



Low-level lead speciation and isotope ratio analysis by GC-MC-ICP-MS

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Goal

To develop a method for simultaneous lead speciation and isotope ratio analysis using the Thermo Scientific™ Neptune XT™ Multicollector ICP-MS coupled with the Thermo Scientific™ Trace™ 1310 GC.

Introduction

Lead has been a major anthropogenic environmental contaminant for centuries, associated with mining, smelting and fossil fuels.¹ Transported via atmospheric aerosols, lead contamination is a global problem, with instances of high lead production measurable within chronometers such as ice cores and peat bogs.

The lead isotope ratio of a material is not constant, but varies by geographical location and the processes (i.e. smelting, geological weathering) it has undergone. The determination of lead isotope ratios of contaminant material therefore can give a good indication of the source. Bulk lead isotope ratio analysis may not provide the complete picture, due to overlapping Pb sources. For organolead compounds, the toxicity of which may differ significantly from inorganic lead, speciation and isotopic ratio analysis of organolead compounds within an environmental sample may determine a distinct source to the bulk analysis.² The Thermo Scientific™ GCI™ Series Interface couples the chromatographic speciation analysis of gas chromatography (GC) to the high sensitivity and simultaneous detection capability of multicollector (MC-) ICP-MS. Employing high gain, Thermo Scientific™ 10^{13} Ω Amplifier Technology™, GC-MC-ICP-MS isotope ratio analysis of even low-level lead samples can be performed to a high degree of precision.

Method

A Thermo Scientific Trace 1310 GC was coupled with a Thermo Scientific Neptune XT MC-ICP-MS via the GCI 300 Interface. Each instrument was operated separately within its own control suite of software.

The GCI 300 is a simple and flexible transfer line that offers easy handling, installation and operation of the GC-MC-ICP-MS system. The instrument configuration and operation parameters are shown in Table 1. The 3 major Pb isotopes were measured on Faraday cup detectors with $10^{13} \Omega$ amplifiers.

Table 1. Instrument configuration and operation parameters.

GC Parameters	Value
Oven program	Initial temp of 50 °C for 0.5 min Ramp at 30 °C/min to 250 °C, hold for 5 min
Column	TG 5MS 5% PMS 30 m × 0.25 mm × 0.25 μm (P/N 26098-1420)
Injection volume	1 μL
Carrier gas	He
Injection mode	PTV, splitless time 0.5 min
Injection port temperature program	Initial temp of 50 °C Ramp at 14.5 °C/min to 250 °C Clean at 270 °C between runs
Carrier pressure program	Initial pressure of 250 kPa for 6.9 min Ramp at 100 kPa/min to 350 kPa, hold for 5.3 min
Septum purge flow	50 mL/min
Split flow	10 mL/min
Transferline	270 °C
ICP-MS Parameters	Value
Interface	Ni-sampler (Std) and Ni-skimmer (H)
RF power	1300 W
Transferline gas flow	Ar at 1.0 L•min ⁻¹
Cup configuration	H1 – ²⁰⁶ Pb ($10^{13} \Omega$), H2 – ²⁰⁷ Pb ($10^{13} \Omega$), H3 – ²⁰⁸ Pb ($10^{13} \Omega$)
Integration time	131 ms
Duration	12 min

Urban Dust reference material (CRM 605) and an environmental dust sample were extracted with 5 mL of a 0.5 M solution of acetic acid in methanol for 12 h with mechanical agitation. The extract was neutralized and the organolead complexed with EDTA before extraction in 2 mL of hexane. The supernatant was derivatized with n-butylmagnesium chloride in tetrahydrofuran. Each sample was run in triplicate with a blank measured before, between and after each sample batch.

Results

The chromatographic data was exported from within the Thermo Scientific Multicollector Software Suite and evaluated. The high thermal stability of the newly developed transferline eluted baseline separated Pb compounds (Figure 1) reproducibly: the compound TML in c3 could be identified from the retention time (Figure 2).

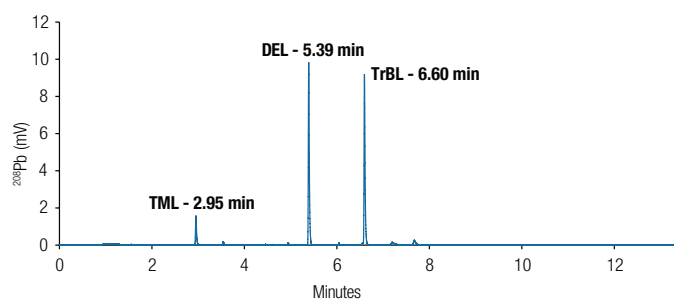


Figure 1. Chromatogram acquired for the SA1 dust sample.

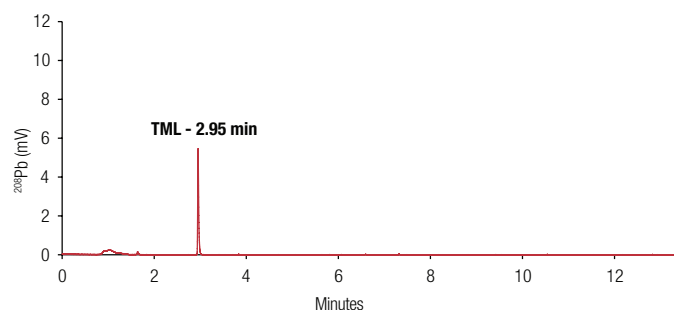


Figure 2. Chromatogram acquired for the c3 dust sample.

The measured Pb isotope ratio uncertainty for each compound were 0.2–3.1%, depending on total signal. The total Pb signal per peak ranged between 60–360 mV.

The 3 compounds above the limit of quantification (0.3 mV) in SA1 had distinct lead isotope ratio values (Figure 3). The compound TML, detectable in both samples SA1 and c3, did not share the same Pb isotope ratio values between samples (Table 1). Thus suggesting a different source for the TML detected at each sample location.

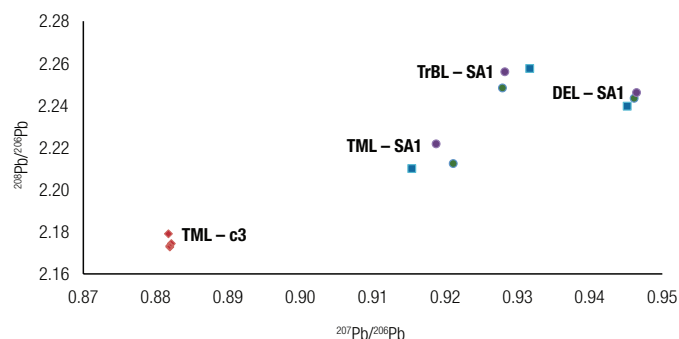


Figure 3. Lead isotope ratios of four quantifiable peaks in samples SA1 and c3.

Table 2. Lead isotope ratios of compounds within two dust samples, SA1 and c3.

Sample	Peak	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
SA1	TML	2.215 ± 0.006	0.918 ± 0.003
	DEL	2.243 ± 0.003	0.946 ± 0.001
	TrBL	2.254 ± 0.005	0.929 ± 0.002
c3	TML	2.176 ± 0.003	0.882 ± 0.0002

Conclusion

With the GCI 300 Interface (P/N BRE0008122), isotope ratio analysis of speciated organometallic compounds is within the scope of the modern environmental laboratory. 10^{13} Ω Amplifier Technology extends the operating range of the high precision Faraday cup detectors to small ion beams. By overcoming the low analyte abundance common in environmental samples the utility of GC-MC-ICP-MS to isotope ratio analysis was further improved.

References

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