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ORGANOMETALLIC GEOCHEMISTRY. ISOLATION AND IDENTIFICATION OF
 ORGANOARSENIC AND INORGANIC ARSENIC COMPOUNDS FROM
 GREEN RIVER FORMATION OIL SHALE

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INTRODUCTION

Transformations and bioaccumulation of trace metals and metalloids, especially arsenic, are well known to occur in modern microorganisms, including the bacteria (1,2) molds (3), and marine plankton or algae (4,5). Such microflora demonstrate capacities for uptake of both inorganic forms of elements, and in some instances, are shown to involve biomethylation of inorganic substrates which result in cellular incorporation of organometal(loid)s, e.g., methylarsonic acid or dimethylarsonic acid (5). Arsenic is known to bioaccumulate in higher marine organisms to a substantial degree (6,7) where it resides in some shellfish tissues as arsenobetaine (8).

Similar considerations for ancient metal(loid) uptake or transformations appear quite reasonable for primordial microflora, especially the algae which account for the present ubiquitous distribution of kerogen in shale rocks (9,10). In general, the fossil deposition record suggests that substantial metal(loid) accumulation also occurred in higher plants which underwent diagenesis to form modern petroleum and coal deposits (11,12). In many instances, various present-day species of plants are known to both selectively and extensively hyperaccumulate various metal(loid)s to such a degree that geochemical prospecting is feasible by correlating metal concentration profiles with local flora (13). It is not unexpected, therefore, to discern characteristic concentration patterns for trace elements in various fossil deposits - whether we regard these as essential or toxic to life - and to expect gross differences in the profiles between the three main types: coal, kerogen, and petroleum, as summarized in Table I (14-18). Similarly expected, though far more subtle, we might anticipate that element distributions for these three main fossil sources also depend upon specific sites, and reflect their terrestrial or marine origins, subsequent geochemical history, and maturation (19-21).

TABLE I
 COMPARISON OF SELECTED ELEMENTAL CONCENTRATIONS* IN
 PETROLEUM, COAL, AND OIL SHALE

| <u>Element</u> | <u>Petroleum</u> | <u>Petroleum</u> | <u>Coal</u> | <u>Oil Shale</u> |
|----------------|------------------|------------------|-------------|------------------|
| As | 0.111 | 0.263 | 15 | 44.3 |
| Be | -- | -- | 2.0 | -- |
| Cd | -- | -- | 1.3 | 0.64 |
| Cr | 0.093 | 0.008 | 15 | 34.2 |
| Fe | 10.8 | 40.7 | 1.6% | 2.07% |
| Ge | -- | -- | 0.71 | -- |
| Hg | 0.051 | 3.236 | 0.18 | 0.089 |
| Ni | 9.38 | 165.8 | 15 | 27.5 |
| S | 0.83% | 1.31% | 2.0% | 0.573% |
| Se | 0.052 | 0.530 | 4.1 | 2.03 |
| Si | -- | -- | 2.6% | 15% |
| U | -- | 0.060 | 1.6 | 4.5 |
| V | 13.6 | 87.7 | 20 | 94.2 |

*Concentrations in ppm except as noted.

The molecular forms of trace metal(loid)s in fossil deposits is doubtless complex, probably consisting of varying proportions of inorganic, metallo-organic (no covalent element-carbon bonds), and true organometallic chemical species residing in unspecified sites within the carbonaceous matrix. Over the years a very substantial solvent differentiation methodology has emerged (22-24), which greatly aids the analyst in assessing the broad matrix categories of fossil materials, and produces reproducible information concerning possible ligation, elements present, and approximate molecular size (weight) of the soluble components.

The determination of the molecular forms of trace metal(loid)s in fossil materials ideally requires a technique with extreme selectivity, lack of interferences, sensitivity to the sub-ppm level, and the ability to deal with heterogeneous samples. The state-of-the-art analytical methods which are capable of meeting these criteria to varying degrees, without extensive sample preparation, are quite limited and have only recently been applied to limited types of fossil samples.

The coupling of chemical separations, which provide selectivity and reduce interferences, with instrumental techniques, which are capable of providing further selectivity and the necessary sensitivity, has been an active area of analytical research, being performed in both off-line and on-line modes. The recent emergence of a number of on-line "hyphenated" techniques (24), GC-MS, MS-MS, LC-ESD (including variable- and scanning UV, IR, NMR, GFAA, FAA and electrochemical detectors) appears to be the most effective and versatile method to quantitate organic, inorganic, organometallic and metallo-organic compounds in complex matrices. Among these, automated coupling of high performance liquid chromatography (HPLC) in normal, reverse phase, ion exchange, or size exclusion modes with element-selective detectors appears most promising for the characterization of metal(loid) containing molecules in complex matrices (25).

RESULTS AND DISCUSSION

Reports of on-line, element-selective detection of chromatographic effluents of fossil materials have appeared more recently and offer the advantages of increased resolution and easier chromatographic optimization because of the real time acquisition of elemental distributions during the chromatographic run. Recently, Brinckman et al. (26), have coupled a graphite furnace atomic absorption (GFAA) spectrometer to a high performance liquid chromatograph, which has been applied by Fish et al. (27), and Weiss et al. (28) to the analysis of arsenic compounds in process waters and oils generated during oil shale retorting.

In order to answer questions on the biogeochemical origin of the methyl and phenylarsonic acids, and arsenate, found in oil shale retorting products (27,28), we extracted a Green River Formation oil shale sample (NBS standard reference material) with refluxing methanol. By using HPLC-GFAA analysis of the extract, and catecholorganoarsonic acid (29) and trimethylsilylation-arsenate derivatization reactions, we have identified, in an unequivocal fashion, methyl- and phenylarsonic acids and arsenate, by the former technique and by capillary column gas chromatography - mass spectrometry analysis with the latter derivatization technique.

Figure 1 gives the arsenic-specific chromatogram of the compounds we identified as methylarsonic acid, phenylarsonic acid, and arsenate, based on retention times of the authentic arsenic compounds. An unknown neutral organoarsenic compound eluted with the solvent front.

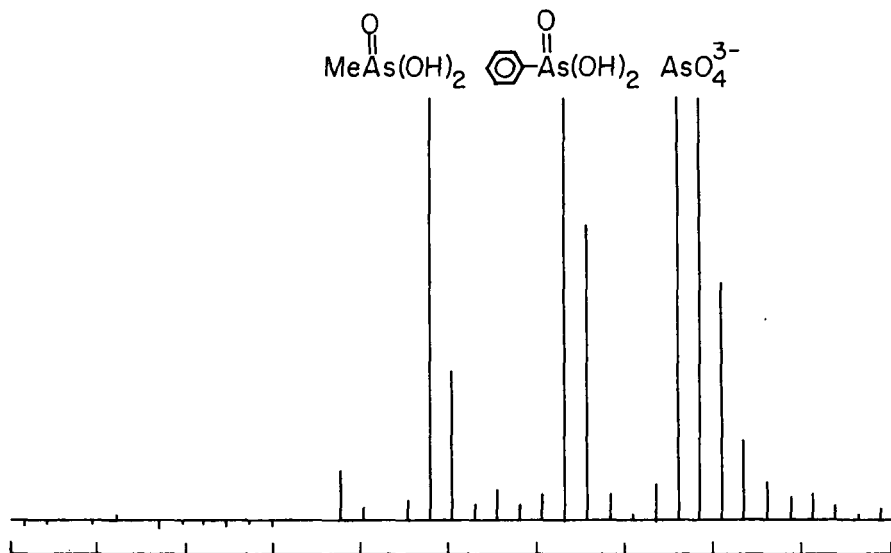
The methanol extract was purified by preparative HPLC (the area from 22 to 35 min. was collected, see Figure 1), lyophilized and dissolved in benzene. To this solution was added excess 3-methylcatechol and the reaction mixture was refluxed for 5 h and worked up to remove the excess 3-methylcatechol. A concentrated sample was subjected to GC-EIMS analysis to provide spectra and scan numbers (retention times) that were identical to the known samples of the 3-methylcatecholates of both methyl- and phenylarsonic acids (29). Additionally, the inorganic anion, arsenate (AsO_4^{3-}), was verified in a similar fashion (preparative HPLC of the region from 35.5-41 min) by preparation of the tris(trimethylsilyl-) derivative of the ammonium salt of arsenate and analyzing the purified extract by GC-EIMS. The organoarsenic compound (Figure 1) that elutes with the solvent front has not been as yet identified and further work is in progress to verify its structure.

We believe these identifications of the organoarsenic acids to be the first such molecular characterizations of trace organometallic compounds to be reported for any fossil fuel precursors and initiates the area of organometallic geochemistry, a field that has hithertofore been totally unexplored (30).

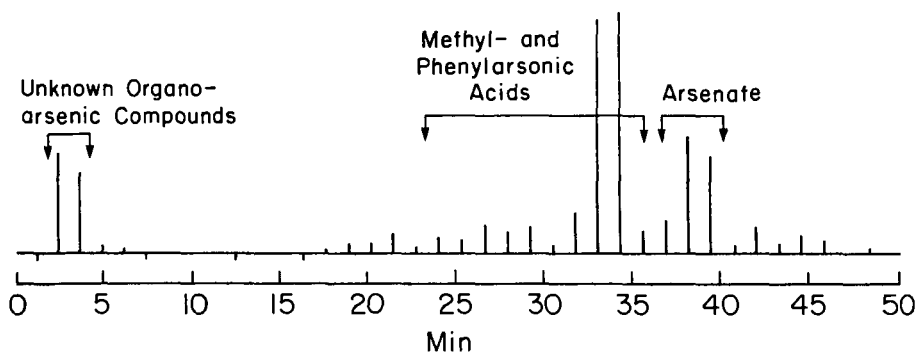
EXPERIMENTAL

The HPLC-GFAA instrumentation and analyses conditions have been described previously (see Literature Cited 25-27). The AA detection of arsenic was at 193.7 nm. The HPLC column was a Dionex anion exchange column with 0.2M $(\text{NH}_4)_2\text{CO}_3$ in aqueous methanol as the eluting solvent. The GC-MS analyses were accomplished using a Finnigan 4023 mass spectrometer system with a 30 m x 0.3 mm DB-5 (J and W) capillary column, conditions: 55° (3 min.) - 300°/min.

Standard



Methanol Extract of Green River Formation Oil Shale



XBL 8210-3116

Figure 1. The HPLC-GFAA analysis of Green River Formation oil shale extracted with refluxing methanol.

Reconstructed ion chromatograms and single ion chromatogram data was done with the INCOS Data System.

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