Validation of the DMA-80 Direct Mercury Analyzer as an Alternate Extraction and Quantification Procedure for the AT593 Passive Mercury Vapor Sampler

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This report documents the validation of the Milestone DMA-80 Direct Mercury Analyzer as an alternate extraction and quantification procedure for the AT593 gold film passive mercury vapor sampler. This report is a companion to the existing Laboratory Validation of AT593 Mercury Vapor Sampler (Manning & Quarles, May 2017), which remains the primary validation document for the AT593 sampler and its original CVAF analytical method. That document is unmodified and should be read alongside this report.

1. Background

The AT593 ChemDisk™ passive mercury vapor sampler (Assay Technology) uses a gold film medium to collect elemental mercury vapor from workplace air through vapor-phase amalgamation. The badge has been validated and commercially available for over two decades. Until 2026, AT Labs analyzed AT593 samples using Cold Vapor Atomic Fluorescence Spectroscopy (CVAF) following acid digestion of the gold film medium, per in-house method AT593 (modified from OSHA 140). The validation basis for that procedure is documented in Manning & Quarles (2017).

In 2026, AT Labs transitioned to the Milestone DMA-80 Direct Mercury Analyzer as the analytical instrument for AT593 mercury badge samples. The DMA-80 performs direct thermal decomposition of the gold film medium in a flowing oxygen atmosphere, followed by amalgamation of released mercury on a secondary gold trap and atomic absorption detection at 253.7 nm. This approach is based on EPA Method 7473 — Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry (EPA SW-846) — with modifications for application to occupational air sampling media. The AT Labs DMA-80 mercury method (SOP L-HgDMA) is accredited by AIHA-LAP under ISO 17025:2017, effective June 2026.

The DMA-80 offers several analytical advantages over CVAF for this application: elimination of the acid digestion step, direct analysis of the gold film medium, reduced sample preparation time, and lower detection limits. Because the DMA-80 thermally decomposes the gold-mercury amalgam directly rather than dissolving it into solution, it more directly interrogates the collected sample matrix.

2. Basis for Method Validity — EPA Method 7473

The analytical principle of the DMA-80 is documented and validated in EPA Method 7473, which provides an independently established basis for the validity of thermal decomposition amalgamation atomic absorption spectroscopy for mercury determination. EPA Method 7473 Section 2.1 describes the interference handling mechanism: decomposition products pass through a catalyst section that traps halogens and nitrogen and sulfur oxides, after which mercury species are reduced to elemental mercury, selectively trapped on a gold amalgamator, released by heating, and measured by atomic absorption at 253.7 nm. The selectivity of the gold amalgamator ensures that only mercury reaches the detector.

The application of EPA Method 7473 to AT593 gold film media constitutes a modification of the original method, which was designed for solid and liquid environmental matrices. AT Labs modifications include: application to industrial hygiene air sampling media; use of small-volume liquid mercury standards introduced into quartz sample boats for calibration and quality control; and calculation and reporting of results as mass per sample (µg/sample) with conversion to air concentration (mg/m³) based on sampling volume. These modifications are documented in the AT Labs Method Modification Summary for EPA 7473 (Modified) and in SOP L-HgDMA.

3. Vapor-Phase Spike Validation

To validate the DMA-80 against a matrix representative of real AT593 workplace samples, AT Labs developed a controlled in-badge vapor-phase spike procedure. This approach was adopted because conventional liquid-phase ionic mercury spikes applied directly to gold film media do not replicate the actual collection mechanism of the AT593 badge, which relies on vapor-phase diffusion of elemental mercury (Hg^0) followed by adsorption and amalgamation

on the gold surface. A liquid spike confirms the instrument can detect mercury present on the media but does not validate the collection and amalgamation process.

3.1 Chemistry

Elemental mercury vapor was generated inside a sealed AT593 badge by the well-established stannous chloride ($SnCl_2$) reduction of ionic mercury (Hg^{2+}):

$$\mathbf{Hg^{2+} + Sn^{2+} \rightarrow Hg^{0}\ (vapor) + Sn^{4+}}$$

The generated Hg^0 diffused within the closed badge headspace and adsorbed onto the gold film, forming a genuine Hg-Au amalgam in the same manner as a workplace sample. The loaded media was then analyzed on the DMA-80, exercising both the collection mechanism and the analytical finish in a single procedure.

3.2 Method Development

Prior to establishing the final validated procedure, iterative development evaluated three agitation methods and two badge assembly configurations. Results are summarized in Table 1.

Table 1. Summary of iterative development results

Configuration	Mean Recovery	Range	Observations
Shaker agitation (5–15 min)	26–34%	12.84–17.17 ng	Liquid contact with media; poor mixing
Sonication (15–30 min)	43–62%	21.07–30.92 ng	Bath-dependent; pressurization at 45°C
Stir bar, no heat (large plate)	84.8%	42.4 ng	Inconsistent with small plate (56.8%)
Stir bar, 35–36°C, 45 min (optimized)	95.93%	43.54–52.81 ng	Best precision; adopted as final method

The use of a perforated grid within the badge assembly was evaluated and found to introduce variability through capillary-driven liquid transport to the gold media surface, causing inconsistent recoveries and potential media damage. Elimination of the grid in favor of a double-spacer configuration (thin spacer below, thicker spacer above, gold side facing down) significantly improved reproducibility by separating the reaction liquid from the media surface while maintaining the vapor pathway.

3.3 Optimized Procedure

The following conditions were adopted for the validated method:

Badge assembly: Double spacer (thin below, thick above), no grid, gold film side facing down

Mercury standard: 5 µL of 10 µg/mL Hg^{2+} standard solution (50 ng theoretical mass), placed on left side of inner chamber

Reducing agent: 50 µL of 2% (w/v) $SnCl_2$ in 10% HCl, placed on right side of inner chamber

Initiation: Badge closed securely before agitation to prevent vapor loss

Agitation: Magnetic stir bar on heated stir plate

Temperature: 35–36°C (mild heat to promote volatilization)

Reaction time: 45 minutes (recovery plateaus beyond this point; condensation observed at 60 min)

Post-reaction: Gold film medium rinsed with 18.2 MΩ·cm ultrapure water prior to DMA-80 analysis

Analysis: DMA-80 Direct Mercury Analyzer per SOP L-HgDMA (EPA Method 7473, Modified)

Note: This vapor-phase spike method is not intended for routine analytical quality control due to the complexity of the procedure. It is documented here as a validation tool demonstrating the DMA-80's ability to accurately quantify mercury from a genuine Hg-Au amalgam matrix. It may be applied as needed for method validation, troubleshooting, or special studies.

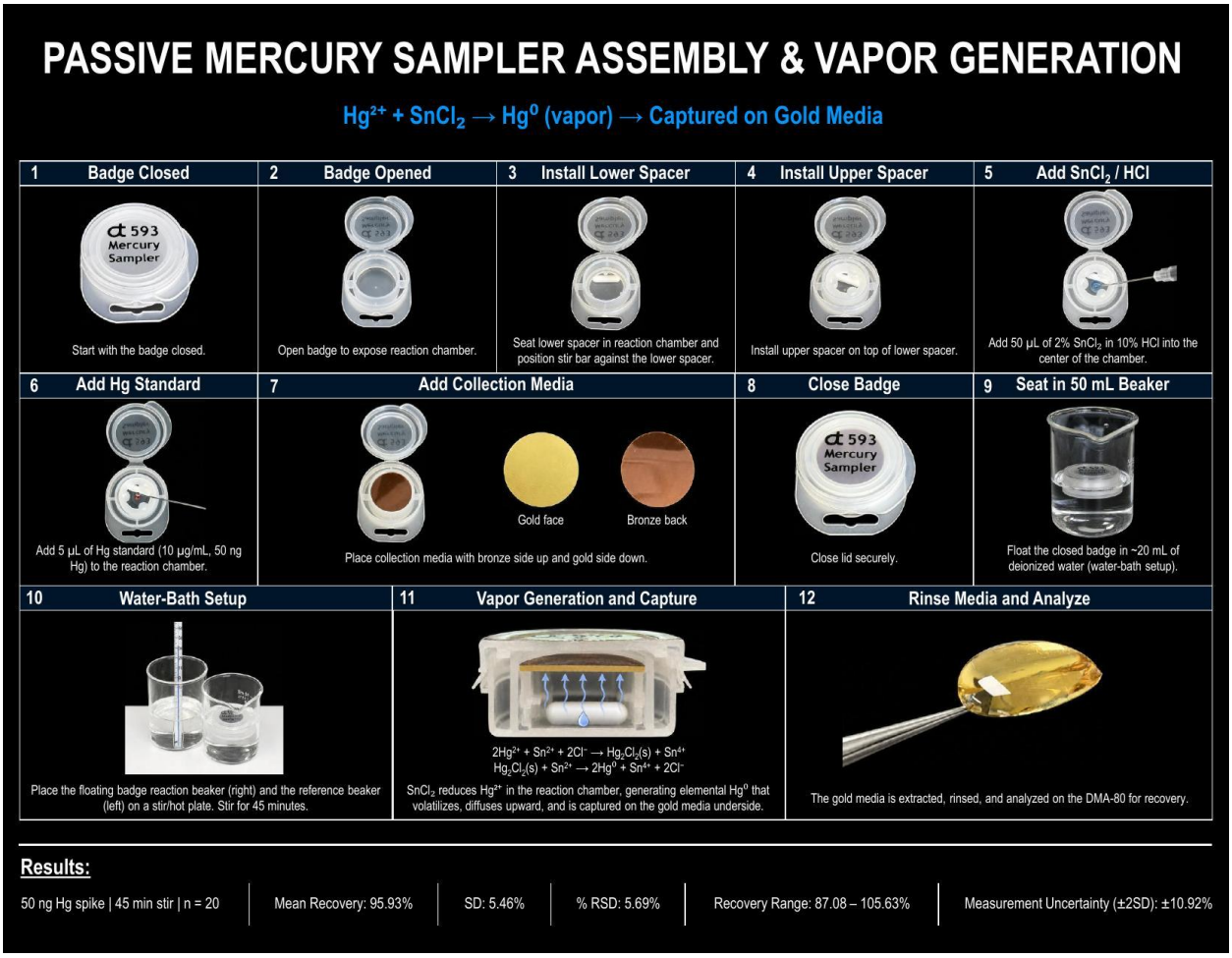

Figure 1. Passive mercury sampler assembly and vapor generation procedure (optimized method). Steps 1–12 illustrate the in-badge $SnCl_2$ reduction spike method. Results shown reflect n = 20 replicates at 50 ng theoretical mass.

4. Results

Twenty replicate vapor-phase spikes were performed using the optimized procedure described in Section 3.3. Each spike used a theoretical mass of 50 ng. Results are presented in Table 2.

Table 2. Vapor-Phase Spike Recovery Data, DMA-80, n = 20

Spike #	Mass Found (ng)	% Recovery	Theoretical (ng)
1	52.1388	104.28%	50.00
2	50.5554	101.11%	50.00
3	52.8140	105.63%	50.00
4	43.8512	87.70%	50.00
5	50.9475	101.89%	50.00
6	48.2943	96.59%	50.00
7	52.1361	104.27%	50.00
8	45.0520	90.10%	50.00
9	46.4558	92.91%	50.00
10	48.8683	97.74%	50.00
11	48.3919	96.78%	50.00

12	46.7890	93.58%	50.00
13	50.1858	100.37%	50.00
14	48.0380	96.08%	50.00
15	46.3223	92.64%	50.00
16	46.9762	93.95%	50.00
17	46.5541	93.11%	50.00
18	47.2298	94.46%	50.00
19	43.5422	87.08%	50.00
20	44.1784	88.36%	50.00
	Mean: 47.97 ng	**Mean: 95.93% SD: 5.46%**	**50.00 ng**

Mean recovery: 95.93% SD: 5.46% %RSD: 5.69% Range: 87.08–105.63% Measurement uncertainty (±2 SD): ±10.92%

5. Discussion

The mean recovery of 95.93% across 20 replicates demonstrates that the DMA-80 accurately quantifies mercury recovered from a genuine gold-mercury amalgam formed by vapor-phase adsorption. The %RSD of 5.69% reflects good precision for a multi-step manual procedure involving volumetric delivery, in-badge vapor generation, diffusive transport, and thermal desorption analysis.

The measurement uncertainty of ±10.92% at the 95% confidence level is well within the OSHA maximum total error (MTE) requirement of ±25% at the permissible exposure limit (PEL). This figure represents the combined uncertainty of the vapor generation, collection, and DMA-80 analytical steps.

An important distinction from the CVAF desorption efficiency data reported in Manning & Quarles (2017) is that the DMA-80 does not involve a liquid extraction step. The 87.7% overall DE reported for CVAF reflected losses inherent to the acid digestion and solution transfer process. The DMA-80 thermally decomposes the gold-mercury amalgam directly, achieving essentially complete recovery of mercury from the medium. The 95.93% mean recovery in this study reflects the combined efficiency of vapor generation, collection, and analysis rather than an extraction loss; the instrument-level desorption efficiency of the DMA-80 for gold-mercury amalgam is effectively 100%.

The validity of the thermal decomposition analytical principle is independently supported by EPA Method 7473, which documents the technique for mercury in solid and liquid environmental matrices. The catalyst section of the DMA-80 traps sulfur and halogen oxides upstream of the gold amalgamator, providing robust interference rejection. This is particularly relevant for the AT593 badge, whose technical insert notes that hydrogen sulfide (H_2S) may be absorbed by the badge in field conditions but does not interfere with analysis. EPA Method 7473 Section 2.1 provides a mechanistic basis for this claim under the DMA-80 analytical method.

6. Conclusions

(1) The Milestone DMA-80 Direct Mercury Analyzer, operated under EPA Method 7473 (Modified) per SOP L-HgDMA, has been validated as an alternate extraction and quantification procedure for the AT593 passive mercury vapor sampler.

(2) Twenty vapor-phase spike replicates at 50 ng theoretical mass yielded a mean recovery of 95.93% (SD 5.46%, %RSD 5.69%), with measurement uncertainty of ±10.92% at the 95% confidence level. These results meet OSHA accuracy requirements.

(3) The DMA-80 directly interrogates the gold-mercury amalgam formed during badge sampling, providing a more representative analytical matrix than liquid-phase ionic spiking under CVAF.

(4) The validity of the analytical principle is supported by EPA Method 7473, an independently established and widely cited reference method for thermal decomposition amalgamation atomic absorption mercury analysis.

(5) The original Laboratory Validation of AT593 Mercury Vapor Sampler (Manning & Quarles, May 2017) remains valid and unchanged. That document continues to serve as the primary validation basis for the AT593 sampler's collection performance and sampling rate. This report addresses only the alternate analytical extraction procedure.

7. References

1. Manning, C.R. and Quarles, B. Laboratory Validation of AT593 Mercury Vapor Sampler. Assay Technology. Revised May 2017.

2. Manning, C.R. Laboratory Evaluation of AT593 Mercury Vapor Sampler Using Dynamically Generated Mercury Atmospheres, in accordance with ANSI/ISEA 104-1998. Assay Technology. November 2012.

3. U.S. EPA Method 7473: Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry. EPA SW-846. https://www.epa.gov/sites/default/files/2015-07/documents/epa-7473.pdf

4. Assay Technology Technical Insert, Item No. 593 ChemDisk™ Monitor for Mercury Vapor, March 2025.

5. AT Labs SOP L-HgDMA: Mercury by Direct Thermal Decomposition (HgDMA), EPA Method 7473 (Modified). AT Labs, a Unit of Assay Technology, Inc.

6. AT Labs Method Modification Summary, EPA 7473 (Modified). AT Labs, a Unit of Assay Technology, Inc., June 2026.