

## **EXTRACTION OF SEDIMENTS FOR BUTYLTINS**

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### **ABSTRACT**

Determining organic contaminant levels in sediments requires extraction, isolation and concentration from the matrix. Butyltins (BT) are extracted from sediments by sonication in a 0.1% tropolone/hexane or 0.1% tropolone/dichloromethane mixture. The extracts are concentrated to 10 mL and pentylated using pentylmagnesium bromide (Grignard reagent), followed by neutralization with hydrochloric acid. The organic fraction is concentrated and purified using silica gel/florisil chromatography columns. The resultant eluent is concentrated to a final volume of 10 mL and submitted for the determination of BT by gas chromatography/flame photometric detection.

### **1.0 INTRODUCTION**

The procedure described is capable of extracting, isolating, purifying and concentrating butyltin (BT) contaminants at the parts per billion level from sediments or soils. Sediment samples are thawed, homogenized and an aliquot of 1-2 g is removed for percent moisture determination. Another aliquot of sediment is oven dried at 40°C prior to extraction. Once samples are dried they are ground and homogenized using a mortar and pestle. Approximately 2 to 15 g of dry sediment is extracted in 60 mL of 0.1% tropolone/hexane or 0.1% tropolone/dichloromethane using a sonic probe. The liquid is decanted and the extraction procedure is repeated twice more. The combined extracts are concentrated to approximately 10 mL. The samples are then pentylated using pentylmagnesium bromide (Grignard reagent) and shaken for 1 hour after which they are neutralized with hydrochloric acid (HCl). The organic layer is drawn off and concentrated to 2 – 4 mL. Samples are purified using silica gel/florisil columns and hexane. The eluent is concentrated to 10 mL, from which 2 mL is prepared for analysis by gas chromatography/flame photometric detection (GC/FPD).

## **2.0 APPARATUS AND MATERIALS**

### **2.1 EQUIPMENT**

- Solvent reduction apparatus, Zymark TurboVap LV concentration workstation
- Sonicator, Tekmar TMX500 sonicator
- Balance, top loading, tare capacity to 300 g, capable of weighing to 1 mg
- Microbalance, capable of weight to 1  $\mu\text{g}$
- Calibrated weights, certified
- Combustion furnace, electric capable of combusting glassware at 400°C for at least 4 hours
- Oven capable of 40°C temperature maintenance
- Conditioning oven, electric, gravity convection, capable of maintaining a stable temperature of up to 200°C
- Concentration tubes, Zymark® 60 mL borosilicate glass
- Concentration tubes, 60 mL certified pre-cleaned VOA tubes with open screw caps and teflon lined VOA septa
- Micropipettors, calibrated, 1% accuracy, disposable tips
- Beakers, 150 mL
- Erlenmeyer flasks, 250 mL
- 2.0 mL amber extract vials with teflon-lined screw caps
- Glasswool

### **2.2 REAGENTS**

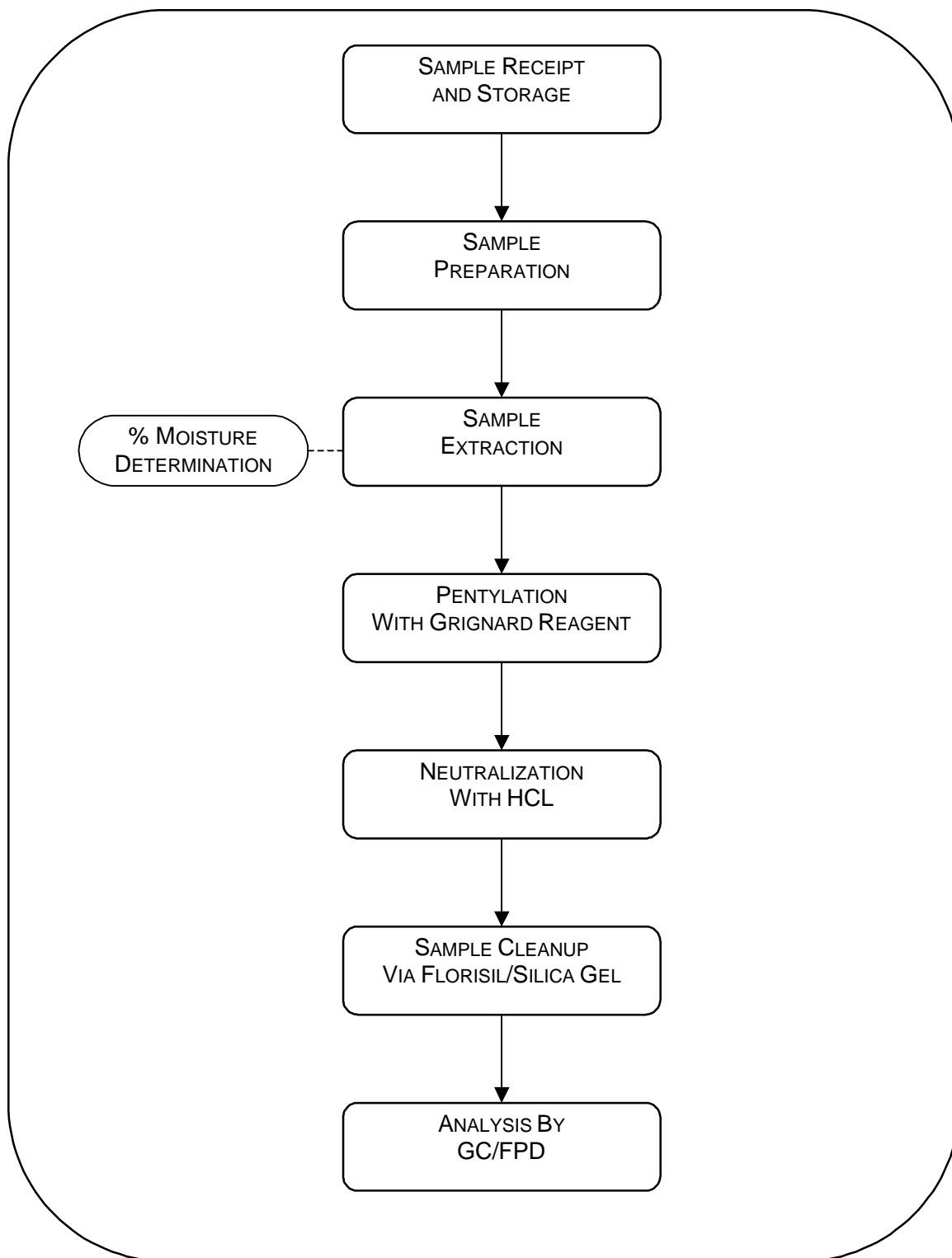
- Silica gel/Florisil columns, Resteck, 16 g florisil and 5 g silica gel
- Dichloromethane, pesticide grade or equivalent purity
- Hexane, pesticide grade or equivalent purity
- Hydrochloric acid, Tracepur® Plus or equivalent purity
- Copper, granular
- Hydrochloric acid
- Topolone, 98% purity
- Grignard reagent, pentylmagnesium bromide
- Nitrogen, 99.8% purity

### **3.0 PROCEDURE**

All glassware used to extract sediments is washed, solvent rinsed or combusted at 400°C for at least 4 hours. All other items that come in contact with sediment samples are washed and solvent rinsed with acetone and dichloromethane. Sediment samples are thawed and homogenized. A portion (1-2 g) is removed for percent moisture determination (see Dry Weight Determination of Sediments). An aliquot is oven-dried at 40°C and then ground and homogenized using a mortar and pestle. Between 2 to 15 g of the dried sediment is weighed into a 150 mL beaker to which 60 mL of 0.1% tropolone in either hexane or dichloromethane is added. Appropriate surrogates and spikes are added to beakers prior to extraction. The sediment/tropolone mixture is sonicated at 50% power, 1 second on and 0.5 second off, for a total of 3 minutes. The extract is decanted into a 250 mL Erlenmeyer flask. The extraction is repeated two more times.

The combined extracts are concentrated to 10 mL using a Zymark TurboVap LV concentration station set at 40°C and 15 psi. An aliquot of extract (between 20 and 45 mL) is added to a 60 mL VOA tube and concentrated. Additional aliquots are added to the tube as the extract volume decreases and concentrates until the entire sample extract has been concentrated to approximately 10 mL. Purified copper is added to the concentration tube to remove sulfur. Copper is added until it no longer turns black, indicating that all sulfur has been bound. Samples extracted in dichloromethane are back extracted into hexane. The sample is quantitatively transferred to a clean 60 mL concentration tube and reduced to 10 mL. The sample extracts are then pentylated by adding 1 mL of pentylmagnesium bromide (Grignard reagent). The sample headspace is purged using nitrogen and then the tubes are capped and shaken for 1 hour on a shaker table. After shaking, the Grignard reagent is neutralized by adding 40 mL of 10% HCl to each tube, in an ice bath. The tubes are shaken and the upper organic layer is transferred to a 50 mL Zymark concentration tube. The acid fraction is rinsed twice more using 10 mL of hexane, each time transferring the organic layer to the concentration tube. The extract is then concentrated to 2 – 4 mL using a Zymark TurboVap LV set at 40°C and 15 psi.

The concentrated extract is purified using silica gel/florisil chromatography columns. The chromatography columns contain 16 g of florisil and 5 g silica gel and are conditioned by flushing with 30 mL of hexane. The sample and solvent rinses are drained to the top of column and 125 mL of hexane is added and eluted until the column is dry. The eluent is collected in 250 mL Erlenmeyer flasks. The eluent is quantitatively transferred to a Zymark concentration tube and concentrated to a final volume of 10 mL. Approximately 2 mL of each extract is transferred to a clean 2 mL amber extract vial to which the appropriate internal standard is added in preparation for instrument analysis.



**Figure 1.** Methodology for Extraction, Isolation and Quantification of Sediment Samples for Butyltins.

#### **4.0 QUALITY CONTROL (QC)**

All reagents used are verified to be contaminant free. All equipment and glassware used to extract samples are thoroughly cleaned by solvent rinsing or combustion at 400°C. The calibration and accuracy of balances, weights, pipettors and thermometers are checked daily. The calibration and accuracy of balances, weight, pipettors and thermometers are verified yearly by independent sources. All samples are shipped and received under chain-of-custody. A series of quality control samples are processed with each batch of 20 samples or less. The following quality controls are used to ensure the accuracy and precision of tissue data.

- **Surrogates.** Solutions containing analytes that do not interfere with the analytes of interest are prepared at concentrations approximately 5 to 10 times the method detection limit (MDL). Specified surrogates are added to each sample extracted, including QC samples, at a specified volume (typically 100 µL), immediately prior to extraction.
- **Method Blank.** Method blanks are extractions of all support material used for extraction of samples, with the exception of sediment. A method blank is analyzed with each extraction batch of 20 or fewer samples. The method blank is extracted and analyzed in a manner identical to samples.
- **Matrix Spike.** Matrix spikes are extractions of sample matrix fortified with spikes of selected target analytes. A matrix spike and matrix spike duplicate are analyzed with each extraction batch of 20 or fewer samples. Matrix spikes are extracted and analyzed in a manner identical to samples.
- **Laboratory Duplicates.** A sample is analyzed in duplicate with each extraction batch of 20 or fewer samples.
- **Standard Reference Material.** A standard reference material is analyzed with each extraction batch of 20 or fewer samples.