

Supporting Information

Online determination of mercury isotopic compositions at ultratrace levels by automated purge and trap coupled with multicollector inductively coupled plasma–mass spectrometry

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Specific description of purge & trap procedure

The sample solution was added into 40 mL sampling vials, followed by the addition of 0.1 mL of SnCl₂ solution (20% in 10% HCl). The sample vials were configured with PTFE caps (24-414 white open top cap, PTFE/Si, Agilent Technologies, USA). These caps were all single-use. After quick capping, the vials were shaken and placed on the autosampler. The gas flows (purge and carrier gas) were controlled by rotameters. During purging, the sweeping gas flowed out from the bottom of the PEEK needle and carried the reduced Hg(0). The Hg(0) was carried by carrier gas after two-stage trap and desorption. The gas flow passed by a soda-lime container (to remove acid gas) and then Hg(0) was concentrated on gold trap (X/Y). Then the Hg(0) was released by heating and absorbed in one analytical gold trap. When the sample sequence is running, the parallel gold traps X and Y alternately work (built-in settings). The purge and trap module is a closed system which can be checked by blocking the outlet of the module as suggested by the Brooks Rand engineers. If there is no air leak in the system, the reading of rotameter will drop to zero.

Sample preparation

The coal standards (NIST 1632e) were pretreated by the double-stage thermal combustion-trapping method¹ for THg and Hg isotope measurements. In detail, approximately 0.2 g of replicated samples was weighed into quartz tubes, and these tubes were placed into the central part of the combustion furnace (Thermo Scientific, USA), with the temperature programmed to increase from room temperature to 1000°C within 4 h: (1) ramping from room temperature to 100°C within 0.5 h; (2) ramping from 100°C to 650°C within 3 h; and (3) ramping from 650°C to 1000°C within 0.5 h. The released Hg was carried out by oxygen (highly purified, flow rate of 25 mL min⁻¹), passed by the decomposition furnace with the temperature held at 1000°C, and finally oxidized to Hg(II) in a 5 mL trapping solution (40% v/v, HNO₃: HCl = 2:1 v/v). The trapping solution was completely transferred into brown borosilicate glass bottles with several rinses.

Biota standards (NRC DORM-4) were treated with microwave digestion.² In

detail, approximately 0.2 g of replicates was weighed into PTFE tubes. Then, 4 mL HNO₃ and 2 mL H₂O₂ were added to the tubes. The mixture was digested in a microwave digestion system (Anton Paar, Austria) following the ramping scheme with max power of 1500 W: (1) ramping from room temperature to 120°C within 20 min and maintained for 5 min; (2) ramping from 120°C to 150°C within 5 min and maintained for 5 min; (3) ramping from 150°C to 180°C within 5 min and maintained for 30 min. The digestion solution was completely transferred into brown borosilicate glass bottles with several rinses after cooling. The solution was added to 5 mL L⁻¹ of BrCl (0.2 N) to fully convert all the Hg species to Hg(II). All the sample solutions were stored at 4°C before THg and isotope analysis.

The water samples were collected and treated following USEPA method 1631. Approximately 500 mL of aquatic samples was collected in brown glass bottles immediately supplemented with 4 mL L⁻¹ HCl. The water samples were filtrated by 0.45 µm PTFE membranes and added to 50 mL L⁻¹ of BrCl (0.2 N) overnight.

Macros for data processing

Specific Macros were used in this work for batch calculating the Hg isotope ratios using LRS method. The processed files were the exported data files from Neptune software-evaluation with an extension “.static.exp”. The macro “Filename” was used for exporting the file name and the macro “Dataprocessing” was used for filtering and calculating the Hg isotope ratios. A “Run.xlsx” file was used for recording the results with buttons that trigger the edited Macros. A “Calculator.xlsx” file was used for calculating the isotope ratios that was corrected by internal Tl standard. It is worth noting that the edited Macros are available for the instrumental and acquisition parameters in the current work but may not be suitable for other conditions. Appropriate modifications could give these Macros more application scenarios.

The visual basic code of the Macros is as follows:

```
Sub Filename() 'Batch exporting the name of each .exp file in a given folder
mypath = "E:\RUN_FOLDER" 'appoint a folder pathway
```

```

mytype = "*.exp" 'appoint file type
myname = Dir(mypath & mytype)
Do While myname <> ""
If myname <> "." And myname <> ".." Then
i = i + 1
Cells(i, 1).Value = Left(myname, InStrRev(myname, ".") - 8)
End If
myname = Dir
Loop
Set mypath = Nothing
Set mytype = Nothing
Set myname = Nothing
End Sub

Sub Dataprocessing() 'Batch calculating Hg isotope ratios for each .exp file
in a given folder using LRS method
Dim exp
exp = Dir("E:\RUN_FOLDER" & "*.exp") 'appoint a folder pathway and file type
Do While exp <> ""
Set exp = Workbooks.Open("E:\RUN_FOLDER" & "\" & exp)
Sheets(1).Select
    Rows("5018:5025").Select
    Selection.delete Shift:=xlUp 'delete the unnecessary data
    Range("H17").Select
    Selection.AutoFilter
    ActiveSheet.Range("$A$17:$O$5017").AutoFilter Field:=8,
Criteria:=">0.01", Operator:=xlAnd 'define a threshold for data filter, for
example, the intensity of 202Hg as 0.01
    Range("A17:J17").Select
    Range(Selection, Selection.End(xlDown)).Select
    Application.CutCopyMode = False
    Selection.Copy
    Windows("Calculator.xlsx").Activate
    Range("A1").Select
    ActiveSheet.Paste 'copy the filtered data to an edited excel file for LRS
calculation
    Range("P9:S9").Select
    Application.CutCopyMode = False
    Selection.Copy
    Range("P10").Select
    Selection.PasteSpecial Paste:=xlPasteValuesAndNumberFormats,
Operation:=xlNone, SkipBlanks:=False, Transpose:=False
    Columns("A:J").Select
    Application.CutCopyMode = False

```

```
Selection.ClearContents 'clear the data in the calculating file
Range("P10:S10").Select
Application.CutCopyMode = False
Selection.Copy
Windows("Run.xlsx").Activate
ActiveSheet.Paste 'copy the calculated ratios in an appointed excel file
ActiveCell.Offset(1).Activate
exp.Close SaveChanges:=False
exp = Dir
Loop
Set exp = Nothing
Windows("Run.xlsx").Activate
ActiveWorkbook.Save
End Sub
```

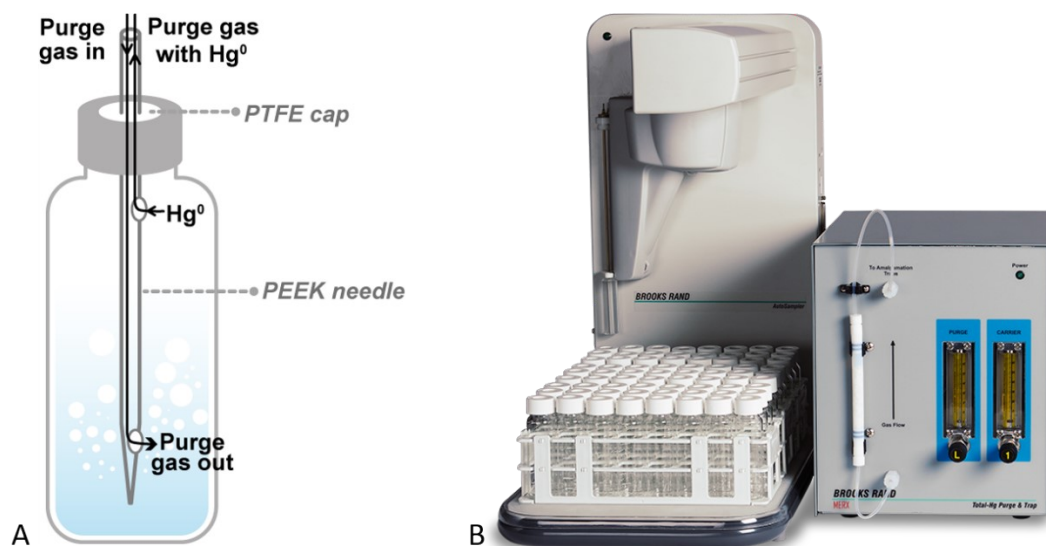


Figure S1. Schematic diagram of the in-vial purge system (A) and a photograph of automated purge and trap module (B).

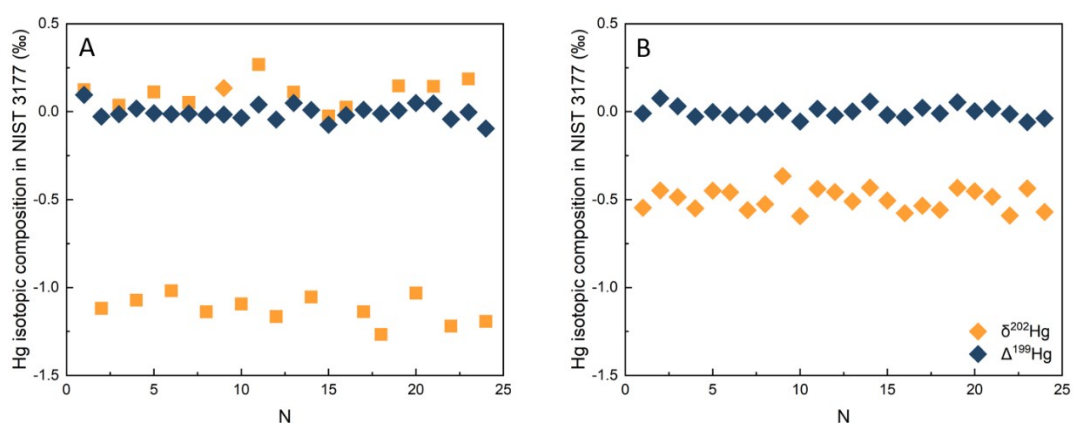


Figure S2. Hg isotopic compositions in NIST 3177 using “SSB” (A) and modified “SSSSSB” (B) analytical sequence. In Figure S2A, the calculated values of NIST 3177 were bracketed with NIST 3133 measuring by the different gold trap (analytical sequence of NIST 3133_x-NIST 3177_y-NIST 3133_x). In Figure S2B, the values of NIST 3177 were bracketed with NIST 3133 measuring by the same gold trap (analytical sequence of NIST 3133_x-NIST 3133_y-NIST 3177_x-NIST 3177_y-NIST 3133_x-NIST 3133_y).

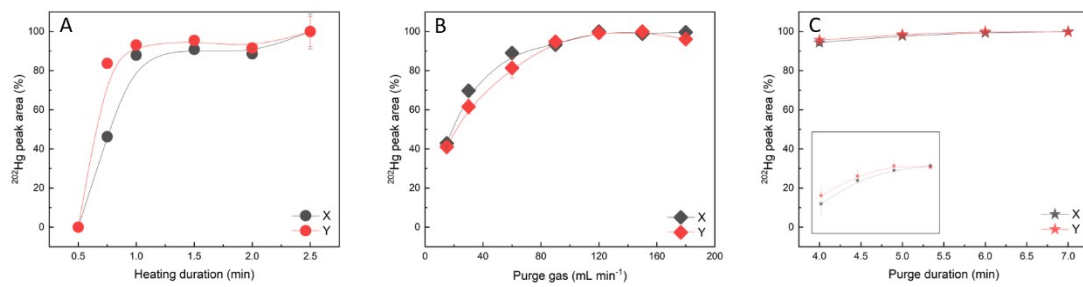


Figure S3. Optimization of the automated P&T unit: (A) heating duration for the gold trap (purge gas flow rate of 150 mL min^{-1} , purge duration of 5 min), (B) flow rate of purge gas (heating duration of 2.5 min, purge duration of 5 min), (C) purge duration of single injection (heating duration of 2.5 min, purge gas flow rate of 180 mL min^{-1}).

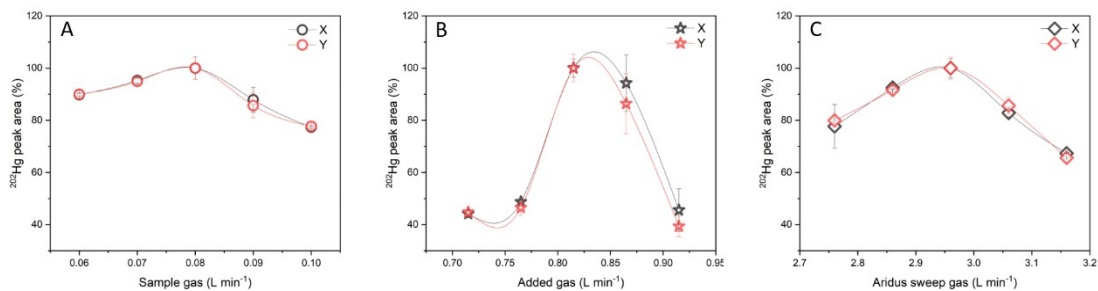


Figure S4. Original optimization of the gas flow parameters in the P&T-MC-ICPMS hyphenated system: (A) flow rate of sample gas (added gas flow rate of 0.89 L min^{-1} , sweep gas flow rate of 3.98 L min^{-1}), (B) flow rate of added gas (sample gas flow rate of 0.08 L min^{-1} , sweep gas flow rate of 3.98 L min^{-1}), (C) flow rate of sweep gas (sample gas flow rate of 0.08 L min^{-1} , added gas flow rate of 0.89 L min^{-1}).

Table S1. Instrumental parameters for the automated P&T-MC-ICPMS system and CV-MC-ICPMS.

Automated P&T module								
Flow rate of purge gas (Ar, mL min ⁻¹)		180						
Flow rate of carrier gas (Ar, mL min ⁻¹)		145						
Purge duration (min)		5.0						
Heating duration (min)		2.5						
Cooling duration (min)		1.0						
Drying duration (min)		3.0						
Aridus II	P&T	CV						
Flow rate of sweep gas (Ar, L min ⁻¹)	3.90-4.00	3.80-4.00						
Flow rate of Nitrogen gas (N ₂ , L min ⁻¹)	-	-						
Neptune Plus	P&T	CV						
RF Power (W)	1296	1296						
Resolution	low	low						
Cool gas (Ar, L min ⁻¹)	16.00	16.00						
Aux gas (Ar, L min ⁻¹)	0.80	0.80						
Sample gas (Ar, L min ⁻¹)	0.08	0.14-0.20						
Added gas (Ar, L min ⁻¹)	0.8~0.9	0.60-0.70						
Blocks	1, 1	2						
Cycles	5000, 1000	50						
Integration time (s)	0.008, 0.066	2						
Faraday Cups Configuration								
L4	L3	L2	L1	C	H1	H2	H3	H4
¹⁹⁶ Hg	¹⁹⁸ Hg	¹⁹⁹ Hg	²⁰⁰ Hg	²⁰¹ Hg	²⁰² Hg	²⁰³ Tl	²⁰⁵ Tl	-

Table S2. Recoveries of THg concentrations in samples with different matrices measuring with automated P&T and CVAFS detector.

CRMs	Type	Pretreatment	N	Recoveries (%) mean \pm 1SD
NRC DORM-4	Fish protein	Microwave digestion	51	97 \pm 5
NRC TORT-3	Lobster hepatopancreas	Microwave digestion	48	100 \pm 3
NIST 1632e	Coal	Double-stage combustion	12	99 \pm 2
NIST 1944	Sediment	Double-stage combustion	48	101 \pm 9
GBW 07310	Sediment	Double-stage combustion	72	104 \pm 6
IRMM BCR-482	Lichen	Double-stage combustion	12	99 \pm 2

Table S3. Parameters for the sensitivity calculation.

	CV	P&T
Hg load for single measurement (pg)	6000	1000
Solution concentration (ng L ⁻¹)	1000	40
Volume for single measurement (mL)	6	25
Maximum intensity of ²⁰² Hg (V)	2.0	12.7
Single injection duration (s)	200	300

Table S4. The calculated Δt values (mean \pm 2SD) of the time-lag corrections A and B.

	N	^{199}Hg (ms)	^{200}Hg (ms)	^{201}Hg (ms)	^{202}Hg (ms)
Correction A	10	-0.06 ± 0.04	1.25 ± 0.28	-3.84 ± 0.83	2.68 ± 0.80
Correction B	62	-0.16 ± 0.04	0.12 ± 0.05	-1.30 ± 0.14	0.39 ± 0.17

Table S5. Information and concentrations (mean \pm SD) of lake water samples.

Sample ID	Location	Latitude (°, N)	Longitude (°, E)	N	THg (ng L⁻¹) mean \pm 1SD
LW-E	East Lake, Wuhan, China	30.54	114.37	2	23.9 \pm 0.3
LW-Y1	Ya-Er Lake, Wuhan, China	30.49	114.64	6	46.1 \pm 0.8
LW-Y2	Ya-Er Lake, Wuhan, China	30.48	114.64	2	10.2 \pm 0.6
LW-S	Sanjiao Lake, Wuhan, China	30.51	114.16	3	13.0 \pm 1.4

Table S6. T-test results for the CRMs measuring with CV and P&T methods
(Independent samples T-test was used).

CRMs	t	p	d
NIST 3177 ^{L, c, 40}	0.000	1.000	0.000
NIST 3177 ^{L, c, 20}	-0.075	0.942	-0.040
NIST 3177 ^{L, c, 8}	0.085	0.934	0.045
NRC DORM-4	0.075	0.942	0.040
NIST 1632e	0.030	0.977	0.016

^{L, c}: acquisition parameter: integration time of 8 ms, cycles of 5000 and conduction of data reduction using 0.01 V as criteria based on ²⁰²Hg in P&T measurements;

^{40/20/8}: introduced Hg concentrations (ng L⁻¹) in P&T measurements.

REFERENCES

1. Liu, H.; Yu, B.; Shi, J.; Zhang, Q.; Jiang, G. *Advance in Polar Science* **2017**, 28 (1), 75-80.
2. Meng, M.; Sun, R.; Liu, H.; Yu, B.; Yin, Y.; Hu, L.; Chen, J.; Shi, J.; Jiang, G. *Journal of hazardous materials* **2020**, 384, 121379.