

Naturally Occurring Arsenic Compounds in a  
Green River Oil Shale

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The distribution of arsenic among the various components of a sample of Green River oil shale has been investigated. A number of arsenic species, some of which have not been previously reported, have been identified. The greatest fraction of arsenic, 65 percent of the total, was found to be present as skutterudite,  $(\text{Co}, \text{Fe}, \text{Ni})\text{As}_3$  and safflorite,  $(\text{Fe}, \text{Co})\text{As}_2$ . About 16 percent was present in an HCl-soluble fraction, very probably in the form of arsenate. Almost nine percent was extracted by HF with the quartz and silicates. The bitumens and kerogens accounted for three and four percent of the total As, respectively, and this was found to exist in the form of methylarsenic and dimethylarsenic compounds. No evidence was found for the residence of arsenic in the pyrite.

Among the fossil fuels, oil shales are known to have the highest concentrations of arsenic, averaging 44 ppm. During recent years, and at the present time, there has existed a great deal of public concern about the contamination of the environment. Also, the refining of shale oils will utilize catalysts which are widely used in petroleum technology, viz., platinum and palladium. Arsenic is well-known to act as a poison toward such catalysts. Primarily for these two reasons information about the modes of occurrence of arsenic in oil shales is of importance.

Fish and co-workers (1) using a high performance liquid chromatograph coupled to a graphite furnace atomic absorption detector were able to confirm the presence of methylarsonic acid, benzenearsonic acid and arsenate in oil shale retort and process waters. Fish and Brinckman (2) studied the methanol extracts obtained from Green River oil shales. They reported the presence of the same three arsenic species in such extracts and the presence of other unidentified organoarsenic compounds. Jeong and Montagna (3) performed a gravitational separation followed by an isodynamic magnetic separation of pulverized Green River oil shale. Based on the enrichment of arsenic in fractions with higher magnetic susceptibility, they concluded that there exists an association between the arsenic content and iron-containing sulfide minerals such as  $\text{Fe}_{1-x}\text{S}$  and  $\text{Fe}(\text{AsS})_2$ .

In this report we describe the results of a systematic study of the distribution of arsenic among the various components which constitute a sample of Green River oil shale. Of the total arsenic, 97 percent was accounted for. The most significant result was the discovery of the presence of two arsenic minerals which account for two thirds of the total arsenic. These had not been previously found in oil shales.

#### EXPERIMENTAL

The oil shale sample used in this study was from the Hell's Hole Canyon of northeast Utah which forms part of the Uinta basin (Mahogany Zone). The sample, after it was disaggregated with a "Shatterbox" and screened through a U.S. standard -100 mesh sieve, had the following proximate analysis:

% moisture,  $0.26 \pm 0.02$ ; % volatiles,  $41.89 \pm 0.14$ ; % ash,  $57.92 \pm 0.24$ ; fixed carbon (by difference),  $0.18 \pm 0.12$ .

**Metal Analyses.** Arsenic and iron in aqueous solutions were determined using a Perkin-Elmer Model 272 graphite furnace atomic absorption spectrometer. Nickel, at a concentration of 400 ppm was added as a matrix modifier in the arsenic analyses. Corroboration of the As and Fe values and the determinations of the other metal ion concentrations were performed with an ARL Model 34000, simultaneous, vacuum inductively coupled argon plasma emission spectrometer (ICPAES).

**Ashing.** A Branson/IPC, Model 4005-448 AN Automated Radio Frequency Plasma Asher was used to prepare the low temperature ash from the raw shale and the residue obtained following each acid demineralization step (Figure 1).

**Arsenic Speciation.** Arsenate, arsenite, methylarsonic and dimethylarsinic species were converted to the hydrides which separated and analyzed for separately. Details of the method are described elsewhere (4, 5). The technique, in addition to being very sensitive, makes possible a differentiation between inorganic As(III) (reduction by  $\text{BH}_4^-$  at pH 6.5) and inorganic As(V) (both As(III) and As(V) are reduced at pH 2). Methylarsenic and dimethylarsenic compounds are reduced to  $\text{MeAsH}_2$  and  $\text{Me}_2\text{AsH}$ , resp. These are trapped at liquid nitrogen temperatures and easily separated by fractional distillation. Control experiments using  $\text{MeAs(O)(OH)}_2$  and  $\text{Me}_2\text{As(O)OH}$  showed that the conditions used for digestion of the kerogens and bitumens, *viz.*, concentrated nitric acid at temperatures not exceeding  $100^\circ\text{C}$  for 2 h in a capped flask followed by the addition of 1 ml. of  $\text{HClO}_4$  (70 percent) at the same temperature for 30 min., does not cause any rupture of  $\text{H}_3\text{C-As}$  or  $\text{H}_3\text{C-As-CH}_3$  bonds. Known compounds were converted quantitatively to the arsines following this treatment.

**X-Ray Diffraction and SEM-EDS Measurements.** Diffractograms of the minerals in the low temperature ash samples, of the raw oil shale and of the residues remaining after successive demineralization treatments were obtained with the use of a Seifert-Scintag PAD II powder diffractometer automated by a DGC Nova 3 computer.

Scanning electron microscopy with energy-dispersive X-ray spectrometric measurements were carried out at the Electron Microscopy Center, Texas A&M University. The instrument used was a JEOL 35CF electron microscope equipped with energy-dispersive and wavelength dispersive spectrometric capabilities, digital beam control and dual wavelength capability.

## RESULTS AND DISCUSSION

Figure 1 outlines a flow diagram which describes the chemical separation sequences used in this study. Powder X-ray diffraction studies revealed the presence of minerals typical of Green River oil shales with albite ( $\text{NaAlSi}_3\text{O}_8$ ), dolomite ( $\text{CaCO}_3\text{-MgCO}_3$ ) and quartz comprising the major mineral phases. Other minerals which were identified and found to be present in significant concentrations were pyrite ( $\text{FeS}_2$ ), orthoclase ( $\text{KAlSi}_3\text{O}_8$ ) and calcite.

Studies of the X-ray powder patterns at various stages of demineralization showed that treatment with 5M HCl was accompanied by the removal of dolomite and calcite. In the HCl-HF treated shale only pyrites appear to remain. The intensities of their characteristic spacings appear to be enhanced, probably due to the removal of other minerals. As expected, following treatment with  $\text{HNO}_3$ , the pyrite peaks disappear. The matter remaining at the end of the successive acid treatments was characterized by the absence of diffraction peaks. This is attributed to the amorphous and micro-crystalline nature of the material.

In Table 1 are listed the concentrations of arsenic and iron in various oil shale components separated according to the Scheme in Fig. 1. The results show that the bulk of the arsenic, ~65 percent of the total, can be extracted by 2M nitric acid. Sixty percent of the iron is also extracted by this reagent.

Identification of Skutterudite and Safflorite. Fragments of the shale were fractured from a large 10 kg sample. Based on visual observation, the fragments collected represented both darker (presumably oil-rich) and lighter layers. The fragments collected were examined as follows: 1. The fragments were embedded in thermoplastic cement (Buehler Sci. Co., Cat. No. 40-8100); 2. the mounted samples were polished with alumina to a grit of 0.3 $\mu$ . 3. in the case of some fragments originating from the more lightly colored layers of the shale sample, lustrous, silver grey mineral particles became visible. 4. the prepared samples were coated with 25A thick layer of carbon and examined by SEM-EDS. 5. based on the x-ray microanalysis, large (1~2 mm) mineral particles of interest were extracted from the SEM specimens after dissolving the cement with acetone; 6. x-ray powder diffractograms were obtained of these particles and, following their dissolution in HNO<sub>3</sub>, metal ion concentrations were determined by ICPAES.

Figure 2 shows the electron micrograph of an arsenic-containing mineral particle and the energy-dispersive x-ray spectrum of the same particle. Several spot analyses on the silver-grey mineral grain indicated, based on a standardless semi-quantitative procedure (SSQ), the following uniform composition: %As, 76.7; %Fe, 8.90; %Co, 10.2, %Ni, 4.1. There was no evidence of the presence of sulfur in these particles. Evidence that these particles were composed of skutterudite and safflorite was obtained from measurements of the d-spacings in their x-ray powder diffractograms as is illustrated in Fig. 3. Further corroboration was obtained from the results of analytical measurements (ICPAES) of the metal ion content of these particles: %As, 71.4; %Fe, 10.4; %Co, 3.9; %Ni, 5.1; %Ca, 4.2. The composition of the arsenide minerals excluding calcium was as follows: %As, 74.6; %Fe, 10.8; %Co, 9.3; %Ni, 5.3 giving a stoichiometry of Fe<sub>1.0</sub>Co<sub>0.82</sub>Ni<sub>0.46</sub>As<sub>5.1</sub>.

Examination of about seventy pyrite particles, by SEM-EDS, with x-ray photons being accumulated, in some cases, for periods as long as 5000 seconds, showed no evidence of the presence of arsenic. These results indicated quite conclusively that in this oil shale sample the arsenic is present as skutterudite, (Co,Fe,Ni)As<sub>3</sub> and safflorite, (Fe,Co)As<sub>2</sub>, but not with pyrite.

Methylated Arsenic Compounds in Bitumen and Kerogen. Samples of bitumen and kerogen were analyzed for total arsenic by digestion with con HNO<sub>3</sub> followed by con HClO<sub>4</sub> and taken to fuming. They were also analyzed by hydride reduction techniques following digestion methods which keep the H<sub>3</sub>CAs and (H<sub>3</sub>C)<sub>2</sub>As bonds intact (see exptl. part). The results of these studies show very clearly that only a minor fraction of the total arsenic in these organic components is present in the form inorganic arsenic(V). This is possibly due to the distribution of small quantities inorganic arsenic minerals with these components. The bulk of the arsenic in both the bitumens and kerogens is present as H<sub>3</sub>C-As and (H<sub>3</sub>C)<sub>2</sub>As species. These results have not yet been quantitated.

## CONCLUSION

The bulk of the arsenic in a sample of Green River oil shale, almost 65 percent of the total, is present as skutterudite and safflorite.

None was found to be associated with the pyrites. About 16 percent of the arsenic is extracted by HCl, and this may be in the form of arsenates. The HF-solubles, primarily quartz and silicates, have about nine percent of the total arsenic. The bitumens and kerogens accounted for three and four percent of the

total original arsenic and this was found to contain significant amounts of methyl and dimethylarsenic compounds.

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Table 1. Distribution of Arsenic and Iron among Oil Shale Components\*

Sample description	As $\mu\text{g/g}$ oil shale		Iron $\text{g}/100 \text{ g}$ oil shale	
	GF-AAS	ICPAES	GF-AAS	ICPAES
Raw shale	72.3 $\pm$ 0.68	68 $\pm$ 1.2	2.23 $\pm$ 0.02	2.24 $\pm$ 0.01
HCl-soluble	13 $\pm$ 0.1	10 $\pm$ 0.1	0.49 $\pm$ 0.003	0.47 $\pm$ 0.004
HF-soluble	6.34 $\pm$ 0.06	-----	0.35 $\pm$ 0.004	-----
HNO <sub>3</sub> -soluble	46 $\pm$ 0.6	47 $\pm$ 0.4	1.34 $\pm$ 0.03	1.31 $\pm$ 0.03
THF-soluble	1.88 $\pm$ 0.11	2.12	-----	-----
R**	3.28 $\pm$ 0.02	3.23 $\pm$ 0.01	-----	-----

\*Each value represents an average of the results of at least three experiments.

\*\* R: HCl-HF-THF-HNO<sub>3</sub>-treated oil shale.

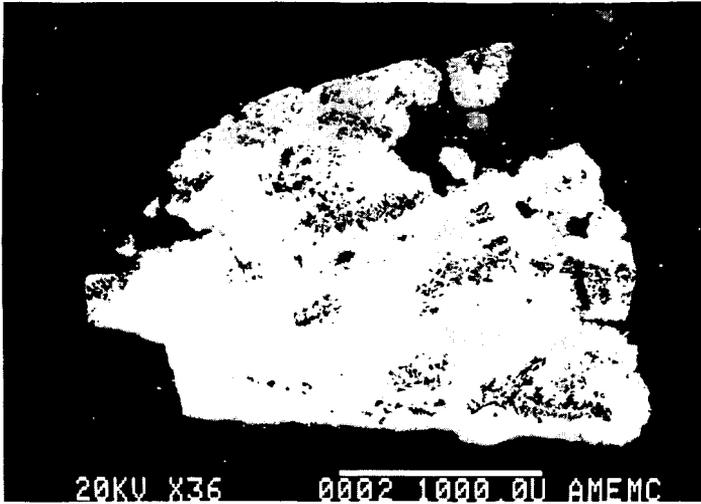


Fig. 2a. Electron micrograph of arsenic-rich mineral, magnification x36.

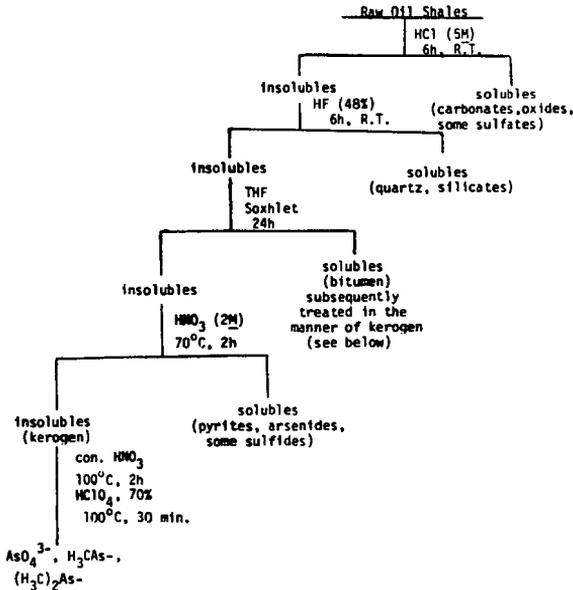


Fig. 1. Flow Diagram of the Sequence of Chemical Separation of Oil Shale Components.

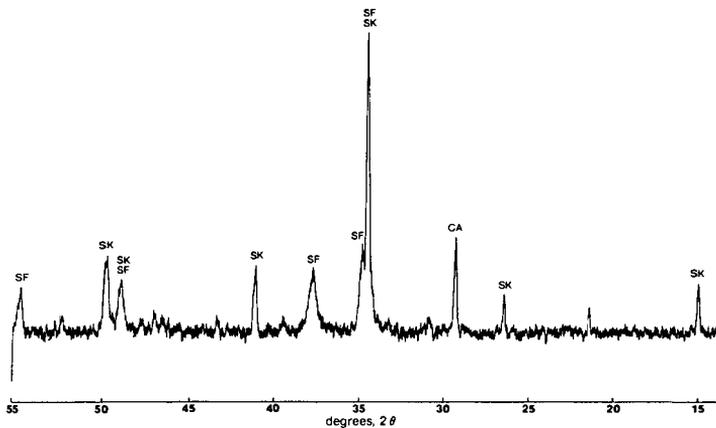


Fig. 3. Powder x-ray diffractogram of the particle in Fig. 2a. Key to symbols: SK, skutterudite; SA, Safflorite; CA, calcite.

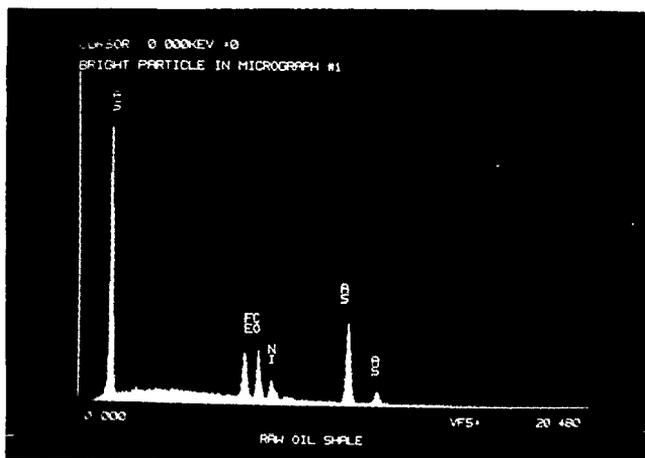


Fig. 2b. Energy-dispersive x-ray spectrum of the particle in Fig. 2a.