



Applied Speciation

Analysis Research Consulting

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



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 alkyllead-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



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)

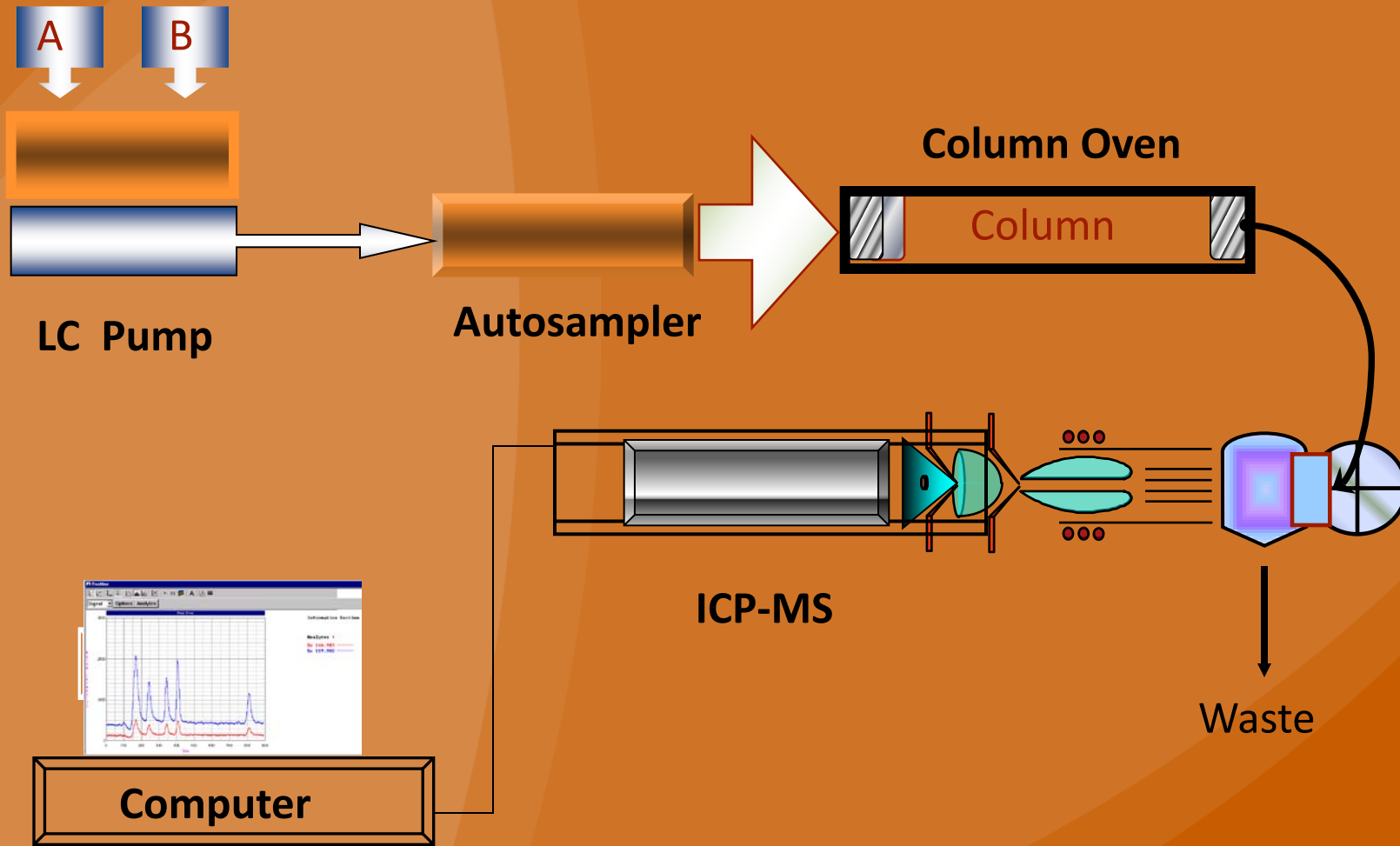


IC-ICP-MS

- 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

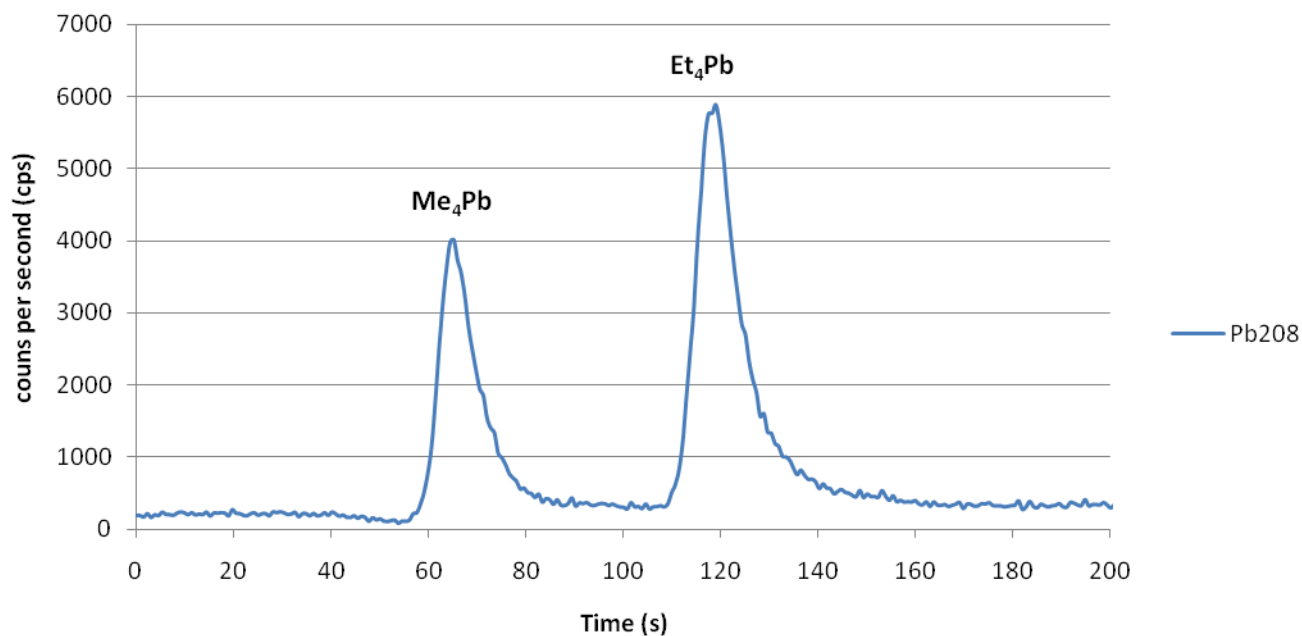


Schematic for HPLC-ICP-MS (RP or IC)



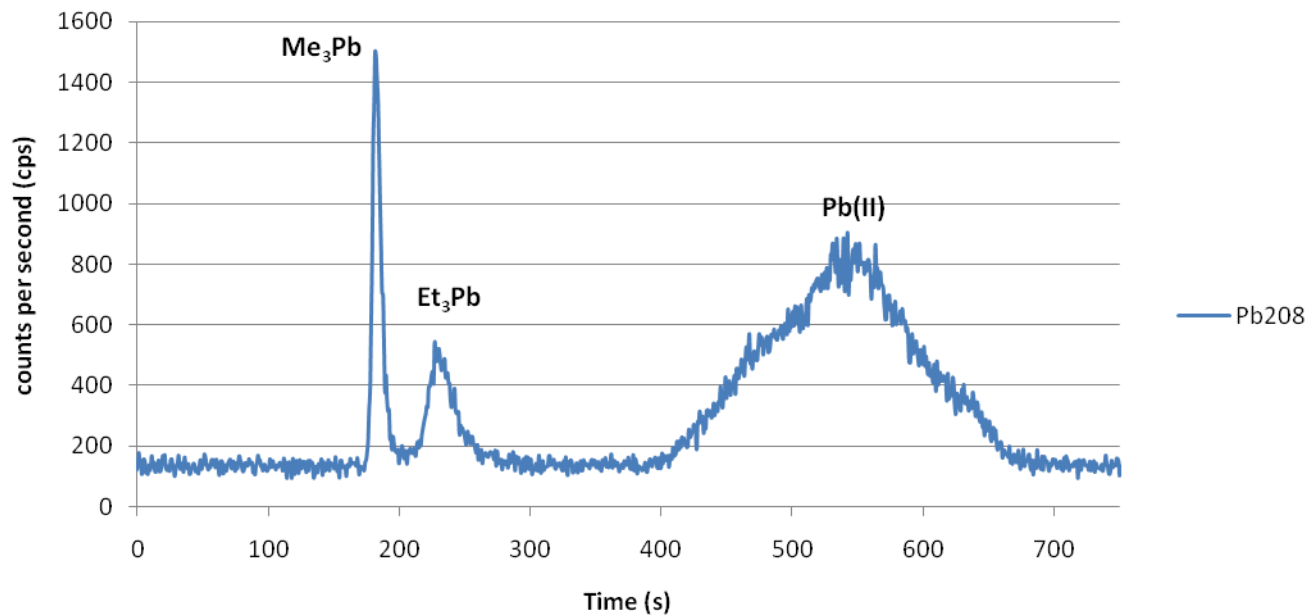
RP-ICP-MS Chromatogram

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

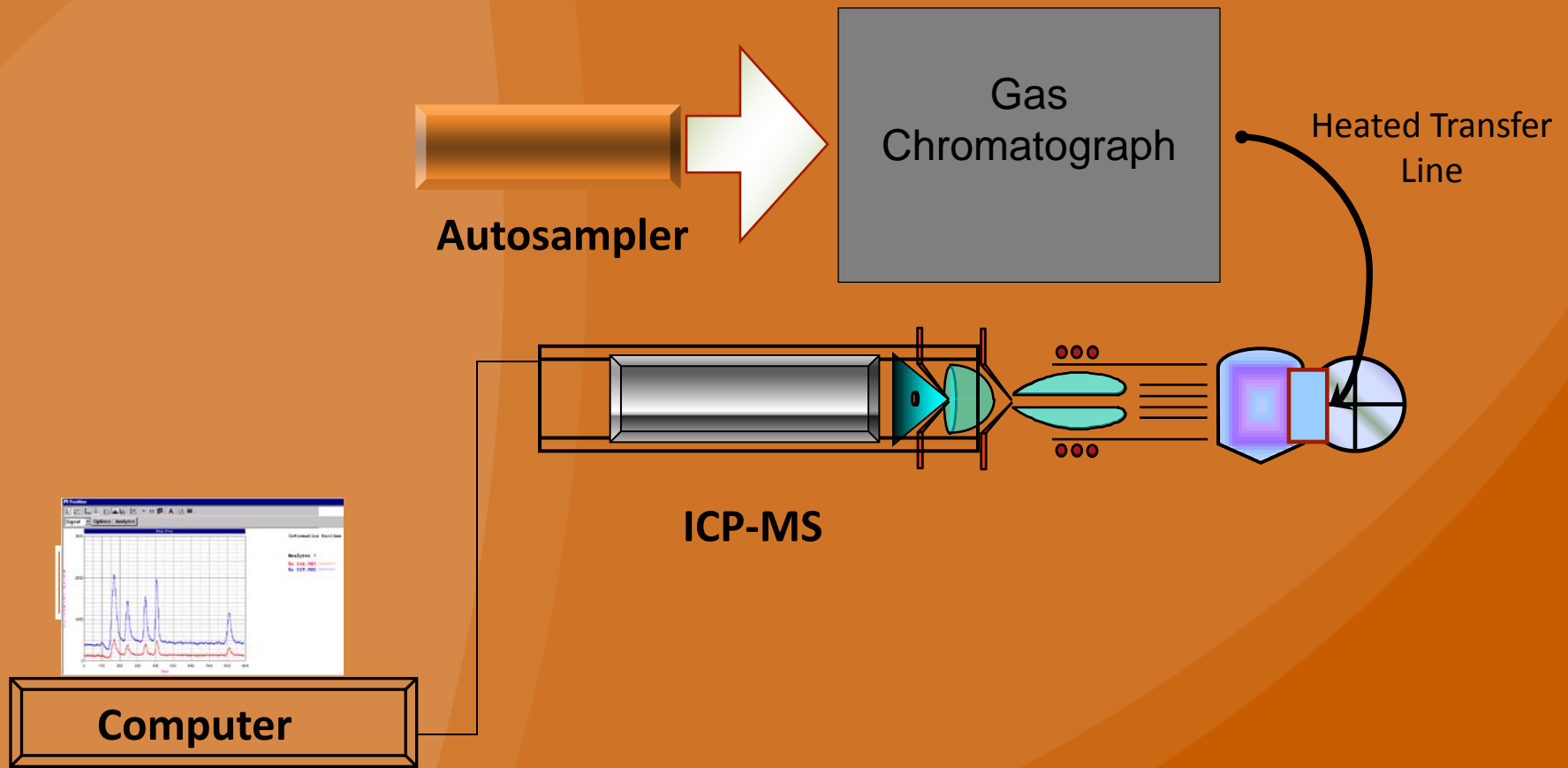


IC-ICP-MS Chromatogram

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



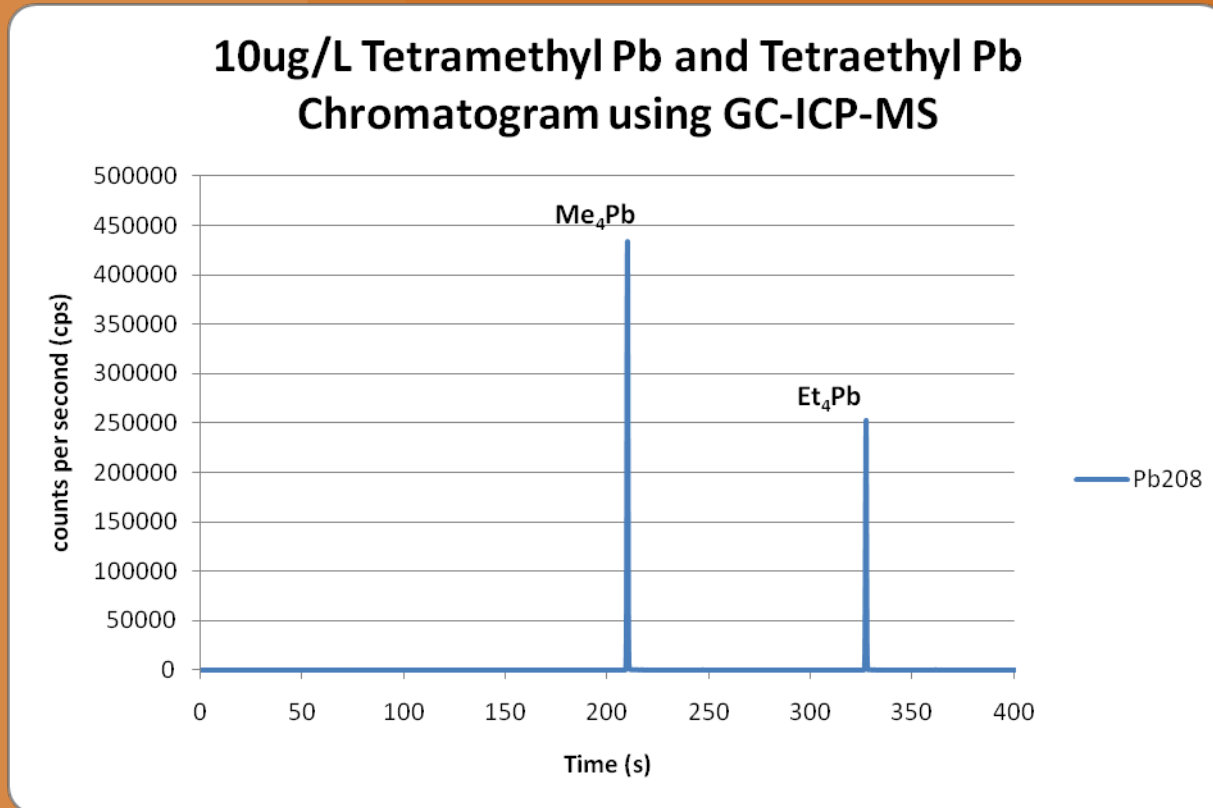
Schematic for GC-ICP-MS



Schematic for GC-ICP-MS



GC-ICP-MS Chromatogram



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 HCl+DIW

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



Soil Sample Results

Comparison of Water Extraction with and Without HCl 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 HCl	
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 significantly improved from GF-AAS
 - GFAAS IDL = 1020mg/L
 - RP-ICP-MS IDL = 0.00002mg/L



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