

QUANTITATIVE DETERMINATION OF BUTYLTINS USING GAS CHROMATOGRAPHY/FLAME PHOTOMETRIC DETECTION

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ABSTRACT

Butyltins are quantitatively determined using a gas chromatograph/flame photometric detector. This method unambiguously detects low concentrations of monobutyltin, dibutyltin, tributyltin and tetrabutyltin in tissues and sediments.

1.0 INTRODUCTION

A gas chromatograph/flame photometric detector (GC/FPD) coupled to a capillary column is used to resolve, detect and quantitate butyltins (BTs) in tissues and sediments at parts per billion levels. Samples are injected into a temperature-programmed GC/FPD. The capillary column is a DB-5 (30 m x 0.25 mm ID and 0.25 μ m film thickness). The data acquisition system continuously acquires and stores all data analyses.

2.0 APPARATUS AND MATERIALS

2.1 EQUIPMENT

- Thermoquest 2000 Series Trace GC equipped with large volume injector, autosampler, electronic pressure control, and a flame photometric detector with a tin selective 610 nm filter
- Data acquisition system, Thermoquest Chromquest software, capable of continuous acquisition and storage of all data during analysis, or equivalent
- Autosampler, Thermoquest AS2000, capable of making 1 to 250 μ L injections
- Capillary column, J&W Scientific DB-5 (30 m x 0.25 mm ID and 0.25 μ m film thickness), or equivalent
- Desolvation column, Supelco fused silica intermediate polarity (15 m long by 0.53 mm ID), or equivalent
- Micropipetters, calibrated, 1% accuracy, disposable tips

2.2 REAGENTS

- Hexane, pesticide grade or equivalent
- Helium, 99.8% purity
- Hydrogen, 99.8% purity
- Nitrogen, 99.8% purity
- Air, 99.8% purity

2.3 STANDARDS

2.3.1 *Surrogate Spiking Solution*

The surrogate spiking solution is prepared with aliquots of pure compounds that are diluted with hexane to a final concentration of 646 ng Sn/mL. The surrogate spiking solution includes tripropyltin chloride. Surrogate solution is added to all samples and all quality control samples prior to extraction. The surrogate is resolved from, but elutes in close proximity to the analytes of interest. The recovery of the surrogate is used to correct analyte concentrations.

2.3.2 *Internal Standard Solution*

The internal standard solution is made from an aliquot of pure compound and diluted with hexane to a final concentration of 1,015 ng Sn/mL. The internal standard compound is tetra-n-propyltin. The internal standard compound is resolved from, but elutes in close proximity to the analytes of interest. The internal standard solution is added to all samples and quality control samples just prior to analysis. The internal standard is used to calculate analyte concentrations.

2.3.3 *Matrix Spiking Solution*

A certified solution containing monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT) and tetrabutyltin (TeBT) is purchased from a commercial vendor and diluted with hexane to prepare the matrix spiking solution. The matrix spike solution is diluted to approximately 10 times the MDL and is added to all matrix spike samples.

2.3.4 *Calibration Solution*

Calibration solutions are prepared at 5 concentrations ranging from approximately 0.5 to 50 ng Sn/mL by diluting a commercially prepared solution containing the analytes of interest.

2.3.5 Retention Index Solutions

The mid-level calibration standard is used as a retention index solution to determine the retention times of analytes of interest.

3.0 QUANTITATIVE DETERMINATION OF BTs BY GC/FPD

3.1 INITIAL CALIBRATION

A 5-point relative response factor (RRF) calibration curve is established for analytes of interest prior to the analysis of samples and quality control samples. A RRF is determined, for each analyte, for each calibration level using the following equation:

$$RRF = \frac{(A_A)(C_{IS})}{(A_{IS})(C_A)}$$

Where:

A_A = the area of the analyte to be measured

A_{IS} = the area of the specific internal standard

C_A = the known concentration of the analyte in the calibration solution (ng Sn/mL)

C_{IS} = the known concentration of the internal standard in the calibration solution (ng Sn/mL)

The response factors determined for each calibration level are averaged to produce a mean relative response factor (\overline{RRF}_i) for each analyte. The percent relative standard deviation (%RSD) for the 5 response factors must be less than or equal to 15%, for each analyte.

$$\%RSD = \frac{\text{Standard Deviation of the RRFs}}{\text{Average of the RRFs}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{(n-1)}}$$

Where:

x_i = each RRF value used to calculate the mean RRF

\bar{x} = the mean of n values

n = total number of values (5)

3.2 CONTINUING CALIBRATION

A mid-level calibration standard is analyzed at the beginning and end of each analytical set, or every 10 samples (whichever is more frequent). The daily relative response factor for each compound is compared to the mean relative response factor from the initial calibration curve and the average percent difference (RPD) of all analytes must be less than 15%. If the calibration check does not meet this criterion then the initial five-point calibration is repeated.

$$RPD = \frac{RRF_c - \overline{RRF}_i}{\overline{RRF}_i} \times 100$$

Where:

\overline{RRF}_i = mean relative response factor from the most recent initial calibration (meeting technical acceptance criteria)

RRF_c = relative response factor from the continuing calibration standard

3.3 GC/FPD ANALYSIS

The initial calibration of the GC/FPD must meet the previously described criteria prior to sample analysis. Samples are analyzed in analytical sets that consist of standards, samples and quality control samples. Quality control samples are method blanks, laboratory duplicates, blank spikes, matrix spikes and standard reference materials. The type and number of quality control samples depend upon client requests and material availability. An autosampler is used to inject 50 μ L of all samples, standards and QC samples into the capillary column of the GC using the following instrument conditions. Slight modifications may be necessary depending upon the analysis.

Inlet: Large volume with solvent vent
Carrier gas: Helium, 1.9 mL/min
Detector gas: Hydrogen 90 mL/min:Air 105 mL/min
Make up gas: Nitrogen 20 mL/min

Temperatures:
Base Temp: 250°C
FPD: 160°C

Oven program:
Initial oven temp: 65°C

Initial hold time: 0.18 minutes
Ramp rate: 10°C/min
Final oven temp: 240°C
Final hold time: 4 minutes

3.4 ANALYTE IDENTIFICATION

The retention time of a sample analyte must fall within 15 seconds of the retention time for the analyte in a calibration standard or retention index solution.

Data not meeting established criteria are appropriately qualified or are re-analyzed.

4.0 QUANTITATION CALCULATIONS

Sample analyte concentrations are calculated based on the concentration and response of the internal standard. The equations in section 3.1 are used to calculate the RRF of each analyte relative to the concentration and area of the internal standard in the initial calibration.

The mass (M_A) of each target analyte (ng), is calculated using the following equation:

$$M_A = \frac{(A_A M_{IS})}{(A_{IS} \overline{RRF}_i)}$$

Where:

A_A = the area of the analyte measured

A_{IS} = the area of the specific internal standard

M_{IS} = mass of internal standard added to the extract (ng)

\overline{RRF}_i = the average relative response factor for the analyte from the current calibration

The concentration (C) of each target analyte in a sample (in ng Sn/g) is calculated using the following equation:

$$C = \frac{(M_A V_E DF)}{(V_{inj} W)}$$

Where:

V_E = final volume of the extract (μ L)

V_{inj} = volume of the sample injected onto the column (μ L)

W = the weight of the sample (g)

DF = the dilution factor applied to the extract

$$DF = \frac{\text{Volume of Extract (uL)}}{\text{Volume of extract used to make dilution (uL)}}$$

Analyte concentrations are reported as corrected for surrogate recovery. Percent surrogate recovery (SU_{Recovery}) is calculated using the following:

$$SU_{\text{Recovery}} = \frac{C_{\text{ESU}}}{C_{\text{SU}}} \times 100$$

Where:

C_{ESU} = calculated surrogate concentration in the extract (ng Sn/mL)

C_{SU} = known concentration of surrogate added to extract (ng Sn/mL)

Analyte concentration corrections ($C_{\text{Corrected}}$) for surrogate recovery are calculated using the following equation:

$$C_{\text{Corrected}} = \frac{C}{SU_{\text{Recovery}}} \times 100$$

5.0 QUALITY CONTROL

The initial calibration must pass established criteria before sample analysis can occur. All continuing calibration checks must pass established criteria for analysis to continue.

An acceptable method-blank analysis may not contain more than one target analyte at concentrations three times greater than the MDL. This criterion does not apply if the analytes detected in the method blank are not detected in the associated samples or if the sample analyte concentrations are 10 times greater than the blank analyte concentration. If the method-blank exceeds these criteria then the analytical procedure is not in control. The source of the contamination must be investigated, and corrective measures taken and documented before further sample analysis occurs.

All samples and quality control samples are spiked with the surrogate compound prior to extraction. The surrogate compound measures sample matrix effects associated with sample preparation and analysis. The recovery of the surrogate compound is monitored in each sample and quality control sample. The laboratory will take corrective action if the average surrogate recovery, with the exception of MBT, is less than 40% or greater than 120%. The following corrective action will be taken if the above criteria are not met:

- 1) Calculations are checked to assure that no errors have been made.
- 2) The internal standard and surrogate solutions are checked for degradation, contamination, etc., and instrument performance is checked.

- 3) If surrogate recovery could not be measured because only a portion of the sample is analyzed (such as sample dilutions) then no corrective action is required. The surrogate recovery is appropriately qualified.
- 4) If the steps above fail to reveal a problem, the extract is re-analyzed, if sufficient material is available. If the sample was completely consumed, the data will be reported but designated outside the quality control criteria.

No more than one individual analyte recovery in a blank spike or valid matrix spike may exceed 40-120% with the exception of monobutyltin. A valid matrix spike is a matrix-spike where the amount of analyte added is at least as much as was present in the sample originally. If the matrix spike is valid and the QC criteria are not met then the quality control sample failing the criteria will be re-analyzed. If the re-analyzed spike meets the criteria, then the data for the re-analyzed quality control sample are reported. If the analytes that are in violation are not present in the samples analyzed with this extraction batch, the violation is noted but no action is required. If upon re-analysis, quality control criteria are still in violation, the entire batch of samples is re-extracted and re-analyzed, if deemed necessary. If sufficient sample is unavailable for re-extraction of the matrix spike, a blank spike may be analyzed. The acceptable average RPD for a valid matrix spike/matrix spike duplicate or blank spike/blank spike duplicate pair is 30%. No more than one individual analyte RPD may exceed 35%.

The average acceptable RPD between the duplicate and original sample, for analytes greater than 10 times the concentration of the MDL, is 30%. No more than one individual analyte RPD can exceed 35%.

When available, an SRM is analyzed with each extraction batch. The average RPD for target compounds in a SRM should not exceed 35% of the upper and lower bounds of the mean certified values.

An SRM may not be available, and in this case a laboratory control sample (LCS) is used to monitor accuracy and precision. A LCS is similar to an SRM in that it is a homogeneous matrix that closely matches the sample matrix analyzed. However, the analyte concentrations in the LCS are not certified but are based on statistically establishing acceptable limits by repeated measurements.

The method detection limit (MDL) is determined following the procedures outlined in Federal Register (1984), Vol. 49, No. 209: 198-199.