

Lawrence Berkeley National Laboratory

Recent Work

Title

FINGERPRINTING AND CHARACTERIZATION OF CARBOXYLIC ACIDS IN IN SITU OIL SHALE RETORT AND PROCESS WATERS BY CAPILLARY COLUMN GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Permalink

<https://escholarship.org/uc/item/2376p6kn>

Authors

Fish, R.H.

Newton, A.S.

Babbitt, P.

Publication Date

1981-06-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

RECEIVED
JUN 30 1981
LIBRARY
DOCUMENTS

Submitted to Fuel

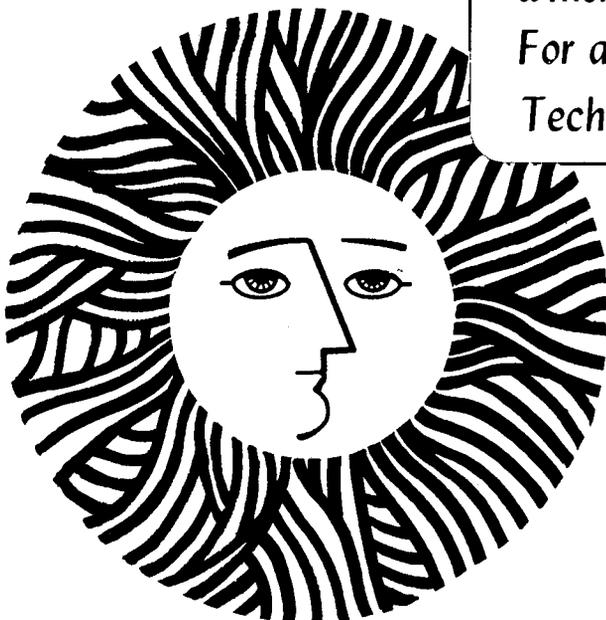
FINGERPRINTING AND CHARACTERIZATION OF CARBOXYLIC
ACIDS IN IN SITU OIL SHALE RETORT AND PROCESS WATERS
BY CAPILLARY COLUMN GAS CHROMATOGRAPHY-MASS
SPECTROMETRY

Richard H. Fish, Amos S. Newton and Patricia Babbitt

June 1981

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*



LBL-12430
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.

Address Correspondence to:

Dr. Richard H. Fish
Energy and Environment Division
18-121
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Manuscript prepared for:

Fuel

Fingerprinting and Characterization of Carboxylic
Acids in In Situ Oil Shale Retort and Process Waters by
Capillary Column Gas Chromatography-Mass Spectrometry

Richard H. Fish, Amos S. Newton and Patricia Babbitt
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

This work was supported by the Assistant Secretary for Fossil Energy,
Office of Oil Shale, Division of Oil, Gas and Shale Technology of the
U.S. Department of Energy under Contract W-7405-ENG-48.

Fingerprinting and Characterization of Carboxylic Acids in
In Situ Oil Shale Retort and Process Waters by Capillary
Column Gas Chromatography - Mass Spectrometry

Richard H. Fish^{*1a}, Amos S. Newton and Patricia C. Babbitt^{1b}

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

Six important in situ oil shale retort and process waters were analyzed for carboxylic acids by capillary column gas chromatography-mass spectrometry. A fingerprint or profile was obtained for Occidental's boiler blowdown process water, retort water and heater-treater process water; Geokinetics' retort water, Laramie Energy Technology Center's Omega-9 and 150 Ton retort waters. The results clearly show significant differences in that each retort or process water contains various mono-, di- and keto-aliphatic carboxylic acids. The Occidental retort and process waters contained normal monocarboxylic acids from C₂-C₁₃ and C₂-C₁₄, while the Geokinetics' retort water contained C₂-C₁₀ 150 Ton retort water C₂-C₁₀ and Omega-9 retort water C₂-C₁₄.

Variations among the retort waters and process waters were more important for the normal dicarboxylic acids. Interestingly, the Occidental retort and process waters contain no C₂-C₇ normal dicarboxylic acids; however, those from C₈-C₁₂ were present. The Omega-9 retort water had all normal

dicarboxylic acids, C₂-C₁₂, that were identified, while the 150 Ton sample contained only C₂ and C₄ dicarboxylic acids and the Geokinetics' sample C₂-C₄ and C₈-C₁₂.

A discussion of these results and their implication in the pyrolysis of oil shale kerogen will be presented.

INTRODUCTION

The oil shale retorting process consists of a pyrolysis of oil shale kerogen and bitumens at 500° thereby producing a shale oil and a retort water². The retort waters emanate from combustion, dehydration, and steam and moisture from added water used to mediate the pyrolysis temperature.

The pyrolysis of oil shale kerogen releases an array of organic compounds, many of which are potential ligands for complexation with trace metals associated with oil shale kerogens^{1a}. One of the more important potential ligands released or synthesized during pyrolysis are the carboxylic acids. This class of ligands has been studied extensively. For example, the carboxylic acids found in Green River Formation oil shale, (Eocene age), have been isolated and identified by a number of methods and groups³⁻⁹. In a similar manner, carboxylic acids, either synthesized or released during oil shale retorting, have not been studied to any significant extent¹⁰⁻¹³.

These latter studies have concentrated on the surface retorting processes and no comprehensive studies of carboxylic acids have been conducted on the in situ retorting processes^{1,11} (Table 1). In this paper, we compare the fingerprints or pro-

files of carboxylic acids isolated and identified in six important in situ oil shale retort and process waters that represent current technology.

RESULTS

Each retort or process water sample was treated in a similar fashion and this sample procedure was analogous to that reported recently by Riley et al.¹³. This entailed lyophilization of a 20 ml sample of the retort or process water, followed by methylation or butylation of the residue, and finally extraction of the resulting reaction mixture with benzene. The concentrated benzene layers were initially analyzed by capillary column gas chromatography using known methyl and butyl esters of carboxylic acids as a tentative indication of sample content. Unequivocal identifications of these carboxylic acids were obtained using capillary column gas chromatography in combination with electron impact mass spectrometry (GC-EIMS). The lower molecular carboxylic acids, from C₂-C₄, could only be detected and identified as their butyl esters not their methyl esters. This was due to the greater volatility and shorter retention times of the methyl esters of C₂-C₄ carboxylic acids, causing them to be masked by the solvent peak in the gas chromatograms.

The fingerprints of all the retort and process waters studied are shown in Figure 1 and the numbered methyl esters in Figure 1 are tabulated in Table 2. The methyl and butyl esters identified by GC-EIMS are tabulated in Table 3 and some were quantified by the internal standard method. Clearly, each retort or process water has a distinct fingerprint of carboxylic

acids with Occidental's retort and two process waters having similar profiles. The boiler blowdown process water contained n-carboxylic acids from C₂-C₁₄ and n-dicarboxylic acids from C₈-C₁₂ and various branched C₅ and C₆ carboxylic acids. Both the retort and the heater-treater process water had n-carboxylic acids from C₂-C₁₃ as well as C₈-C₁₂ n-dicarboxylic acids, but no C₅-C₆ branched carboxylic acids.

The LETC 150 Ton retort water sample had n-carboxylic acids from C₂-C₁₀ and only C₂ and C₄ n-dicarboxylic acids, while the LETC's Omega-9 retort water had all identified n-carboxylic acids and n-dicarboxylic acids (C₂-C₁₄). The Geokinetics' retort water contained n-carboxylic acids C₂-C₁₀ and dicarboxylic acids C₂-C₄ and C₈-C₁₄.

Interestingly, the retort waters contained few branched carboxylic acids and only the Omega-9 retort water had a keto-substituted carboxylic acid - 4-ketopentanoic acid. Moreover, only the Occidental boiler-blowdown process water and the Omega retort water contained a cyclic aliphatic carboxylic acid - cyclohexanecarboxylic acid.

All the aromatic carboxylic acids identified were present in the Omega-9 retort water sample, while the other samples contained benzoic acid or a substituted benzoic acid. The only benzenedicarboxylic acid identified, 4-methyl-1,2-benzenedicarboxylic acid, was found in LETC's 150 Ton and Omega-9 retort waters. There were other carboxylic acids that could not be identified due to their very low concentrations, which caused their mass spectra to be difficult to interpret.

DISCUSSION

Previous investigations on Green River Formation Oil Shale identified the following carboxylic acids: normal, C₅-C₃₂ (C₂₂ maximum); branched, C₅-C₂₂ (C₁₆); di, C₅-C₂₅ (C₁₄); keto, C₄-C₂₀ (C₆ and C₁₄); isoprenoid, C₁₄-C₂₂ (C₁₆), phenylalkenoic, C₇-C₁₈ (C₉) (see reference 7 and references therein). These investigations have provided insights into the Green River Formation kerogen structures and the relevant conclusions suggest a rather predominant aliphatic macromolecular cross-linking with lesser aromatic groups within the matrix. The pertinent finding of a decreasing relative abundance of isoprenoid acids, under the longer oxidation conditions used to isolate the carboxylic acids, and the dramatic increase of normal, and in particular dicarboxylic acids, substantiates these conclusions.

Alternatively, these mild oxidizing conditions^{6,7}, used to ascertain the structure of kerogen, may not be entirely comparable to the rather stringent conditions used to pyrolyze Green River Oil Shale, i.e., 500 to 1000°C in the presence of air or air/stream^{2,12}. A perusal of our results show definitively that the ranges of both normal and dicarboxylic acids are lower than those obtained under the mild oxidizing conditions of Burlingame and Simoneit^{6,7} and are devoid of isoprenoid acids. The latter result is consistent with the longer chemical oxidation conditions used by these workers^{6,7}, which showed a dramatic decrease in concentration of this class of carboxylic acids.

A better comparison of our results would entail looking at the range and results of previous analyses of oil shale retort waters¹⁰⁻¹³. A rather superficial study was done on a surface retort sample from the TOSCO II process¹⁰. The butyl esters of n-carboxylic acids identified were from C₂-C₈ with di-, branched and aromatic carboxylic acids not accounted for. In a more recent study on another surface retort process water, Parahoe retort water, n-carboxylic acids from C₇-C₁₀ and n-dicarboxylic acids from C₄ to C₁₄ were identified by GC-MS analysis¹³. The only published analysis of an in situ retort water was that of Ho et al.¹¹ who identified n-carboxylic acids from C₂ to C₁₀ in a LETC 150 Ton retort water.

Our results (Table 3) demonstrate the presence of a wider diversity of carboxylic acids in in situ oil shale retort and process waters than has previously been reported. Thus, dicarboxylic acids (C₂-C₁₄), branched carboxylic acids (C₅-C₈) a keto carboxylic acid and several substituted benzoic acids are present along with the previously known n-carboxylic acids (C₂-C₁₄). Moreover, the dicarboxylic acids, also recently identified for the first time in a surface retort water sample¹³, were dramatically different in the samples we analyzed. These differences (Table 3) are emphasized with the Occidental samples containing C₈-C₁₂, LETC 150 Ton C₂ and C₄, LETC Omega-9 C₂-C₁₄ and Geokinetic C₂-C₄ and C₈-C₁₂ dicarboxylic acids.

The n-carboxylic acids we were able to semiquantitate provided a maximum for the Occidental samples at C₈, as was the case for the LETC 150 Ton sample, while the Omega-9 sample peaked at

C₉ and Geokinetics' sample at C₇. We could not easily compare these results to the only other study of an in situ retort water, LETC's 150 Ton retort water¹¹, since the C₂-C₄ carboxylic acids (analyzed as butyl esters in our studies) were not quantified.

The lack of significant amounts of aromatic acids seems to be consistent with other results on Green River Oil Shale kerogen³⁻⁹, while the exact biogeochemical origin of our identified carboxylic acids is more tenuous. This is due to the fact that some of these carboxylic acids were probably formed during the oxidation of the oil shale kerogens and others such as the isoprenoid acids were degraded to lower molecular weight acids such as the C₂-C₄ carboxylic acids.

Another aspect of this study was to fingerprint the retort process waters and demonstrate the usefulness of these profiles for future environmental monitoring needs. It is important to note that these profiles (Figure 1) possibly represent the different operating conditions used in the retorting of oil shale kerogen and this is reflected, as stated before, in the dramatic differences of the dicarboxylic acids identified.

ACKNOWLEDGMENTS

We wish to thank Ms. Lisa Bowles and Ms. Laura Joseph for technical assistance. The work was supported by the Assistant Secretary for Fossil Energy, Office of Oil Shale, Division of Oil, Gas and Shale Technology of the U.S. Department of Energy under contract W-7405-ENG-48.

EXPERIMENTAL SECTION

Materials and Instrumentation

A 14% solution of boron trifluoride in methanol (Aldrich) was used for the methylation reactions and a saturated hydrogen chloride solution in butanol was used in the butylation reactions. Standard methyl esters of mono-, di-, and branched carboxylic acids for GC and GC-MS analysis were obtained from Analabs Inc., and Chem. Services Corp. Gas chromatographic analyses were performed on a Hewlett-Packard 5840 gas chromatograph equipped with FID detection and capillary column capabilities. The gas chromatography-mass spectrometry analyses were performed on a Finnigan 4023 in the electron impact mode with capillary column gas chromatographic capabilities and interfaced with the INCOS Data Collection and Reduction System.

Methods and Procedures

The six retort or process waters had been stored at 4°C and prior to use each sample was filtered through glass-wool and a 0.45 µm millipore filter. A sample of Geokinetics' retort water will be described as an example of the procedure used to derivatize the carboxylic acids: a 20 ml filtered sample of Geokinetics' retort water was frozen at -20°C and lyophilized to give a powder (0.45 g). The lyophilized sample, 0.45 g, was placed in 20 ml of a 14% boron trifluoride solution in methanol and refluxed for 5 hr. The excess boron trifluoride was decomposed by the addition of 20 ml of quartz distilled water and the reaction mixture was extracted thrice

with 10 ml portions of benzene. The benzene extracts of the methyl esters were concentrated to 1 ml (30x) by short-path distillation and then analyzed by glass capillary column (30 m × 0.25 mm, i.d., SP 2100) gas chromatography. The GC conditions were as follows: temperature programming - 70°C (4.5 min) to 265°C (3°/min) with the FID detector at 250°C. After capillary column gas chromatographic analysis, the retention time verifications of unknown methyl esters of acids were achieved by using standard methyl esters of mono-, di- and branched carboxylic acids. Further unequivocal verification of these tentative assignments was carried out by GC-MS analysis. The glass capillary column used was a 30m × 0.25 mm i.d. WCOT OV 101 with temperature programming from 45° for 2 min to 270° at 5.0°/min. The unknown methyl esters were matched (INCOS Data System) to methyl esters in the NBS mass spectrometry library data file. All compounds identified were matched at the 95% confidence level (fit and refit).

A similar procedure was used for the preparation and identification of the butyl esters of acetic, propionic and butyric acids except that hydrochloric acid was the catalyst. The methyl esters were quantified by the internal standard (IS) method (Figure 1), where a comparison of areas of the IS (C₁₇ n-carboxylic acid methyl ester) to the identified methyl ester gave a semi-quantitative value. The areas were read directly from the Hewlett-Packard programmed recorder.

REFERENCES

- 1 (a) A preliminary account of this work was presented at the 13th Oil Shale Symposium, Golden, CO, April 16-18, 1980. Fish, R. H., Proceedings of the 13th Oil Shale Symposium, 1980, 385.
(b) Department of Energy cooperative student researcher (1979-80).
- 2 Yen, T. F. and Chilingarian, G. V., ed, Developments in Petroleum Science, 1976, 5, Oil Shale, Elsevier Scientific Publishing Co., Amsterdam.
- 3 Lawler, D. L. and Robinson, W. E., Div. Petroleum Chem. Abstracts American Chem. Soc. April 1965, 10(1), 5.
- 4 Leo, R. F. and Parker, P. I., Science 1966, 152, 649.
- 5 Eglinton, G., Douglas, A.G., Maxwell, J. R., Ramsey, J. N., and Stallberg-Stenhagen, S., Science 1966, 153, 1133.
- 6 Burlingame, A. L. and Simoneit, B. R., Nature 1968, 218, 252.
- 7 Burlingame, A. L. and Simoneit, B. R., *ibid.* 1969, 222, 741.
- 8 Djuricic, M. V., Murphy, R. C., Vitorvic, D. and Biemann, K., Geochim. Cosmoch. Acta 1971, 35, 1201.
- 9 Philp, R. P., Brown, S., and Calvin, M., Energy Sources 1978 4, No. 2, 113.
- 10 Cook, E. W., Chem. Ind. 1971, 485.
- 11 Ho, C. H., Clark, B. R., and Guerin, M. R., J. Environ. Sci. Health 1976, All, 481 and references therein.

12. Wen, C. S., Yen, T. F., Knight, J. B., and Poulsen, R. E.,
172nd National Meeting ACS Division of Fuel Chem. 1976, Vol.
21, No. 6.
13. Riley, R. G., Shiosaki, K., Bean, R. M. and Schoengold, D. M.,
Anal. Chem. 1979, 51, 1995.

FIGURE LEGEND

Figure 1. Fingerprints of six in situ oil shale retort and process waters including Occidental's, Geokinetics', LETC's Omega and 150 Ton samples. The concentration differences should be noted with Occidental's retort and process waters and Geokinetics' retort water concentrated to a similar extent (30x), LETC's Omega-9 (60x) and 150 ton retort water samples (100x).

Table 1. Water types and sources and retort operating conditions for samples used to identify carboxylic acids

Water	Retort/ Process	Shale Source	Retorting Atmosphere	Retorting Temperature
SIMULATED IN-SITU RETORTS				
150-ton retort Water (Run 13)	LETC 150-ton/ modified in situ	Anvil Points, Colorado	air	816°C
FIELD IN-SITU RETORTS				
Omega-9 Retort Water	LETC Site 9/ true in situ	Rock Springs, Wyoming	air	(a)
Geokinetics Retort Water	Retort 16 true in situ	Book Cliffs, Utah	air	(a)
Occidental Retort Water	Retort 6 modified in situ	Logan Wash, Colorado	air/steam	(a)
Occidental Boiler Blowdown	Retort 6 modified in situ	Logan Wash, Colorado	air/steam	(a)
Occidental Heater-Treater	Retort 6 modified in situ	Logan Wash, Colorado	air/steam	(a)

(a) Field retorting temperatures are not accurately known due to corrosion problems with thermocouples. However, mineral analyses of spent shales from the Geokinetics and Occidental processes suggest temperatures may locally reach 1000°C.

Table 2

Designation of Methyl Esters Separated on a Glass Capillary Column and Correlated with Each Retort Water Fingerprint^a

Compound Number ^b	Compound Name	R.T. (min)
1	n-pentanoic acid	5.9
2	ethanedioic acid	6.2
3	2,3-dimethylbutanoic acid	6.7
4	2-ethylbutanoic acid	7.0
5	2-methylpentanoic acid	7.3
6	3-methylpentanoic acid	7.7
7	branched hexanoic acid	7.9
8	hexanoic acid	9.3
9	propanedioic acid	10.6
10	4-ketopentanoic acid	11.3
11	heptanoic acid	13.4
12	butanedioic acid	13.5
13	cyclohexanecarboxylic acid	14.0
14	methylbutanedioic acid	14.6
16	branched octanoic acid	15.4
19	benzoic acid	16.8
20	octanoic acid	18.4
21	pentanedioic acid	18.5
22	unidentified dicarboxylic acid	18.9
23	unidentified dicarboxylic acid	20.3
24	3-methylbenzoic acid	22.0
25	substituted methylbenzoic acid	22.4
26	nonanoic acid	23.4
27	unidentified branched carboxylic acid	23.6
28	hexanedioic acid	23.7
29	decanoic acid	28.3
30	heptanedioic acid	28.6
31	3,5-dimethylbenzoic acid	28.8
32	undecanoic acid	32.9
33	octanedioic acid	33.4
34	substituted methylbenzoic acid	35.2
35	dodecanoic acid	37.4
36	nonanedioic acid	37.8
37	4-methyl-1,2-benzene dicarboxylic acid	38.7
38	tridecanoic acid	41.6
39	decanedioic acid	42.0
40	undecanedioic acid	46.0
41	dodecanedioic acid	49.8
42	heptadecanoic acid (internal standard)	56.5

^a30 m x .025 mm SP 2100 glass capillary column (70°-265°, 3.0°/min after 4.5 min).

^bSee Figure 1 for compound number. Compounds numbered 15 and 17 in Figure 1 have been identified by GC-EIMS as α,β -unsaturated cyclic ketones.

Table 3

Identification of Normal and Branched Mono- and Dicarboxylic Acids; Keto, Cyclic and Aromatic Carboxylic Acids;
Found in Six In Situ Oil Shale Retort or Process Waters by GC-EIMS

Compounds	In Situ Oil Shale Retort or Process Waters						
	<u>n-Carboxylic Acids (ppm)</u>	<u>Occidental Boiler Blowdown</u>	<u>Occidental Heater-Treater</u>	<u>Occidental Retort Water</u>	<u>LETC 150 Ton Retort Water</u>	<u>LETC Omega-9 Retort Water</u>	<u>Geokinetic Retort Water</u>
C ₂		+	+	+	+	+	+
C ₃		+	+	+	+	+	+
C ₄		+	+	+	+	+	+
C ₅		+ (28.6)	+ (3.4)	+ (1.8)	+	+	+ (0.5)
C ₆		+ (45.0)	+ (10.2)	+ (9.0)	+ (0.7)	+	+ (3.0)
C ₇		+ (64.0)	+ (28.0)	+ (34.5)	+ (1.8)	+ (0.2)	+ (14.0)
C ₈		+ (72.4)	+ (48.9)	+ (54.6)	+ (3.6)	+ (0.9)	+ (9.5)
C ₉		+ (42.6)	+ (32.5)	+ (35.4)	+ 2.7	+ (1.0)	+ (4.1)
C ₁₀		+ (31.8)	+ (18.0)	+ (17.8)	+ (1.3)	+ (0.9)	+ (1.1)
C ₁₁		+ (8.0)	+ (2.8)	+ (2.9)	-	+ (0.2)	-
C ₁₂		+	+ (1.3)	+ (1.0)	-	+ (0.3)	-
C ₁₃		+	+	+	-	+	-
C ₁₄		+	-	-	-	+	-
<u>n-dicarboxylic acids</u>							
C ₂		-	-	-	+ (0.4)	+ (0.3)	+
C ₃		-	-	-	-	+ (0.4)	+ (0.2)
C ₄		-	-	-	+ (2.5)	+ (1.7)	+ (1.2)
C ₅		-	-	-	-	+ (0.7)	-
C ₆		-	-	-	-	+ (0.6)	-
C ₇		-	-	-	-	+ (0.4)	-
C ₈		+	+ (2.2)	+ (2.2)	-	+ (0.6)	+ (0.6)
C ₉		+	+ (2.7)	+ (3.0)	-	+ (0.8)	+ (0.7)
C ₁₀		+	+ (2.7)	+ (2.9)	-	+ (0.8)	+ (0.6)
C ₁₁		+	+ (2.2)	+ (2.7)	-	+	+ (0.52)
C ₁₂		+	+	+ (0.99)	-	+	+
C ₁₃		-	-	-	-	+	-
C ₁₄		-	-	-	-	+	-

Table 3 (continued)

<u>Branched Carboxylic Acids</u>	<u>Occidental Boiler Blowdown</u>	<u>Occidental Heater- Treater</u>	<u>Occidental Retort Water</u>	<u>LETC 150 Ton Retort Water</u>	<u>LETC Omega-9 Retort Water</u>	<u>Geokinetic Retort Water</u>
2-methylpentanoic Acid	+	-	-	+		+ (0.12)
3-methylpentanoic Acid	+	-	-	+	+ (0.14)	+
5-methylheptanoic Acid	+	-	-	-	+ (0.23)	+ (0.22)
2,3-dimethylbutanoic Acid	+	-	-	-	-	-
2-ethylbutanoic Acid	+	-	-	-	-	-
unidentified C ₆ Acid	+	-	-	-	-	-
unidentified C ₈ Acid	+	+	+ (4.1)	-	-	-
methylbutanedioic Acid	-	-	-	+ (0.89)	+ (0.51)	+
 <u>Keto-Substituted Carboxylic Acids</u>						
4-ketopentanoic acid	-	-	-	-	+ (1.09)	-
 <u>Cyclic Aliphatic Carboxylic Acids</u>						
cyclohexanecarboxylic acid	+	-	-	-	+	-
 <u>Aromatic Carboxylic Acids</u>						
benzoic acid	+	+	+ (2.7)	-	+	+
3-methylbenzoic acid	-	-	-	-	+ (0.19)	+ (0.89)
substituted benzoic acid	-	+	-	+	+ (0.38)	-
3,5-dimethylbenzoic acid	-	-	-	-	+ (0.12)	-
4-methyl-1,2-benzene dicarboxylic acid	-	-	-	+	+ (0.16)	-

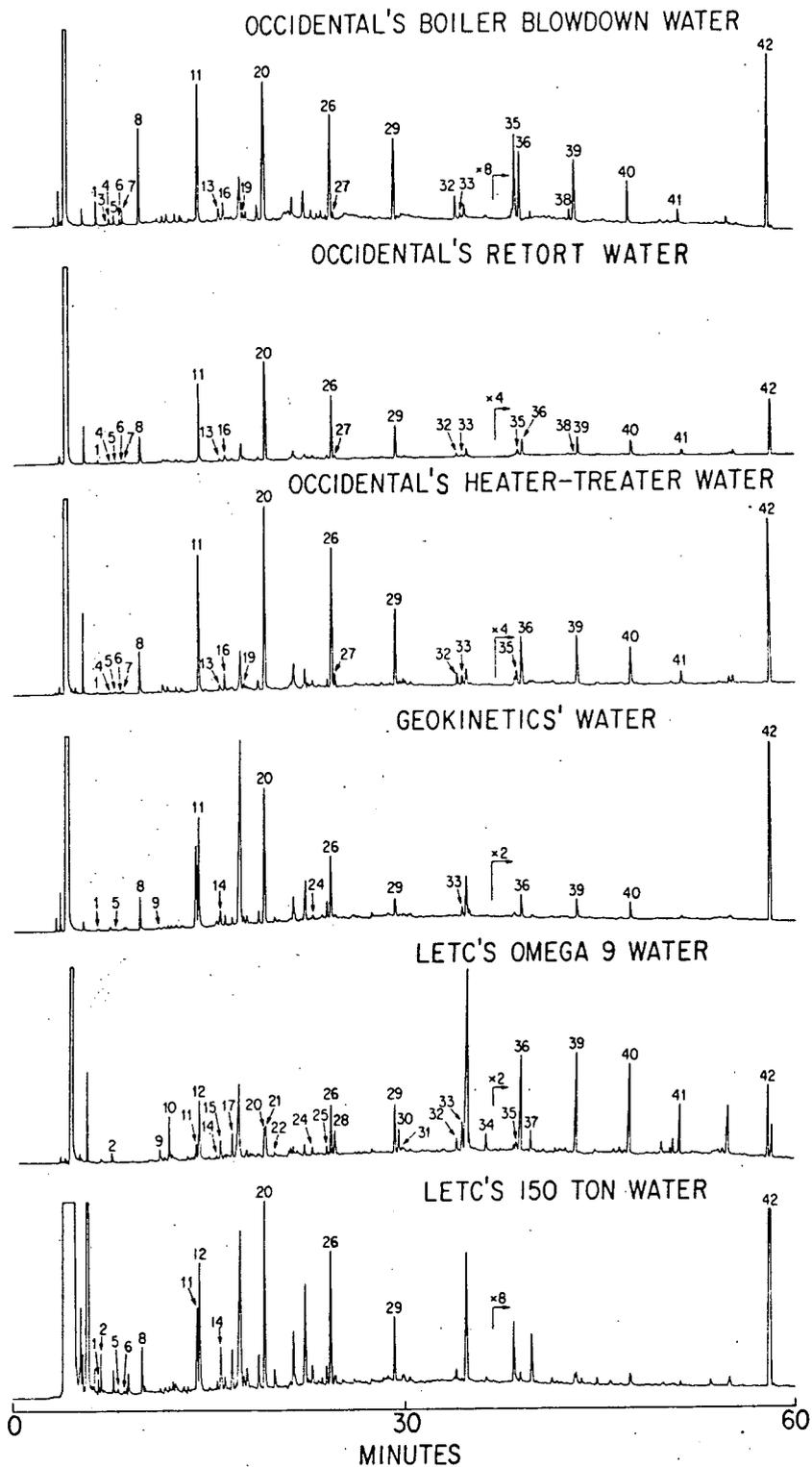


Figure 1

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