Supporting Information for: Improved Methods for Signal Processing in Measurements of Elemental Mercury Vapor by Tekran® 2537A and 2537B Instruments

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S1 Details on the Format of the Tekran® Analyzer’s Serial Data Output

The serial data output ("RAWDUMP" format) from the Tekran® analyzer can be parsed into the components listed below. (A more detailed description is provided in the Tekran® user manuals [c.f., Tekran Corporation, 2006, 2007].)

I. A “Raw data” string, which consists of Hg atomic fluorescence signal values, recorded at 10 Hz over a user-defined interval of the sample analysis cycle.

II. A “Peak table” string, which consists of a header and parameters defining the Hg thermal desorption peak profile (e.g., the peak start and end times) according to the Tekran® analyzer’s internal signal processing method.

III. A “Final data” string, which consists of a header and the following components (not ordered exactly as in the string): the timestamp; the cycle type flag (“CLN”, clean cycle; “CONT”, continuous ambient air analysis cycle; “SPAN”, calibration gas analysis cycle; “ZERO”, zero air blank cycle); the Au trap identity (“A” or “B”); the sample duration (seconds) and volume (standard liters); the area of the Hg TD peak, as determined by the Tekran® analyzer’s internal signal processing method, and the corresponding Hg concentration, calculated based on the sample volume, Hg TD peak area, and internal calibration data (see below); and some diagnostic parameters (e.g., the baseline standard deviation).

An example string for a single sample cycle is shown in Fig. S1. An additional “Calibration data” string is generated when a calibration gas analysis cycle is executed (Fig. S2).
Figure S1: An example of the Tekran® 2537B instrument’s serial data output (“RAWDUMP” format). The string of 10 Hz Hg fluorescence signal values in the “Raw data” string is delimited at the beginning and end by lines reading “RAWDUMP:” and “-9999”, respectively. The data values in the “Peak table” string are delimited at the beginning by a line reading “-” and at the end by a line reading “RAW END:” in the “Final data” string. The “Final data” string is delimited at the beginning by the line reading “RAW END:” and at the end by the line reading “RAWDUMP:” from the subsequent sample’s “Raw data” string. Note that the lines containing the dash, “-”, and the data header in the “Final data” string are only written with the raw data for the first sample analyzed. The same formatting is used with the 2537A instrument. Further information is provided in the Tekran® user manuals (Tekran Corporation, 2006, 2007).
Figure S2: An example of the “Calibration data” string in the Tekran® analyzer’s serial data output (“RAWDUMP” format). Further information is provided in the Tekran® user manuals (Tekran Corporation, 2006, 2007).
S2 Details on Tekran® Operating Parameters Employed in This Work

Instrument operating parameters and Hg thermal desorption peak integration parameters employed with the Tekran® 2537A and 2537B instruments I tested are given in Table S1.

Table S1. Operating parameters and Hg TD peak integration parameters employed with the Tekran® 2537A and 2537B instruments I tested.ª

<table>
<thead>
<tr>
<th>Flow Parameters (mL/min)</th>
<th>Car-Meas</th>
<th>Car-Idle</th>
<th>Car-Flush</th>
<th>Smpl-Rateᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80.0</td>
<td>15.0</td>
<td>160.0</td>
<td>1.00</td>
</tr>
</tbody>
</table>

| Analysis Timing Parameters (sec) | Sample Flush-Hi Meas-dly BL-time Intg-dly Pk-time |
|----------------------------------|---------|----------|----------|----------|-----------|
|                                  | 150.0   | 30.0     | 5.0      | 10.0     | 10.0      | 19.0      |

<table>
<thead>
<tr>
<th>Integration Parametersª</th>
<th>N-up</th>
<th>V-up (LSB)</th>
<th>N-dn</th>
<th>V-dn (LSB)</th>
<th>N-base</th>
<th>V-base (LSB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>8</td>
</tr>
</tbody>
</table>

ªParameters are defined in the Tekran® instrument manuals (Tekran Corporation, 2006, 2007). Flows are referenced to standard temperature and pressure of 273.15 K and 1.01325 bar.
bUnits are liters/min.
cLSB: least significant bit (1 LSB = 5 μV).

S3 Details on Constraining the Hg Thermal Desorption Peak End Time

For the dataset represented in Fig. 2 in the main manuscript, the preliminary Hg TD peak height value is negative for one blank sample (VIa,a method only). Only the SPAN samples (Hg loadings ≈ 150 pg) have peak heights that are large enough that it is necessary to constrain $t_{\text{end}}$ so that it is no later than 10 ds before the upper bound time, $t_n$, of the interval during which the Hg atomic fluorescence signal was recorded. No samples have peak heights that are small enough that it is necessary to constrain $t_{\text{end}}$ so that it is no earlier than 10 ds after the peak maximum time.

For the dataset represented in Fig. S3, the preliminary peak height value is negative for seven blank samples (VIa,a method only). Only the SPAN samples (Hg loadings ≈ 100 pg) have peak heights that are large enough that it is necessary to constrain $t_{\text{end}}$ so that it is no later than 10 ds before the upper bound time, $t_n$, of the interval during which the Hg AF signal was recorded. Sixteen blank samples have peak heights that are small enough that it is necessary to constrain $t_{\text{end}}$ so that it is no earlier than 10 ds after the peak maximum time (VIa,a method only).
S4 Details on Estimating the Baseline Standard Deviation

LabVIEW calculates the mean Bisquare regression residual, $r_{\text{mean}}$, from eq. 1:

\[ r_{\text{mean}} = \frac{1}{N} \times \left( \sum_{n=0}^{N-1} w_n (f_n - y_n)^2 \right) \]  

(1)

Here, $N$ is the number of data points in the regression, $w_n$ is the weight of the $n^{th}$ data point, $f_n$ is the value of the $n^{th}$ data point predicted by the regression equation, $y_n$ is the true value of the $n^{th}$ data point, and the summation is over all data points.

Accordingly, I estimate the baseline standard deviation from $r_{\text{mean}}$ using eq. 2:

\[ \sigma_{\text{bl}} = \left( r_{\text{mean}} \times \frac{N}{N-1} \right)^{0.5} \]  

(2)
S5 Results Obtained with a Tekran® 2537B Hg Vapor Analyzer

The test dataset collected with the 2537B instrument is shown as a time series in Fig. S3. Figure S4 shows the Hg thermal desorption profile recorded for a calibration gas analysis cycle. Figure S5 compares Hg loadings derived from the Tekran® method with concentrations derived from the VI₉₉ method (dataset shown in Fig. S3, excluding SPANs).

![Graph showing Hg thermal desorption profile](image)

**Figure S3:** Test dataset collected with a Tekran® 2537B instrument, represented as Hg loadings derived from my VI-based manual, semi-automated, and automated peak height determination methods (the VI₉₉, VI₉₉, and VI₉₉ methods, respectively), and by the Tekran® method. Mercury thermal desorption peaks not detected by the Tekran® method are assigned a value of 0.0001 pg. The pair of data points at ~100 pg corresponds with a pair of calibration gas analysis cycles (SPAN samples), which I use to initialize the VI. I use response factors calculated from the SPAN samples (and the preceding pair of blanks) to calculate Hg loadings for all other samples in the dataset. The sets of data points at ~25 pg correspond with calibration gas analysis cycles using an external calibration unit (external SPAN samples). The external calibration unit is described in Ambrose et al. (2015). The mean value of the baseline standard deviation, σₙ (defined in Sect. 2.1.1 in the main manuscript), is ~0.19 mV (equal to ~0.02 pg). The corresponding estimated lower-limit f value (mean ± 2σ) is 1.36(5) × 10⁻⁴.
Figure S4: (a) Example Hg thermal desorption profile during a calibration gas analysis cycle on a Tekran® 2537B instrument. Also shown is the corresponding 150 point exponential Bisquare (unweighted) regression (eq. 1 in the main manuscript; $r^2 = 0.997$) used to derive the decay constant ($b = -0.0308 \pm 0.0004 \, \text{ds}^{-1}$) during initialization of the VI’s signal processing method. (b) Comparison between the calculated (fit) and observed Hg atomic fluorescence signal values in (a). The slope and intercept of the linear regression are $1.00 \pm 0.01$ and $0 \pm 7 \, \text{mV}$, respectively.
Figure S5: (a) Comparison of Hg loadings derived from measurements made with a Tekran® 2537B instrument using the Tekran® method and my VI-based peak height determination method (dataset shown in Fig. S3, excluding SPANS), with the peaks defined manually (the VI_{m,m} method). The equation of the linear regression is $y = 0.95(1)x - 0.09(5)$ pg ($r^2 = 0.994, n = 110$). The fit includes only the data derived from detected peaks (represented by the filled symbols). (b) Absolute and relative biases in the Tekran® derived loadings, based on the fit in panel (a), where absolute bias $\equiv Hg_{\text{Tekran}} - Hg_{\text{Benchmark}}$, and relative bias $\equiv 100 \times (Hg_{\text{Tekran}} - Hg_{\text{Benchmark}}) / Hg_{\text{Benchmark}}$. Here “Hg_{\text{Tekran}}” and “Hg_{\text{Benchmark}}” represent Hg loadings derived from the Tekran and VI_{m,m} methods, respectively. Grey bands represent propagated uncertainties (95% confidence intervals) in the fit parameters. (c) Distribution of residuals from panel (a), including only data derived from detected peaks.

The nominal Hg limit of detection for the Tekran® method is 0.5 pg (see Sect. S7). While many Hg thermal desorption peaks in the 2537B dataset are detected by the Tekran® method at Hg loadings <0.5 pg, some Hg TD peaks are undetected by the Tekran® method for loadings ≤0.20 pg (Fig. S3). The results suggest that the actual Hg LOD achieved with the Tekran® method is ~0.2 pg, which is lower than the nominal value (and lower than observed for the 2573A instrument) as a result of modifications that were made to the 2537B instrument to improve its signal-to-noise ratio (Ambrose et al., 2013).
Figure S6: (a) Comparison of Hg loadings derived from measurements made with a Tekran® 2537B instrument using my VI-based automated and manual peak height determination methods (the VI$_{a,a}$ and VI$_{m,m}$ methods, respectively; dataset shown in Fig. S3, excluding SPANs). The equation of the linear regression is $y = 1.015(2)x - 0.017(8)$ pg ($r^2 = 0.9998$, $n = 132$). (b) Absolute and relative biases in the VI-based Hg loadings, based on the fit in panel (a), where absolute bias $\equiv Hg_{Auto} - Hg_{Benchmark}$, and relative bias $\equiv 100 \times (Hg_{Auto} - Hg_{Benchmark}) / Hg_{Benchmark}$. Here “Hg$_{Auto}$” and “Hg$_{Benchmark}$” represent Hg loadings derived from the VI$_{a,a}$ and VI$_{m,m}$ methods, respectively. Grey bands represents propagated uncertainties (95% confidence intervals) in the fit parameters. (c) Distribution of residuals from panel (a).
Table S2. Bias in Hg loadings derived by applying automated and semi-automated Hg atomic fluorescence signal processing methods to measurements made with a Tekran® 2537B instrument.

<table>
<thead>
<tr>
<th>Method</th>
<th>Hg (pg, ng/m³)</th>
<th>Bias (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5, 1</td>
<td>3.75, 0.75</td>
</tr>
<tr>
<td>Tekran®</td>
<td>−7 ± 2</td>
<td>−7 ± 2</td>
</tr>
<tr>
<td>VIₐₐ</td>
<td>1.1 ± 0.3</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>VIₘₐ</td>
<td>0.7 ± 0.2</td>
<td>0.7 ± 0.2</td>
</tr>
</tbody>
</table>

⁹Bias values for the Tekran® and VIₐₐ methods are calculated from the equations of the linear regressions in Figs. S5a and S6a, respectively. Bias values for the VIₘₐ method are similarly calculated from the linear regression equation given in Table S6 (“Standard” configuration). All bias values are expressed relative to Hg loadings derived by processing the data using manual peak definition (the VIₘₘ method).

⁹Hg loadings are also expressed in terms of concentrations under the typical Tekran® operating parameters.

ⅡTekran® operating and peak integration parameters are defined in Table S1.

ⅡMy new VI-based peak height determination method, with peak start and end times determined automatically (VIₐₐ).

ⅡMy VI-based peak height determination method, with peak start times determined manually and peak end times determined automatically (VIₘₐ).

ⅢFor Hg < the estimated 0.2 pg Tekran® LOD, the true bias is −100%. For clarity, the true bias is substituted for the calculated value.

S6 Details on Reproducing Hg Thermal Desorption Peak Baselines Calculated by the Tekran® Method

I reproduced the Hg thermal desorption peak areas (and thereby the baselines) calculated by the Tekran® method by doing the following: linearly interpolating between consecutive Hg atomic fluorescence signal values; carrying out a stepwise integration over the interval between the baseline start and end times (“STM” and “ETM” in the “Peak table” string in Fig. S1), with the baseline signal values calculated by linearly interpolating between the baseline start and end values (“SBL” and “EBL” in the “Peak table” string in Fig. S1); summing the resulting integrals and multiplying by a factor of 2.5. I found that the values of “SBL” and “EBL” (Fig. S1) are not the same as the signal values recorded at “STM” and “ETM”.

S7 Details on Estimating the Nominal Hg Limit of Detection for the Tekran® Method

The Tekran® manuals (Tekran Corporation, 2006, 2007) state a Hg limit of detection for the Tekran® analyzer of 0.1 ng/m³ for typical operating conditions, which include a sample flow rate of 1.0 liter/min (at standard temperature and pressure of 273.17 K and 1.01325 bar) and a sample duration of 5 min. These conditions yield a sample volume of 5 standard liters. In terms of Hg loading, the nominal LOD is therefore 0.5 pg.
S8 Details on Sensitivity Tests Carried Out with the VI\(_{a,a}\) and VI\(_{m,a}\) Methods

Tables S3 and S4 show the results of sensitivity tests carried out with the VI\(_{a,a}\) and VI\(_{m,a}\) methods, respectively, applied to the 2537A dataset. Following each listed modification to the “Standard” VI\(_{a,a}\) configuration, I determine \(\sigma_{\text{blank}}\) and the parameters of a linear regression of “Hg\(_{\text{Auto}}\)” vs. “Hg\(_{\text{Benchmark}}\)” (as in Fig. S6a). For all sensitivity tests, the fit parameters are indistinguishable (at the 95% confidence interval) from those obtained from the values derived from the “Standard” VI\(_{a,a}\) configuration (Fig. 5 in the main manuscript).

Table S3. Results of sensitivity tests carried out with the VI\(_{a,a}\) method applied to the 2537A dataset (Fig. 2 in the main manuscript).

<table>
<thead>
<tr>
<th>VI(_{a,a}) Configuration</th>
<th>Fit Equation(^a)</th>
<th>(r^2)</th>
<th>Hg LOD(^b) (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard(^c)</td>
<td>(y = 1.001(1)x + 0.000(6))</td>
<td>0.99992</td>
<td>0.12</td>
</tr>
<tr>
<td>(-\delta t_{\text{end}})</td>
<td>(y = 1.002(2)x - 0.007(7))</td>
<td>0.9989</td>
<td>0.13</td>
</tr>
<tr>
<td>(+\delta t_{\text{end}})</td>
<td>(y = 1.001(2)x + 0.003(6))</td>
<td>0.99991</td>
<td>0.11</td>
</tr>
<tr>
<td>(\Delta t_{\text{start}})</td>
<td>(y = 1.000(2)x + 0.001(8))</td>
<td>0.9988</td>
<td>0.13</td>
</tr>
<tr>
<td>(-\delta t_{\text{end}}, \Delta t_{\text{start}})</td>
<td>(y = 1.001(2)x - 0.01(1))</td>
<td>0.9998</td>
<td>0.17</td>
</tr>
<tr>
<td>(+\delta t_{\text{end}}, \Delta t_{\text{start}})</td>
<td>(y = 1.000(2)x + 0.005(8))</td>
<td>0.9988</td>
<td>0.12</td>
</tr>
<tr>
<td>Second SPANs(^m)</td>
<td>(y = 1.000(2)x + 0.001(8))</td>
<td>0.9987</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\(\text{aUnits of } y \text{ are pg. Errors are quoted at the 95\% confidence interval (} n = 152).\)

\(\text{bEstimated as twice the standard deviation in blank samples (} n = 62).\)

\(\text{cVI}_{a,a} \text{ method initialized with the first pair of SPAN samples in Fig. 2 in the main manuscript.}\)

\(\text{dSame as "Standard" but with } \delta t_{\text{end}}\text{ subtracted from calculated } t_{\text{end}}\text{ values.}\)

\(\text{eThe estimated range in } \delta t_{\text{end}}\text{ is 7–49 ds.}\)

\(\text{fThe value of } \delta t_{\text{end}}\text{ is } > \delta t_{\text{end}}\text{ for five samples. In these cases, } t_{\text{end}}\text{ is forced to 0 ds.}\)

\(\text{gSame as "} -\delta t_{\text{end}}\text{" but with } \delta t_{\text{end}}\text{ added to calculated } t_{\text{end}}\text{ values.}\)

\(\text{hThe value of } t_{\text{end}}\text{ is } <10\text{ ds for one sample. In this cases, } \delta t_{\text{end}}\text{ is set to 49 ds (} i.e.,\text{ the value estimated for a peak height equal to } \sigma_{\text{bl}}).\)

\(\text{iSame as "} -\delta t_{\text{end}}\text{" but with } t_{\text{start}}\text{ values taken from the second pair of SPAN samples in Fig. 2.}\)

\(\text{jThe values of } t_{\text{start}}\text{ for the first pair of SPAN samples are 123 ds (Au trap A) and 145 ds (Au trap B). For the second pair of SPAN samples, the values are shifted by } -9\text{ and } -5\text{ ds to 114 ds and 140 ds for Au traps A and B, respectively.}\)

\(\text{kSame as "} -\delta t_{\text{end}}\text{" but with } t_{\text{start}}\text{ values taken from the second pair of SPAN samples in Fig. 2.}\)

\(\text{lSame as "} +\delta t_{\text{end}}\text{" but with } t_{\text{start}}\text{ values taken from the second pair of SPAN samples in Fig. 2.}\)

\(\text{mSame as "Standard", but with the VI}_{a,a}\text{ method initialized with the second pair of SPAN samples in Fig. 2.}\)
Table S4. Results of sensitivity tests carried out with the VI_{m,a} method applied to the 2537A dataset (Fig. 2 in the main manuscript).

<table>
<thead>
<tr>
<th>VI_{m,a} Configuration</th>
<th>Fit Equation(^a)</th>
<th>(r^2)</th>
<th>Hg LOD(^b) (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard(^c)</td>
<td>(y = 1.001(1)x + 0.004(3))</td>
<td>0.99998</td>
<td>0.10</td>
</tr>
<tr>
<td>(-\delta t_{\text{end}})^(d,e)</td>
<td>(y = 1.000(1)x + 0.001(3))</td>
<td>0.99998</td>
<td>0.10</td>
</tr>
<tr>
<td>(+\delta t_{\text{end}})^(e,f)</td>
<td>(y = 1.000(1)x + 0.008(3))</td>
<td>0.99998</td>
<td>0.10</td>
</tr>
<tr>
<td>Second SPANs(^g)</td>
<td>(y = 1.001(1)x + 0.007(3))</td>
<td>0.99998</td>
<td>0.10</td>
</tr>
</tbody>
</table>

\(^a\)Units of \(y\) are pg. Errors are quoted at the 95% CI (\(n = 152\)).  
\(^b\)Estimated as twice the standard deviation in blank samples (\(n = 62\)).  
\(^c\)VI\(_{m,a}\) method initialized with the first pair of SPAN samples in Fig. 2 in main manuscript.  
\(^d\)Same as "Standard" but with \(\delta t_{\text{end}}\) subtracted from calculated \(t_{\text{end}}\) values.  
\(^e\)The estimated range in \(\delta t_{\text{end}}\) is 7–16 ds.  
\(^f\)Same as "\(-\delta t_{\text{end}}\)" but with \(\delta t_{\text{end}}\) added to calculated \(t_{\text{end}}\) values.  
\(^g\)Same as "Standard", but with the VI\(_{m,a}\) method initialized with the second pair of SPAN samples in Fig. 2.

Tables S5 and S6 show the results of sensitivity tests carried out with the VI\(_{a,a}\) and VI\(_{m,a}\) methods, respectively, applied to the 2537B dataset. Following each listed modification to the “Standard” VI\(_{a,a}\) configuration, I determine \(\sigma_{\text{blank}}\) and the parameters of a linear regression of “Hg\(_{\text{Auto}}\)” vs. “Hg\(_{\text{Benchmark}}\)”. Because only one pair of SPAN samples was analyzed, the sensitivity of the results to variability in \(t_{\text{start}}\) can’t be tested as is done for the 2537A dataset. However, the values of \(t_{\text{start}}\) calculated for external standard samples falls within a range of ±5 ds from one another, suggesting that derived Hg loadings would be insensitive to the choice of calibration standard samples used to initialize the VI.

For all sensitivity runs (except the “\(+\delta t_{\text{end}}\)” run) carried out with the VI\(_{a,a}\) method, and for all sensitivity runs carried out with the VI\(_{m,a}\) method, the fit parameters are indistinguishable (at the 95% CI) from those obtained from the values derived from the “Standard” VI\(_{a,a}\) and VI\(_{m,a}\) configurations. For the “\(+\delta t_{\text{end}}\)” sensitivity run carried out with the VI\(_{a,a}\) method, bias in “Hg\(_{\text{Auto}}\)” is slightly lower at high loading and slightly higher at low loading than for the “Standard” VI configuration.
Table S5. Results of sensitivity tests carried out with the VI<sub>a,a</sub> method applied to the 2537B dataset (Fig. S3).

<table>
<thead>
<tr>
<th>VI&lt;sub&gt;a,a&lt;/sub&gt; Configuration</th>
<th>Fit Equation&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( r^2 )</th>
<th>Hg LOD&lt;sup&gt;b&lt;/sup&gt; (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard&lt;sup&gt;c&lt;/sup&gt;</td>
<td>( y = 1.015(2)x - 0.017(8) )</td>
<td>0.9998</td>
<td>0.13</td>
</tr>
<tr>
<td>(-\delta_t&lt;sub&gt;end&lt;/sub&gt;&lt;sup&gt;d,e,f&lt;/sup&gt;)</td>
<td>( y = 1.017(2)x - 0.027(9) )</td>
<td>0.9998</td>
<td>0.13</td>
</tr>
<tr>
<td>(+\delta_t&lt;sub&gt;end&lt;/sub&gt;&lt;sup&gt;e,g,h&lt;/sup&gt;)</td>
<td>( y = 1.007(3)x + 0.016(9) )</td>
<td>0.9998</td>
<td>0.15</td>
</tr>
<tr>
<td>External SPANs&lt;sup&gt;i&lt;/sup&gt;</td>
<td>( y = 1.008(2)x - 0.002(7) )</td>
<td>0.99988</td>
<td>0.12</td>
</tr>
</tbody>
</table>

<sup>a</sup>Units of \( y \) are pg. Errors are quoted at the 95% CI (\( n = 132 \)).

<sup>b</sup>Estimated as twice the standard deviation in blank samples (\( n = 39 \)).

<sup>c</sup>VI<sub>a,a</sub> method initialized with the pair of SPAN samples in Fig. S3.

<sup>d</sup>Same as "Standard" but with \( \delta_t<sub>end</sub> \) subtracted from calculated \( t<sub>end</sub> \) values.

<sup>e</sup>The estimated range in \( \delta_t<sub>end</sub> \) is 2–65 ds.

<sup>f</sup>The value of \( \delta_t<sub>end</sub> \) was > \( t<sub>end</sub> \) for 24 samples. In these cases, \( t<sub>end</sub> \) was forced to 0 ds.

<sup>g</sup>Same as "−\( \delta_t<sub>end</sub> \)" but with \( \delta_t<sub>end</sub> \) added to calculated \( t<sub>end</sub> \) values.

<sup>h</sup>The value of \( t<sub>end</sub> \) was <10 ds for 16 samples. In these cases, \( \delta_t<sub>end</sub> \) was set to 65 ds (i.e., the value estimated for a peak height equal to \( \sigma_{bl} \)).

<sup>i</sup>Same as "Standard", but with the VI<sub>a,a</sub> method initialized with the last pair in the first set of external SPAN samples in Fig. S3.

Table S6. Results of sensitivity tests carried out with the VI<sub>m,a</sub> method applied to the 2537B dataset (Fig. S3).

<table>
<thead>
<tr>
<th>VI&lt;sub&gt;m,a&lt;/sub&gt; Configuration</th>
<th>Fit Equation&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( r^2 )</th>
<th>Hg LOD&lt;sup&gt;b&lt;/sup&gt; (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard&lt;sup&gt;c&lt;/sup&gt;</td>
<td>( y = 1.005(1)x + 0.009(5) )</td>
<td>0.99994</td>
<td>0.10</td>
</tr>
<tr>
<td>(-\delta_t&lt;sub&gt;end&lt;/sub&gt;&lt;sup&gt;d,e,f&lt;/sup&gt;)</td>
<td>( y = 1.006(1)x + 0.004(5) )</td>
<td>0.99993</td>
<td>0.11</td>
</tr>
<tr>
<td>(+\delta_t&lt;sub&gt;end&lt;/sub&gt;&lt;sup&gt;e,g,h&lt;/sup&gt;)</td>
<td>( y = 1.004(1)x + 0.014(4) )</td>
<td>0.99994</td>
<td>0.10</td>
</tr>
<tr>
<td>External SPANs&lt;sup&gt;i&lt;/sup&gt;</td>
<td>( y = 1.005(1)x + 0.011(4) )</td>
<td>0.99995</td>
<td>0.10</td>
</tr>
</tbody>
</table>

<sup>a</sup>Units of \( y \) are pg. Errors are quoted at the 95% CI (\( n = 132 \)).

<sup>b</sup>Estimated as twice the standard deviation in blank samples (\( n = 39 \)).

<sup>c</sup>VI<sub>m,a</sub> method initialized with the pair of SPAN samples in Fig. S3.

<sup>d</sup>Same as "Standard" but with \( \delta_t<sub>end</sub> \) subtracted from calculated \( t<sub>end</sub> \) values.

<sup>e</sup>The estimated range in \( \delta_t<sub>end</sub> \) is 2–65 ds.

<sup>f</sup>The value of \( \delta_t<sub>end</sub> \) was > \( t<sub>end</sub> \) for four samples. In these cases, \( t<sub>end</sub> \) was forced to 0 ds.

<sup>g</sup>Same as "−\( \delta_t<sub>end</sub> \)" but with \( \delta_t<sub>end</sub> \) added to calculated \( t<sub>end</sub> \) values.

<sup>h</sup>The value of \( t<sub>end</sub> \) was <10 ds for one sample. In these cases, \( \delta_t<sub>end</sub> \) was set to 65 ds (i.e., the value estimated for a peak height equal to \( \sigma_{ul} \)).

<sup>i</sup>Same as "Standard", but with the VI<sub>m,a</sub> method initialized with the last pair in the first set of external SPAN samples in Fig. S3.
References