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US EPA RECORDS CENTER REGION 5
513915

July 31, 1981

Mr. James Pankanin
U.S. Environmental Protection Agency
5 EWHME
230 South Dearborn
Chicago, Illinois 60604

Subject: Letter Report of Results for the Analysis of 5 Soil Samples from EPA Region V (from St. Louis Park, Minnesota) for Polycyclic Aromatic Compounds (hydrocarbons, azaarenes, and phenols). EPA Contract No. 68-02-2814, Assignment No. 21, MRI Project No. 4468-L-21.

Dear Mr. Pankanin:

This report gives the results of the analysis of five soil samples for polycyclic aromatic hydrocarbons (PAH) (hydrocarbons, azaarenes, and phenols). The samples were sent by the Region V Office of the U.S. Environmental Protection Agency and were received and inventoried on December 1, 1980. Copies of the chain-of-custody forms are enclosed.

Presented in this report are a description of the analytical procedures, the results of the analyses, and conclusions and recommendations. Attached to this report are reconstructed ion chromatograms (RIC's) of samples and standards and extracted ion current plots (EICP's) of all the PAH priority pollutants found in the samples, as well as EICP's of the corresponding standard compounds. The EICP's of other compounds identified in the extracts of the samples are also included (Figures 1 through 59).

I. Sample Preparation and Analysis

The soil samples were air dried at room temperature overnight before being extracted for organic pollutants. The water content of the samples was determined separately by air-drying 5 g of each sample overnight at room temperature and then at 110°C for 3 hr. The moisture content is reported in Table 1.

For extraction of the PAH compounds from the soil, 50 g of air-dried soil sample was weighed into a glass jar having a Teflon-lined lid and then spiked with 250 μg each of the surrogate compounds. The surrogates used for this purpose were decafluorobiphenyl and pentafluorophenol. A glass ball was added and the sample was placed on a roller mill for 4 hr. It was then transferred to the sample cup of Soxhlet apparatus and Soxhlet-extracted with about 200 ml of methanol for 16 hr. The methanol was then replaced with methylene chloride and the sample further Soxhlet-extracted for 16 hr. A glassware-solvent blank was run concurrently with the samples.

The methanol extract was concentrated in a Kuderna-Danish (KD) apparatus to a volume of 5 to 8 ml and this volume was added to the methylene chloride extract. During this concentration step, Samples Nos. 1 and 3 formed a yellow, oily precipitate. This material was soluble in methylene chloride and these methanol concentrates were added to the corresponding methylene chloride extracts along with methylene chloride rinses of the KD apparatus.

The methylene chloride solution was partitioned three times with 100 ml of aqueous base (pH = 11). Then the aqueous solution was made acidic (pH = 2) and back-extracted three times with 100 ml of fresh methylene chloride. All the methylene chloride solutions were then combined, dried with Na_2SO_4 and reduced in volume in a KD apparatus. Samples Nos. 2, 4 and 5 were concentrated in a KD apparatus to about 5 ml and then concentrated further to a final volume of 1 ml in a stream of nitrogen. The methylene chloride solutions of Samples Nos. 1 and 3 were reduced to approximately 5 ml in a KD apparatus and then concentrated to less than 5 ml in a stream of nitrogen. The volume of this extract was adjusted to exactly 5 ml by addition of methylene chloride.

These solutions were analyzed by gas chromatography/mass spectrometry (GC/MS).

The GC/MS analyses were carried out with the following conditions.

Column: 30 ft fused silica capillary, 0.25 mm I.D., SE-54 coating

Temperature Program: 60°C for 2 min, then 4°C/min to 300°C, hold for 10 min.

Injector Temperature: 225°C

GC/MS Interface Temperature: 275°C

Detector: Finnigan 4000 Mass Spectrometer with Incos 23 Data System.

Two microliters each of Samples Nos. 2, 4 and 5 were analyzed under the GC conditions above, and these samples produced reconstructed ion chromatograms (RIC's) which generally did not present difficulties in interpretation. However, Samples Nos. 1 and 3 gave RIC's with high backgrounds from unresolved high-mass impurities which interfered with identification and measurement of the peaks in the ion chromatograms. Chromatograms obtained after Samples Nos. 1 and 3 were diluted still showed an unacceptably high background.

Aliquots of the solutions of Samples Nos. 1 and 3 were fractionated by gel-permeation chromatography (size-exclusion chromatography) but this cleanup process did not sufficiently improve the chromatograms of Samples Nos. 1 and 3. These two samples were then carried through the Florisil cleanup as described below.

A 1-ml aliquot of the methylene chloride soil extract was deposited on 1 g of Florisil and the methylene chloride was evaporated under a gentle stream of dry nitrogen. This Florisil was deposited on top of a prepared Florisil column (10 cm long x 2 cm diameter). The column was eluted successively with 100 ml of hexane, 100 ml of methylene chloride, 50 ml of 1% methanol in methylene chloride. The methylene chloride eluate was concentrated in a KD apparatus to 1 ml and then taken for reanalysis by GC/MS. The extracts were diluted 1:5 before the GC/MS analysis.

These cleaned-up sample extracts produced interpretable ion chromatograms.

Results of the GC/MS analyses for polycyclic aromatic hydrocarbons are given in Table 2.

Copies of the reconstructed ion chromatograms of the samples and extracted ion current plots of analytes in the standards and samples are presented in Figures 1 through 59.

After completion of the analyses of the samples, one sample (No. 4) was spiked in duplicate with 5 ppm of PAH compounds and these spiked duplicates were analyzed as described above for Samples Nos. 2, 4 and 5. The results of this duplicate recovery determination are given in Table 3. As mentioned above, all samples were spiked with surrogate compounds. Recoveries of the surrogate compounds are given in Table 4.

II. Results and Discussion

A. Results

Some polycyclic aromatic hydrocarbons were found in all the samples, but Sample No. 4 contained only a trace (11 ng/g) of naphthalene and thus could be considered virtually free of PAH contamination. Only two PAH at low levels were found in Sample No. 2. These were naphthalene at 11 ng/g and dibenz[a,h]anthracene at 157 ng/g. Sample No. 3 contained five PAH; phenanthrene, fluorene, pyrene, chrysene and benzo[g,h,i]perylene (see Table 2).

Sample No. 1 was found to contain numerous PAH at the nanograms/gram level (acenaphthene, fluorene, phenanthrene, pyrene, chrysene, benzo[k]fluoranthene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, acenaphthylene, naphthalene, and benzo[a]pyrene) and also fluoranthene at the micrograms/ gram level (1,800 ng/g = 1.8 μg/g) (see Table 2). Sample No. 1 also contained a compound tentatively identified from its mass spectrum as cyclobutanethiol.

Sample No. 5 was found to contain numerous PAH at the nanogram/gram level (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, fluoranthene, pyrene, chrysene, benzo[a]pyrene, benzo[k]fluoranthene, dibenz-[a,h]anthracene, and benzo[g,h,i]perylene) (see Table 1). This sample also showed several identifiable non-PAH peaks in the ion chromatogram of the sample. We identified elemental sulfur (commonly found in soil samples), dibutylphthalate, tributylphosphate and a methyl carbazole (the specific isomer cannot be identified). The EICP's of these compounds found in Sample No. 5 are enclosed (Figures 43 through 45).

No phenolic compounds were detected in any of the soil samples. The methyl carbazole (undetermined isomer) found in Sample No. 5 was the only azaarene found in any of the samples.

The results of the recovery of PAH during analysis of duplicate spiked samples of soil (Sample No. 4) as given in Table 3 are considered to be good recovery results for analysis of soil samples.

Recoveries of the surrogate compounds which were added to all samples as described earlier are given in Table 4. They are at satisfactory levels except for those samples (Nos. 1 and 3) which were carried through the Florisil cleanup. We surmise that the surrogate compounds were not well recovered during this step. If this is so, then similar compounds, and specifically PAH compounds, may also have suffered from poor recovery during the Florisil cleanup step of Samples Nos. 1 and 3. The spiked samples for which recoveries of PAH analytes are good, were however not subjected to Florisil cleanup.

B. Discussion

During the analyses, we encountered two problems with Samples Nos. 1 and 3. The first problem was the interference in the mass spectra of these samples caused by unresolved substances giving a high background signal. This high background problem was solved by cleaning up the sample extracts as described. However, as noted above, the cleanup step may have resulted in diminished analyte recovery.

The other problem occurred during the GC/MS analysis of Samples Nos. 1 and 3 (and to a lesser extent during the GC/MS analysis of Sample No. 5) using the 30-meter capillary column. It was observed that some analyte peaks in the ion chromatograms of these samples appeared to be doubled;

that is, chromatographic peaks arising from the same compound appeared at two different retention times in the same chromatogram. This phenomenon was not observed for peaks of analytes during chromatography of standard solutions.

This doubling phenomenon has been observed by other workers using capillary columns in this and other laboratories. A completely satisfactory explanation has not been offered. The evidence indicates that it is an overloading phenomenon since the peak doubling can be diminished or eliminated by reducing the volume of the solution injected or diluting the sample solution or both. Both of these potential remedies reduce the sensitivity of the method, and reducing the injection volume decreases the reproducibility of the results as well. We diluted Samples Nos. 1, 3 and 5 and continued to use an injection volume of 2 µl.

In Samples Nos. 2 and 4 and spiked Sample No. 4 we were able to obtain chromatograms without peak doubling. In chromatograms of Sample Nos. 1, 3 and 5 some peaks of analytes were doubled even after diluting the sample. These peaks were measured for quantitation by measuring both peaks of a doublet and adding their peak heights, provided that height of the smaller peak was 25% or more of the height of the larger peak. If the height of the smaller peak was less than 25% of the height of the larger peak it was disregarded.

III. Summary and Conclusion

The soil samples received for analysis contained varying amounts of PAH ranging from low levels for Sample No. 4 (one PAH at the 10 ng/g level) to rather high levels for Samples Nos. 1 and 5. No priority pollutant phenols were found in any of the samples. Only Sample No. 5 was found to contain any azaarene. In this case an unspecified isomer of methyl carbazole was identified.

Recoveries of the polycyclic aromatic compounds spiked into Sample No. 4 are considered good. Recoveries of the two surrogate compounds pentafluorophenol and decafluorophenyl spiked into all the samples are acceptable except for Samples Nos. 1 and 3.

Samples Nos. 1 and 3 were carried through a gel permeation cleanup and a florisil cleanup which were not applied to Samples Nos. 2, 4 and 5. Our experience with extracts of many samples analyzed for PAH and phenols has shown that they pass through gel permeation cleanups with good recovery. Therefore, we concluse that the loss of the surrogate took place during the florisil cleanup.

The low recoveries of the surrogate compounds in Samples Nos. 1 and 3 implies that quantitative recovery for other compounds may be low and these values should be regarded as minimums.

If you have any questions concerning these results, please do not hesitate to call us.

Sincerely yours,

MIDWEST RESEARCH INSTITUTE

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TABLE 1. MOISTURE CONTENT OF SAMPLES, PERCENT

Sample No.	% Moisture
1	7.7
2	10.5
3	5.5
4	7.7
5	9.4

TABLE 2. RESULTS OF THE ANALYSIS OF THE ST. LOUIS PARK SOIL SAMPLES FOR POLYCYCLIC AROMATIC COMPOUNDS (PAH)

Compound	Concentration, ng/g
Sample No. 1	
Naphthalene	14
Acenaphthylene	900
Acenaphthene	23
Fluorene	77
Phenanthrene	500
Fluoranthene	1,800
Pyrene	500
Chrysene	190
Benzo[k]fluoranthene	300
Dibenz[a,h]anthracene	95
Benzo[a]pyrene	270
Benzo[b,h,i]perylene	180
Sample No. 2	
Naphthalene	11
Dibenz[a,h]anthracene	157
Sample No. 3	
Phenanthrene	70
Fluoranthene	620
Pyrene	160
Chrysene	220
Benzo[g,h,i]perylene	34
Sample No. 4	
Naphthalene	11
Sample No. 5	
Naphthalene	88
Acenaphthylene	16
Acenaphthene	7
Fluorene	9
Phenanthrene	200
Fluoranthene	550
Pyrene	600
Chrysene	630
Benzo[a]pyrene	690
Benzo[k]fluoranthene	480
Dibenz[a,h]anthracene	350
Benzo[g,h,i]perylene	230

TABLE 3. PERCENT RECOVERY OF POLYCYCLIC AROMATIC COMPOUNDS FROM DUPLICATE SPIKED SAMPLES

Compound	Sample No. 4, Sample No. 1	Sample No. 4, Sample No. 2
Naphthalene	40	60
Acenaphthene	43	56
Acenaphthylene	54	69
Fluorene	39	57
Phenanthrene	50	63
Fluoranthene	50	59
Pyrene	46	58
Chrysene	50	64
Benzo[a]pyrene	90	100
Benzo[k]fluoranthene	90	90
Dibenz[a,h]anthracene	71	93
Benzo[g,h,i]perylene	72	95
Carbazole	47	60
Indole	41	57
Quinoline	51	70
Acridine	48	62
Phenol	85	77
2,4-Dimethylphenol	8	10
2,4,6-Trichlorophenol	60	64
Cresol	54	66

TABLE 4. PERCENT RECOVERY OF SURROGATE COMPOUNDS ADDED TO SAMPLES AT 5 μg/g

Sample No.	Decafluorobiphenyl	Pentafluorophenol
Blank	39	64
No. 1	< 1	0
No. 2	29	56
No. 3	2	0
No. 4	23	57
No. 5	51	65
No. 4 Spike No. 1	48	120
No. 4 Spike No. 2	59	110

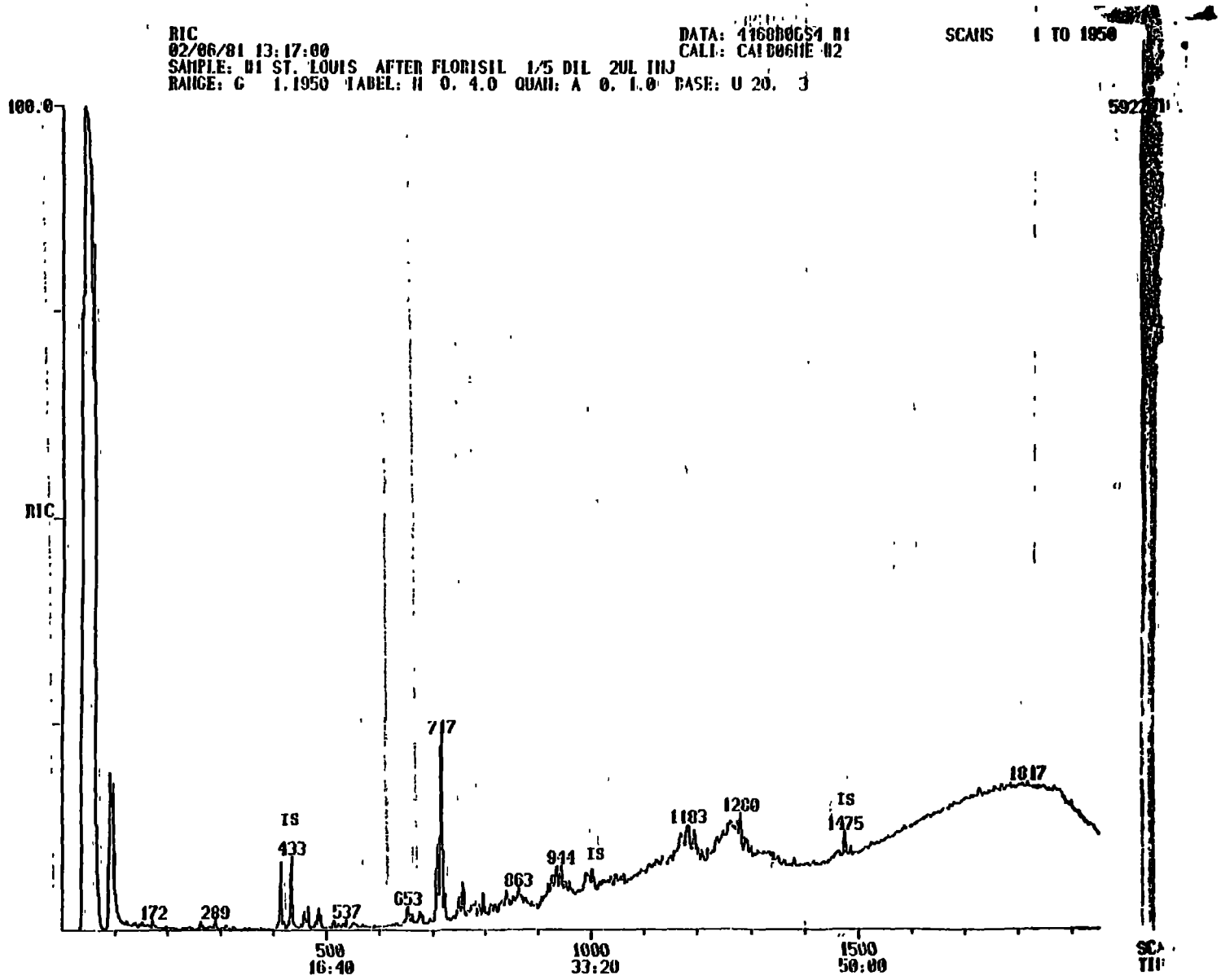

Figure 1 - RIC of Sample No. 1

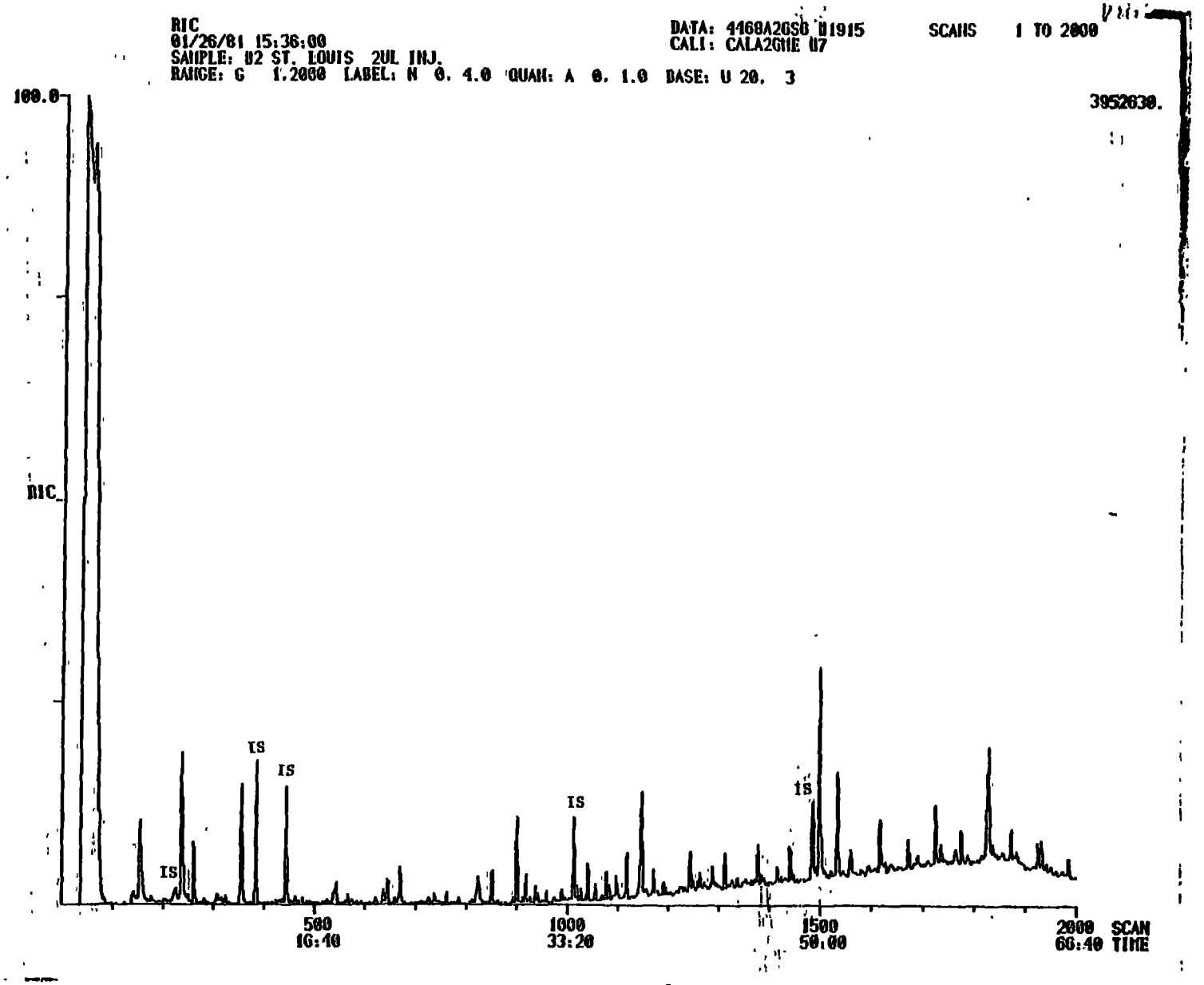

Figure 2 - RIC of Sample No. 2

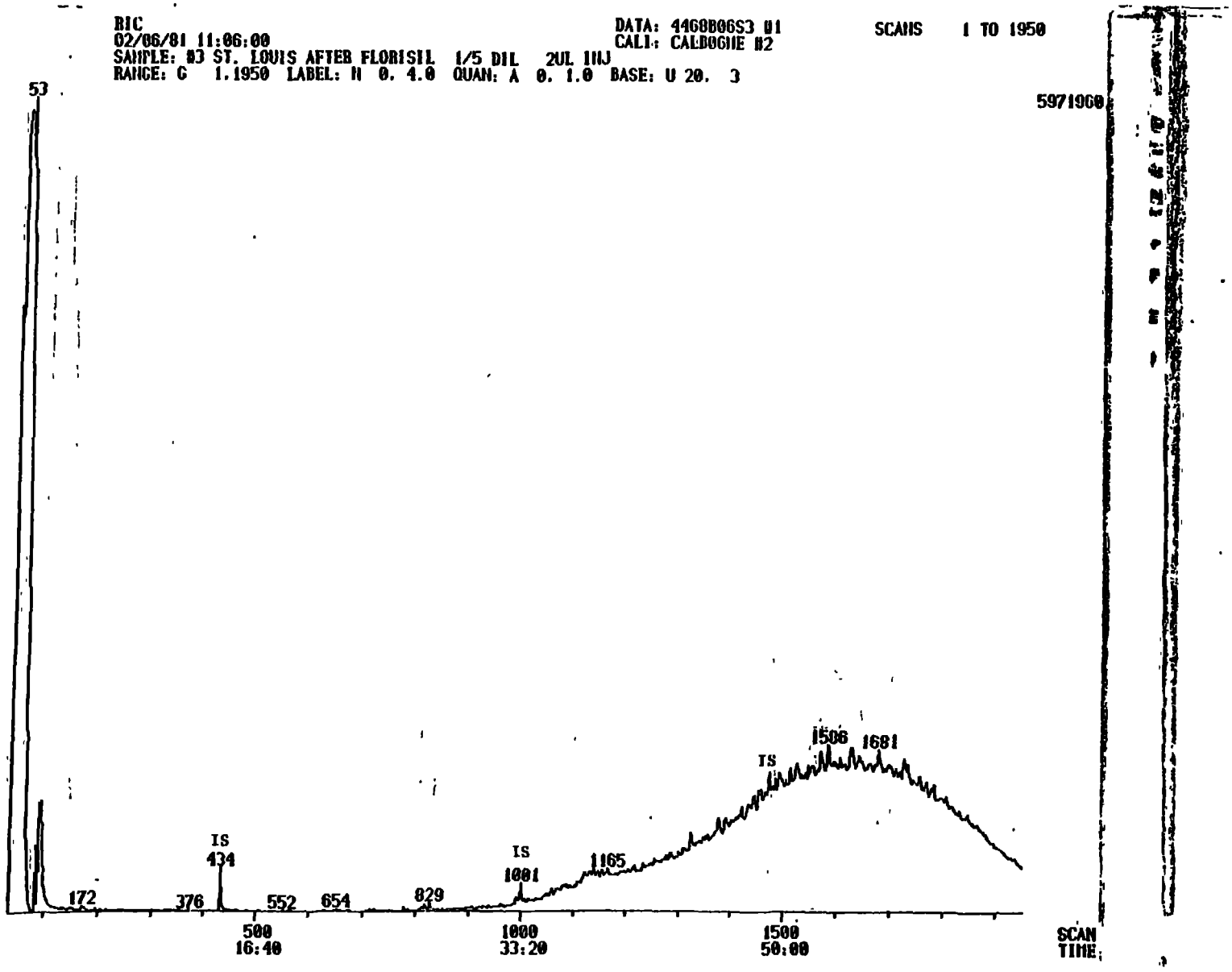

Figure 3 - RIC of Sample No. 3

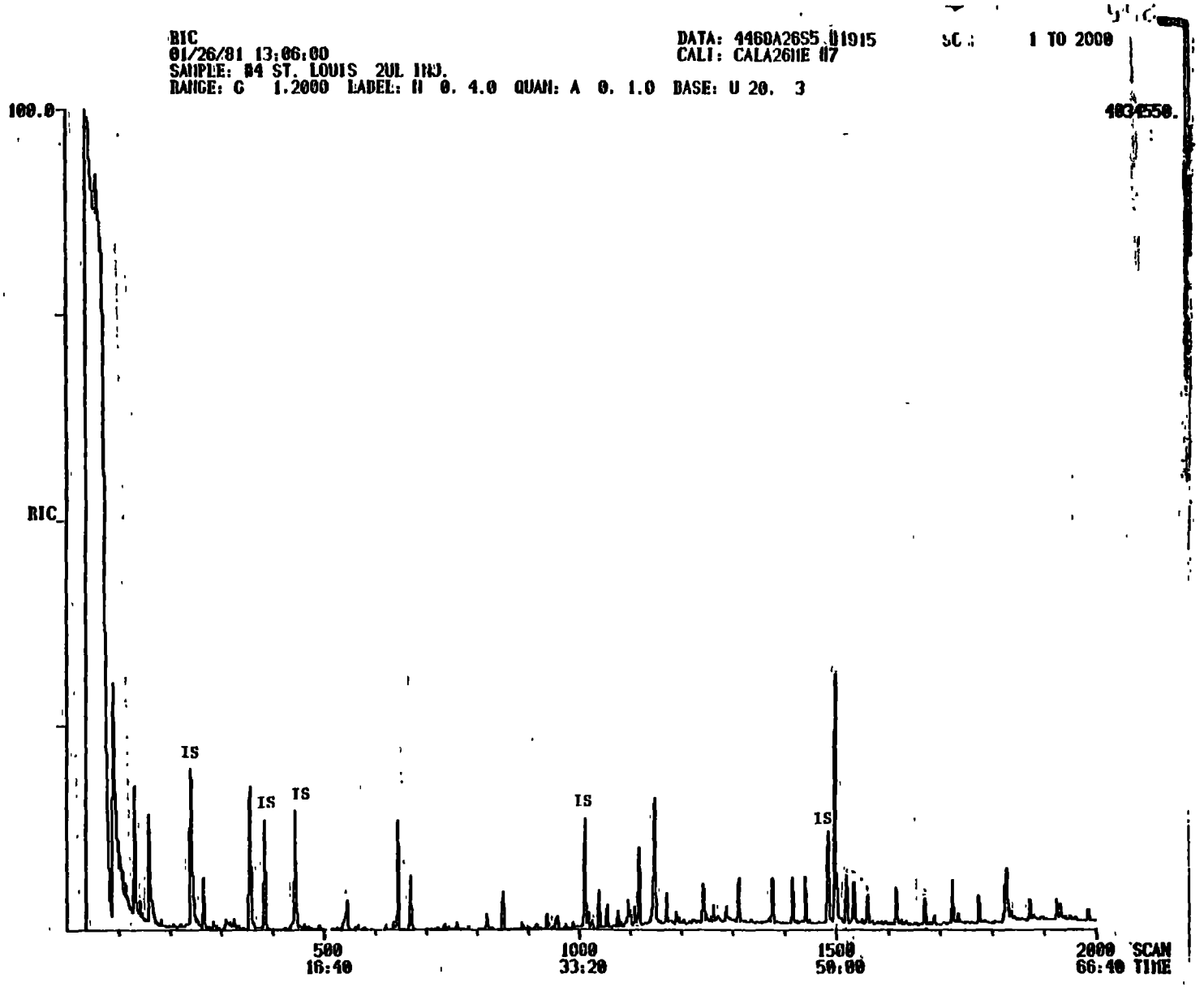

Figure 4 - RIC of Sample No. 4

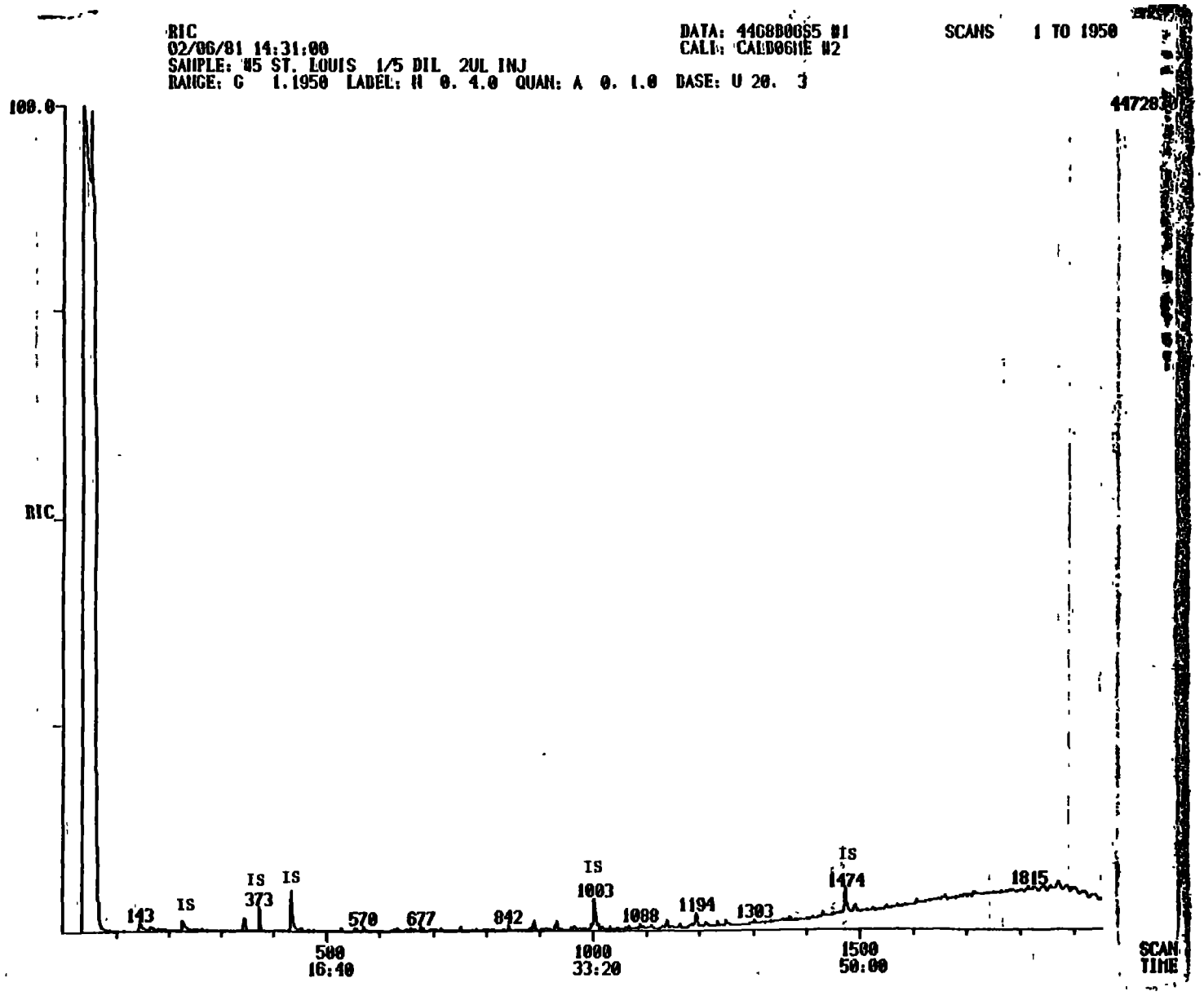

Figure 5 - RIC of Sample No. 5

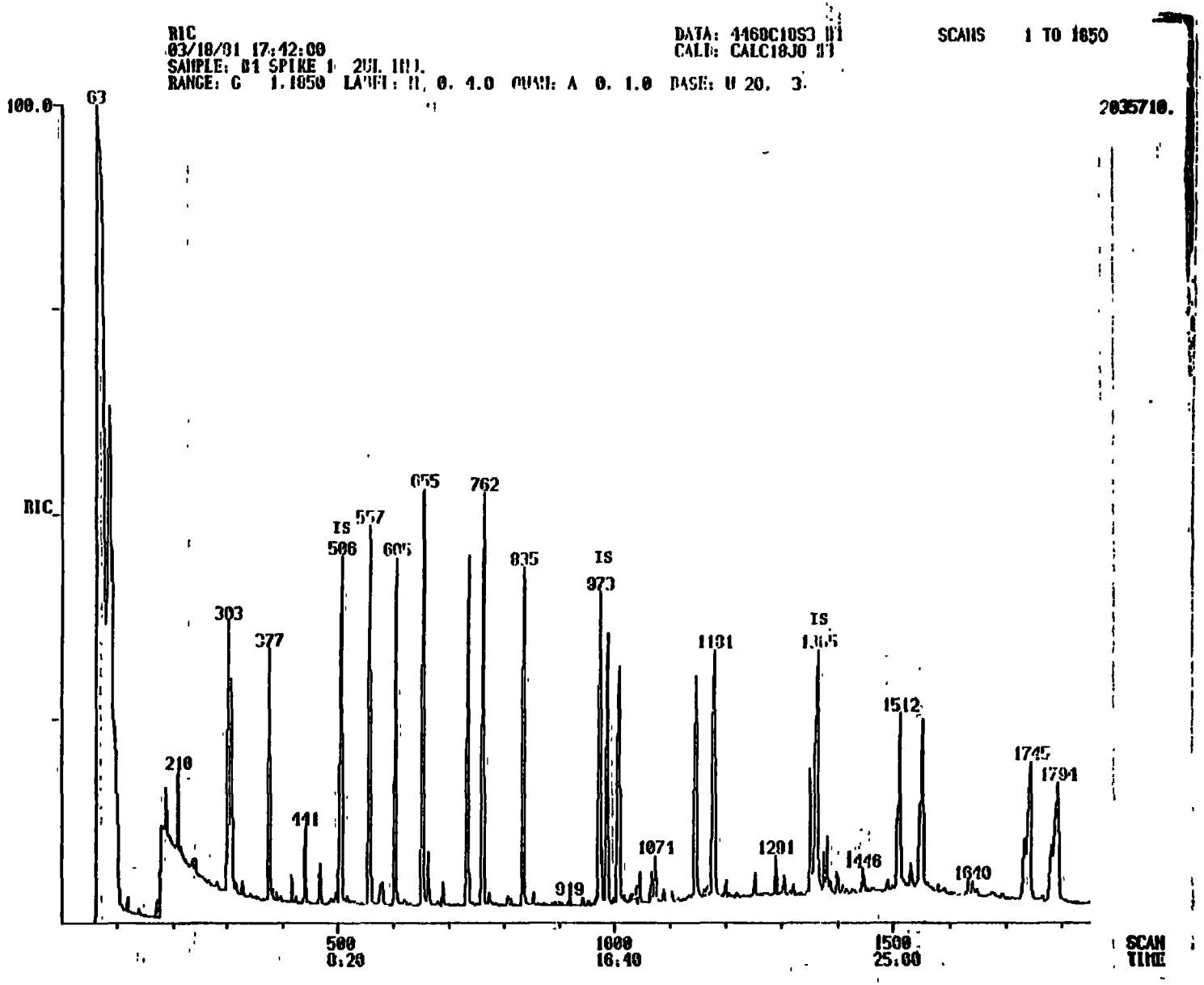

Figure 6 - RIC of Sample No. 4, Spike No. 1

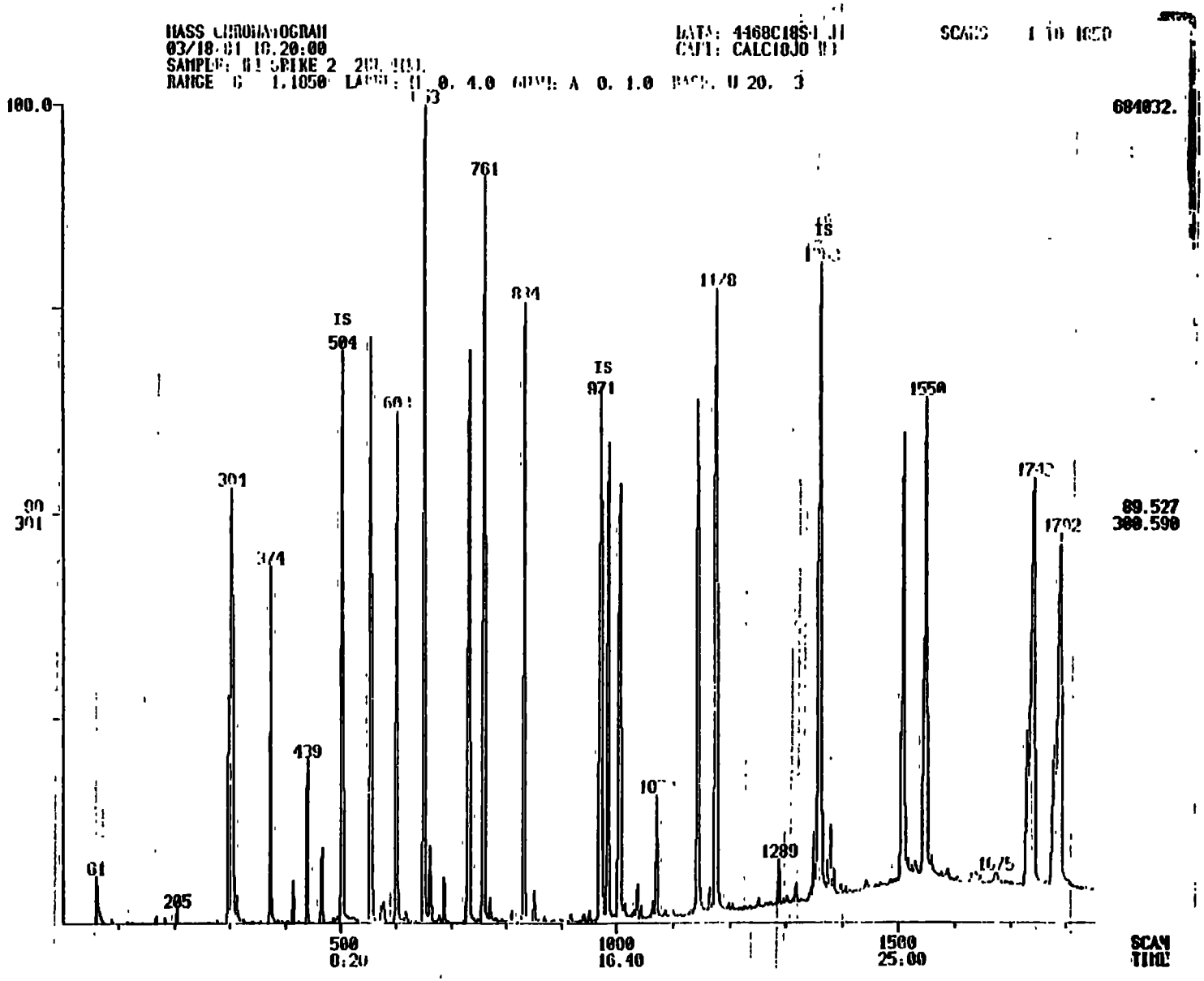

Figure 7 - RIC of Sample No. 4, Spike No. 2

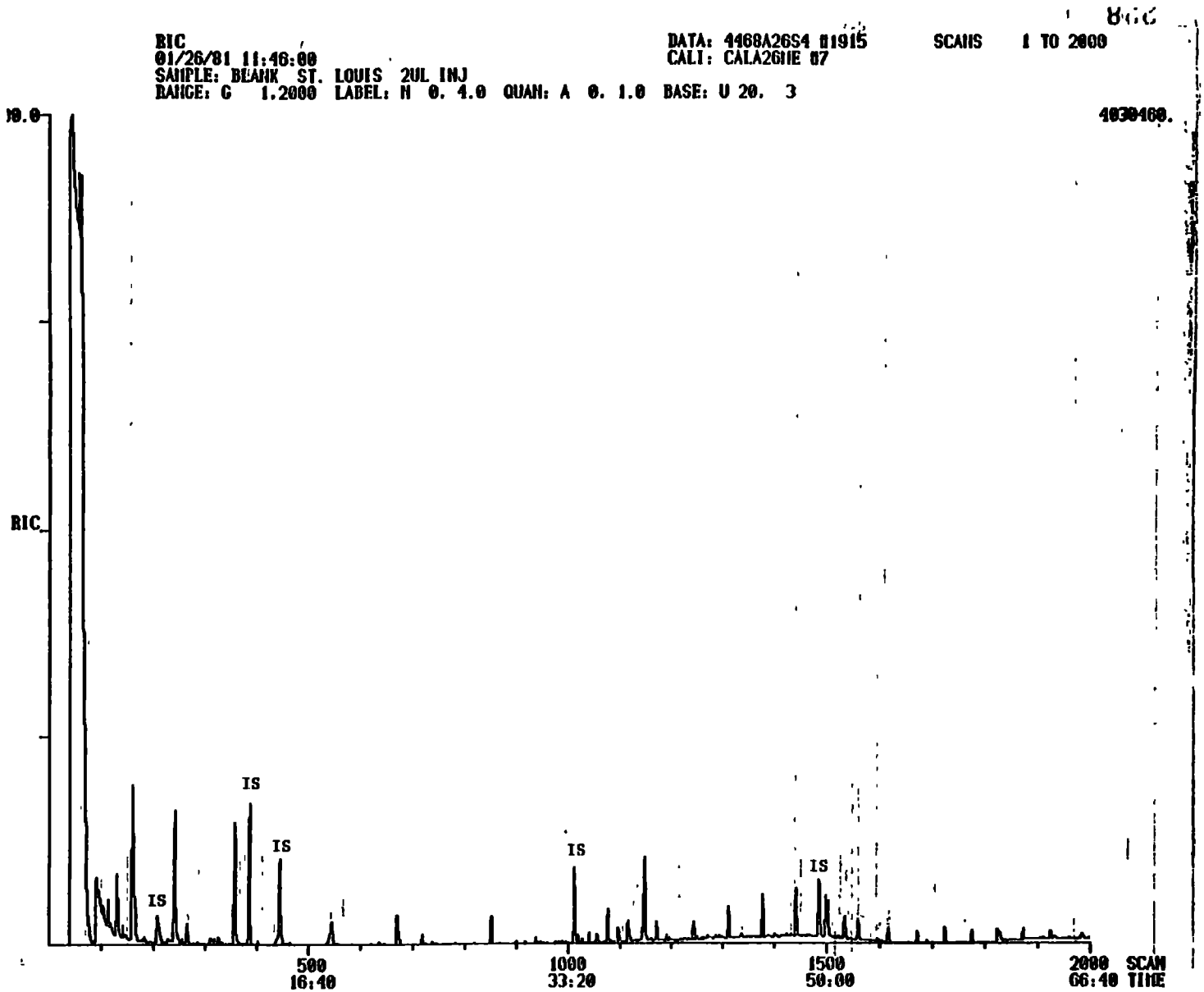

Figure 8 - RIC of Solvent Blank

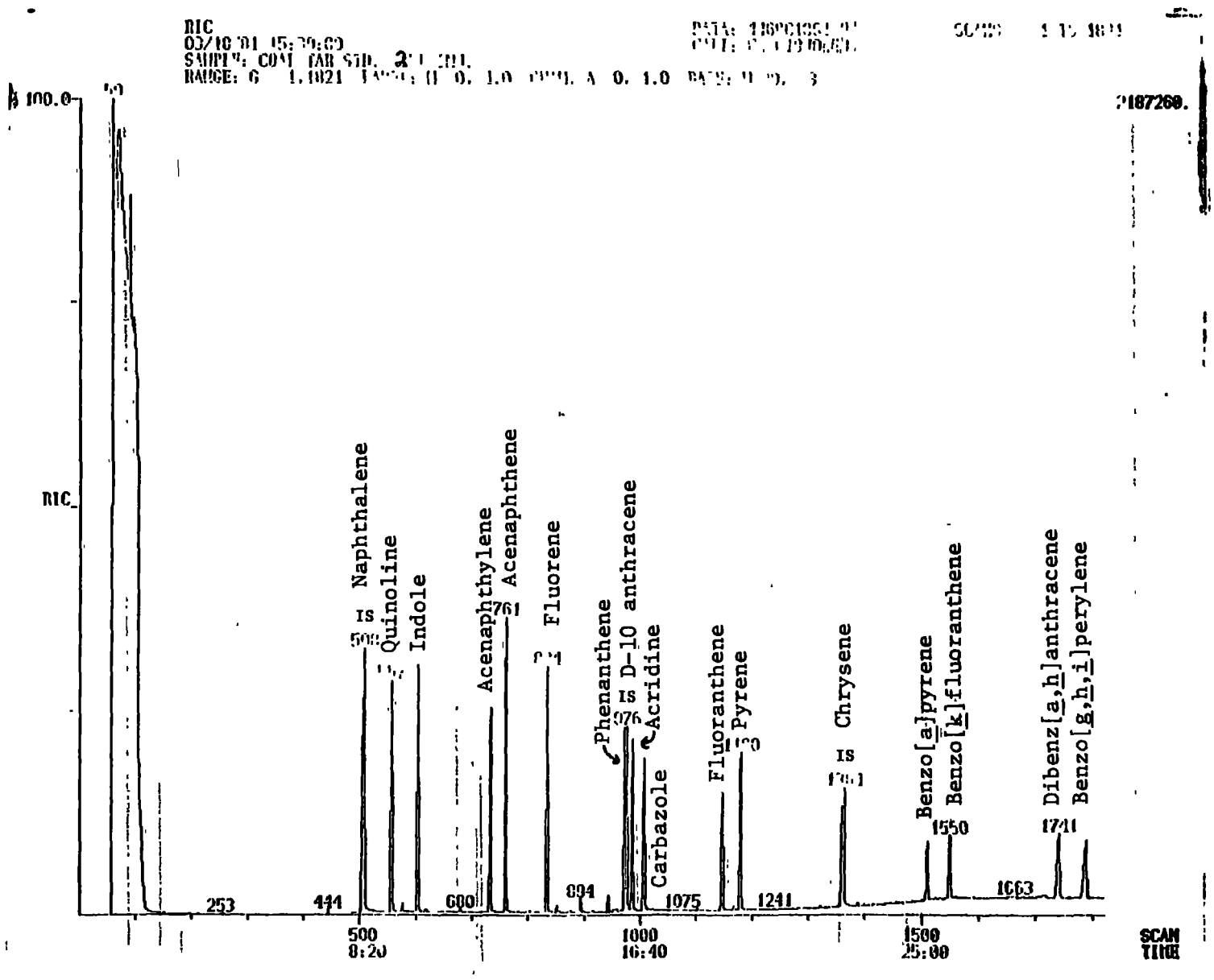

Figure 9 - RIC of Standard of PAHs and Coal Tar Bases, 3/18/81

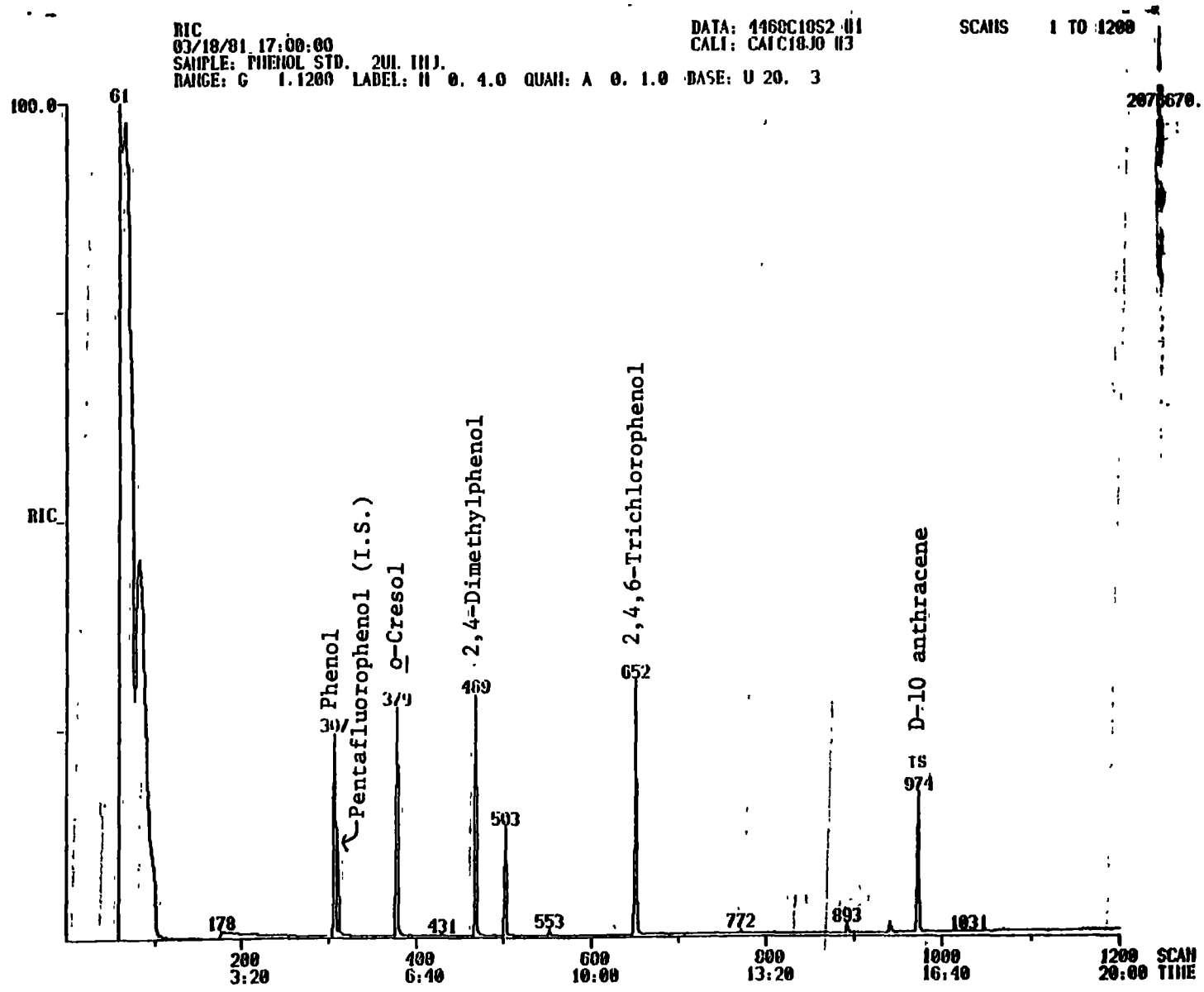

Figure 10 - RIC of Standard of Phenols, 3/18/81

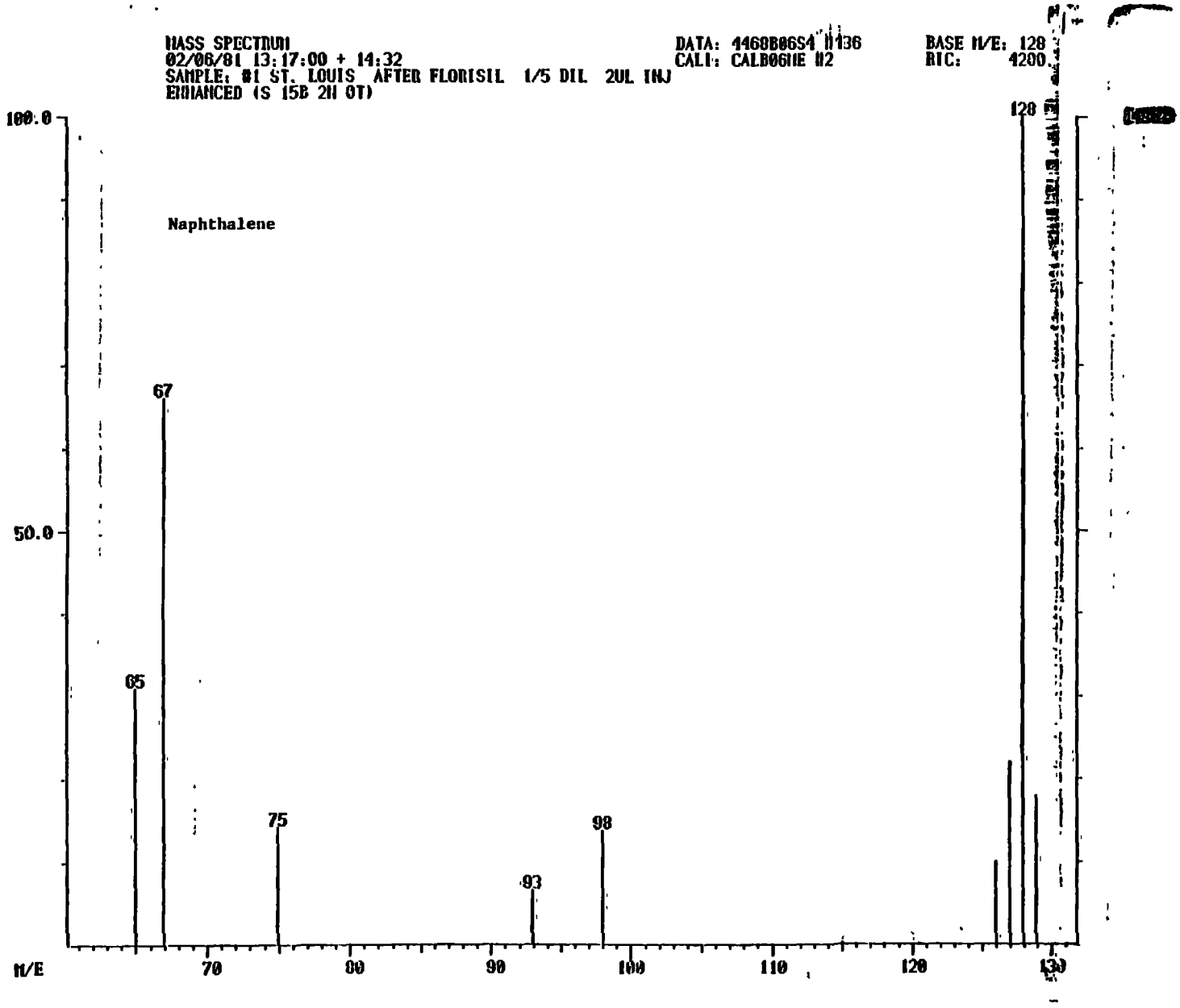

Figure 11 - Naphthalene in Sample No. 1

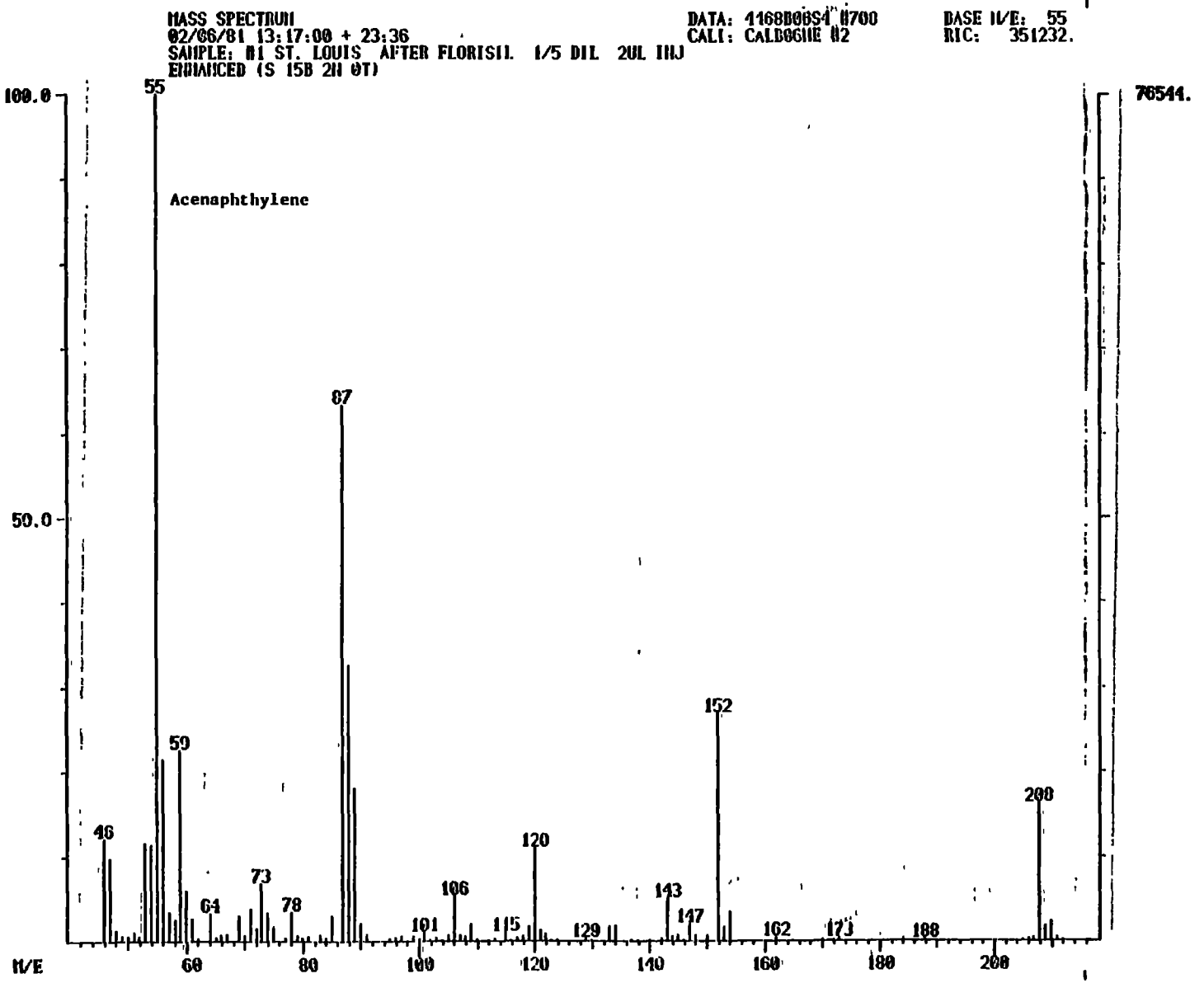

Figure 12 - Acenaphthylene in Sample No. 1

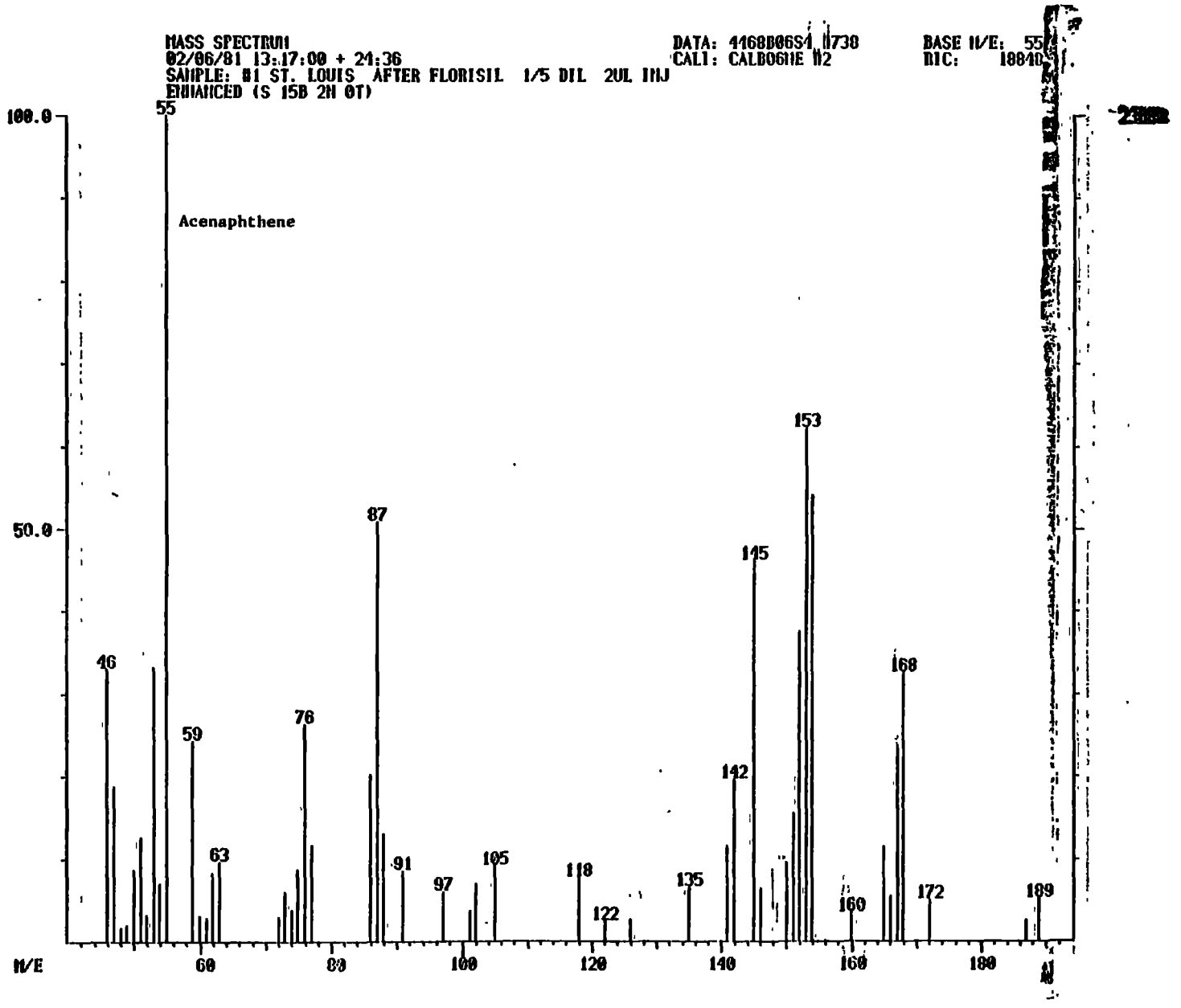

Figure 13 - Acenaphthene in Sample No. 1

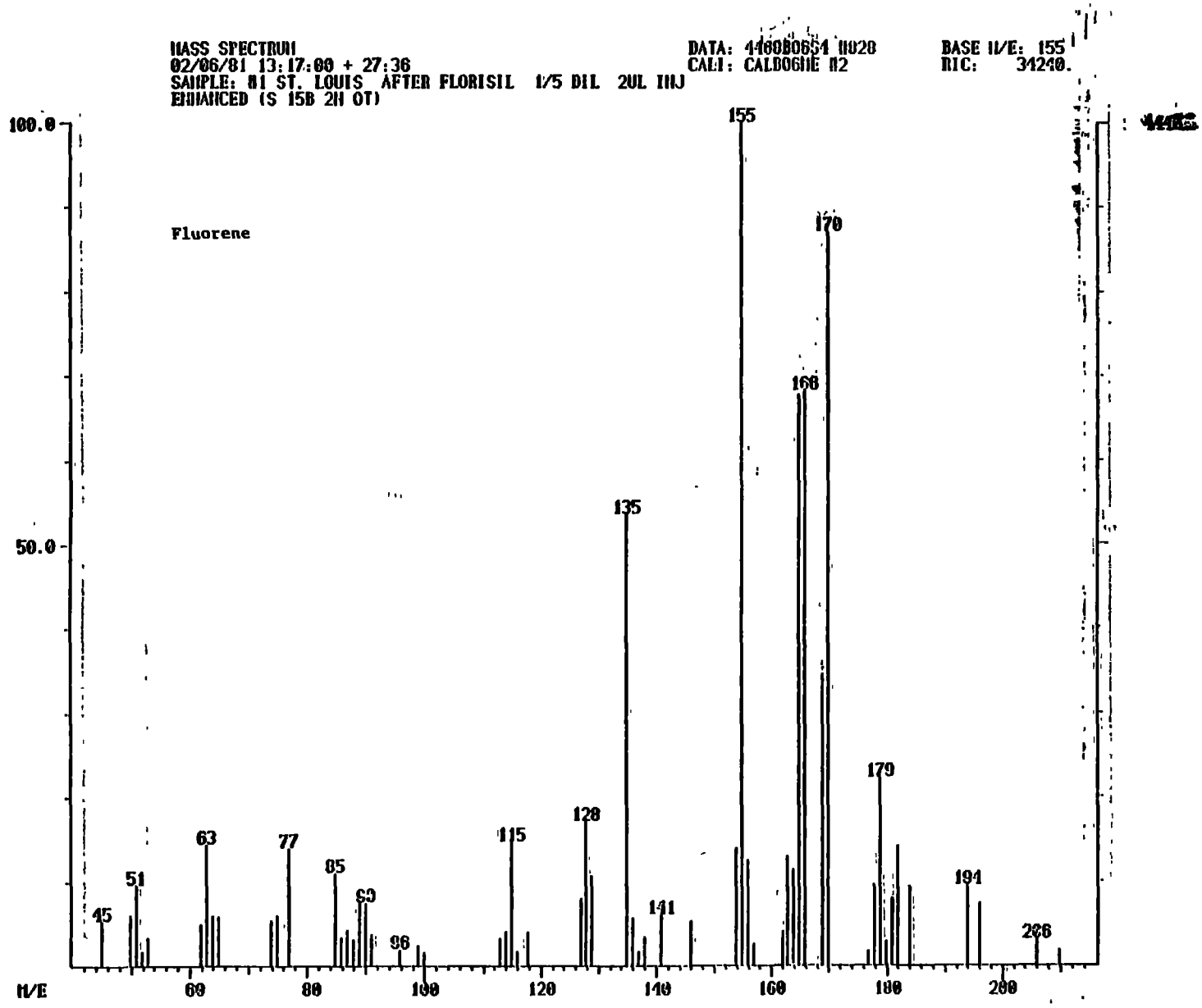

Figure 14 - Fluorene in Sample No. 1

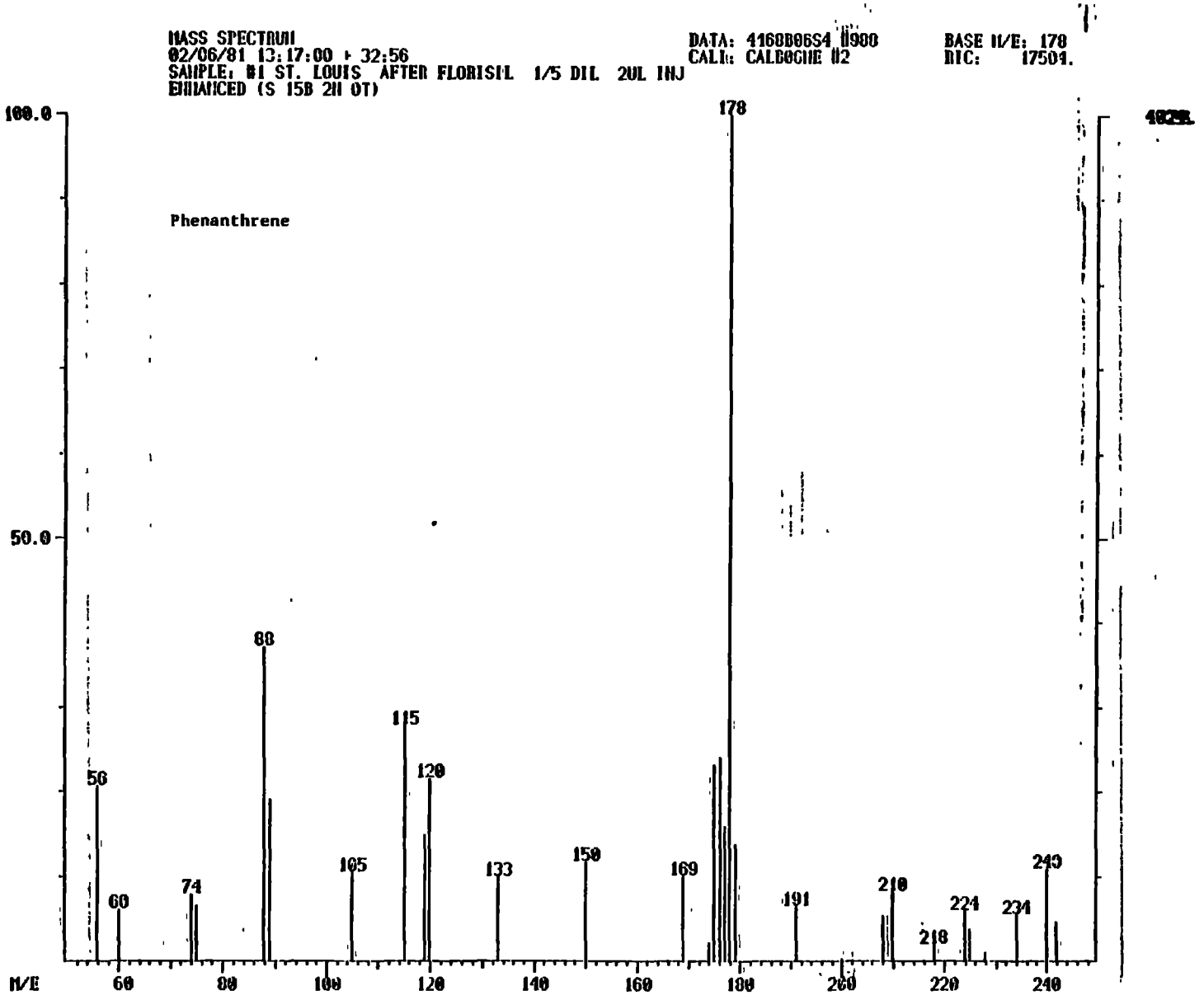

Figure 15 - Phenanthrene in Sample No. 1

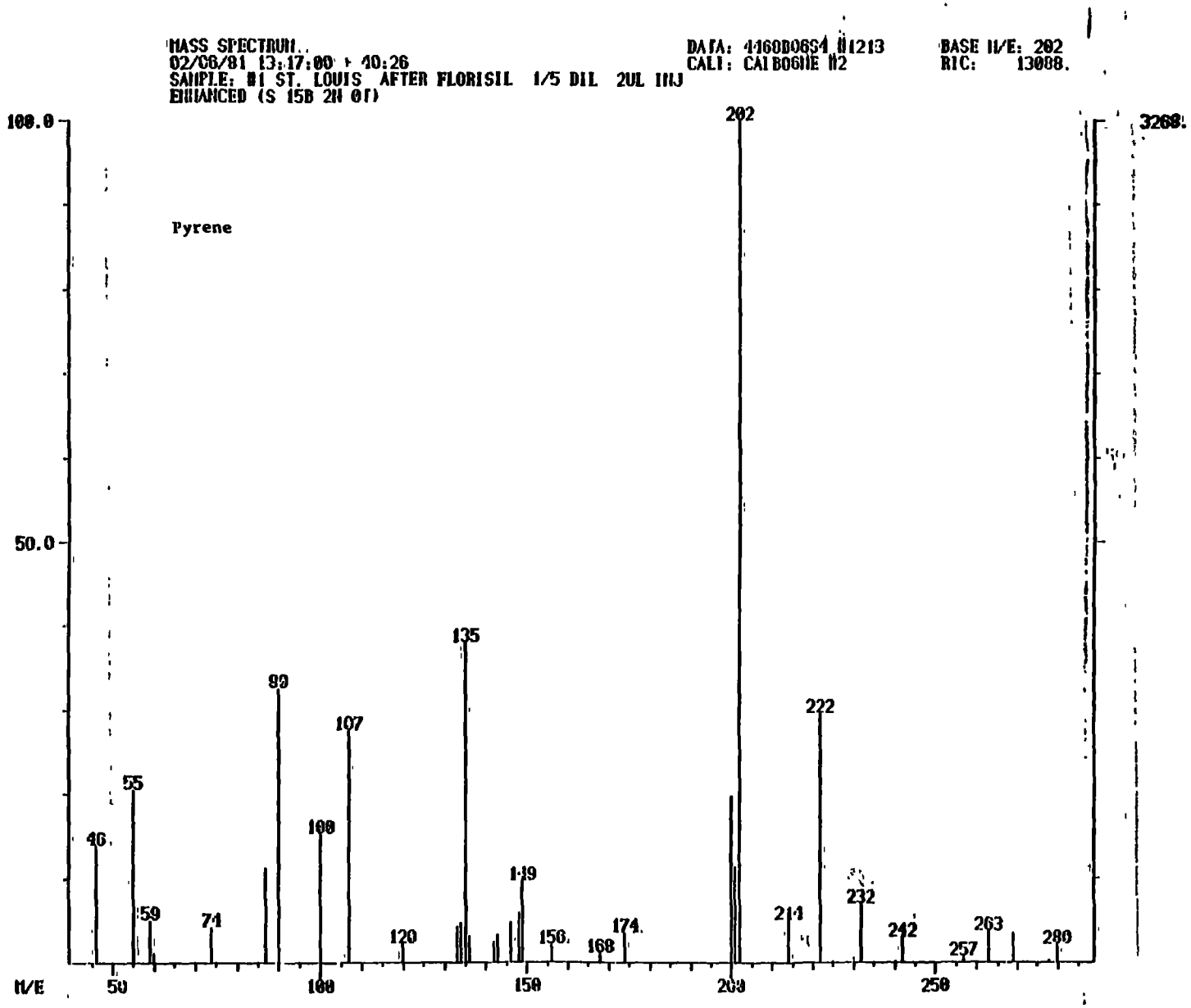

Figure 16 - Pyrene in Sample No. 1

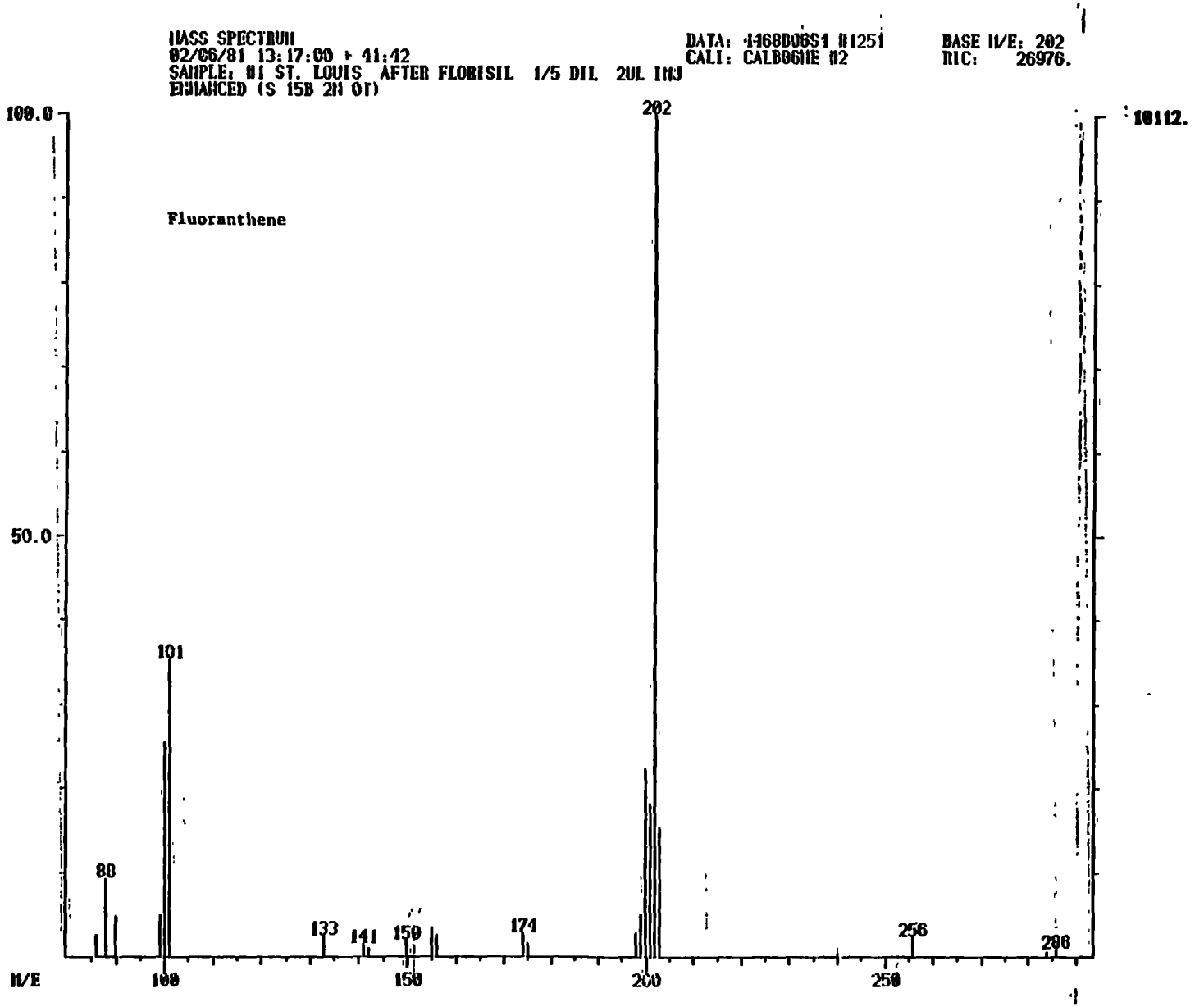

Figure 17 - Fluoranthene in Sample No. 1

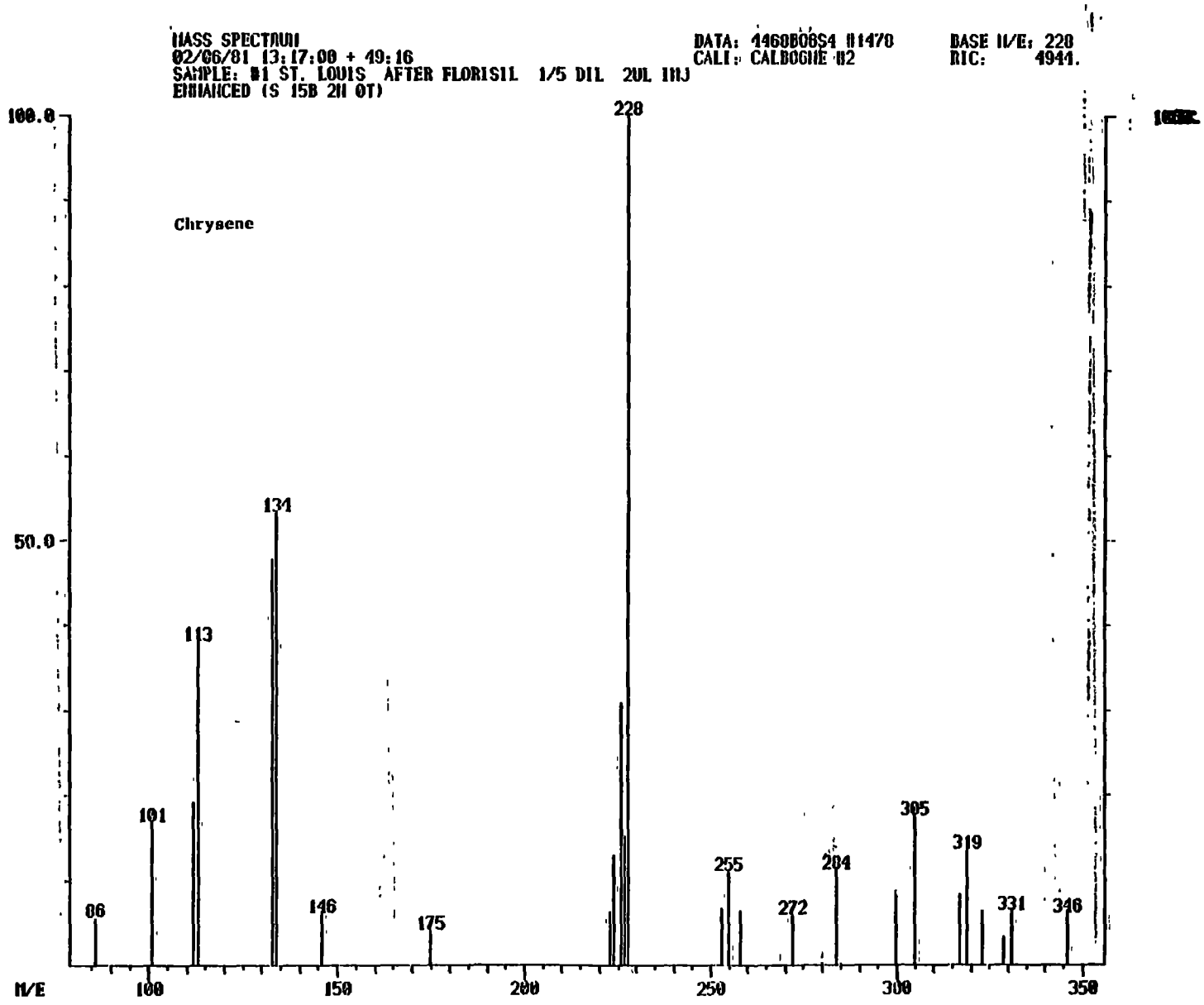

Figure 18 - Chrysene in Sample No. 1

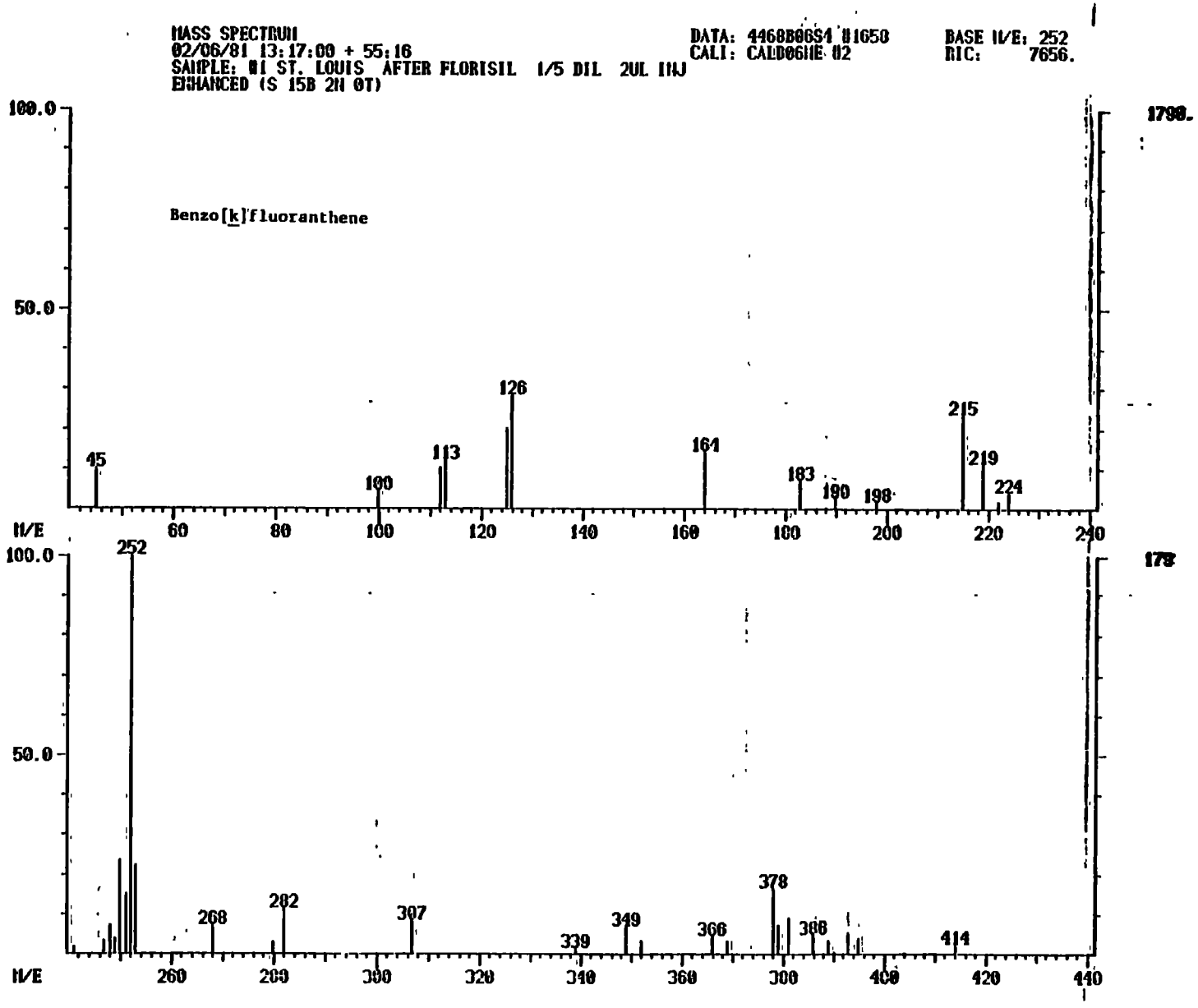

Figure 19 - Benzo[k]fluoranthene in Sample No. 1

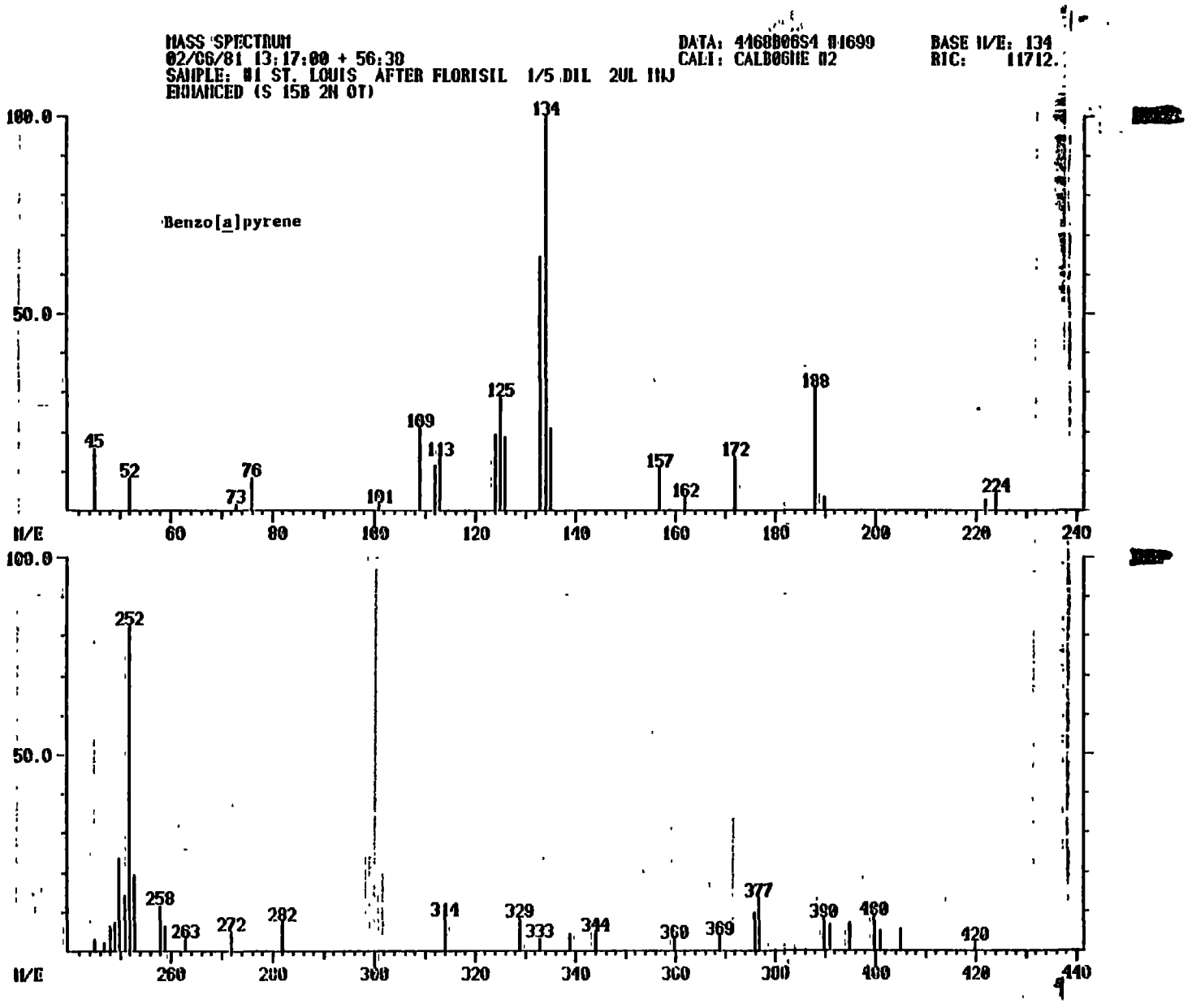

Figure 20 - Benzo[a]pyrene in Sample No. 1

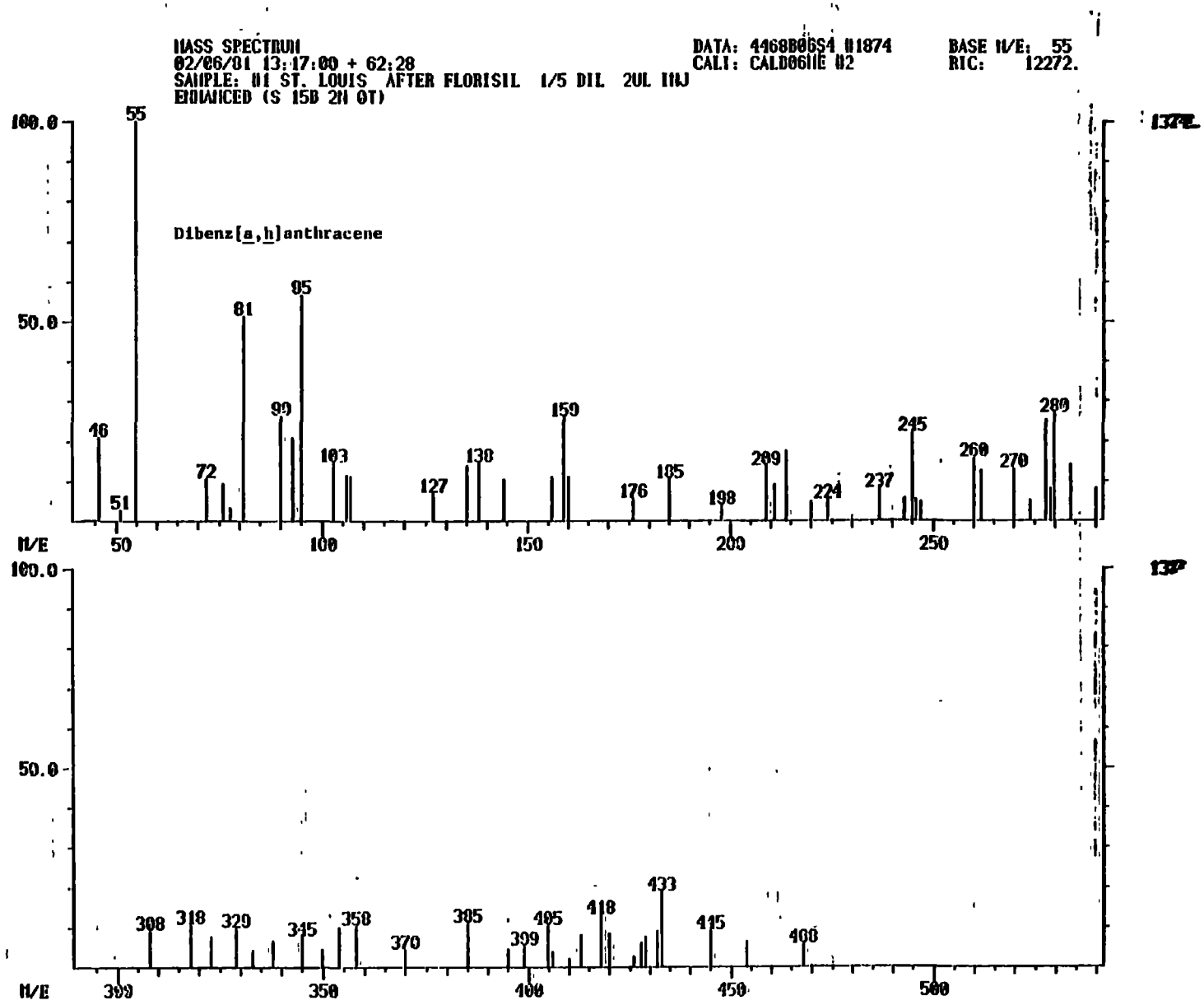

Figure 21 - Dibenz[a,h]anthracene in Sample No. 1

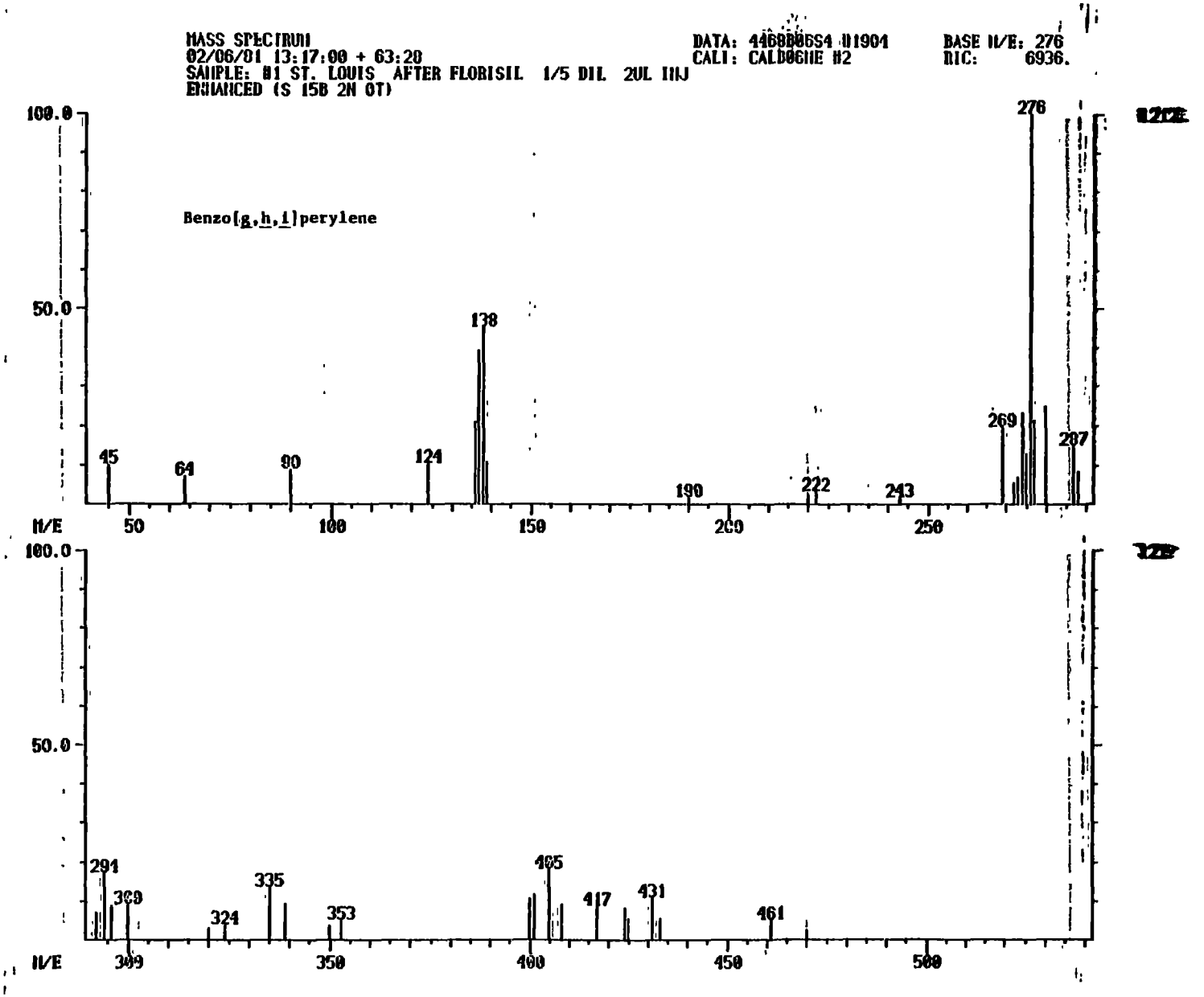

Figure 22 - Benzo[g,h,i]perylene in Sample No. 1

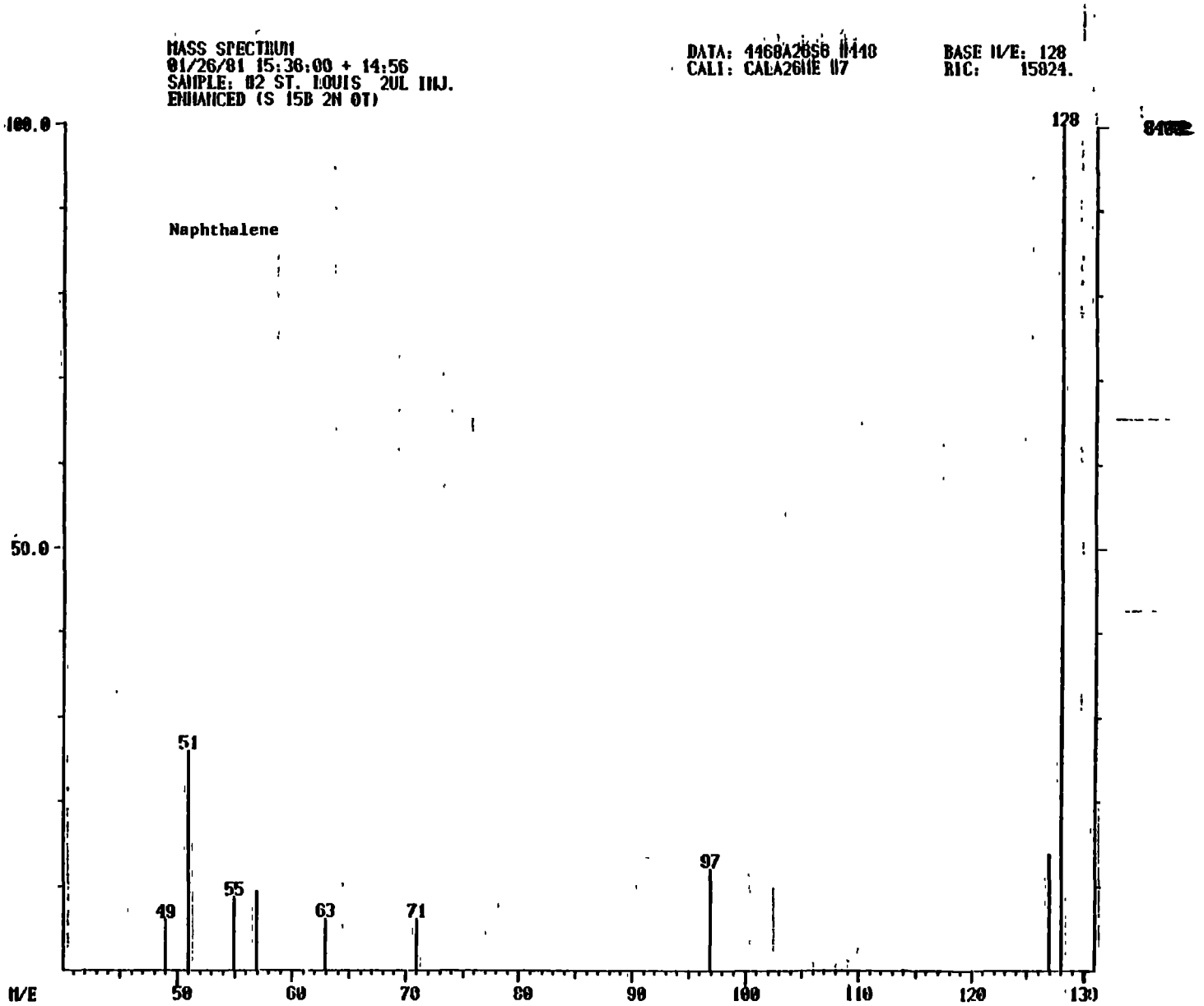

Figure 23 - Naphthalene in Sample No. 2

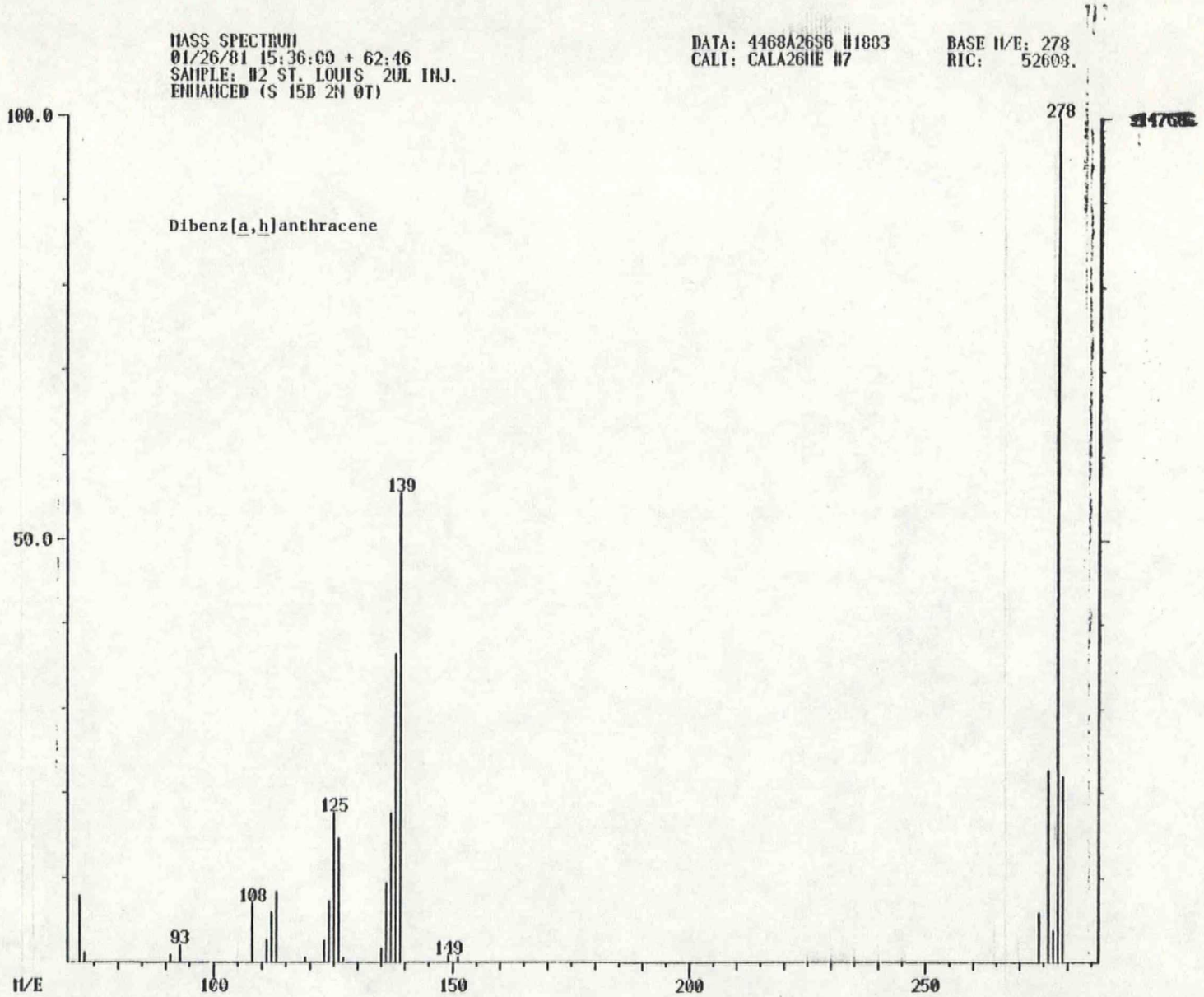

Figure 24 - Dibenz[a,h]anthracene in Sample No. 2

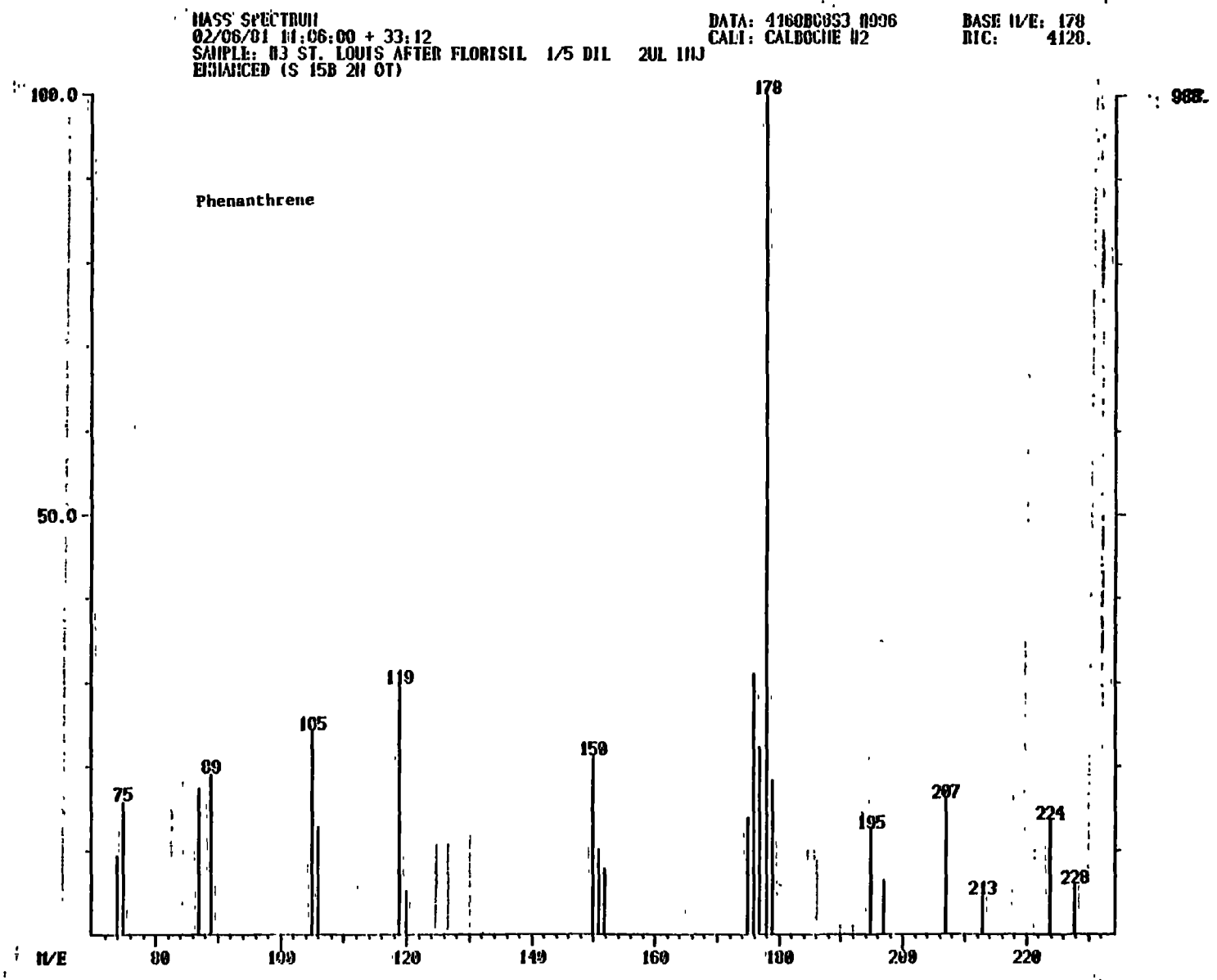

Figure 25 - Phenanthrene in Sample No. 3

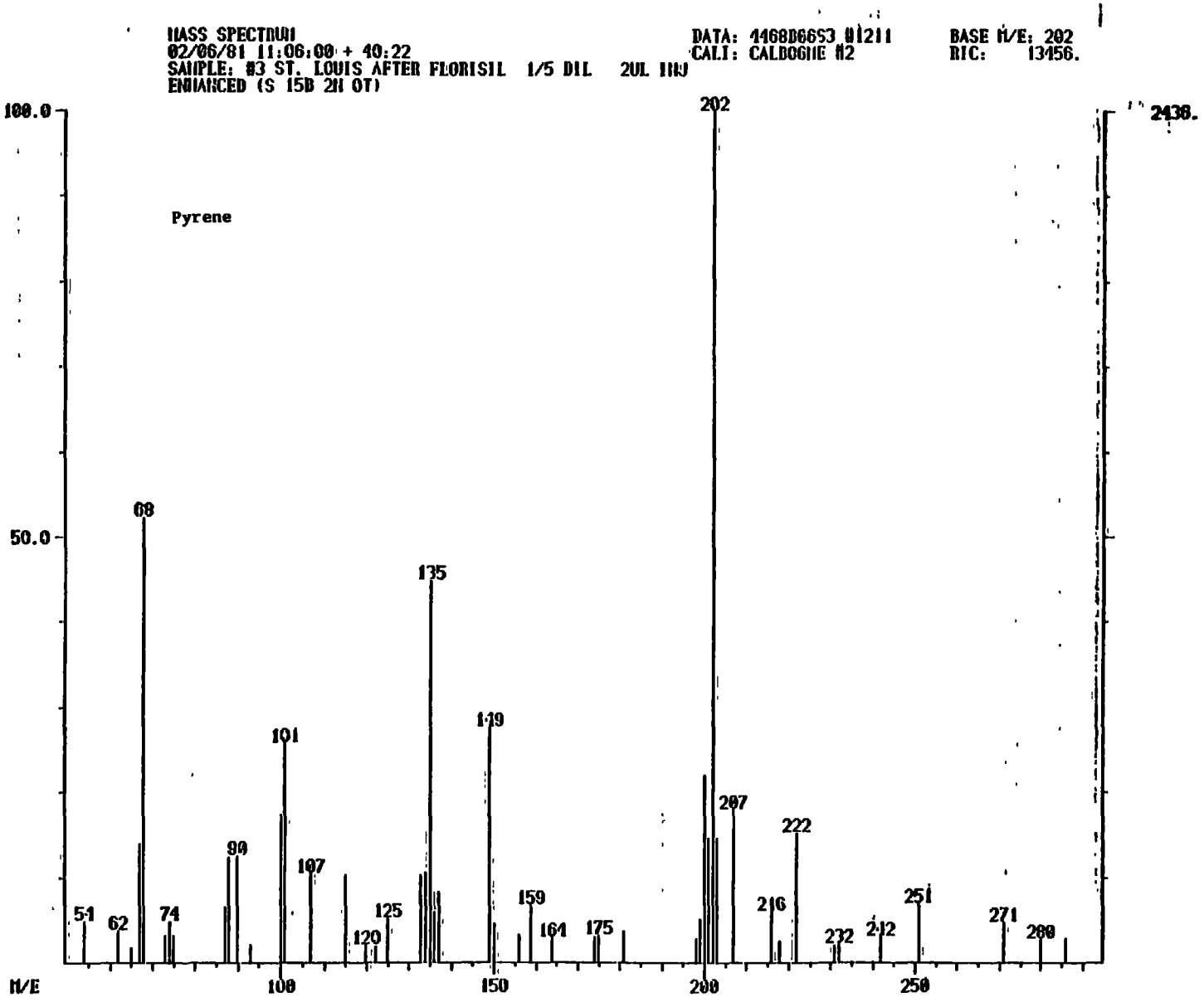

Figure 26 - Pyrene in Sample No. 3

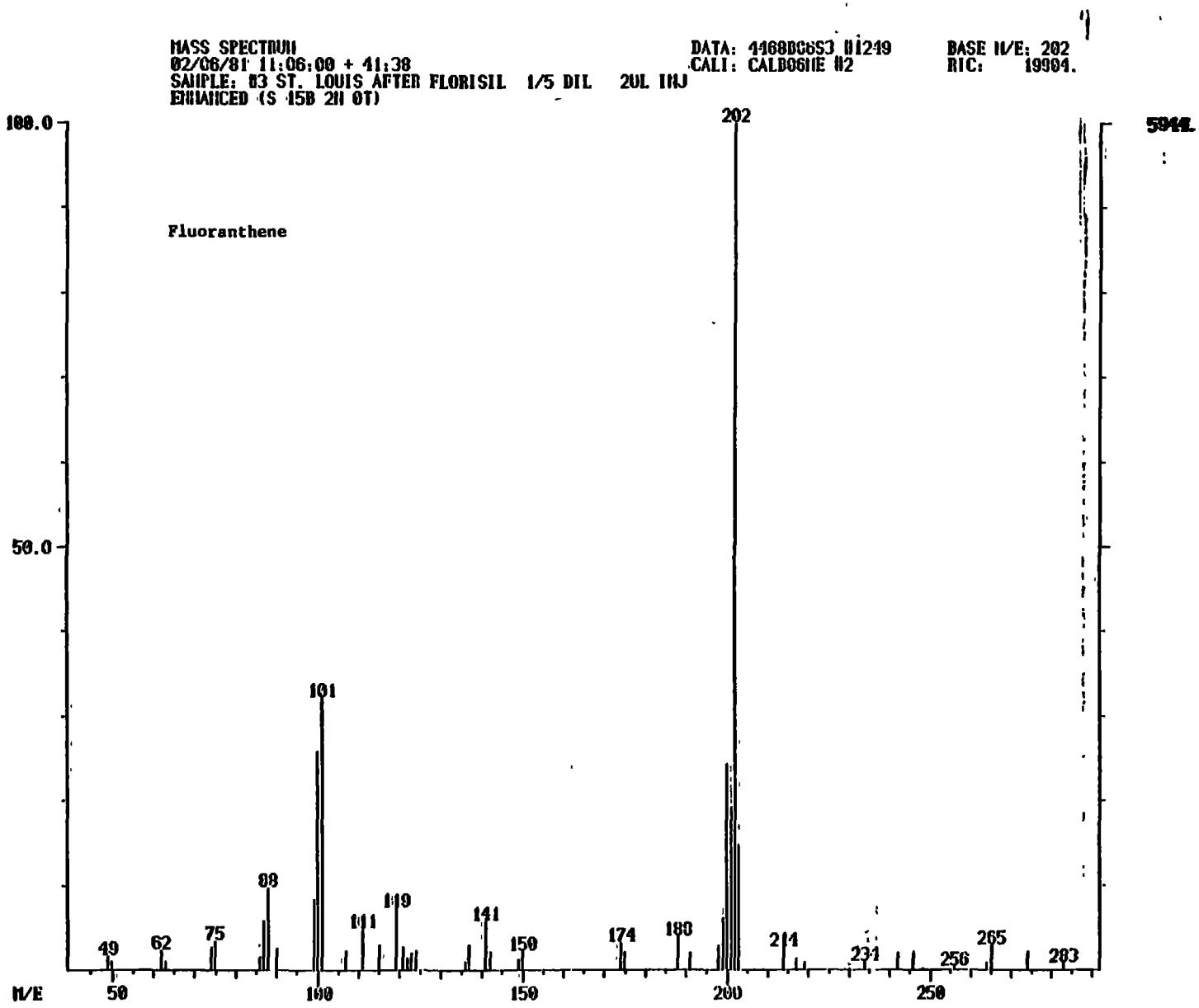

Figure 27 - Fluoranthene in Sample No. 3

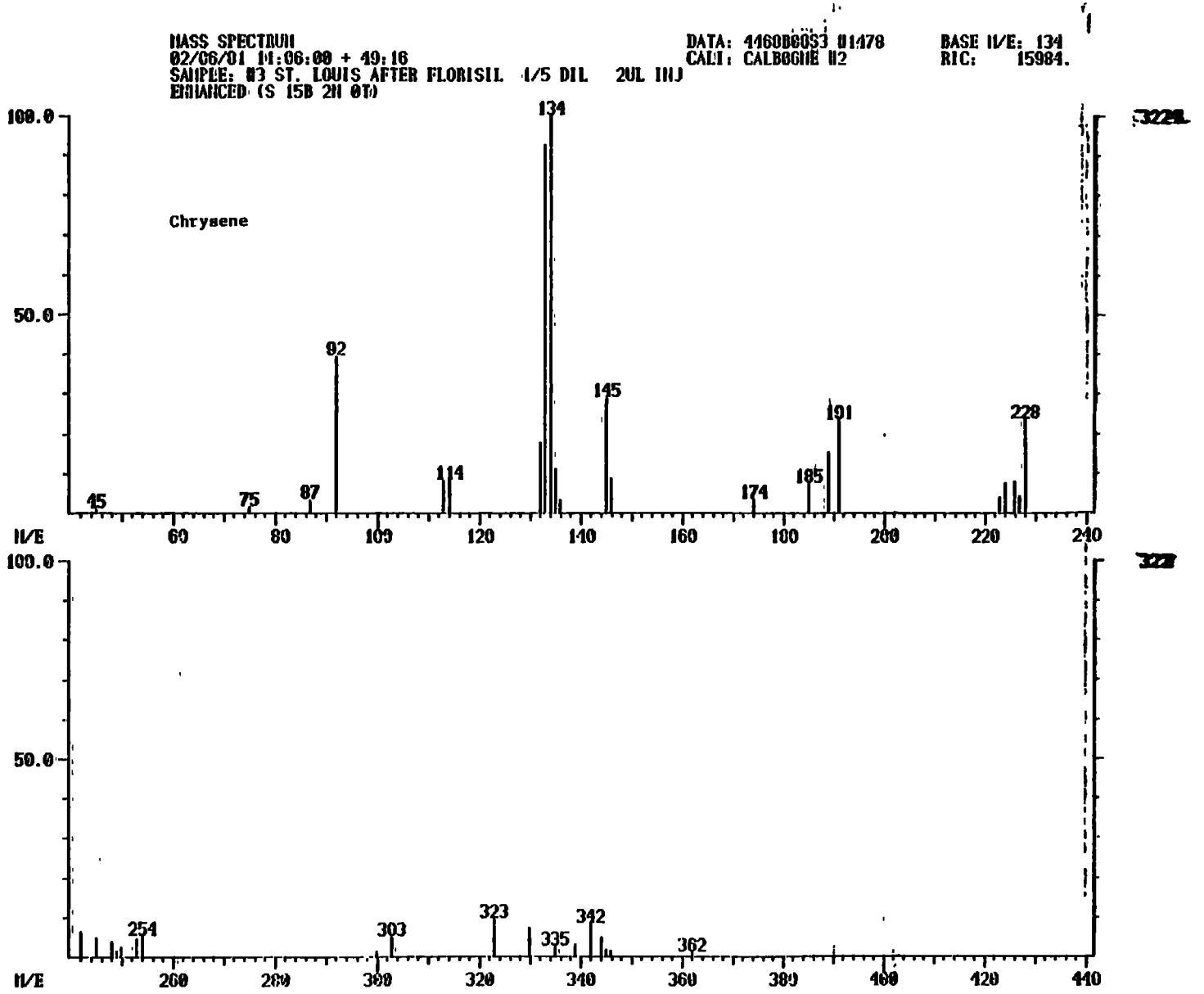

Figure 28 - Chrysene in Sample No. 3

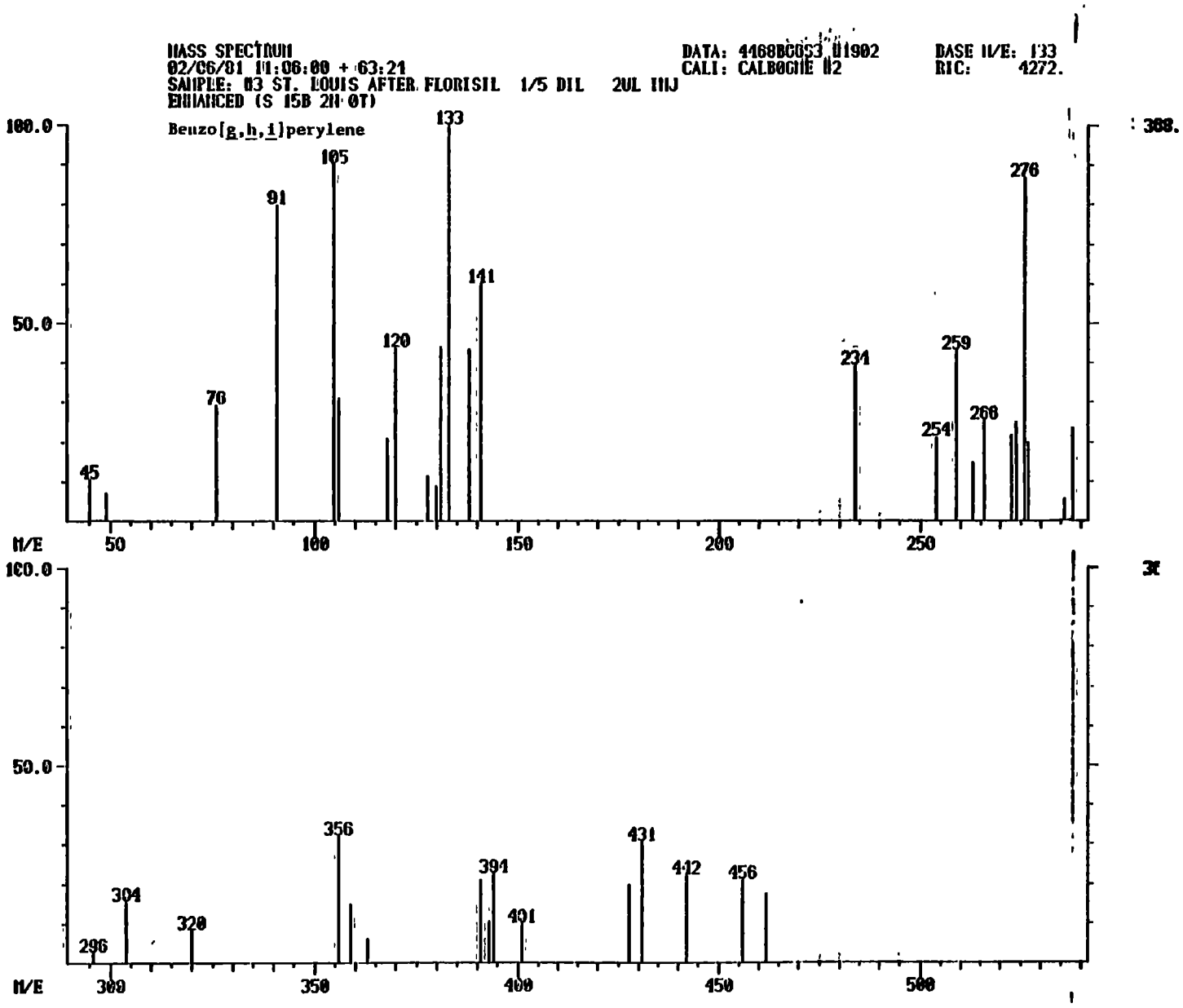

Figure [illegible] - Benzo[g,h,i]perylene in Sampl[illegible] No. 3

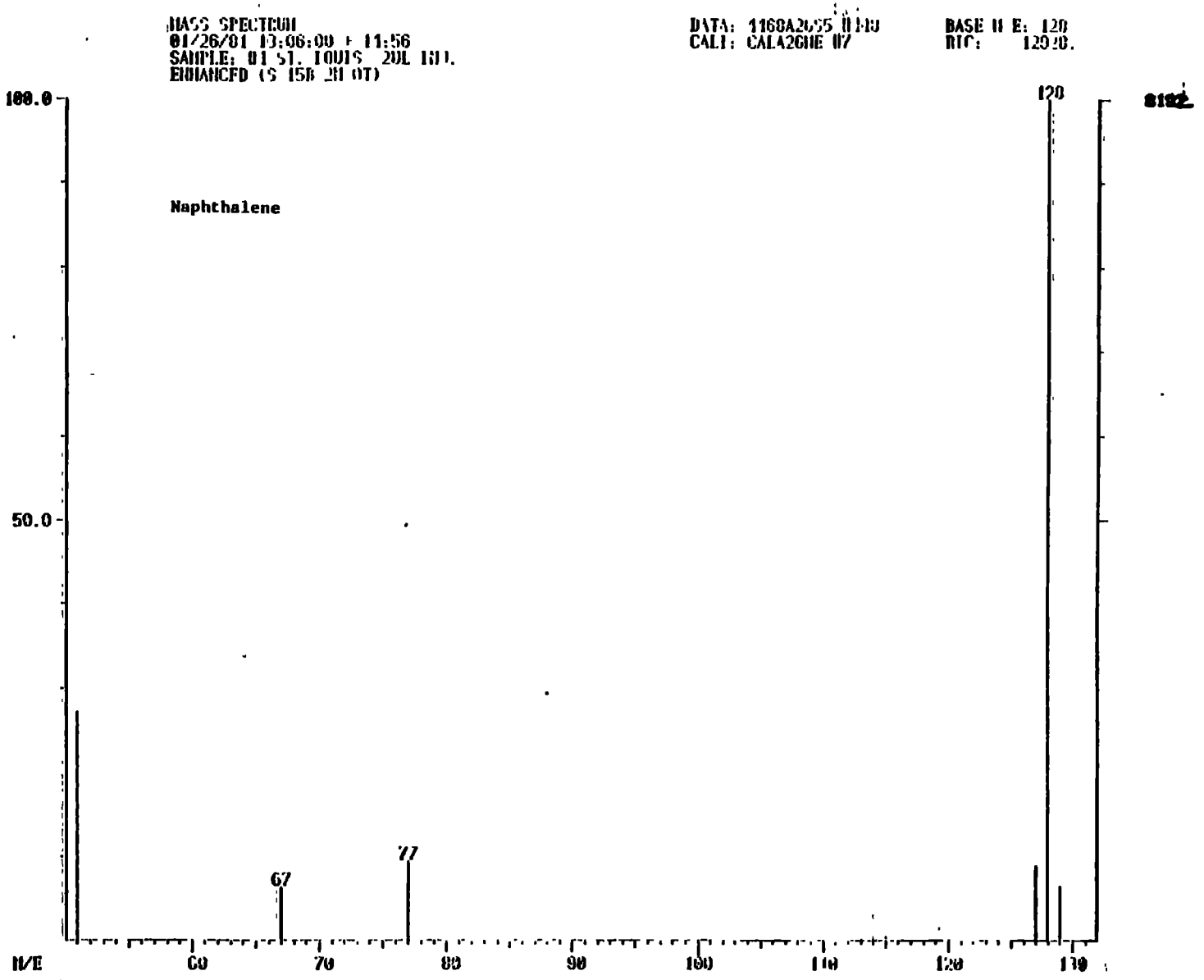

Figure 30 - Naphthalene in Sample No. 4

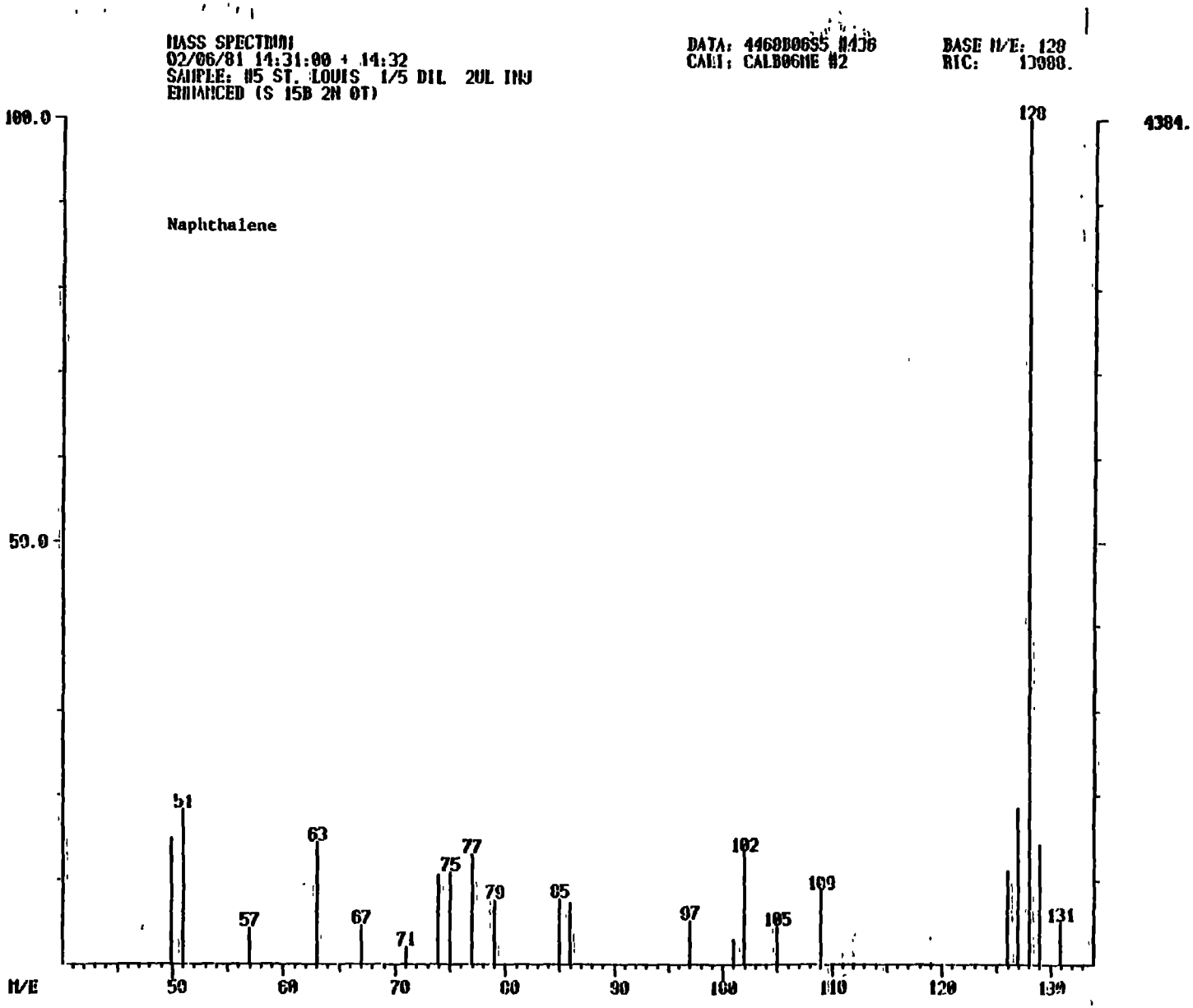

Figure 31 - Naphthalene in Sample No. 5

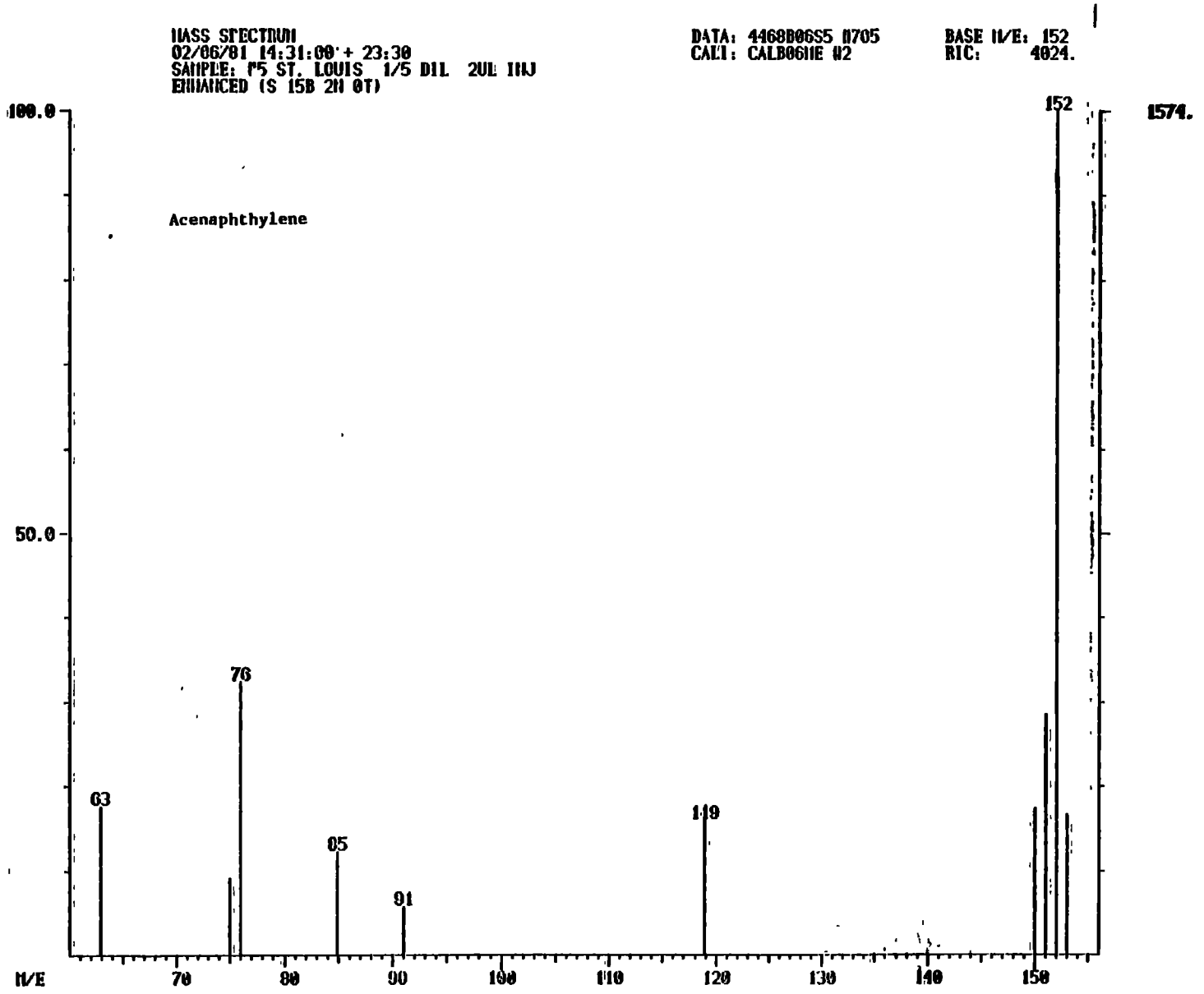

Figure 32 - Acenaphthylene in Sample No. 5

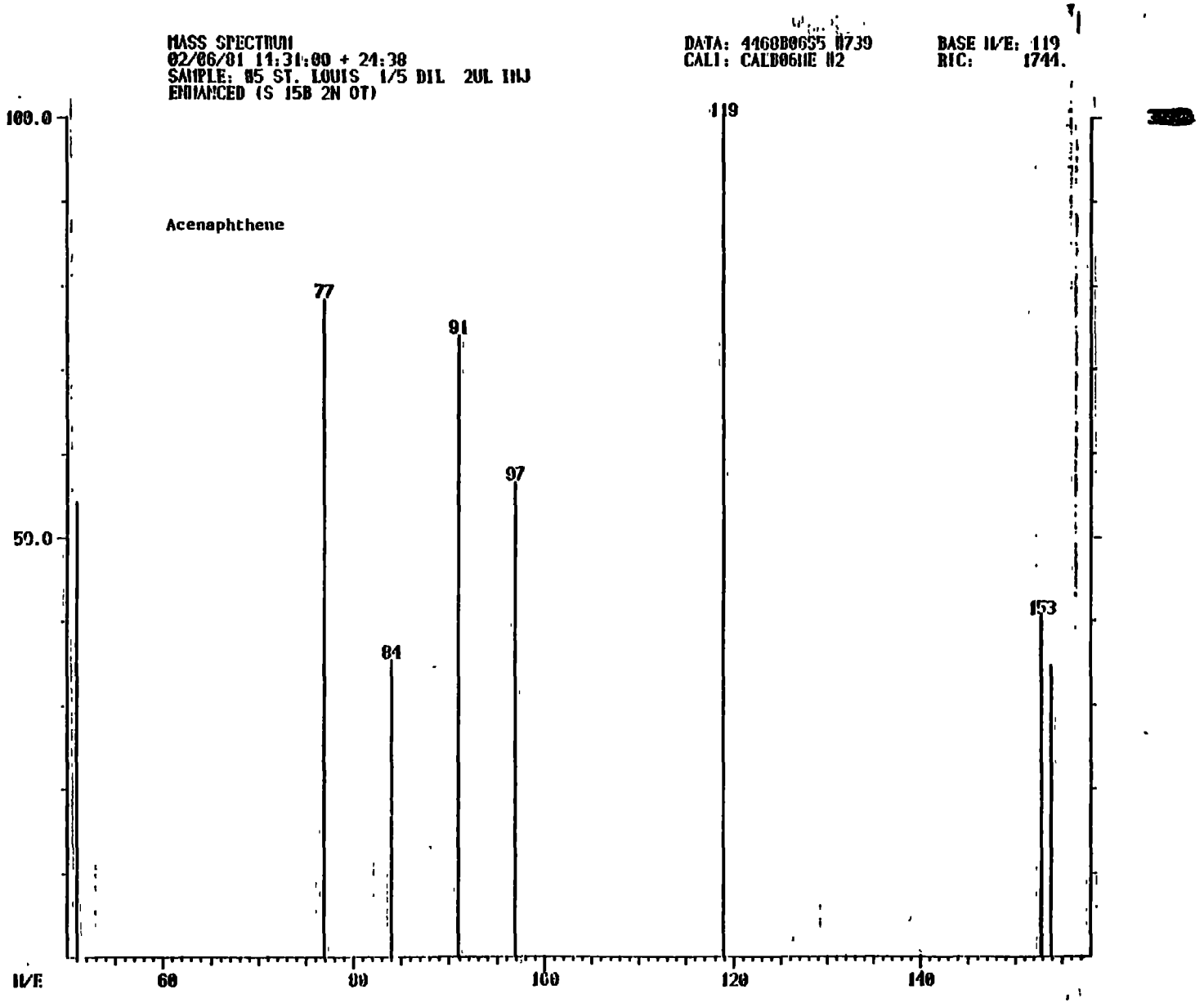

Figure 23 - Acenaphthene in Sample No. 5

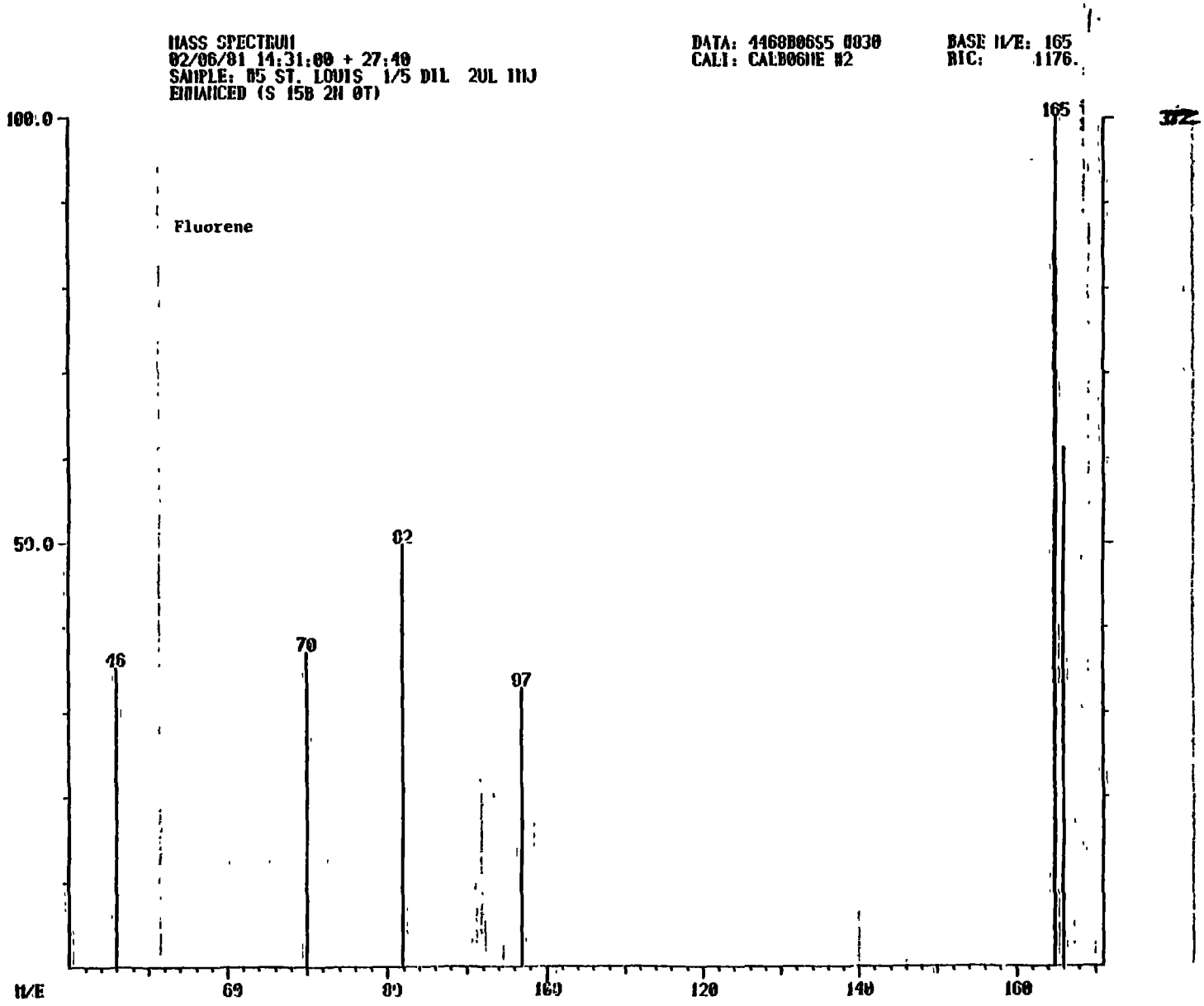

Figure 34 - Fluorene in Sample No. 5

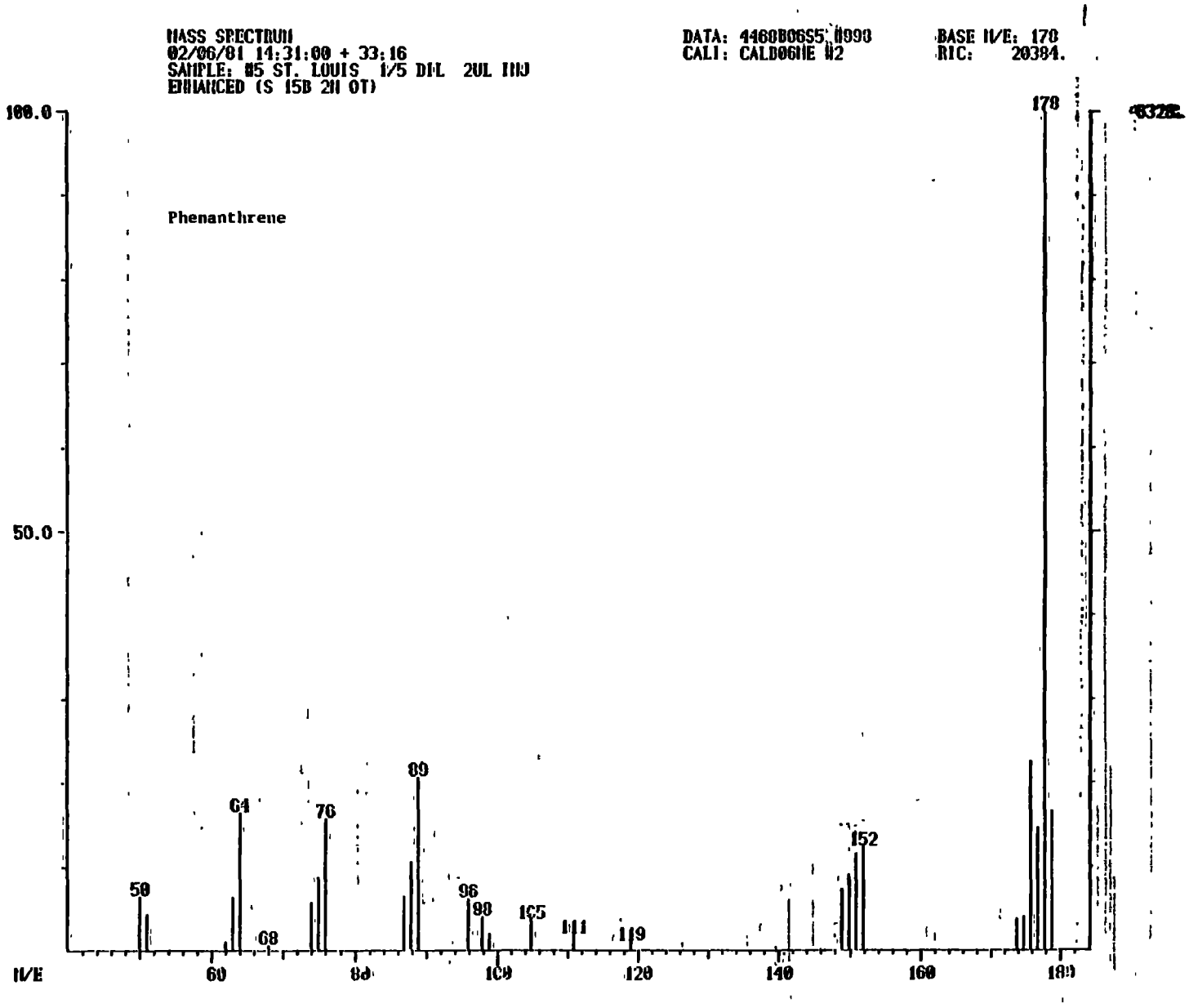

Figure 35 - Phenanthrene in Sample No. 5

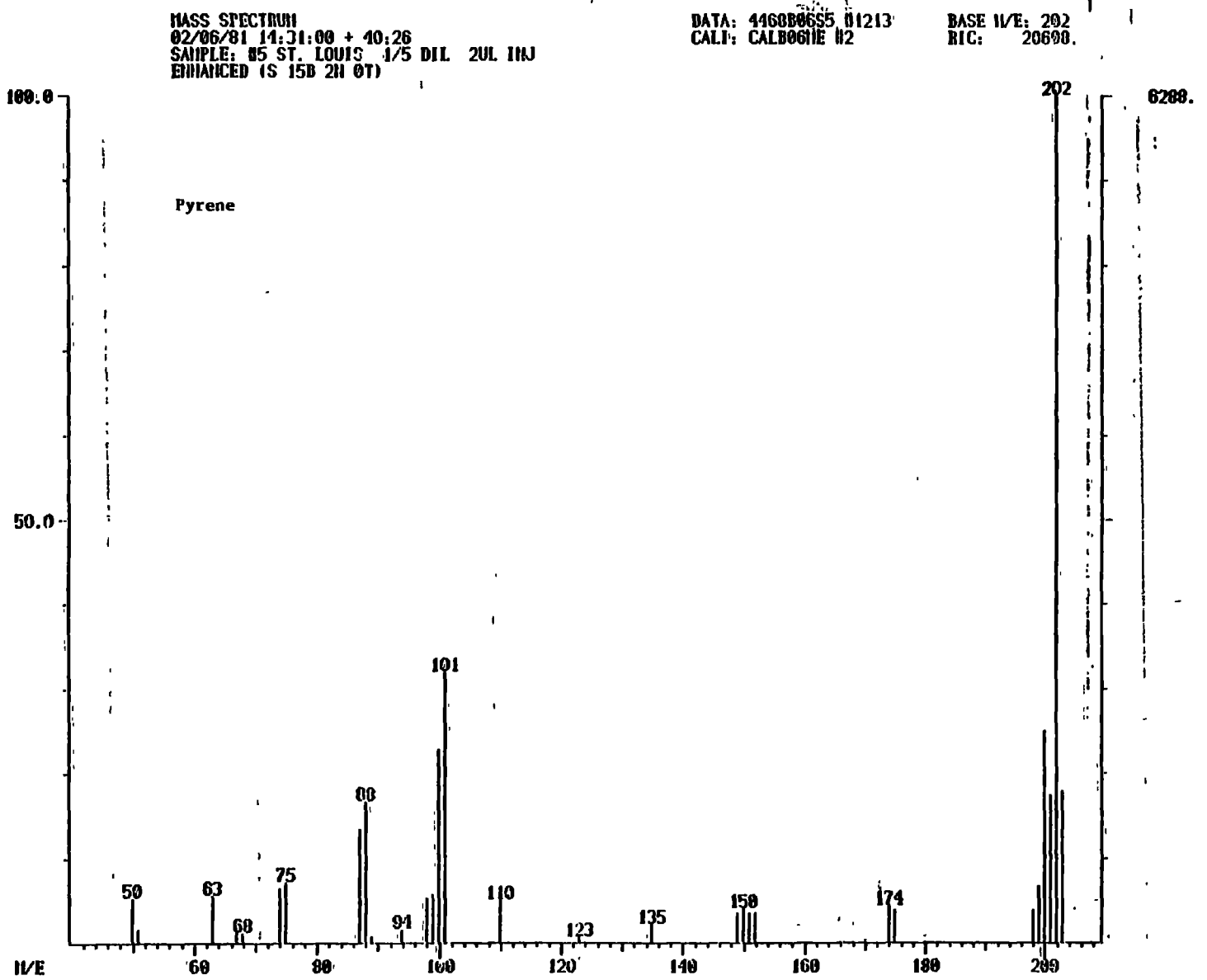

Figure 36 - Pyrene in Sample No. 5

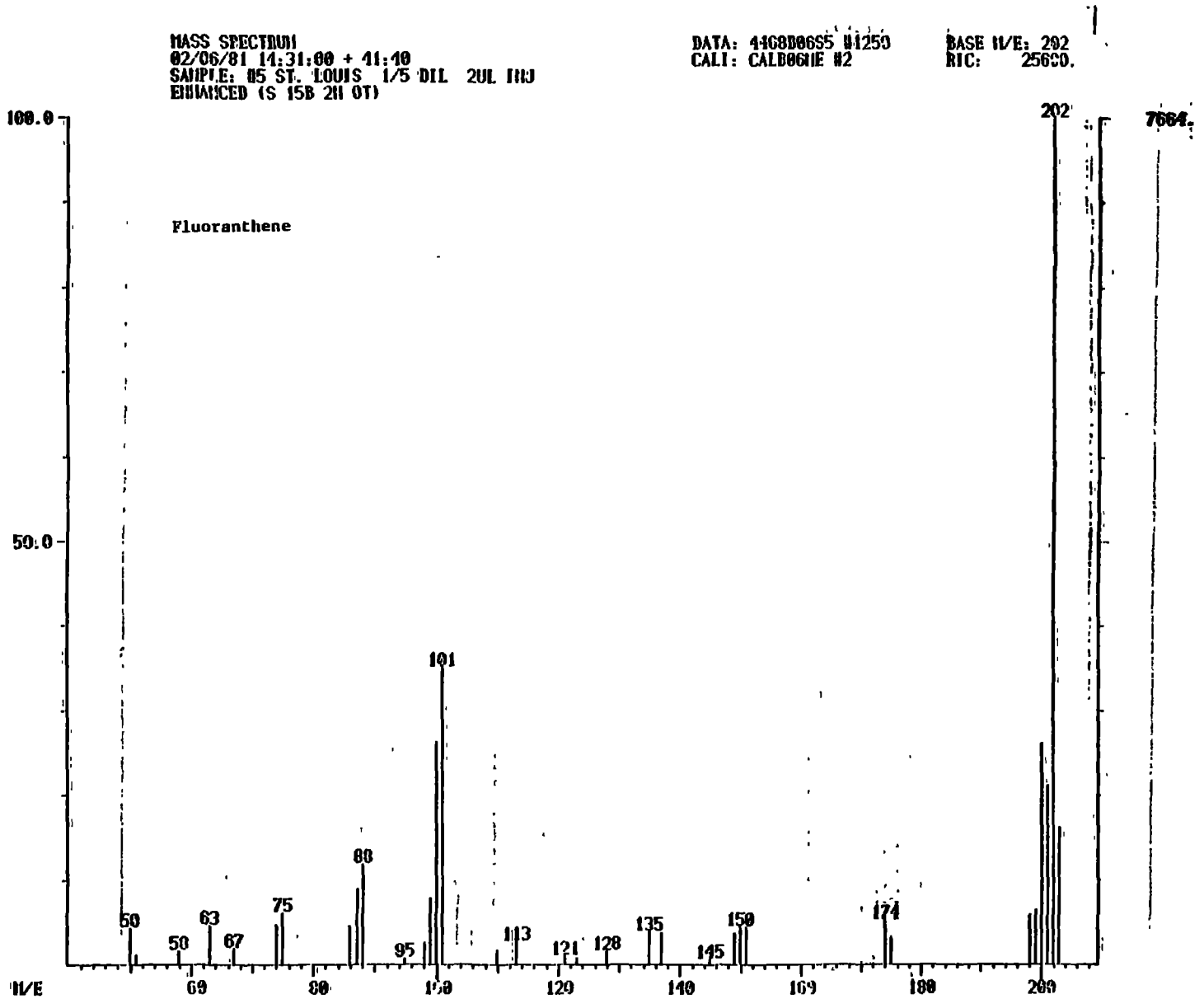

Figure 37 - Fluoranthene in Sample No. 5

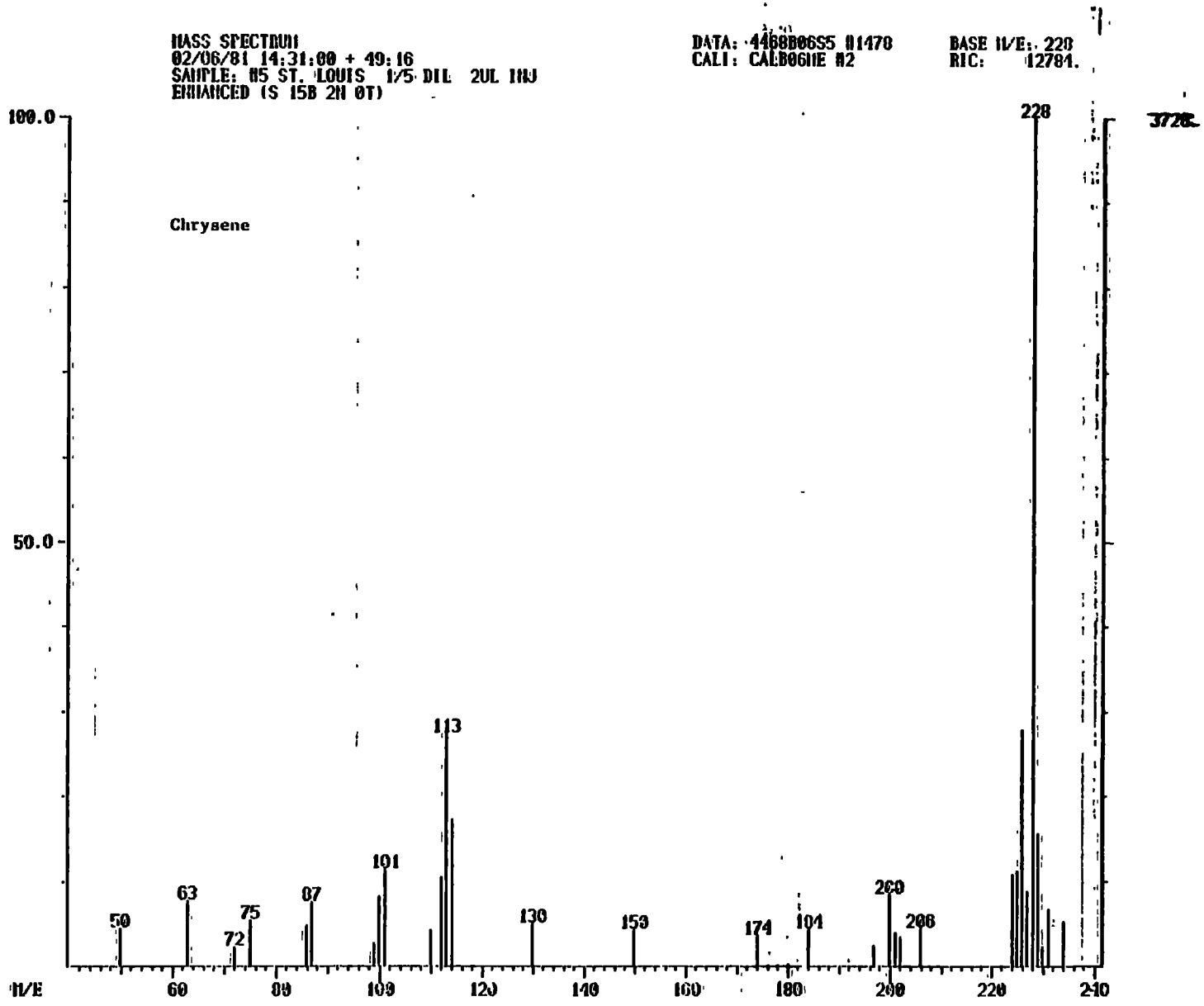

Figure 38 - Chrysene in Sample No. 5

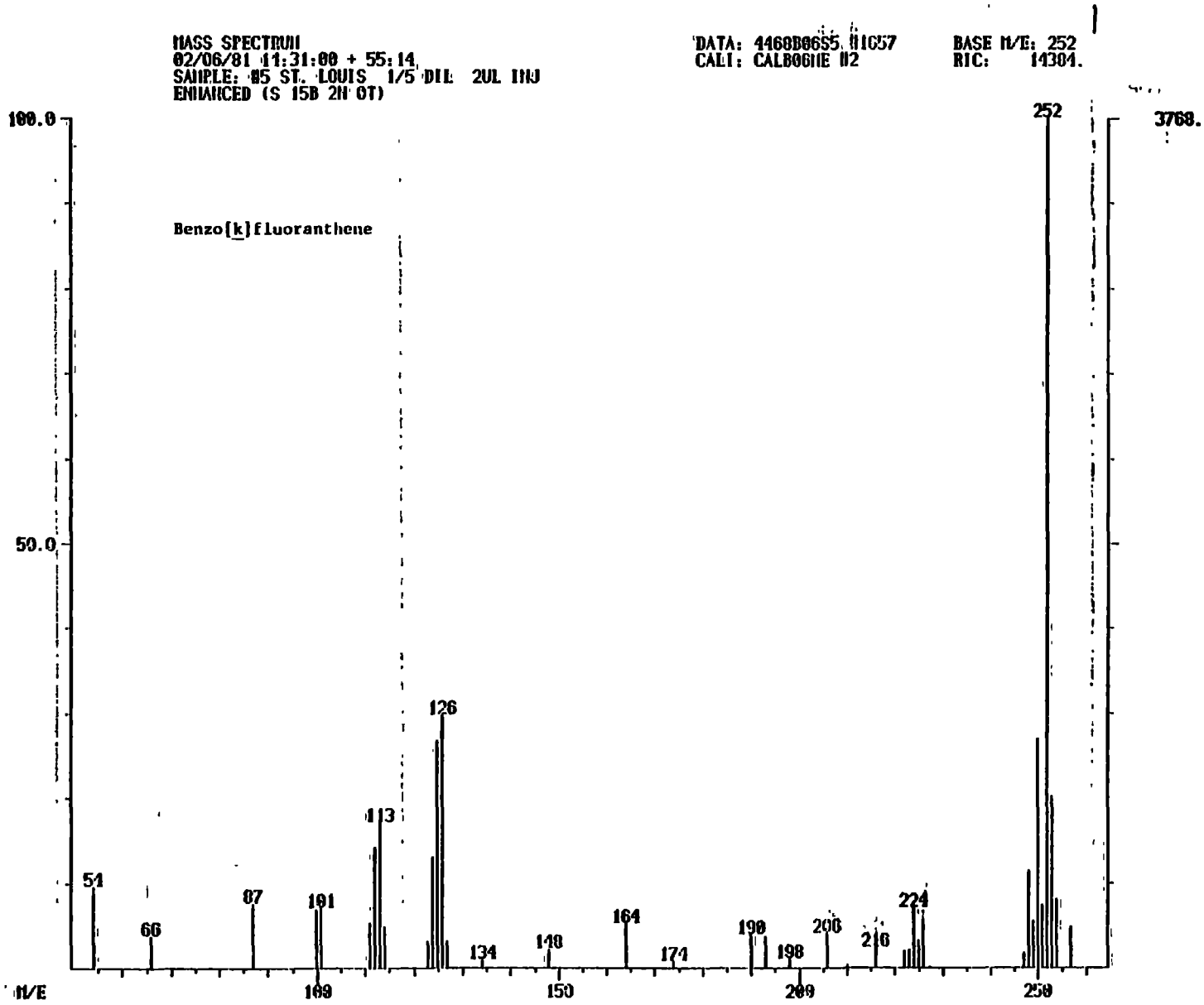

Figure 39 - Benzo[k]fluoranthene in Sample No. 5

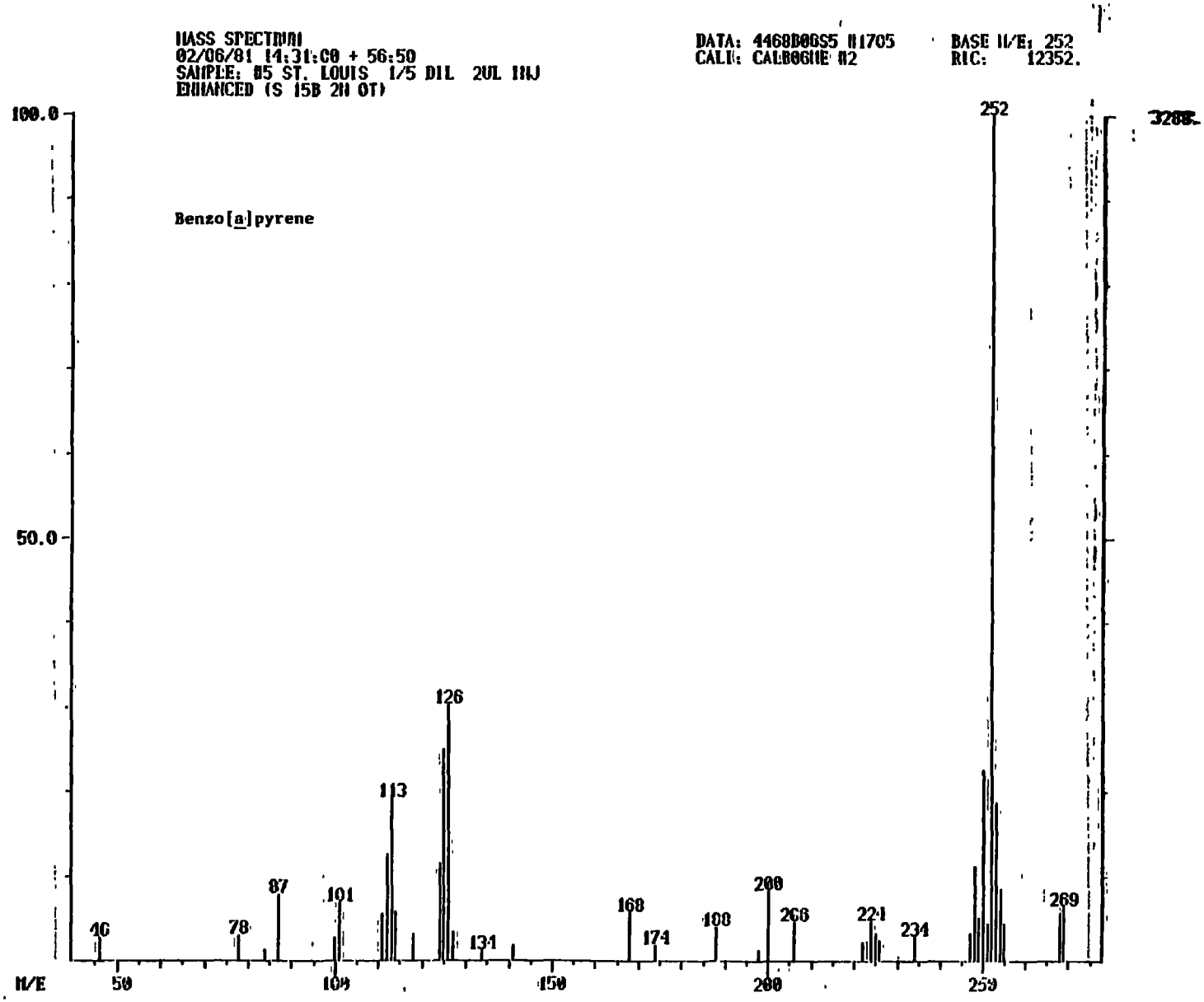

Figure 40 - Benzo[a]pyrene in Sample No. 5

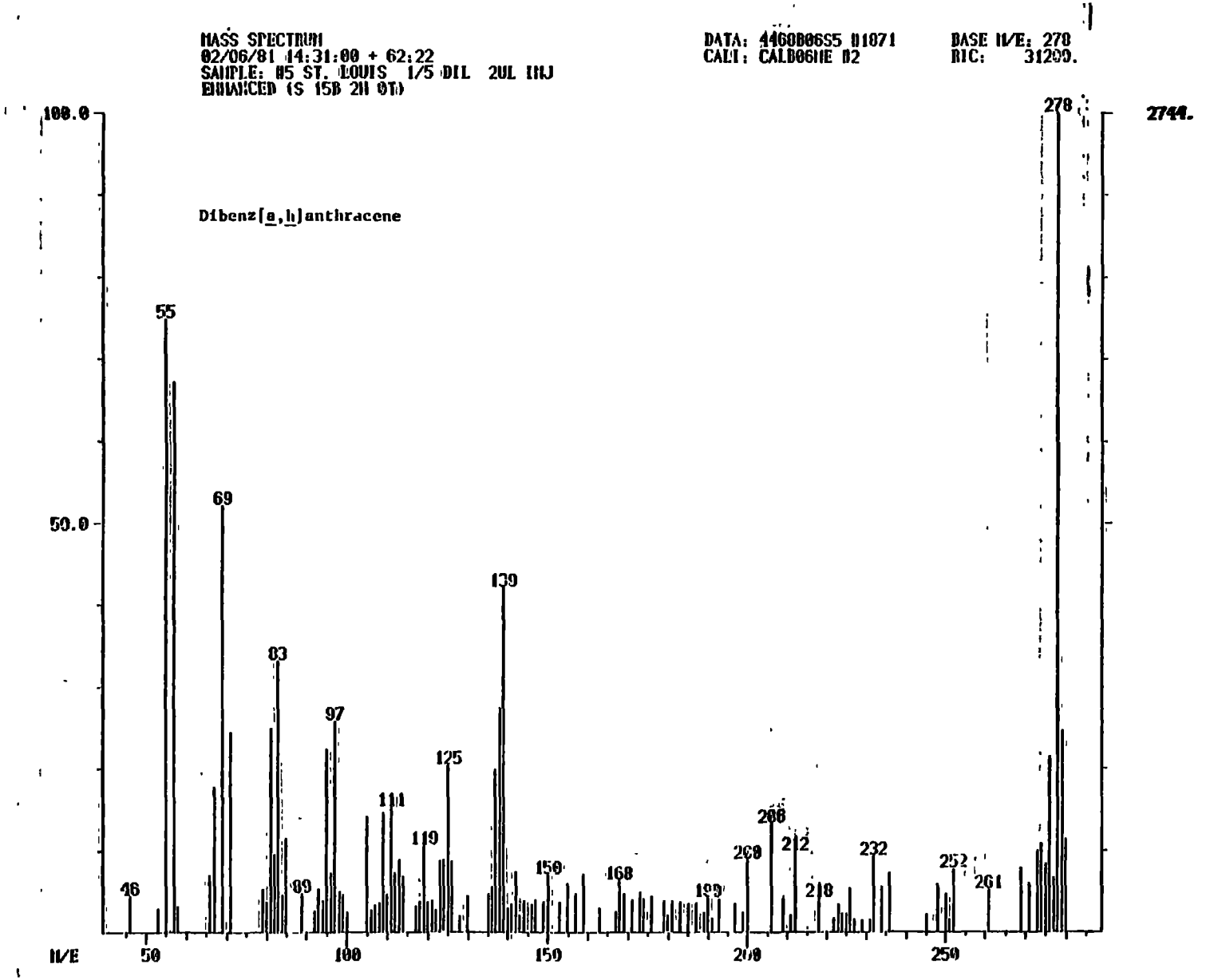

Figure 41 - Dibenz[a,h]anthracene in Sample No. 5

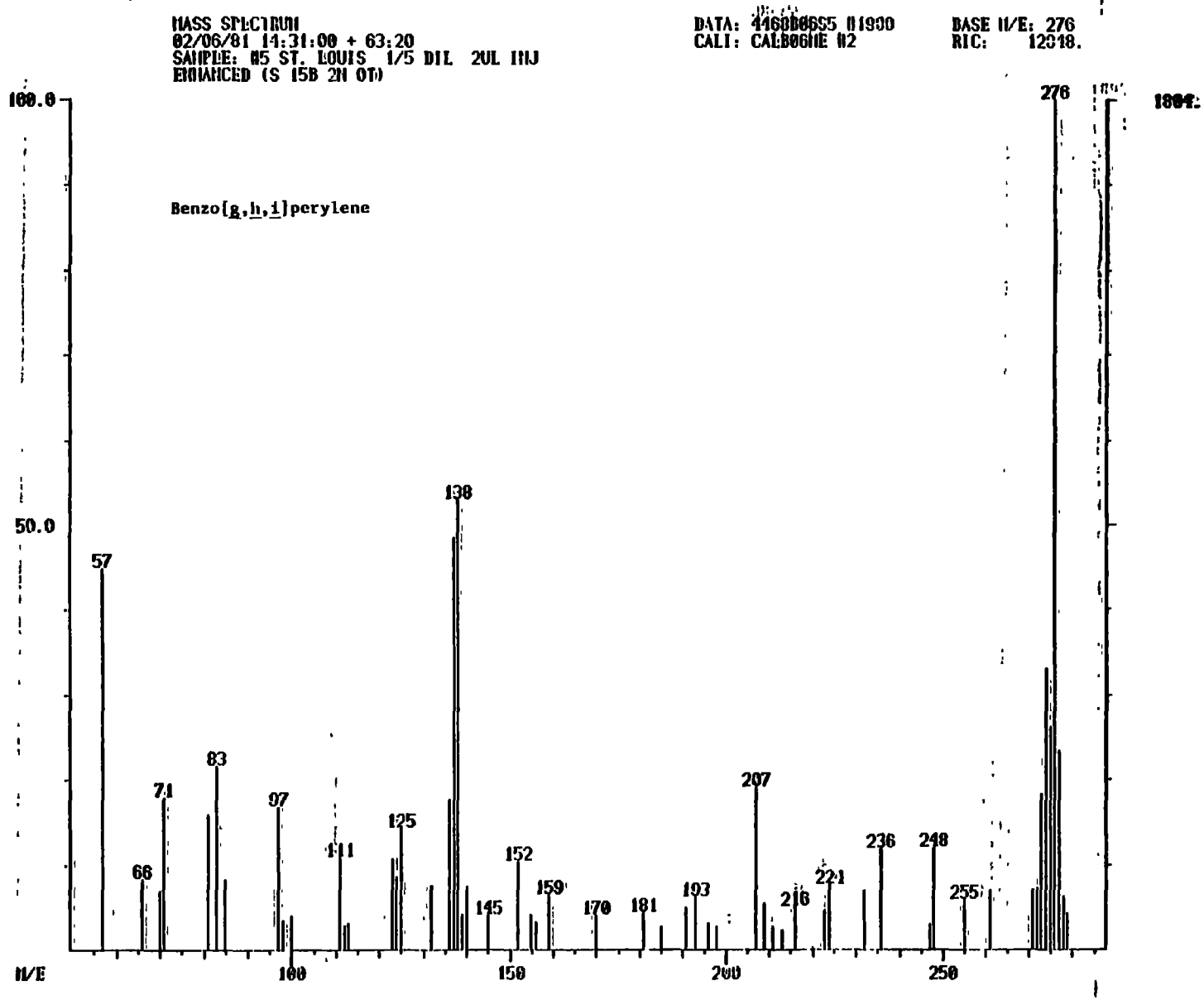

Figure 42 - Benzo[g,h,i]perylene in Sample No. 5

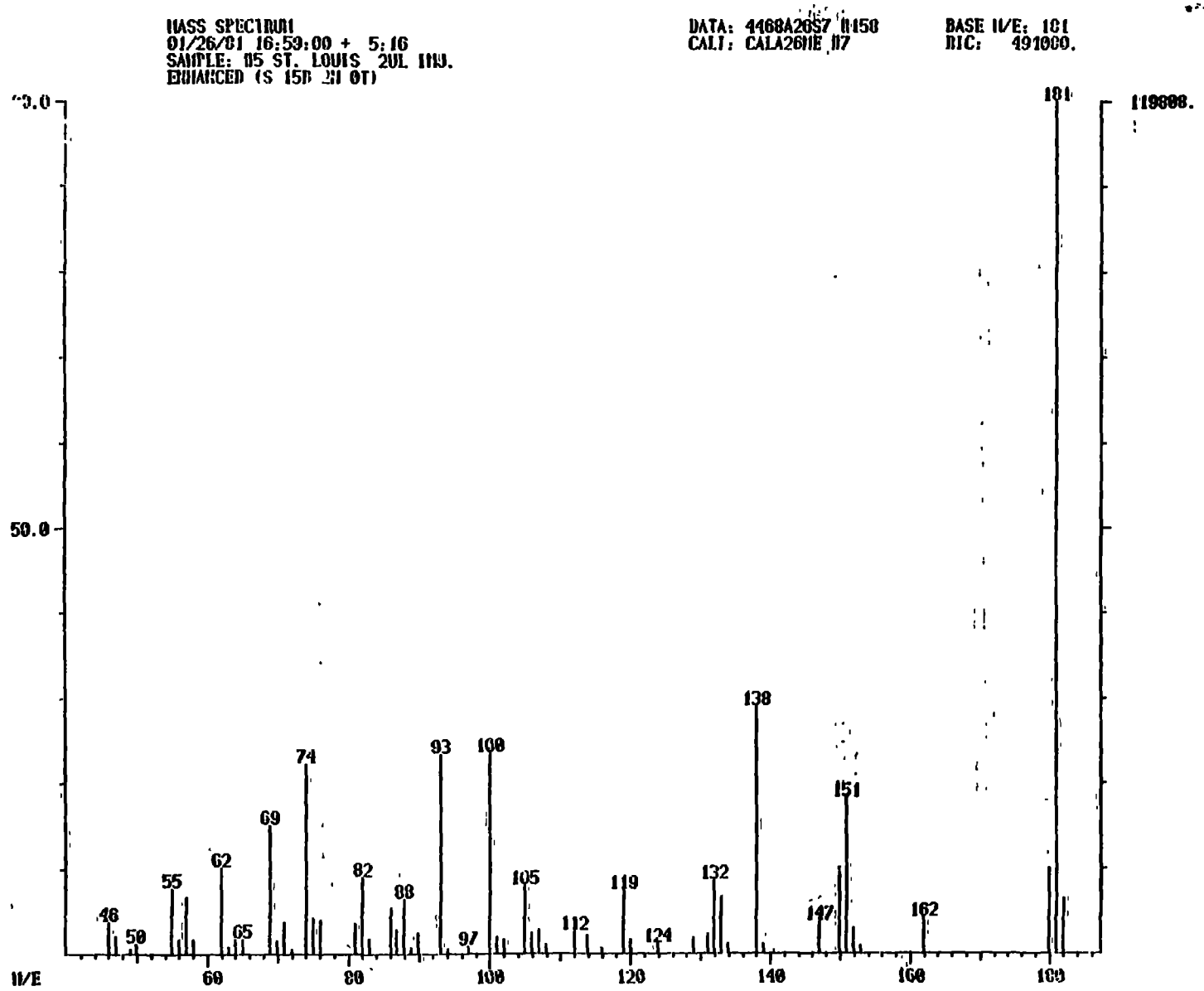

Figure 43 - A Methyl Carbazole in Sample No. 5

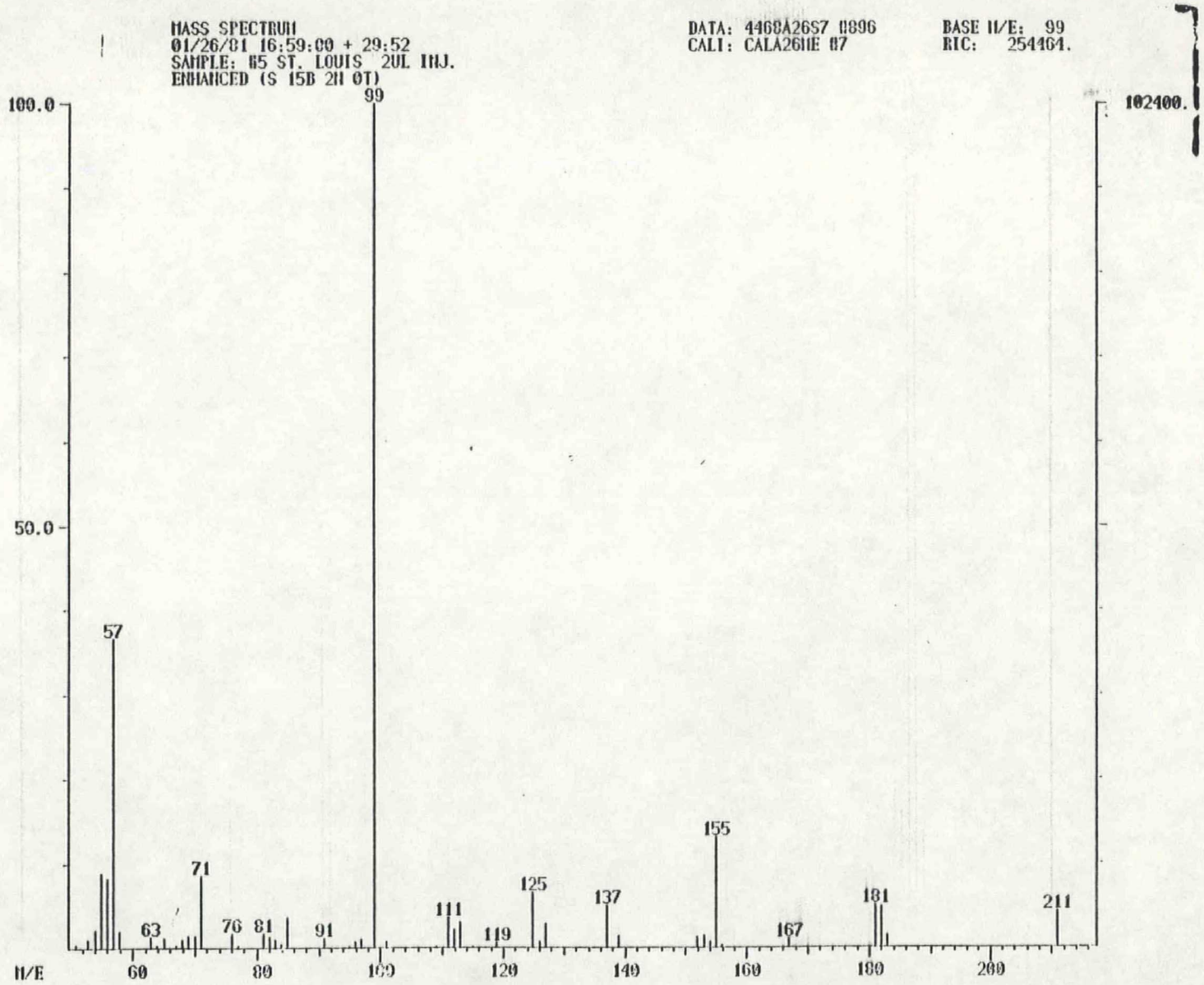

Figure 44 - Tributylphosphate in Sample No. 5

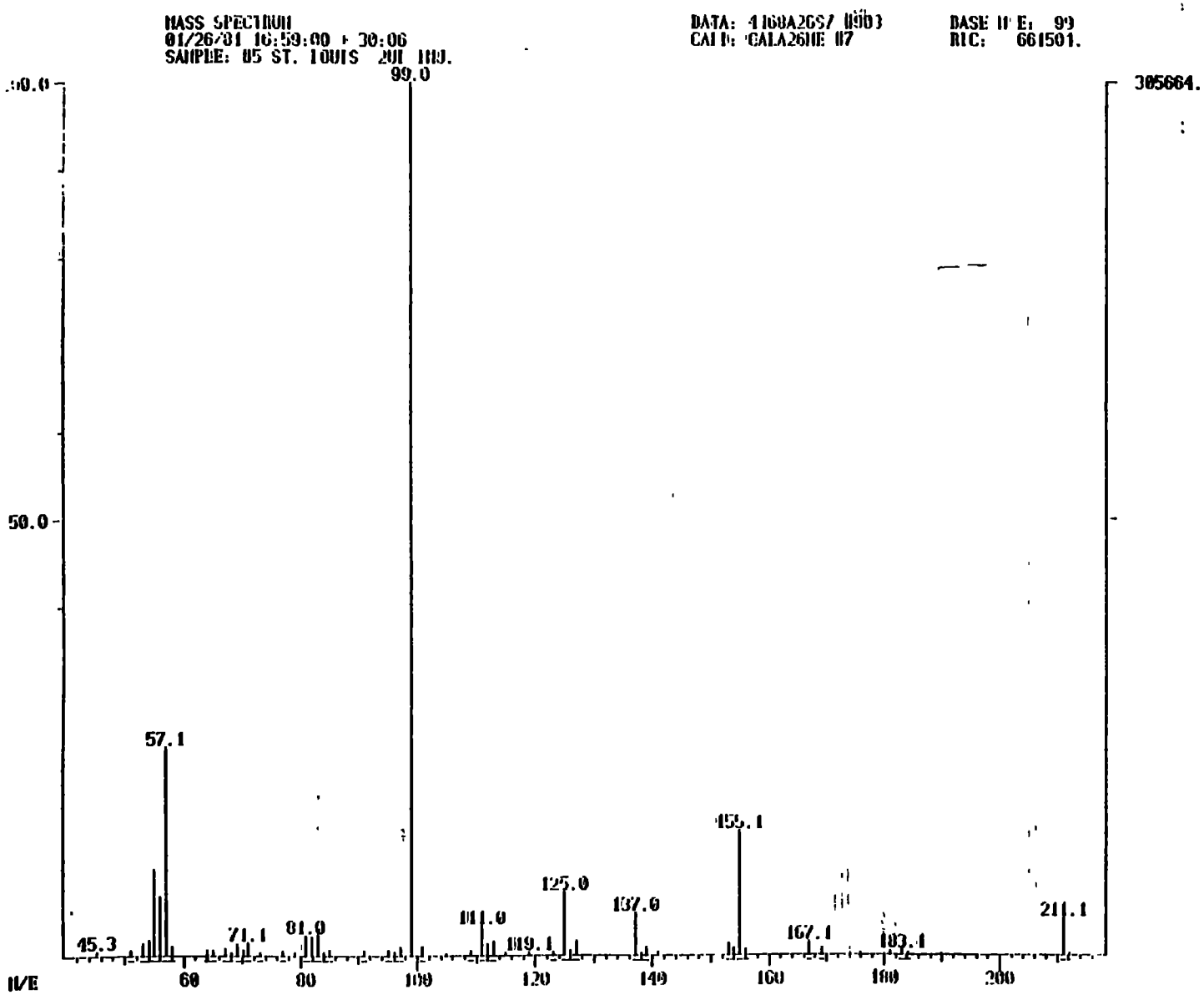

Figure 45 - Tributylphosphate from Computer Library

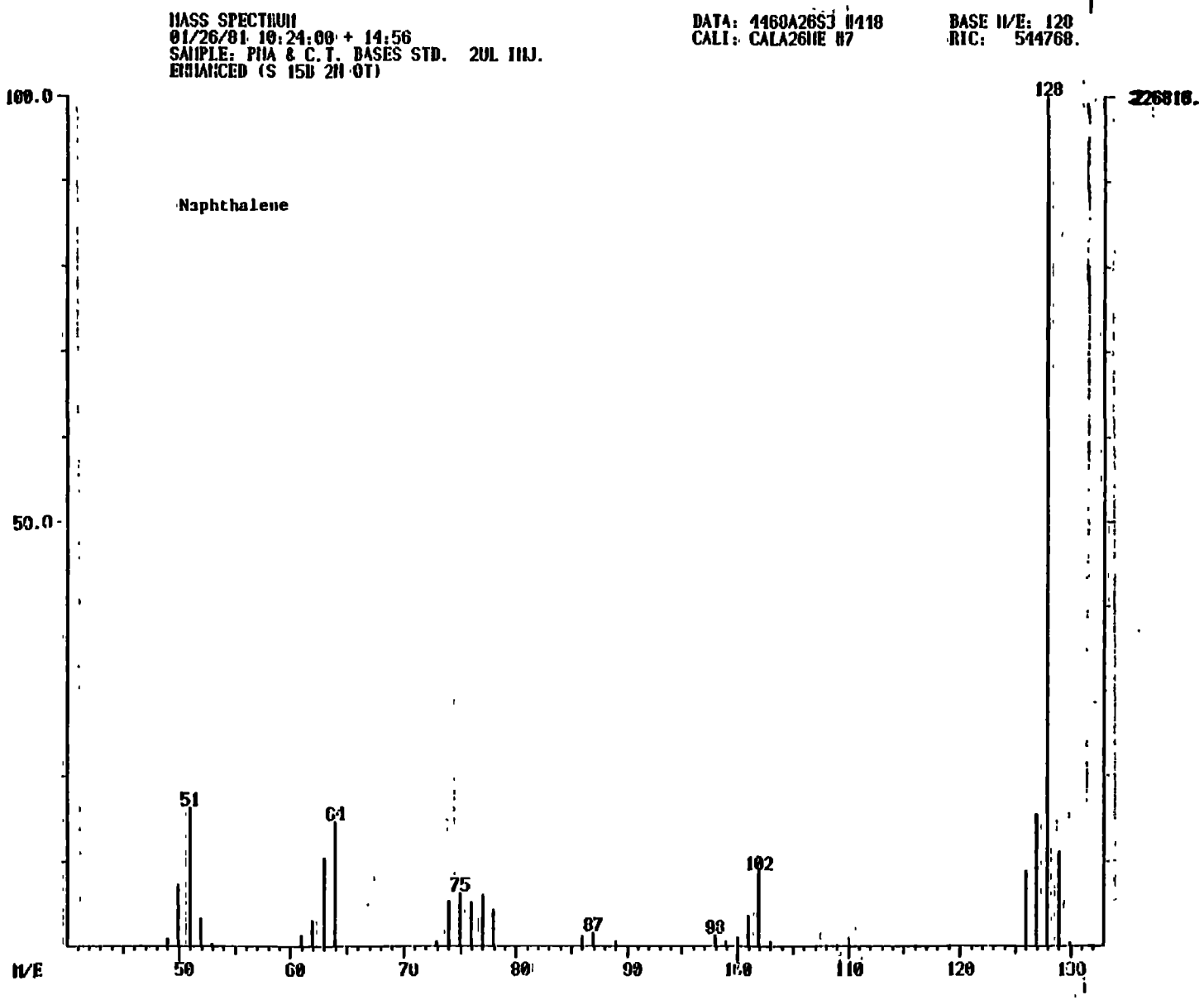

Figure 46 - Naphthalene in Standard (1/26/81)

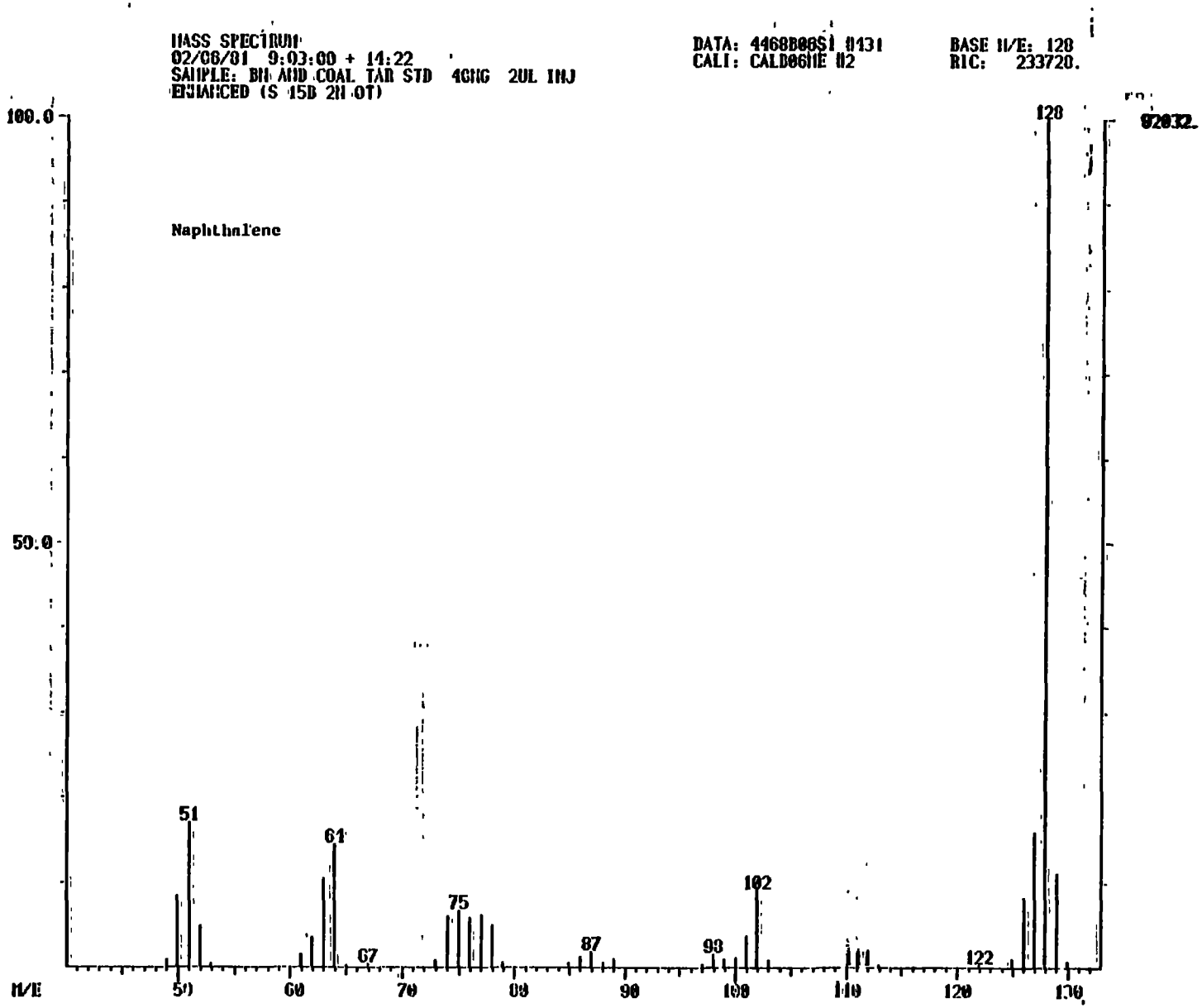

Figure 47 - Naphthalene in Standard (2/6/81)

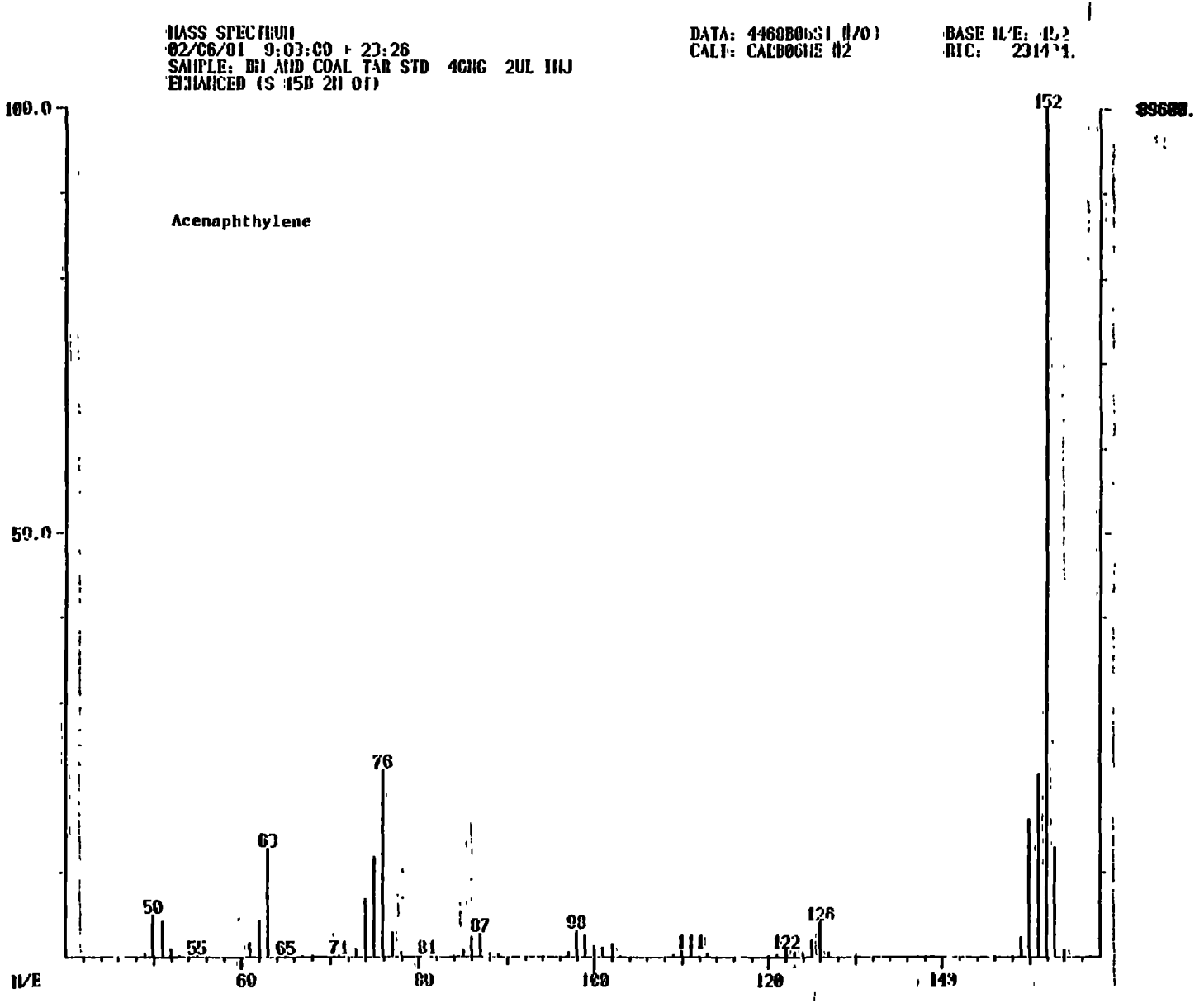

Figure 48 - Acenaphthylene in Standard (2/6/81)

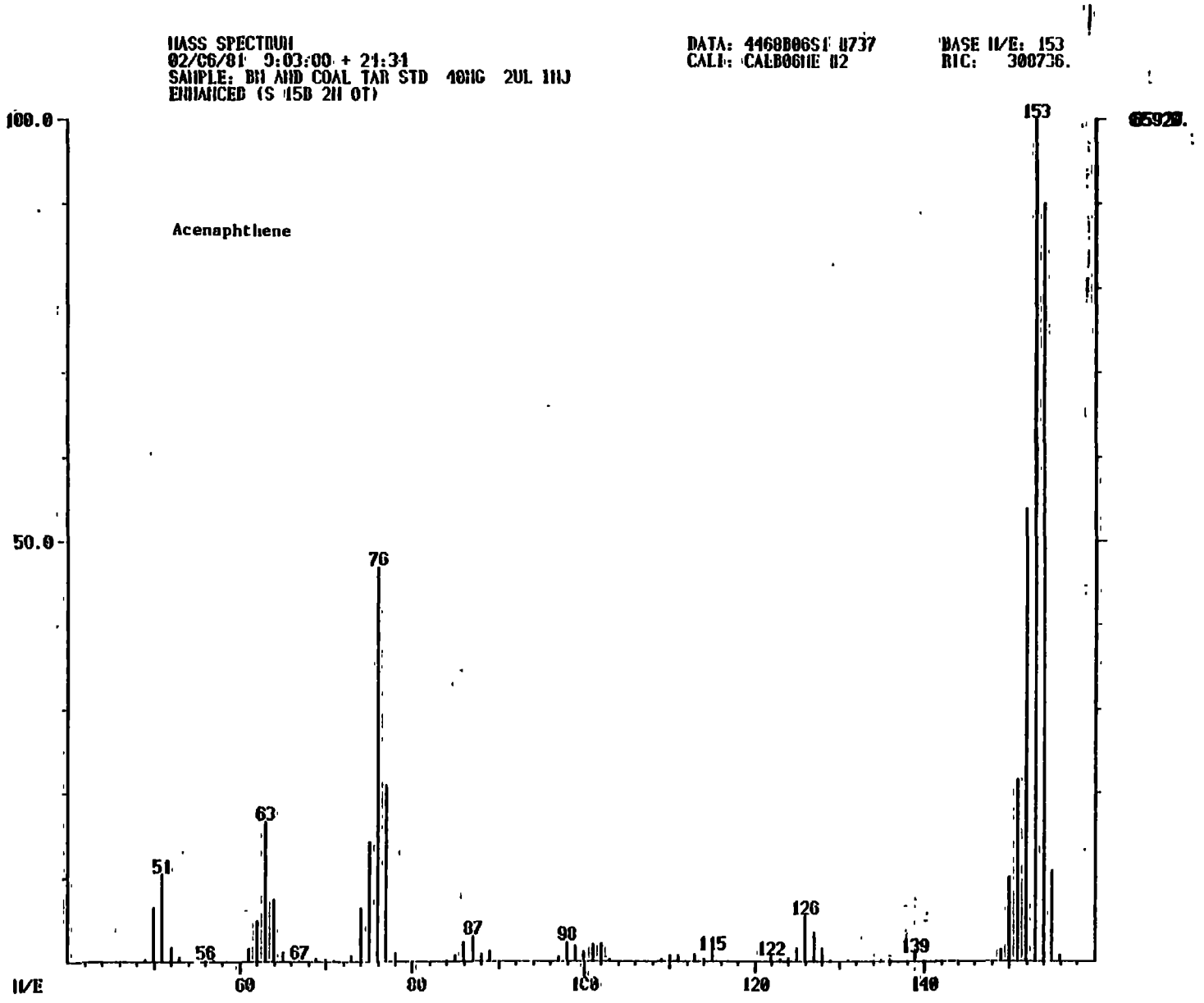

Figure 49 - Acenaphthene in Standard (2/6/81)

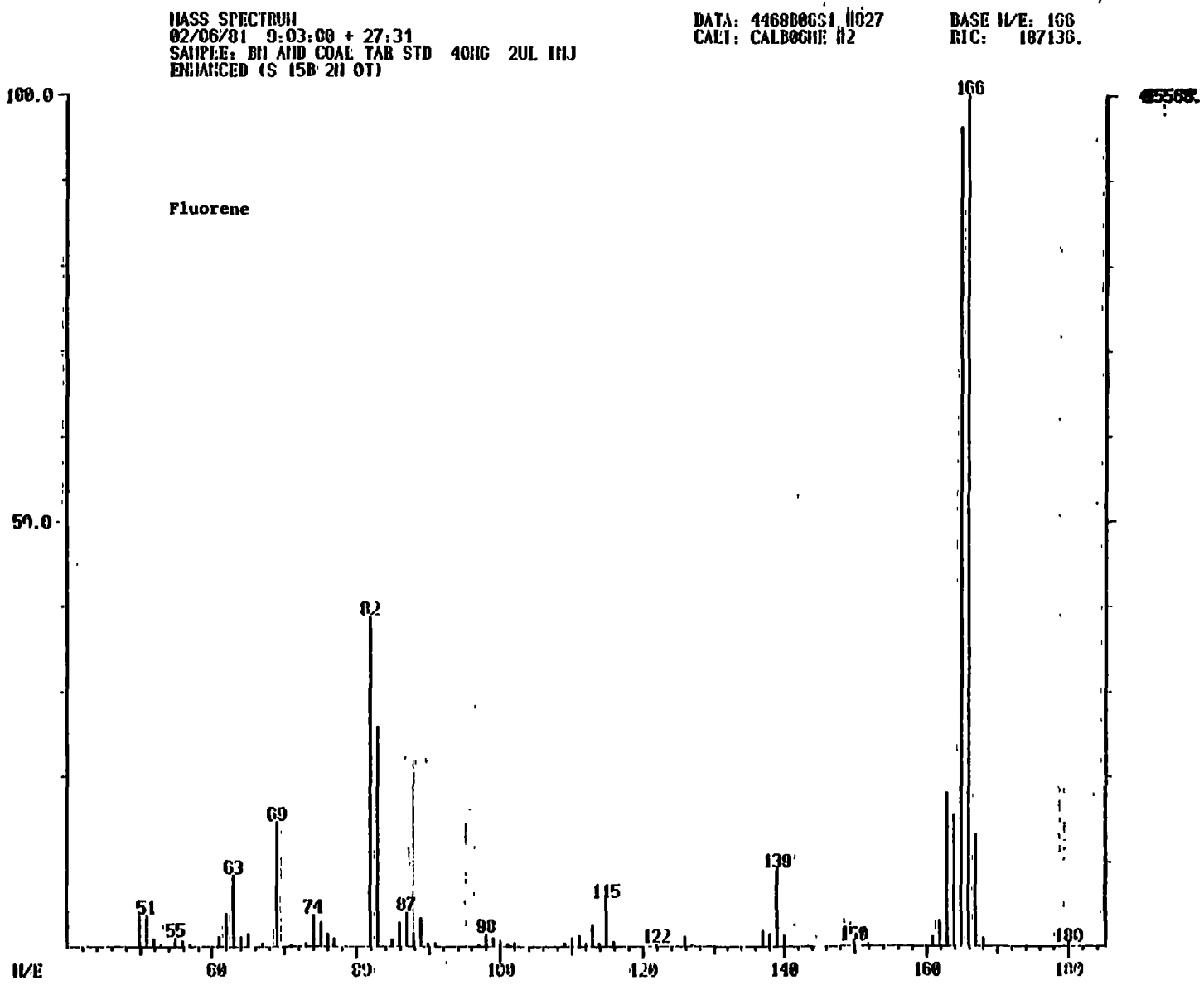

Figure 50 - Fluorene in Standard (2/6/81)

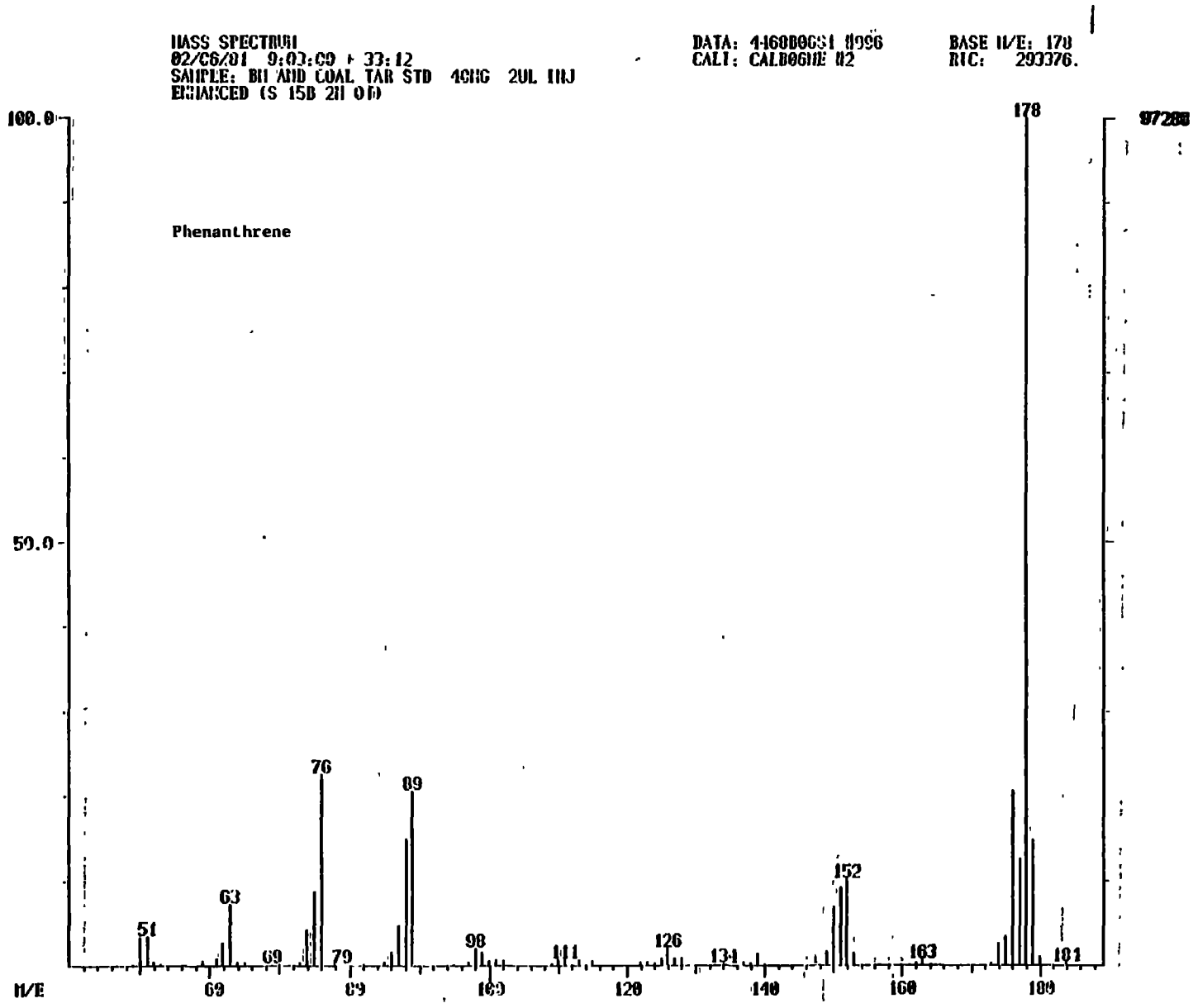

Figure 51 - Phenanthrene in Standard (2/6/81)

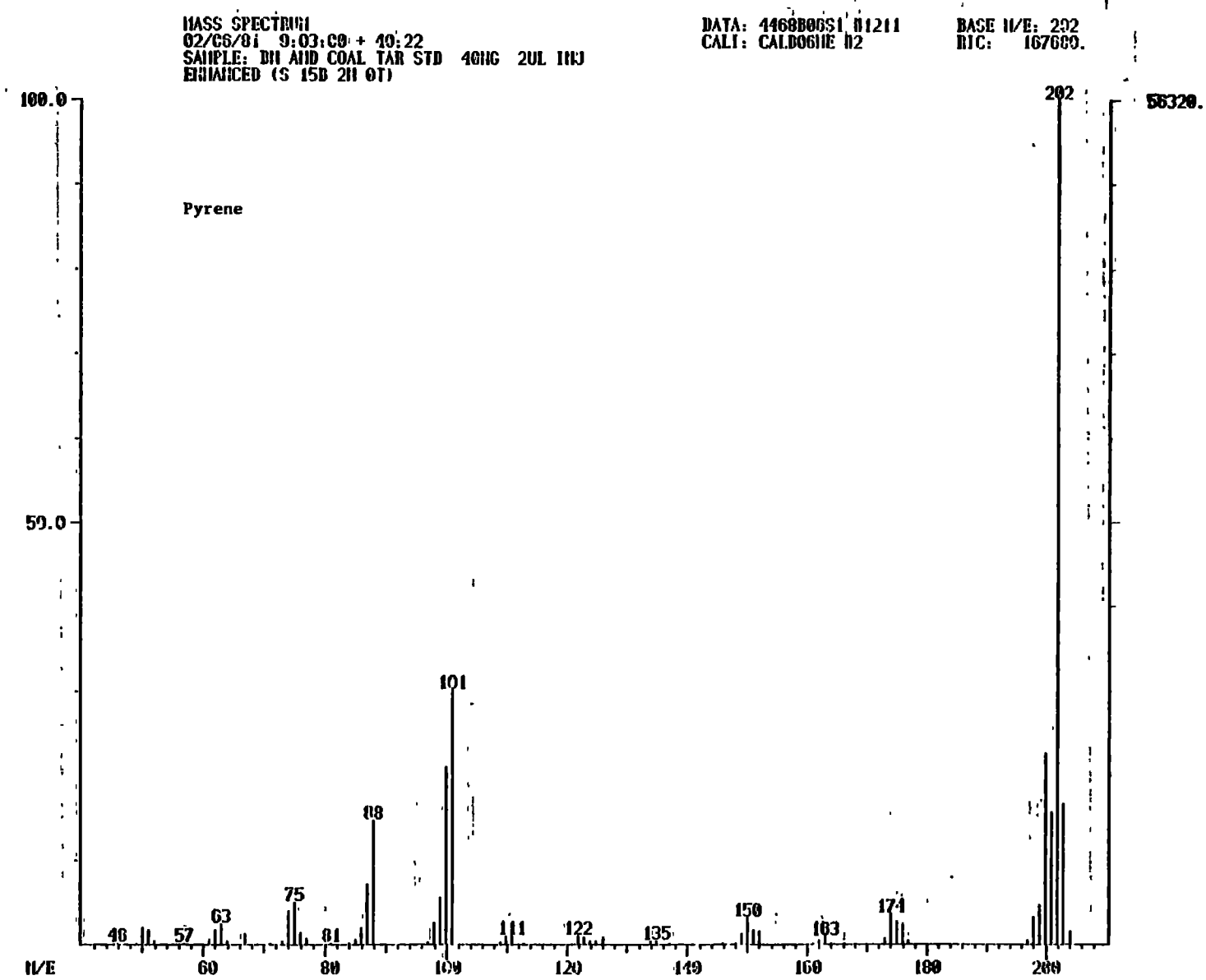

Figure 52 - Pyrene in Standard (2/6/81)

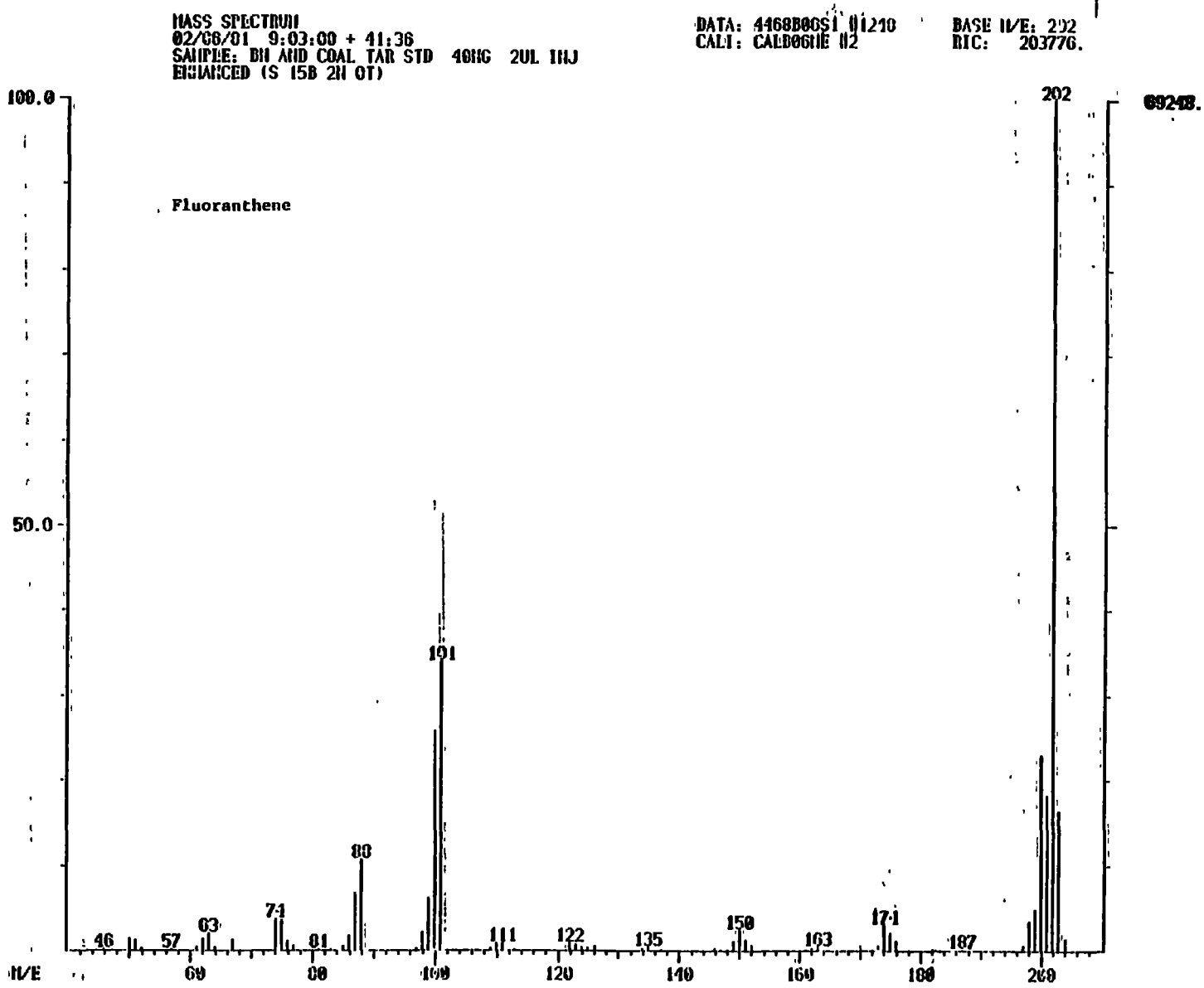

Figure 53 -- Fluoranthene in Standard (2/6/81)

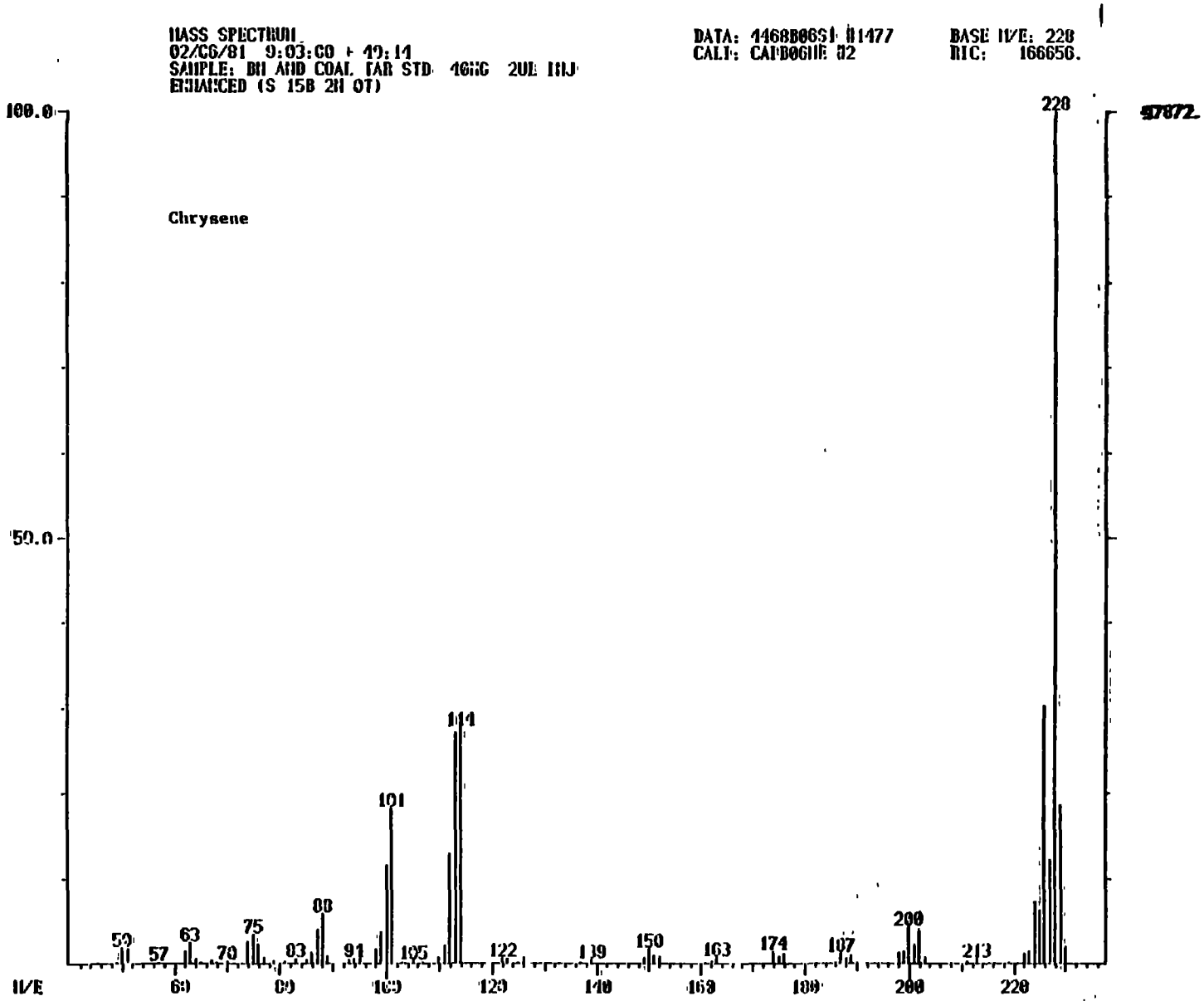

Figure 54 - Chrysene in Standard (2/6/81)

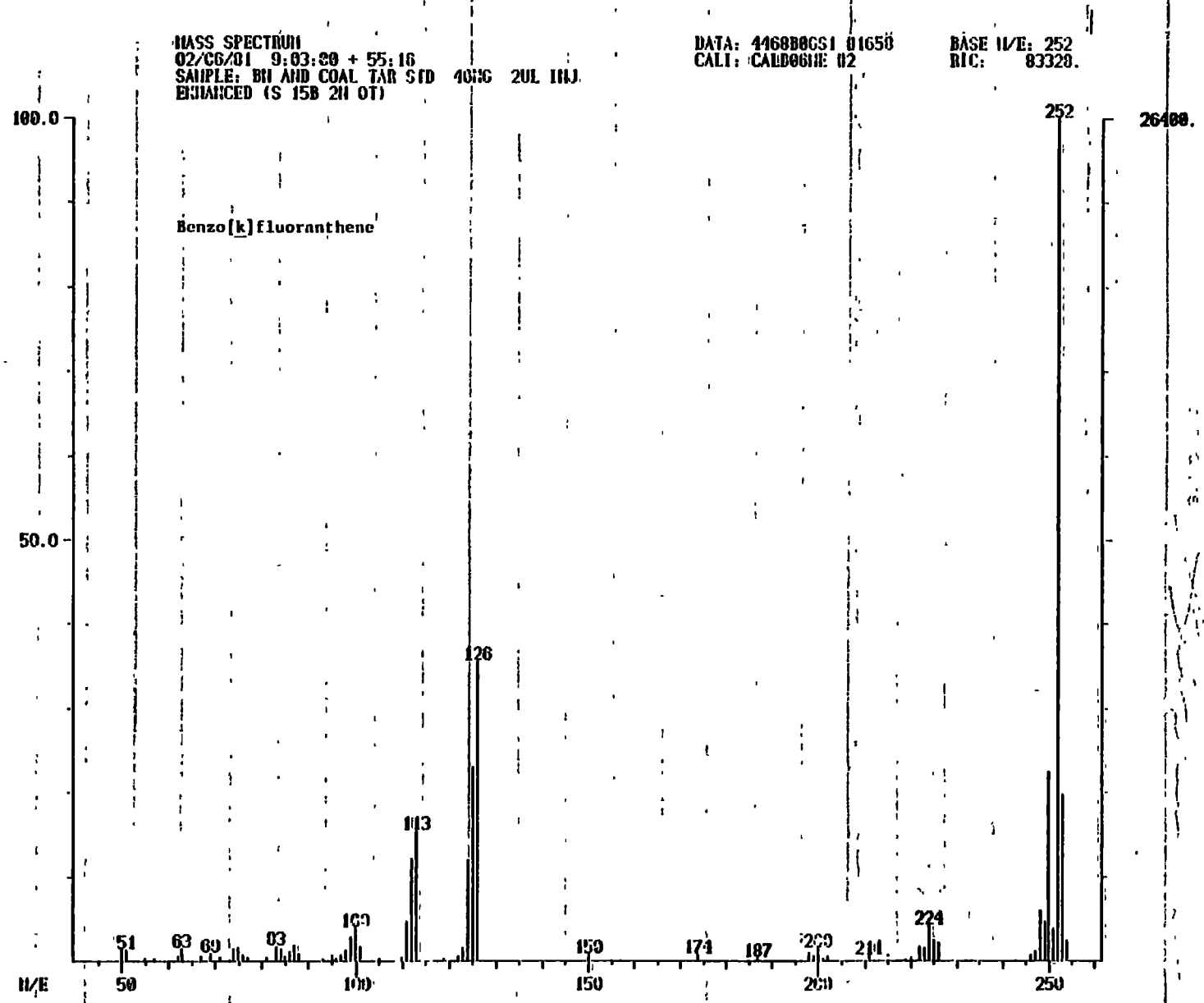

Figure 55 - Benzo[k]fluoranthene in Standard (2/6/81)

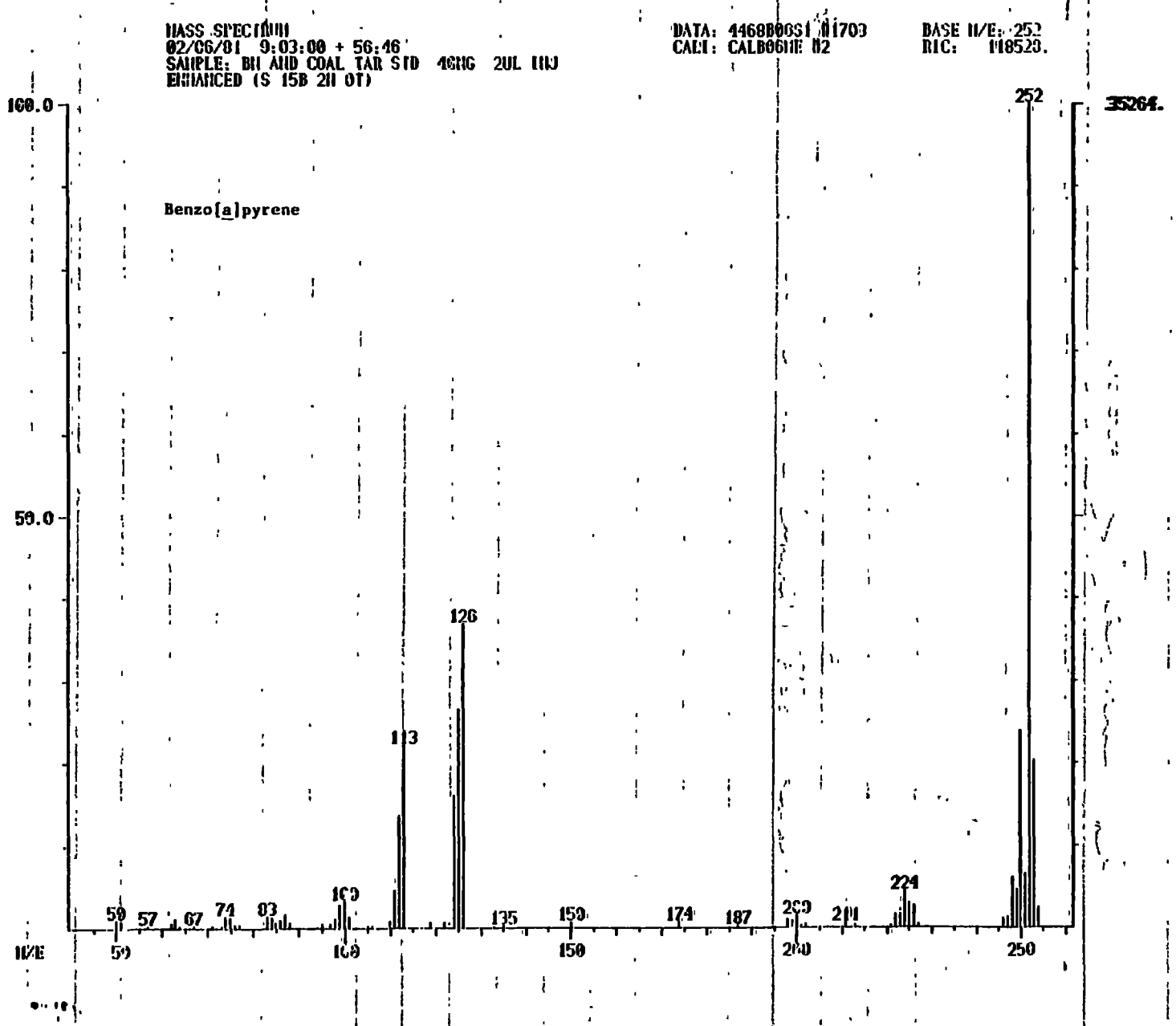

Figure 5[illegible] Benzo[a]pyrene in Standard (2[illegible]81)

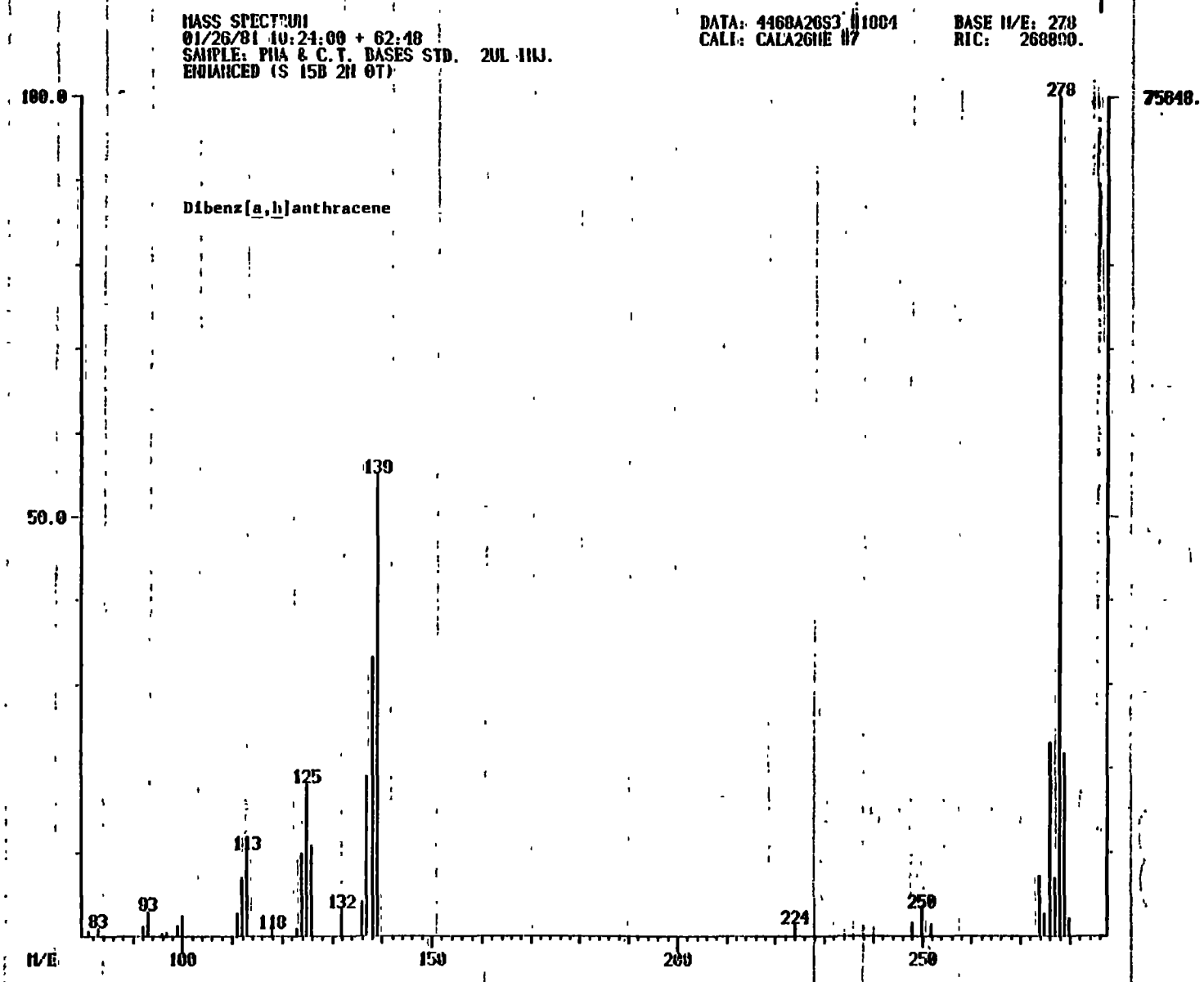

Figure 57 - Dibenz[a,h]anthracene in Standard (1/26/81)

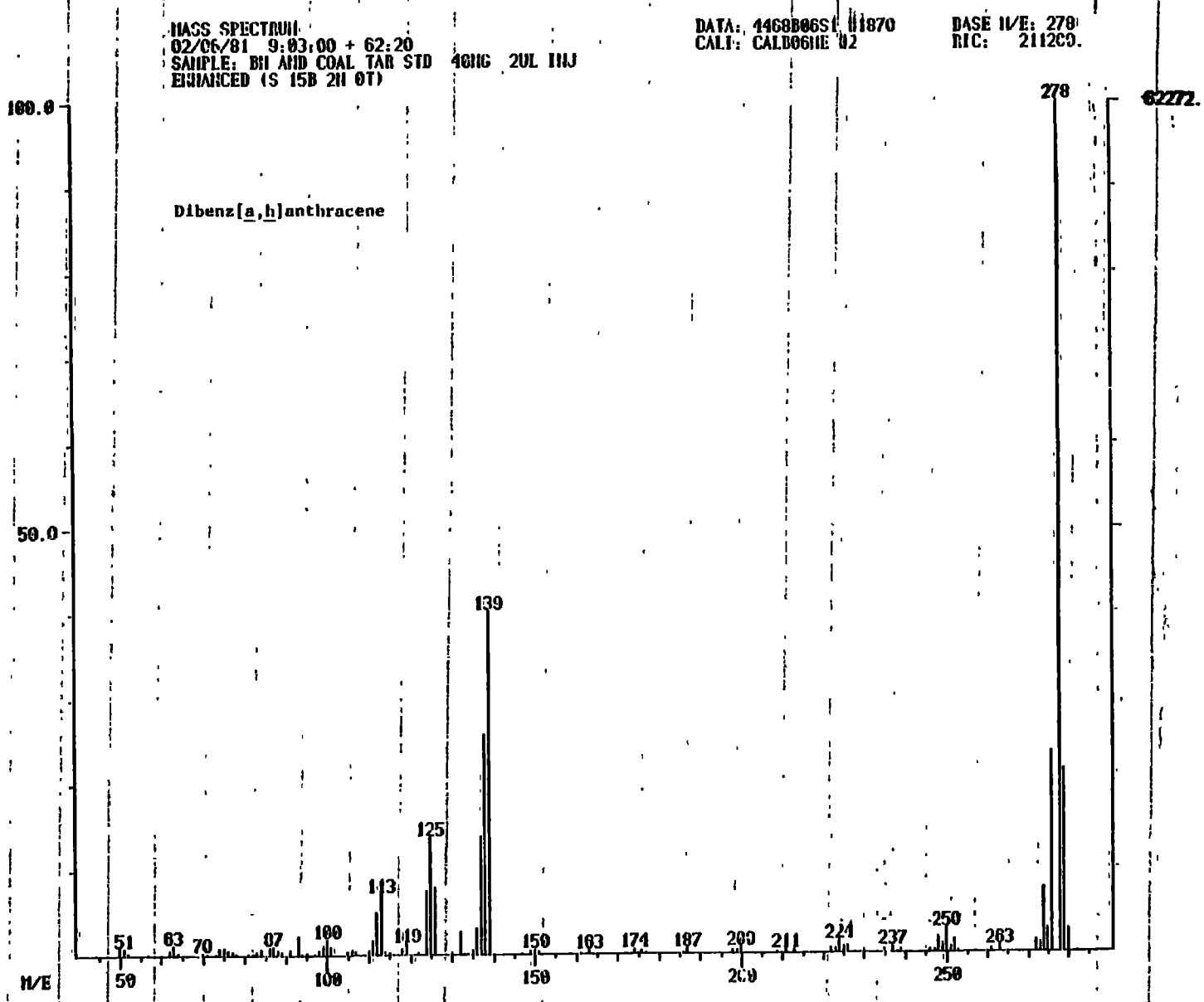

Figure 58 - Dibenz[a,h]anthracene in Standard (2/6/81)

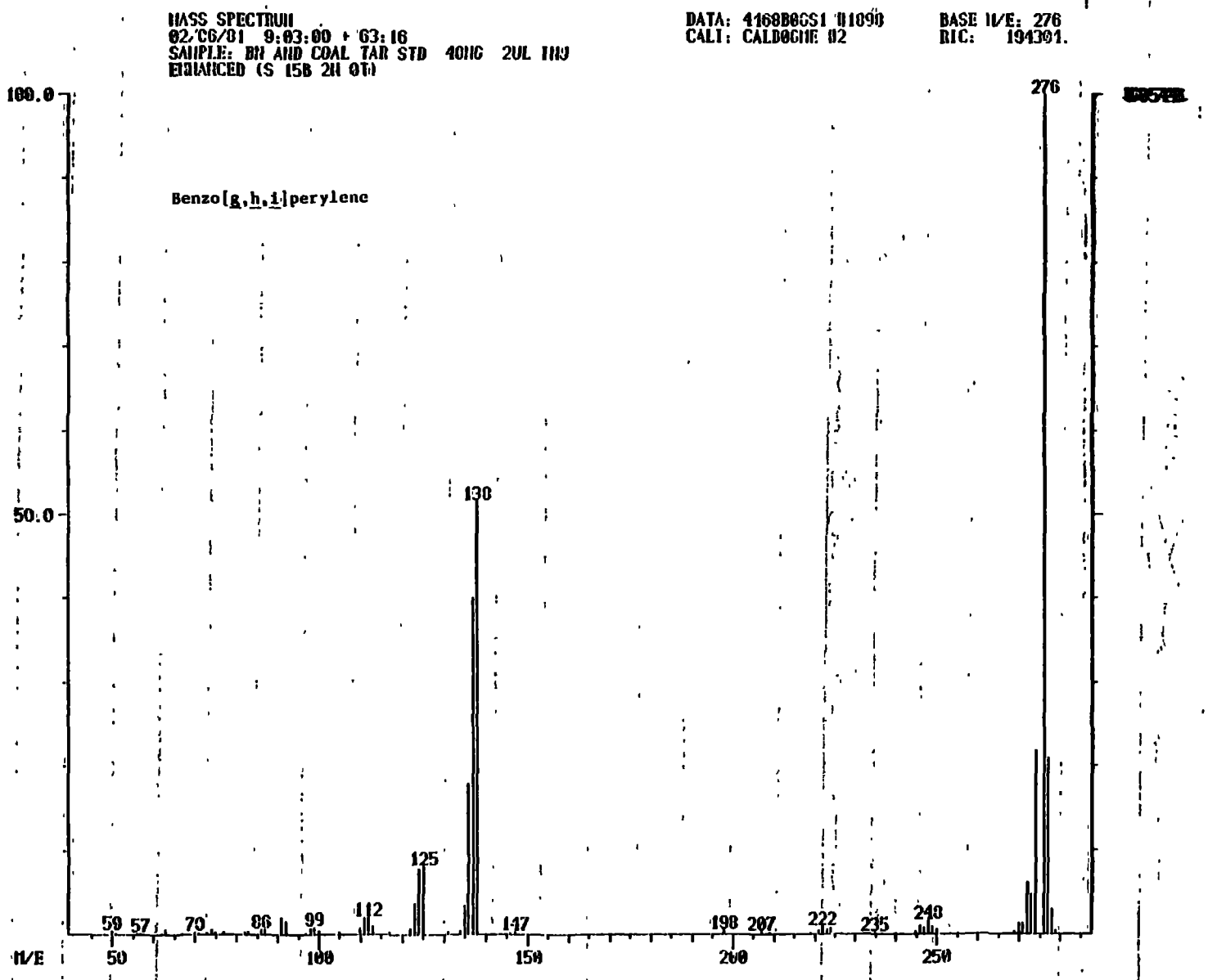

Figure 59 - Benzo[g,h,i]perylene in Standard (2/6/81)

CHAIN-OF-CUSTODY SHEETS

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

MRI

CHAIN OF CUSTODY RECORD

Project No.:	Samplers: (Signature) Stephen Lee

Sample No. _____ Field No. #1

boring #1, sample #1/2-3

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Date/Time	Comments (Changes, Volume Removed, Dilutions, etc.)
Stephen Lee	11-24-80 3 PM	Edward P. Olson	11-24-80 3 PM	Storage
[illegible]	11-26-80 3PM	Earl M. Horte	11-26-80 3PM	Transp. to K.C.
Earl M. Horte	12-1-80 8:20 Am	Evelyn E Conrad	12-1-80 8:20	storage

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

MRI

CHAIN OF CUSTODY RECORD

Project No.:	Samplers: (Signature) Stephen Lee

Sample No. _____ Field No. #2

boring 1 sample day

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Date/Time	Comments (Changes, Volume Removed, Dilutions, etc.)
Stephen Lee	11-24-80 3 PM	Edward P. Olson	11-24-80 3PM	Storage
James L. Neal	11-26-80 3 PM	Earl Hanke	11-26-80 3PM	Transp. to K.C. Mo
Earl M. Hanke	12-1-80 8:20 AM	Evelyn E. Conrad	12-1-80 8:20	Storage

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Kansas City, Missouri 64110

MRI

CHAIN OF CUSTODY RECORD

Project No.:	Samplers: (Signature) Stephen Lee

Sample No. _____ Field No. #3
boring 2 1½-3

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Date/Time	Comments (Changes, Volume Removed, Dilutions, etc.)
Stephen Lee	11-24-80 3PM	Edward F. Olson	11-24-80 3PM	Storage
James J. Neil	11-26-80 3PM	Earl M. Henke	11-26-80 3PM	Transp. to K.C. Mo
Earl M. Henke	12-1-80 8:20 Am	Evelyn E. Conrad	12-1-80 8:20	Storage

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Kansas City, Missouri 64110

MRI

CHAIN OF CUSTODY RECORD

Project No.:	Samplers: (Signature) Stephen Lee

Sample No. _____ Field No. #5 boring 3 1½-3

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Date/Time	Comments (Changes, Volume Removed, Dilutions, etc.)
Stephen Lee	11-24-80 3 PM	Edward Gibson	11-24-80 3 PM	Storage
James L. Neel	11-26-80 3 PM	Carl M. Hanse	11-26-80 3PM	Transp. to K.C. Mo.
Carl M. Hanse	8:20 12-1-80	Evelyn E Conrad	12-1-80 8:20	Storage,

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CHAIN OF CUSTODY RECORD

Project No.:	Samplers: (Signature) Stephen Lee

Sample No. _____ Field No. #4 boring 2 deep

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Date/Time	Comments (Changes, Volume Removed, Dilutions, etc.)
Stephen Lee	11-24-80 3 PM	Edward H. Olson	11-24-80 3 PM	Storage
James L. Neal	11-26-80 3 PM	Earl M. Honser	11-26-80 3 PM	Transp. to K.C. Mo.
Earl M. Honser	12-1-80 8:20 AM	Evelyn E. Conrad	12-1-80 8:20	Storage