The Determination of Mercury in Synthetic Gypsum by Thermal Decomposition, Amalgamation, and Cold Vapor Atomic Absorption Spectroscopy

Application Note #1301

Introduction

Synthetic gypsum is a byproduct of some coal fired power plant operation using flue gas desulfurization (FGD). Recently, concern is growing that this byproduct may contain higher levels of mercury, particularly as the amount of mercury emitted with other stack gases is reduced in compliance with the Clean Air Mercury Rule (CAMR) and Clean Air Interstate Rule (CAIR). Much of the synthetic gypsum created today is used to produce wallboard, a common construction material used in homes and offices. It would be tragic if the mercury removed from the stack emissions ended up re-entering the environment as the gypsum is converted to wallboard. In this study samples were collected from various gypsum areas of a coal fired power plant and analyzed for mercury using the technique of thermal decomposition, gold amalgamation, and cold vapor atomic absorption.

Thermal Decomposition Principle

Principle of Operation

A small amount of sample (typically 0.05 to 1 gram) is weighed and deposited into a sample boat. The weighed sample is then introduced into the Hydra II$_C$ (Figure 1) 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 (Hg^0) 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.

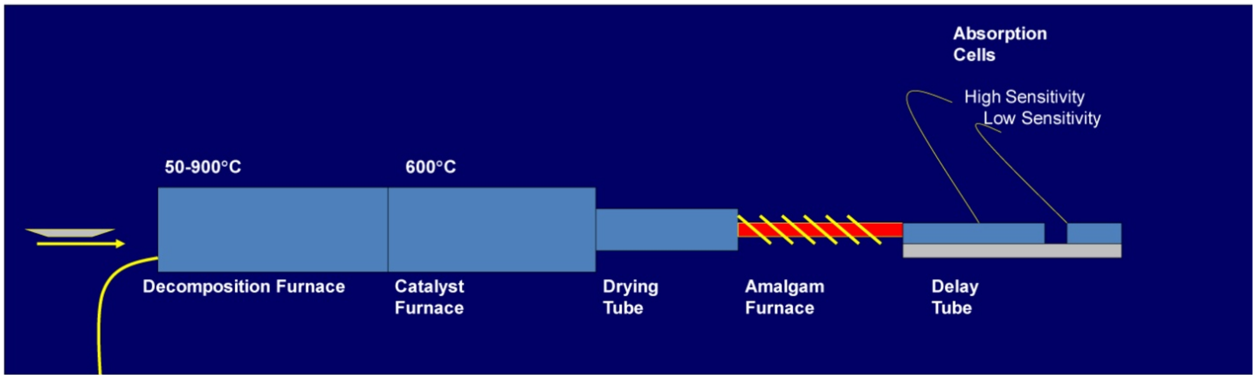

Figure 1: The Thermal Decomposition Principle

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Sample and Standard Preparation

About 0.1-0.2 gm of each sample was placed into a tared nickel boat. Aqueous standards were prepared in 1% HNO_3 for system calibration. Working standards included a blank, 1.0 and 10.0 ppm (w/w) mercury solution with differing weights of standard injected.

Instrumental

For this report the Hydra II_C direct mercury analyzer was used. Table 1 shows the instrument parameters employed for the analysis. Nickel boats were used for all the samples in this analysis.

Phase	Temperature (^oC)	Time (s)
Drying	300	TBD
Decomposition	800	150
Catalyst Temperature	600	
Wait Time		60
Amalgamator	600	30
Measurement		120

Table 1: System Parameters

Calibration

The Hydra II_C employs two optical paths of differing lengths for extended dynamic range; however, all the sample concentrations were low enough to measure in the high sensitivity mode using an optical path length of 10". Absorbance results are reported as the sum of the area under the peak. See Figure 2.

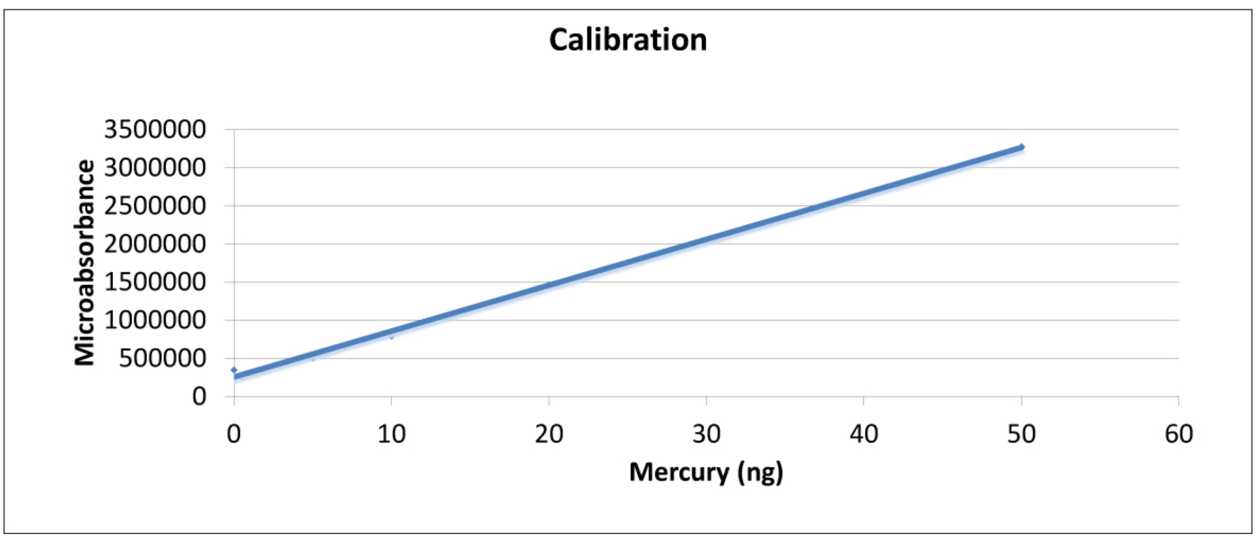

Figure 2: Calibration

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Results

82 gypsum samples were analyzed. A recovery study was performed by spiking several samples with 20 ng mercury. A summary of this study appears in Table 2.

Replicate 1 (ng/g)	Replicate 2 (ng/g)	Sample Mean (ng/g)	Spike Weight (g)	Hg Sample Mass in Spike (ng)	Measured Spike Total Hg Mass (ng)
118.8	117.2	118.0	0.1002	11.8	33.1
117.2	115.6	116.4	0.1022	11.9	31.1
98.4	107.6	103.0	0.1001	10.3	28.4
57.9	63.2	60.6	0.1044	6.3	33.5
87.7	80.8	84.3	0.1065	9.0	32.3

Table 2: Hydra II_c Recovery Study

Mass	
20.41 ng	
30.31	
20.49	
20.33	
20.82	
21.22	
21.52	
21.03	
22.14	
20.91889	Avg.
0.625069	Std. Dev.

Stability was confirmed by running a recurring quality control check of 20 ng Hg every ten samples. The results appear in Table 3 along with the mean and standard deviation of the readings.

The samples analyzed produced a mean concentration of 170 ng/g Hg or 0.170 parts per million and a median value of 157.5 ng/g.

When you consider that every year 7.5 million tons of gypsum# is used in the production of wallboard alone and gypsum has an average concentration of 170 ng/g Hg, this wallboard corresponds to about 1.275 tons of mercury re-introduced into the environment.

$$Hg/yr = (0.170 \times 10^{-6} ton\ Hg/ton)(7.5 \times 10^{6} ton/yr) = 1.275\ ton/yr$$

 # Based on ACAA 2006 Coal Combustion Product (CCP) Production and Use Survey – 7,579,187 short tons used in wallboard production.

Table 3: Stability

Discussion

As mentioned in earlier reports[1] the amount of mercury found in synthetic gypsum varies significantly based on several factors including the emissions controls employed at the power plant and the type of coal consumed. Furthermore, in the wallboard production process some of the high temperature steps may release much of the inherent mercury present in the synthetic gypsum. What mercury remains in the wallboard will be used in homes or offices and eventually end up as landfill. The fate of the mercury in the final product deserves more investigation. 1.275 tons of mercury produced in wallboard manufacture is significantly less than the 15 tons anticipated from coal fired power plants after full implementation of CAMR and CAIR or the approximately 60 tons introduced by all man-made sources. Nonetheless, wallboard production could still contribute 1-2% of the total mercury released unless attention is paid to controlling the process.

Reference

1. Fate of Mercury in Synthetic Gypsum Used for Wallboard Production, Agricultural and Industrial Uses of FGD Gypsum Workshop, Gary Blythe & Mandi Richardson, URS Corporation, Jessica Sanderson, USG Corporation, Charles Miller, Department of Energy, NETL, October 23, 2007