

Alkylated Lead Speciation Analysis in Soil, Sediment, and Aqueous Samples Using Selective Extraction Followed by IC/RP-ICP-MS

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What are Alkylated Lead Species?

 Alkylated Lead Species = compounds are man-made compounds in which a carbon atom of one or more organic molecules is bound to a lead atom (EPA definition). Ligands are typically methyl or ethyl groups when pertaining to petroleum additives.

Examples:

- Tetraethyl lead
- Tetramethyl lead
- Trimethyl lead
- Triethyl lead
- Monomethyltriethyl lead
- Monoethyltrimethyl lead
- Dimethyldiethyl lead



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Why is Metal Speciation Analysis so Important?

- Most lead in ground is mineralogical and in the inorganic form
- Lead concentrations in subsurface can be heterogeneous
- Accepted method (HML-939) only supports non-ionic lead species (e.g. tetramethyl and tetraethyl lead)
- Site remediation can be expensive
 - Confirm culpability
 - Apply appropriate remediation measures



Current Method HML-939

California Department of Toxic Substances Control

"Determination of Organic Lead Compounds by Graphite Furnace Atomic Absorption Spectrometry"

- p-xylene extraction for solids and aqueous samples
- Add iodine and Aliquat 336 to form alkylead-iodine-aliquat 336 complex
- Recommends use of SRM 2715 (Lead in Reference Fuel)
 SRM 2715 only contains one lead species (tetramethyl lead)

Instrument Detection Limit (IDL) for GFAAS is 1020mg/L (ppm)



Problems with Current Approach

• Method only uses one organic lead species (tetramethyl Pb) and assumes performance for all other species

- Detection limit is extremely high (1020mg/L)
- Method does not support degradation components

 Ozone and hydroxyl groups can induce demethylation producing trialkylated species

 Biological systems can demethylate via reactions with thiol groups in proteins and enzymes

 Trialkyl and dialkyl lead species are ionic and not readily extracted using HML-939 method



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Solutions to Resolve Limitations

 Total Pb method needed to support mass balance confirmation in extracts such as flow injection inductively coupled plasma mass spectrometry (FI-ICP-MS)

•Extraction Method must support ionic and non-ionic lead species

- Solvent extraction
- Water Extraction (standardize ion concentration to maximize desorption of target lead species)

• Need analytical method which can provide species specific results

 Non-ionic lead species - Reverse Phase Chromatography coupled to Inductively Coupled Plasma Mass Spectrometer (RP-ICP-MS)

non-ionic lead species – Gas Chromatography coupled to Inductively Coupled Plasma Mass Spectrometer (GC-ICP-MS)
Ionic lead species – Ion Chromatography coupled to Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS)



New Method Approach

• Solvent Extraction with p-xylene to support non-ionic lead species (tetramethyl and tetraethyl lead)

 Increased chloride concentration in original sample or use chloride in extraction for solids to support ionic lead species (Pb(II), trimethyl lead, triethyl lead, other degradation compounds)

• Analyze all extracts using FI-ICP-MS to confirm extraction efficiency and mass balance of quality control parameters

- Analyze solvent extracts using RP-ICP-MS
- Analyze water extract using IC-ICP-MS



Flow Injection Inductively Coupled Plasma Mass Spectrometry

• Flow injection uses an injection loop to collect sample which is swept into organic solvent carrier and transported into the ICP-MS for detection.

 Application of FI-ICP-MS reduces carryover and matrix effects on plasma



RP-ICP-MS

Reverse Phase Chromatography Inductively Coupled Plasma Mass Spectrometry (RP-ICP-MS)

Ionic interactions between lead species and chromatographic column are limited

Uses a C-18 or other carbon based column instead of an anion or cation column for species retention

Requires ion pairing agent to provide acceptable species resolution for most ionic lead species (not supported with this method)

Can require high concentrations of organic solvents to elute highly retained organic lead species (ICP-MS issue)



IC-ICP-MS

Ion Chromatography Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS)

Non-ionic species are unretained; thus, no resolution between species

Uses a cation based column for species retention



Schematic for HPLC-ICP-MS (RP or IC)



RP-ICP-MS Chromatogram

0.20 ug/L Tetramethyl Pb and Tetraethyl Pb Chromatogram using RP-ICP-MS





IC-ICP-MS Chromatogram

0.10ug/L Pb(II), Trimethyl Pb, and Triethyl Pb Chromatogram using IC-ICP-MS





Schematic for GC-ICP-MS



Schematic for GC-ICP-MS





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GC-ICP-MS Chromatogram

10ug/L Tetramethyl Pb and Tetraethyl Pb Chromatogram using GC-ICP-MS





Groundwater Sample Results Solvent Extraction with p-xylene

FI-ICP-MS Results (aqueous samples)	% Recovery
LCS Inorganic Pb	0%
LCS TriMethyl Pb	1%
LCS Triethyl Pb	46%
LCS Tetramethyl Pb	101%
MS Pb(II)	0%
MSD Pb(II)	0%
MS Trimethyl Pb	3%
MSD Trimethyl Pb	3%
MS Triethyl Pb	46%
MSD Triethyl Pb	45%
MS Tetramethyl Pb	101%
MSD Tetraethyl Pb	100%

RP-ICP-MS Results (aqueous samples)	% Recovery
Tetraethyl Pb	103%
Tetramethyl lead	76%



Groundwater Sample Results

Water Extraction with HCI+DIW

IC-ICP-MS Results (aqueous samples)	% Recovery
LCS Trimethyl Pb	100%
LCS Triethyl Pb	105%
MS Trimethl Pb	80%
MSD Trimethyl Pb	80%
MS Triethyl Pb	76%
MSD Triethyl Pb	77%



Soil Sample Results

Comparison of Water Extraction with and Without HCI Addition

Water extraction with DIW only	
IC-ICP-MS Results (soil samples)	% Recovery
LCS -Pb2-1	90%
LCS -TriM-1	98%
LCS -TriE-1	92%
MS Pb(II)	-1%
MSD Pb(II)	45%
MS Trimethyl Pb	17%
MSD Trimethyl Pb	23%
MS Triethyl Pb	6%
MSD Triethyl Pb	5%

Water extraction with DIW and HCI	
IC-ICP-MS Results (soil samples)	% Recovery
LCS -Pb2	88%
LCS -TriM	93%
LCS -TriE	99%
MS Pb(II)	111%
MSD Pb(II)	98%
MS Trimethyl Pb	87%
MSD Trimethyl Pb	97%
MS Triethyl Pb	92%
MSD Triethyl Pb	90%



Soil Sample Results

Solvent Extraction with p-xylene

RP-ICP-MS Results (soil samples)	% Recovery
LCS -Pb2-3	0%
LCS -TriE-3	2%
LCS -TetE-3	104%
MS Pb(II)	0%
MSD Pb(II)	0%
MS Triethyl Pb	1%
MSD Triethyl Pb	1%
MS Tetraethyl Pb	116%
MSD Tetraethyl Pb	115%



Conclusions

- Technology is available to support lead speciation in groundwater
- Existing HML-939 method does not support degradation compounds which can lead to poor conclusions regarding remediation and culpability
- Extraction and analytical methods must be specific to target molecules
 - Solvent extractions for non-ionic species
 - Water based extractions for ionic species
- Appropriate method must be available for total Pb confirmation in extracts for mass balance purposes
- Different approaches are available for quantitation of tetraalkylated lead species (liquid and gas chromatography)
- Detection limits have significant improved from GF-AAS
 - GFAAS IDL = 1020mg/L
 - RP-ICP-MS IDL = 0.00002mg/L



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