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## Recent Work

### Title

APRIL MONTHLY PROGRESS REPORT - DISTRIBUTION OF AS, Cd, Hg, Pb, Sb, AND Se DURING SIMULATED IN-SITU OIL SHALE RETORTING

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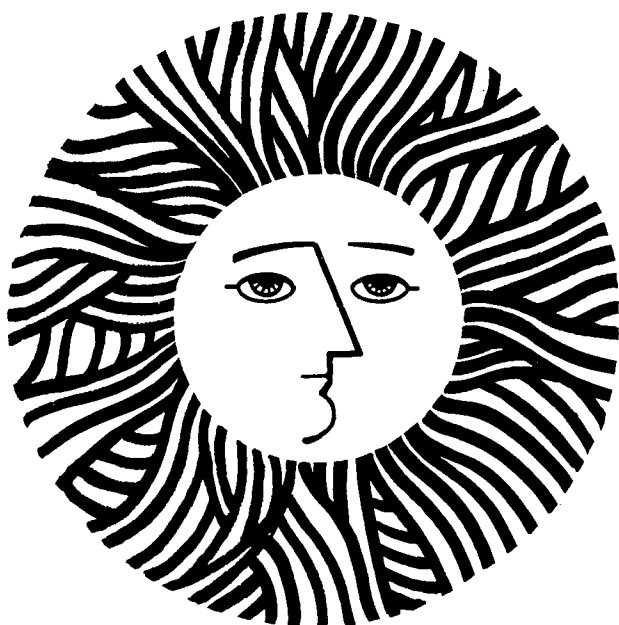


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May 13, 1980

TO: Bob Thurnau

FROM: D. C. Girvin and A. T. Hodgson

RE: April Monthly Progress Report  
Distribution of As, Cd, Hg, Pb, Sb, and Se  
During Simulated In-Situ Oil Shale Retorting  
LBID-204

TASK 1. ANALYTICAL METHODS FOR OIL AND WATER

In March, a distilled water sample was spiked with 10 ng Hg/ml, preserved with 5% (v/v)  $\text{HNO}_3$  plus 0.05%  $\text{K}_2\text{CR}_2\text{O}_7$ , and stored in an acid-cleaned glass container. This sample was analyzed in April after storage at 4°C for 38 days. Mercury concentration in this sample was found to be 9.8 ng/ml with a coefficient of variation of 5%. Consequently, the above procedure appears to be adequate for preservation and short-term storage of water samples intended for Hg analysis.

We previously reported that direct analysis of undiluted oil samples for Hg with the batch-sample ZAA spectrometer resulted in severe matrix suppression. In April, several oil samples were diluted with xylene (1:2 w/v) and analyzed by the method of additions using a commercial 100 ppm Hg in oil standard which was also diluted in xylene. Quantitative results were obtained; however, the analytical error at 100 ng/g was approximately 25%. The relatively large error and the difficulty of analysis led us to search for an alternate procedure. We subsequently initiated an evaluation of Parr acid digestion bombs for the decomposition of oil samples prior to Hg analysis. Several investigators have successfully used similar acid digestion bombs to decompose solid samples prior to Hg determinations (Holak et al. 1972; Trujillo and Campbell 1975; and Greenburg 1980). Our first attempts using the bombs also appeared to be successful; however, a recovery experiment must be performed to determine if any Hg is lost during digestion.

The Hg amalgamation, thermal desorption, cold-vapor atomic absorption detection method which we intended for use primarily with gaseous samples (see Task 2 below) is readily adaptable to the quantitation of Hg in other

matrices. We have used a stannous chloride bubbler system similar to the one described by Trujillo and Campbell (1975) to evolve Hg from acidified water samples and from diluted, acid-digested oil samples. The Hg is collected on amalgamation tubes packed with silver-plated quartz wool and analyzed by thermal desorption, ZAA cold-vapor detection. Using the batch-type ZAA spectrometer equipped with a 30 cm long optical tube, the workable linear concentration range of the method is from 2 to at least 50 ng of Hg. Calibration curves are prepared by injecting and analyzing known volumes of air which are saturated with Hg in a closed 2 l glass container. Agreement with  $\pm 5\%$  was obtained between selected points on these curves and aqueous standards by evolving Hg from diluted standards with the bubbler system.

No attempt was made to analyze shale oil samples for Cd and Pb. This analytical work will be postponed until the Hg retort runs are complete.

#### TASK 2. ANALYTICAL METHODS FOR GAS SAMPLES

The mercury amalgamation method was tested in conjunction with both conventional atomic absorption and ZAA cold-vapor detection and was found to be a useful analytical procedure. The amalgamator-ZAA combination was used to check the accuracy of the dynamic calibration device. Nitrogen flow rates through the calibration device were varied between 25 and 400 cc/min to determine if Hg saturation in the calibration gas was affected by flow rate. Discrete gas samples were collected from the calibration gas stream both before and after dilution with another nitrogen stream. A standard curve was prepared using saturated Hg vapor from the 2 l glass container as noted in Task 1. Measured Hg concentrations in the calibration gas average  $102 \pm 4\%$  ( $n=7$ ) of calculated concentrations. These calculated concentrations were based upon the temperature of the gas exiting the dynamic calibration device and the saturation vapor pressure of mercury at that temperature. The above results clearly demonstrate the accuracy of the dynamic calibration device up to a flow rate of 400 cc/min.

#### TASK 4. LABORATORY PARTITIONING STUDIES

In March, we initiated analytical work on subsamples of raw shale prepared for the next 15 retort runs. This shale originated from the Colony Mine.

Fischer Assay shale grade is 34.8 gallons per ton. Table 1 gives the trace element analytical results obtained to date.

Table 1. Elemental concentrations in raw shale prepared for retorting.

	ELEMENT			
	As	Hg	Pb	Se
Method	XRF	ZAA	XRF	XRF
No. Replicates	5	5	5	5
Mean ( $\mu\text{g/g}$ )	68.5	0.149	27.8	3.4
Std. Deviation ( $\mu\text{g/g}$ )	1.2	0.006	1.1	0.6

Three retort runs to determine the mass balance and partitioning of Hg were originally scheduled to begin in April. These runs have been rescheduled to begin in May. This decision was made to facilitate further evaluation of methods for Hg analysis in oil samples to make preparations for the collection of offgas particulate samples.

#### PROJECTED WORK

The projected work for May is as follows:

##### Task 1. Analytical Methods for Oil and Water Samples

- We will evaluate the use of acid digestion bombs for the decomposition of shale oil samples prior to Hg analysis.

##### Task 4. Laboratory Partitioning Studies

- The series of three inert gas retort runs which was originally scheduled for April has been rescheduled for May and early June. The scope of these runs has been expanded to include the collection and Hg analysis of offgas particulate samples. The majority of the month's efforts will be devoted to preparation and execution of the retort runs.

#### REFERENCES

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Trujillo, P. E. and E. E. Campbell, 1975. Development of a multistage air sampler for mercury. Anal. Chem. 47:1629-1634

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