

Supplementary Information

Direct determination of Pb isotope ratios in archaeological materials by coupling Liquid Chromatography to Multicollector ICP-MS.

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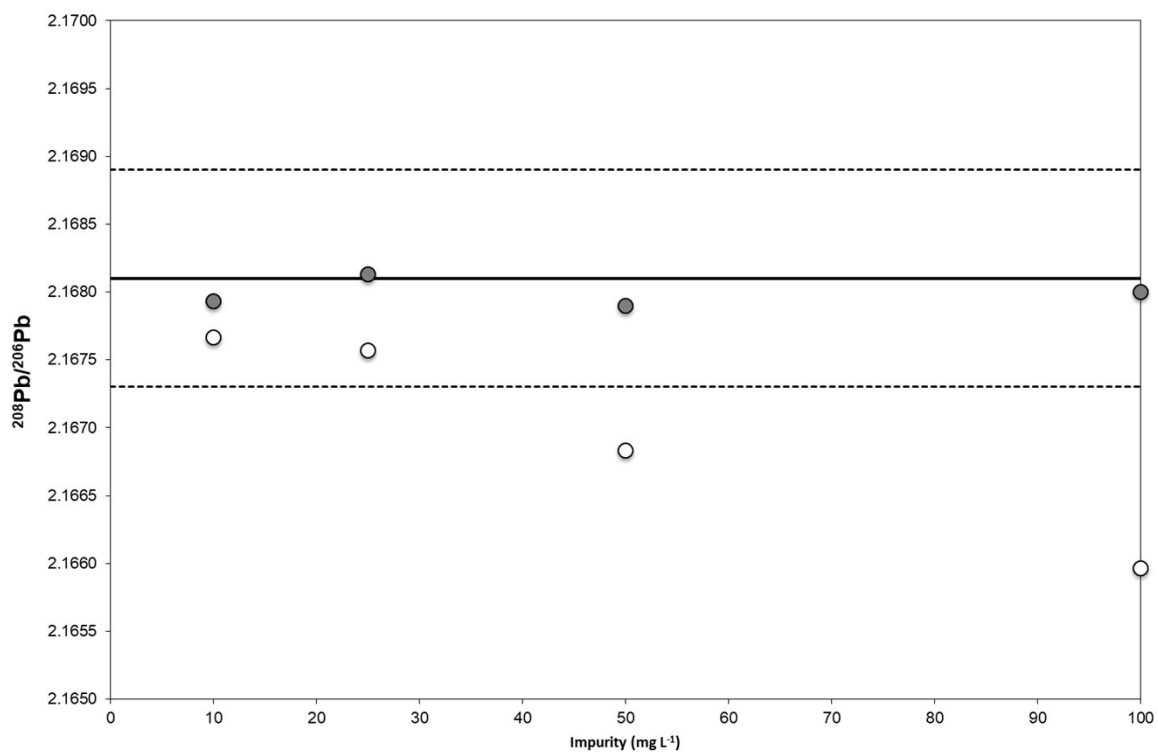


Figure S1. Effect of Cu (white dots) and NaCl (grey dots) on the measured $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratio on NIST 981 reference material. The horizontal lines correspond to the reference value and the acceptance interval.

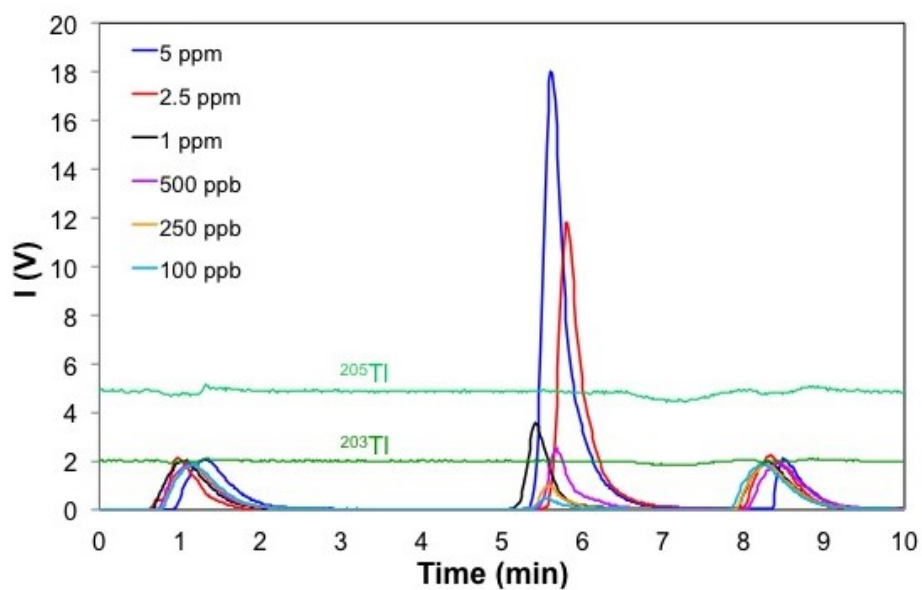


Figure S2: Chromatogram overlapping the different peaks for the different concentrations under study of the NIST 981 reference material injected through the HPLC system.

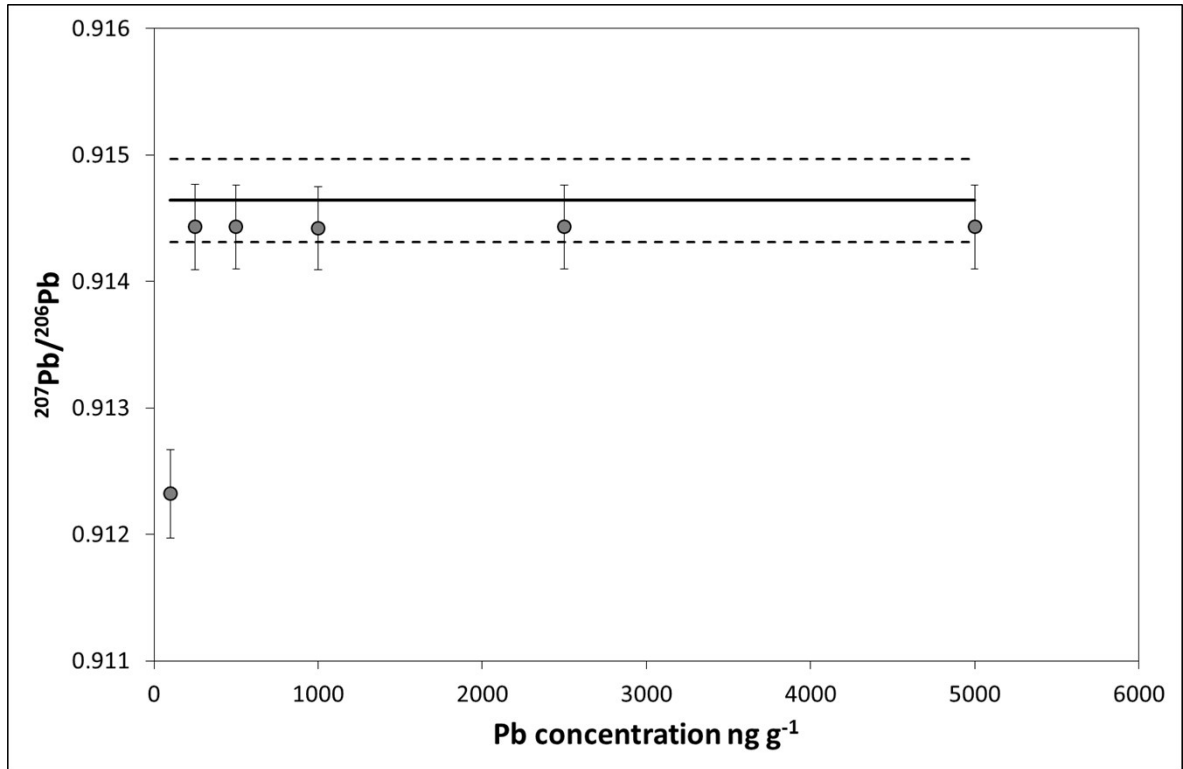


Figure S3: Results for the measurement (in triplicate) of $^{207}\text{Pb}/^{206}\text{Pb}$ ratio in different solutions of SRM 981 at different concentrations in order to check the limiting concentrations.

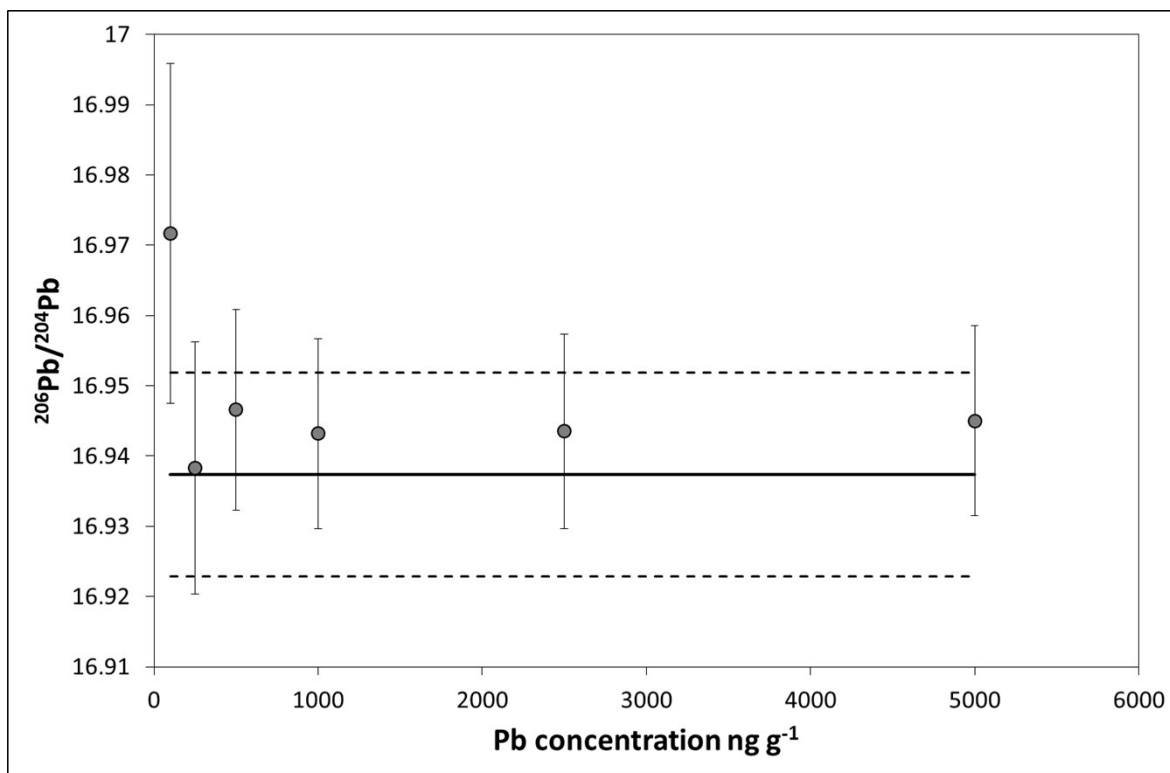


Figure S4: Results for the measurement (in triplicate) of $^{206}\text{Pb}/^{204}\text{Pb}$ ratio in different solutions of SRM 981 at different concentrations in order to check the limiting concentrations.

Table S1: ^{208}Pb maximum intensity for each concentration.

[Pb]	Intensity ^{208}Pb (V)
100 $\mu\text{g L}^{-1}$	0.46
250 $\mu\text{g L}^{-1}$	0.97
500 $\mu\text{g L}^{-1}$	2.25
1 mg L^{-1}	4.57
2.5 mg L^{-1}	11.4
5 mg L^{-1}	18

Table S2: $^{208}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ values for each individual replicate injected through the chromatographic column for the optimisation of the limiting concentration. The uncertainty of each isotope ratio, u_i , is the combined uncertainty of the raw isotope ratio, the uncertainty of the measurements of the NIST SRM 981 for bracketing correction and the uncertainty of the certified reference material.

Sample	$^{208}\text{Pb}/^{206}\text{Pb}$	u_i	$^{207}\text{Pb}/^{206}\text{Pb}$	u_i	$^{206}\text{Pb}/^{204}\text{Pb}$	u_i
100 $\mu\text{g L}^{-1}$ (1)	2.16528	0.00082	0.91234	0.00034	16.9549	0.0219
100 $\mu\text{g L}^{-1}$ (2)	2.16549	0.00083	0.91219	0.00035	16.9784	0.0235
100 $\mu\text{g L}^{-1}$ (3)	2.16587	0.00082	0.91243	0.00034	16.9818	0.0226
250 $\mu\text{g L}^{-1}$ (1)	2.16764	0.00081	0.91443	0.00034	16.9231	0.0151
250 $\mu\text{g L}^{-1}$ (2)	2.16730	0.00081	0.91443	0.00034	16.9379	0.0156
250 $\mu\text{g L}^{-1}$ (3)	2.16745	0.00081	0.91442	0.00034	16.9539	0.0159
500 $\mu\text{g L}^{-1}$ (1)	2.16772	0.00081	0.91443	0.00033	16.9446	0.0137
500 $\mu\text{g L}^{-1}$ (2)	2.16760	0.00081	0.91443	0.00034	16.9537	0.0140
500 $\mu\text{g L}^{-1}$ (3)	2.16775	0.00081	0.91443	0.00033	16.9416	0.0140
1 $\mu\text{g L}^{-1}$ (1)	2.16751	0.00081	0.91443	0.00033	16.9440	0.0135
1 $\mu\text{g L}^{-1}$ (2)	2.16748	0.00081	0.91443	0.00033	16.9443	0.0135
1 $\mu\text{g L}^{-1}$ (3)	2.16729	0.00081	0.91441	0.00033	16.9414	0.0135
2.5 $\mu\text{g L}^{-1}$ (1)	2.16738	0.00081	0.91440	0.00033	16.9485	0.0134
2.5 $\mu\text{g L}^{-1}$ (2)	2.16787	0.00081	0.91445	0.00033	16.9369	0.0133
2.5 $\mu\text{g L}^{-1}$ (3)	2.16766	0.00081	0.91443	0.00033	16.9451	0.0134
5 $\mu\text{g L}^{-1}$ (1)	2.16747	0.00081	0.91442	0.00033	16.9491	0.0134
5 $\mu\text{g L}^{-1}$ (2)	2.16765	0.00081	0.91444	0.00033	16.9433	0.0134
5 $\mu\text{g L}^{-1}$ (3)	2.16758	0.00081	0.91443	0.00033	16.9427	0.0133

Table S3: Average $^{208}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ with the corresponding final combined uncertainties, u_f , calculated taking into account the standard deviation of the three replicates and the uncertainty of each individual measurement.

Sample	$^{208}\text{Pb}/^{206}\text{Pb}$	u_f	$^{207}\text{Pb}/^{206}\text{Pb}$	u_f	$^{206}\text{Pb}/^{204}\text{Pb}$	u_f
100 $\mu\text{g L}^{-1}$	2.16554	0.00084	0.91232	0.00035	16.9717	0.0242
250 $\mu\text{g L}^{-1}$	2.16746	0.00082	0.91443	0.00034	16.9383	0.0179
500 $\mu\text{g L}^{-1}$	2.16769	0.00081	0.91443	0.00033	16.9466	0.0143
1 mg L^{-1}	2.16743	0.00081	0.91442	0.00033	16.9432	0.0135
2.5 mg L^{-1}	2.16764	0.00082	0.91443	0.00033	16.9435	0.0138
5 mg L^{-1}	2.16757	0.00081	0.91443	0.00033	16.9450	0.0135