

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

MONTHLY PROGRESS REPORT FOR OCTOBER - THE PARTITIONING OF MAJOR, MINOR AND TRACE ELEMENTS DURING SIMULATED IN SITU OIL SHALE RETORTING

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1979-11-01



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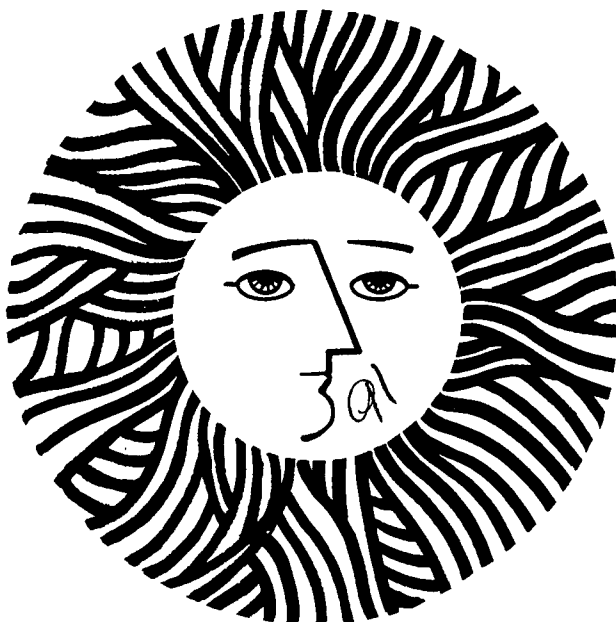
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November 9, 1979

TO: Art Hartstein

FROM: Phyllis Fox and Richard Fish

RE: Monthly Progress Report for October  
The Partitioning of Major, Minor and Trace Elements  
during Simulated In Situ Oil Shale Retorting  
LBID-135

Navy Core Project

Characterization studies of two cores from the Naval Oil Shale Reserve No. 1 are being carried out in a joint program with LETC. These cores have been composited (280 samples) vertically based on the retorting technology likely to be used in each zone, pulverized and characterized chemically. X-ray diffraction analyses, Fischer Assays and major, minor and trace element analyses have been completed on both cores. During the past month, these data were reduced, quality control checks performed and work continued to develop statistical analysis packages and plotting routines to analyze the resulting data.

Mass Balance Studies

Elemental mass balance studies of 23 runs of the LETC controlled-state retort and LLL's 125-kg and 6000-kg retort for 52 major, minor and trace elements have been completed and work is in progress to analyze and interpret the resulting data. Experiments have been initiated to determine the origin of As, Se and other trace elements in in-situ retort water. It is hypothesized that these elements are incorporated into the retort water by solubilization from raw shale and shale oil.

Weighted quantities of raw oil shale and of shale oil are being mixed with fixed volumes of  $\text{NH}_4\text{HCO}_3$  solution for time periods and at temperatures which simulate in situ retorting conditions. The aqueous phase will be separated from the solids and oil and analyzed for trace elements.

#### Organometallic Speciation Studies

Previous work revealed that a significant fraction of the As, Se and Zn exists in the organic fraction of oil shale by-product waters. Work is in progress to identify the chemical forms of these elements using high performance liquid chromatography (HPLC), gas chromatography (GC), mass spectrometry (MS), Zeeman atomic absorption spectroscopy (ZAA) and other techniques.

Work this month focused on the identification and quantification of arsenic compounds in Heater Treater Water (HTW) from Room 6 of Occidental's Logan Wash site. We believe these compounds are present in the methylene chloride extracts of both the acidic ( $\sim 2$  ppm) and basic ( $\sim 0.5$  ppm) components of HTW samples. The HTW samples were extracted with methylene chloride at pH 2.0 and 9.2 and eluted on a florisil column with hexane, hexane-methylene chloride, methylene chloride and methylene chloride-methanol. HPLC was used to identify fractions with products, and these were then analyzed by capillary gas chromatography in combination with a quadrupole mass spectrometer in the electron impact mode (GC-EIMS). The results of these analyses for the pH 9.2 extracts are summarized in Tables 1 and 2 and Figures 1 and 2. The hexane eluates provided the long chain alkenes and alkanes and the hexane-methylene chloride (50/50) eluates provided the heterocyclic aromatic bases. Carboxylic acids have been identified in the pH 2.0 extract and GC-EIMS analysis is in progress.

Work was initiated on another separation technique, the combination of HPLC with ZAA. Strong anion and cation exchange chromatography columns are being used to separate known arsenates, arsenites, alkylarsonic, arylarsonic and arsenic acids. The As content of these eluates will be determined by ZAA. If this technique is successful, it will be extended to Zn, Se and other toxic trace elements.

Work was also initiated to characterize toxic trace metals in retort waters by chelation followed by analysis using capillary gas chromatography in combination with chemical ionization (CI) and electron impact mass spectrometry (EI-MS). The ligand-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (HFOD), was used to remove inorganic and organometallic compounds from the HTW samples by refluxing in 50% ethanol and extraction into hexane. We are presently examining pure compounds of FOD by CI and EI-MS to facilitate identification of some metal species suspected as being present in retort waters.

Table 1. Alkanes and Alkenes found  
in pH 9.2 Methylene Chloride Extract of Heater Treater Waters by  
GC-EIMS<sup>a</sup>

Scan Number <sup>b</sup>	Formula	Compound <sup>c</sup>
1359	C <sub>14</sub> H <sub>28</sub>	1-Tetradecene
1442	C <sub>14</sub> H <sub>28</sub>	Octylcyclohexane
1662	C <sub>16</sub> H <sub>32</sub>	1-Hexadecene
1933	C <sub>18</sub> H <sub>36</sub>	1-Octadecene
2179	C <sub>16</sub> H <sub>34</sub>	Hexadecane

- a) Finnigan 4023 equipped with a 30m x 0.25 mm glass capillary column coated with OV 101. Programmed from 40-250<sup>o</sup> at 5<sup>o</sup>/min.
- b) See Figure 1 for scan number (MS) assignment of a particular peak for the GC analysis.
- c) From the file of known compounds and the best fit for the mass spectrum.

Table 2. Substituted Pyridines and  
Quinolines found in pH 9.2 Methylene Chloride Extract of  
Heater Treater Water by GC-EIMS<sup>a</sup>

Scan Number <sup>b</sup>	Formula	Compound <sup>c</sup>
628	$C_8H_{11}N$	2,3,5-trimethylpyridine
772	-	Not assigned accurately
802	$C_{18}H_{13}ON$	2-pentan-1-onepyridine
815	-	Not assigned accurately
890	-	Not assigned accurately
901	$C_8H_{17}N$	1-ethyl-2-methylpiperidine
926	$C_9H_{19}N$	3-methyl-1,2-diisopropyl- aziridine
1050	-	Not assigned accurately
1108	-	Not assigned accurately
1183	$C_{10}H_9N$	2-methylquinoline
1202	$C_9H_{19}N$	Not assigned accurately
1279	$C_7H_{12}O$	Not assigned accurately
1401	$C_{11}H_{11}N$	2,4-dimethylquinoline

- a) Finnigan 4023 equipped with a 30m x 0.25 mm glass capillary column coated with OV101. Programmed from 40-250<sup>o</sup> at 5<sup>o</sup>/min.
- b) See Figure 2 for scan number (MS) assignment of a particular peak for the GC analysis.
- c) From data base of known compounds.



RIC  
09/17/79 13:37:00  
SAMPLE: COL CHRO XPT 1, HTW EXT  
RANGE: G 1.4918 LABEL: N 0. 4.0

DATA: FISHHTW1X9B #1  
CALI: CAL17SEP #1

SCANS 1200 TO 2500

798720.

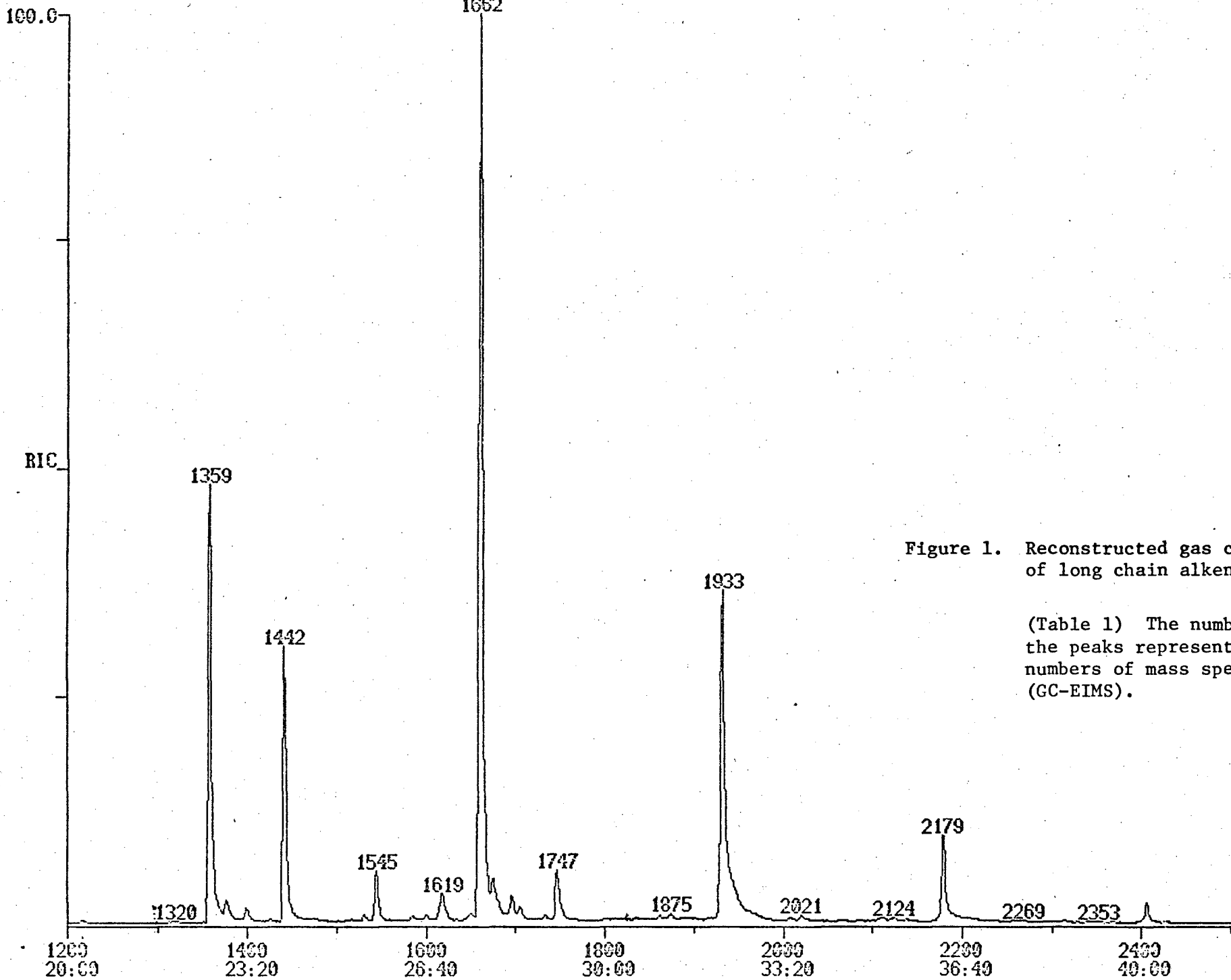


Figure 1. Reconstructed gas chromatogram of long chain alkenes

(Table 1) The numbers above the peaks represent scan numbers of mass spectrum (GC-EIMS).

RIC  
09/17/79 15:21:00  
SAMPLE: COL CHRO XPT 1. HTU EXT  
RANGE: G 400.2300

DATA: FISHHTU38\$ #1.  
ENHANCED ( 5B 2N 0T)

SCANS 400 TO 2300

LABEL: N G. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

14192.

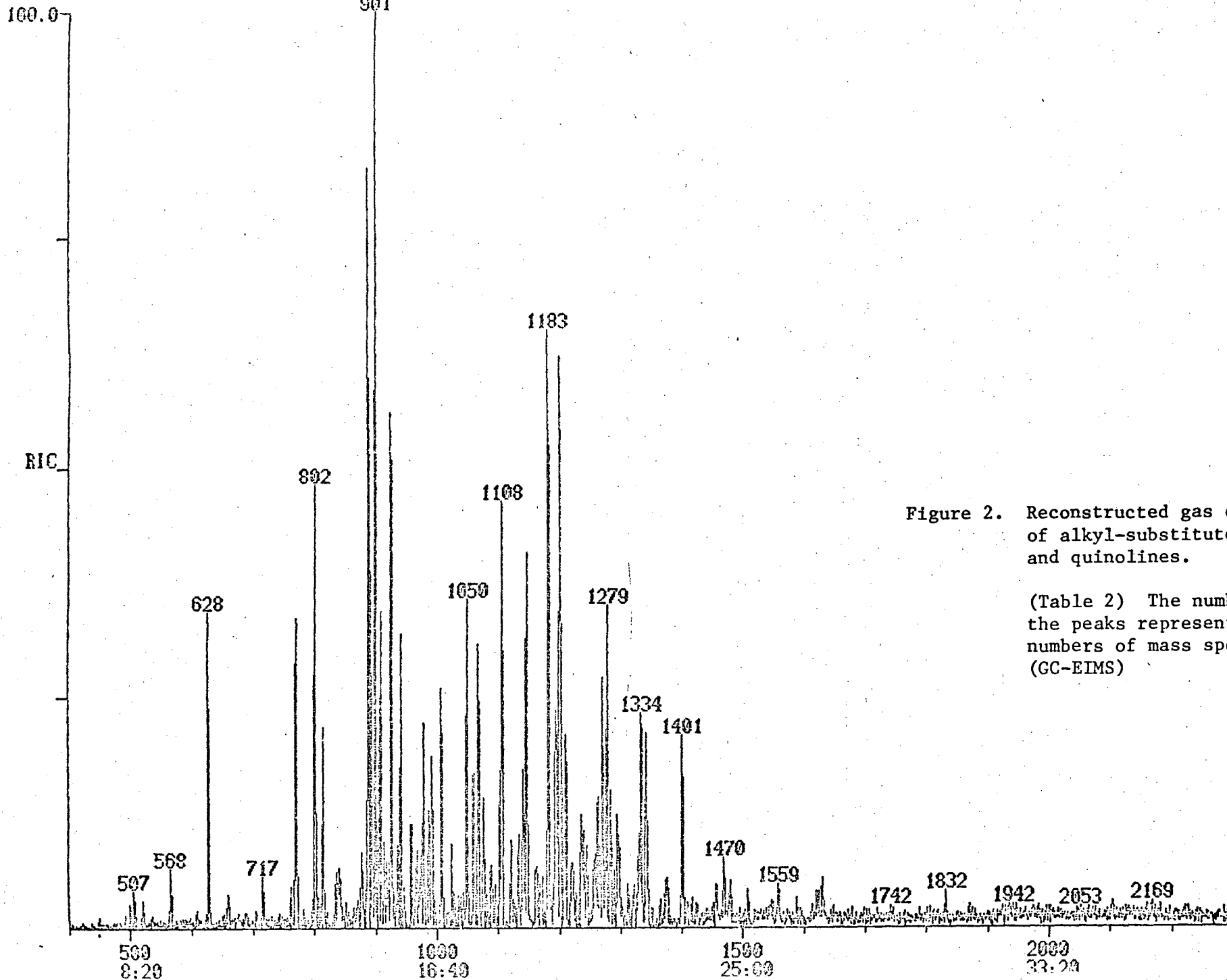


Figure 2. Reconstructed gas chromatogram of alkyl-substituted pyridines and quinolines.

(Table 2) The numbers above the peaks represent scan numbers of mass spectrum (GC-EIMS)

SCAN  
TIME

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