

DETERMINATION OF TOTAL MERCURY IN COAL

Lori J. Blanchard and J. David Robertson
Department of Chemistry
University of Kentucky
Lexington, KY 40506-0055

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INTRODUCTION

The determination of mercury in coal is of interest due to its extreme volatility during coal combustion and its potential to be toxic if released into the environment. However, the low concentration of mercury in coal, frequently at the low ng/g level, makes analysis extremely difficult. In addition, mercury's volatility makes sample cross-contamination more likely. Despite the emphasis placed on mercury analysis, the analytical method of choice to give accurate, reproducible results for coal samples remains debatable. In 1988, 18 independent laboratories participated in an interlaboratory comparison of EPA Method 245.5 (sample digestion/dissolution followed by amalgamation/CVAA) for the analysis of mercury in NIST-SRM 1633a coal fly ash which has a certified value of $0.16 \pm 0.01 \mu\text{g/g}$. The results gave a mean that was 230% of the true value with an overall standard deviation of 200%.¹ More recently, an extensive round robin experiment on Hg analysis was carried out in which 11 laboratories were supplied with three different coals for analysis. The analytical methods employed were cold vapor atomic absorption spectroscopy (CVAAS), cold vapor atomic fluorescence spectroscopy (CVAFS), and instrumental neutron activation analysis (INAA). The study showed that there was approximately a 50% inter-laboratory variability corresponding to a reproducibility of $0.04 \mu\text{g/g}$ for a coal with an approximate Hg concentration of $0.08 \mu\text{g/g}$.²

INAA is one method that has commonly been used for mercury analysis in coal. NAA has the advantage over other analytical methods in that once the sample is sealed in the irradiation vial sample cross-contamination is prevented. However, the ⁷⁵Se ($t_{1/2}=120 \text{ d}$) 279.5 keV γ -ray is a direct spectral interferant for the ²⁰³Hg ($t_{1/2}=47 \text{ d}$) 279.2 keV γ -ray. The interference can be mathematically corrected for using the ⁷⁵Se 264.7 keV γ -ray, but this can result in large uncertainties associated with the mercury values, particularly in coal samples where the selenium concentration is many times larger than the mercury concentration.

Our laboratory has developed a new radiochemical neutron activation analysis (RNAA) method based on pyrolysis followed by double gold amalgamation. During pyrolysis the more volatile elements, such as mercury and selenium, are liberated from the coal sample, and the mercury is preferentially collected by amalgamation with gold. While this procedure does not completely separate the mercury from the selenium it does greatly increase the Hg-to-Se ratio in the 279 keV peak, thereby reducing the measurement's uncertainty. Furthermore, since other elements in the sample are not amalgamated with the gold, the spectrum background is drastically reduced which results in a greater sensitivity for mercury.

EXPERIMENTAL

Sample Preparation

Samples of NIST SRM 1632a were dried at 105°C overnight and cooled. 10.00 $\mu\text{g/mL}$ and 50.00 $\mu\text{g/mL}$ Hg solutions were prepared from a $1000 \pm 3 \mu\text{g/mL}$ Hg in 2% HNO₃ certified standard (High Purity Standards). Appropriate amounts were added to

known quantities of dry SRM 1632a to obtain spike concentrations of approximately 200, 400, 650, and 1000 ng/g. The spiked samples were dried at 35-45°C overnight. After cooling, the samples were shaken on a mixer mill for twenty, 2-3 minute intervals.

Irradiation

Approximately 70-100 mg of the spiked standards were placed in acid washed quartz vials (4 mm i.d., 6 mm o.d.) and sealed. Samples were irradiated at the University of Missouri Research Reactor (MURR) for 48 hours at a thermal flux of 5.150×10^{13} n/cm²/sec. One to two weeks after irradiation the vials were washed with aqua regia.

Radiochemical Separations

Apparatus. The experimental setup is shown in Figure 1. All glassware was constructed of quartz and was soaked overnight in 10% HNO₃ prior to analysis. Quartz wool was placed in the tube furnace downstream from the sample to trap coal particulates and ensure complete pyrolysis.

Gold traps were prepared by folding a 10 cm x 10 cm gold mesh in half and rolling lengthwise. These gold mesh "cylinders" were blanked by heating to 800°C for 1 hour. After cooling, each mesh was placed inside a 6 mm i.d. quartz tube with quartz wool plugs at each end to keep the mesh in place.

Procedure. Sample vials were cooled in liquid nitrogen for several minutes, wrapped in a thin layer of quartz wool, and rolled in aluminum foil. The vials were crushed and the foil was partially unwrapped before being placed inside the tube furnace. Samples were then heated to 550°C for 1 hour. After the furnace had cooled to <90°C, the heating tape wrapped around the first gold mesh was heated to 400°C for 30 minutes. Throughout the procedure the nitrogen flow rate was kept constant at about 250 mL/min.

Counting

Activated samples were counted prior to being opened (as in INAA) for 6 hours with a HPGe detector. After radiochemical separation the second amalgamated gold mesh was counted for 4 hours with a larger, higher efficiency HPGe detector.

RESULTS & DISCUSSION

Typical γ -ray spectra obtain before and after radiochemical separation are shown in Figures 2 & 3. The reduction in the spectral background results in a lowering of the sensitivity for mercury from about 190 ng/g for INAA to about 15 ng/g for RNAA (calculated using the $3\sigma_{\text{bkg}}$ method).

The radiochemical separation also greatly reduces the uncertainty associated with a mercury determination due to the increase in the Hg-to-Se ratio in the 279 keV peak. Prior to separation, the relative standard deviation (rsd) in the specific activities (counts in the 279 keV peak per gram of sample) ranged from 12% for the 1000 ng/g spiked sample to 75% for the 200 ng/g spike sample. After separation, the rsd of the specific activities ranged from 1-4%.

The accuracy of the method was evaluated with SRM 1632a. RNAA analysis yielded an experimental value of 114 ± 13 ng/g, well within the certified Hg concentration of 130 ± 30 ng/g. Although only one sample of the standard has been analyzed thus far the results are very promising, and repeat analyses of the SRM are planned in the future.

The linearity and reproducibility for the method are illustrated in Figure 4. The correlation coefficient for these results was calculated to be 0.916 suggesting reasonable linearity. The discrepancy seen in the reproducibility is most

likely introduced during the opening of the vials. It is possible that some sample was lost during the breaking of the vial and/or placement in the tube furnace.

SUMMARY

As increasing emphasis is placed on sensitive and accurate mercury determinations, analytical methods will be placed under more scrutiny and current methods have already been shown to yield inconsistent results. To meet future requirements, either current methods must be revised or new methods must be developed.

In the development of this analytical method the greatest obstacle encountered thus far has been devising a process that ensures quantitative sample recovery during vial opening. The focus of future research will be on refining this aspect of the procedure.

Despite this difficulty, performing radiochemical separations using pyrolysis and amalgamation on irradiated coal yielded accurate results and resulted in significant improvements in sensitivity and the relative standard deviation in mercury determinations. Both of these characteristics are critical in yielding reliable, accurate results for the analysis of mercury in coal.

ACKNOWLEDGMENTS

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REFERENCES

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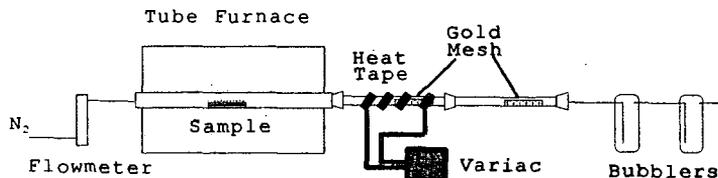


Figure 1. A schematic of the experimental setup for the radiochemical separation of mercury.

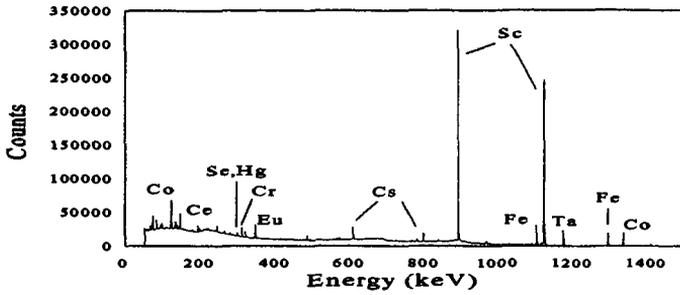


Figure 2. γ -ray spectra of irradiated coal. (48 hour irradiation, 80 day decay, 6 hour count).

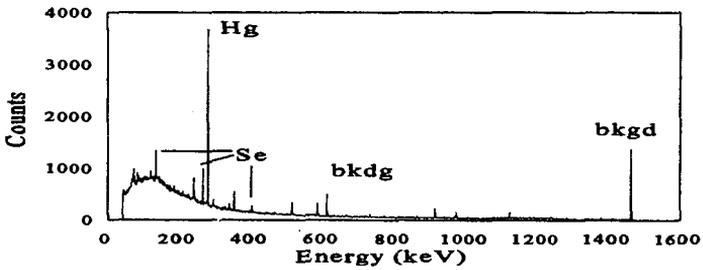


Figure 3. γ -ray spectra of amalgamated gold containing mercury from coal sample. (75 day decay, 4 hour count).

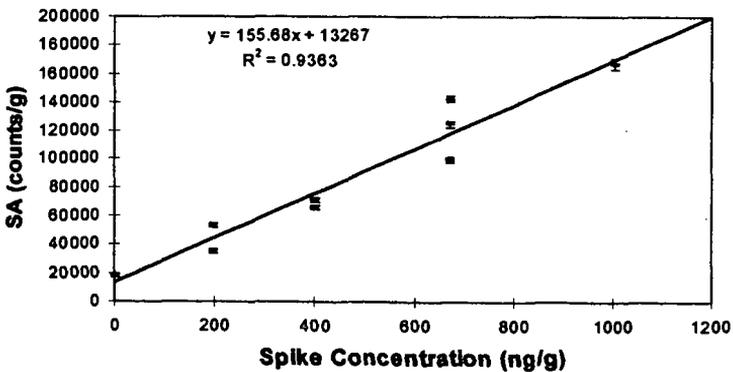


Figure 4. Graph of specific activity vs. Spike concentration.