Lawrence Berkeley National Laboratory
Recent Work

Title

ORGANOMETALLIC GEOCHEMISTRY. 1. ISOLATION AND IDENTIFICATION OF ORGANOARSENIC COMPOUNDS FROM GREEN RIVER FORMATION OIL SHALE.

Permalink

https://escholarship.org/uc/item/5fp565xq

Author

Fish, R.H.

Publication Date

1982-11-01

eScholarship.org Powered by the California Digital Library
University of California

LBL-15060
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY
JAN 11 1983
LIBRARY AND
DOCUMENTS SECTION

Submitted to Organometallics

ORGANOMETALLIC GEOCHEMISTRY. 1. ISOLATION AND IDENTIFICATION OF ORGANOARSENIC COMPOUNDS FROM GREEN RIVER FORMATION OIL SHALE

Richard H. Fish, Raja S. Tannous, Wayman Walker, Carl S. Weiss, and Frederick E. Brinckman

November 1982

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

ENERGY AND ENVIRONMENT DIVISION

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-15060
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-15060

ORGANOMETALLIC GEOCHEMISTRY. 1. ISOLATION AND IDENTIFICATION OF ORGANOARSENIC COMPOUNDS FROM GREEN RIVER FORMATION OIL SHALE

Richard H. Fish, Raja S. Tannous,
and Wayman Walker

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Carl S. Weiss and Frederick E. Brinckman

Chemical and Biodegration Processes Group
Center for Material Science
National Bureau of Standards
Washington, DC 20234

November 1982

Organometallic Geochemistry. 1. Isolation and Identification of Organoarsenic Compounds from Green River Formation Oil Shale

Richard H. Fish*[1], Raja S. Tannous, and Wayman Walker

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Carl S. Weiss and Frederick E. Brinckman

Chemical and Biodegradation Processes Group
Center for Material Science
National Bureau of Standards
Washington, DC 20234

Summary:

A Green River Formation oil shale sample was crushed and extracted with refluxing methanol. The extract was analyzed by high performance liquid chromatography in combination with graphite furnace atomic absorption detection (HPLC-GFAA). The HPLC-GFAA analysis provided evidence for the identification of methyl- and phenylarsonic acids and arsenate. Further unequivocal evidence for the methyl- and phenylarsonic acids identification was provided by reaction of HPLC purified fractions of the total extract with excess 3-methylcatechol followed by capillary column gas chromatography - electron impact mass spectrometry (GC-EIMS) analysis. The GC-EIMS analysis demonstrated the presence of methyl- and phenylarsonic acids as there five-coordinate organoarsenic catecholates. The significant implication for the biogeochemical origin of these organoarsenic compounds will be discussed.

The molecular characterization of organometallic compounds which occur as natural products in fossil fuel precursors is becoming a significant area to research due to the importance of these compounds in emerging synthetic fuel processes as well as their impact on the environment.[2]

Recently, we identified, using a high performance liquid chromatograph coupled to a graphite furnace atomic absorption spectrometer as an element-selective detector (HPLC-GFAA), methyl- and phenylarsonic acids as well as arsenate in oil shale retort waters.[3] We also have analyzed the shale oils produced by pyrolysis of oil shale and have found that the above-mentioned organoarsonic acids also occur, but in association with iron-containing macro-molecules with molecular weights in the range of 2,000-4,000 daltons.[4a,b]

In order to discern whether these compounds were natural products in the precursor of the shale oil and the retort waters or were formed during pyrolysis, we examined a Green River Formation oil shale. Oil shale from the Green River Formation is a fine-grained sedimentary rock, which contains appreciable quantities of organic material. It consists of three fractions - kerogen, bitumen and an inert substance. Kerogen and bitumen, which constitutes the organic material, generally are regarded as biogeochemical fossil products, emanating largely from lipid fractions of ancient algae and forming the ubiquitous oil source matrix in shales.[5]

The Green River Formation oil shale sample (10 g) was crushed and Soxhlet extracted with 500 mL of methanol for 48 hours. This effectively removed about 20% of the total arsenic contained in this oil

shale.[6] Following evaporation (25 mL) and filtration, we speciated the extract by HPLC, using a Dionex anion exchange column with 0.2M ammonium carbonate in water/methanol (85:15) as the eluting solvent. The arsenic compounds were detected via automatic GFAA analysis at 197.3 nm.[2,3]

Figure 1 gives the arsenic-specific chromotogram of the compounds we identified as methylarsonic acid, phenylarsonic acid, and arsenate, based on retention times of the authentic arsenic compounds.[7] An unknown neutral organoarsenic compound eluted with the solvent front.[8]

We recently have studied the reactions of methyl- and phenylarsonic acids with substituted catechols, and established that they provide five-coordinate organoarsenic catecholates.[9] Since many of these organoarsenic catecholates could be gas chromatographed on fused silica capillary columns and characterized by electron impact mass spectroscopy (GC-EIMS), we decided to apply this derivitization technique for the unequivocal identification of methyl- and phenylarsonic acids present in the oil shale extract.

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[10] 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.

Figure 2(A) shows the reconstructed ion chromatogram of the two standards, 3-methylcatecholates of methyl- and phenylarsonic acids, and

the single ion chromatograms show pertinent fragments of interest at m/e 197 and 212 for the methylarsonic acid derivative (Figure 2 B,C) and m/e 197 and 274 for the phenylarsonic acid derivative (Figure 2 B,D). Figure 3(C) shows the region we purified by HPLC containing the organoarsonic acids, which were derivatized, and the expanded sections of this chromotogram containing the organoarsenic catecholates with the important ions, m/e 197, 212 and 274, clearly evident for the 3-methylcatecholates of methyl- (Figure 3 A) and phenylarsonic (Figure 3 B) acids. 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 for ions at m/e 207, 343, and 358.[11] The organoarsenic compound(s) that elutes with the solvent front (Figure 1) has not been as yet identified and further work is in progress to verify its structure.[8]

We believe these identifications of the organoarsonic 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.

The implications are that these organoarsonic acids are natural products and hence have a biogeochemical origin in the oil shale taphonomy process. It is also interesting to note that no examples of biophenylation have been reported, whereas biomethylation of arsenic compounds is a well known reaction.[12] How the phenylarsonic acid forms will have to be answered with the examination of precursors to the oil

shale such as freshwater marine algal mats as well as other biogeochemical samples.

Finally, the fact that these organoarsonic acids are released upon oil shale pyrolysis has important implications in the various synthetic fuel processes where the role of organometallic compounds in poisoning process catalysts and contribute to environmental problems is paramount.

Acknowledgements

The work at LBL was supported by the Assistant Secretaries of Fossil Energy and Oil, Gas and Shale Technology, and the Bartlesville Energy Technology Center (Project Manager, Dexter Sutterfield) of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. A portion of the NBS study was supported by the NBS Office of Standard Reference Materials. C.S.W. was a National Research Council-National Bureau of Standards Postdoctoral Research Associate (1980-82).

References

(1) Author to whom correspondence should be addressed.

(2) Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy-Related Processes, Brinckman, F.E. and Fish, R.H., editors, National Bureau of Standards Special Publication 618 (1981).

(3) Fish, R.H., Jewett, K.L., and Brinckman, F.E., Environ. Sci, and Tech. 1982, 16 174 and references therein.

(4) a) Brinckman, F.E., Weiss, C.S., and Fish, R.H., in: "Chemical and Geochemical Aspects of Fossil Energy Extraction," Yen, T.F. ed., Ann Arbor Science

(1982).

b) Weiss, C.S., Parks, E.J., and Brinckman, F.E., in: Arsenic: Industrial, Biomedical, and Environmental Perspectives, Lederer, W.H. and Fensterheim, R.J., Eds., Van Rostrand-Reinhold Co., New York (1982).

(5) Yen, T.F., Chilingarian G.V., Ed., Developments in Petroleum Science, Elsevier, Amsterdam, 1976; Vol. 5.

(6) The Green River oil shale sample from Anvil Points, CO (NBS Standard Reference Material) was found to contain approximately 20 ppm of total arsenic.

(7) See Reference 2, p. 197.

(8) We examined this material, after preparative HPLC isolation, on a C-18 reverse phase HPLC column with methanol as solvent and determined that the compound(s) in Figure 1 eluting at the solvent front was not triphenylarsine or triphenylarsine oxide. It might possibly be a mixed methyl- and phenylarsine and we are in the process of trying to determine the identity of these neutral organoarsenic compounds.

(9) Fish, R.H. and Tannous, R.S. Organometallics 1982, 1 1238.

(10) The GC-MS analyses were run on a Finnigan 4023 mass spectrometer system with a 30 m x 0.3 mm DB-5 (J&W) capillary column, conditions: 55° (3 min.) - 300°C at 4°/min. Data analysis and preparation were performed using the INCOS Data system.

(11) Butts, W.C. and Rainey, Jr., W.T., .Anal Chem. 1979, 43 538.

(12) McBride, B.C., Merilees, H., Cullen W.R. and Pickett, W., ACS Symposium Series 82 p94 (1978) Organometals and Organometalloids Occurrence and Fate in the Environment, Brinckman, F.E. and Bellama, J.M. editors.

Figure Captions

Figure 1 The HPLC-GFAA analysis of Green River Formation oil shale extracted with refluxing methanol. The AA detection of arsenic was at 193.7 nm. The HPLC column was a Dionex anion exchange column with 0.2M $(NH_4)_2CO_3$ in aqueous methanol as the eluting solvent. The bracketed areas were isolated by preparative HPLC.

Figure 2 GC-EIMS analysis of the 3-methylcatecholates of methyl- and phenylarsonic acids. (A) Reconstructed ion chromatogram of known methyl- and phenylarsonic acids derivatives of 3-methylcatechol. (B) Selected ion chromatogram showing m/e 197 for each derivative. (C) Selected ion chromatogram for methylarsonic acid-3-methylcatecholate at m/e 212. (D) Selected ion chromatogram for phenylarsonic acid-3-methylcatecholate at m/e 274.

Figure 3 GC-EIMS analysis of the derivatized, HPLC purified, methanol extract. (A) Selected ion chromatograms near Scan 1137 for m/e 197 and m/e 212 confirming the identification of the 3-methylcatecholate of methylarsonic acid in the expanded reconstructed ion chromatogram. (B) Selected ion chromatograms near Scan 2030 for m/e 197 and m/e 274 confirming the identification of the 3-methylcatecholate of phenylarsonic acid in the expanded reconstructed ion chromotogram. (C) Reconstructed ion chromatogram of HPLC purified methanol extract with arrow on left designating methylarsonic acid-3-methyl catecholate and arrow on right designating phenylarsonic acid-3-methyl catecholate.

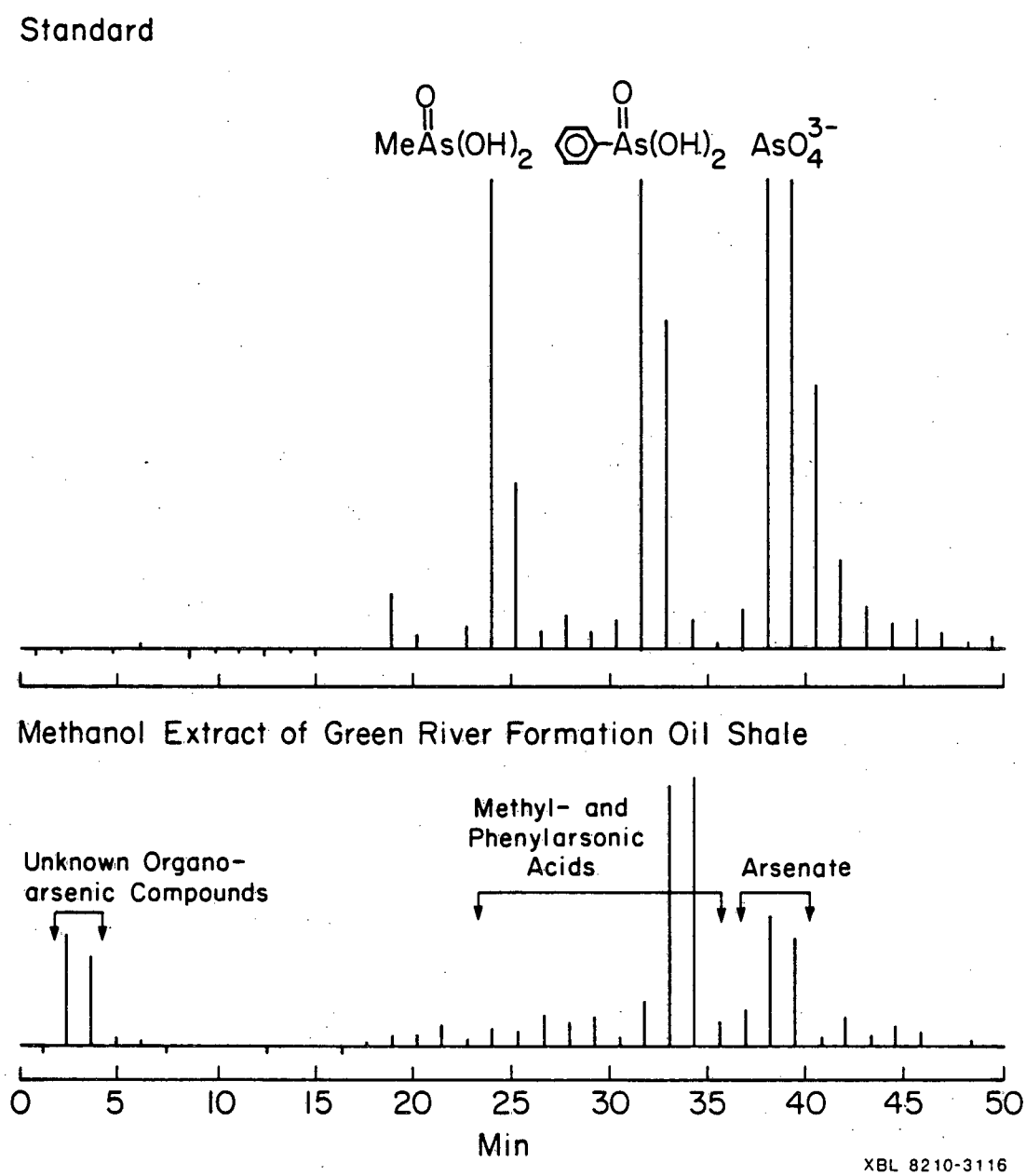
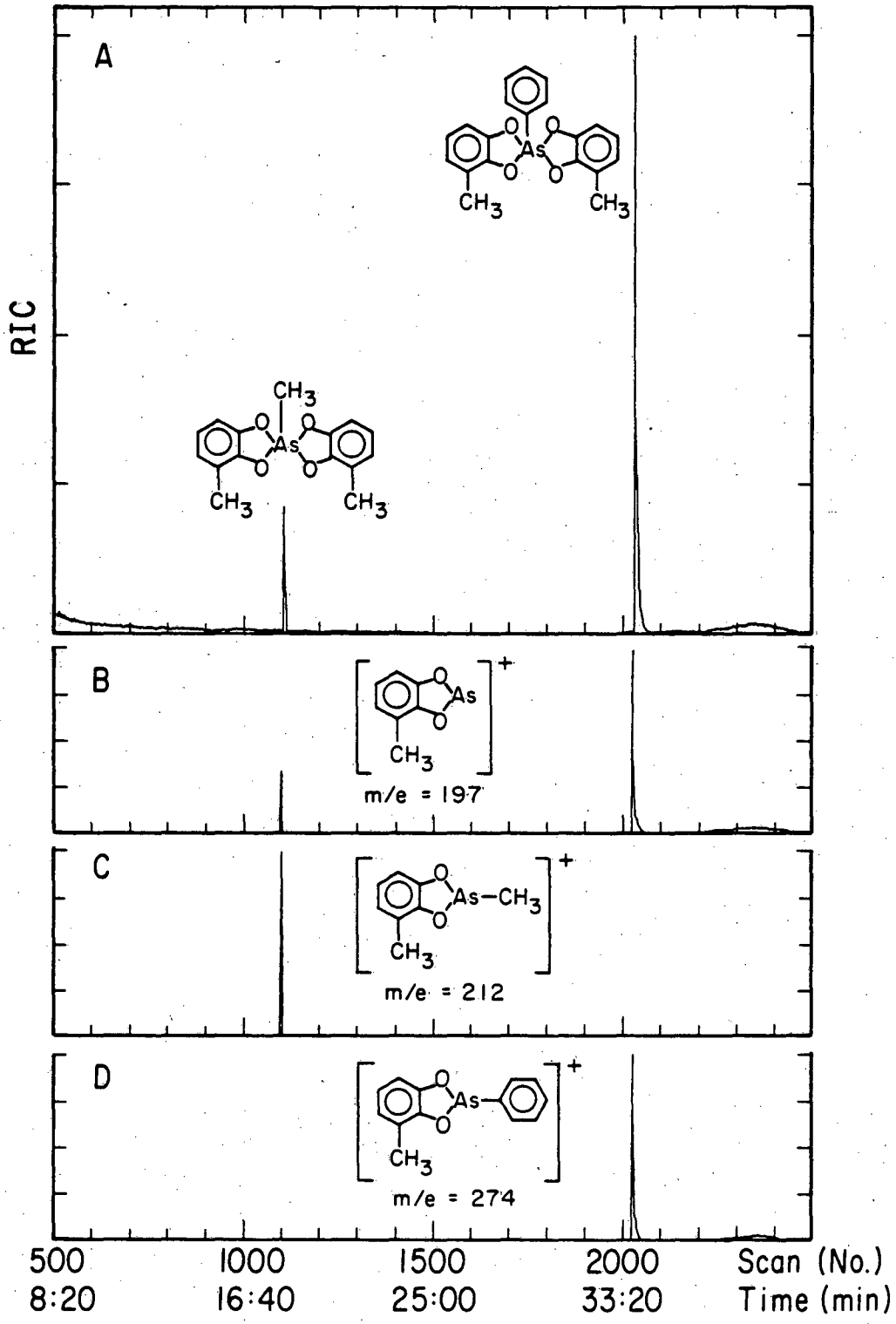

Standard
MeAs(OH)2
As(OH)2
AsO4 3-
Methanol Extract of Green River Formation Oil Shale
Unknown Organo-arsenic Compounds
Methyl- and Phenylarsonic Acids
Arsenate
0
5
10
15
20
25
30
35
40
45
50
Min
XBL 8210-3116

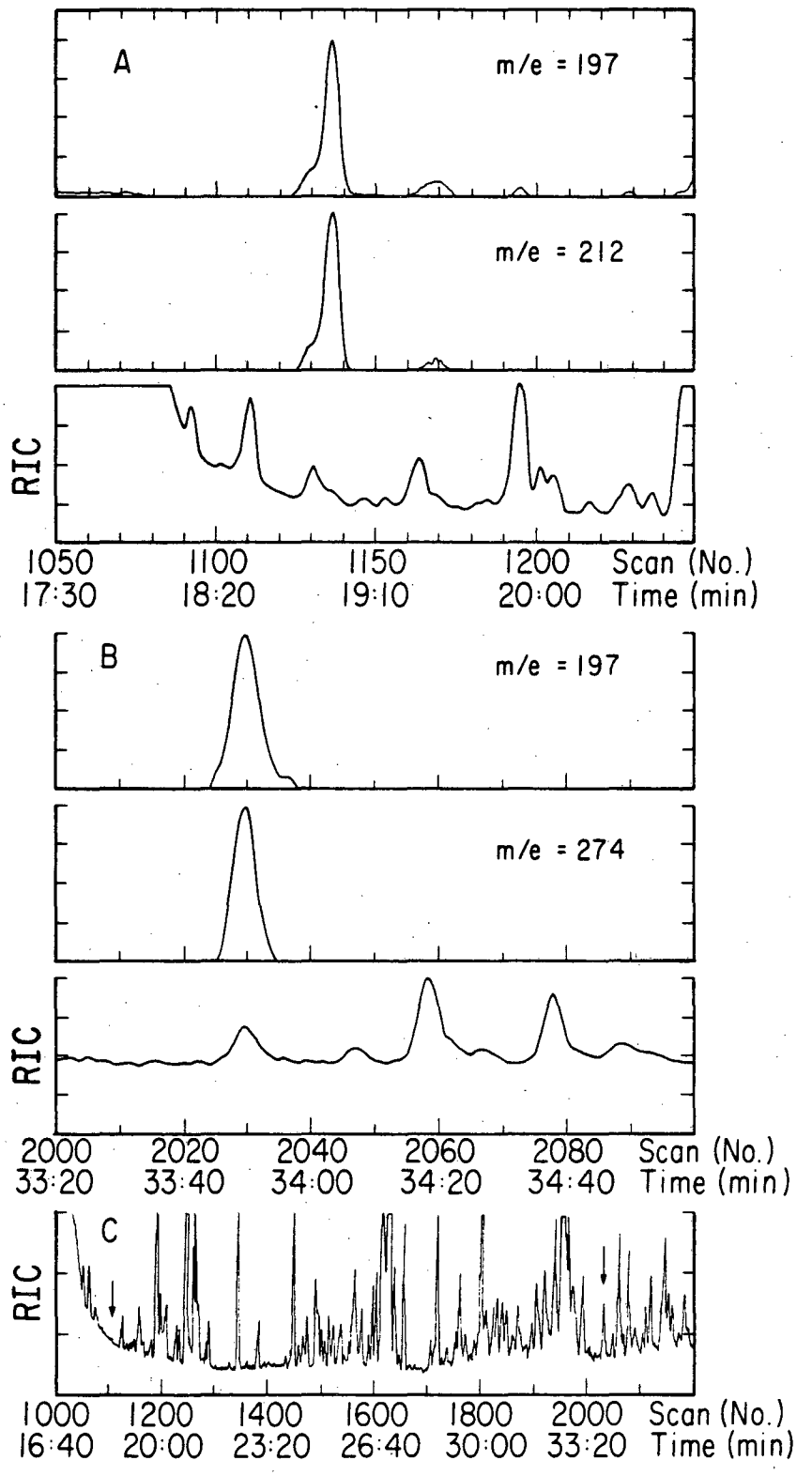
Figure 1

Figure 2



XBL 828-10938a

Figure 3



XBL 828-10939a

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720