial additions of 0.1% tropolone in hexane, 60mL each, using sonication for 2 minutes.*
5. Collect extract into Kuderna-Danish (KD) concentrator, passing through granular sodium sulfate 10-60 mesh, in a funnel.
6. Rinse funnel with additional extraction solvent.
7. Concentrate extract to approximately 5mL and transfer to 20mL vial.



Sample Extract Derivatization and Cleanup:

1. Add 0.8mL 2M n-hexyl magnesium bromide.
2. Place vial on wrist shaker for 30 min., or agitate by hand.
3. Place vial in ice bath, and add HCl to dissolve precipitate.
4. Pipet off hexane layer and transfer to KD concentrator.
5. Concentrate extract to approximately 1mL.
6. Add extract to 16gm/5gm Florisil®/silica-gel SPE tube. (Restek cat.# 24049). May use prep-scale chromatography column.
7. Elute with 100mL hexane, collecting eluent in KD concentrator.
8. Spike internal standard as appropriate.
9. Concentrate extract to 1.0mL.

This method combines methods previously reported.²⁻⁴ It was designed for use with equipment that exists in most commercial environmental laboratories. The method is applicable to water, soil, or biota samples, and is compatible with the monoalkyl through tetraalkyl tin compounds. The following is a step-by-step extraction procedure for the various matrices.

Deactivation Procedure

Prior to analysis by GC, it is critical to derivatize the organo tin chlorides and process the sample extracts using sorbent cleanup. Although several techniques are available, the following procedure works well for all compounds in any matrix. (Note: This method uses a commercially available Grignard reagent. Because this reagent is moisture-sensitive, keep exposure to the atmosphere to a minimum by handling the solution in a syringe.) The goal of this reaction is to replace all chlorides on the tin with an n-hexyl group. It is very important to minimize potential contamination. The primary interference is caused by sulfur-containing compounds. These occur in relatively high concentration in comparison with the organo tin compounds. If these compounds are not extracted, they will cause considerable interference, especially in soil or biota matrices. The large-capacity cleanup described below will remove these nontarget compounds. SPE tubes for this cleanup are available from Restek (cat.# 24049).

Prior to final volume adjustment, internal standards can be added. Tetra-n-propyl tin is the recommended internal standard. All standards used in this method are solutions of organo tin chlorides. Calibration standards must be either derivatized by the same procedure, or they can be purchased as neat-derivatized material from Restek. Tropolone and Grignard reagents are available from Aldrich, among others. Since alkyl tin compounds exhibit ligand exchange, the samples and standards should be kept in a cool (4°C), dark place until used. If properly stored, the standards should be stable for six months; but if left at room temperature, the compounds will exchange alkyl groups peaks from additional organo tin compounds may be observed in the chromatogram. The use of at least one surrogate compound, such as tripropyl tin chloride, is suggested to allow extraction recovery calculations.

References

1. *Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis*, EPA/630/R-96/012, Feb. 1997.
2. Unger, M.A, MacIntyre, W.G., Greaves, J., and Huggett, R.J., *Chemosphere*, 15 (4), pp 461-70, 1986.
3. *Sampling and Analytical Methods of the National Status and Trends Program*, National Benthic Surveillance and Mussel Watch Projects, 1984-1992, Vol. IV, NOAA Technical Memorandum, NOS ORCA 71.
4. Jaima Conference, Tokyo, Japan. Nov. 1998.
5. STL-Burlington, 208 South Park Dr. Suite 1, Colchester, VT 05446.

Sample Analysis

The GC analysis is relatively simple. The flame photometric detector (FPD) must be operated under fuel-rich conditions for efficient conversion of the alkyl tin compounds to tin hydrides. The only modification needed is a 610nm wavelength filter in the FPD, to collect the molecular emission for tin hydride. This filter can be obtained from Oriel Corporation, Stratford, CT, (203) 377-8282 (cat.# 53925) or other optics supply companies.

Figure 1 shows a simultaneous analysis using two capillary columns of differing selectivity. This provides both a primary and a confirmation analysis from a single injection. The compounds are injected at 500pg on-column.

Using the procedure detailed in this note, a commercial laboratory⁵ obtained the data shown in Table I. The results easily meet the method detection limit requirements of 50ng/L. Should your laboratory need to meet a 1ng/L detection limit, some modification of the method will be necessary. The simplest and least expensive way to meet a lower detection limit would be to switch from using an FPD to a Pulsed FPD (PFPD). This detector can give a sensitivity enhancement of 10 to 100 times over a standard FPD. Figure 2 shows the chromatogram obtained from an injection of an organo tin calibration standard with 5pg on-column for each compound. A comparison of this chromatogram to Figure 1 reveals that a similar signal-to-noise ratio can be obtained with 100 times less analyte. This demonstrates an increase in sensitivity (or lower reporting limit) of roughly 100 times using the PFPD and the preparation method outlined above.

This method is adaptable to most commercial laboratories and uses common glassware and equipment. If this is your first time using this method, you will not need to purchase a specialized instrument because the PFPD detector provides the sensitivity to meet even the lowest of proposed detection limits. The use of equipment such as tandem mass spectrometers (MS/MS/MS) or microwave induced plasma detectors (MIP or AED) is not necessary. Both are expensive and require much more operator skill. Finally, Restek is available to provide additional training on this and other methods to eliminate the need for literature and vendor research—please contact us for more information.

Table I Commercial laboratory results using the proposed method.⁵

Compound	Water Extraction Recovery (%)	Soil Extraction Recovery (%)	Restek SPE-Cleanup Recovery (%)	MDL Liquid (ng/L)	MDL Soil (µg/Kg)
tetrabutyl tin	83	86	92	29.9	0.45
tributyl tin	110	96	99	20.9	0.39
dibutyl tin	75	66	96	15.7	0.46
tripentyl tin (SSTD)	NA	NA	101	NA	NA
monobutyl tin	38	36	118	19.6	0.14

Figure 1 500pg of derivatized organo tin compounds separated well on Rtx®-5 and Rtx®-35 columns, using GC/FPD.

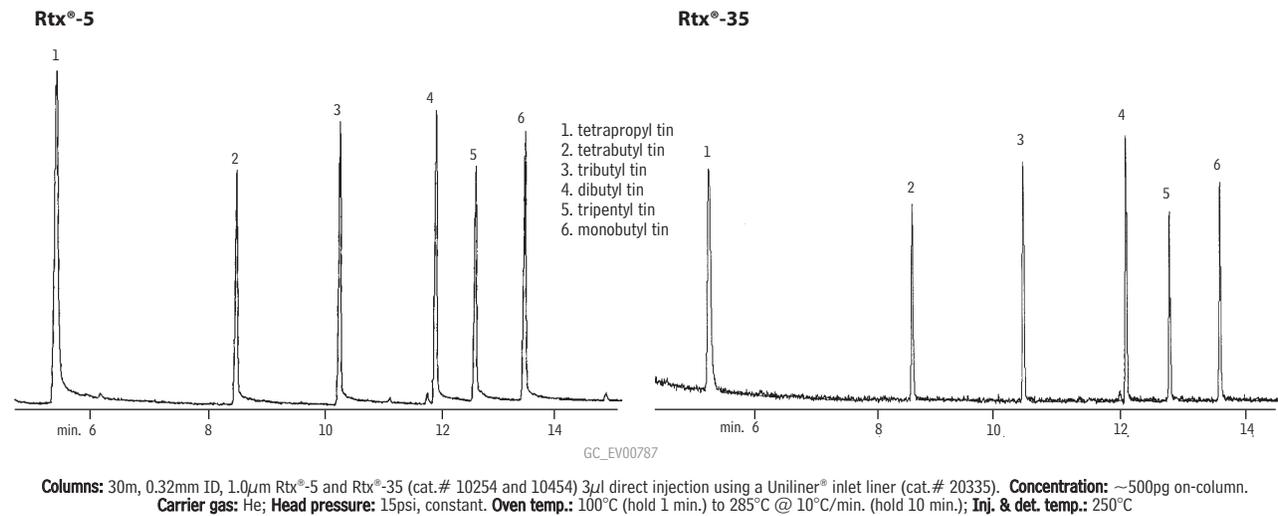
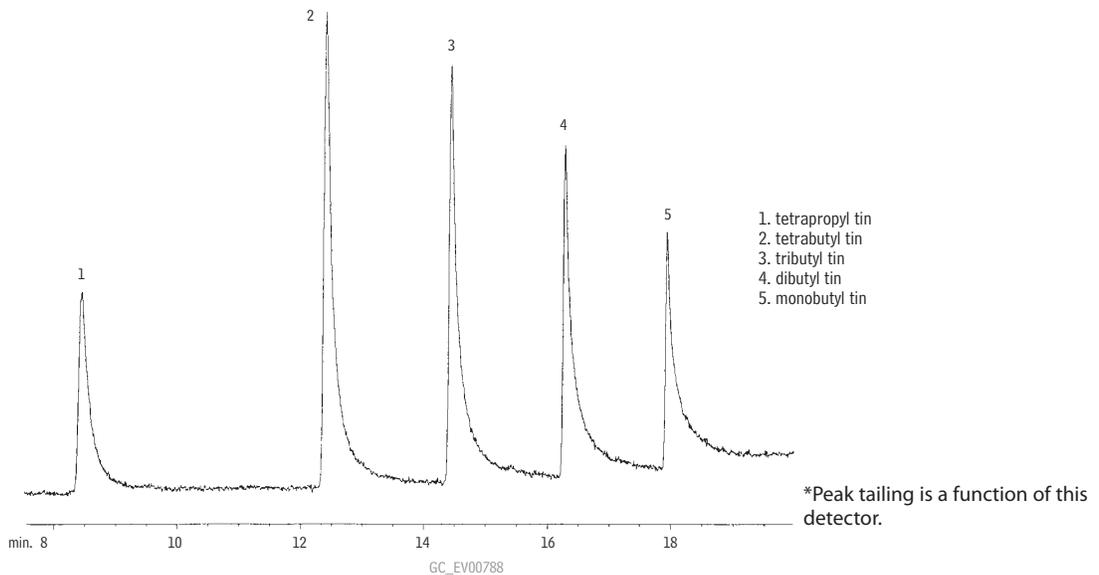


Figure 2 PFPD* Increases sensitivity by 100 times when analyzing organo tin compounds by this method.



Column: 30m, 0.32mm ID, 1.0µm Rtx®-35 (cat.# 10454). Direct injection using a Uniliner® inlet liner (cat.# 20335). Concentration: 5pg on-column. Carrier gas: He; Head pressure: 15psi, constant. Oven temp.: 100°C (hold 1 min.) to 285°C @ 10°C/min. (hold 10 min.); Detector: PFPD Model 5380 courtesy of O.I. Analytical Corp., College Station, TX.

Surrogate Mixtures

Tri-*n*-propyltin Chloride Surrogate

2,000 μ g/mL in methylene chloride, 1mL/ampul cat.# 31476 (ea.)

Triphenyltin Chloride Surrogate

2,000 μ g/mL in methylene chloride, 1mL/ampul cat.# 31477 (ea.)

Individual Calibration Compounds for Environmental Analysis and the Electronics Industry

Tributyltin Chloride Calibration Mixture

2,000 μ g/mL in methylene chloride, 1mL/ampul cat.# 31478 (ea.)

Calibration Mixes

Butyltin Chloride Calibration Mixture

butyltin trichloride tetrabutyltin
dibutyltin dichloride tributyltin chloride
2,000 μ g/mL each in methylene chloride,
1mL/ampul cat.# 31472 (ea.)

Phenyltin Chloride Calibration Mixture

diphenyltin dichloride tetraphenyltin
phenyltin trichloride triphenyltin chloride
2,000 μ g/mL each in methylene chloride,
1mL/ampul cat.# 31473 (ea.)

Internal Standard Mixes

Tetra-*n*-propyltin Internal Standard

2,000 μ g/mL in methylene chloride, 1mL/ampul cat.# 31474 (ea.)

Tetraphenyltin Internal Standard

2,000 μ g/mL in methylene chloride, 1mL/ampul cat.# 31475 (ea.)

Organo Tins Reference Materials

- Organo tin analysis technical training offered. Please contact Restek, or your Restek representative.

Resprep™ 12- or 24-Port Tube Manifolds

Complete manifold includes glass basin with built-in vacuum regulator, polypropylene top plate with 12 or 24 individual control valves, 12- or 24-position collection rack, and 12 or 24 Teflon® sample guides.



Description	qty.	cat.#
Resprep™ 12-Port Manifold	kit	26077
Resprep™ 24-Port Manifold	kit	26080

Resprep™ Organo Tin SPE Cartridge

Applications	Tube Volume	qty.	cat.#
High-capacity cleanup of butyl and phenyl tin compounds from soil, water, and biota. Mixed bed.	60mL	16-pk.	24049

Rtx®-5 Column (fused silica)

(Crossbond® 5% diphenyl/95% dimethyl polysiloxane)

ID	df (μ m)	temp. limits	length	cat. #
0.32mm	1.00	-60 to 330/350°C	30-Meter	10254

Rtx®-35 Column (fused silica)

(Crossbond® 35% diphenyl/65% dimethyl polysiloxane)

ID	df (μ m)	temp. limits	length	cat. #
0.32mm	1.00	0 to 290°C	30-Meter	10454



Lit. Cat.# 59550A

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