CONOCO

Technical Service Report

Continental Oil Company
Research and Development Department
Analytical Research Section
Ponca City, Oklahoma

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Report No. 242-79-350-2

To R. E. Laramy

From G. W. Keen

Date April 12, 1979

Subject THE GCMS ANALYSIS OF WATER SAMPLES FROM THE LAKE CHARLES REFINERY

OBJECT: To identify organic impurities in the effluent water samples

CONCLUSIONS:

Most of the components were typical of crude oils or heat exchanger fluids. Many aromatic compounds that were below the 10 ppb level were not listed.

The following priority pollutants were detected:

Component	Approximate Concentration
diethyl phthalate	7 ppb
dibutyl phthalate	4 ppb
fluoranthene	1 ppb
chrysene	16 ppb
dioctyl phthalate	4 ppb
benzofluoranthene	12 ppb
benzopyrene	7 ppb
phenol	10 ppb
Cyanide	

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Distribution: FK-EAS-RLH

DISCUSSION:

The quantitative data in this report have been back-calculated and reported on an original-sample basis. Several assumptions have been made. We have assumed 100% extraction efficiencies, no losses in the extraction and Kuderna-Danish concentration steps, 100% purging efficiencies, 100% trapping efficiencies and equal mass spectrometry response factors.

The concentrations of the extractable organics were calculated through the use of a D_{10}-anthracene internal standard. The solutions were injected with a sample size that would insure the detection of this internal standard and priority pollutants at the 5 ppb level. This obviously leads to extrapolation problems when the sample contains contaminants at the several-thousand ppb level. The reported concentrations, especially the high ones, should be considered order-of-magnitude estimates.

Therefore, the quantitative data contained in this report can only be used as a guide to the relative amounts of material in the samples analyzed. The nature of the samples and the intended use of the analytical data obtained do not justify the cost required to obtain strenuous quantitative results.

The EPA protocol methods call for reporting "between 10 and 100 ppb" or "greater than 100 ppb" for selected priority pollutants. We have chosen to depart from the EPA protocol-reporting procedure by including all organic materials and by reporting rough quantitative information about these contaminants so that intelligent decisions can be made about ways to clean up the plant effluents. If more accurate determinations are needed, cost and manpower estimates can be provided.

The Research Triangle Institute and the Gulf South Research Institute have been awarded a $750,000 contract to develop the Master Analytical Scheme (MAS) for the analysis of organics in water. Their procedures are expected to be incorporated into the new EPA protocol. It should be advantageous for us to wait for the MAS, since it is expected to utilize a glass capillary gas chromatography electron impact mass spectrometry data system (GCGCEIMSDS) finish.

Lake Charles Refinery Blank (Base-Neutral) 3/79

See Figures 1 and 2.

Scan #	ID	Concentration
751	butyl-capped nonionic	300 ppb
791	isooctanol	30 ppb
1036	isodecanol	10 ppb

Lake Charles Refinery Blank (Acids) 3/79

See Figure 3.

No significant components were observed.

Lake Charles Refinery Influent (Base-Neutral) 3/79

See Figure 4.

No significant components were observed.

Lake Charles Refinery Influent (Acids) 3/79

See Figure 5.

Scan #	ID	Concentration
2009	di-2-ethylhexyl phthalate	1 ppb

Lake Charles Refinery Effluent (Base Neutral) 3/79

See Figures 6 and 7.

Scan #	ID	Concentration
396	possible amino acid	25 ppb
527	butyl-capped nonionic	80 ppb
619	butyl-capped nonionic	26 ppb
696	tridecane	10 ppb
762	butyl-capped nonionic	1400 ppb
824	tetradecane	21 ppb
903	branched paraffin	13 ppb
946	pentadecane	24 ppb
1008	diethyl phthalate	7 ppb
1063	hexadecane	25 ppb
1120	branched paraffin	16 ppb
1174	heptadecane	24 ppb
1184	pristane	25 ppb
1215	biphenylcarbaldehyde	10 ppb
1279	octadecane	21 ppb
1292	branched paraffin	12 ppb
1306	dibutyl phthalate	4 ppb
1379	nonodecane	23 ppb
1479	eicosane	19 ppb
1553	fluoranthene	1 ppb
1578	heneicosane	14 ppb
1592	trimethylphenanthrene	5 ppb
1602	trimethylphenanthrene	7 ppb
1680	docosane	14 ppb
1700	methylpyrene	10 ppb
1777	terphenyl	10 ppb
1786	tricosane	12 ppb
1805	terphenyl	16 ppb
1896	tetracosane	11 ppb
1908	chrysene	16 ppb
2012	pentacosane	14 ppb
2018	dioctyl phthalate	4 ppb
2048	methylbenzanthracene	18 ppb
2134	hexacosane	10 ppb
2265	heptacosane	8 ppb
2278	benzopyrene	7 ppb
2373	benzofluoranthrene	12 ppb

Lake Charles Refinery Effluent (Acids) 3/79

See Figure 8 .

Scan #	ID	Concentration
524	butyl-capped nonionic	40 ppb
741	butyl-capped nonionic	60 ppb

Lake Charles Refinery Volatile Organics 3/79

See Figure 9.

Scan #	ID	Concentration
79	carbon dioxide	200 ppb
129	internal standard	20 ppb
193	branched C_6 olefin	10 ppb
310	hexane	210 ppb
541	internal standard	20 ppb
822	phenol	10 ppb

EXPERIMENTAL:

Base neutral and acid extracts were provided by the Separations Analysis Group.

The extracted base-neutral and acid concentrates were spiked with deuterated anthracene, which served as an internal standard.

These extracts were analyzed with the Finnigan 4023 GCMS-DS. The 30M SP2100 glass capillary column was programmed from 60° to 260°C at 6°/minute.

Internal standards of bromochloromethane and 1,4-dichlorobutane were added to 5 ml of water, the volatile organics were purged with helium, trapped in a silica gel-Tenax absorber tube at room temperature and driven onto the packed column injector by heating the Tenax tube rapidly to 180°C. The GC column was a 14" Carbowax (3%) on Chromosorb W followed by 4' Carbowax (.2%) on Carbopack C. The 1/4" thick walled glass column was held below room temperature during the thermal elution of the sample from the Tenax column. It was heated rapidly to 60°C, held there for .8 minutes, then programmed to 170°C at 8°/minute. It was held at 170° until the run was finished. Mass spectra were recorded at 1.1 second intervals.

REFERENCES:

File of GCMS data: G213A-217A, G219A, G241A,B

FIGURE 1

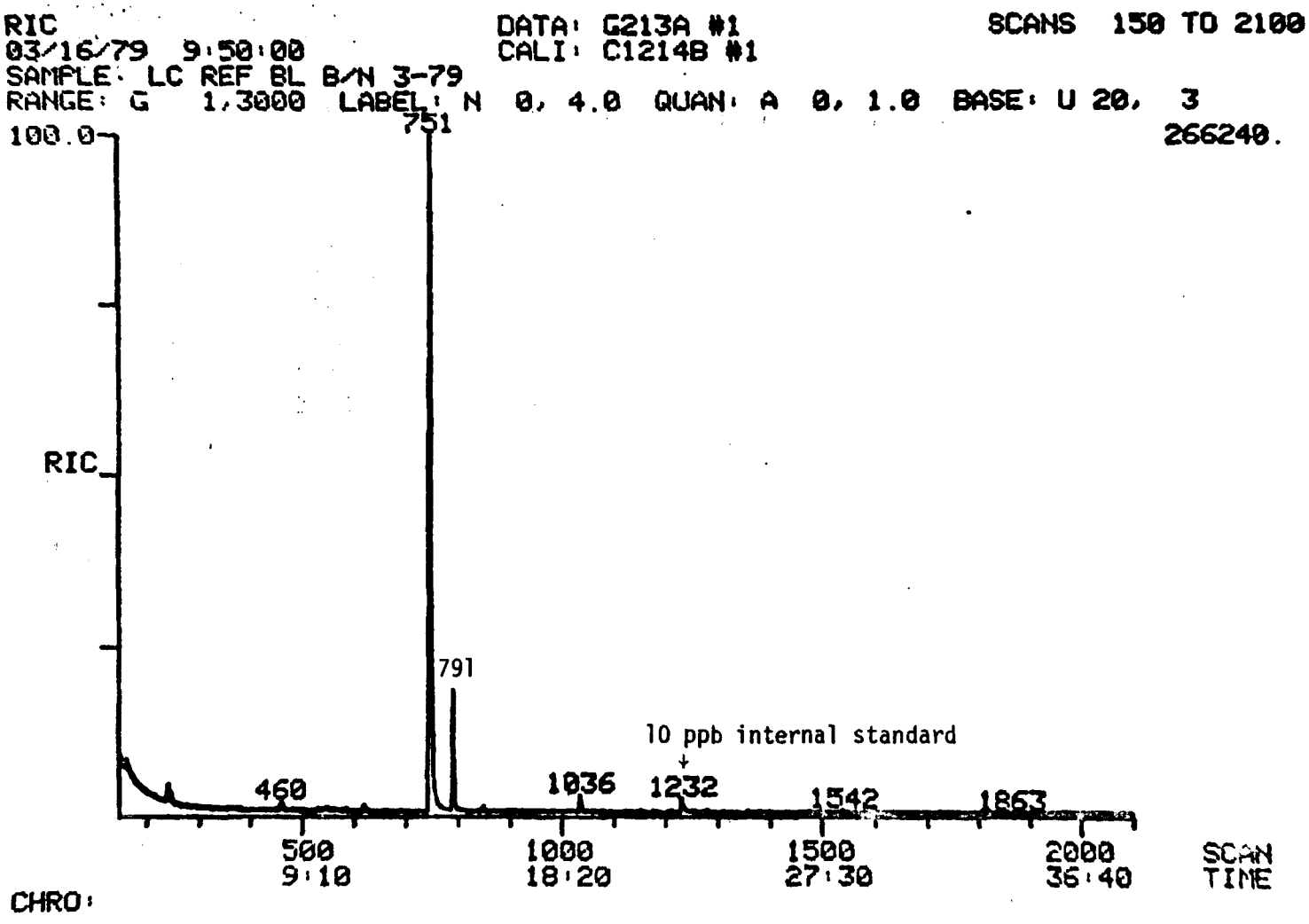


FIGURE 2

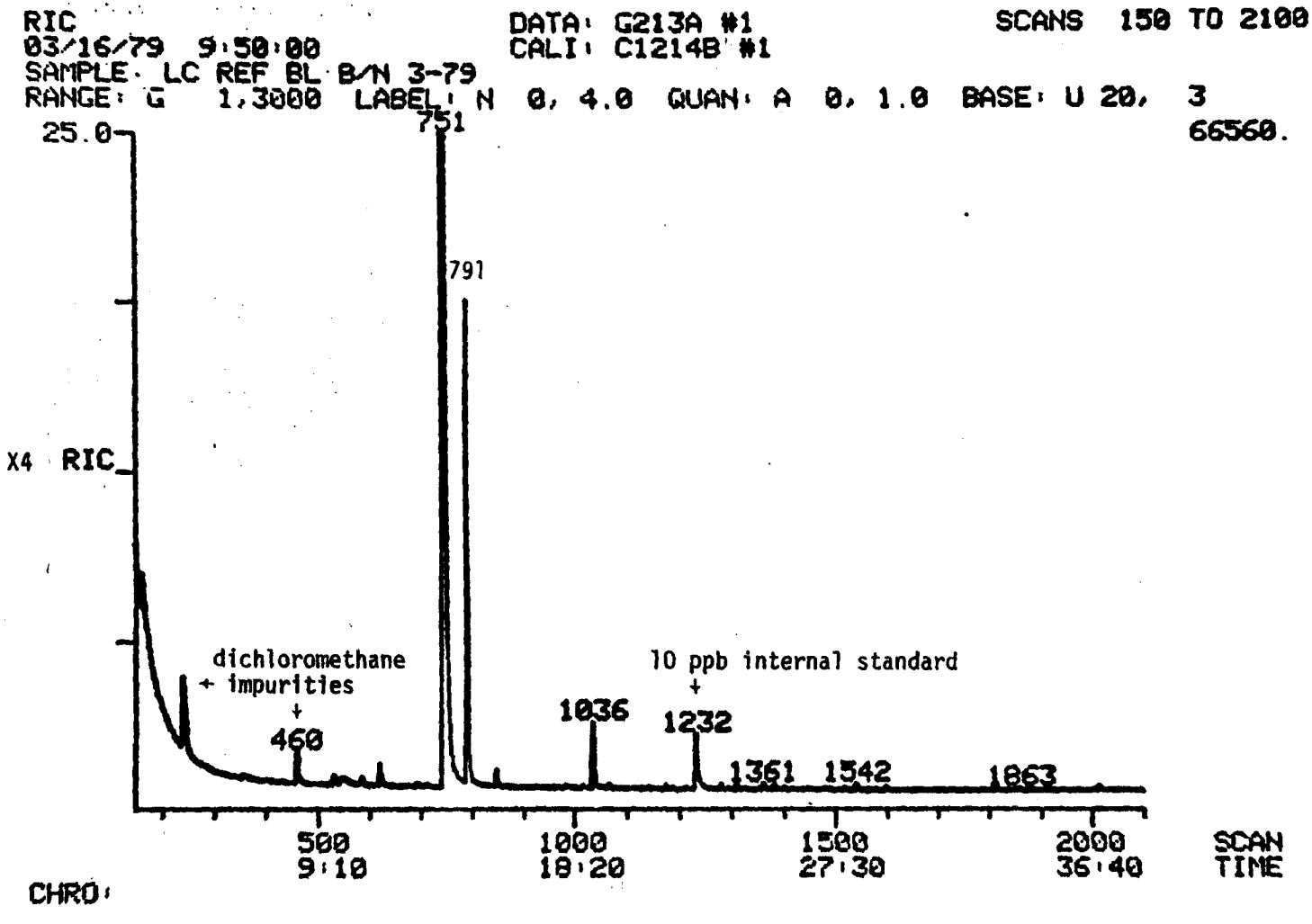
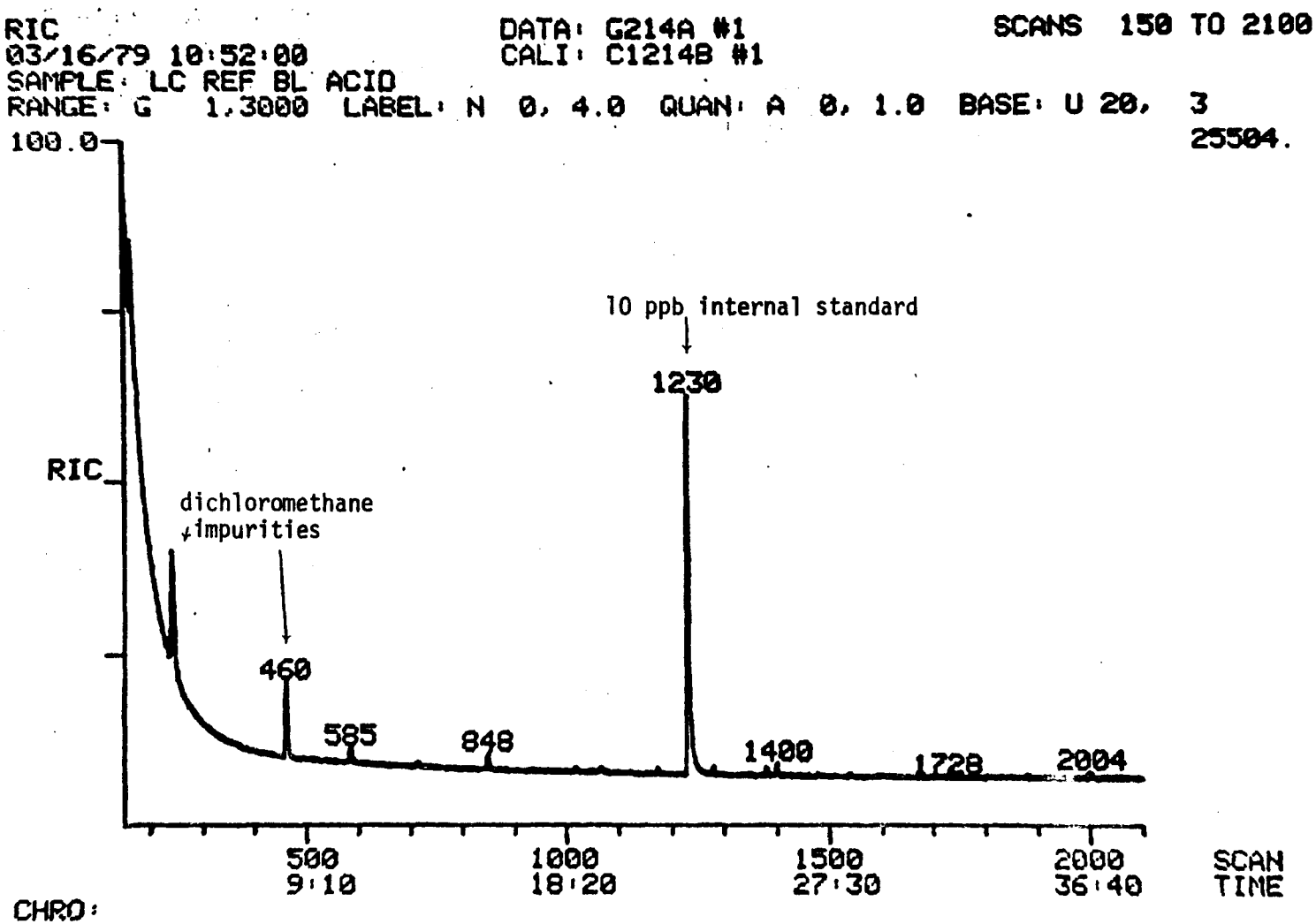


FIGURE 3



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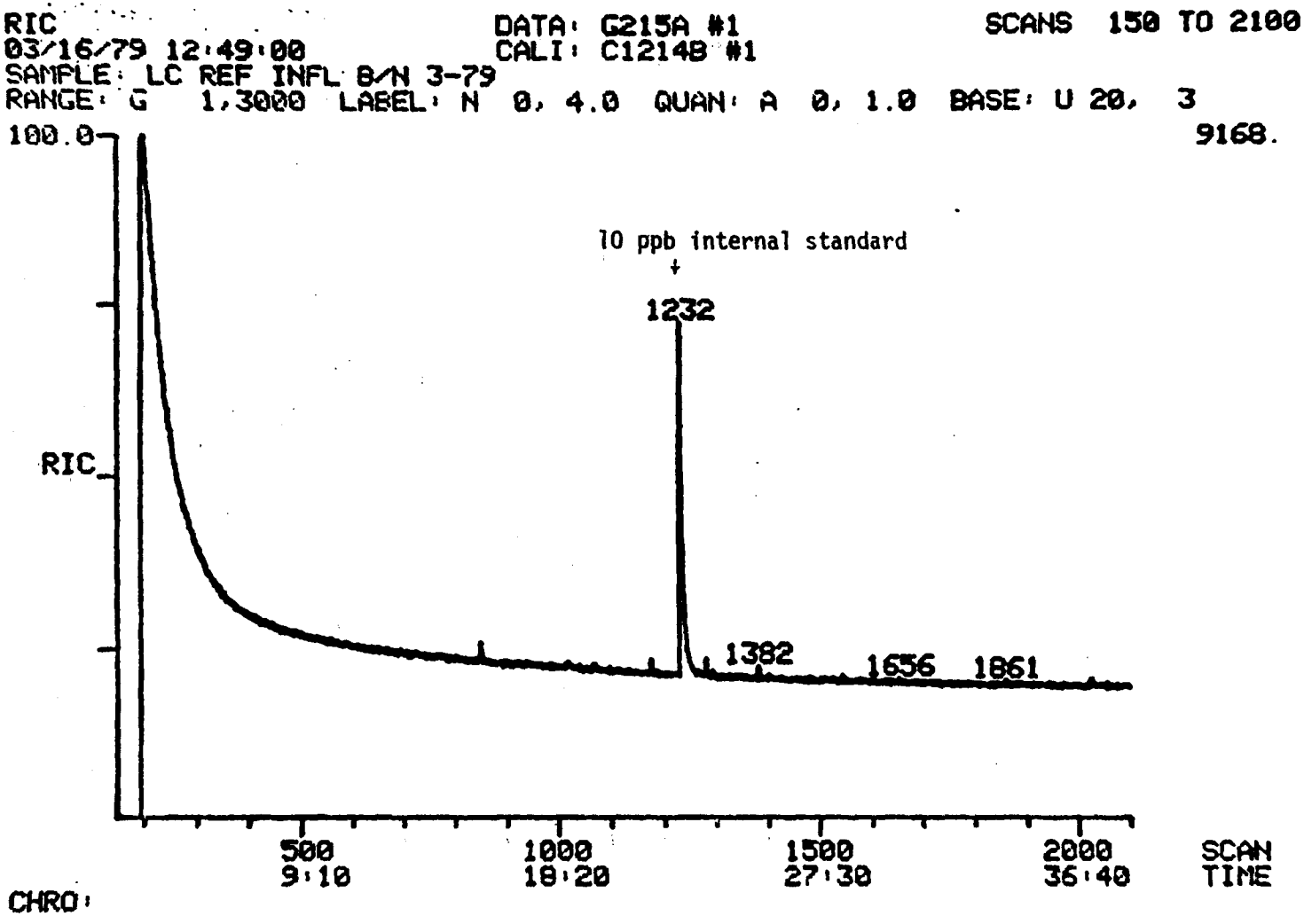

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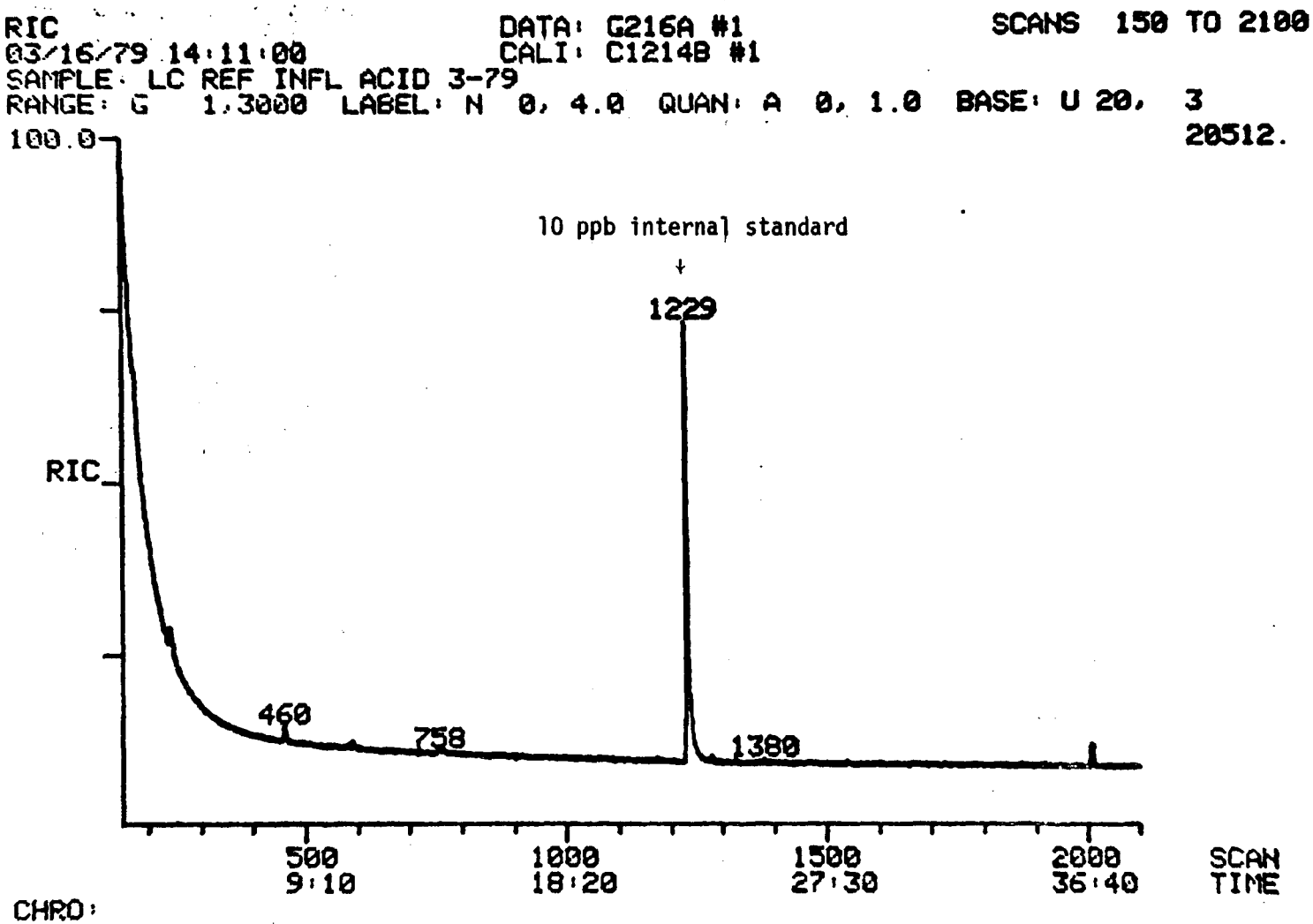
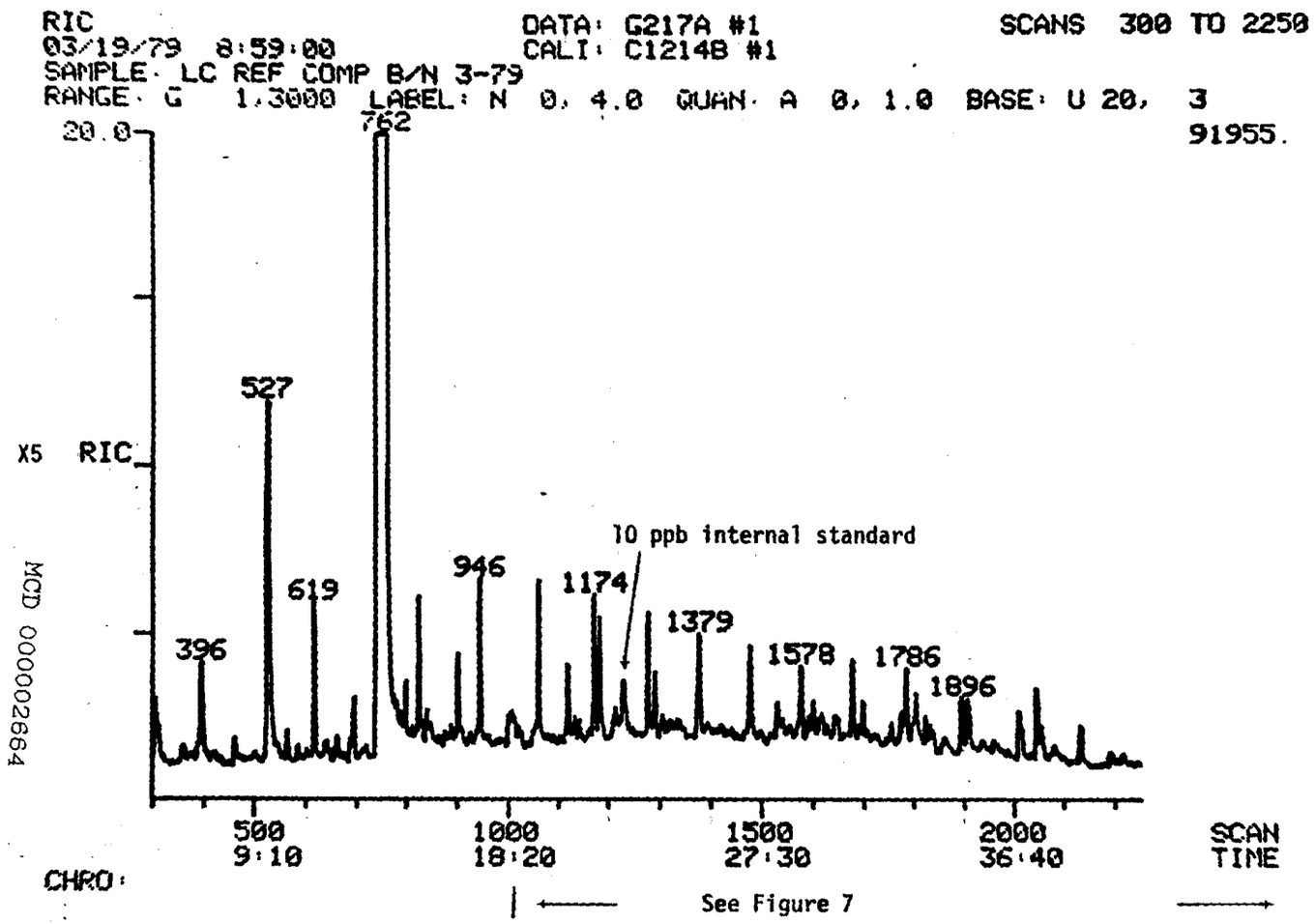


FIGURE 6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03/19/79 8:59:00
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CALI: C1214B #1
SCANS 300 TO 2250
SAMPLE: LC REF COMP B/N 3-79
RANGE: G 1.3000 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3
91955.
20.0
762
527
X5 RIC
946
619
1174
10 ppb internal standard
1379
396
1578
1786
1896
MCD 000002664
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9:10
1000
18:20
1500
27:30
2000
36:40
SCAN
TIME
CHRO:
See Figure 7

FIGURE 7

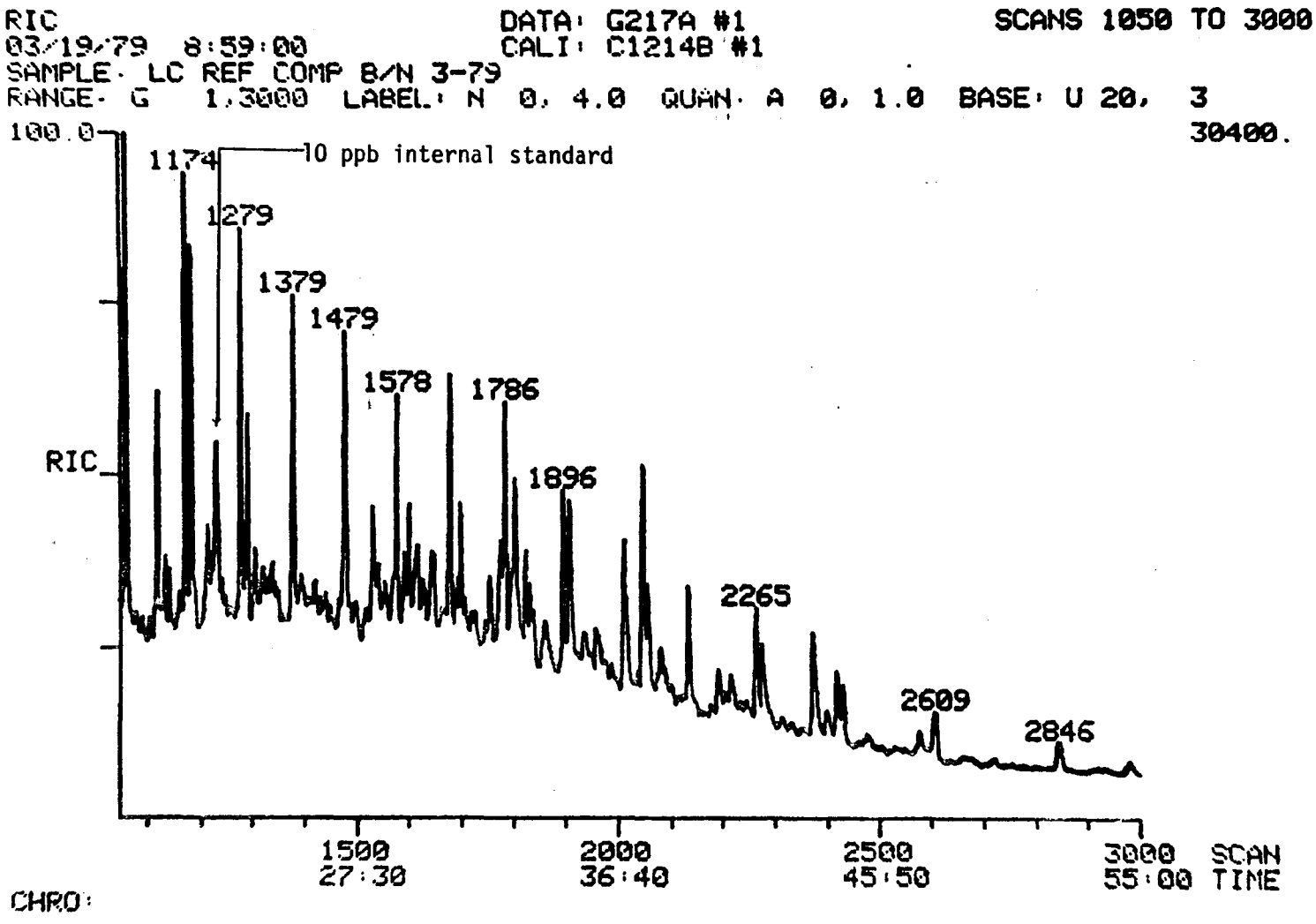

FIGURE 8

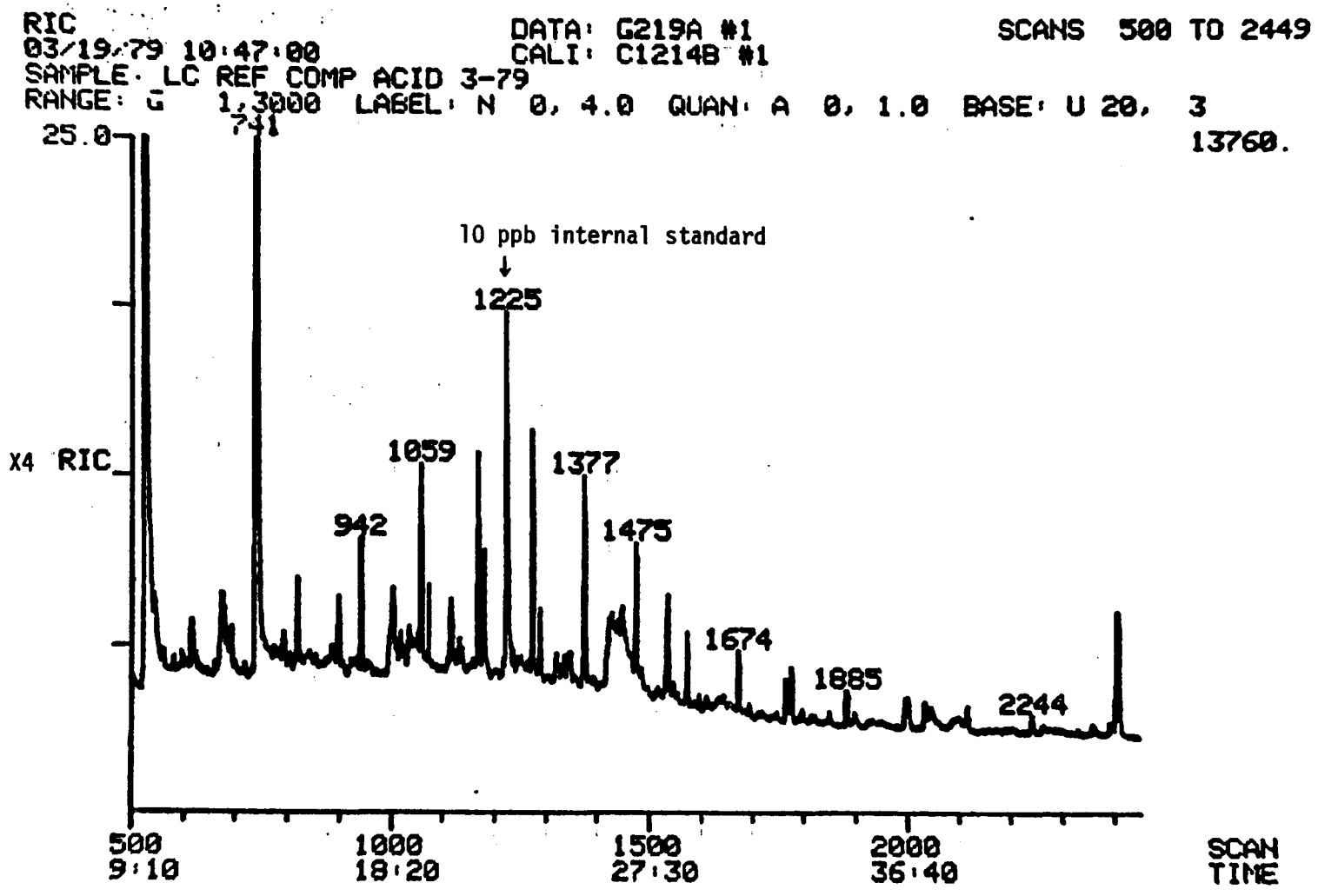

FIGURE 9