



Ultra-Trace Mercury Analysis in Waters

Frequently Asked Questions (FAQ's)

What is Method 1631 ?	1
What is Method 245.7 ?	2
What are the differences between Method 1631 and Method 245.7?.....	2
Does this mean that I have to spend 20 minutes per sample with Method 1631 ?...	2
Do I have to manually change bubblers when using Method 1631 ?.....	3
How do these methods compare with the old style Method 245.1 (AA based) analysis?.....	3
Is Method 1631 recognized in all jurisdictions ?	3
If I buy a Method 1631 system, will I still have to buy an old style AA system?.....	3
Do I need a Class 100 clean room ?	3
What about clean room garb ?	4
Will I ever see No Detects (N/D's) again ?	4
What grade of water will I require ?	4
Where do I obtain low mercury reagents ?	4

What is Method 1631 ?

Method 1631 is a new US EPA method for determining low level total mercury in wastewater. It has a detection limit of 0.2 ng/l (0.2 ppt). The method specifies digestion using bromine monochloride. The sample is treated with hydroxylamine hydrochloride and then reduced by the addition of stannous chloride. The sample is placed into a bubbler and purged with an inert carrier gas. The eluted mercury is captured on a gold coated cartridge. This first stage cartridge is then thermally desorbed onto a second, analytical gold cartridge. The second cartridge is then thermally desorbed into an atomic fluorescence detector.

This method has been used by mercury researchers for over two decades to determine total mercury levels in a wide variety of matrices, including surface waters, seawaters, wastewater, industrial effluents, etc. (Dual stage gold preconcentration has also long been used for determining mercury levels in ambient air.) The method allows routine measurement of mercury concentrations in the parts per quadrillion range.

This EPA method is *performance based*, allowing modifications to the procedures and apparatus, as long as they meet or exceed the original performance specifications. As such, Tekran has developed a fully automated implementation of the method using *continuous flow* techniques.



The full text of Method 1631, together with other valuable information, is available on the US EPA website, <http://www.epa.gov/ost/methods/1631method.html>.

What is Method 245.7 ?

Method 245.7 is a proposed EPA method that also can be used for low level mercury analysis. The digestion and chemistry is similar to the previous method, however, gold preconcentration is not used. A permeation dryer is used to remove water vapor from the sample before sending the carrier gas directly to a CVAF detector.

The method is less sensitive and less robust than the previous method, however some groups favor it in the belief that less intrinsic sensitivity in a method allows for easier analysis.

What are the differences between Method 1631 and Method 245.7?

Both methods use atomic fluorescence detection. They differ in that Method 1631 is written as a purge and trap method. It bubbles the digested and reduced sample in an impinger for 20 minutes and collects the eluted mercury onto a gold trap. It uses two stage preconcentration of the mercury onto a gold substrate.

Method 245.7 uses a gas/liquid separator to strip mercury from a sample. A permeation dryer is used to remove water vapor from the sample. The sample is then passed directly into an AF detector.

Both methods use similar chemistry. Digestion is performed using bromine monochloride. Hydroxylamine hydrochloride is then used to neutralize the BrCl. Final reduction is done with stannous chloride. The concentrations of reagents are different in the two methods.

Method 1631 has already been promulgated in the Federal Register (June 1999). Method 245.7 is still undergoing validation and will not be adopted until 2001 or later. (if the validation indicates that the method is acceptable for widespread use)

Method 1631 is more sensitive than 245.7. Tests at Tekran have shown that Method 1631 is more rugged and less susceptible to interferences. Method 1631 also uses less gas for analysis than 245.7 since a source of dry dryer purge flow is not required. Analytical time for Method 245.7 is shorter since no heating/cooling of the traps is required. (Analytical times are typically 3 minutes per sample for Method 245.7 vs. 5 minutes with Method 1631.)

Both methods require clean sampling techniques and a clean environment in which to digest and run the samples.

Does this mean that it takes 20 minutes per sample with Method 1631 ?

No! This is a common misconception about Method 1631! Although written as a manual purge and trap method, the method is also *performance based*. This means that you can change the implementation as long as you can demonstrate equivalent or superior performance.

The **Series 2600** uses continuous flow techniques. A gas liquid (phase) separator is used instead of a manual bubbler. The analysis sequence is completely automated, and requires about 5 minutes per sample. Depending on the size of sample you elect to run, the autosampler can



hold from 48 to 176 tubes. When it is finished running the last sample, the system shuts off all gasses and stops all reagent pump channels.

The **Series 2600** has a typical MDL of < 0.05 ng/l (0.05 ppt). This is four times lower than called for in Method 1631.

Do I have to manually change bubblers when using Method 1631 ?

No! See answer immediately above.

How do these methods compare with the old style Method 245.1 (AA based) analysis?

Both of these new methods are many times more sensitive than the old, cold vapor atomic absorption (CVAA) based method known as **Method 245.1**. Despite an unfortunate similarity in the EPA method numbering scheme, **Method 245.1** and **Method 245.7** have little in common.

The older method uses potassium permanganate digestion, stannous chloride reduction, and direct flameless AA detection. The newer AF based methods are also more selective and are linear over a much wider range. (AF is inherently linear; AA is not.)

Is Method 1631 recognized in all jurisdictions ?

The method is published in the Federal Register. More and more states are recognizing the superiority of AF methods over AA based methods and are formally recognizing the new method. In some states, entities that have low level effluent limits are being required to use Method 1631. For others, its use is still voluntary.

If I buy a Method 1631 system, will I still have to buy an old style AA system?

Some older operating permits *require* older methods such as 245.1. In virtually all cases, a simple written request to the regulating body will allow substitution of a newer, superior method for an older, less sensitive method.

Do I need a Class 100 clean room ?

No! Although the methods mention Class 100 clean rooms, virtually no one has found the use of a certified Class 100 clean room necessary. However, reasonable care must be taken to ensure that the environment is suitable. Clean laboratory techniques are required to perform any type of ultra-trace analysis, but these can be much simpler and cheaper to implement than you would think.

Particulates in your air will result in the occasional whopping large peak as airborne particles fall into a sample tube and get digested. We have generally found that ambient gaseous mercury levels are far less of a problem than particulates.

Most customers use a laminar flow fume hood. These units have a HEPA (high efficiency particulate) filter on the inlet and blow a curtain of clean air down through the workspace. Ideally, you would have two separate clean areas. One would be used for the digestion and



would be vented outdoors. (The digestion process liberates copious quantities of halogen gases (chlorine and bromine) and this will corrode both your analytical equipment and your highly trained analyst if not dealt with properly.)

A second fume hood is often be used to hold your analytical equipment. This will prevent the samples from being contaminated while awaiting processing by the autosampler.

You don't want to attempt sub-ppt mercury analysis (or any other type of ultra-trace work for that matter) in an area with high traffic. Use a dedicated room with access only by suitably trained personnel

A sticky mat at the entrance to your clean area will help keep it clean. Oh, and don't forget to wash the floors and walls occasionally. Just because an area starts clean doesn't mean that it will stay clean forever.

What about clean room garb ?

Tyvek® or similar clothing that do not emit huge amounts of fibers is required. Lab coats, head coverings, powder free latex gloves, and boot covers are generally required. (You would be surprised to see how much stuff comes off the average person's clothing. If you don't believe this, try patting down someone's clothes while they illuminated in a strong beam of sunlight.)

This laboratory clothing is relatively inexpensive and lasts a long time. You can get either the limited use disposable type of garment or the permanent type. If you have a beard, wear a facemask. Otherwise all sorts of stuff will drop into your samples. If you have several dental amalgam fillings, don't speak or spit over your samples.

Will I ever see No Detects (N/D's) again ?

Probably not. Method 1631 is so sensitive that you will probably never see **N/D** as a result of an analysis ever again. However, don't despair. The method has blank correction to correct for background levels. If using a **Series 2600**, your overall method detection limits (MDLs) will be limited by the blank levels of your reagents rather than by instrument sensitivity.

Many analysts assume that, Method 245.7, being inherently less sensitive, will result in more N/D levels. This isn't necessarily true since you might get N/D on your blanks but not on your samples. It is then possible to under correct for background reagent levels.

What grade of water will I require ?

You will need a high quality DI water system to produce low mercury DI water. Many manufacturers make two stage reverse osmosis systems that provide acceptable water. Most labs already have such systems in house.

Where do I obtain low mercury reagents ?

Method 1631 was designed to use reagents that are either commonly available with low mercury levels, or can be easily cleaned to acceptable levels. Even though the reagents may be cleaned, you want to start with low mercury chemicals. Tekran maintains a list some of the best suppliers of low mercury reagents.