HYDRARGYRUM AT LARGE ...

mercury analysis ..

A look at the analytical laboratory techniques;
Gravimetric, titimetric & instrumental approaches.

The presence of mercury - in several forms - in any substance that we deal with is a concern raised by the possible toxicity of many of the mercury forms. Environmental analytical laboratories regularly analyze soil, lake or potable water, fish and other seafood products and several other samples for mercury contamination.

Such contamination is usually caused by industrial and residential waste dumping. As a result, I have personally seen alarming levels of mercury in fish and water samples I analyzed during the past decade.

This paper will deal with the technical aspect of laboratory analysis SOPs and will examine several options.

The emphasis will be on cold vapour atomic absorption technique whereby mercury ions in an acidic solution are reduced by reaction with stannous chloride to ground state atoms. The solution is vigorously stirred until the mercury vapor over the solution reaches equilibrium with the mercury left in the solution. The total Mercury atoms (atomic mercury vapor) is driven {by use of purge gas: nitrogen or argon} into a quartz absorption cell located in the optical path of AAS. Hg, being in a ground atomic state is amenable to atomic absorption of radiation and Hg atoms are monitored at 253.7 nm wavelength. This is the basis of the SOP theory.

The author - an authority on the subject, has structured this book to provide a complete reference for junior chemists and laboratory technicians; as well as environmental and health & safety technical staff.

It's a must for every science library.

Synopsis:

Mercury minerals in ore deposits in nature consist mainly of corderiote ($Hg_3S_2CL_2$), livingstonite ($HgSb_4S_7$), montroydite (HgO), terlinguaite (Hg_2OCL) and calomel (HgCL).

Mercury exists in two oxidation states: mercurous (valence +1) and mercuric (valence +2). Organic compound of weak reducing activity such as amines, aldehydes and ketones often break mercury compounds to compounds of lower oxidation state and metal.

Mercury use, as well as many of its treatment techniques are in fact as ancient as the Pharaohs and the Romans. Recorded history proves that the Egyptians followed by the Greeks and Romans used mercury for cosmetic and medical preparations over five thousand years ago!

In fact, one of the orthodox refinery procedures still being used today involving mercury and gold amalgamation is recorded in hieroglyphic and is dated back to year 2800 B.C. It was not however until this century when mercury treatment techniques witnessed its sudden technological peak .

The toxicity of mercury compounds is not a recent discovery either! Galen, who died about 200 A.D. wrote about the toxicity of mercurials. As to the therapeutic uses of mercury compounds, the "Chemical technology reference" makes this statement: ".. in the 13th century, as a result of Arabian influence, such therapeutic uses of mercury were finally recognized by Western Europe."

Some of these uses are specifically supported by recorded history in Egypt 5000 years ago, and in China and India dating over 4000 years ago.

However, having said that, the wide attention was not focused on the toxicity of mercury until the recent famous industrial Japanese tragedy. It seems however - at least at times - that the media attention surrounding the toxicity of mercury is associated with more than one misconception.

Contrary to common belief, metallic mercury is not highly toxic. In fact, a suicidal attempt by injection of two grams of mercury failed to produce more than a rather minor trouble.

Meanwhile, organic mercury compounds [and fumes, such as dimethyl-mercury $(CH_3)Hg$] are extremely toxic. Such compounds have been found in fish. PMA [phenyl mercury acetate] $C_6H_5HgCOOCH_3$ is also very poisonous.

Modern technology has also utilized mercury in a negative, destructive way with the use of mercury fluminate $Hg(ONC)_2$ as a detonator for explosives.

The discovery of biomethylation of mercury and the realization of the role of certain chemical moieties not only as toxic sources but also as potential carcinogens and mutagens are behind the rapid development of powerful analytical instrumentation capable of detection of mercury compounds in ranges of fractional parts per billion {ppb}

Within a rather short period, numerous techniques, including chromatography, micrometry, radiometry, spectrography and titrimetry were developed. In this paper, I shall lead the reader into a tour, scanning through several analytical approaches.

The liquid silver in action:

Mercury, in the +2 state is frequently present as the simple ion Hg^{2+}. It is however usually found in the form of complex ions, insoluble solids or weak salts. In fact, in a solution of the weak salt mercuric chloride, the concentration of Hg^{2+} is much smaller than the concentration of non-dissociated $HgCL_2$ molecules. With excess chloride ion, the complex $HgCL_{3-}$ and $HgCL_4^{2-}$ are also formed.

In Ammonia solutions complex ions containing one to four NH_3 molecules are expected. For a complete dissociation of $Hg(NH_3)_4^{2+}$ the constant is 5.2×10^{-20}. The complex $Hg(CN)_4^{-2}$ is even more stable.

Mercuric sulphide as found in nature is a red salt, however, when is passed through a mercuric solution, a black precipitate of HgS is obtained. The colour difference is due to difference in crystal structure. The solubility product of black HgS is very low {1.6×10^{-54} }. Such insoluble sulphide will not dissolve even in boiling nitric acid. Aqua regia however, which supplies both nitrate for oxidizing the sulphide and chloride for complexing the mercuric, does take it into solution.

The electrode potentials are so close that any reducing agent is able to reduce mercuric ion to mercurous ion can also reduce mercurous ion to mercury. Thus, if a limited amount of reducing agent solution such as Sn^{2+} {stannous ion} is added to a mercuric solution, only Hg_2^{2+} is formed, but if Sn^{2+} is added in excess, the reduction goes all the way to Hg .

$2\ Hg^{2+} + 2\ e^- = Hg_2^{2+}$

$Hg_2^{2+} + 2\ e^- = 2\ Hg$

Mercury analysis, now and then:

As I indicated earlier, mercury analysis developed considerably within the past few years to meet the new and much tighter environmental specifications. Not too long ago, I reported Hg in ppm using conventional FAA "flame atomic absorption". Mercury analysis by flame absorption using a concentration of 5 mg 1^{-1} in solution produced an absorbency signal of only **.**0050. This is obviously is not good enough for today's specification level.

In fact, not too long ago I analyzed several sediment and industrial sludge samples strictly in one fume-hood in the lab, with just a few test-tubes, beakers, flasks and funnels; applying titrimetric / volumetric approaches - reporting a final concentration in Fns. & % . Now a days such concentration is rare and we can only hope that the reason for that is the right reason!

Gravimtetric procedures:

Only a few years ago colorimetric tests such as cinnabar / black HgS test, and $HgNH_2CL$ test were commonly accepted as orthodox methodology!

Titration / volumetric as well as gravimetric methods to analyze Hg were justified by the high level of mercury present in alloys and industrial samples. In **the calciunation method**, mercury and a deficiency of hot, concentrated nitric acid react to form mercurous nitrate:

$6\ Hg + 8\ HNO_3 \rightarrow 3\ Hg_2(NO_3)_2 + 2(NO3)2 + 2NO + 4H_2O$

Water and nitrogen oxide are driven off ($\xrightarrow{\triangle}$) Continued heating drives off NO_2 and several other NOx:

$Hg(NO_3)_2 \rightarrow 2HgO + 2NO_2$

In **the hot precipitation method**, sodium carbonate solution is added slowly to a refluxing solution of mercuric chloride, followed by an additional reflux for 1-2 hours. The washed precipitate is then dried.

Another approach {***the EGM method***} is to separate mercurous ion from cations by adding HCL to precipitate white, insoluble **$_2H_2g_2CL$**. When NH_3 is added to a mixture of this chloride, a black colour appears indicating the formation of Hg and **$HgNH_2CL$.**

If H_2S is added to an acidic solution containing Hg^{2+} {and other elements: e.g. Cd^{2+}, Cu^{2+}, Zn^{2+} ..} insoluble sulfides are precipitated:

black HgS,
yellow CdS,
black CuS.. etc. "The bench chemist needs to follow up with further test-tube approaches to determine what he has. I'll illustrate."

The residual solution is made basic with NH_3 and white ZnS is formed.

The next step involves a confirmatory test to separate other elements and isolate mercury. ZnS is dissolved in HCL. Evaporated to dryness and re-precipitated by addition of H_2S in a SO_4^{2-} - $H_2SO_4^-$ buffer.

The separation of HgS, CdS, CuS makes use of the fact that CdS and CuS are soluble in boiling HNO_3 where HgS is not. Residual HgS can then be confirmed by dissolving it in aqua regia and reducing it with $SnCL_2$ into **Hg_2CL_2 + Hg.**

Hg is then separated as indicated and reprecipitated while Hg in Hg_2Cl_2 is calculated. The total Hg recovery is then achieved.

Such gravimetric bench-chemistry methods for Hg analysis are almost a thing of the past when it comes to environmental samples. However, I must admit, I still now and then resort to such methods as a confirmatory test on high concentration alloy samples and Hg salts such as $HgCl_2$ when used for certain SOP standards. It still feels good when a gravimetric straight test-tube recovery of near 100% is obtained!

Volumetric approaches:

The titration approach, obviously for high level of concentration, had more than one common execution method. The tartaric acid & sodium bicarbonate titration method widely adopted by many laboratories until a few years ago became unsuitable for today's expectation of DL "Detection Level". Like most analytical chemists, I personally experimented with more than one method.

The common method involves heating the sample to volatilize mercury and collect it as metal, which is then dissolved in hot HNO_3.

$KMNO_4$ is added to oxidize the mercury, and peroxide to destroy excess permanganate.

Ferric sulphate is added [nitrate indicator] and the solution is titrated with standard potassium thiocynate solution to a faint pink end-point.

Dithizone method:

The next stage of development witnessed approaches such as the **diphenylthiocarbazone** [dithizone] method which became commonly utilized. More than one approach was introduced.

A finely powdered sample is treated with sulphuric acid, hydrobromic acid and bromine to give a solution adjusted to pH 4. The solution is treated with dithizone in n-hexane to form mercuric dithizonate. Typical detection limit was reported to be 0.02 ppm.

The ECS diphenylthiocarbazone determination is simply based on mercury ions' reaction with dithizone solution in chloroform producing an orange colour. The development of

much more sensitive spectrophotometry contributed to the wider use of the dithizone method; however, certain factors remained to be major obstacles; namely:

1- ***Interference*** by Pd, Cu, Au, Ag & divalent Pt which react with dithizone in acidic solutions.

2- **Cu in dithizone extract remains in the organic phase while Hg dissolves in the aqueous phase**. Since mercury dithizonate is very photosenitive, it must be measured quickly.

3- The expected ***detection limit*** even with the aid of good spectrophotometer providing a light path of 1 cm or longer at 492 nm is still much higher than the concentration level needed to be monitored in order to meet the environmental expectation.

The dithizone method is similar in several aspects to the now widely applied cold vapour procedure adopted by (but not invented by) the North American Environmental Agency [EPA] and documented as method # 245.1 & 245.2 .

The reagents utilized by ***the Dithizone method*** are potassium permanganate / potassium persulfate & potassium bromide , hydroxylamine hydrochloride, phosphate-carbonate, sodium sulphate, dithizone in chloroform solution and sulphuric acid as indicated below:

5% $KMnO_4$,

5% $K_2S_2O_8$,

40% KBr,

50% $NH_2OH.HCL$,

15% $Na_2HPO_4.12H_2O$ &

3.8% anhydrous K_2CO_3 {extract with 10-ml portions of dithizone until the last portion remains blue,then wash with $CHCL_3$ to remove excess dithizone},

Na_2SO_4 anhydrous,

60 ml of stock dithizone solution in $CHCL_3$ to produce 1 ml = 6 ug dithizone, H_2SO_4 conc.& 0.25N.

The method is obviously quite lengthy and time consuming; however it was the most successful determination of low level mercury specially with organic mercury compounds such as methyl mercuric chloride at concentration level of 250 ug / l where a recovery >95% was achieved. At a time when concentration < 1 ppm was considered and reported as BDL, the dithizone set-up was certainly the epitome of ultra-trace analysis.

The neutron activation method was never widely adopted by commercial analytical labs for obvious reasons. The method is based on activating the sample by neutron bombardment to emit gammarays. This still left the analytical industry with a need for a more analytically and economically sound approach.

ppt recovery:

The next development of cold vapour / atomic absorption technique was able to secure accurate determination of mercury at trace ppb level. The commonly expected environmental detection limit is in the area of 1 ppb. The EPA 245 cold vapor method secures a detection limit of 0.2 ppb or even lower.

This AAS detection limit can be improved further to as low as 0.01 ppb (ppt level) under certain analytical conditions and using the newly proposed signal enhancement technique.
The approach is based on the fact that mercury forms **an amalgam with Au**.

A collecting surface is inserted into mercury vapor flow then heated to drive off trapped mercury. The procedure is known as MAT ***"mercury amalgamation trap"*** and uses a thin layer of gold plated on a large surface.

The reagents used are the same as per cold vapor EPA 245, in fact, the procedure utilizes the same vapor generator unit introduced by Varian for cold vapor AAS determination with the addition of a tube inside which the collecting sheet is placed.

The procedure is referred to herein for documentary and reference purposes only. It does however, in my opinion, have its share of difficulties including the need for a very long period of collecting time per each determination to deal with the ubiquitous nature of Hg; not to mention that ultra-pure reagents and even a distillation process become a must.

This is only logical since a 99.999 % pure reagent could mean an impurity level of 10 ppm!! When one views the fact that such impressive yet ridiculous level of detection is

likely beyond reasonable need; one is left with the conclusion that the present cold vapor-AA technique is actually the best approach available.

Having said that, let's then scan through the cold vapor technique that apparently seems to be our best bet!

Cold vapour .. Theory & principal:

Let scan both sides of the method. It must be stated that today's demanding application requires an analytical chemist with a fresh knowledge of both the theory and the practical aspects of Hg analysis.

This method is the focus of this research paper. I'll explain why.

The theory behind the cold vapour technique:

Mercury ions in an acidic solution are reduced by reaction with stannous chloride to ground state atoms. The solution is vigorously stirred until the mercury vapor over the solution reaches equilibrium with the mercury left in the solution. The total Mercury atoms (atomic mercury vapor) is driven {by use of purge gas: nitrogen or argon} into a quartz absorption cell located in the optical path of AAS. Hg, being in a ground atomic state is amenable to atomic absorption of radiation and Hg atoms are monitored at 253.7 nm wavelength.

The educated approach:

As indicated below, special effort {**during wet preparation as well as during instrumentation**} is essential to achieve good analysis. Educated instrumentation must be aimed at maximizng the utilization of the AAS to its fullest: e.g. alteration of spectral bandwidth / gain / cathode lamp current ..etc. - based on sample needs when necessary .

As well, **the digestion scheme** may also have to be altered from one sample to another.

Generally, the adopted wet procedure and a good computerized AA programme constitute a solid guideline. However, having said that, it must be stated that as in any analytical performance, understanding the nature and the chemistry of the sample and altering both the wet and the instrumental approaches taken to treat and to monitor the sample are not only expected but also imperative.

No flame stoichiometry:

The nature of the cold vapour procedure eliminates several common AA concerns associated with flame stoichiometry - including several ***cationic & anionic interference*** and other common problems that may rise when monitoring the excited atoms in the flame.

At the same time, traditional Hg analysis {as **Hg I** or **Hg II**: $\mathbf{Hg^{2+2} ---- Hg^{2} + Hg^{0}}$} by flame atomization does not produce the required detection limit sensitive enough for environmental research {typical FAA -Hg recovery is in ppm: > 1 mg/L } and introduces additional C_2H_2 negative side effects.

The cold vapour - near **BDL** recovery method - despite the fact that it is a straightforward procedure, yet it does however have its "imperfections." In this report, I shall provide examples of practical experience to elucidate the intricacies of the analytical approach and to illustrate the necessity of understanding all active factors involved -e.g. ***background interference, chemical and spectral*** suppressants or false positives and all other possible analytical scenarios.
This understanding is a must in order to be able to manipulate the conventional and the instrumental analytical approach and thus monitor and capture the right peak.

Today's analytical chemist faces a challenge!

Indeed as with all AAS analytes, one cannot depend on a blind routine application of a parameter method. Hg - CVA is certainly no exception. The variety of samples representing different natures and different active backgrounds necessitates, at times, individual attention given to a specific sample. Without such individual treatment one

may only reach a semi-reasonable or in fact a totally wrong figure, and certainly one will not capture the perfect result. Those who understand the nature of instrumental analysis would surely agree that this statement is indeed not a hallow theory .. it's a practical fact that must be observed.

A blind routine application of the method, regardless of the sample's matrix, concentration, nature, interfering factors, chemical side-effects and other details of the analysis picture can mean a meaningless figure. Such figure will vary - for obvious reasons - from an organic to an inorganic sample, vitreous / amorphous solids to crystalline solids .. a soil sample to an industrial solution sample, or from a metal to a fish sample.

The specific reagents often used to produce a good result, can cause complications if applied blindly to another sample. For example, sulphuric acid can introduce side reactions that, in turn, would create other reactions ..

$$\mathbf{H_2SO_4 + NaCL = Na_2SO_4 + HCL}.$$

Also, the role of KNO_3 + NaCL .. depending on other agents taking direct or indirect active participation, can introduce several cases of unwanted situations....and ..
the ionization of $\mathbf{KNO_3 = NO_{3-} + K^+}$,

or .. $\mathbf{NaCL = Na^+ + CL-}$ .. or .. $\mathbf{HCL = CL- + H^+}$ ..

or .. the decomposition of $\mathbf{HgO = Hg + O_2}$ ..

and several other possible interference by the dichromate $K_2Cr_2O_7$ or by the ammonium salt $(NH_4)_2Cr_2O_7$ ...all such scenarios must be examined closely from one sample to another.

I will specify a few selected examples of cases I ran into personally and cases that have been reported by other analytical chemists through established experimentation. These notes are supported by the basic principals of chemistry, documented methodology, established research literature and personal experience. I shall focus in this part of the "paper" on cold vapor approach as being - as stated earlier - the most suitable candidate for this field of analyses. But, first, let's establish a couple of basic facts.

Fundamentals:

Hydrargyrum compounds show both +1 mercurous & +2 mercuric oxidation states. The mercurous compounds contain two Hg atoms bound together. In aqueous solutions, the ion is double ion corresponding to Hg^{2+}_2 in which there is a covalent Q bond between the two atoms.

Experimental evidence for this is the lack of paramangnetism of mercurous compounds. The ion Hg+ would have one unpaired electron in its 6s orbital and would be paramagnetic, whereas ion Hg^{2+}_2 would have the two electrons paired in a Q bonding molecular orbital and would form an equilibrium between liquid mercury, mercuric ion, and mecurous ion as follows:

$Hg + Hg^{2+} = Hg^{2+}_2$

$Hg + Hg^{2} = 2Hg^{+}$

Mercurous ion behaves much like Ag+, e.g. it reacts with chloride ion to precipitate white mercurous chloride, Hg_2CL_2 (calomel). When exposed to light, calomel darkens by partial disproportional into Hg and $HgCL_2$. Just as silver halides decrease in solubility in going from AgF to AgI, so do mercurous halides.

Mercurous fluoride, Hg_2F_2, is quite soluble in H_2O, but the solution quickly decomposes to form HF and insoluble black Hg_2O. For the other halides the solubility products are as follows:

$Hg_2CL_2 = Hg^{2+}{}_2 + 2\ CL^{-}$

$Hg_2Br_2 = Hg^{2+}_2 + 2Br^{-}$

$Hg_2I_2 = Hg^{2+}_2 + 2\ I^{-}$

Unlike Ag+, mercurous ion does not form an ammonia complex. When aqueous ammonia is added to Hg_2CL_2 the solid turns black because of the formation of finely divided mercury :

$$Hg_2CL_2 + NH_3 = HgNH_2CL + Hg + NH^+_4 + CL^-$$

When performing test-tube bench chemistry, note that the compound **$HgNH_2CL_2$**, mercuric ammonobasic chloride, is white, yet its colour is obstructed by the intense black of the mercury.

In the +2 state, mercury is frequently represented as the simple ion Hg^{2+} , although it is usually in the form of complex ions, insoluble solids or weak salts. For example, in a solution of the weak salt mercuric chloride, the concentration of Hg^{2+} is much smaller than the concentration of non-dissociated $HgCL_2$ molecules. With excess chloride ion the complex $HgCL_{3-}$ and $HgCL_4^{2-}$ are also formed.

Well .. having said all that, let us get back to the cold vapour technique ....

Cold vapour ***- general analytical notes***:

As stated earlier, the "cold vapor" technique is based on the fact that mercury is reduced to the elemental state. Elemental mercury vapor is aerated from solution in a closed system and absorption (peak height or peak area) is measured as the function of mercury concentration.

The following technical notes are pertinent facts & factors:

* Hg atomic absorption at 253.7 nm wavelength constitutes no ***complex spectra*** concern. Specific interferences are indicated in this paper.

* Standard solutions / Q. C. references need be prepared from different sources for cross-check purposes. Typical references are 1000 ppm solutions from 2 sources {such as BDH, Plazmachem and Optimum Green.} and at least one source - typically a salt, e.g. **$HgCL_2$, $Hg(NPO_3)_2$ or CH_3HgCL .**

* Aqueous samples are first acidified to pH < 2 with HNO_3. Non-aqueous samples are refrigerated. **K_2Cr2O_7** is used as a preservative when preparing stock standard solutions.

It is of course important that samples and QC standards undergo the same treatment; e.g. the same K_2Cr2O_7 solution, out of the same bottle would be used in the preparation the blank standard and Hg QC samples as well as additional spiked samples. In the attached analysis illustration, chemist-author Paul Gouda named the zero-blank: Q1, calibration standard closest to sample concentration (or two standards below and above sample concentration): Q2, spiked sample: Q3 (including spiked blank, applicable to both sets of samples; strict standards and matrix match standards.

* **Organic mercury compounds will not respond to cold vapor technique unless first broken down and converted to mercuric ions vulnerable to reduction to ground state atoms by $SnCL_2$. $KMnO_4$ acts as a strong oxidant to serve this purpose**.

Some organic mercurial *such as phenyl mercuric acetate and methyl mercuric chloride* may require a second treatment with potassium persulphate (as an additional oxidant) added after the regular treatment with $KMnO_4$ in order to complete the oxidation.

Potassium permanganate will also remove most of the aromatic and nitrogen compounds that could interfere with the photo-metric measurement.

* The method known here in North America as EPA #245 uses sample aliquots weighed into digestion test tubes. The preparative digestion varies based on sample matrix/nature. The procedure provides a sound guideline, again, with the understanding that individual samples may require **individual attention.** Usually a sample of 25ml or 0.5g is treated with 2ml of HNO_3 and 5ml of H_2SO_4, followed by 5ml of 5% $KMnO_4$ solution.

Depending on the sample, an additional volume of an oxidising agent (e.g. HNO_3) may be required. In some cases up to 20ml of $KMnO_4$ had to be added to ensure complete oxidation (purple colour persists). The sample is often digested in a water bath (at 80 degree Celsius) for 90 minutes.

* Special attention to the temperature and method of heating is necessary to prevent **volatile mercury in elemental state** from escaping. Some organic samples (where Hg is in a compound form, not in elementary state) require heat block digestion at a higher temperature and over a longer time in order to break down the organic compound. Clearly high temperature digestion is ideal for some samples while low temperature digestion is a must for others as I'll explain latter.

Preparative digestion in biological samples is designed for degradation of samples to free mercury from chemical bonds and biological matrices. Fuming with H_2SO_4 at a temperature as high as 260 ^{O}C produced 97 % recovery. Without such fuming the organic compounds did not breakdown and recovery was < 45 %.
At the same time, samples with volatile mercury in elementary state need close temperature control . One must keep in mind that the solid method is based on dealing with mercury in Hg II state.

Other methods use a ***perchloric digestion*** at 200 - 260 C . This is reported to succeed with organic Hg compounds such as methylmercury. It has also been reported that **$HCLO_4$ + HNO_3 digestion** followed with **H_2O_2** treatment recorded good recovery. I have experimented with ***aqua regia*** digestion and obtained very good recovery; which I'll address in details in part-II of this study "next publication".

* Digestion is carried out in 50ml test-tubes. Samples are allowed to cool to room temperature and 5ml of 12% hydroxlamine solution (12% w/v sodium chloride & 12% w/v hydroxlammonium chloride) is added to reduce excess of permaganate {reddish colour clears}.

In some cases up to 15ml of NaCL.HO-NH_3CL had to be added. Individual attention in terms of digestion approach, i.e. volume of and specific oxidising and reducing agents utilized, temperature and length of digestion, is a crucial judgement call and a vital factor in achieving successful oxidation and reduction and thus a good result.

* When working on highly organic samples [e.g. fish and lobster] it is necessary to digest the sample with HNO_3 [conc./neat] on hot block for a longer period of time until **NOx** are expelled (brown fumes cleared). An additional volume of $KMnO_4$ is a precaution against possible mercury dissipation.

This will especially be necessary for samples containing high fat and cellulose because lipids / complex compounds are not easily broken down especially at a lower temperature.

It should also be noted that with some samples, the permanganate solution used in digestion should be allowed to sit at room temperature [exposed to light] for some two days to allow MnO_4 that may form to settle out.

Generally, a saturated permaganate solution (or 5% w/v) is used as a second oxidant especially to complete the oxidation of organic material. An additional volume of $KMnO_4$ is often needed during digestion when there is a possibility of formation of

nitrogen compounds that could interfere with the photo measurement by AAS. This is only one of many examples of the importance of the often necessary individual treatment to certain samples.

* The hydroxylamine solution is used mainly to reduce excess permanganate.
Experiments indicate that a concentration of 12% w/v concentration [12% sodium chloride and 12% hydroxylam - ammonium chloride]. **NaCL.HO-NH_3CL** is a sound guide-line.

* ***Major reagents***:

HCL: neat {conc.}

$SnCL_2$: 5 % w/v depending on sample as explained below.
The common Tin [II] chloride concentration is 10 % $SnCL_2.2H_2O$ in 20 % HCL.

H_2O: distilled and deionized.

(NaCL+NH_2OH.HCL): 12% w/v

$KMnO_4$: 5%

H_2SO_4: neat-conc.

Argon gas is the medium by which Hg atomic vapour is swept into the cell [using a peristaltic pump producing a rate of 1L/min.] Nitrogen can be used as an insert gas. In addition, compressed air can be used as a substitute carrying agent, however it has to be treated to ensure being moisture free [e.g. filtration through magnesium perchlorate]. Special attention should be given to the cell to ensure being dry and clean and thus avoid spectrophotometric interference.

Condensation of water vapour in the cell can cause attenuation of the light beam. This problem can be circumvented with proper handling technique of the vapour generator including allowing for the final post-delivery gas purge which, in this stage, is not impregnated with moisture. Also proper maintenance, pump calibration [reagent control & reaction time], argon pressure, setting of the generator unit...etc. are all contributing factors to successful analysis.

The pump can be easily calibrated using 100ml of H_2O in the empty reducing agent reservoir. The Varian generator accessory used in this experiment is calibrated by placing a funnel over it, and place the sample fleaker cap over the funnel. Press start/reset button and hold the head over the funnel until the circle is complete and the pump ceases to operate.
The volume of H_2O in the graduated cylinder should be approximately 5ml. Special attention should be given to securing the fleaker cap to prevent mercury vapour from escaping.

* It is important to prepare fresh reducing agent [Stannous Chloride] to ensure stability of $SnCL_2$. The agent is normally prepared in 5 M HCL. Practically 5 % v/v of Hydrochloric acid is sufficient to keep the Stannous Chloride in solution, however it should be noted that an *increase of $SnCL_2$ concentration contributes to increasing the absorption sensitivity.*

Experiments indicate that raising the Stannous Chloride up to 20% w/v gives the highest signal. No improvement in sensitivity was detected beyond 25% $SnCL_2$ concentration. 25% $SnCL_2$ solution can be easily kept in 20% HCL. Most of the time a 10 % $SnCL_2$ in 10% HCL is sufficient. There are however samples that require a higher concentration of $SnCL_2$ solution when a higher signal / better sensitivity is needed even at the cost of a slightly higher background noise and / or a less stable curve.

The analyst has to consider his options and balance his approach accordingly. It is one of those judgement calls by the chemist who has to consider the factors involved and the special application of the sample. It must however be noted that consistent calibration is imperative. EPA method #245 recommends 20% $SnCL_2$ w/v in 25% HCL v/v for reason of solubility and stability.

H_2O condensation is reported as a major spectra interference. This necessitated ensuring the use of dry compressed air via **dehydration with granular calcium sulphate trap ($CaSO_4$) or $Mg(CLO_4)_2$.** The use of argon to substitute the compressed air appears to be a safer choice. As I indicated, nitrogen can also be used as a purge gas. A 30 psi pressure setting is reported to be ideal.

* The extreme sensitivity of the analytical procedure and the omnipresence of Hg necessitate extreme care to avoid extraneous contamination. Glassware need to be cleaned in HNO_3 for 30 minutes. Deionized - distilled H_2O {ideally 3 times} is used, and when necessary soaking in a 20% w/v sodium EDTA for 1 hour would be a good approach .

* ***Methyl mercuric chloride*** is partially retained on the sample and is, therefore a potential interference. A number of organo - mercury compounds including phenyl mercuric acetate and methylmercuric chloride are only partially oxidized by potassium permanganate.
Experiments show that using potassium persulfate {in addition to and following $KMnO_4$} insures that such organic Hg compounds are oxidized to mercuric ions. This is the recommendation of the EPA method which claims that the addition of the persulfate as a second oxidant increased recovery up to 98% when treating difficult organic samples.

Personal experience indicates that this is only true with very specific sample matrix (this issue will addressed in paper II), otherwise, the difference is very insignificant when treating inorganic samples with "permanganate only" as opposed to addition of both "permanganate and persulfate" - provided that the chemist has done everything right; and I'll elaborate further in paper II.

* Sea water, brines and industrial effluents high in chloride require additional permanganate {up to 25 ml}. *During the oxidation, chlorides are converted to* ***free chloride*** *which will absorb radiation at 253 nm.* **Care must be taken to assure that free chlorine is absent before mercury is reduced and swept into atomic absorption cell**. This can be accomplished by using an excess of hydroxylamine solution {up to 25 ml}.

* Possible **interference from sulphide** is eliminated by $KMnO_4$. Experiments show that concentration as high as 20 ppm of sulphide (sodium sulphide} did not interfere with the recovery of added inorganic mercury using spiked distilled water samples.

* **Cu interferes** with Hg recovery, however, experiments show that Cu as high as 10 ppm has no effect whatsoever on the recovery of spiked samples. No Cu interference was detected until its concentration reached the high Fns. level.

* Interference from certain ***volatile organic materials which will absorb radiation at this wavelength*** has been reported. This necessitates a preliminary matrix-match background run {analytical blank} to determine if such interference is present {false positives}. I'll address the concerns related to suppressants {false negatives} in a future article. Meanwhile, matrix match blank will aim at the false positive concern, and the

standard addition approach would be the obvious recommendation to determine if false negative is a problem.

It must also be noted that reduction techniques that produce a transient - i.e. short-lived absorbance signal, create a need for a suitable auto integration time set up {and a fast-response recorder, of course}. This becomes a major factor when comparing two different cold vapour approaches such as method ESS # H10 referred to in last fall's issue of "The European scientist" magazine as opposed to the method referred to here in as adopted by EPA.

* When organic material interfere, it is advisable to analyse the sample both by using the **regular procedure and again under oxidising conditions only** - that is without the reducing reagents. The true Hg value would be the difference between the two values.

* **Typical interference** were found to exist within this guideline:

Ni^{+2} : 20% enhancement

Cr^{+6} : 200 ppm

Fe^{+3} : none // 1000 ppm

Cu^{+2} : none / 1000 ppm

KI : 1 ppm

HNO_3 : none / 20 %

H_2SO_4 : none / 20 %

Other interference:

1) H_2O vapour condensation.

2) Chlorides and oxides of nitrogen.

3) Some diatomic gases such as CL_2.

4) Volatile aromatics such as acetone and chloroform

5) Certain elements are also reported to interfere chemically causing a low bias, e.g. Se, Te , Sb, Bi and As.

HCL is the orthodox choice of acid. "Varian" experiments show that 5% HCL + 5% HNO_3 matrix gave the best sensitivity while 5% HNO_3 gave the poorest signal. "The British report" indicated that dichromate used for stabalization of mercury standard solutions causes a drop of 7% in sensitivity at the concentration level of 0.1% and this is corrected by preparing Hg standard solution at higher concentration level (to necessitate a higher dilution for working standard solution, i.e. lower $K_2Cr_2O_7$, and, if necessary, increasing the HNO_3 in the stock standard solution to a much higher level. The European method recommends a 40% HNO_3 for stock Hg standard solutions.

* A major control sample is the spike Q.C. for obvious reasons. Spike recovery will give a good indication whether the sample matrix is acting as a suppressant. The sample is spiked with a known value of mercury and the ideal recovery would of course be the total of original sample concentration plus the injected additional spike value. Resorting to comparing the absorbance difference between sample slope and correction curve corrects the problem. The correct graph should consist of at least 3 different spiked values.

In addition, the graph must present the difference between the two blanks {**analytical blank and arbitrary blank**}. This will ensure producing a confirmed, stable actual calibration curve with > 95% correction factor.

The sensitivity of the method is also affected by other parameters such as **temperature** of the reducing solution and the flow of the carrying gas. An increase of the temperature of the solution produces more sensitivity. As indicated, concentration of the Tin II chloride solution and concentration of HCL contribute to signal sensitivity.

* The majority of sample preparations, at the AAS stage, are likely to contain trace level Hg < 0.5 ppb in solution. Increasing Hg level too high in the prepared sample by taking a large sample, in most cases, will introduce larger background factor. The practical detection limit of the method is said to be 0.2 ppb, hence, readings below 0.2 ppb can be technically dismissed and reported as **BDL** {below detection limit}. However, with proper sample digestion and instrument operation, the chemist can easily determine an obvious 0.1 ppb peak with obvious certainty; and; I personally, so did fellow chemist at 2 laboratories, have repeatedly, consistently and positively detected a 0.05 ppb presence with satisfactory assurance. My Q.C. references have always included a 0.05, 0.1, 0.25 and 0.5 ppb standards all of which have given obvious confirmed reference

peaks. With the addition to the reference "0" sample {blank} and spiked samples at the corresponding level of concentration, the chemist can easily determine trace level 0.05 - 0.2 ppb with great certainty.

* A typical calibration curve is 0 "blank", .5, 1, 2, 3, & 5 ppb standards with **a minimum correlation coefficient factor of 0.995**. The base line must be monitored and any shift must be corrected. It must also be determined whether a deviation at base line is a calibration shift or a fluctuation and thus data must be edited accordingly after a confirmatory test using known standards is established.

* Experiments show that other reducing agents such as hydrazine hydrate 40% or sodium borohydride 5% do not produce as good recovery as Tin II chloride {$SnCl_2$ 10% in 10% HCL}:

$$Sn^{2+} + 2HgCL_2 = Hg_2CL_2 + Sn^{4+} + 2\,CL^-$$

$$Sn^{2+} + HgCL_2 = Hg + Sn^{4+} + 2CL^-$$

AAS setting:

pattern: gain; 550 / cathode lamp: 5 / bandwidth: 0.3

The bench chemist must keep in mind that the baseline absorbance noise is related to the light source intensity Io {$n\alpha \sqrt{1/\ Io}$ }. The baseline noise decreases as the source intensity increases. Intensity of light source I_o is proportional to the square of lamp current. Accordingly, when lamp current is increased, the baseline noise level decreases. However, if the lamp current is over increased, the phenomenon known as self absorbance becomes a concern.

In one case, while using an old lamp, spectral interference was obvious with a couple of samples.
The standard addition approach (blank and known QC) confirmed that there is a problem. The false reading was a result of a different atomic absorbance that fell within the width of the monitored element's absorbance line. This, of course, resulted in a "false positive" and one would have to review that sample's digestion and preparation process form step one to the atomic absorbance stage.

The analyst must also keep in mind that the cathode lamp can be affected by metal impurity in the cathode itself (or infected from the "W" anode). This is a common case that happen with old lamps. Narrowing the slit width would correct the problem and eliminate the false positive. A spiked Q.C. sample should then be repeatedly used as confirmatory test.

Another common problem that was experienced with a deteriorating lamp was its inability to produce sufficient voltage impressed across the electrodes, i.e. its **inability to ionise sufficient Ar atoms enough to bombard the cathode and thus produce an effective electromagnetic radiation (energy beam)**. This necessitates alterations to the AA setting to compensate for the problem. Of course, this shouldn't happen - as the analyst must use a healthy cathode lamp.

Of course, when making such adjustments, the analyst again must keep in mind that an increase in hollow cathode current results in an increase in the kinetic energy of the ionised fill gas "Ar" causing more atoms to be sputtered.

As the population of the sputtered atoms increases, the residual unexcited atoms cool and a cloud of neutral atoms in front the cathode is formed. These neutral atoms absorb some of the lamp light which results in an attenuation of the resonance radiation resulting in a classic case of self-reversal or self-absorption.

It should also be noted that spectral band width is also a major factor in signal-to-noise ratio. **A large spectral width will generate an excellent ratio, however, the resonance line may not be isolated from other lines and as a result, the calibration curve will not be as linear. At the same time, the good resolution of a "too narrow" spectral band width will not compensate for the poor signal-to-noise ratio due to the considerate reduction of light.**

With certain samples {trace level recovery when it is necessary to determine near BDL concentration} the spectral band has to be opened wider in order to lower the background noise.
In such a case, the sample has to be re-examined under a narrower bandwidth to make certain that the wider monochromater slit did not admit **non-absorbable radiation defraying linear range.**

Voltage / gain for a CV-AAS must be set to compromise allowing the photomultipllier to give sufficiently high current output without adding excessive noise. That is not to say

that it must be always set blindly in the centre of the traditional (green zone).. nor does it mean that it should always be set on - say "620" just because the analysis involves the same parameter! A judgement call is often needed based on the needs and nature of a specific matrix. At times, raising the actual signal peak at the expense of raising the baseline noise is a good choice, while a lower peak that minimizes background noise may in another case be the right choice.

Mercury salts:

Among many inorganic and organic mercury compounds, a few are commonly precipitated or interfere during analysis of the "odd" sample. The following notes will help the analyst spot such salt and approach his sample accordingly:

- Mercuric acetate: **$Hg(C_2H_3O_2)_2$**. White water-soluble crystalline powder.
- Mercuric carbonate (basic): **$HgCO_3$.3HGO**. Brown precipitate.

- Mercurous chloride: **Hg_2CL_2**. White powder insoluble in water.

- Mercuric chloride: **$HgCL_2$**. Very soluble in water or methyl alcohol or ethyl alcohol.

- Mercurous iodide: **Hg_2I_2**. Bright yellow amorphous powder.

- Mercuric iodide: **HgI_2**. Bright red tetragonal powder dissolves in alkalis to form complex salts: **$NaHgI_4$ or K_2HgI_4**.

- Potassium iodomecurate dihydrate: **$K_2(HgI_4).2H_2O$**. Yellow water-soluble.

- Cuprous iodomercurate: **$Cu_2(HgI_4)$**. Bright red, water-insoluble.

- Mercurous nitrate: **$Hg_2(NO_3)_2$**. White monoclinic crystalline, soluble in cold dilute nitric acid.

- Mercuric nitrate: **$Hg(NO_3)_2$**. Colourless deliquescent crystalline.

- Mercurous sulphate: **Hg_2SO_4**. Pale yellow.

- Mercuric sulphate: **$HgSO_4$**. Colourless compound soluble in acidic solutions, but

decomposes by water to form yellow, water-insoluble basic sulfate **$HgSO_4.2HgO$**.

- Mercuric sulfide: **HgS**. Exists in two stable forms, the black cubic tetrahedral form (soluble mercuric salts + sulfides) and red hexagonal form (cinnabar/vermilion as found in nature).

…

In conclusion, I'll present a few selected facts and factors that constitute problems in areas that I have often been consulted with by laboratories and refinery operations.

High temperature digestion without careful preparation is risky and should be limited to such samples as fish or with high fat content. Chemist Jim Bishop, in his paper ***"high temperature acid digestion of mercury in environmental samples* - 1975"** referred to researches conducted by the Canadian Fisheries Research as well as by EPA.

The researches conclude the following:

- High temperature digestion - hot plate / 260 ^{o}C / 4:1 sulphuric & nitric- gave better recovery than water bath digestion .

- The experiments included the following mercury compounds:

Methyl mercury chloride

Methyl mercury bromide

Phenyl mercuric acetate

Mercuric chloride

Mercuric sulfate

Mercuric nitrate

Mercuric oxide

The experiments also involved oily fish samples such as sturgeon (Acipenser fulvescens) and crap (Cyprinus carpio). The average result was 99.6 % recovery at 5.7 % RSD with **no measurable loses of mercury due to volatilization** despite the high temperature of the aluminium hot plate digestion.

The paper argues that high temperature digestion is certainly more successful than the low temperature (80 ^{O}C) water bath treatment. Many laboratories have a misconception about how and when mercury is volatile; properly not truly understanding the difference between being in an elemental state versus an organo compound!

Several universities in Canada, Ireland, England, USA, Austria, Egypt and Spain published lengthy reports on their in-house research. Several approaches were experimented with, including:

- Powerful oxidants such as vanadium pentoxide
- Potassium permanganate + sulfuric acid {and hydroxylamine hydrochloride}
- Sulfuric + nitric + sodium molybdate
- 1:1 nitric + perchloric
- Nitric + hydrogen peroxide {260 0C / potassium permanganate / hydroxlamine}
- Aqua regia .....

.. As well, another issue that must be addressed is the fact that there are several other organo mercury compounds that may take active part in routine test-tube digestion including **phenylmercuric acetatate, chloro-methoxypropylmercuric acetate and alkyl mercuric compounds.**

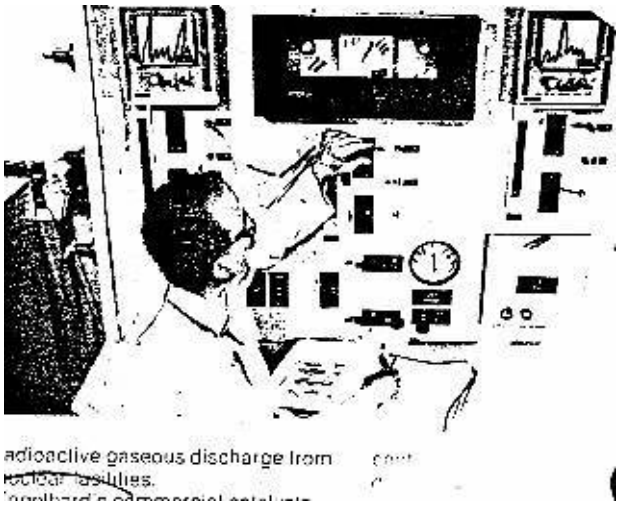
However, having said that, the practical need to worry about such treatment when dealing with common mercury samples during test-tube digestion and analysis is rare; and, chances are, a good beaker or test-tube digestion - especially with the precautions I addressed under cold vapour - atomic absorption, when applied correctly to the nature of the individual sample by a keen chemist, would eliminate such interference factors. QC records prove this claim to be true.

This book however is meant to provide a complete reference covering all the **rare (yet real)** possible complications that have been experienced or reported by or to the author.

I intend to write a comparative study addressing the use of the preceding oxidants and analyzing each approach's advantages and disadvantages.

In conclusion, I can simply state that cold vapour technique, when applied correctly, is a reliable atomic absorption choice for ultra trace analysis of mercury contaminated samples.

Dr. Paul Gouda, C.Chem.; Ph.D.

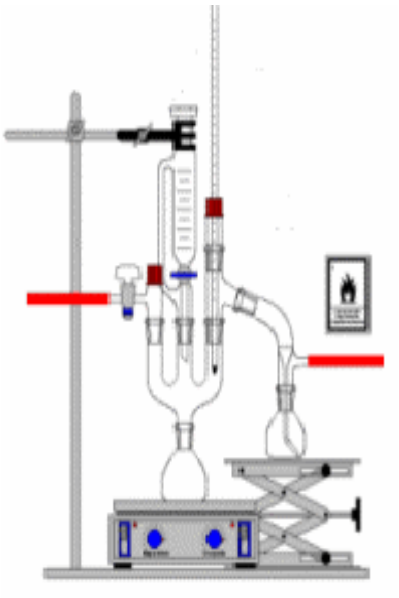


Inorganic chemist, Paul. Gouda, comparing ICP recovery of ultra trace mercury in fish to confirmed analysis results conducted by cold vapour AAS.

HYDRARGYRUM AT LARGE ...

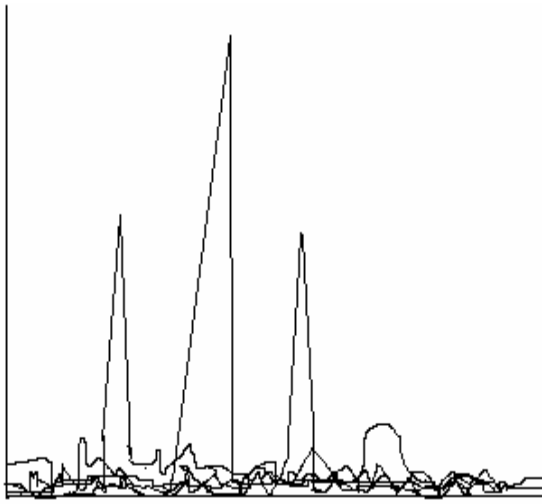
A paper on ultra trace analysis of mercury analysis.

Analytical notes on
gravimetric, titimetric & instrumental approaches.



With a special paper on:

Cold Vapour technique by Atomic Absorption.



By: ***Dr. Paul Gouda, C.Chem. / Ph.D.***.
Analytical inorganic chemist
Consultant / Instructor.
Chief chemist, Optimum Green Environmental

About the author:

* Chemist Paul Gouda, Ph.D. in analytical, inorganic ultra trace analysis.

* Written several papers on analytical laboratory SOPs of several inorganic parameters, including the analysis of As, Se, Sb, Au, Ag, Hg, Cd, Cu .. and other elements presents in environmental and industrial samples - water, soil, sludge, alloys - at both instrumental ultra trace and bench high concentration levels.

* Chief chemist - scientist of Optimum Green Environmental Laboratories Int. - Canadian Branch.

* Presently resides in British Columbia, Canada and operates both a chemical consulting firm and a hospitality business. On a personal note, he is a single parent to a 9 years old son and his limited personal recreational time is shared between football (soccer, that is), chess, poker and cooking. His web site presents a wide scope of background arenas including psychology, theology, teaching, soccer (real football!) and more: **www.gouda.cc**

To the left, the author, surrounded by the EIC laboratory chemists & staff at Dr. Gouda's second graduation in Toronto, Ont. Canada.

.. Below, the author, with his son, Pele'.