Tetraethyllead in Water – PBM (DRAFT)

Parameter
Tetraethyllead (TEL)

Analytical Method
Solvent Extraction, GC-MS/MS, GC-ICPMS

Introduction
This method is applicable to the quantitative determination of Tetraethyllead (TEL) in Water.

Alkylated lead compounds are anthropogenic organometallic substances which have been in use since the 1920’s, primarily associated with their use in leaded gasolines as anti-knock agents, which protect against engine damage due to premature ignition. Tetraethyllead was the primary alkyl lead substance used in gasolines, but tetramethyllead was also used for this purpose. Due to its link to severe health risks and issues, TEL was banned for automotive use across North America in the early to mid 1990’s, and an almost total global ban was achieved by the early 2000’s. TEL is still used with aviation fuels.

TEL is a moderately volatile substance with a boiling point of approximately 200°C (decomposition occurs at ~200°C according to the CRC handbook), which puts it on the cusp between semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs). For purposes of sample handling and preservation protocols, this method treats TEL as an SVOC.

Method Summary
Solvent extraction (with isotope dilution and derivatization if necessary) followed by GC-MS/MS or GC-ICPMS instrumental analysis.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes*

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CAS No.</th>
<th>Approx. MDL (ug/L)</th>
<th>EMS Analyte Code*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraethyllead</td>
<td>78-00-2</td>
<td>0.0005</td>
<td>To be determined</td>
</tr>
</tbody>
</table>

EMS Method Code(s)*
To be determined

*Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.

Matrix
Fresh Water, Wastewater, Marine water.

Interferences and Precautions
Contaminants present in solvents, reagents and sample processing hardware may cause interferences or yield artifacts. These must be monitored and demonstrated to be free of interferences under the conditions of the analysis by the routine analysis of method blanks.

Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

TEL is thermally labile, with decomposition reported to occur beginning at temperatures as low as 110°C. It has also been shown to be inherently unstable in acidic conditions.

GC-MS/MS and GC-ICPMS are both highly selective analytical techniques with very limited potential for positive interferences.

Sample Handling and Preservation
Collect samples in amber glass bottles with Teflon-lined silicone septa (e.g. 250 mL bottles, 2 per sample; contact laboratory for lab-specific sample requirements). Collect samples with zero headspace. A small air bubble of up to 5% of sample volume may appear after sampling, and is acceptable.

All samples must be field preserved by addition of base to pH ≥ 12 using NaOH or KOH as a microbial inhibitor and stabilizer. Field preservation with 2 mL 6N NaOH or KOH per 250 mL sample is recommended.
Holding Time: 14 days to extraction if field preserved to pH ≥ 12. Extract hold time is 40 days.

Storage: Sample temperature should be chilled to ≤ 10°C after sampling and for transit to the laboratory. In the laboratory, samples must be refrigerated at ≤ 6°C. Avoid freezing to prevent sample breakage.

Procedure

Reagents:

a) Solvents, distilled in glass, or pesticide grade, or equivalent: Dichloromethane (DCM), and Iso-Octane or Toluene.

b) Sodium sulfate, anhydrous, reagent grade.

Extraction:

a) Accurately measure the sample volume and pour the entire contents of the sample bottle into a Teflon or glass separatory funnel. Include all suspended and settled materials, surface film, or non-aqueous phase layer (NAPL). If solids content is too great for extraction in this manner, then the solids should be extracted separately from the water phase and the extracts combined. Ensure sample pH is ≥ 10. If necessary, adjust pH using KOH or NaOH solution.

b) Spike the sample with at least 1 non-naturally occurring surrogate compound with physical properties (e.g. boiling point) similar to TEL. Refer to Quality Control section for requirements.

c) For a 250 mL sample, add 15 mL of DCM to the sample bottle and rinse contents into the separatory funnel (i.e. use 60 mL DCM / liter of sample). Shake vigorously for at least one minute with frequent venting. Allow layers to separate and drain the DCM (bottom layer) through anhydrous sodium sulfate into a glass collection flask.

d) Repeat step c) twice more, combining all extracts.

e) Concentrate the combined extracts to a known final volume using an appropriate concentration apparatus (e.g. rotary evaporator, turbo evaporator, nitrogen evaporator, Kuderna Danish evaporator) ensuring that method performance requirements are met. It is recommended that a low volatility keeper solvent such as toluene or iso-octane be employed to prevent loss of tetraethyllead during concentration. Use care during solvent concentration due to the volatility of TEL. Avoid concentration to dryness or near dryness.

Instrumental Analysis:

This method requires gas chromatography to physically separate organolead species from any potential interferences. Detailed gas chromatographic conditions are not provided in this method. Refer to US EPA 8270E for more detailed guidance. The on-column injection technique may reduce potential degradation issues due to the thermal lability of TEL.

For GC-MS/MS detection and quantitation, at least two multiple reaction monitoring (MRM) transitions are monitored to ensure a very high degree of specificity and freedom from interferences. The recommended MRM transitions for quantitation and confirmation are as follows:

Quantitation: Precursor ion 295 amu > Product ion 237 amu
Confirmation: Precursor ion 237 amu > Product ion 209 amu

For GC-ICPMS detection and quantitation, the recommended quantitation mass for lead is 208 amu (52.4% isotopic abundance). Two qualifier ions should be monitored for confirmation purposes, at 206 amu (24.1% isotopic abundance) and 207 amu (22.1% isotopic abundance). The high temperature of the ICPMS plasma destroys all organic molecules, and acts as a highly specific elemental detector for this application.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing
method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

**Accuracy Requirement:** Laboratories must demonstrate method accuracy (measured as average recovery) of 50-130% or better for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

**Precision Requirement:** Laboratories must demonstrate method precision equal to or better than 20% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

**Sensitivity Requirement:** Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

### Quality Control

#### Summary of QC Requirements

<table>
<thead>
<tr>
<th>QC Component</th>
<th>Minimum Frequency</th>
<th>Minimum Data Quality Objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration Verification Standard (CVS) – 2nd source</td>
<td>1 per initial calibration</td>
<td>80-120%</td>
</tr>
<tr>
<td>Detection Limit Check Std</td>
<td>1 per initial calibration</td>
<td>50-130%</td>
</tr>
<tr>
<td>Continuing Calibration Verification (CCV)</td>
<td>At least every 12 hours (max 20 samples), and at end of each batch.</td>
<td>80-120% for mid-level standards</td>
</tr>
<tr>
<td>Method Blank (MB)</td>
<td>One per batch (max 20 samples)</td>
<td>Less than reported DL</td>
</tr>
<tr>
<td>Lab Control Sample (LCS)</td>
<td>One per batch (max 20 samples)</td>
<td>50 – 130%</td>
</tr>
<tr>
<td>Field Duplicate (DUP)</td>
<td>Greater of 1 per submission or 10% of samples recommended</td>
<td>see below</td>
</tr>
<tr>
<td>Matrix Spike (MS) or Reference Material (RM)</td>
<td>One per batch (max 20 samples)</td>
<td>40 – 130%</td>
</tr>
<tr>
<td>Surrogate Compound(s)</td>
<td>All samples (max 20 samples)</td>
<td>50 – 130%</td>
</tr>
<tr>
<td></td>
<td>Minimum 1 per sample</td>
<td></td>
</tr>
</tbody>
</table>

If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.

**Recommended Surrogate Compounds:** Acenaphthylene-d8 is recommended as a GC-MS/MS surrogate (boiling point is similar to TEL, and can be analyzed without derivatization). For GC-ICPMS any semi-volatile organometallic or ICPMS-measurable non-naturally occurring surrogate with similar physical properties to TEL (e.g. boiling point) may be used.

**Field Duplicates:** A minimum of 1 field duplicate or 10% of samples per submission (whichever is greater) is recommended to be submitted to the laboratory. Recommended DQO is 40% RPD for field splits (greater for co-located field duplicates), or within 2x reported DL for low level results.

### Prescribed Elements

The following components of this method are mandatory:

1. Analysis must be by Triple Quadrupole GC-MS/MS or GC-ICPMS. At least one additional qualifier ion or MRM transition must be monitored for confirmation purposes.
2. Initial calibrations must include at least 5 points.
3. All specified Sample Handling and Preservation requirements, Performance Requirements, and Quality Control requirements must be met.
4. Due to the low water solubility of TEL, the entire contents of the sample container must
be analyzed, including any accompanying suspended or settled material and any surface film that may exist. Should this not be possible, the client must be contacted for direction and any method deviations must be clearly qualified on the final report.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References


Revision History
Dec 20, 2019   Draft method, reviewed by BCELTAC, for public comment.