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A Comparison between Atomic Fluorescence (AF) Based and Atomic Absorption (AA) Based Mercury Monitors

Atomic Absorption (AA) based mercury analyzers have been commercially available for several decades. Mercury is well known for an extremely strong emission/absorption line at 253.7 nm, and this is why spectroscopic methods have traditionally been used.

However, it was long standing problems with AA instrumentation that led to the development of manual atomic fluorescence methods in the mid 1980's and gave rise to the Model 2537 automated AF analyzer in the 1990's.

There are two basic classes of AA analyzers.

1. Direct AA Analyzers

These analyzers directly measure the absorbance of light at 253.7 nm in the sample air stream. The problem is that an extremely wide variety of compounds also absorb at these wavelengths. (e.g. Ozone, SO_2, hydrocarbons) Often these compounds are present at concentrations many thousands of times higher than mercury. As a result, these devices are unsuitable for ambient air monitoring. They have, however been widely used in applications such as industrial monitoring where mercury is in the microgram/m^3 range and where few potential interferences exist.

A number of compensation and correction schemes have been tried over the years in attempts to improve the performance of AA analyzers.

1.1. No Compensation

Several simple UV absorption spectrophotometers with no compensation are available. (e.g. Seefelder) These units generally have detection limits in the 1 – 2 ug/m^3 range and will respond to other compounds that absorb radiation at 253.7 nm.

1.2. Dual Path

These analyzers (e.g. EPM) use a gold or charcoal cartridge to absorb mercury in the sample that is then fed to a second (compensation) photometer path. The intent is to allow the second path to give a reading of the absorbance of the air matrix except for the mercury in the original sample. The two absorbances are then subtracted to yield the absorbance due to mercury.

This approach will not increase the sensitivity of the analyzer since this is a function of path length. The background correction approach helps reject some interferences, but is not accurate or precise enough to allow use for environmental applications. Compensation requires that the absorber between the sample path and the compensation path be a perfect absorber of mercury while not impacting the composition of the matrix in any other way. Such an absorber does not exist. Even if it did, the inaccuracies inherent in subtracting two large absorbances in an attempt to determine the small absorbance due to mercury would result in large errors.

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1.3. Zeeman Correction

Scintrex first used this background correction scheme in the mid 1960's. The Zeeman effect uses frequency splitting that occurs when mercury atoms are placed in a powerful magnetic field. The total absorbance of the sample gas is measured at the centre frequency. The absorbance of everything except for mercury is measured on the slightly shifted frequency. The results are subtracted to yield the absorbance due to mercury. This background correction can be effective, however, the detection limit of the system and the accuracy of the result will vary with the amount of background interference that is present in the sample. Newer Zeeman units can operate in the ng/m^3 range; however, they suffer from a number of shortcomings.

- Short lamp lifetime
- Special Hg isotopes are required for the lamps
- Results are reported as concentration at *current* conditions. Reading by reading temperature and pressure correction is required to convert to accepted units. (The literature and most environmental standards are specified in units of ng/m^3 at 760 mm Hg, 0°C.)

2. Gold Preconcentration AA Analyzers

This class of analyzers uses one or two stages of gold preconcentration before attempting to quantify the mercury with an AA detector. Various makes and models of such analyzers have been around since well before the advent of the Model 2537. (Gardis, NIC) Newer models have more sophisticated data displays and slightly shorter cycle times, but are virtually identical in the principle of operation. (UT-3000) The Gardis has two stages gold amalgamation, the UT-3000 only one stage. The comments below apply to both types of analyzers but the problems will be more severe with only one stage of sample cleanup.

This type of device seems to offer many advantages:

- They can be quite compact, even portable
- They do not require argon gas
- Lower cost

However, despite these advantages, researchers and governments in over 20 countries have used, and continue to use, AF instruments. Many Tekran customers (GKSS, Germany; Environment Canada; IVL, Sweden) have bought one of these AA based units. However, they have always purchased more Tekran analyzers afterwards.

There are good reasons for this:

Interferences

While gold goes an excellent job of absorbing and retaining mercury, it is not specific to this compound. A range of other compounds will absorb into, or deposit onto the gold cartridge. These compounds are then co-eluted with the mercury during the thermal desorption process.

These compounds can either positively or negatively influence the AA detector, resulting in readings that are artificially high or low. Since the presence of these compounds will vary with time, there is no way to know when an artefact is occurring.

This is why researchers performing ambient air analysis using manual gold cartridges long ago switched from AA to AF detectors. (Fiztgerald, 1979, US EPA IO-5) Current low level methods for aqueous analysis also use AF detection. (US EPA Methods 1631 and 245.7)

Heated in Air

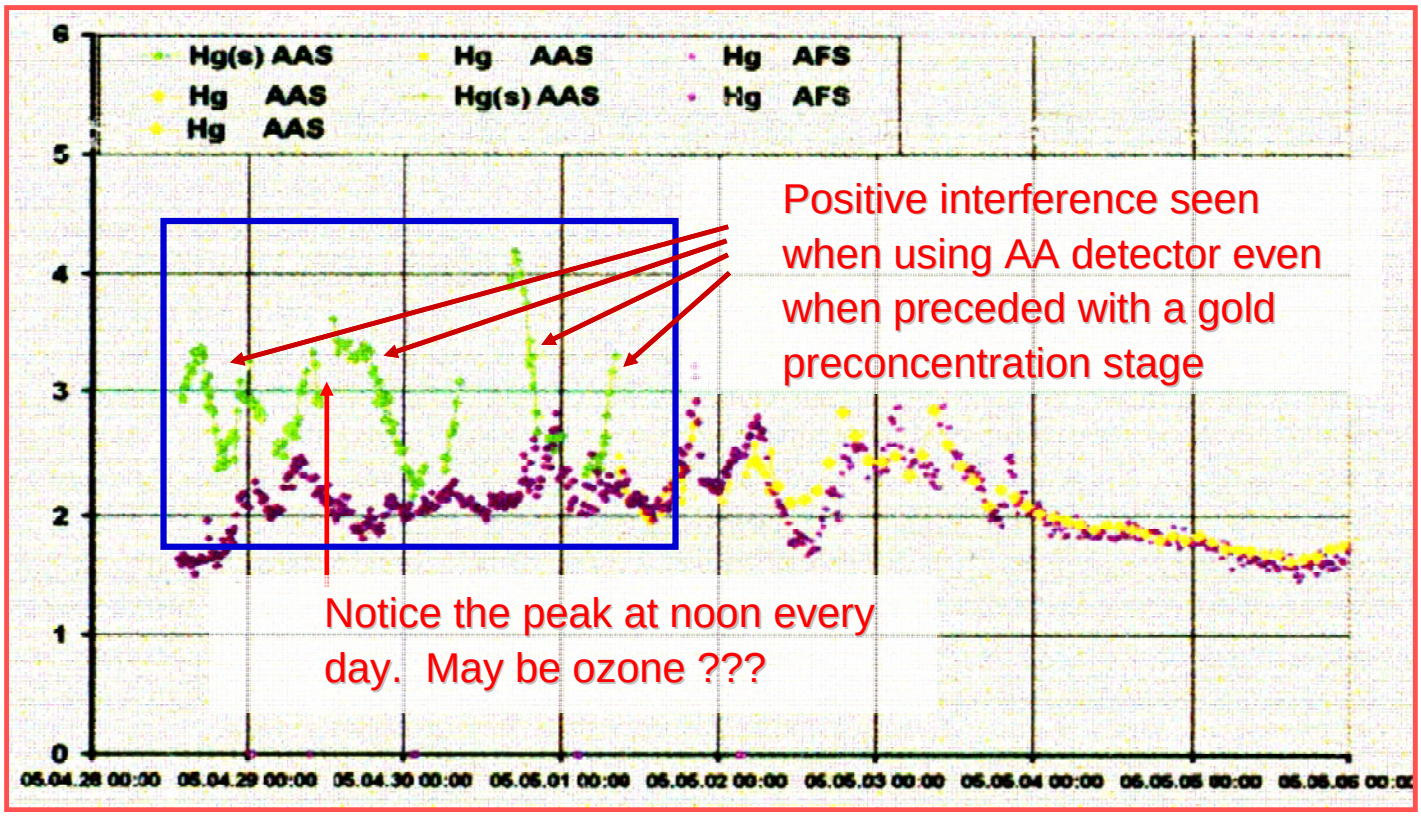
The gold cartridges are heated in air, rather than in argon. This will result in the pyrolysis and subsequent deposition of compounds onto the gold itself and downstream of the cartridge. This deposition can influence the mercury readings.

Single Cartridge

These analyzers have only a single ambient measurement cartridge. This results in gaps in the ambient data. It would be extremely difficult to implement a dual cartridge system as used on the Tekran Model 2537 since the problems mentioned above would make agreement between the two cartridges problematic.

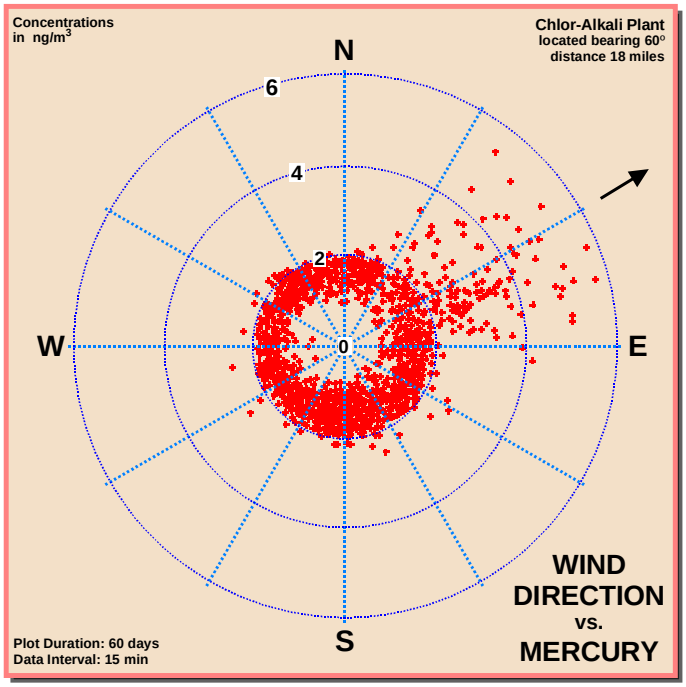
2.1. Summary

Gold preconcentration/AA systems will occasionally produce results comparable to the Tekran 2537. More often, results can differ dramatically. When performing elemental mercury injections into zero air, good agreement will likely be obtained. It is when analyzing actual ***ambient air*** that agreement will vary. The ***green*** curve below shows the very large differences that can manifest themselves when a gold preconcentration system with an **AA** detector is used to measure ambient air. *(Source: International Conference on Mercury as a Global Pollutant, Madison Wisconsin, 2006.)*



3. Tekran Model 2537 - AF Analyzer

The Tekran Model 2537 continues to be the analyzer to which others are compared. It's reputation of accuracy, stability, and reliability has made it the international standard. There are good reasons for this.



3.1. Do Low Mercury Levels Really Matter?

The question is often asked whether low ambient levels (in the 1 to 5 ng/m^3 range) actually matter. Why do they need to be measured at all?

The graph at left is a "radar plot" showing the measured mercury levels at a site plotted as a function of wind direction. The plot clearly shows slightly elevated readings when the wind was blowing from the northeast, the result of emissions from a Chlor-Alkali plant located 29 km away. All of the fish in lakes located around this site were found to have mercury levels many times the maximum acceptable level for human consumption. Clearly even slight elevations of mercury over background levels have major environmental impact.

How meaningful would such results be if the analyzer were subject to periodic random biases (errors) of ±2 ng/m^3?

3.2. Guaranteed Accuracy of Results

The graph below reveals one of the most significant discoveries regarding mercury in the last decade. It shows one of the first Mercury Depletion Episodes (MDE's) ever recorded. At the time, this finding was totally unexpected. In the years since the initial observations by Dr. W.H. Schroeder, this phenomenon has been observed in all Arctic and Antarctic regions where monitoring has been done. It has since been determined to be the major reason why wildlife in polar regions around the world had always been found to be extremely high in mercury despite being great distances from natural or anthropogenic sources.

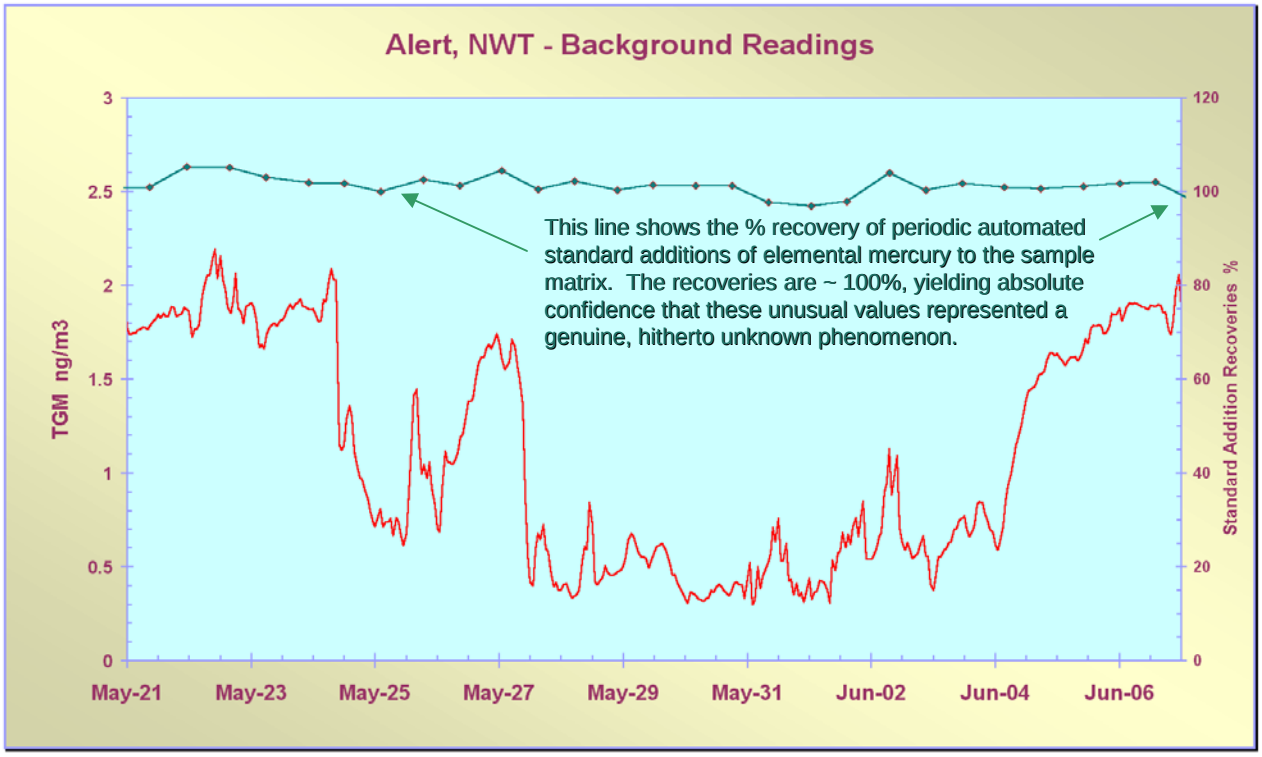
The graph reveals several unique capabilities of the Tekran Model 2537 analyzer.

Ability to quantitate accurately at very low levels

The detection limit of the Model 2537 is stated at 0.1 ng/m^3, however, this is a very conservative figure. The quantitation methods used in the analyzer allow it to quantitate very accurately at levels only slightly above the peak detection threshold.

Std Additions

An inexpensive option, the **Model 1120 Standard Addition Unit** allows periodic activation of the internal permeation source of the Model 2537 late in a measurement cycle. This allows determination of the percent recoveries of the injected mercury. This provides strong evidence that the analyzer is performing properly *while measuring the ambient air stream.*



3.3. Intercomparability of Data

Governments and researchers in at least eight countries in the European Union have standardized on the Model 2537, in some cases after a year of exhaustive testing. An agency using an analyzer with different detection principles would have to justify the correctness of their data. This might prove especially difficult if the test protocol was not sufficiently rigorous. It would be almost impossible to justify ambient readings if the analyzers had been found to occasionally differ by 50% while monitoring outdoor or lab air! (This periodic difference was also observed in a presentation at a major international mercury conference in Madison Wisconsin in 2006. An AA based system using gold preconcentration occasionally reported numbers twice as high as the Model 2537.)

The Model 2537 is also widely used in Asia (e.g: CREIPI, Japan and the PRC) and North America. It is widely cited in peer reviewed journals dealing with environmental atmospheric mercury.

3.4. Reporting Basis

The Model 2537 contains a high precision mass flowmeter to totalize sample flow. Readings are based on sample volumes corrected to 0°C, 760 mm. (All Hg concentrations in the literature are reported on this volume basis.) Reporting at other conditions (e.g. 20 °C) is possible simply by changing internal menu setting.

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3.5. Mercury Speciation

The Tekran Model 2537 is the only analyzer that can be expanded to provide ***speciated*** mercury readings. A **Model 1130** will differentiate between ionic and elemental gaseous forms. The addition of a **Model 1135** will also provide information on particulate bound mercury. The apparatus and process

that allow these automated methods to be made were developed by Tekran and are patented worldwide. (The patent applies to all thermal regenerable denuder RGM monitoring, both manual and automated.)

In the last years, researchers have realized that measuring only elemental or total mercury will not provide the information required to determine the biological impact of mercury. Examples:

Florida Everglades

In the early 1990's, mercury levels in this area were found to be high enough to have killed top predators (panthers) in the food chain. Years of measuring total mercury using conventional techniques failed to reveal the cause of these high levels. The problems were subsequently traced to the emission of large amounts of mercury chloride from local sources. These sources have been remediated and mercury levels are now falling.

Alert

The depletions found in Alert raised the question of what was happening to the missing mercury. It was subsequently found (through use of the 1130 and 1135) that enormous amounts of ionic (reactive) and particulate mercury were being produced during these depletion episodes. These species were deposited into the snow and subsequently entered the biosphere.