FINAL REPORT

FOR

STUDY OF OUTGASSING AND DECOMPOSITION OF SPACE SHUTTLE HEAT PROTECTION TILES, FILLERS, AND ADHESIVE

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COMPOUNDS DESORBING FROM THE SPACE SHUTTLE TILES

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N85-21242#

The purpose of this project was to determine the chemicals desorbing from the space shuttle heat protection tiles. The original protocol for this project involved direct insertion probe mass spectrometry (DIPMS) analysis of the outgassing products from the tiles. This procedure allowed us to examine the desorbing chemicals for the tile material subjected to temperatures ranging between ambient temperature to 500°C at a pressure of 10^{-3} torr. However, this method proved unsatisfactory due to the large number of compounds desorbing from the tiles. Analysis by DIPMS does not allow for separation of compounds with the same volatility (1). The large number of compounds desorbing from the tile material resulted in unresolved complex organic mixture.

A purge and trap technique (2) was then employed to collect and separate the chemicals desorbing from the tiles. The maximum temperature in this analysis was 280°C which is the gas chromatograph fused silica capillary column's temperature limit. The desorption was also carried out at atmospheric pressure with helium as the purge gas. A description of the modified protocol is given below. All compounds are tentatively identified and have not been confirmed.

Material and Methods

Sample Collection

Interior Tile Material: A tared, preconditioned (1 hour at 550°C) quartz tube (3 mm I.D. x 5 cm) was inserted directly into the tiles to a depth ranging between 3-4.5 cm. The black protective skin on the surface of the tiles was removed prior to insertion of the quartz sample tube. Care was also taken to avoid the adhesive material on the bottom of the tiles. Samples represented a vertical profile of the upper half of most tiles tested. Aliquots of the tile material ranged between 0.8-1.1 grams. After collection of tile material the samples were placed in the purge and trap chamber for analysis.

Exterior Tile Materials: The black protective skin (0.3-0.5 mm thick) on the surface of the tiles was carefully removed and quantitatively transferred to the quartz desorption tubes. Aliquots of this material weighed between 0.3-0.45 grams. It should be noted that it was virtually impossible to separate all of the black skin from the white subsurface tile material.

Method

Purge: The quartz tube containing the tile material was heated to 280°C and held at that temperature for 15 minutes. There was a constant flow of helium through the purge chamber to sweep the desorbing compounds into the gas chromatograph where they were cryogenically trapped onto the fused silica capillary column. The inlet of the column was held at -30°C throughout the desorption phase. After desorption the purge chamber was cooled to room temperature and the trapped compounds separated and analyzed by gas chromatography-mass spectrometry (GC-MS).

Instrumentation and Conditions;

Mass Spectrometer	Nermag R-10-10
Conditions	Electron Impact Mode Filiment current 70eV Mass Range 60-500 amu Scan Rate 2 msec per amu
Gas Chromatograph:	Carlo Erba (model 4160) equipped with a purge and trap unit constructed at UT-Dallas.
Conditions	Column: 30 meter-bonded fused silica capillary column DB5 (J&W) Carrier Gas: He.
Temperature Program:	The initial column temperature of 0°C was maintained for one minute. The oven temperature was then raised at a rate of 5°C per minute to a final temperature of 280°C. The final temperature was maintained for 15 minutes.

Results

Numerous compounds desorbed from both the protective skin and interior tile matrix. However, composition of the two matrices differed. Desorbing compounds from the interior tile matrix were more numerous and varied than from the protective skin. All chromatograms and mass spectrum presented in this paper are from analysis of a nose tile. All compounds are tentatively identified and have not been confirmed.

Interior tile material

The GC-MS chromatograms (total ion current) for the interior tile matrix is given in Figure I. Four major or unusual groups of compounds were found desorbing from the interior tile matrix. They include silicon (Si) containing organic compounds, hydrocarbons (aliphatic and aromatic), phthalates and several halogenated organic compounds.

Silicon containing compounds represented over 50% of the peaks sampled. These compounds are readily distinguishable due to the isotope abundance pattern of Silicon (28 = 100%; 29 = 5.1%; 30 = 3.4%)(3).

Mass spectrum for several silicon containing compounds are presented in Figure 2. Tentative identification by computer search of the EPA/NIH library are also given for several of the compounds. These possible compound identification lists from the search of the EPA/NIH library are probably incorrect (DI > .4). However, they do indicate the probable type of compound. Our EPA/NIH library is limited to 31,000 compounds and probably does not contain many of the desorbed silicon containing compounds.

Both aromatic and aliphatic hydrocarbons and substituted hydrocarbons were found desorbing from the tile matrix. Figure 3 contains several mass spectrum of these types of hydrocarbons. These compounds were the second most abundant group of compounds.

Numerous phthalates were found in the interior tile matrix. In fact, phthalates were found in higher concentrations than any other compound (assuming a uniform response factor). Figure 4 shows a partial total ion current for desorbing material from interior tile matrix and the selective ion current for ion 149, (base peak for phthalates). Mass Spectrum for the two most prevalent phthalates are given in Figure 5. Phthalates are fairly ubiquitious in the environemnt. However, we were surprised to find them at such levels in the interior tile matrix.

Several chlorinated organic compounds were also found in the tile material. Figure 6 presents the mass spectrum of a trichlorobiphenyl (PCB) found in tile matrix. Figure 7 presents a partial total ion current and single ion current for ions 256, 258, 260 (identifying peaks for trichlorobiphenyl). Note that several isomers of this PCB appear to be present. These compounds also were found in replicate.

Tetra chloroethylene (Figure 8) was also found in <u>both</u> the interior tile matrix (white) and the protective skin (black).

These chlorinated compounds were <u>not</u> found in any of the blanks.

<u>Protective Skin</u>

The thin (0.3-0.5 mm) protective skin on the surface of the tiles was also analyzed. The GC-MS chromatogram (total ion current, 60-500 amu) from the analysis of this material is presented in Figure 9. Numerous compounds were desorbed from this material. The total ion current (TIC) from this protective skin was 26.49 x 10^6. The TIC generated from the analysis of the interior matrix material was an order of magnitude higher (24.99 x 10^7) indicating either larger number of compounds and/or higher levels (concentration) of compounds desorbing from the interior matrix.

Polychlorinated biphenyls were not found in the skin matrix. However, tetrachloroethylene and two phthalates were identified as desorbing compounds.

The major group of compounds desorbing from this matrix were hydrocarbons. Representative mass spectrum and EPA/NIH library search are given in Figure 10.

If the protective skin was applied to the surface of the tiles by a flame spray technique; many of the more volatile compounds were probably lost.

Conclusion

At 280°C many compounds desorb from the tile interior and protective skin. Classes of compounds desorbing from these matrices vary but hydrocarbons, substituted hydrocarbons, phthalates, and tetrachloroethylene were common to both matrices.

The major group of compounds desorbing from the interior tile matrix were Silicon (Si) containing organics. Numerous phthalates and several isomers of trichlorobiphenyl were also found in interior tile matrix.

It should be emphasized that none of the chlorinated hydrocarbons, phthalates or silicon containing compounds were present in the blanks.

REFERENCES

1. Cotter, R.J., and A.L. Yerger. 1982 . Thermally Produced Ions Desorptive Mass Spectrometry. Anal. Chem. 53:1306-1308

2. Keith, L.H.(Ed) 1981.Advances In The Identification And Analysis of Organic Pollutants in Water Vol II. pp.713-830 Ann Arbor Sci.

3. McLafferty,F.W. 1980. Interpretation of Mass Spectra 3rd. Edition University Science Books

FIGURE I Total Ion Current for Interior Tile Matrix

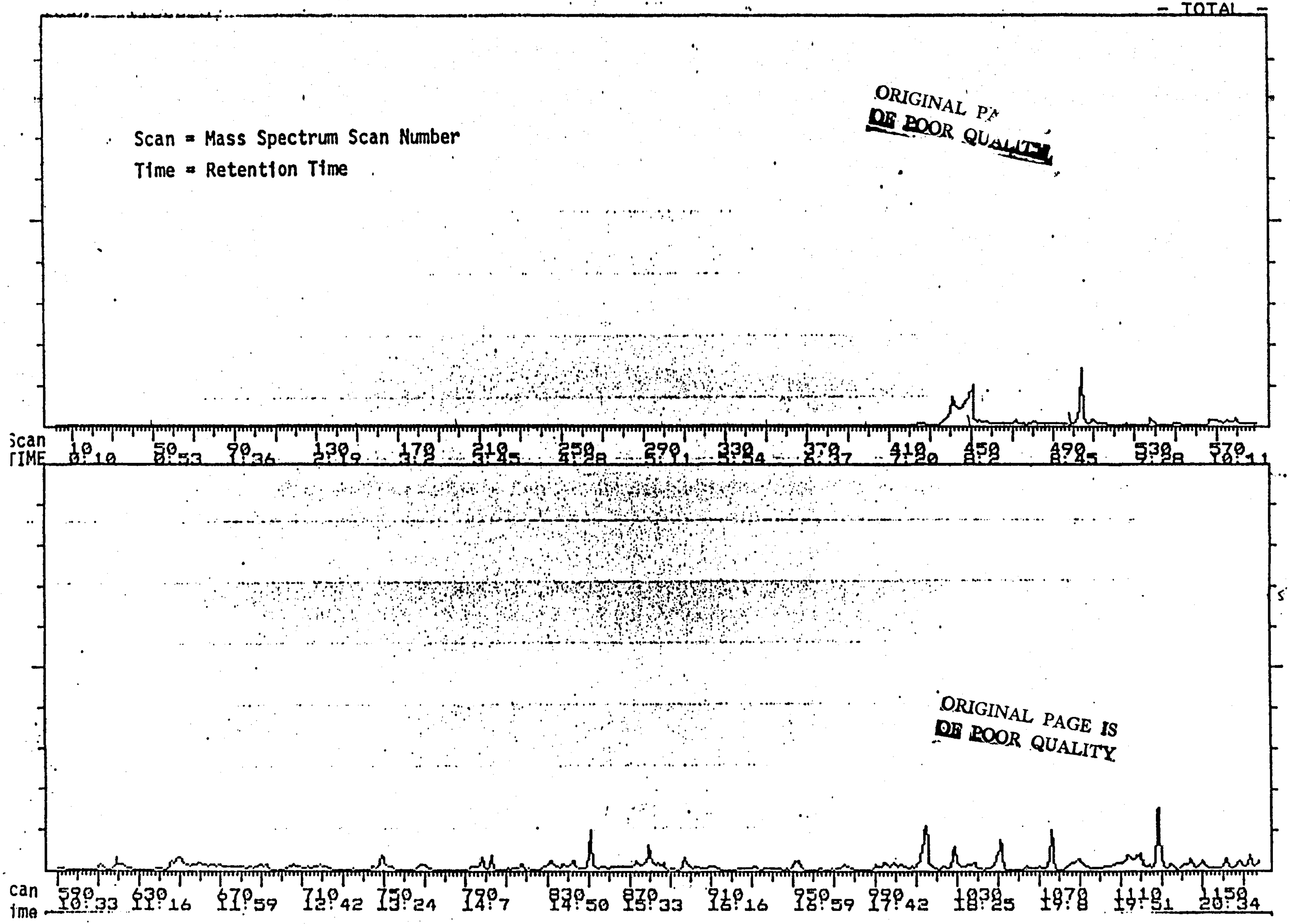
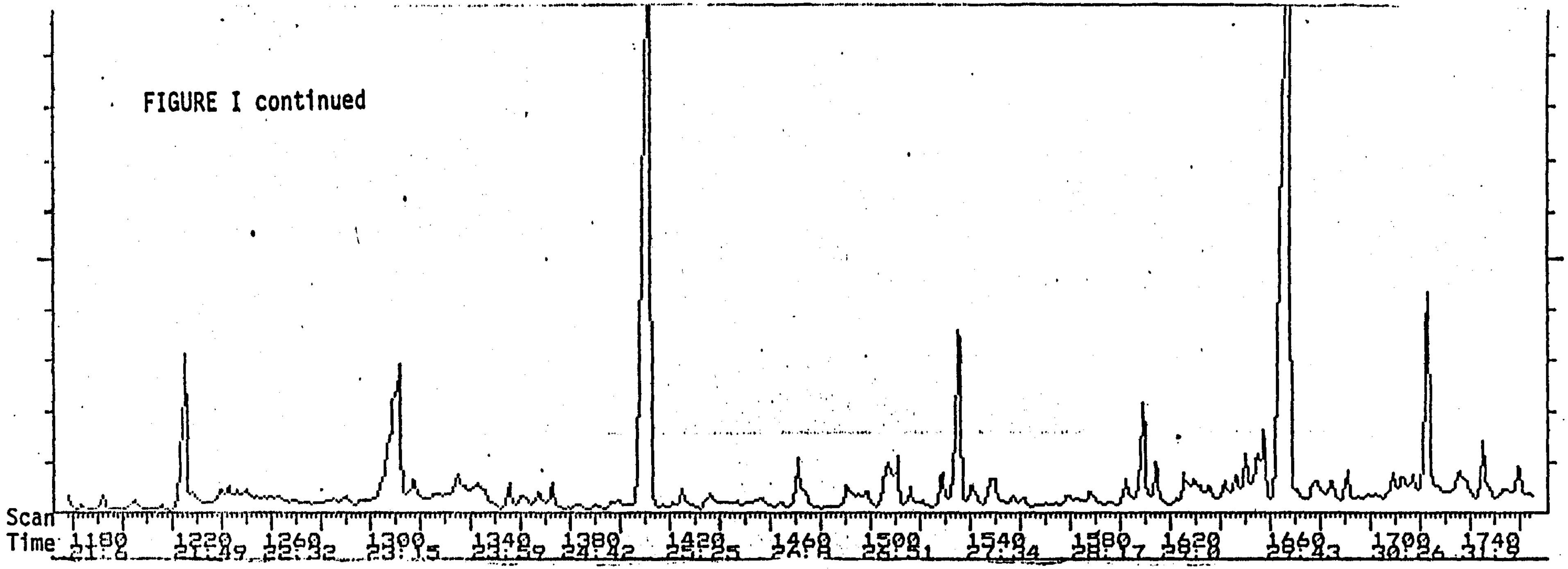


FIGURE I continued



* due to computer software problem

ADJUSTMENT*

Retention Time plus 40 minutes

Mass Spectrum Scan Number add 1760

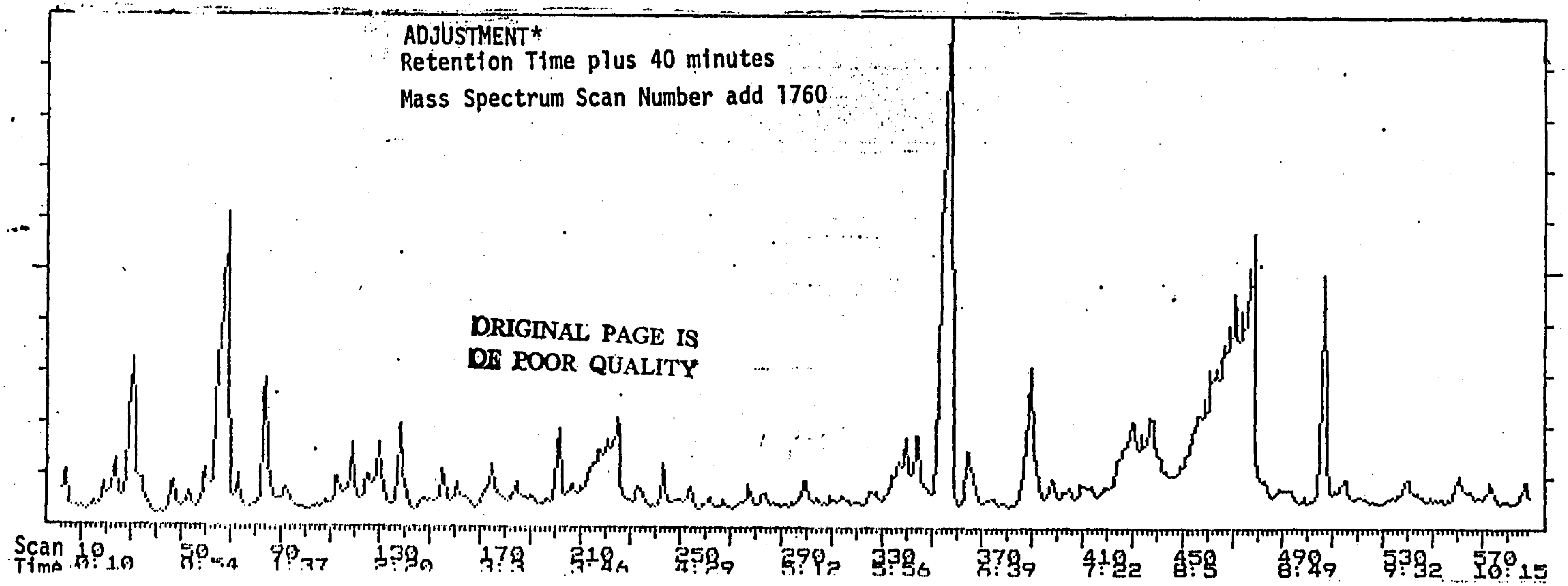


FIGURE I continued (Adjusted Retention Time add 40 minutes, Adjusted Mass Spectrum Number Plus 1760)

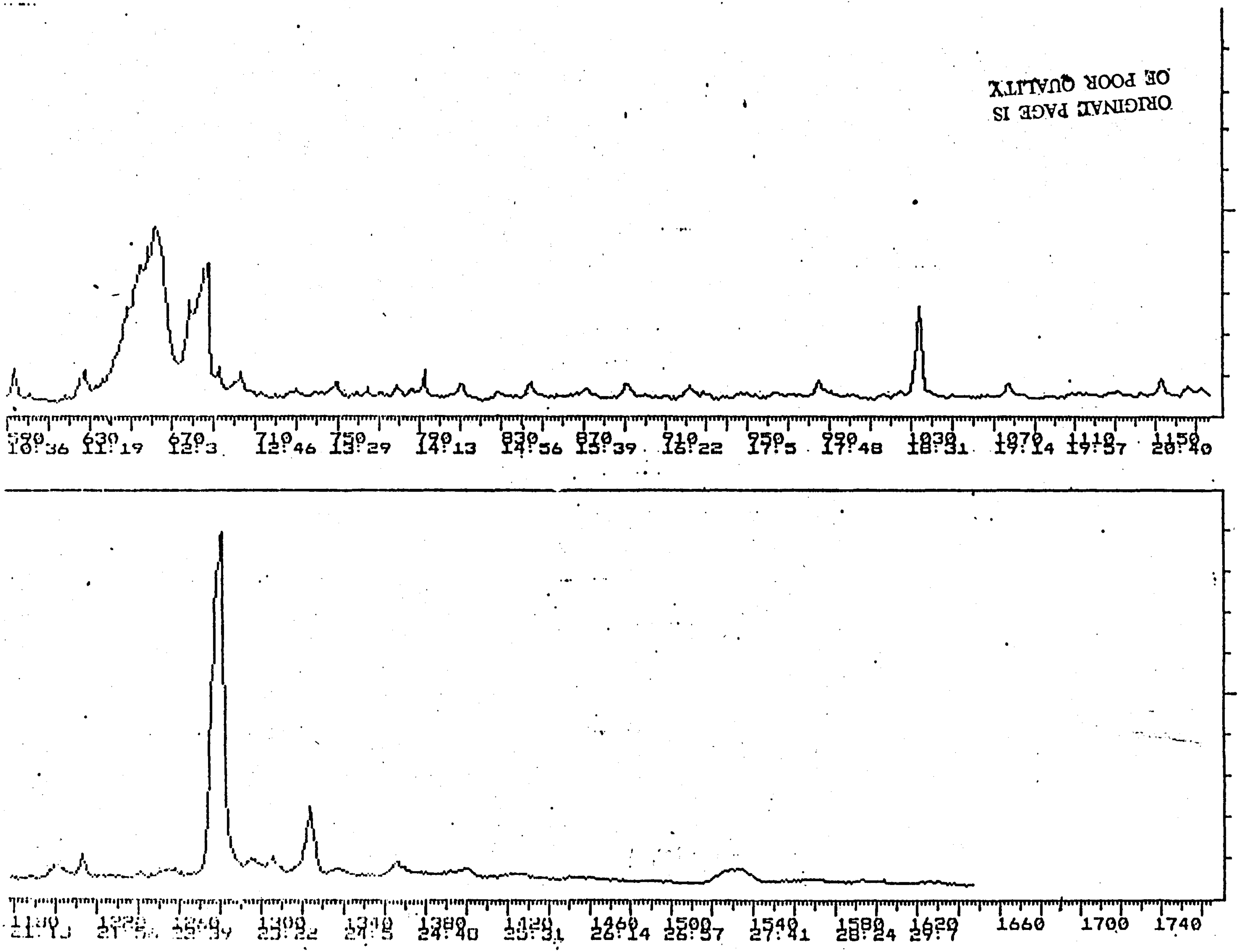
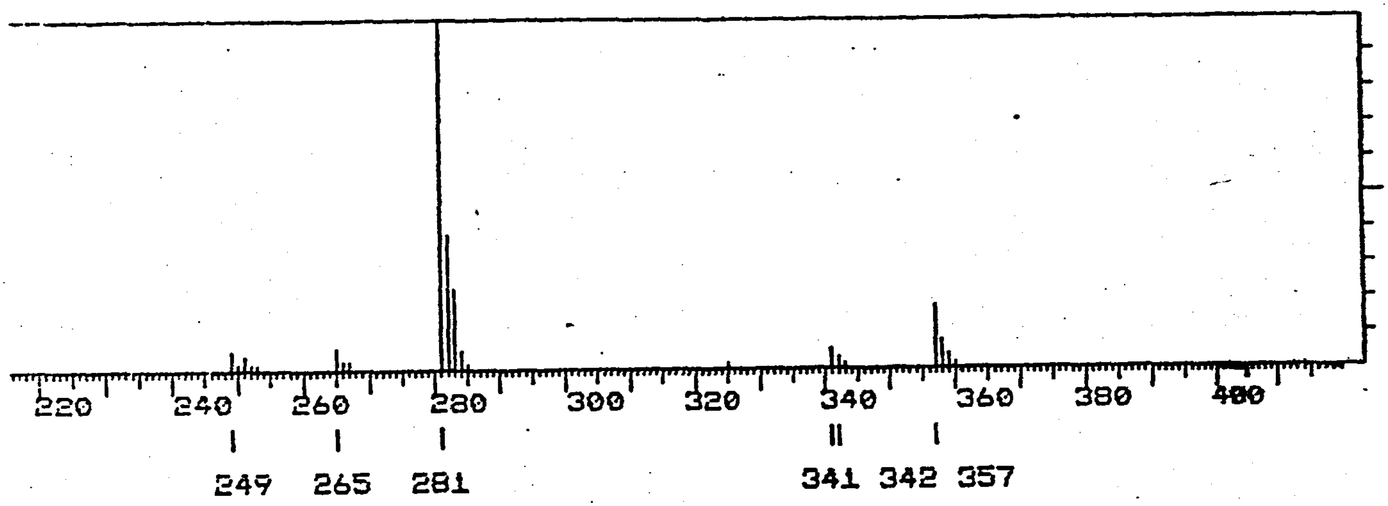


FIGURE 2 Mass Spectra and EPA/NIH Library Search for Selected Silicon Containing Compounds Found in the Interior Tile Matrix



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NBS/EPA/NIH LIBRARY

  77  HITS

CYCLOTETRASILOXANE, OCTAMETHYL-  C8H24O4SI4 296 #55667
NUM    23309 DI= .493
PENTASILOXANE, DODECAMETHYL-  C12H36O4SI5 384 #14163
NUM    28655 DI= .646

1-PROPANONE, 1-[2, 4-BIS[(TRIMETHYLSILYL)OXY]PHENYL]-  C15H26O3SI2 310 #5
572493
NUM    24341 DI= .662

1, 1'-BINAPHTHALENE, 3, 3'-DIMETHYL-  C22H18  282 #34042825
NUM    22084 DI= .729

ISOFLAVONE, 6, 7-DIMETHOXY-  C17H14O4  282 #24195173
NUM    22024 DI= .744

TRICYCLO[10. 2. 2. 25, 8]OCTADECA-5, 7, 12, 14, 15, 17-HEXAENE, 6-NITRO-  C18H19N
O2 281 #24777320
NUM    21958 DI= .748
18, 19-SECO-15. B*. -YOHIMBAN-19-OIC ACID, 20, 21-DIDEHYDRO-16. B*. -(HYDROXY
METHYL)-, METHYL  ESTER C21H26N2O3 354 #555225
NUM    372[illegible] DI= .753

CHOLESTA-5, 17(20)-DIEN-3-OL, ACETATE, (3. B*. , 17E)-  C29H46O2 426 #5631272

NUM    [illegible]
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FIGURE 2 Continued

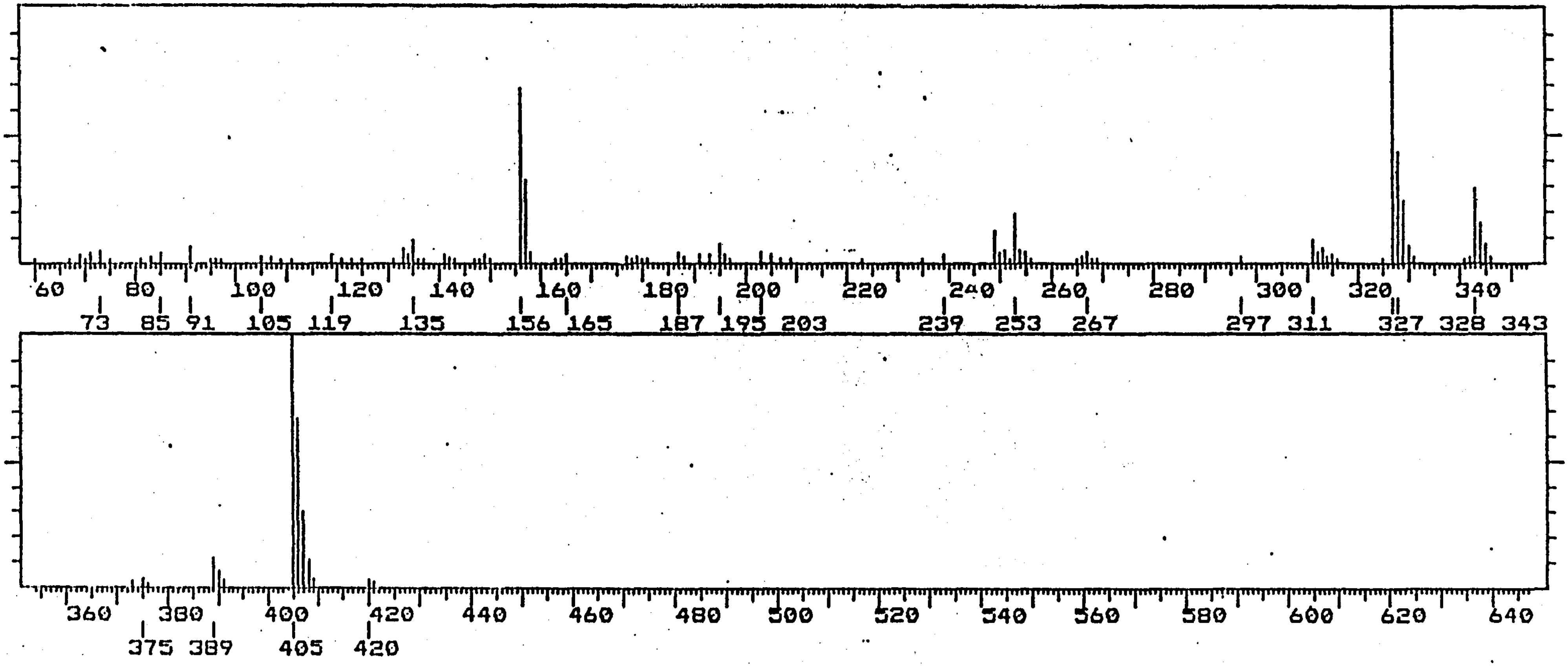


FIGURE 3 Mass Spectra of Hydrocarbons Desorbing From the Interior Tile Matrix

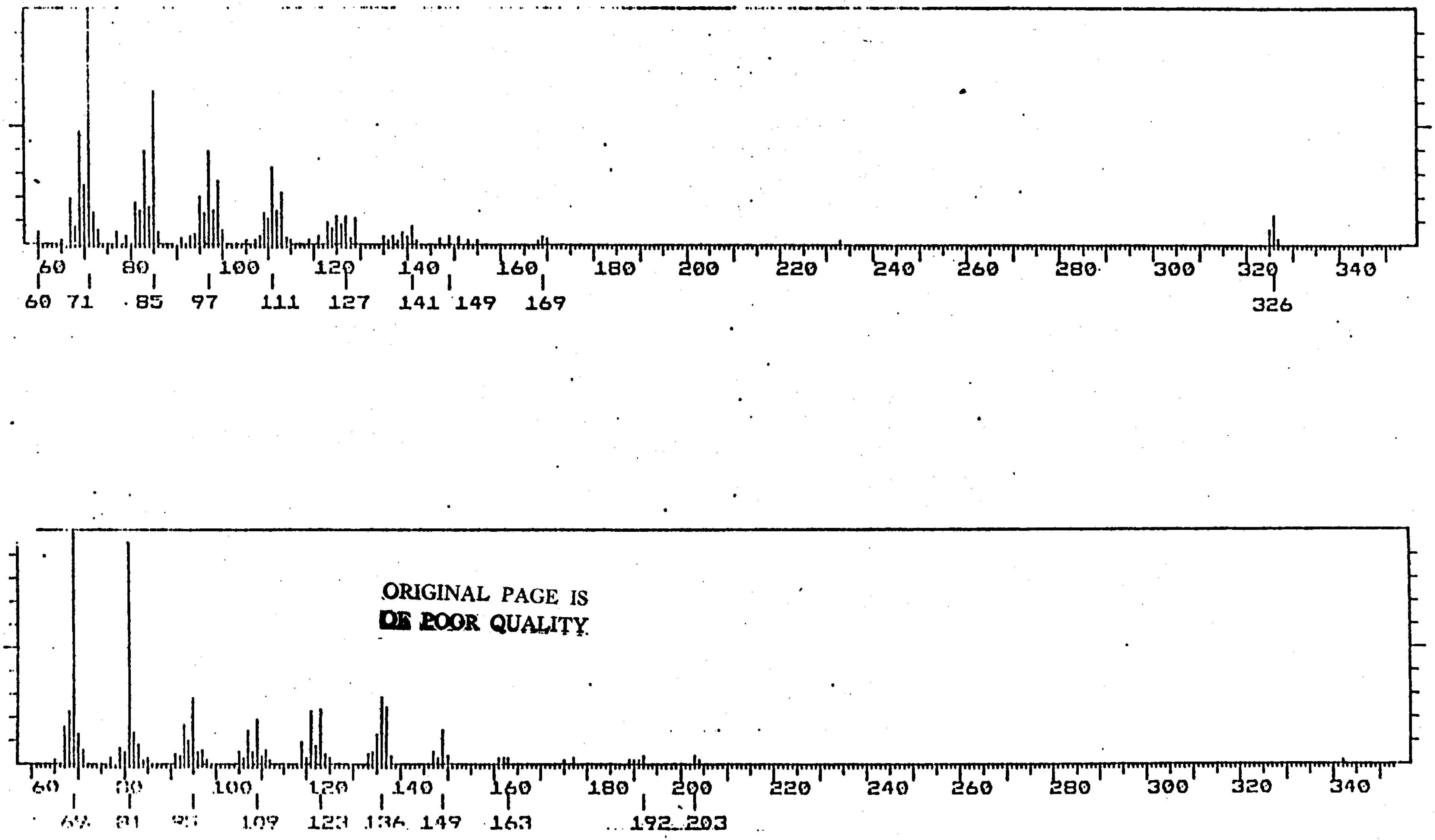


FIGURE 4 Total Ion Current and Single Ion Current for Ion 149, Base Peak for Phthalates

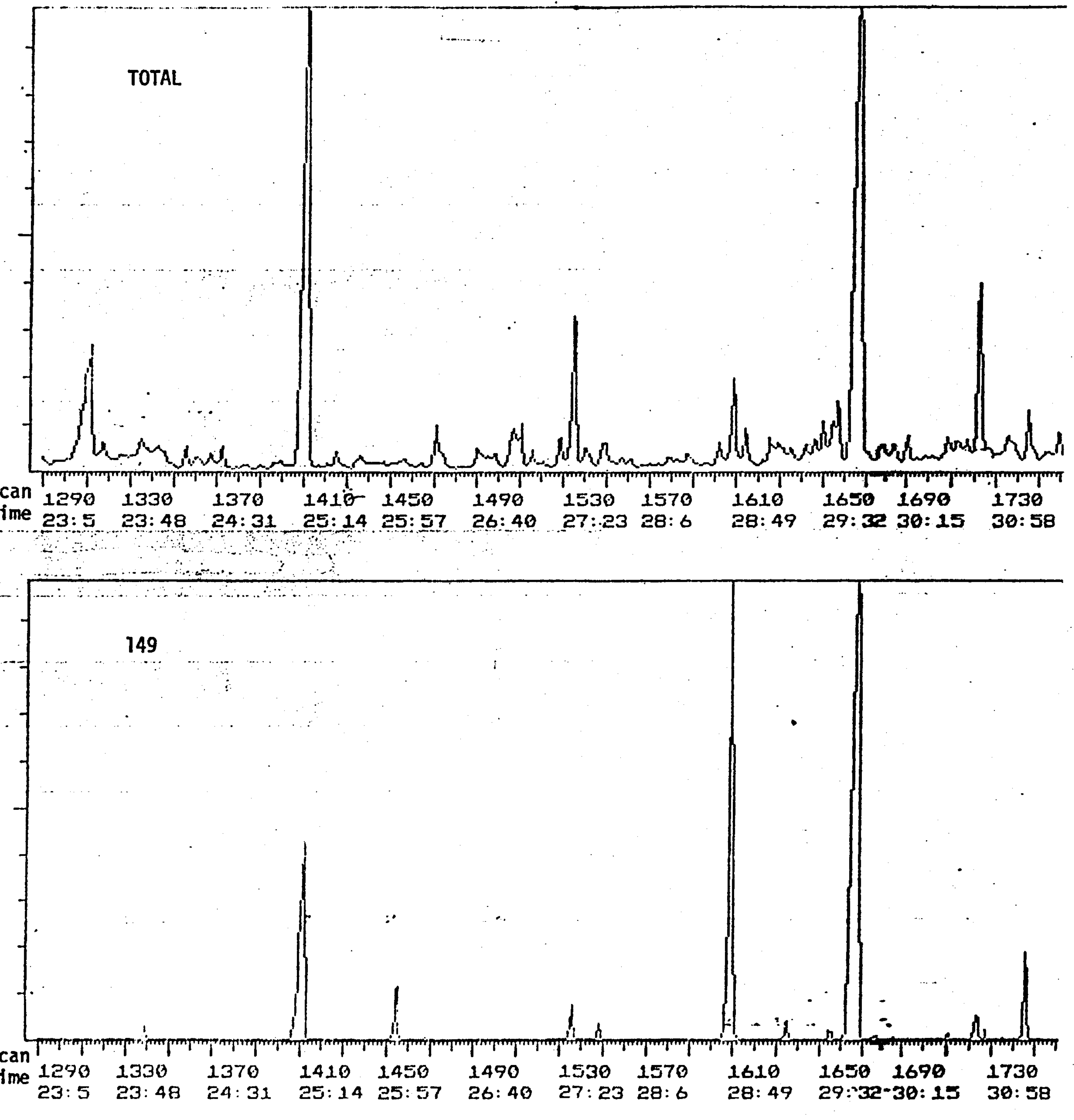
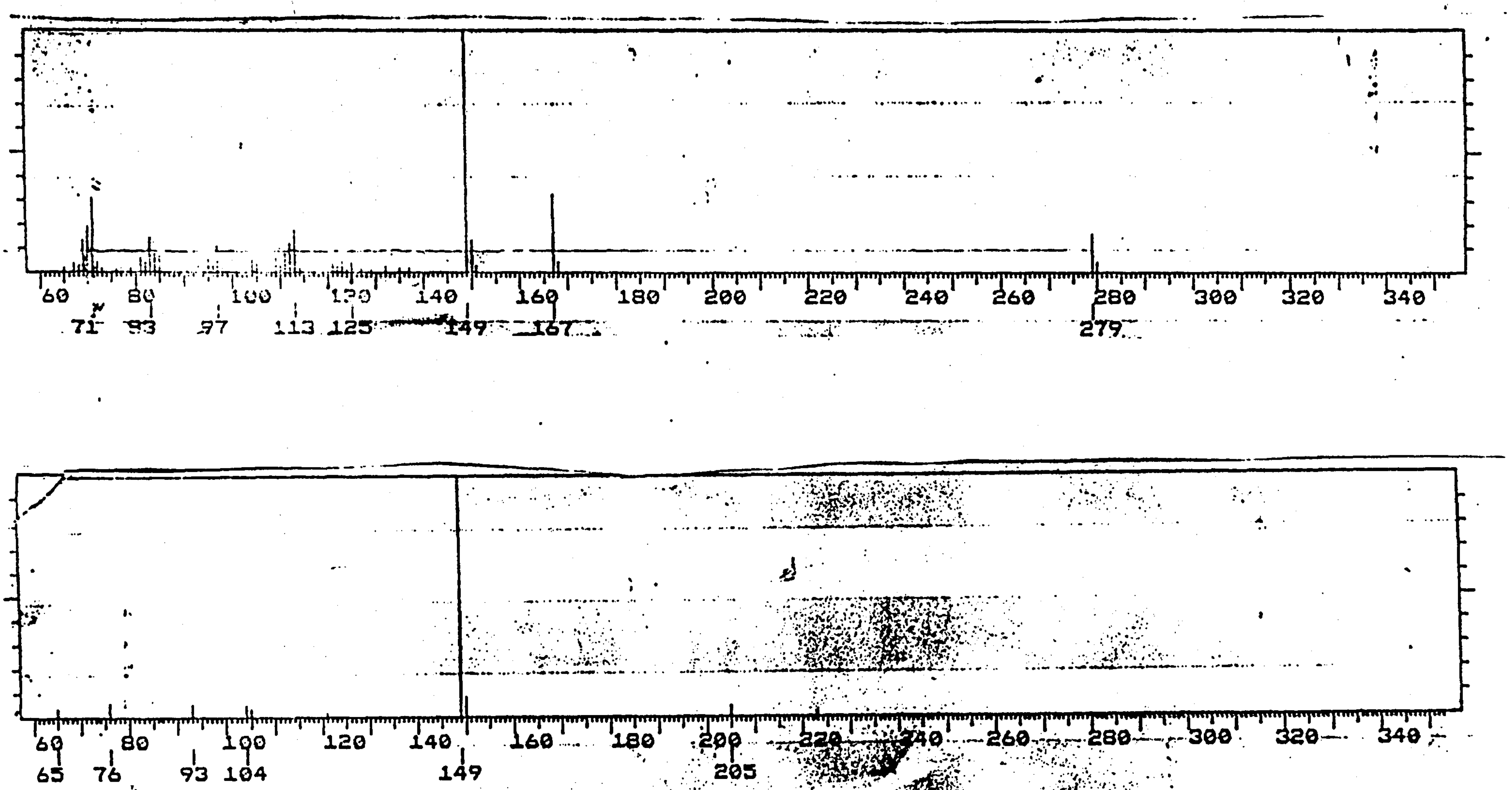


FIGURE 5 Mass Spectra of the Most Abundant Phthalates in Interior Tile Matrix



in Interior Tile Matrix.

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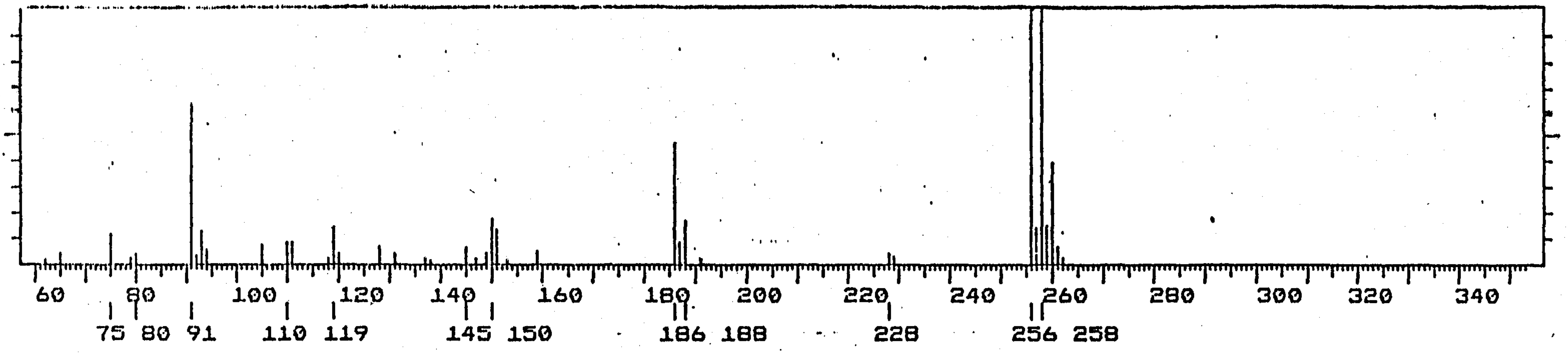

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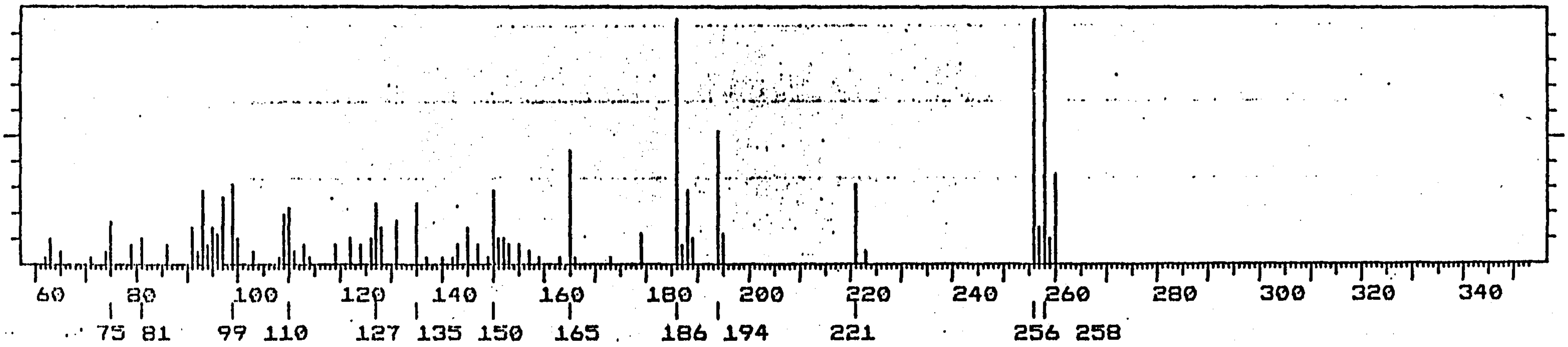

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NUM   19713 DI= 377
1,1'-BIPHENYL, 2',3,4-TRICHLORO- C12H7CL3 256 #38444869
NUM   19710 DI= 405
1,1'-BIPHENYL, 2,3',5-TRICHLORO- C12H7CL3 256 #38444814
NUM   19709 DI= 410
1,1'-BIPHENYL, 2,4,5-TRICHLORO- C12H7CL3 256 #1586207
NUM   19705 DI= 412
1,1'-BIPHENYL, TRICHLORO- C12H7CL3 256 #2532368
NUM   19707 DI= 475
1,1'-BIPHENYL, 2,4',5-TRICHLORO- C12H7CL3 256 #16606023
NUM   19704 DI= 478
1,1'-BIPHENYL, 2,2',6-TRICHLORO- C12H7CL3 256 #38444734
NUM   19708 DI= 480
1,1'-BIPHENYL, 2,4,6-TRICHLORO- C12H7CL3 256 #3569392
NUM   19706 DI= 486
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FIGURE 7 Total Ion Current and Single Ion Current for Ions 256,258, and 260 indicating PCBs in Interior Tile Matrix.

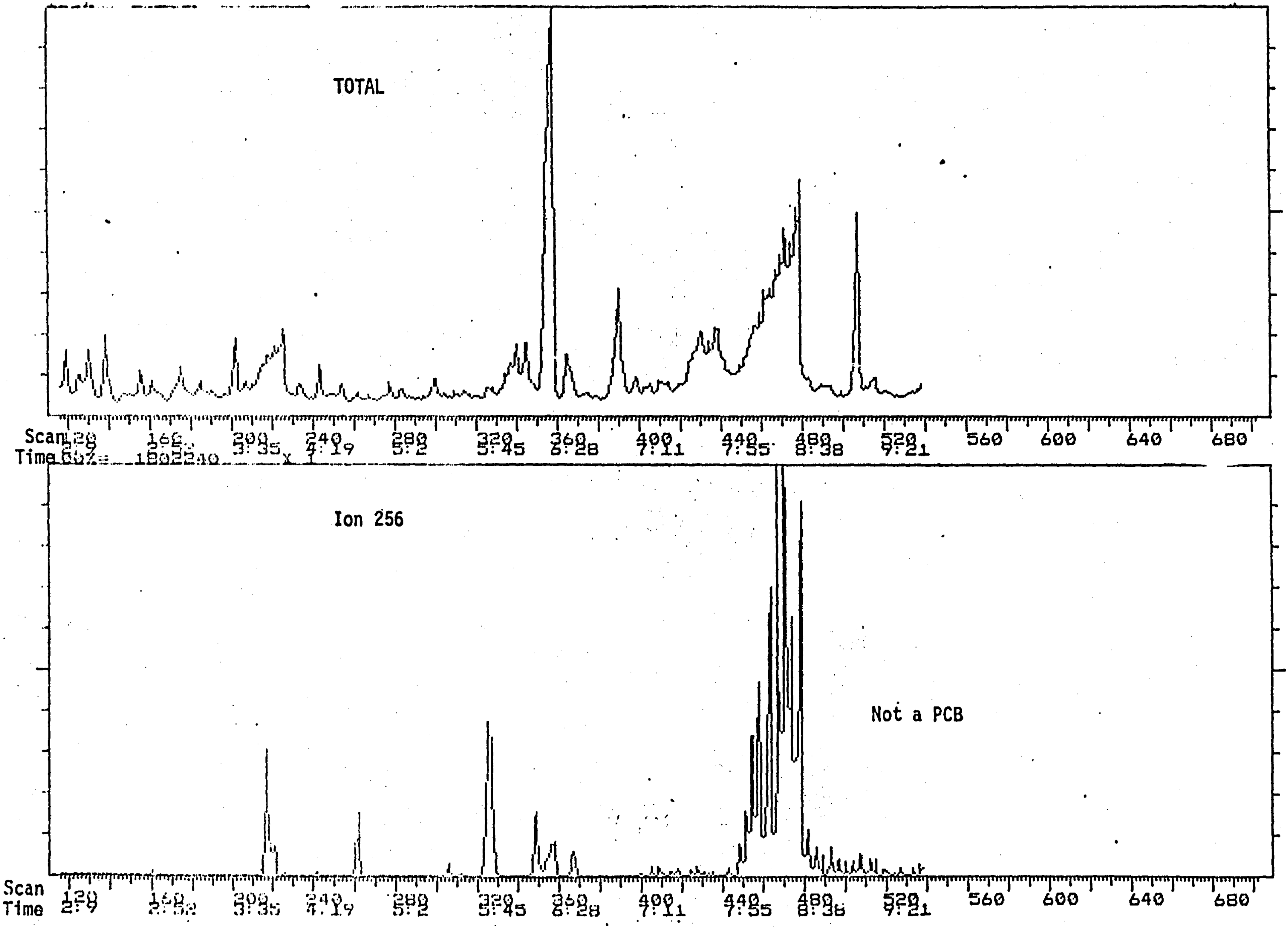


FIGURE 7 continued

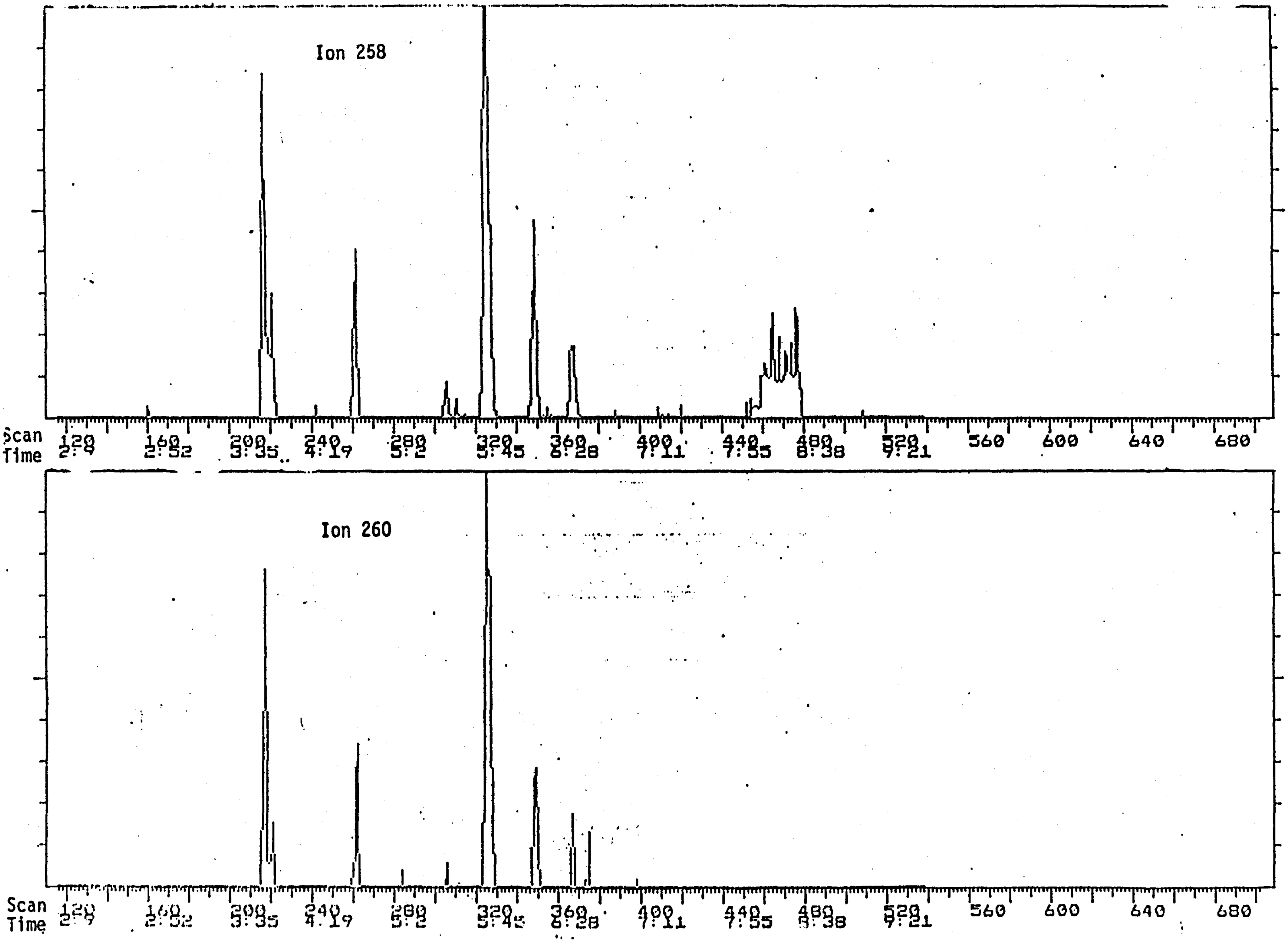
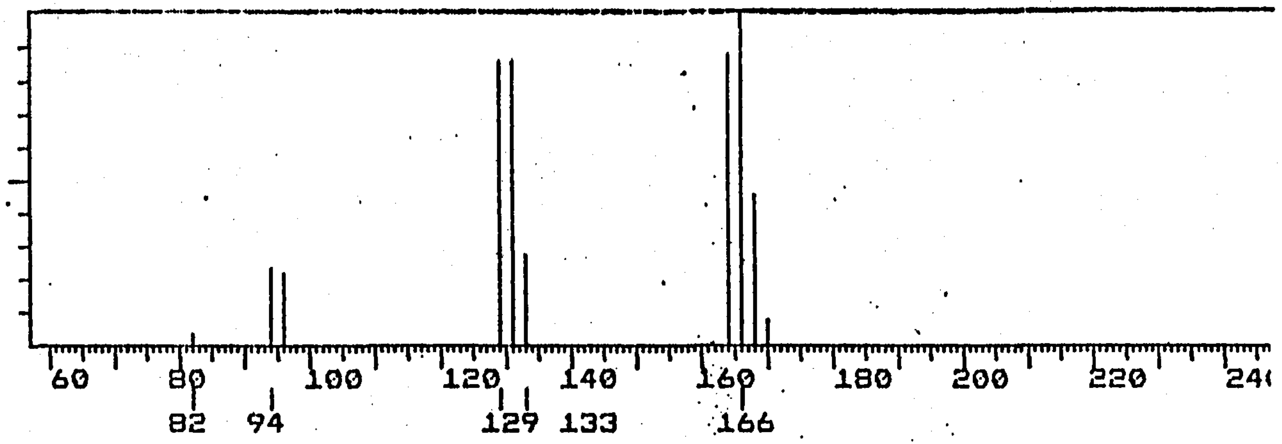


FIGURE 8 Mass Spectrum of Tetrachloroethylene



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QUINAZOLINE, 4-CHLORO- C8H5CLN2 164 #519068
NUM     8583 DI= .607
PHOSPHORODICHLORIDOTHIOIC ACID, O-METHYL ESTER CH3CL2OPS 164 #2523946
NUM     8416 DI= .622
QUINAZOLINE, 2-CHLORO- C8H5CLN2 164 #614113
NUM     8584 DI= .628
1, 3, 5-TRIAZIN-2-AMINE, 4, 6-DICHLORO- C3H2CL2N4 164 #93320
NUM     8535 DI= .630
PROPENE, 1, 2-DICHLORO-3, 3, 3-TRIFLUORO- C3HCL2F3 164 #431276
NUM     8532 DI= .652
2, 5-FURANDIONE, 3, 4-DICHLORO- C4CL2O3 166 #112217
NUM     8827 DI= .714
1, 2-DITHIANE-4-CARBOXYLIC ACID C5H8O2S2 164 #1409199
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FIGURE 9 Total Ion Current for Protective Skin on Tiles

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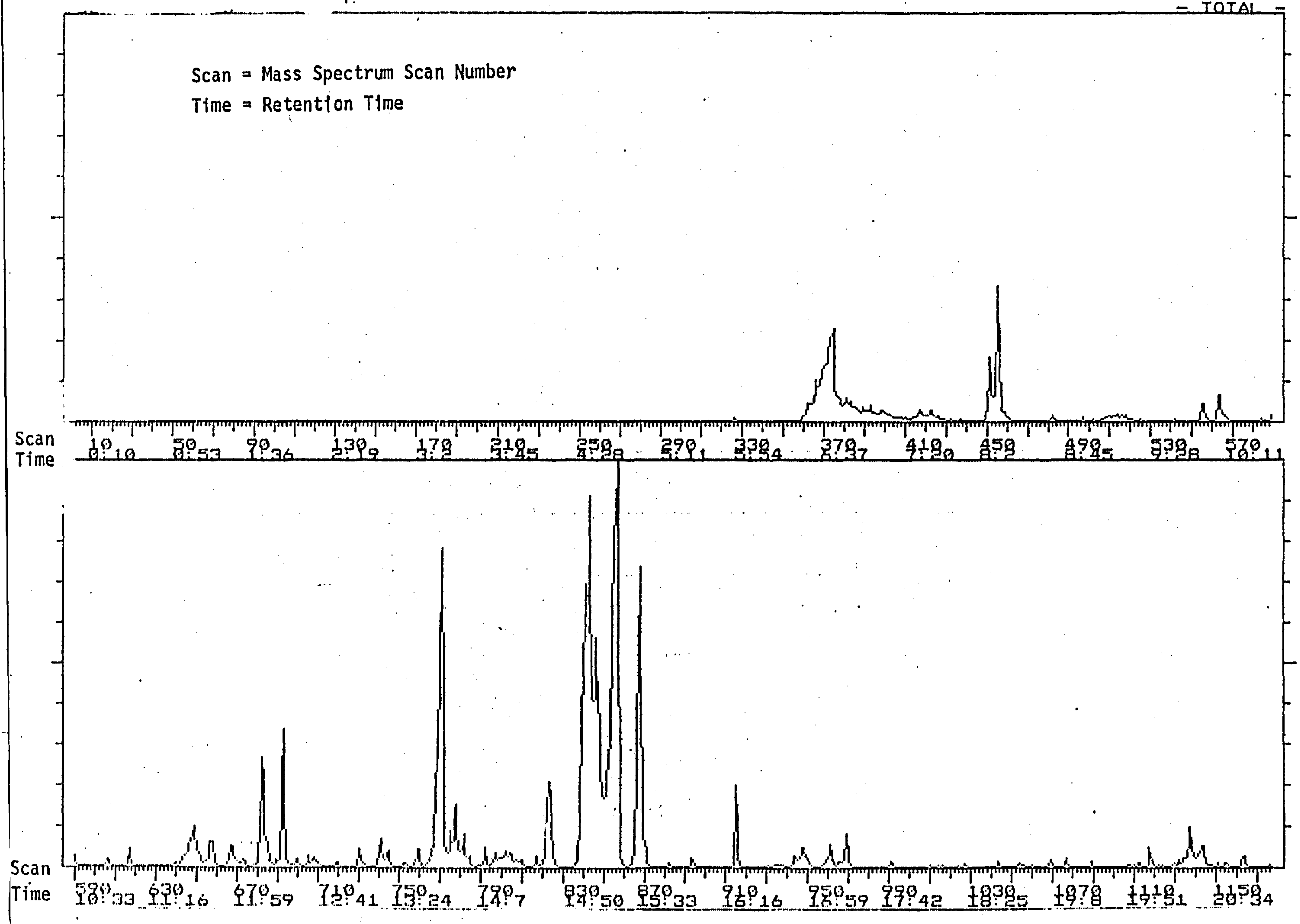
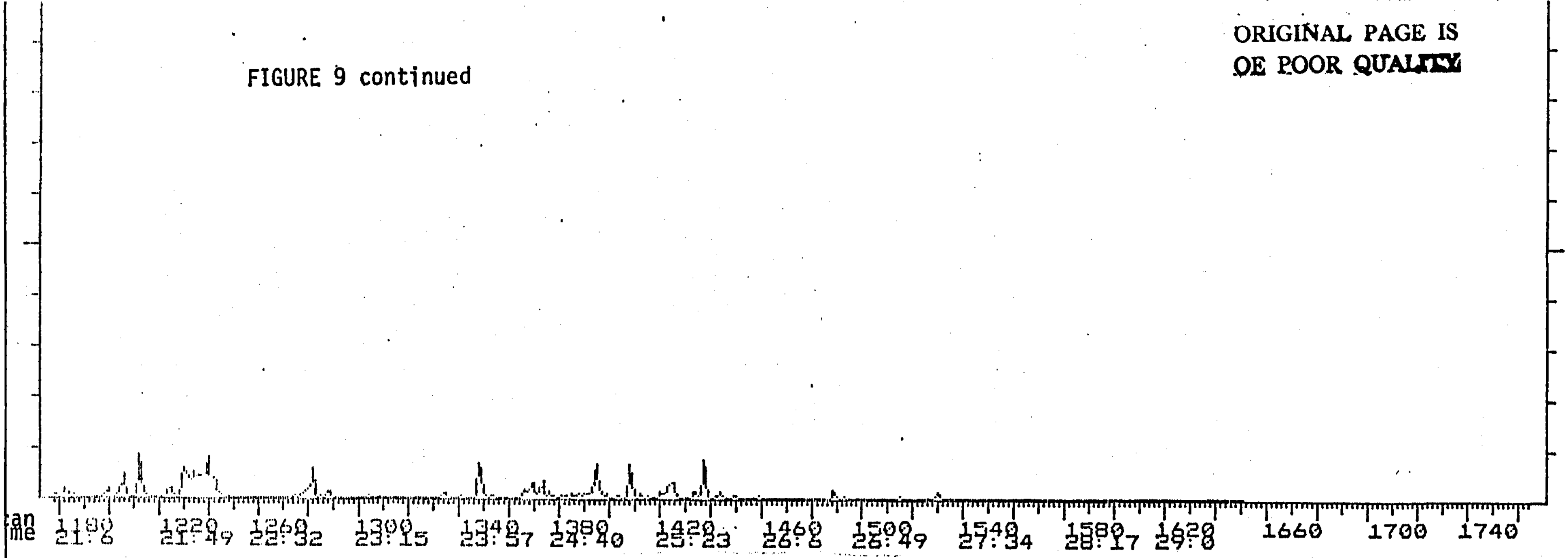


FIGURE 9 continued



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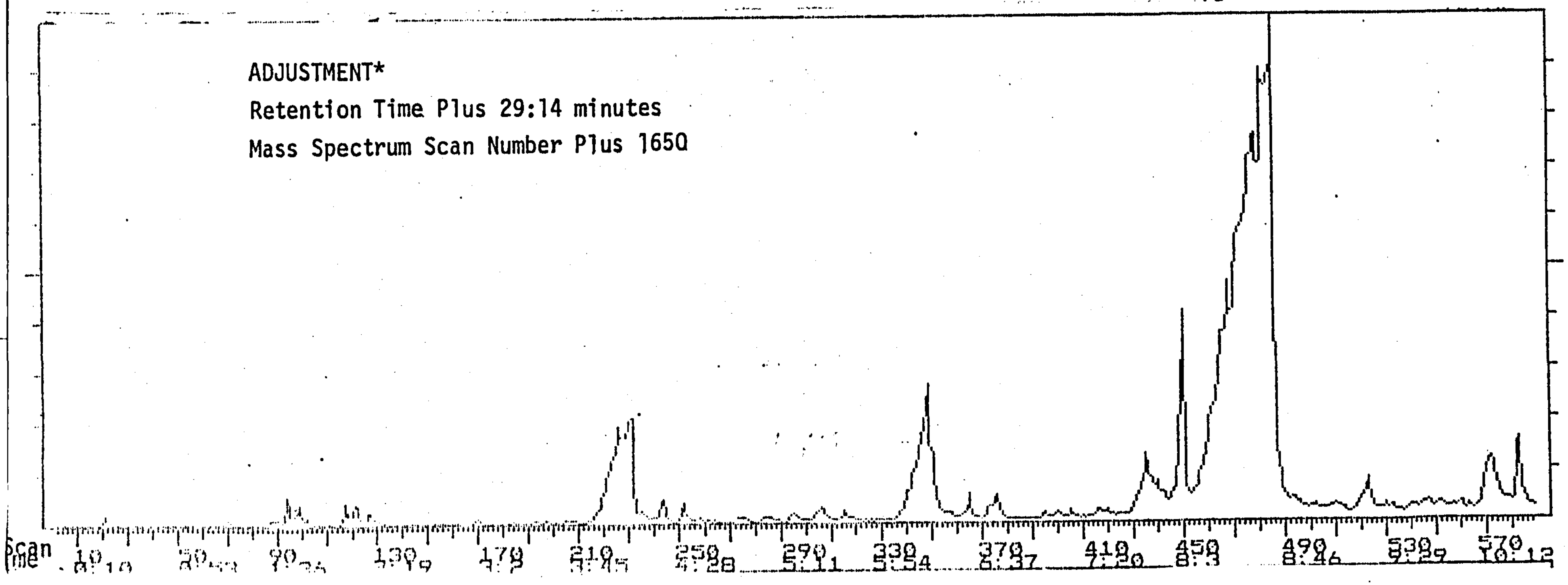
ADJUSTMENT*

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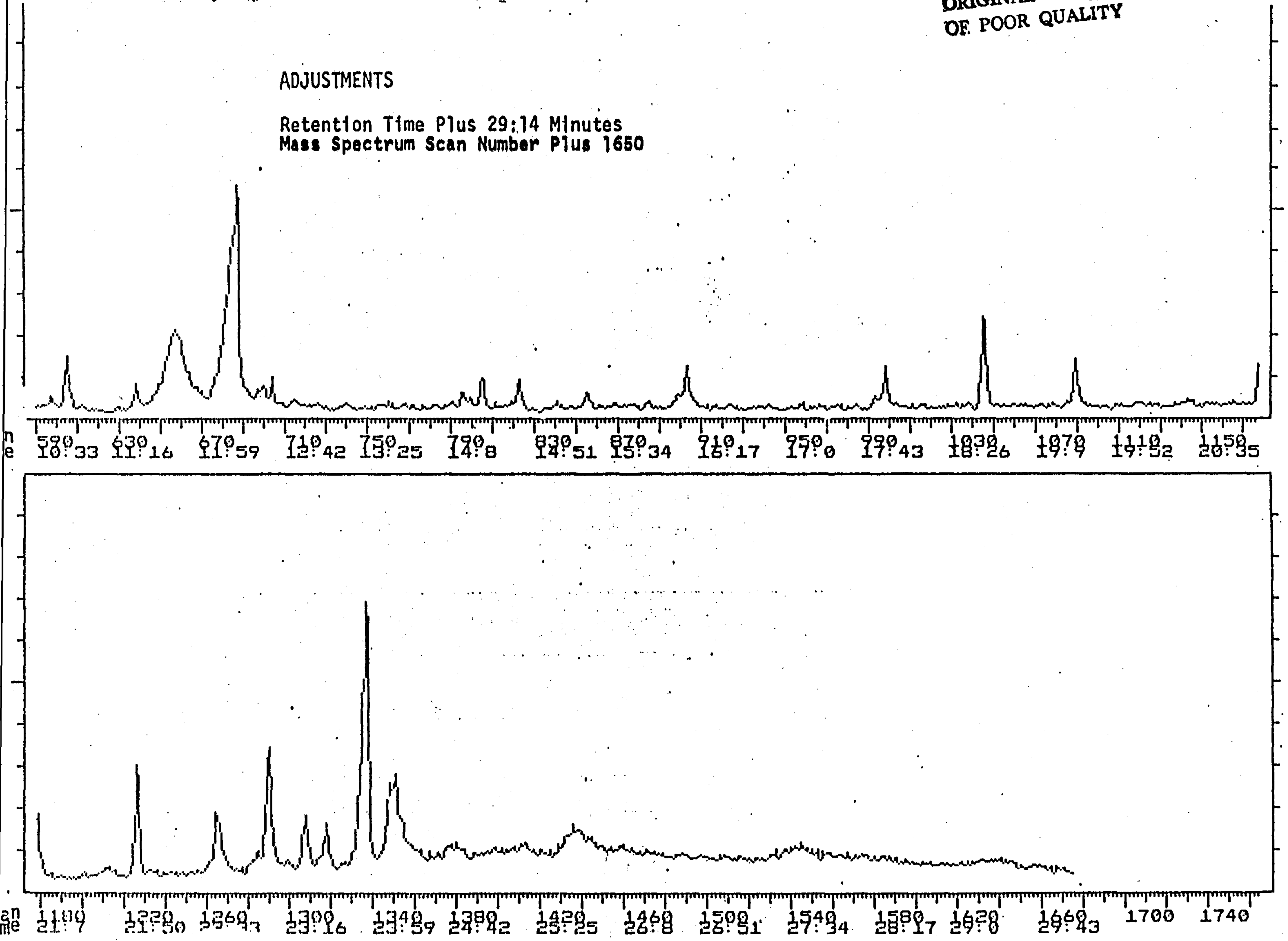
Mass Spectrum Scan Number Plus 1650

FIGURE 9 continued



ADJUSTMENTS

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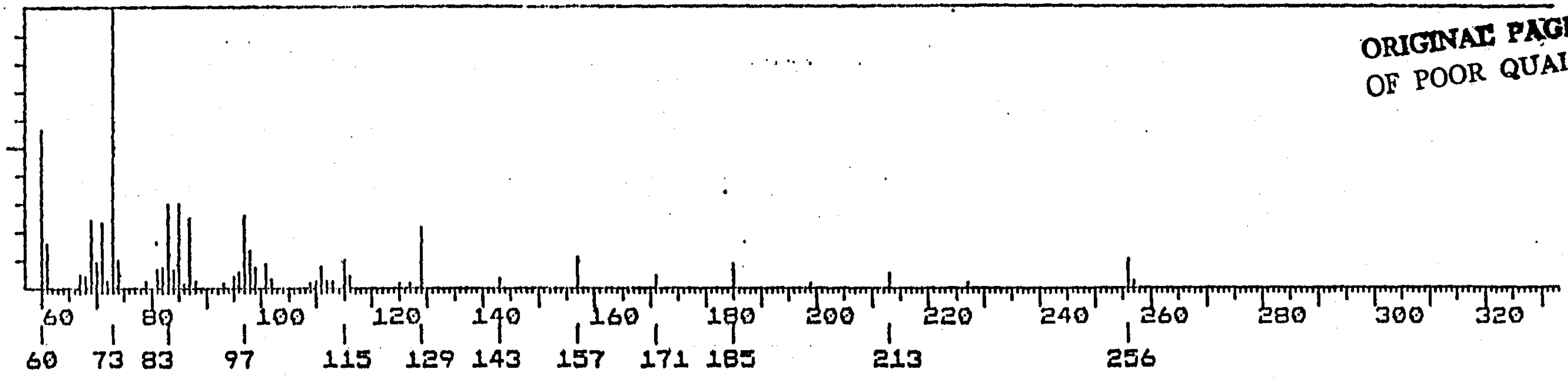
Mass Spectrum Scan Number Plus 1650

FIGURE 10 Mass Spectrum and EPA/NIH Library Search of Hydrocarbons Found in Skin on Tiles.



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NUM 20832 DI= 416
TETRADECANOIC ACID C14H2802 228 #54463
NUM 16936 DI= 443
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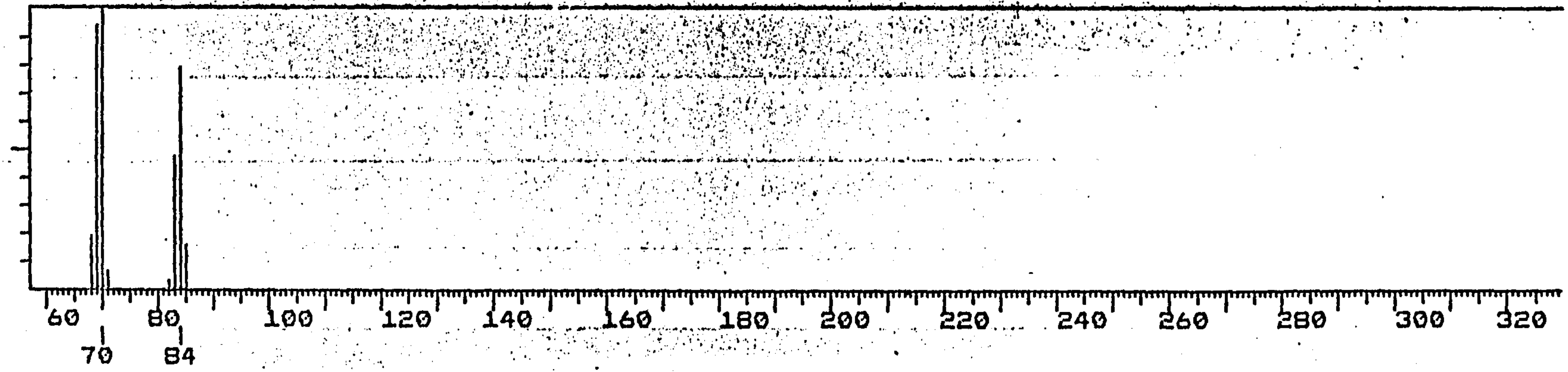

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650731 120 #620235474O 114 #35217175
NUM 3148 DI= 399
2-AZETIDINONE,3,3,4,4-TETRAMETHYL-1-(PHENYLMETHYL)- C14H19NO 217 #2260
7030
NUM 15590 DI= 515
2-AZETIDINONE,3,3,4,4-TETRAMETHYL- C7H13NO 127 #13423228
NUM 3284 DI= 541
CYCLOPENTANE,1,1,3,4-TETRAMETHYL-,CIS- C9H18 126 #53907601
NUM 3238 DI= 549
2-OCTENE,2,3,7-TRIMETHYL- C11H22 154 #33933754
NUM 6253 DI= 551
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