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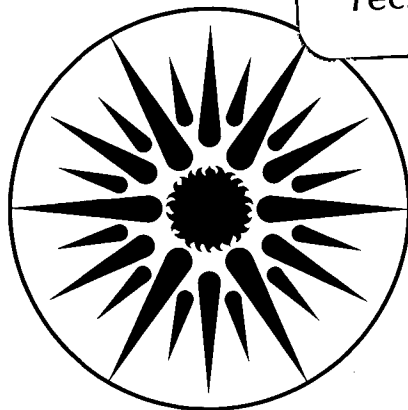
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MEASUREMENT OF MERCURY EMISSIONS FROM A MODIFIED IN-SITU OIL SHALE RETORT

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Abstract --Commercial oil shale production has the potential to release significant amounts of mercury to the atmosphere. Two techniques to measure mercury in oil shale retort offgas, Zeeman atomic absorption spectroscopy and gold bead amalgamation collection and analysis, are discussed and compared. A technique for speciating between organic and atomic forms of Hg is also discussed. The measured mercury emission rates and speciation results are presented.

This study was supported by the Assistant Secretary for Fossil Energy; Office of Oil Shale; Oil, Gas and Shale Technology Division and by the Assistant Secretary for Environment, Office of Environmental Compliance and Overview, Environmental Control Technology Division of the United States Department of Energy under Contract No. DE-AC03-76SF00098. This work was also supported by the Office of Research and Development, Industrial Environmental Research Laboratory, Energy Pollution Control Division of the United States Environmental Protection Agency under Contract No. AD-89-F-0-062-0.

Mercury is the most volatile of the toxic trace elements commonly found in oil shale. Various simulated retorting experiments have shown that most, if not all of the mercury present in the shale will be volatilized and released at typical retorting temperatures of 500–1000°C. Mercury concentrations in oil shale are only on the order of several hundred nanograms per gram. Mercury emissions from projected commercial production could be significant since an enormous mass of shale will be processed. Consequently interest in assessing potential Hg emissions prompted the development of a continuous real-time mercury monitor which was developed and tested on a laboratory scale retort to measure mercury emissions in a retorting environment.(1) The burning of a semi-commercial size modified *in-situ* (MIS) retort by the Rio Blanco Oil Shale Company (18 × 18 × 122 m³) between June and December 1981 provided an opportunity to test the continuous mercury monitor and to make extensive mercury concentration measurements in the offgas under actual retorting conditions.

The continuous monitoring technique is based on Zeeman atomic absorption spectroscopy (ZAA). The fundamental basis of the ZAA technique is atomic absorption spectroscopy with a unique method of background correction (2). The major difference between this technique and conventional atomic absorption spectroscopy techniques is the means by which the background correcting signal is generated. By placing a mercury lamp in a magnetic field (≈15 Kg) the atomic energy levels are split according to the Zeeman effect. Figure 1 shows the emission spectrum of the $^1S_0 \rightarrow ^3P_1$ transition corresponding to the 253.7 nm Hg line in a direction of observation perpendicular to the magnetic field. The unshifted component is designated π and the two shifted components are designated σ^+ and σ^- . The separation of the π and σ components is proportional to the magnetic field strength.

The relative transmission of the π and σ components through gaseous mercury is also shown on Figure 1. Both the π and σ components are equally absorbed and scattered by background components in the offgas such as water, oil mist, and particulates, but the π component is more strongly absorbed since it is at the resonant frequency with the Hg absorption transitions in the sample gas. By observing the difference between the π and σ transmission through the offgas we eliminate the background components of absorption and obtain a signal that corresponds only to absorption due atomic mercury.

The ZAA spectrometer is fitted with a corrosion resistant furnace-absorption tube. The sample gas flows into the furnace section of the tube, which is maintained at 800–900°C, then into a 5 cm path length absorption chamber with gas tight quartz glass windows. The total flow rate of the gas sampled through the ZAA is maintained by

an electronic flow controller which is continuously calibrated by a wet test meter and a Hewlett-Packard 85 computer and an Hewlett-Packard model 3054 Data Logger. Mercury calibration gas is generated by a device similar to the system described by Nelson (3) and is injected into the offgas line before the furnace.

A discrete sampling technique, based on mercury amalgamation on gold beads (4), was used along with the continuous mercury monitor to validate our measurements. Mercury is collected by inserting a quartz glass tube, with a 25 mm section of gold beads, into the offgas sample line for a measured flow rate and time period. The column is analyzed in the thermal desorption system shown in Figure 2. The sample collection tube, or transfer column, is quickly heated to 400°C in N₂ carrier gas; the mercury is desorbed and transferred to the analytical column downstream. The Hg is similarly desorbed from the analytical column and then analyzed by passing it into the ZAA spectrometer for detection. Calibrations are obtained by injecting gaseous Hg through the septum onto the analytical column followed by thermal desorption. Two stage desorption of samples is used since analytical response varies from column to column.

Speciation measurements of atomic and organic mercury were made using a the method adapted from Trujillo and Campbell (5). A quartz tube containing Carbosieve B is placed in front of the gold bead sampling column in the offgas sampling line. After sample collection, the atomic mercury remaining on the Carbosieve is transferred to the gold bead column by purging the Carbosieve with 10 liters of N₂ at room temperature. The organic mercury is retained on the Carbosieve B. Both the Carbosieve B and gold bead columns are analyzed in the same manner. No attempt was made to separate and identify the organic species.

A schematic of the Rio Blanco Oil Shale Company facility is shown in Figure 3. The MIS retort is an underground rubblized column of shale. The retort is burned from top to bottom with air and steam injected as shown. Shale oil is collected at the bottom of the retort and the offgas is directed to the ground surface through the offgas pipe. The primary sampling point is located in this pipe at the ground surface. The secondary sampling point is located in the offgas stack after the incinerator and desulfurization unit.

The sample offgas for the ZAA spectrometer and the discrete sampling columns were pulled from the center of the offgas pipe through a 0.63 cm Teflon tube supported by an outer stainless steel tube. It was then passed through a condenser, the sample line, the analytical instrumentation, and a peristaltic pump.

The Zeeman technique can quantitatively detect Hg in the untreated offgas and correct for background absorption due to the water vapor, oil mist, and particulates. However, sample line problems prevented the addition of mercury calibration gas in the presence of water vapor. The resistance heated stainless steel sample line (150°C) passed the water in the gas phase but condensation at the unheated fittings to the furnace-absorption tube interfered with the addition of calibration gas. The erratic addition of mercury calibration gas resulted in an extremely "noisy" calibration signal. Since we were unable to solve this problem under field conditions the offgas to the ZAA monitor was passed through a condenser. The condenser consisted of a glass bubbler packed with glass wool. It was immersed in an ice bath. This was sufficient to remove most of the water in the offgas which varied from 24 to 70% of the total offgas volume.

The stainless steel sample line was heated to prevent Hg condensation. An ambient temperature Teflon line was run in parallel to the heated stainless steel line. A comparison of the Hg signals from these sample lines showed that there were losses to the stainless steel line despite laboratory tests that showed that temperatures >100°C were sufficient to pass atomic mercury vapor with no losses to the line. The Hg signals for the Teflon and stainless steel sample lines are shown in Figure 4. The N₂ base line represents gas with no mercury vapor. When the offgas was sampled through the heated stainless steel line there was a 20-30% drop in the absorption signal relative to the Teflon line indicating loss of mercury to the stainless steel line. Since a condenser was being used to remove water, a heated line was no longer necessary. Consequently, the Teflon sample line was used for the remaining mercury measurements.

Figure 5 shows the results of the ZAA monitor mercury measurements at the primary sampling point. The current emission rates, in g day⁻¹, were obtained by multiplying the Hg concentration in the offgas times the dry offgas flow rates from the retort. The vertical bars represent the range of emission rates obtained throughout each day. The horizontal bars are the weighted mean average emission rate for each day. The rates are highly variable within each day and between days. There is no correlation between the emission rates and the air and steam input to the retort. Laboratory experiments indicate that Hg emissions should increase toward the end of the retort burn (6,7) yet no long-term trends to the emissions rates were seen during the period of this investigation. It should be noted that the measurement period extended over 35 days during the latter part of the retort burn and that the measurements were stopped prior to termination of the burning of the retort.

Au-bead amalgamation samples were taken on one day at the secondary sampling point. After experiencing losses to our stainless steel sampling line and from experience with the laboratory retorting experiments it was expected that a significant portion of the mercury in the offgas would be lost to the surface plumbing of the retorting facility. Only an estimate of the offgas flow rate at the secondary sample point was available but qualitative results indicate that no mercury was lost to the retort plumbing.

Gold-amalgamation samples were taken on seven days. Figure 6 shows a comparison between Mercury concentrations measured by analysis of the amalgamation columns and the ZAA mercury monitor. The sample measurements used for comparison in Figure 6 were taken within one hour of each other. The error bars are two standard deviations from the measured value. The variations may be due to the non-concurrent times at which the samples were collected. Never-the-less there is generally good agreement between the two methods, and neither technique gives consistently high or low results.

The results of the speciation sample, taken on four days with the Carbosieve B columns, are shown in Table 1. The total Hg concentrations agreed well with the concentrations measured with the ZAA Hg monitor on the same days. Of the total Hg in the offgas, 52-82% of the Hg is in the form of organic compounds.

Summary

There is very good agreement between the two techniques, Zeeman atomic absorption spectroscopy and Au-bead amalgamation, for the measurement of mercury concentrations in oil shale offgas but there are a number of differences that point to the ZAA technique to be superior to Au-amalgamation columns. The primary advantage of the ZAA monitor is the ability measure Hg directly in the untreated offgas. We were unable to do this because of sample line problems that interfered with our calibrations but those problems can be solved. Au-amalgamation requires that water be removed before sampling and this water must be analyzed at a later time. Background correction is an intrinsic feature of the ZAA technique. A background correcting spectrometer should be use for the analysis of the Au-amalgamation columns. Also, successful use of the amalgamation columns requires some prior knowledge of the Hg concentration in the offgas so as not to collect too small a sample nor to exceed the breakthrough volume of the column. This is not a problem with the ZAA Hg monitor which has a large analytical range. The continuous measurement capability of the

ZAA mercury monitor makes it a superior technique for reliable measurements of daily mercury emissions rates and a superior research instrument to follow mercury emissions with the process control of the retort. In addition the technique is easily adaptable to the measurement of other atoms and some molecules.

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FIGURE CAPTIONS

Figure 1. Mercury transmission profile

Figure 2. The two-stage thermal desorption system for the analysis of the Au-amalgamation columns.

Figure 3. Schematic of the Rio Blanco Retort facility.

Figure 4. Typical ZAA spectrometer signal for Hg-free N₂ and for Hg in Retort 1 offgas. Standard addition calibration points and the effect of sample line material are shown.

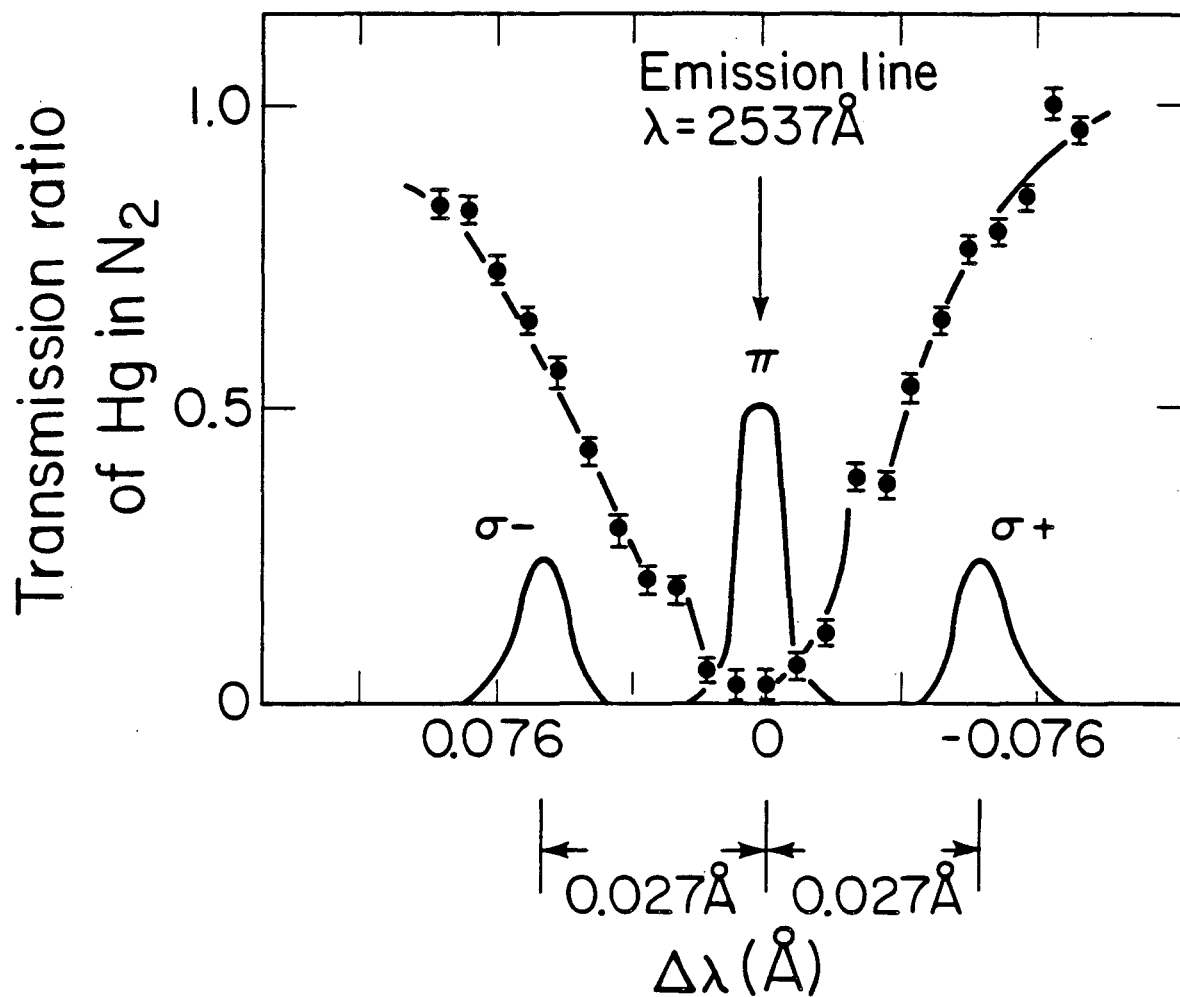
Figure 5. Mean daily Hg mass emission rates and daily mass emission rate ranges.

Figure 6. Comparison of Au-amalgamation and ZAA monitor mercury measurements.

TABLE LEGENDS

Table 1. Speciation of Hg in retort offgas.

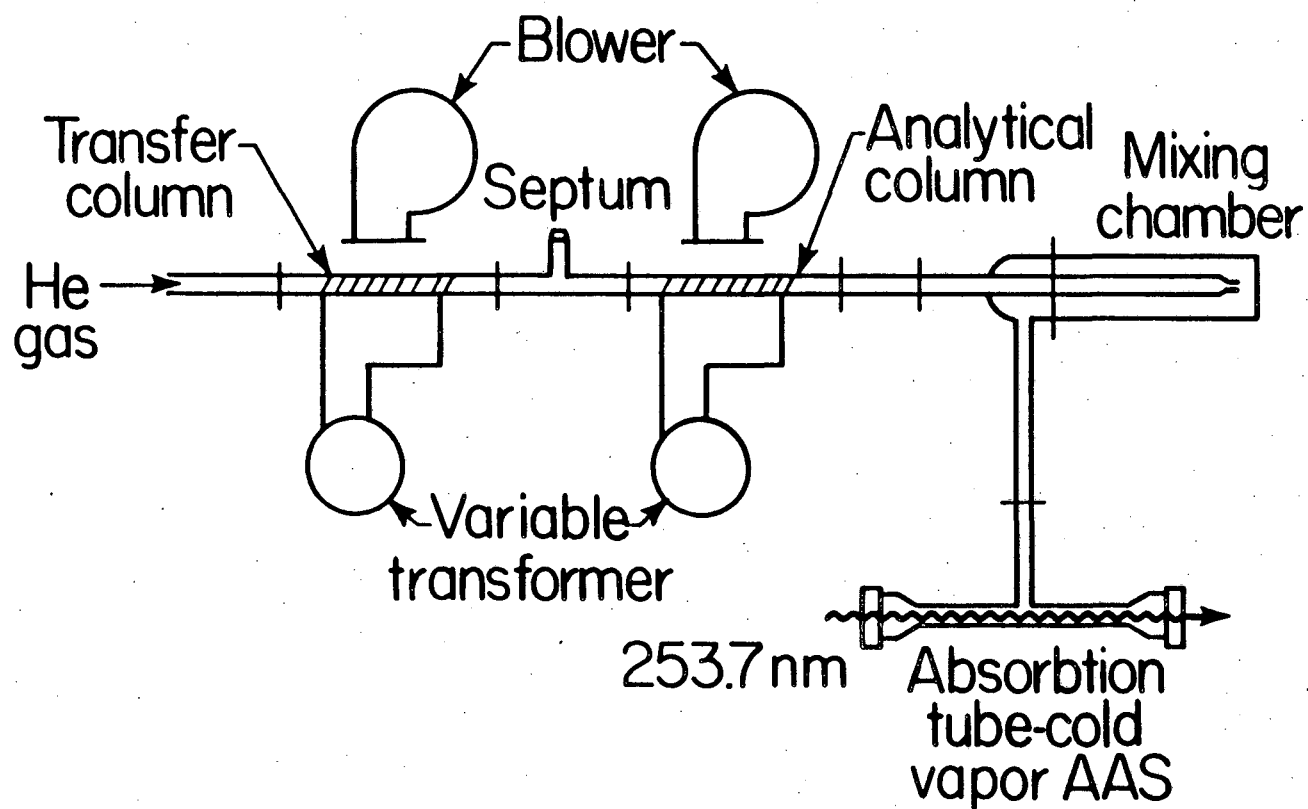
MERCURY TRANSMISSION PROFILE



XBL 834-1587A

FIGURE 1

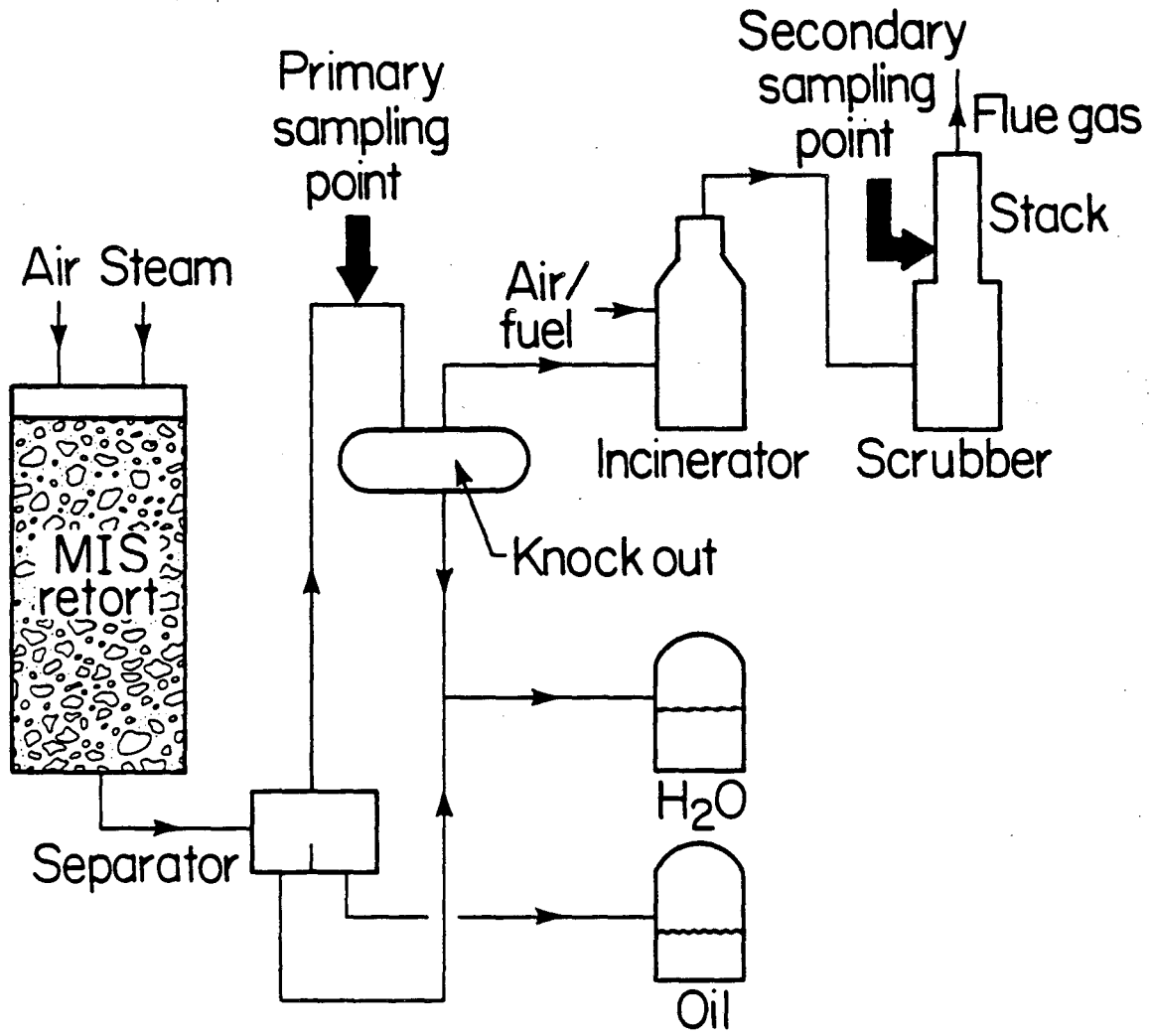
TWO-STAGE THERMAL DESORPTION SYSTEM



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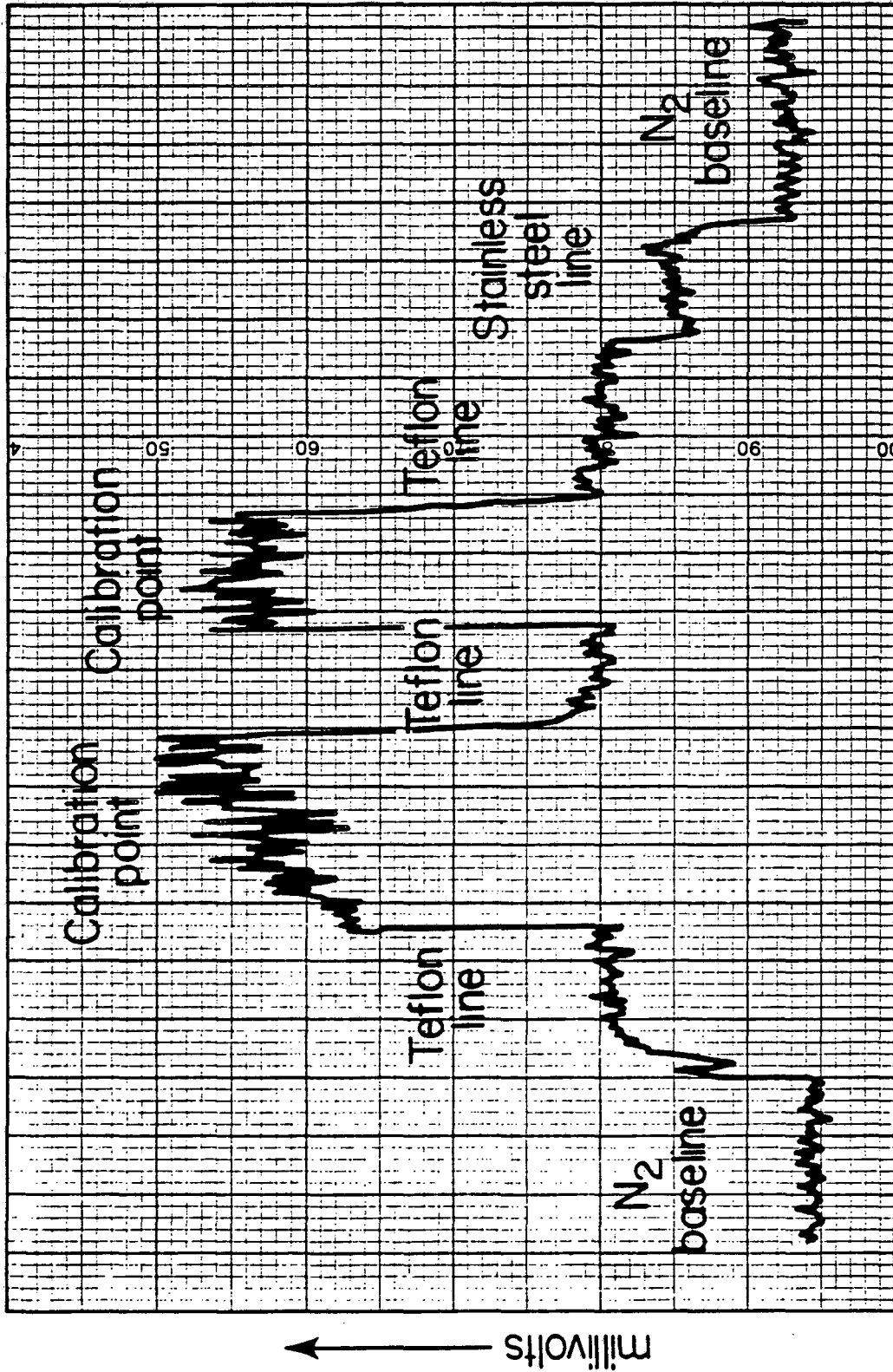
XBL 834-1583A

FIGURE 2



XBL 834-1585

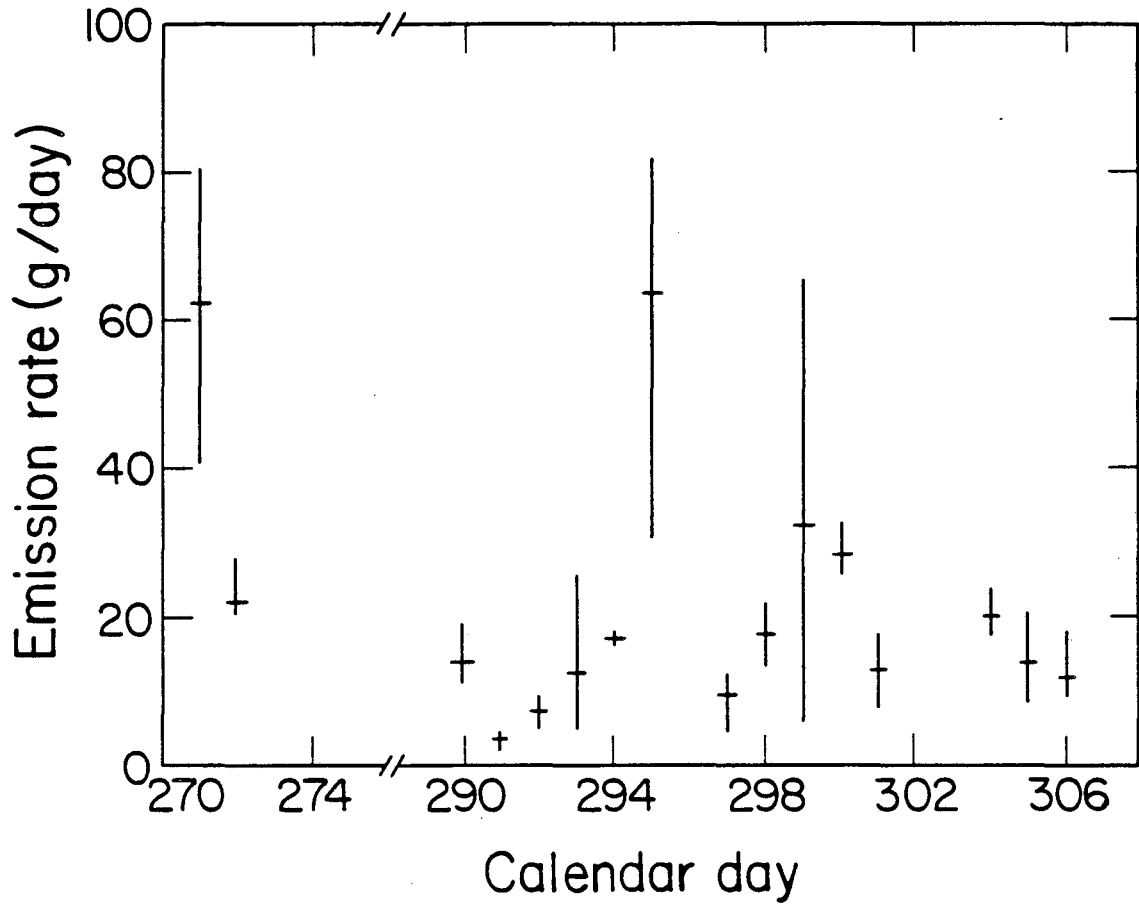
FIGURE 3



XBL 834-9298

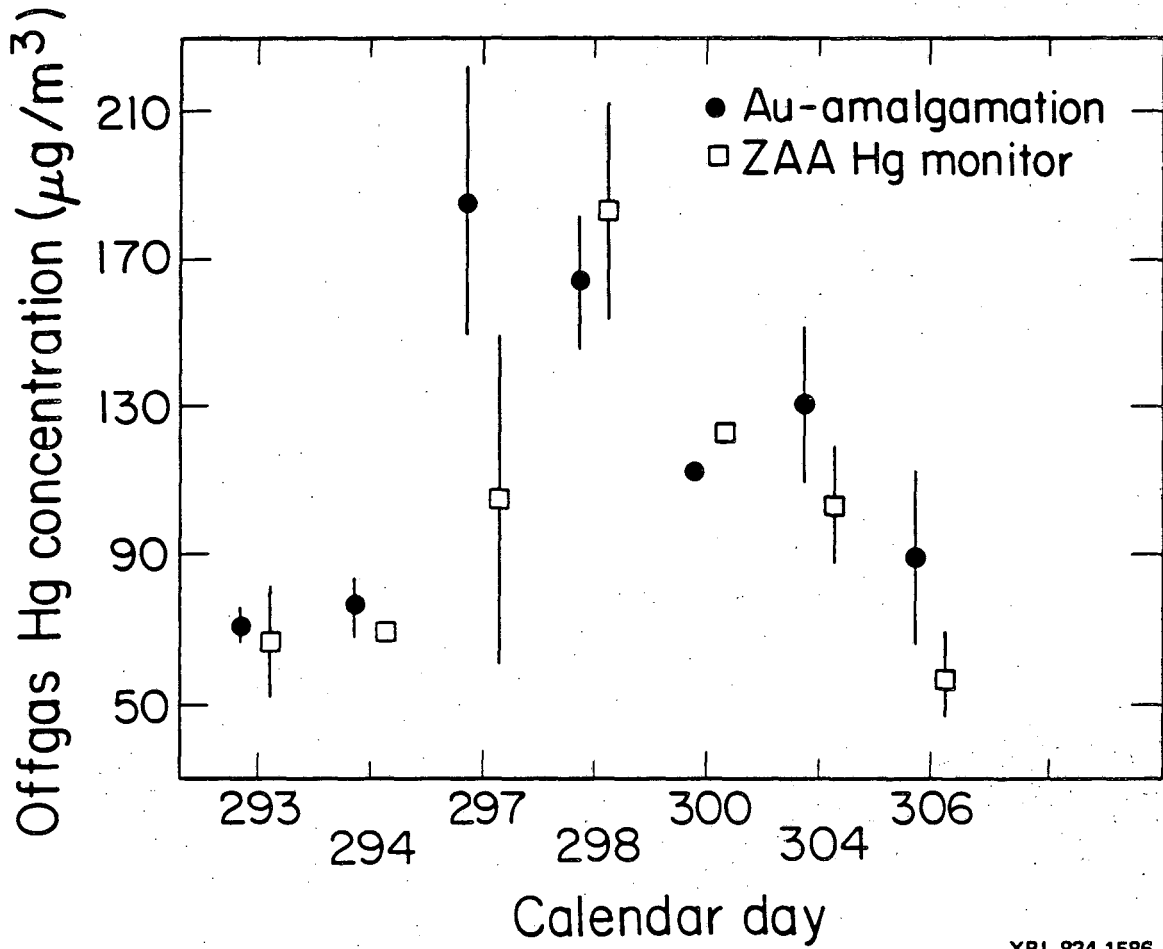
FIGURE 4

MERCURY MASS EMISSION RATE



XBL 834-1584

FIGURE 5

COMPARISON: Au-AMALGAMATION
AND ZAA MONITOR

XBL 834-1586

FIGURE 6

TABLE 1. MERCURY SPECIATION IN
UNTREATED OFFGAS

Day	n	Hg Concentration			Organic Hg (%)
		Atomic ($\mu\text{g m}^{-3}$)	Organic ($\mu\text{g m}^{-3}$)	Total	
297	2	93.5	102	196	52
298	2	30.0	138	168	82
304	3	39.9	94.9	135	70
306	3	31.3	66.2	97.5	68

XBL 836-10170

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