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Evaluation of X-Ray Fluorescence Analysis for the Determination of Mercury in Coal

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ABSTRACT

Limits of detection for mercury in coal have been determined on both a wavelength-dispersive and an energy-dispersive x-ray spectrometer. They are between 2 and 3 ppm under best conditions for both spectrometers. Techniques for reducing the background intensity measured by the energy-dispersive system are discussed along with methods of preparing coal specimens for analysis in both instruments.

1. INTRODUCTION

The mercury content of natural coal ranges between 0.05 and 0.4 parts per million (ppm) according to both atomic absorption analysis and neutron activation analysis [1]. Even though the mercury concentration is so low, the large amount of coal burned each year liberates tons of mercury into the environment. Many different analytical procedures are needed to monitor both the sources and the emissions of toxic materials such as mercury. The primary objective of this work is to experimentally ascertain the sensitivity, by x-ray fluorescence analysis, for the detection of mercury in coal.

We have selected two instrumental arrangements for testing the limit of detection of mercury in coal by x-ray fluorescence. The data thus produced should serve as a guide to the configuration of apparatus most appropriate and sensitive for trace determinations by x-ray spectrometry.

The first (energy-dispersive) arrangement consisted mainly of an x-ray tube and a Si(Li) detector with a multichannel pulse height analyzer. Primary x-rays emitted by the tube excite the specimen which emits an x-ray spectrum characteristic of the elements in the specimen. The secondary x-rays are analyzed by the Si(Li) detector which produces electrical pulses proportional in height to the energy of the

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respective x-ray photons. After amplification, these pulses
are sorted and stored by the multichannel analyzer. Since
this system simultaneously collects all of the x-ray lines
emitted by the specimen, the concentration of every element
for which there is an x-ray line may be determined at the
same time. Therefore, this system is useful for the analysis
of the major constituents in a multi-element specimen. The
scattering by the specimen of continuous radiation generated
in the x-ray tube produces a background which makes it dif-
ficult to detect elements present in trace quantities. To
reduce this scattering and thus the background, either second-
ary x-ray targets or x-ray filters can be introduced between
the x-ray tube and the specimen.

The second (wavelength-dispersive) arrangement is a
commercial single-channel x-ray spectrometer with crystal
dispersion. Primary x-rays emitted by an x-ray tube are
also used to excite the specimen. The crystal spectrometer
is aligned so that the characteristic x-ray line to be mea-
sured is diffracted by the analyzing crystal into the scintil-
lation detector. The pulses from the detector are amplified
and counted. Since this detector is not flooded with x-rays
other than the line of interest, and has a considerable loss
in intensity due to diffraction by the analyzing crystal, a
higher power may be used on the x-ray tube than with the
energy-dispersive system. The peak signal measured with this
system is generally higher than that measured with the energy-
dispersive system.

Since the peak signal and background signal are measured
consecutively with the wavelength-dispersive system, any
instrumental drift limits the useful length of time for mea-
surements. Drift is not a limitation with the energy-dispersive
system since both the peak signal and background signal may
be simultaneously measured. We found that the limit of
detection for mercury in coal is about 2 ppm with either

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system. However, to obtain similar results, the energy-dispersive system must operate for about ten times as long as the wavelength-dispersive system. These results are in agreement with the conclusions reached by Gilfrich et al. [2] who made similar comparisons of equipment for the analysis of air pollution samples, and with the conclusions of Leyden [3] on environmental water analysis.

The techniques employed in this work are now being applied to determine the limits of detection of other elements (Pb, As, Cd and V) in coal and in several other materials, such as fly ash, Fe_2O_3, PbO and CuO. We are also trying to further improve both of our systems.

2.   EXPERIMENTAL

2.1   Energy-Dispersive System

The primary x-rays emitted by the x-ray tube contain both characteristic x-ray lines from the target (Mo, Pt, etc.) and continuous radiation. The most efficient excitation of an x-ray line in a specimen is obtained when the energy of a strong primary x-ray line from the tube is slightly higher than the excitation potential of the x-ray line in the specimen. The continuum generated by the tube also excites x-ray lines in the specimen; however, part of it is scattered by the specimen, particularly from one of low atomic number, such as coal. This scattered radiation produces a high x-ray background (figure 2a). Since, at a given signal intensity, the limits of detection of any element are lowest when the line-to-background ratio is highest, it is desirable to decrease the background. Three methods of separating the continuum component from primary x-rays can be employed:

1.   Use the x-ray tube to excite a secondary target which in turn excites the specimen (figure 2b).

2.   Use a filter between the x-ray tube and the specimen to preferentially absorb the continuum (figure 2c).

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3. Use a crystal monochromator to diffract a primary x-ray line from the tube onto the specimen.

The first two methods have been applied to measure the limit of detection for mercury in coal. With the energy-dispersive system, we have produced efficient excitation of both the HgLα and HgLβ_1 x-ray lines while reducing background radiation. The first apparatus constructed used a silver anode x-ray tube to excite a pure secondary molybdenum target (see fig. 1). X-rays from this target are in an efficient energy interval (12-15 keV) and do not cause line interferences. A Si(Li) solid-state detector and multichannel pulse-height analyzer (MCA) are used for detection.

We have replaced the original device by a more permanent and versatile configuration. Since molybdenum tubes are more common for x-ray fluorescence than silver tubes, a molybdenum anode x-ray tube has been substituted for the silver anode tube, and a pressed pellet of Y_2O_3 has replaced the molybdenum secondary target (fig. 2b). The HgLα x-ray line is effectively excited by the yttrium K-lines from the Y_2O_3 target which have an energy of about 15 keV and are strongly excited by the molybdenum tube.

In another modification to the system, the Y_2O_3 pellet was placed directly in front of the window of the x-ray tube (fig. 2c). In this arrangement, most of the x-ray radiation generated by the tube is absorbed in the 1 mm thick Y_2O_3 pellet. The YKα x-rays generated in the pellet are of sufficient intensity to efficiently excite the HgLα x-ray line in the specimen.

2.2 Wavelength-Dispersive System

The wavelength-dispersive system used was a standard commercial x-ray fluorescence unit. For the measurement of the HgLα_1 x-ray line, a LiF crystal and a scintillation detector were used. Since a molybdenum anode x-ray tube
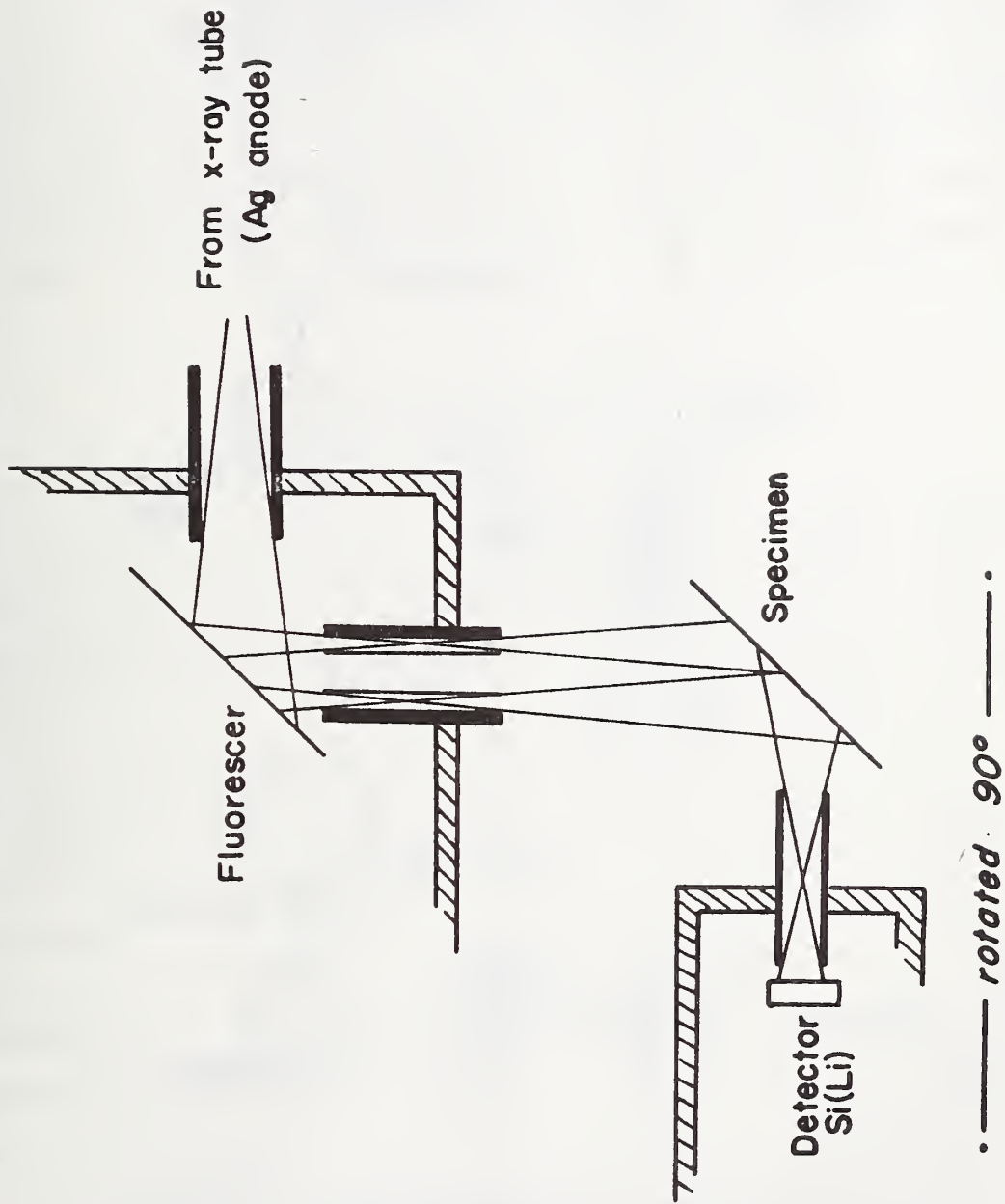
NON-DIFFRACTIVE APPARATUS

Figure 1. NBS energy-dispersive (non-diffractive) x-ray fluorescence apparatus.
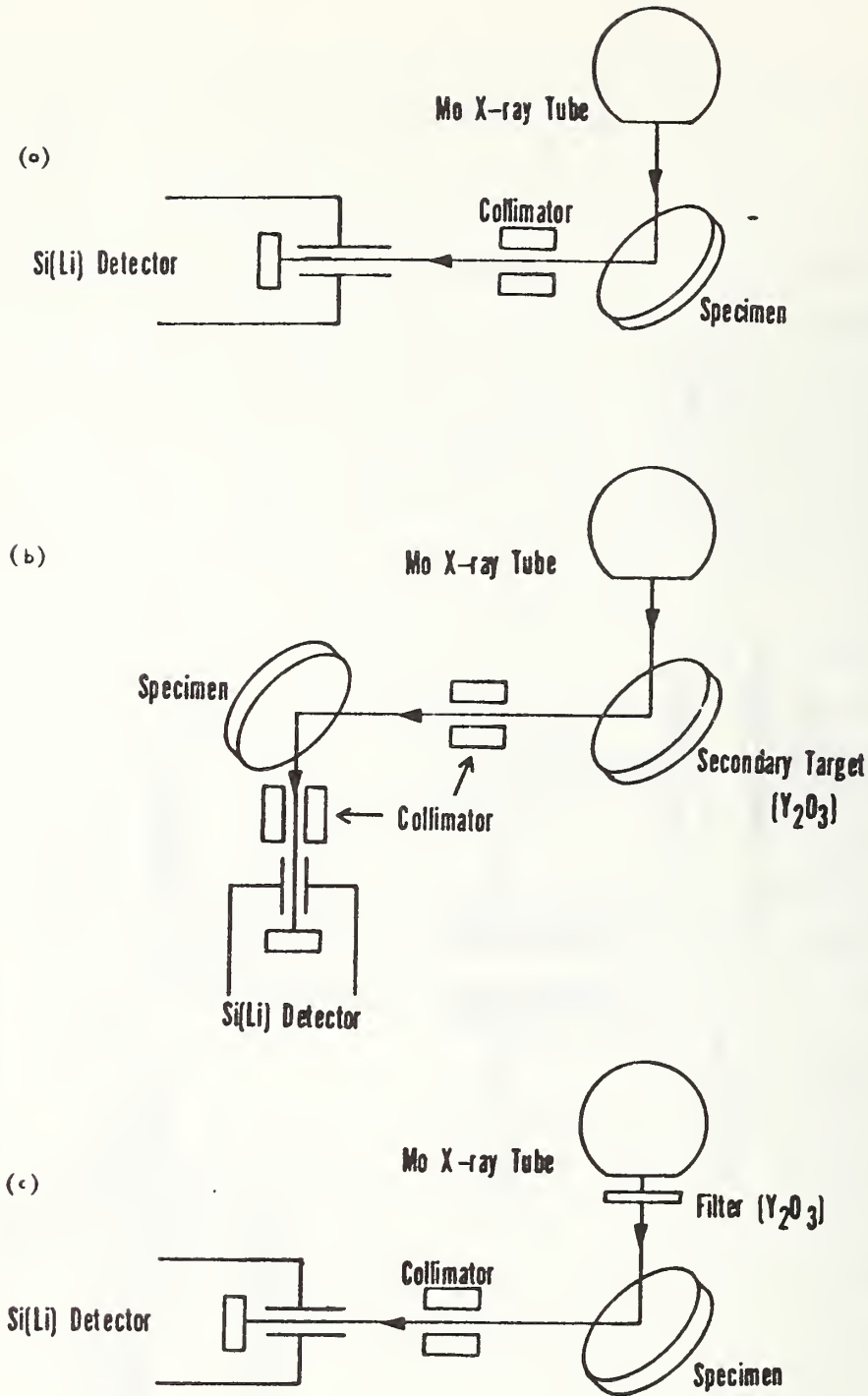
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Figure 2.   Instrumental arrangements of the energy-
dispersive x-ray fluorescence equipment.
(a) direct excitation of specimen by x-ray
tube; (b) excitation of specimen by secondary
target; (c) excitation of specimen by x-rays
filtered to remove continuum.

produces energies in the range efficient for the excitation
of the mercury lines without generating any interfering
x-ray lines, this tube was selected for the work.

In addition to the molybdenum tube, platinum, tungsten
and chromium tubes were available. The chromium anode tube
could not be used since it does not emit an x-ray line of
sufficient energy to excite HgLα. Both the platinum anode
and tungsten anode tubes had to be ruled out because of
interferences with the analytical x-ray lines of mercury.
A brief comparison of the tried configurations is shown in
table 1.

Table 1

Comparison of Equipment

	EDS[a]-1	EDS-2	EDS-3	WDS[b]
X-ray tube	Ag	Mo	Mo	Mo
Secondary fluorescer	Mo	Y_2O_3	Y_2O_3	--
Filter	--	--	Y_2O_3	--
Fluorescent x-ray line	MoK_α	YK_α	YK_α	MoK_α
Crystal	--	--	--	LiF
Detector	Si(Li)	Si(Li)	Si(Li)	Scintilla-tion
Read-out	MCA	MCA	MCA	Scaler
Line measured	HgLα	HgLα	HgLα	HgLα

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[a] EDS is Energy-Dispersive System

[b] WDS is Wavelength-Dispersive System

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2.3   Specimen Preparation

One NBS Standard Reference Material (SRM 1630)** was available for the determination of mercury in coal. This SRM contained 0.13 ppm of mercury, and was used as a base material to which known amounts of mercury were added. For example, a 100 mg specimen was prepared by placing 100 mg of SRM 1630 powder (-325 mesh) on a sheet of 6 μm Mylar* and adding 0.1 ml of trichloroethylene which, upon drying, causes the powder to form a cake. After it had dried, 0.001 to 0.025 ml of a solution of mercuric cyclohexanebutyrate (NBS SRM 1064) in toluene was added to the cake.

Several different methods of mounting specimens for x-ray fluorescence analysis were tried.

1. The specimen was confined to a diameter of 13 mm and held between two sheets of Mylar.

2. The specimen was confined to a diameter of 25 mm and held between a sheet of Mylar and a filter paper backing.

3. The specimen was confined to a diameter of 25 mm and held between two sheets of Mylar.

4. The specimen was pressed into a pellet 12.5 mm in diameter and held between Mylar sheets.

Homogeneity tests were made on three 500 mg specimens mounted by method 3 and on two 500 mg specimens mounted by method 4 (all doped at the 50 ppm Hg level). In the case of method 3, the specimens were prepared and the mercury measured. They were then stirred while in their same mounts and remeasured. No significant difference in the mercury

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*Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

**Available from The Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234.

measurements was observed. Measurements on both sides of
two different pellets mounted by method 4 also showed no
significant differences.

Coal specimens containing 10, 20 and 50 ppm of mercury
were mounted by the four techniques above. Specimens of
20 mg, 100 mg and 500 mg were mounted by methods 1, 2 and 3.
For method 4, 100 mg, 300 mg and 500 mg specimens were
pressed. The 100 mg specimens were very thin and difficult
to handle.

3. MEASUREMENTS AND RESULTS

The theoretical limit of detection will be defined as
that concentration which yields a signal three times as high
as the background [4]. Individual pulses arrive at a sta-
tistically varying rate, and the number of pulses accumulated
in fixed time intervals, for a given specimen and stable
instrumental conditions, varies according to a Poisson dis-
tribution. Therefore, the theoretical standard deviation
of the measured background is equal to the square root of
the number of pulses collected from the background.

If N_o is the total number of counts collected at the
background, the theoretical limit of detection (C_{tl}) for one
measurement can be calculated with the following equation:

$$C_{tl} = C_{std} \frac{3\sqrt{N_o}}{N_{std} - N_o}$$

where C_{std} is the concentration of the measured element
in the standard, and N_{std} is the number of counts collected
from the standard in the same time interval from that element
in the standard. This equation is based on the fact that at
low concentrations, the calibration curves are linear in x-ray
fluorescence analysis.

If multiple measurements are made on the blank and on
the specimen, the experimental limit of detection may be

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calculated from the standard deviation (σ) of the mean of
the blank determinations. If we have n measurements of
the background (X_i), σ may be calculated with the following
equation:

$$\sigma = \frac{n \sum\limits_{i=1}^{n} X_i^2 - (\sum\limits_{i=1}^{n} X_i)^2}{n(n-1)}.$$

If the mean of the background counts is estimated as:

$$\overline{X} = \frac{1}{n} (\sum\limits_{i=1}^{n} X_i)$$

we can calculate an interval from $\overline{X} - t\sigma/\sqrt{n}$ to $\overline{X} + t\sigma/\sqrt{n}$ which
we expect, with a certain confidence, to bracket the true
background. The factor t is a function of the number of
measurements and of the confidence level desired [5]. There-
fore, for an element to be detected, the line signal must
exceed the mean of the background measurement by more than
$t\,\sigma/\sqrt{n}$. The true limit of detection may then be calculated
with the following equation:

$$C_{el} = C_{std} \frac{t\,\sigma/\sqrt{n}}{N_{std} - N_o}.$$

Several experiments were performed on the wavelength-
dispersive apparatus to determine the experimental limit of
detection for mercury in coal. A 200 mg specimen containing
0.125 weight percent of mercury was mounted by method 2 dis-
cussed earlier and a wavelength scan was made to check for
any possible interferences (see fig. 3). As can be seen in
this figure, the background for HgLα is much lower than the
background for HgLβ_1. For this reason, the HgLα x-ray line
was chosen for all analyses.
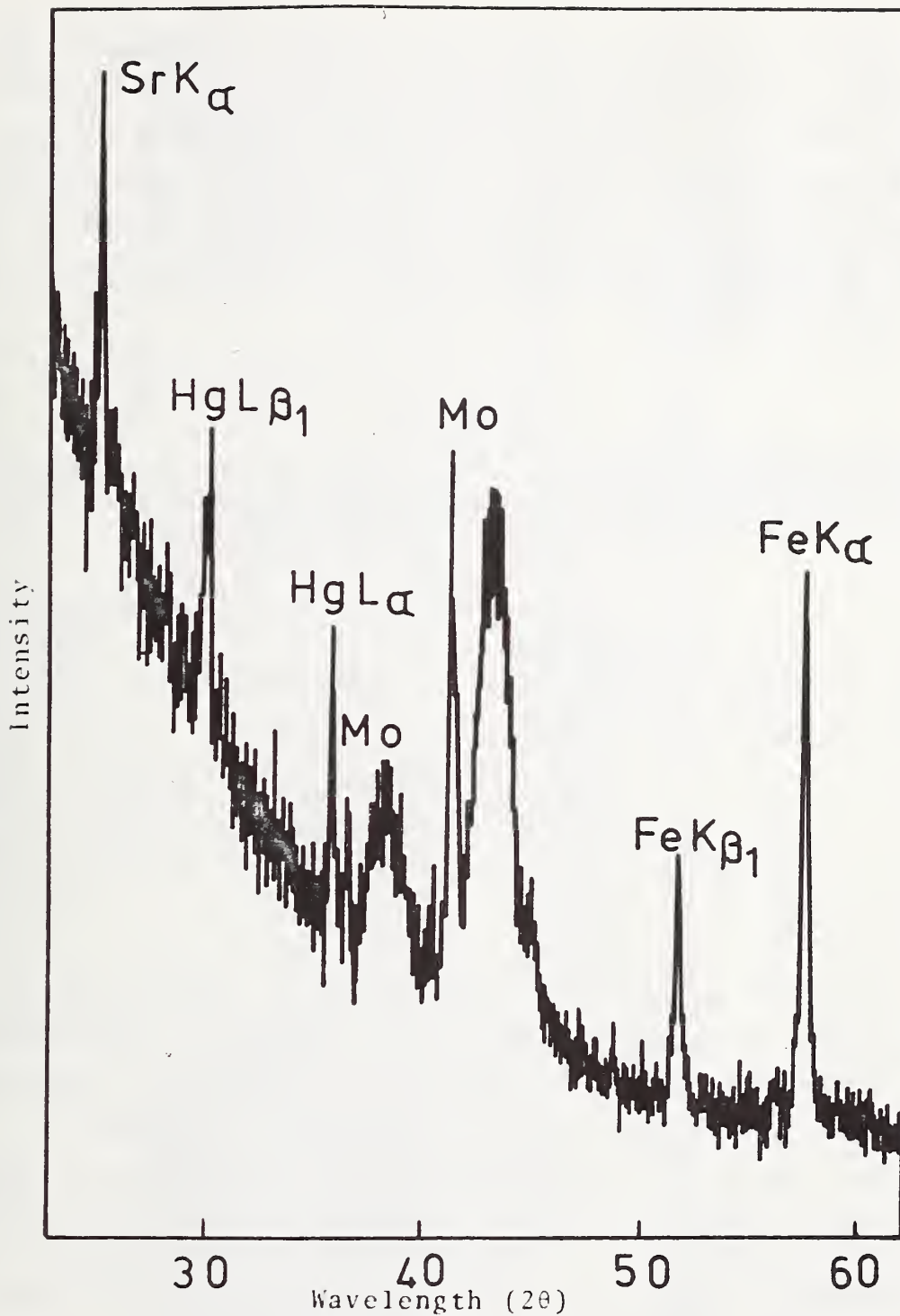
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Figure 3.   Wavelength scan of coal containing
            0.125% Hg.

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Optimum operating conditions for the molybdenum x-ray
tube were determined by measuring the peak signal-to-back-
ground ratio on a 500 mg coal specimen containing 10 ppm
mercury mounted by method 2, and on a similar coal specimen
without mercury. On the basis of the results listed in table
2, all subsequent wavelength-dispersive measurements were made
at 45 keV and 40 mA.

Table 2

100-Second Measurements of 10 ppm HgLα in Coal with Different
Operating Conditions for the Molybdenum Anode X-ray Tube
Wavelength-Diffraction (LiF) Technique

keV	mA	Background on Blank	HgLα Peak	Theoretical Limit of Detection
50	40	16584	1524	2.5 ppm
45	40	13410	1508	2.3 ppm
45	30	10289	950	3.2 ppm
35	35	8090	585	4.6 ppm

Three 500 mg specimens containing 10, 20 and 50 ppm
mercury were prepared and mounted by method 2. The results
of 100-s measurements are summarized in table 3. The lowest
achievable theoretical limit of detection for mercury is
2-3 ppm. The 50 ppm specimen and the blank were each measured
five times. The experimental limit of detection for a 99%
confidence interval was 7.5 ppm mercury for the mean of five
measurements; however, when the blank was measured 15 times,
this limit of detection decreased to 1.6 ppm.

The various specimen-mounting procedures are compared
in table 4. Each point is the result of a single 100 s count.
Since methods 1 and 3 give the best results, they appear to
be the best techniques for sample preparation.

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Table 3

Theoretical Limits of Detection in One 100-s Measurement
Wavelength-Dispersive Technique
on 500 mg Specimens with Paper Backing

	50 ppm	20 ppm	10 ppm
Signal (counts)	3092	2112	1574
Background (counts)	13414	13429	13579
Standard Deviation $(\sigma)^t$	115.8	115.9	115.7
S/N (Signal/σ)	26.7	18.2	13.6
Theoretical Limit of Detection	5.6 ppm	3.3 ppm	2.2 ppm

Table 4

Theoretical Limits of Detection in One 100-s Measurement
Wavelength-Dispersive Technique
with 50 ppm Hg Specimens

Mounting Method	A (100 mg)	B (500 mg)	C (100 mg)	D (100 mg)
Signal (counts)	3953	3092	3620	1031
Background (counts)	10746	13414	8082	8600
Standard Deviation $(\sigma)^t$	103.6	115.8	89.9	92.7
S/N (Signal/σ)	38.2	26.7	40.3	11.1
Theoretical Limit of Detection	3.9 ppm	5.6 ppm	3.7 ppm	13.5 ppm

With the energy-dispersive apparatus, shown in figure 1, several different preparations were also tried. Method 1 was selected for these measurements. Specimens of 500 mg, 200 mg, 100 mg and 20 mg were tried (all doped with mercury at the 50 ppm level). The best signal-to-background ratio was achieved with the 100 mg specimen. The theoretical limit of detection with this specimen was 2.6 ppm mercury for a one-hour measurement.

After the energy-dispersive system was modified, specimens with a larger diameter could more easily be used. Coal specimens of 500 mg mounted by method 3 were found to give the highest signal-to-background ratio for mercury (fig. 4).

To obtain similar limits of detection from both energy-dispersive and wavelength-dispersive systems, sufficient counts must be accumulated by each system to give equivalent statistical results. Since the energy-dispersive system collects information on the whole x-ray spectrum, only a small portion of the signal is within the peak of interest while the wavelength-dispersive system collects information on only the peak of interest [2]. Therefore, with the energy-dispersive system, counts must be accumulated for a longer period of time than with the wavelength-dispersive system.

The theoretical limit of detection can be improved by counting for longer periods of time. For a 50 ppm mercury specimen, the theoretical limit of detection was 3.9 ppm for a 500 s counting time. When the time was doubled to 1000 s, the limit of detection dropped to 2.5 ppm; however, to further lower the limit of detection requires very long counting times (see fig. 5). The experimental limit of detection for the average of seven measurements for 500 s each was calculated to be 2.2 ppm at a 99% confidence interval.

There were no significant differences in the results obtained from either of the two experimental arrangements of the Y_2O_3 pellet. However, significantly lower backgrounds
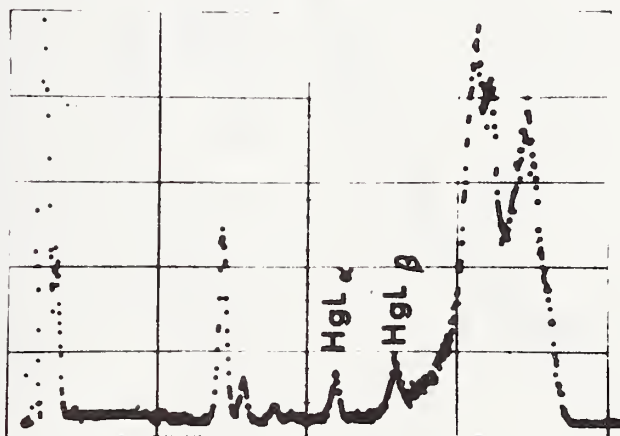
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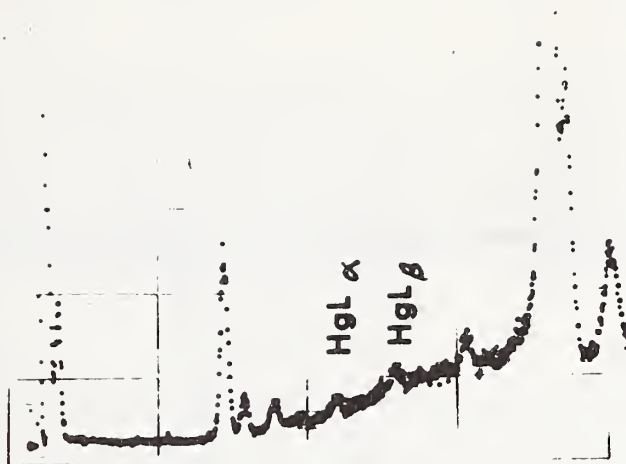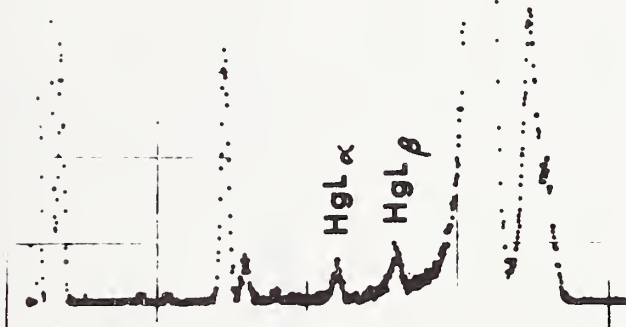
Figure 4. Energy-dispersive spectra of 0.125 weight percent mercury in coal. (a) direct excitation by Mo x-ray tube; (b) excitation by Y_2O_3 secondary target; (c) excitation by Y_2O_3 filtered radiation.
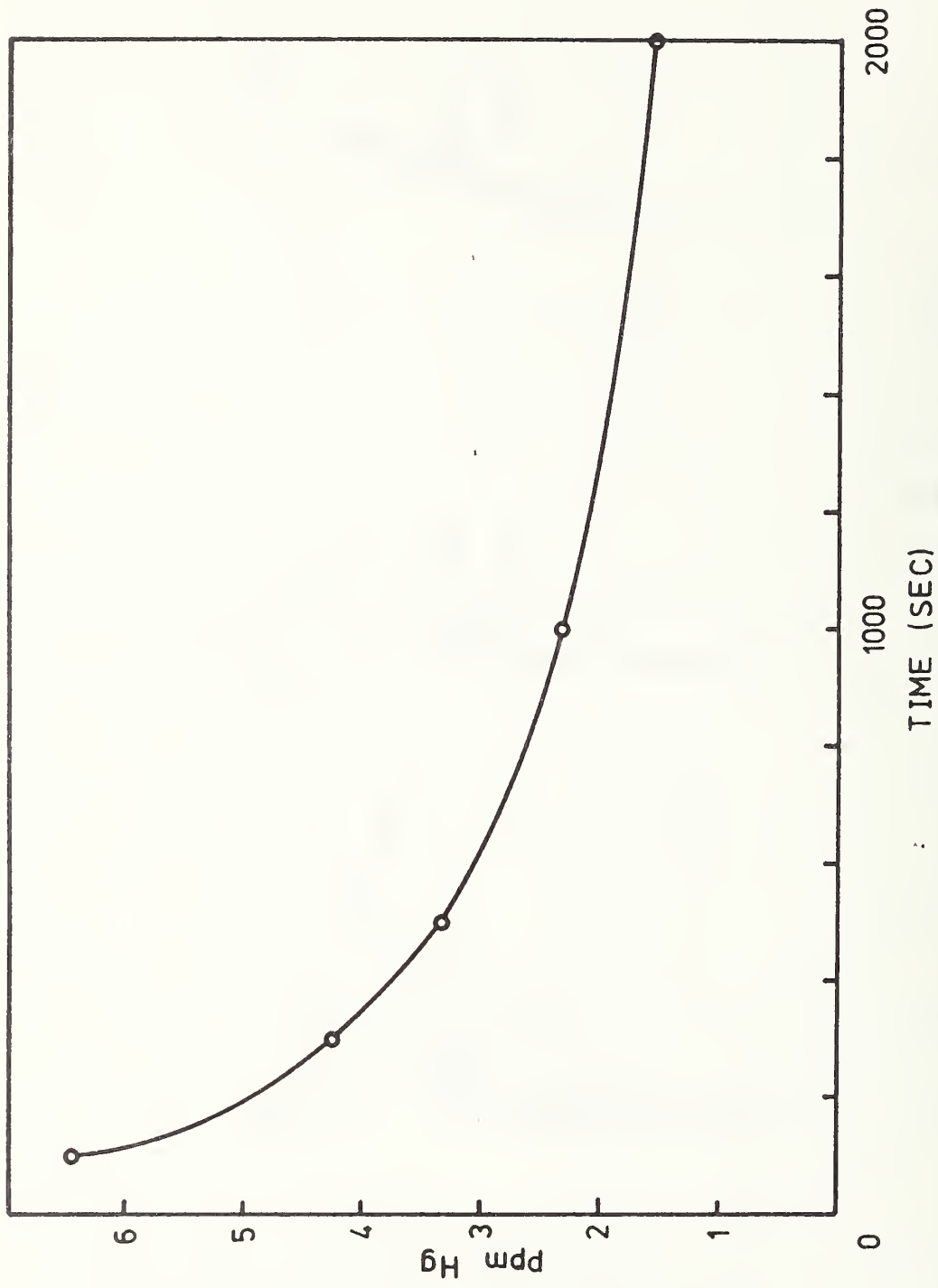
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Figure 5. Limit of detecting as a function of time for Hg in coal. Energy-dispersive analysis on 50 ppm Hg specimen.

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were obtained by carefully collimating the x-rays to reduce scattered x-rays in the specimen chamber. Collimators were placed between the secondary fluorescer and the specimen, and between the specimen and the detector (fig. 2b).

4. CONCLUSIONS

The lowest limit of detection determined by both the wavelength-dispersive and the energy-dispersive systems is approximately 2 ppm mercury in coal. For such results, the counting time with the energy-dispersive system must be increased by a factor of ten over that with the wavelength-dispersive system. However, with the energy-dispersive system, the concentrations of other elements may be simultaneously determined along with mercury. With a wavelength-dispersive system, the number of elements simultaneously determined is limited to the number of crystal spectrometers on the system.

At the present time, neither of these x-ray fluorescence techniques is sensitive enough to determine mercury in natural coal; however, these techniques may be satisfactory for other materials. Besides coal, the limit of detection for mercury will be determined in fly ash, Fe_2O_3, PbO and CuO. Several other elements (such as lead, arsenic, cadmium and vanadium) are also important in these materials, and will be determined. Along with these measurements, we will continue to examine further techniques for improving our limits of detection.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Limits of detection for mercury in coal have been determined on both a wavelength-dispersive and an energy-dispersive x-ray spectrometer. They are between 2 and 3 ppm under best conditions for both spectrometers. Techniques for reducing the background intensity measured by the energy-dispersive system are discussed along with methods of preparing coal specimens for analysis in both instruments.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Background; mercury in coal; trace analysis; x-ray fluorescence; x-ray spectrography.

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