



Tips for Successfully Using Method 30-B to Perform Mercury RATAs at Low-Level Sources (It's Easier than You Think)

A lot of frustration has been reported from crews attempting to complete mercury RATAs using method 30-B at sources where the mercury levels are low. Successfully completing one of these RATAs with minimal frustration can be achieved by focusing on strategies in 2 key areas:

- Optimizing the measurement system
- Being aware of and taking advantage of the method's built-in leniency for low-level sources

Method Information

Method 30-B has actually been well crafted to deal with the challenges of low-level sources. Let's review some of the provisions of the method and how they can help with low-level measurements.

Low Level Standard

One of the least understood parts of the method is the provision to allow quantification of low level samples using a one-point calibration based on a low-level standard that should be run each day analysis are performed at a level > the MDL level and < the lowest point in the Initial Calibration. This is explained in section 11.3 of the method. The response factor from this low-level standard should be used to quantify anything analyzed that produces a response less than that of the lowest point in the multi-point calibration. This includes blanks, section-2 breakthrough amounts, and most importantly, for section-1 sample amounts that are very low.

Looking at table 9-1 in the method, we see that sample analysis only have to be within the "valid calibration range" if the mercury concentration of the source is greater than or equal to 0.5 ug/dscm. We also see that section-1 sample amounts only have to be within the bounds of the Bias Test if the source is greater than or equal to 0.5 ug/dscm. In other words, according to the method, section-1 sample amounts do not have to be bracketed by the multi-point calibration or the Bias Test for sources that are < 0.5 ug/dscm. This means that you don't have to make heroic efforts to successfully perform a special Bias Test or Initial Calibration at very low levels for these sources.

Section-2 Breakthrough and Paired Trap Relative Deviation

Further review of table 9-1 shows that for sources where the mercury concentration is ≤ 1.0 ug/dscm, the limits for acceptable breakthrough and Relative

Deviation for paired trap agreement double from 10% to 20%. This is a big help especially when dealing with breakthrough for section-1 amounts that are very small.

Field Recovery Test

The method requires that the spike levels for the Field Recovery Test must be within 50% to 150% of the “expected “ sample amount, but not the actual sample amount, and there is no penalty for falling outside these bounds. Also, since Field Recovery Test values are calculated using the average of the 3 runs and since the limits are 85% to 115% of the spiked value, it is not difficult to meet these requirements even at very low-level sources.

Relative Accuracy

According to CFR 40, part 75 Appendices B and K, a RATA passes if the 30-B measurements and the audited measuring system have a relative accuracy of $\leq 20\%$ **or** if they agree within 1.0 ug/dscm. This is a pretty big “barn door” to hit. For low-level sources, the 2 measurement systems could differ by a factor of 10 and still pass the RATA.

The full leniency of the method comes into play below 0.5 ug/dscm. At this level, sampling at 2 L/min, 60 ng can be collected in an hour, which is a sufficiently high mass to make things work easily. Below this level the changes in the method constraints detailed above compensate for any difficulties associated with the smaller mass loadings.

Performing RATAs on Appendix-K Systems

Unfortunately, the Appendix-K method was not as well written in regards to low-level sources and especially lacks provisions that would be helpful when doing shorter term low mass loading samples during a RATA test. However there are some helpful provisions in the method.

Paired Trap Relative Deviation

Like 30-B, the Appendix-K method increases the permissible Relative Deviation limits for sources that are ≤ 1.0 ug/dscm to 20% from 10 %. This method also allows for the use of an absolute agreement of 0.03 ug/dscm.

Spike Recovery

Similar to method 30-B, the Appendix-K method says that spike levels should be matched to the “expected” sample amounts $\pm 50\%$, and similarly there is no penalty for failure. The Appendix-K spike recovery limits are calculated on each trap but are wider than the 30-B limits at 75% to 125% of the actual spike amount. These things make it difficult to fail the spike recovery provisions of this method.

Appendix-K Sample Amount

Keep in mind that for Appendix-K, the sample amount is defined as the sum of the section-1 and section-2 mercury masses.

Breakthrough

The worst part of the Appendix-K method for analyzing short-duration RATA samples at low-level sources and one that will hopefully be changed in future revisions (If the method survives) is a strict limit on breakthrough at 5% for all sources high level or low. Meeting these breakthrough criteria is in fact the most difficult thing in performing a RATA on an Appendix-K system at a low-level source. Until some relief comes in the form of a method revision, any one performing such a RATA would need to follow all the other guidelines listed here to best deal with being able to meet the breakthrough requirements.

Optimizing the Measurement System for Low-Level Analysis

While optimizing the measurement system used for 30-B analysis is always beneficial, it is crucial for success at low-level sources.

Sorbent Traps

Utilizing good quality well-designed sorbent traps can prevent many problems with breakthrough, spike recovery, the ability to collect sufficient mercury mass and other issues. It is important that the sorbent material used in the traps has a low native mercury level and it should be assured that spiked traps have been prepared using guidelines that assure that the spike levels are accurate. Using traps that can allow higher flow levels when sampling can allow the capture of a suitably high level of mercury in a shorter time. If a RATA is being done on an Appendix-K system, Appendix-K RATA traps should be used. These traps have less resistance and can be used at higher flow rates to make analysis easier.

Probes and Sampling Pumps

As with the traps, low-level testing is quicker if the sampling pumps used can sample at higher flow rates. At least one company sells a booster pump that can be used in conjunction with your existing pumps if they are not up to the task. The accuracy and precision of your sampling equipment is particularly critical when sampling at these low-level sources so extra attention to maintenance and calibration is called for.

Moisture

Excessive water in the traps can cause breakthrough and poor dual-trap agreement. Moisture is best dealt with by making sure that your probe temperature is high enough to eliminate liquid water in the trap sections. The working range for good quality traps is quite large, up to 450° C, so it should be easy to find a temperature to prevent water in the traps. Shrouds on the probe can prevent liquid water from being

sucked into the traps. Moisture resistant traps are also available and can be used in situations where in-stack water levels are causing problems.

Optimizing the Thermal Zeeman AA Analyzer

For low-level sources, the analyzer like the sampling components should be in top shape and well maintained. Additionally there are a few techniques that can help with these sources.

Lowering the flow on the analyzer will increase the sensitivity and precision and make analysis of lower mercury amounts easier. Make sure the cell windows are clean and all parts are in good working order. The baseline should be stable with a steady state RSD of < 1 or 2 %. Make sure that the standards being used are good and run a 5 or 6-point calibration ranging from 5 to 500 or 1,000 ng using proper pipetting techniques. Use the average of the response factors of your standards to determine your calibration curve. The RSD of these response factors should not be more than 5 or 6 % if the analyzer is operating properly. Run a continuing calibration verification standard after each pair of traps to limit the amount of data lost if a standard fails.

Method Detection Limit

It is important to have a good MDL determination. Weighing out the amount of carbon used in each replicate can decrease precision variances due to the native mercury present in the carbon. To assure that the area for each replicate represents mercury measured and not baseline noise, you need to isolate the baseline from the peak either by manually integrating the peaks or just waiting 30 to 35 seconds before starting integration after the sample has been inserted in the oven. Standards at 3 ng are frequently used for MDL studies.

Sample Preparation

When traps are analyzed, the glass can be cut after removing the section-1 materials so that the section-2 materials can be removed without dragging them through any debris that may be in the front half of the glass tube. This can help avoid false high breakthrough readings.

30-B is the Reference Method

Keep in mind when performing RATAs against CEMMs that below a certain level the CEMM will not be able to measure as accurately as the sorbent traps. Even if the data passes, the numbers might not match. Remember, 30-B is the reference method and if all is working properly, the CEMM must match the 30-B results and not the other way around.

Summary of Low-Level Techniques-Method

- Samples from Sources < 0.5 ug/dscm don't have to be within the bounds of the Initial Calibration or the Bias Test
- Calculate Low-Level Samples with the Low-Level Standard

- The Breakthrough Limit Increases from 10% to 20% for Sources that are ≤ 1.0 ug/dscm
- The Limit for Relative Deviation for Paired Traps Increases from 10% to 20% for sources that are ≤ 1.0 ug/dscm
- Spike Levels are Based on “Expected” Sample amounts, no Penalty for Failing
- Field Recovery is Calculated using the Average of the 3 Runs
- CFR-40 Only Requires Agreement Within 1.0 ug/dscm

Summary of Low-Level Techniques-Appendix-K

- Sources ≤ 1.0 ug/dscm are allowed up to 20% Relative Deviation Between Paired Traps (or 0.03 ug/dscm maximum variance)
- Spike Levels Should be 50% to 150% of “Expected” Sample Amount, No Penalty for Missing
- Spike Recovery must be a Generous 75% to 125%
- Sample Amount = Section-1 plus Section-2
- Unfortunately, Breakthrough is limited to 5% for all samples

Summary of Low-Level Techniques-Measurement Optimization

Use Good Quality Traps

- Low Native Mercury
- Accurately Spiked
- Amenable to Higher Flow Rates
- Use Appendix-K RATA Traps for Appendix-K Systems

Sampling Equipment

- Use Sampling Pumps that can Accommodate Higher Flow Rates or a Booster Pump
- In Good Repair

Moisture

- Use Sufficient Probe Temperature
- Use Moisture Resistant Traps
- Probe Shrouds

Thermal Zeeman AA Analyzer Optimization

- In Good Repair
- Use Lowest Flow
- Make Sure Cell Windows are Clean
- Assure that Baseline RSD is less than 1-2%
- Use Good Standards
- Use a 5 or 6 Point Calibration, 5 ng to 500 or 1,000 ng

- Use Average RF Calibration Calculation
- Assure that the RSD of the Calibration RFs is < 5-6%
- Don't Forget to Run the Low-Level Standard
- Analyze a CCVS after each Pair of Traps
- Have a Good MDL Determination
- Cut Traps if Needed to Remove Section-2

In Summary

Using Method 30-B to perform mercury RATAs at low-level sources will continue to be somewhat more challenging than those at other sources. For a power plant, this is a good thing because the ultimate goal will be low mercury emissions. Hopefully, this information on system optimization and the details of the methods will make performing RATAs on even very low-level mercury sources easier.