

The Determination of Mercury in Some American Coals

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This study deals with the use of three different analytical methods for the determination of mercury in coals: (a) double gold amalgamation, flameless atomic absorption, (b) neutron activation and (c) combustion-solution, flameless atomic absorption. Ten coal samples of varying rank were analyzed and comparisons are drawn between the various analytical procedures. The distribution of mercury in coals is discussed briefly.

INDEX HEADINGS: Mercury; Coals; Atomic absorption; Flameless; Double gold amalgamation; Comparison of techniques.

INTRODUCTION

The increased awareness of mercury pollution which is a matter of serious international concern has recently prompted investigations into the mercury levels present in coals. Although a considerable volume of literature has appeared on the trace elements in U. S. coals, the data available on the mercury concentrations in coals are very limited. This was primarily due to the analytical difficulties encountered in determining mercury in coals. However, the recent advent of several new flameless atomic absorption procedures now permits its rapid determination.

I. LITERATURE REVIEW

As early as 1927 Kirby¹ reported that condensing units in a British gas works that utilized coal were known to accumulate mercury. Goldschmidt² in 1954 postulated that the mercury found in air and rain-water could result from the burning of coal. In a review of the more recent literature it was apparent that very little is known concerning the mercury content of U. S. coals. Mercury figures were reported by Headlee and Hunter³ for several West Virginia coals. Ruch *et al.*⁴ recently analyzed 55 samples of raw coal from ten coal seams in Illinois and found a mean mercury concentration of 0.18 ppm. Joensuu⁵ reports that the mercury content of a random selection of some 36 American coals varied between 0.07 and 33 ppm. However, most of the values appearing in the literature are of Russian origin, and some of these are worthy of note.

Karasik *et al.*⁶ analyzed 3000 samples of Donets coking coals; the mercury content was found to vary between 0.7–1.33 ppm, with an average of 0.86 ppm. The mercury occurred mainly in the form of organic compounds and sulfides, with small amounts of metallic mercury. During coking, the mercury was transferred to the volatile products, especially tar

and tar water. When these coals were cleaned it was found that 50% to 60% of the mercury present remained in the concentrate. Previously, Karasik *et al.*⁷ had reported on the mercury in coals of the southeastern parts of the Donets basin. On the basis of greater than 1000 mercury determinations, the mercury content was found to vary from 0.05 to 10 ppm, and a few samples contained >25–30 ppm. As a rule, it was found that samples containing >1 ppm of mercury originated in parts of the coal bed that were adjacent to known mercury deposits.

Dvornikov⁸ in a study of the coals of the East Donets basin (Rostov region) showed that mercury content varied within a large range of 0.02 to 20 ppm (756 samples). The distribution of mercury in mine waters was also studied by the same author.⁹ The mine waters contained 0.001–0.01 ppm mercury and the distribution of mercury was very nonuniform. Three samples of water were specially analyzed to detect the form of mercury in the waters: 44–61% of the total mercury was in the form of organomercury compounds, 22.5–24.6% in the form of HgS_2^- , and 8.9–25% in the form of Hg^{++} . Dvornikov¹⁰ also reports that mercury, during coking of coals, was extracted into coke gas at 1230 to 1300°C. Upon cooling, the mercury concentrated in the tar, water, polymers, other products of coking, and in the wastes.

Pakter *et al.*¹¹ also studied mercury in coking plant by-products. Coal charges going into 80% of the by-product coking plants in the U.S.S.R. were analyzed. Mercury was detected in practically all of them but in relatively small amounts, the average value being 0.28 ppm. Pakter *et al.*¹² later determined the mercury content of various products of coking and showed that considerable amounts were concentrated only in coal tar, in some sediments, and acid resins from sulfate separation. Vasilevskaya *et al.*¹³ determined mercury in coal by extracting the mercury with a saturated aqueous solution of sodium sulfide. The mercury was subsequently extracted from this solution using dithizone dissolved in carbon tetrachloride and determined colorimetrically with the aid of a spectrophotometer. Pakter¹⁴ utilized a combustion procedure

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for the determination of mercury in coke and chemical products. The coal sample was ignited in a stream of air, the mercury vapor was absorbed in potassium permanganate solution, and the mercury content was determined colorimetrically using dithizone. A modification of this latter procedure was employed in this study; details of the method are included in the experimental procedures.

II. EXPERIMENTAL PROCEDURES

The following experimental techniques were utilized to determine mercury: (a) *Double Gold Amalgamation—Atomic Absorption*. Joensuu¹⁵ has described in some detail a mercury vapor detector system. The method involves the trapping of the mercury vapor by amalgamating it with gold and subsequent thermal release of the mercury into an absorption cell. With some modifications this was essentially the method employed for the determinations. Briefly our method is as follows: A 10–200-mg sample of coal in a nickel boat is burned in a stream of oxygen. The resultant vapors are passed over hot (400°C) silver wire coils to help oxidation, after which an amalgamator packed with gold wire traps all the mercury while most of the interfering substances pass through the apparatus and are vented. Unless these substances are removed, they may subsequently absorb radiation at the mercury 2537-Å resonance line, thus giving rise to erroneous peak heights. Among these substances are volatile organics, sulfides, and water vapor. To ensure complete removal of these interferents, the mercury is driven off the gold by heating to between 600 and 700°C and reamalgamated on a second gold amalgamator. From the second amalgamator the mercury is again released by heating and passed into an 18-cm long cell fitted in the optical path of the spectrophotometer. This chamber takes the place of the usual flame. Since the mercury is driven off the gold consistently at the same time and rather rapidly, a sharp peak is obtained on the strip chart recorder. Indeed a leak in the system is easily detected in the flattening out of the peak.

In this flameless technique advantage is taken of two somewhat unique properties of the element, i.e., its high volatility and its ability to form mercury atoms without the use of a flame. The principal advantages of this method are better sensitivity and improved detection limits. Determinations were made with a Perkin-Elmer model 303 atomic absorption spectrophotometer; details of the instrumental operating parameters are given in Table I. Depending on

Table I. Instrumental operating parameters for mercury determination.

Wavelength	2536.5 Å
Lamp current	8 mA
Slit setting	4 (1 mm)
Scale expansion	1×
Oxygen flow	1.25 ft ³ /hr

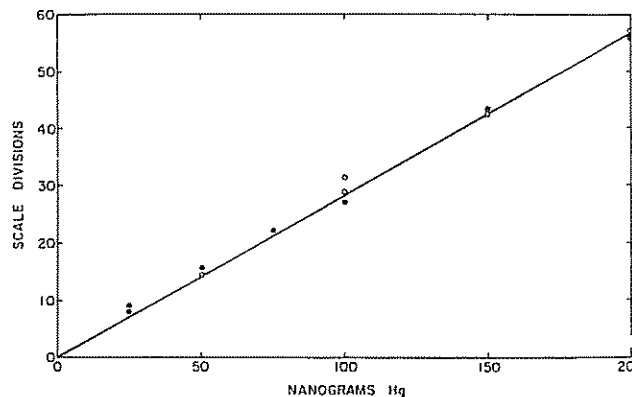


Fig. 1. Calibration curve, method (a); filled circles, HgS in graphite; open circles, standard Hg solutions; scale expansion: 3×.

the sample weight taken, the average time for a single determination was between 6–8 min.

For calibration purposes synthetic standards were prepared by hand blending mercuric sulfide with high-purity graphite (Union Carbide Carbon Products Division SP-2) in a mortar and pestle. From a standard containing 10 ppm Hg, 5-, 10-, 15-, and 20-mg samples were weighed out into nickel boats and put through the combustion unit in an identical manner to that of the test samples.

The calibration curve thus obtained was checked against a curve prepared by using measured volumes of mercury-saturated air. From a plastic bottle containing a few drops of mercury, a known volume of air was extracted through a diaphragm by means of a hypodermic syringe. The ambient temperature was read to the nearest 0.25°C and with the aid of the gas formula the vapor pressure of mercury saturation was converted to weight per unit volume of mercury. The mercury saturated air was injected into the system and again passed through each step of the double amalgamation procedure. The resultant calibration curve obtained by utilizing both of these methods is illustrated in Fig. 1.

(b) *Neutron Activation*. Neutron activation analyses were carried out by Gulf Radiation Technology, San Diego, California. The coal samples together with a mercury comparator standard were irradiated for 3 days at a flux of 10^{13} thermal neutrons $\text{cm}^{-2} \text{sec}^{-1}$. The irradiated samples were digested in an acid mixture in the presence of a mercury carrier and the mercury was distilled off as mercuric chloride. The mercury was then electroplated from the distillate, and multichannel gamma ray spectrometry was utilized to obtain the quantitative data.

(c) *Combustion-Solution Technique*. The combustion unit of this system consisted of a 155-mm length of quartz tubing (16 mm i.d.) around which wire heating coils were wrapped. The heating rate was controlled by a Variac transformer. A 20–400-mg sample of coal contained in a nickel sample boat was placed in the combustion train and oxygen passed over the sample at a rate of 1.25 ft³/hr. Heating was

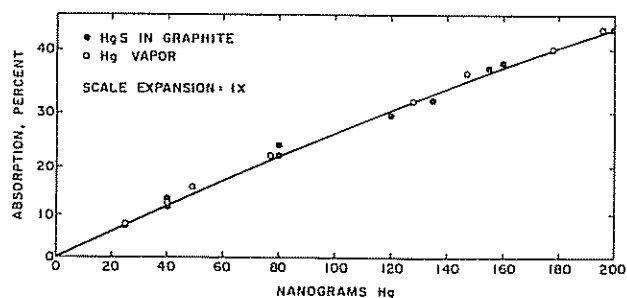


Fig. 2. Calibration curve, method (c); filled circles, HgS in graphite; open circle, Hg vapor; scale expansion: 1X.

continued until complete combustion was achieved. The combustion gases containing the mercury vapor were passed through two absorption bottles each containing 5 ml of an absorbent solution of potassium permanganate. Upon completion, the absorbent solutions and washings were combined and decolorized with 10 drops of 20% hydroxylamine hydrochloride. The solution was then made up to a final volume of 100 ml with distilled water.

Fifty milliliters of the sample solution were transferred to an aeration bottle fitted with a fritted bubbler. The solution was acidified with 5 ml of concentrated nitric acid and the mercury compounds in the solution were reduced to metallic mercury on the addition of 2 ml of stannous chloride solution. The aeration bottle was immediately stoppered and the bottle swirled to ensure adequate mixing of the reagents. The solution was aerated utilizing an air-flow rate of 3 ft³/hr. The mercury now in the air stream passed through an empty bottle to condense any water droplets formed then through a drying column of anhydrous magnesium perchlorate. It was finally measured in the absorption cell of the atomic absorption unit.

From a standard solution of mercuric nitrate (1 ml = 200 μ g Hg) a mercury standard solution (1 ml = 50 μ g Hg) was prepared fresh daily by making the appropriate dilutions. Aliquots of 1, 2, 3, and 4 ml of this solution were then utilized to prepare the calibration curve. In addition, samples of the mercuric sulfide/graphite standard were also run to check the recovery obtainable in the absorbent solutions. The resultant calibration plots are shown in Fig. 2. With

Table II. Details of coal samples studied.

Sample No.	ASTM rank	Sample type	% Ash ^a	% Total sulfur ^a
1	High vol. A	Lithotype	2.1	0.86
2	High vol. B	Channel	10.8	6.66
3	Anthracite	Channel	27.7	2.17
4	Lignite	Lithotype	9.4	0.92
5	High vol. A	Lithotype	9.5	3.13
6	High vol. A	Lithotype	5.2	0.64
7	High vol. A	Lithotype	6.2	1.24
8	High vol. A	Lithotype	6.9	1.59
9	High vol. A	Lithotype	9.4	0.99
10	Medium vol. B	Lithotype	2.4	0.58

^a On dry coal basis.

this technique it was necessary to use a scale expansion of 3X with the atomic absorption unit. The time required for a determination utilizing this procedure was about 20 min.

Reagents:

- 1% wt/vol potassium permanganate in 0.5 N sulfuric acid,
- 20% wt/vol hydroxylamine hydrochloride, nitric acid (concentrated)
- 20% wt/vol stannous chloride, magnesium perchlorate (anhydrous),
- 0.1 N mercuric nitrate stock solution. Dissolve 1.71 g of mercuric nitrate (Hg(NO₃)₂·H₂O) in 50 ml of distilled water, containing 2 ml of concentrated nitric acid, and make up to 100 ml with distilled water.

Mercury Standard Solution, 200 ppm. Pipette 5 ml of 0.1 N mercuric nitrate into a 250-ml volumetric flask and dilute to volume with distilled water.

Mercury Standard Solution, 1 ppm. Pipette 1 ml of the 200-ppm Hg standard into a 200-ml volumetric flask and dilute to volume with distilled water (1 ml = 1 μ g Hg).

Mercury Standard Solution, 0.05 ppm. Pipette 5 ml of the 1-ppm Hg standard into a 100-ml volumetric flask and dilute to volume with distilled water (1 ml = 50 μ g Hg).

III. RESULTS AND DISCUSSION

In Table II the coal samples studied are identified and data for the ash and total sulfur contents are included. Only two of the samples (Nos. 2 and 3) are representative whole seam samples. Samples Nos. 5, 6, 7, and 8 are lithotypes taken at an increasing and continuous depth from a particular seam; they represent a total seam depth of 6 ft.

Headlee and Hunter³ reported mercury in West Virginia coal samples which had been ashed at 740°C using a spectrographic technique. However, the quantitative determination of mercury in a coal ash does

Table III. Mercury content of coals, ppm.

Sample No.	Method (a) ^a	Method (b) ^b	Method (c) ^c	LTA material single gold amalgamation ^d
1	0.12	0.10	0.06	...
2	0.36	0.40	0.23	...
3	0.67	0.66	0.59	0.62
4	13.3	13.3	9.76	2.48
5	0.73	0.71	0.62	...
6	0.91	0.82	0.71	0.34
7	10.7	9.20	7.73	...
8	8.40	7.60	5.66	0.11
9	5.82	4.80	3.30	1.12
10	0.11	0.11	0.11	0.05

^a Averages of 10 determinations, 10–200-mg sample.

^b One determination, 200-mg sample.

^c Average of 4 determinations, 20–400-mg sample.

^d Average of duplicate determination, although No. 4 was run several more times in order to verify low value.

Table IV. Data on precision of selected measurements.

Sample No.	Method (a)				Method (c)	
	3		4		3	
Mesh size	65×100	−200	65×100	−200	65×100	
Sample size, mg	100	100	10	10	200	
Hg, ppm	0.59	0.67	13.4	13.3	0.59	
Standard deviation	0.078	0.12	3.43	0.31	0.055	
No. of determinations	10	10	10	10	10	

not seem possible due to the loss of mercury upon ashing. In a separate study¹⁶ coal samples were ashed at a temperature of 600°C prior to spectrographic analysis, but an evaluation of the photographic plates failed to reveal the presence of mercury in the samples. From this it would appear that the highly volatile mercury is lost in the ashing process. This is also borne out by the figures shown in column 5 of Table III. The LTA material referred to is in fact the mineral matter fraction separated from the coal substance by means of a low-temperature (~150°C) ashing technique (Tracer-lab model LTA-600 low-temperature asher). With this technique, reactive oxygen species are obtained when molecular oxygen is passed through a high-energy electromagnetic field produced by a rf oscillator. The reactive oxygen species removed the coal substance and left relatively unaltered mineral matter behind.

The mercury content of the mineral matter was then determined by method (a) with only a single gold amalgamation step being required. With the exception of sample No. 3, the remaining values are considerably lower than those obtained for the actual coals. This could be interpreted to mean that a considerable percentage of the mercury present is organically bound and is preferentially removed with the coal substance on ashing. In the case of the anthracite sample (No. 3) it is possible to speculate that this sample contains little or no organically bound mercury and that the mercury compounds present are relatively unaffected by the temperature achieved in the low temperature ashing process.

In comparing the three methods (see Table III), the agreement achieved between methods (a) and (b) is reasonably good; whereas method (c) appears to give somewhat lower values. The most marked discrepancies occur with the high volatile samples of comparatively high mercury content. One possible explanation for the large discrepancies found with method (c) is that the reducing species present in the combustion gases cause a reduction of the permanganate to manganese dioxide and consequently cause a decrease in the absorptive capacity of the absorbent solutions. Such a discrepancy was not noted when the mercuric sulfide-graphite standards were utilized in conjunction with method (c); the permanganate solutions appeared to absorb all the mercury released on combustion. This is evident from the calibration curve shown in Fig. 2 and also illustrates that good agreement is achievable between the mercuric sulfide-graphite standards and the mercury standard solu-

tions. Similarly, for method (a) the correlation between the mercuric sulfide-graphite standards and the mercury vapor was excellent (see Fig. 1).

Some tests were also made using a Parr oxygen bomb for the combustion step, but again low values resulted using this procedure. There was some evidence for mercury loss when releasing the vapors under pressure on completion of combustion. Both potassium permanganate and the hydroxylamine hydrochloride-nitric acid mixture were used as absorbing solutions in the bomb. Their absorptive capacities for mercury were found to be similar.

The initial mesh size of our coal samples were either 65×100 or −100 mesh. However, a notable improvement was made in terms of precision for some samples when they were brought to −200 mesh. Table IV illustrates the precision obtained on 65×100 and −200 mesh coals for a few samples. It is difficult to see why the precision was not improved in all cases by going to −200 mesh, but perhaps other errors masked out any improvement obtained by better sampling statistics.

The mercury mineral cinnabar (HgS) is frequently found to occur in nature associated with pyrite. In a study of the geochemical characteristics of mercury distribution in coal beds, Tkach¹⁷ reports that a direct relation was detected between the mercury content in coal and the content of secondary pyrites and carbonates in the coal bed. No such relationship was evident among the limited number of samples covered in this study. In addition Ruch *et al.*⁴ found that no correlation of mercury content with ash, total sulfur, or pyritic sulfur was discernible in their analyses of Illinois coals.

For sample No. 2 which has a relatively high total sulfur and pyritic sulfur content, an anomalous value for mercury content was not in evidence. The agreement between the analyses for sample No. 3 is quite good; the fact that this sample is an anthracite, may be of some significance. In contrast, coal No. 4 is a low-rank coal and the agreement is rather poor between method (c) and the other methods. In the four lithotypes represented by samples No. 5, 6, 7, and 8, all taken from the same coal seam but at increasing depths, it appears that the mercury is concentrated in the bottom half of the seam. As compared to the top two lithotypes (Nos. 5 and 6), the concentration of mercury increases by a factor about 10. Sample No. 19 also contained mercury at a level >1 ppm, whereas samples Nos. 1 and 10 displayed comparatively low mercury values.

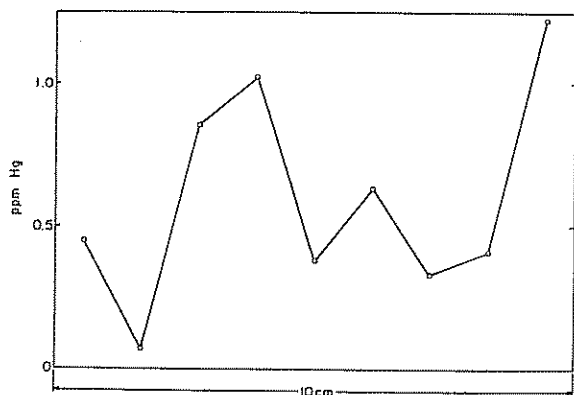


Fig. 3. Mercury distribution in a vertical section of a block of Sample No. 5 coal.

To ascertain what variation in mercury content could be expected in a particular coal, a further series of analyses were made on a small block ($10 \times 6 \times 4\frac{1}{2}$ cm) of No. 5 coal. Drillings were made at intervals of 1 cm along the $10 \times 4\frac{1}{2}$ -cm face, yielding 9 samples. The drillings were then analyzed for mercury utilizing method (a). The results obtained are shown in Fig. 3. The mercury contents were found to vary over a wide range from a low of 0.07 ppm to a high of 1.22 ppm. The average value for the mercury content of the block was 0.59 ppm, contrasted with the value of 0.73 ppm for the whole sample.

IV. CONCLUSIONS

It appears that the dispersion of mercury in coals is very nonuniform and the mercury contents may vary over quite a wide range. This can be attributed in part to the rather heterogeneous nature of the coal substance. Therefore, in order to obtain proper sampling extreme care is needed and in many instances utilizing a -200-mesh material will be an advantage.

From an evaluation of the analytical techniques the double gold amalgamation procedure is the best. The advantages of this method are (1) it is rapid; (2) when compared with the neutron activation results, it shows better agreement than the combustion-solution procedure; (3) it is less expensive than a neutron activation analysis, and (4) it is less susceptible to loss of mercury or to contamination because of sample handling (fewer steps in analytical procedure).

From the somewhat lower values obtained by the combustion-solution technique, a loss of mercury appears to be indicated. Mercury cannot be determined on the mineral matter separated from coals by low-temperature ashing or on coals ashed at higher temperatures because of the volatility of this element.

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