

A Comparison of Wet Digestion and Thermal Decomposition Techniques

Mercury is widely recognized as a persistent, bio-accumulative, and toxic pollutant (PBT). There are numerous sources of mercury from both natural and anthropogenic activities; however, amongst all the human activities releasing mercury, the burning of coal is far and away the most significant source.

As governments work to control and minimize the environmental burden of mercury emissions from smoke stacks, more efficient, and costly, abatement techniques will be employed. Because mercury is a common contaminant in coal, knowing the mercury content in the coal prior to its combustion will be critical to achieving the desired reductions in mercury emissions and

in controlling the cost of the abatement technologies.

Two commonly used analytical methods for the determination of mercury in coal and combustion residue are ASTM D6414-99 (wet digestion) and ASTM 6722-01 (thermal decomposition). This paper describes the procedures employed and results obtained with each method.

Wet Digestion Method

A Teledyne Leeman Labs Hydra II_{AA} Mercury Analyzer was used for wet digestions analysis. The instrument and its operational schematic are shown in figures 1a and b, below. For this work, four coal samples of differing mercury content were digested and analyzed. Five separate aliquots of each sample were prepared by placing approximately one gram of each into a 50mL polypropylene tube followed by 2mL of 15N HNO₃ and 6mL of 12N HCL. All the tubes were held at 80°C for one hour. Next, 36.5mL of de-ionized water was added to each tube followed by 5mL of 5% KMnO₄. After allowing ten minutes for oxidation each tube was examined to ensure that there was an excess of oxidant (purple color). 0.5mL of 12%NaCl:12%NH₂OH removed the excess oxidant and completed the digestion.

Standards and samples were added to the Hydra II_{AA} autosampler. As shown in Figure 1b, the Hydra II_{AA} pumps stannous chloride solution

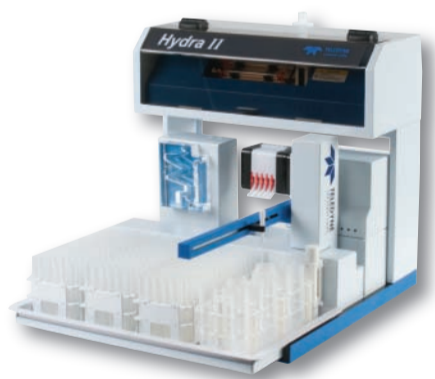


Figure 1a: Teledyne Leeman Labs Hydra II_{AA} Mercury Analyzer

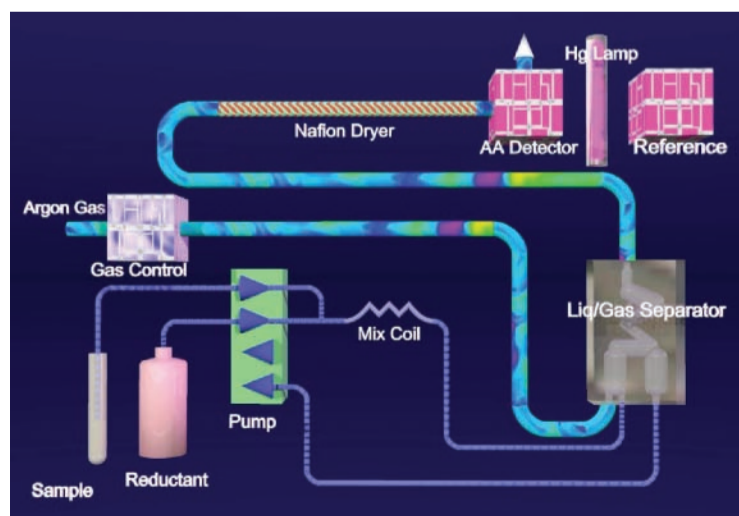


Figure 1b: Hydra II_{AA} Schematic

(10%) and either standard or sample solution into a gas/liquid separator to produce free mercury. The Hydra II_{AA} bubbles argon through the liquid mixture to extract the mercury and carry it to an atomic absorption cell for quantification. The operational parameters for the Hydra II_{AA} appear below in Table 1.

Argon Flow Rate	0.05LPM
Peristaltic Pump Speed	7mL/min
Rinse Time	60sec.
Uptake Time	50sec.
Integration Time	20sec.

Table 1: Hydra II_{AA} Operational Parameters

Thermal Decomposition Method

A Teledyne Leeman Labs Hydra-C Direct Mercury Analyzer was used for the thermal decomposition method. The instrument and its operational schematic are shown in figures 2a and b, below.

An additional important capability of the Hydra-C for the coal-fired power generation industry is that this instrument also permits the measurement of Hg in sorbent traps used for direct stack emission monitoring.

For the coal samples, approximately, 0.5gm of each sample was deposited into the Hydra-C combustion furnace for analysis. For the determination of method precision, five replicates of each sample were injected.



Figure 2a: Hydra-C Mercury Analyzer

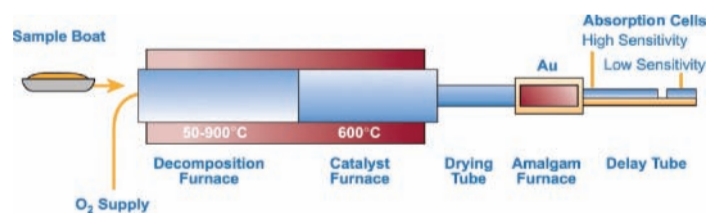


Figure 2b: Principle of the Hydra-C

As shown in Figure 2b, the principle of the Hydra-C is quite simple. A weighed sample is deposited into a sample boat and then introduced into the Hydra-C where oxygen begins to flow over the sample. The decomposition furnace temperature is then increased in two stages; first to dry the sample, then to decompose it. The evolved gases are carried through a heated catalyst to produce free mercury while removing halogens, nitrogen oxides, and sulfur oxides. The remaining combustion products including elemental mercury (Hg⁰) are swept through a gold amalgamation trap where elemental Hg is trapped and concentrated. After the amalgamation step, the trap is heated to release the mercury into a carrier gas which transports it into an atomic absorption spectrometer.

The operational parameters appear in Table 2.

Oxygen flow rate	350mL/min
Dry Temperature	300°C
Dry Time	30sec.
Decomposition Temperature	800°C
Decomposition Time	250sec.
Catalyst Temperature	600°C
Catalyst Delay Time	60sec.
Amalgamator Temperature	600°C
Amalgamator Time	20sec.
Integration Time	100sec.

Table 2: Hydra-C Operational Parameters

Results

Table 3 shows the results obtained from each technique. Both methods have similar precision and the average value obtained by each method is well within confidence limits of the coal reference materials. Figure 3 compares the average values for both techniques graphically.

Hydra II _{AA} with digestion runs 1-5				
	20025B	20100B	30075B	40150B
Run1	81.5	64.5	58.5	ND
Run2	85.0	78.9	56.2	ND
Run3	75.2	73.8	56.5	ND
Run4	79.0	65.2	48.6	ND
Run5	81.3	64.0	51.1	ND
Average	80.4	69.3	54.2	ND
Std Dev	3.62	6.71	4.16	NA

Hydra-C solid analysis 5 replicates				
	20025B	20100B	30075B	40150B
Run1	80.4	76.4	65.6	3.1
Run2	77.5	84.9	54.7	2.8
Run3	84.1	69.1	46.4	2.4
Run4	77.1	70.1	60.0	2.5
Run5	75.0	71.0	53.3	2.3
Average	78.8	74.3	56.0	2.6
Std Dev	3.54	6.57	7.22	0.32

ND = less than method detection limit NA = Not Applicable

Table 3: Results Summary

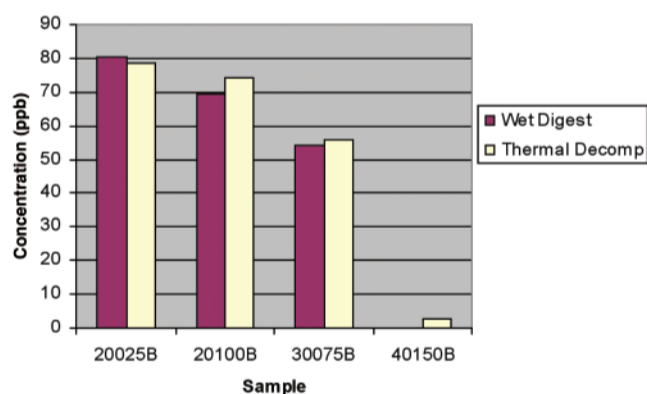


Figure 3: Method Correlation(Average Values)

Conclusions

Despite the fundamental differences between the wet digestion and the thermal decomposition approaches to mercury analysis, excellent correlation is achieved between the two techniques. Comparative results presented here showed no analytical bias and were well within confidence limits for the two techniques.

It is interesting to note that the thermal decomposition technique is capable of determining mercury in coal to lower concentrations than the wet digestion technique. In the case of coal samples, the wet digestion process results in about a 50-fold dilution of the sample while no dilution occurs with thermal decomposition. Further, with the thermal decomposition technique, all of the mercury contained in each sample is collected (i.e. preconcentrated) on the amalgam tube before analysis further helping to lower detection limits for Hg in coal.

The thermal decomposition technique has two additional benefits that some laboratories may appreciate. First, with thermal decomposition no concentrated mineral acids or strong redox reagents are used. Such chemicals must be handled with care by qualified personnel and with appropriate attention to safety. Second, because the aqueous digestion step is eliminated, no aqueous hazardous waste is produced. Specifically, there are no acidic wastes high in metal content (tin, manganese, sodium & potassium) requiring disposal.

For most samples either technique will suffice and the decision of which to use will be based on practical and not analytical considerations. For many laboratories previously acquired instrumentation or legislative requirements may dictate one of the described techniques over the other. In some applications, such as process control, minimizing the total time required from sampling to report generation may be the deciding factor. Others may prefer to keep things simple for operators who lack a strong background in chemistry and to avoid the complexity involved in the reduction technique with its reactive reagents and hazardous waste. If your lab has an interest in using sorbent trapping to monitor stack emissions directly, then the decomposition approach may be well suited to your needs.

Table 4 below offers some points to consider when deciding which technique to use.

Thermal Decomposition	Wet Digestion
No sample preparation	Best detection limit for waters
No hazardous chemicals or waste	Dedicated Instrument or AA attachment
About 5 minutes/sample	Rapid analysis after digestion
Same calibration for various matrices	Dilutions of high samples possible
Capable of direct stack monitoring with sorbent traps	

Table 4: Practical Considerations

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Mercury Content in Petrochemicals

PS Analytical (UK) specialise in the determination of Mercury and hydride forming elements such as Arsenic, Selenium and Antimony. We have been supplying laboratory and online process equipment for the Petrochemical Industry for over 25 years. Knowledge of the mercury content in petrochemicals is extremely important not only because of the environmental concern but also because of the damage mercury can cause to petrochemical plants.

PSA are proud to announce the first ever Online Process Analyser for Hg in Liquid Hydrocarbons (PSA 50.116). The instrumentation is based on the hugely successful 10.515 Hg pre-concentrator and 10.525 Sir Galahad Hg Analyser. Liquid samples at line pressure are delivered using a specially designed sampling arrangement that provides a truly representative sample. The sample at line pressure is injected into a flash vaporization chamber where the Hg is collected on a high temperature adsorbent tube. The mercury is then measured by thermal desorption atomic fluorescence spectrometry. The system comes complete with an automated calibration system, multi-stream functionality and various process control protocols.

This approach provides accurate and rapid unattended online measurements with sub ppb detection limits with linearity to the ppm levels for a wide range of liquid and gaseous hydrocarbon samples.

The system is supplied in purged cabinets that allow the instrumentation to be located in Zone 1, Class 1, Div 1 Hazardous Area locations.

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