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NATIONAL TRANSPORTATION SAFETY BOARD
WASHINGTON, D.C.

EVANS EAST
TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY
ANALYTICAL REPORT
19 PAGES

PREPARED FOR: JEAN BERNSTEIN

EVANS EAST
SPECIALISTS IN MATERIALS CHARACTERIZATION

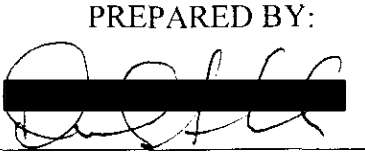
TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY ANALYTICAL REPORT

October 10, 1996

PREPARED FOR:

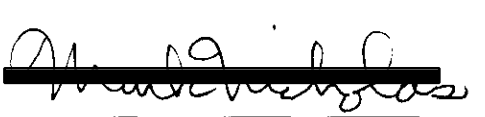
Ms. Jean Bernstein
United States of America
National Transportation Safety Board

PREPARED BY:



David A. Cole
Manager, TOF-SIMS

REVIEWED BY:



Mark Nicholas
Analyst, TOF-SIMS

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TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY

October 10, 1996

RE: Invoice #: 96-1857
Problem #: 24-139
PO #: to be received

Purpose: To determine whether a dye penetrant is present on one (1) failed metal surface.

Analytical conditions:

Instrument	Physical Electronics, PHI-Evans TFS-2000
Primary ion beam	$^{69}Ga^{+}$ liquid metal ion gun
Primary beam voltage	15 kV bunched
Nominal analysis region	$(240\ \mu m)^2$ - metal failure, $(80\ \mu m)^2$ - dye penetrants
Charge neutralization	no
Post acceleration	8000 V
Contrast diaphragm	0
Energy slit	no
Gun aperture	2

Experimental:

The as-received failed metal surface was loaded into the spectrometer as a single sample and analyzed before the analysis of the control dyes, thus preventing any possibility of cross contamination. Positive TOF-SIMS spectra were acquired at five locations which were referenced to the "origin" shown in the enclosed photograph. Thin films of the dye penetrants were prepared by placing a drop of the liquid on a silver sheet (previously etched with nitric acid) and blotting the excess with a Kim-wipe tissue. Positive and negative TOF-SIMS spectra were acquired on both dye penetrants.

Typical primary ion doses were on the order of 10^{12} ions/cm^2 for the analyses. This assures that the data were collected within the static limit, i.e., less than 1% of a monolayer was sputtered. Thus, all molecular fragments are indicative of species existing on the surfaces prior to analysis. (Under these conditions, the sampling depth of TOF-SIMS is 1 monolayer for molecular fragment ions and 1-3 monolayers for atomic species.). Mass spectra are plotted as the number of secondary ions detected (Y-axis) versus the mass-to-charge ratio of the ions (X-axis).

Results:

P-41H1, Class 1 Dye Penetrant. The MSDS for this liquid indicates it contains: dipropylene glycol dibenzoate; octyl epoxy tallate which is most likely a beta ester of octanol with the ester chain made from stearic, oleic, linoleic and linolenic acids; and epoxidized soybean oil which would be a derivative of triglycerides of stearic, oleic, linoleic, and linolenic acids. The approximate molecular weight for these three materials would be 326.15, ≈412, and ≈890 amu, respectively. Because the last two materials are derivatives of natural products we expect to see a distribution of molecular weights. As you can see from figures 1-2, this liquid contains H, C, O, and Si. Although $(CH_3)_xSi$ fragments were detected, the actual silicone could not be determined. However, it does not appear to polydimethyl siloxane. The most unique feature of the positive mass spectrum is the series of peaks between 350 and 450 m/z. These clusters are separated by 14 m/z indicating chain lengthening by CH_2. The best assignment for these ions are parent ions or fragments of octyl epoxy tallate. There is no evidence in either the positive or negative TOF-SIMS spectra for either the dipropylene glycol dibenzoate or the epoxidized soybean oil. Thus the best tags for this dye penetrant are the positive ions between 350 and 450 m/z. Note that several peaks such as 325, 343, 517, 575, 633, and 647 in the positive spectrum and 261, 409, 419, 433, 517, and 591 in the negative spectrum could not be identified. These ions are common to both class 1 (figures 1-2) and class 2 (figures (7-8) dye penetrants but are not found on the control silver sheet (figures 10-11). These peaks might be due to the solvents since they are the only ingredient common to both dye penetrants.

P-60H2, Class 2 Dye Penetrant. The MSDS for this liquid indicates it contains isodecyl biphenyl phosphate which would have a molecular weight of 390.20 amu. Figures 8-9 indicate this liquid contains H, C, O, Si, and P. The positive ions at 391.2 and 251.05 m/z are the protonated phosphate, and the protonated phosphate minus the isodecyl chain, respectively. Both of these ions are very intense and would be excellent tags for the dye penetrant. Negative ions at 249.0 and 285.1 are the deprotonated phosphate minus the isodecyl chain and one phenyl group, respectively. Negative ions at 361.2, 377.2 and 389.2 are the phosphate minus C_2H_6, CH_2 and H, respectively, and the negative ion at 391.2 is the protonated phosphate. All six peaks are unique to the dye and could be used as tags in negative TOF-SIMS spectra. As noted above there are several positive and negative ions which are assumed to be solvent residues. Similar to the class 1 dye, the specific identity of the siloxane could not be determined.

Metal Failure Surfaces. Four (Origin 1-3 and Inboard) of the five region examined on the metal failure surface were nearly identical. These regions contained Na, Ti, polydimethyl siloxane, and polyethylene glycol, see Figures 3-6. The "Aft" region is similar but contains additional species due to fluorocarbons (69, 100, and 169 m/z), C_{36} and C_{38} amines (522 and 550 m/z), and what appears to be an amide of behenic acid (338 m/z).

While the spectra from the metal failure surface are rich with structure, it is not clear whether the failure surface contains the P-41H1 dye penetrant. This is best shown in figures A-B where the top panel presents the positive spectrum of the pure dye from 350 to 450 m/z and the lower panels present the corresponding spectra for the metal failure surfaces. The difficulty in

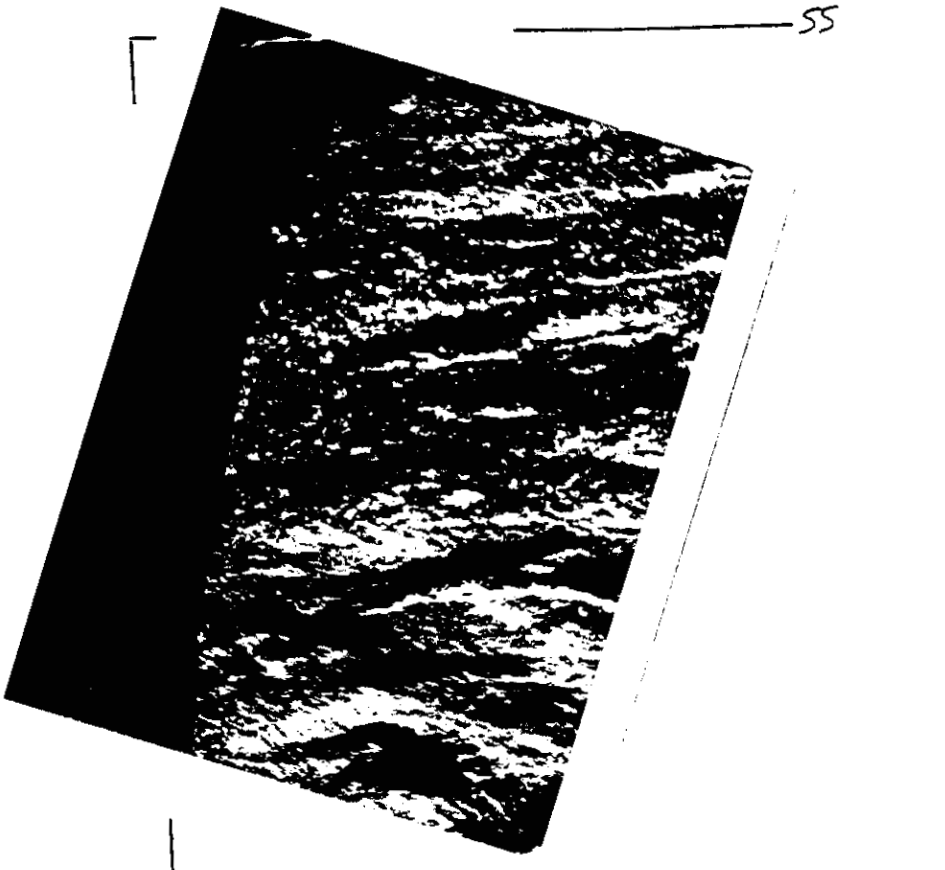
making a definitive statement lies in the interference created by fragments of polyethylene glycol (PEG) which gives a series of strong peaks at 331, 375, 419, 463, 507, 551, 595, 639 and 683 due to $(C_2H_4O)_xNa^+$ where x ranges from 7 to 15, and many minor peaks between each of the large peaks. A close examination of each PEG series shows minor peaks at $-H_2$, $-H_4$ and $-H_6$, each decreasing in intensity relative to the parent $(C_2H_4O)_xNa^+$ peaks. The parent at 419 minus H_6 gives a peak at the same nominal mass as octyl epoxy tallate plus hydrogen, i.e. 413 m/z. The intensity of the 413 peak relative to the 419 peak is however larger than the corresponding ratios of the minus H_6 peaks relative to the main $(C_2H_4O)_xNa^+$ peaks. This suggests that octyl epoxy tallate might be present. Confirmation would require an exact mass measurement. Unfortunately due to the relatively large raster used and the surface roughness, the mass resolution in these spectra is not sufficient to make the distinction between PEG fragments and octyl epoxy tallate from the P-41H1 dye penetrant.

Conclusions:

The best tag for P-41H1, class 1 dye penetrant appears to be the octyl epoxy tallate component which gives a series of peaks between 350 and 450 m/z in the positive TOF-SIMS spectra. While these peaks could be present on the metal failure surface, an unambiguous identification could not be made. The major complication is caused by interferences caused by polyethylene glycol (PEG) fragments which can only be resolved from octyl epoxy tallate if the mass resolution is around 8,000 M/ΔM. Due to surface roughness and relatively large $(240\ \mu m)^2$ analysis areas, the mass resolution is only around 3,000. There are two ways in which the analysis could be improved: (1) obtain TOF-SIMS spectra from much smaller areas (around $40\ \mu m)^2$ while selecting areas which are a flat as possible, and (2) attempt to remove the PEG with a suitable washing methods prior to analysis.

If you have any questions after you have examined the data, please feel free to contact me or Mark Nicholas at (609) 799-1904. Thank you for choosing Evans East.

Table of Contents



55

origin was 8.5 mm from sample holder top edge and 2 mm inboard from left edge of sample

55

Sample Holder

inboard direction

aft direction

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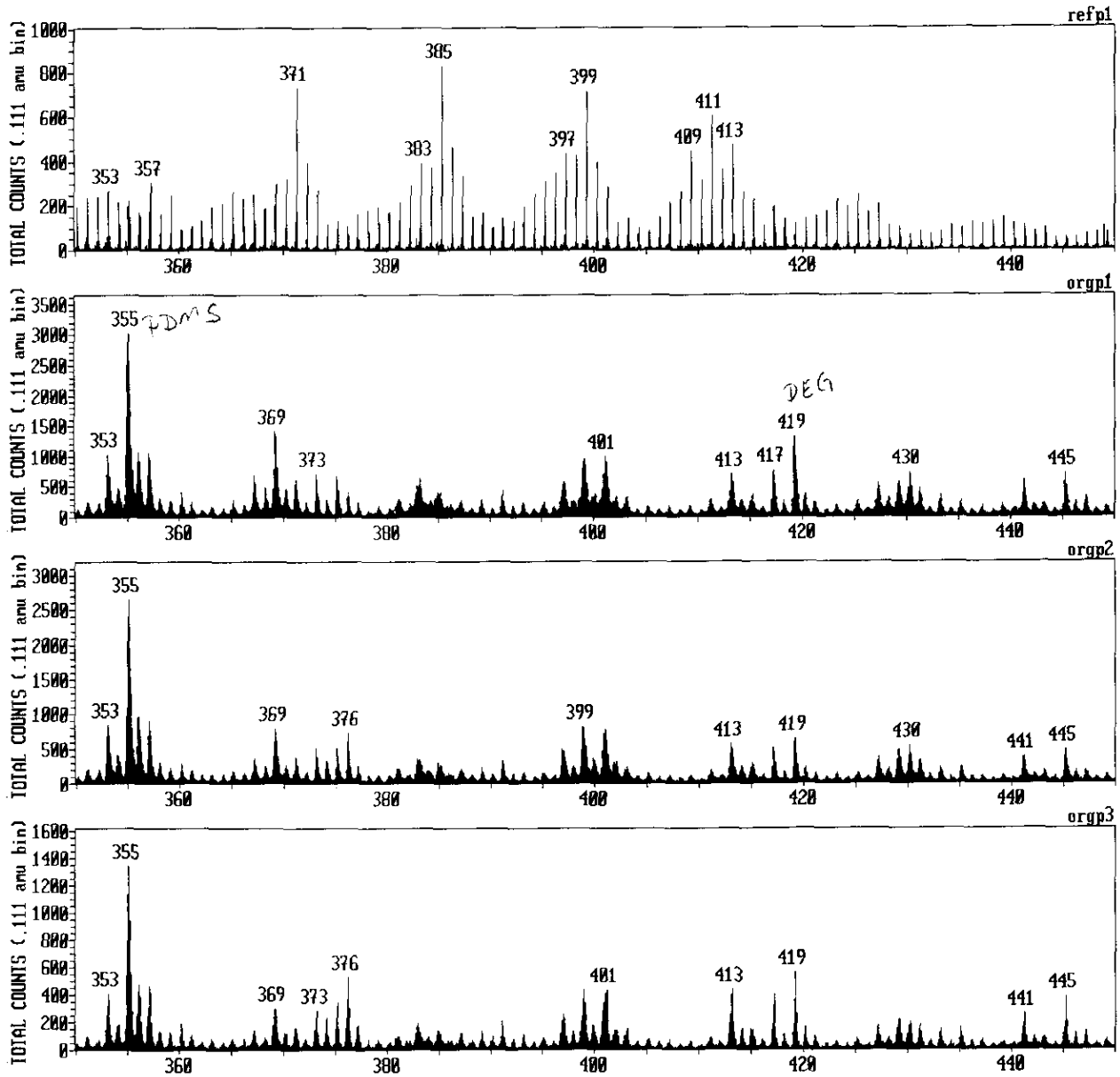

FILE NAME: refp1 *DATE : 3 Oct 96 12:58* *ACQUISITION TIME: 15.0 MIN.* *SPECTRUM INTEGRAL : 6705791*
reference, class 1 dye penetrant; cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS *PRIMARY GUN: LMIG* *TIME RECORDER: Multi-Stop TDC* *X-Y SOURCE: Raster* *TIME PER CHANNEL: 138 ps*
DATA SET: 1 Spectra; 0 Image(s) *RASTER SIZE: 81µm* *RASTER TYPE: 81*

FILE NAME: orgp1 *DATE : 3 Oct 96 10:21* *ACQUISITION TIME: 15.9 MIN.* *SPECTRUM INTEGRAL : 12078391*
Origin (8.5 mm down from frame, 3 mm in); cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS *PRIMARY GUN: LMIG* *TIME RECORDER: Multi-Stop TDC* *X-Y SOURCE: Raster* *TIME PER CHANNEL: 138 ps*
DATA SET: 1 Spectra; 9 Image(s) *RASTER SIZE: 242µm* *RASTER TYPE: 242*

FILE NAME: orgp2 *DATE : 3 Oct 96 10:50* *ACQUISITION TIME: 15.0 MIN.* *SPECTRUM INTEGRAL : 11839259*
Origin (8.5 mm down from frame, 5 mm in); cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS *PRIMARY GUN: LMIG* *TIME RECORDER: Multi-Stop TDC* *X-Y SOURCE: Raster* *TIME PER CHANNEL: 138 ps*
DATA SET: 1 Spectra; 9 Image(s) *RASTER SIZE: 242µm* *RASTER TYPE: 242*

FILE NAME: orgp3 *DATE : 3 Oct 96 11:13* *ACQUISITION TIME: 7.7 MIN.* *SPECTRUM INTEGRAL : 7074587*
Origin (8.5 mm down from frame, 7 mm in); cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS *PRIMARY GUN: LMIG* *TIME RECORDER: Multi-Stop TDC* *X-Y SOURCE: Raster* *TIME PER CHANNEL: 138 ps*
DATA SET: 1 Spectra;10 Image(s) *RASTER SIZE: 242µm* *RASTER TYPE: 242*

FIGURE A

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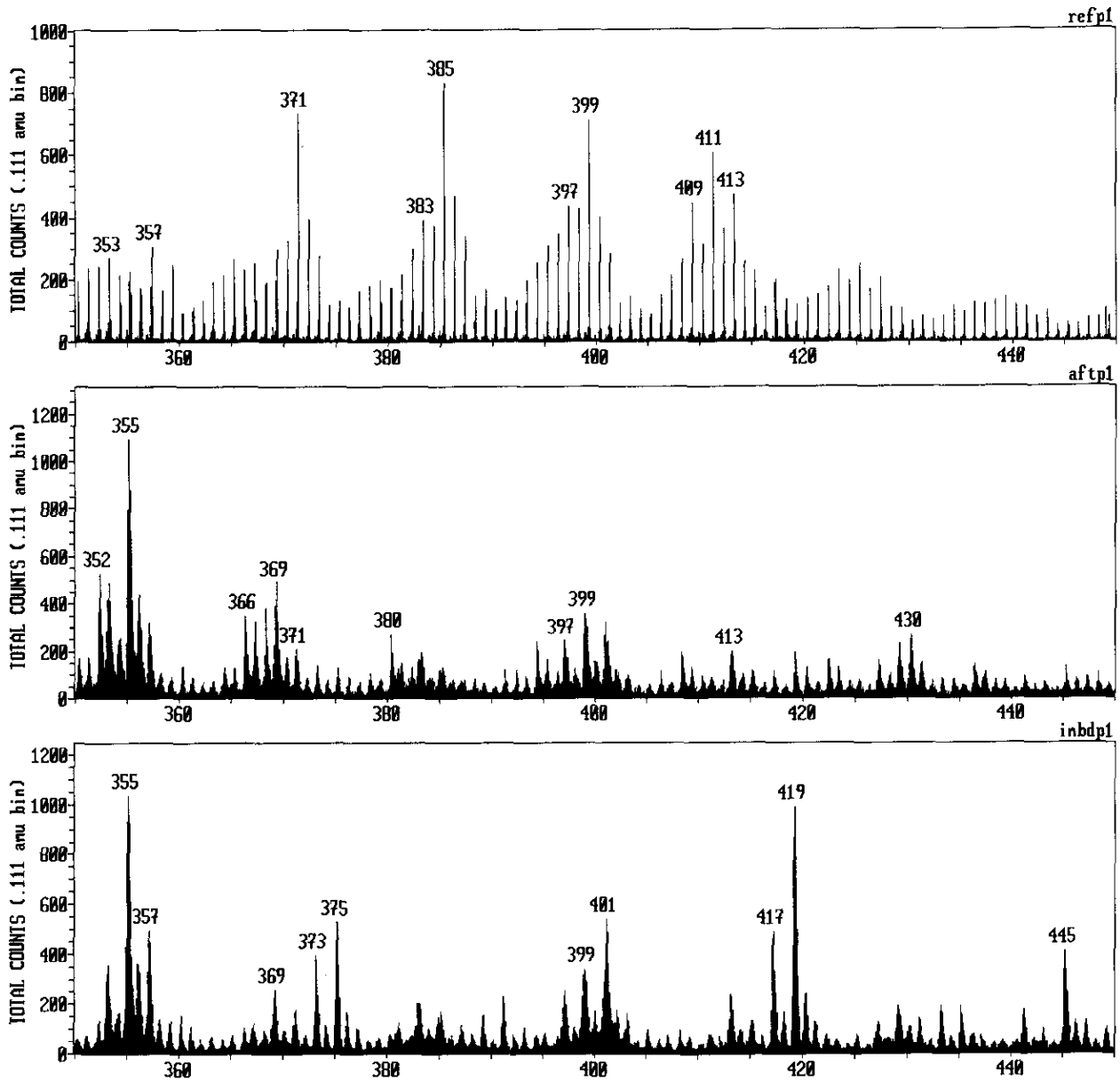

FILE NAME: refp1 DATE : 3 Oct 96 12:58 ACQUISITION TIME: 15.0 MIN. SPECTRUM INTEGRAL : 6705791
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+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 0 Image(s) RASTER SIZE: 81µm RASTER TYPE: 81

FILE NAME: aftp1 DATE : 3 Oct 96 11:57 ACQUISITION TIME: 15.0 MIN. SPECTRUM INTEGRAL : 9135058
Aft (8 mm aft from origin); cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 9 Image(s) RASTER SIZE: 242µm RASTER TYPE: 242

FILE NAME: inbdp1 DATE : 3 Oct 96 11:30 ACQUISITION TIME: 15.0 MIN. SPECTRUM INTEGRAL : 7474205
Inboard (30.5 mm inboard from origin, 5.3 mm forward from origin; cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 9 Image(s) RASTER SIZE: 242µm RASTER TYPE: 242

FIGURE B

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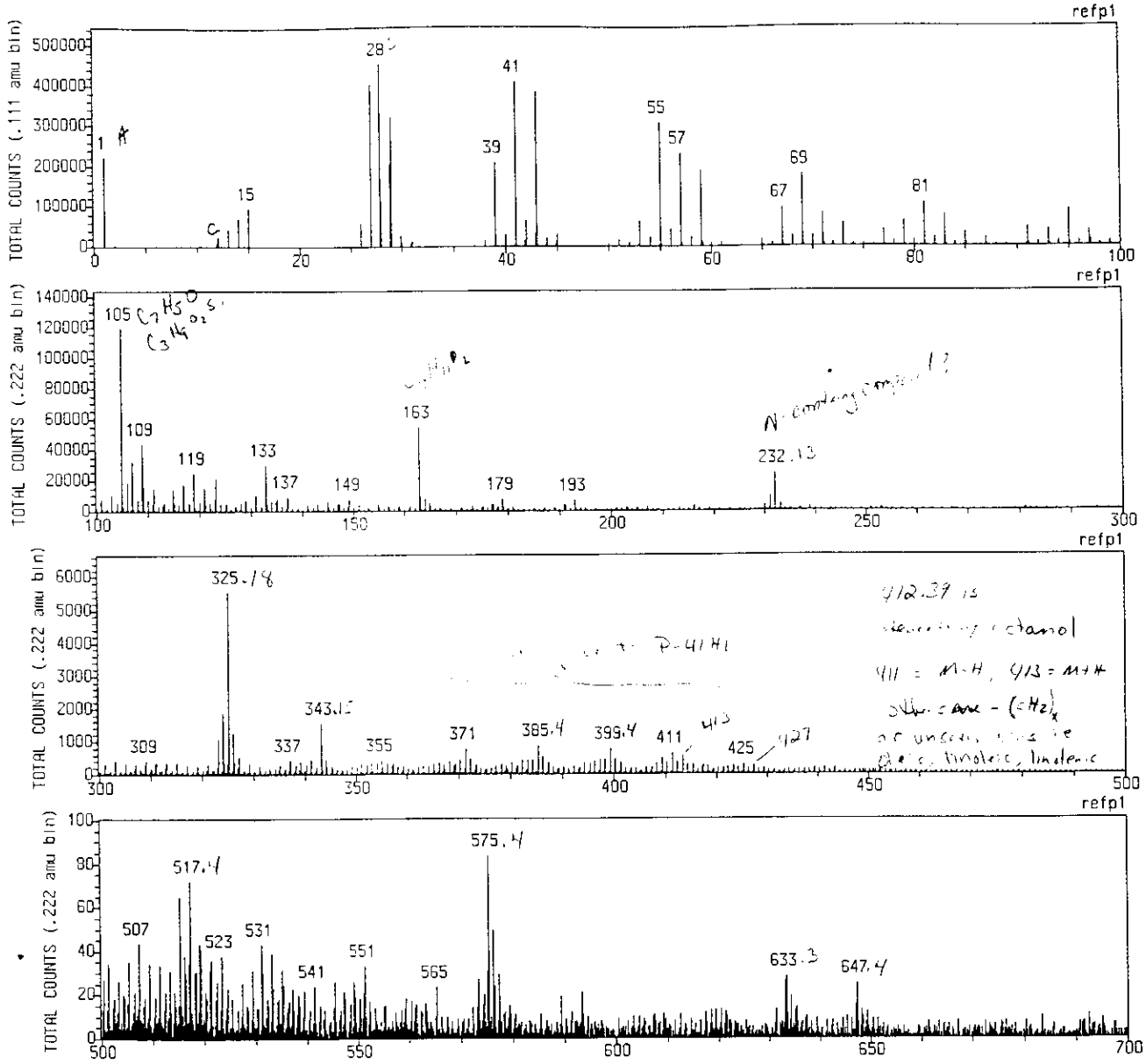

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+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 0 Image(s) RASTER SIZE: 81µm RASTER TYPE: 81

class 1 dye penetrant

FIGURE 1

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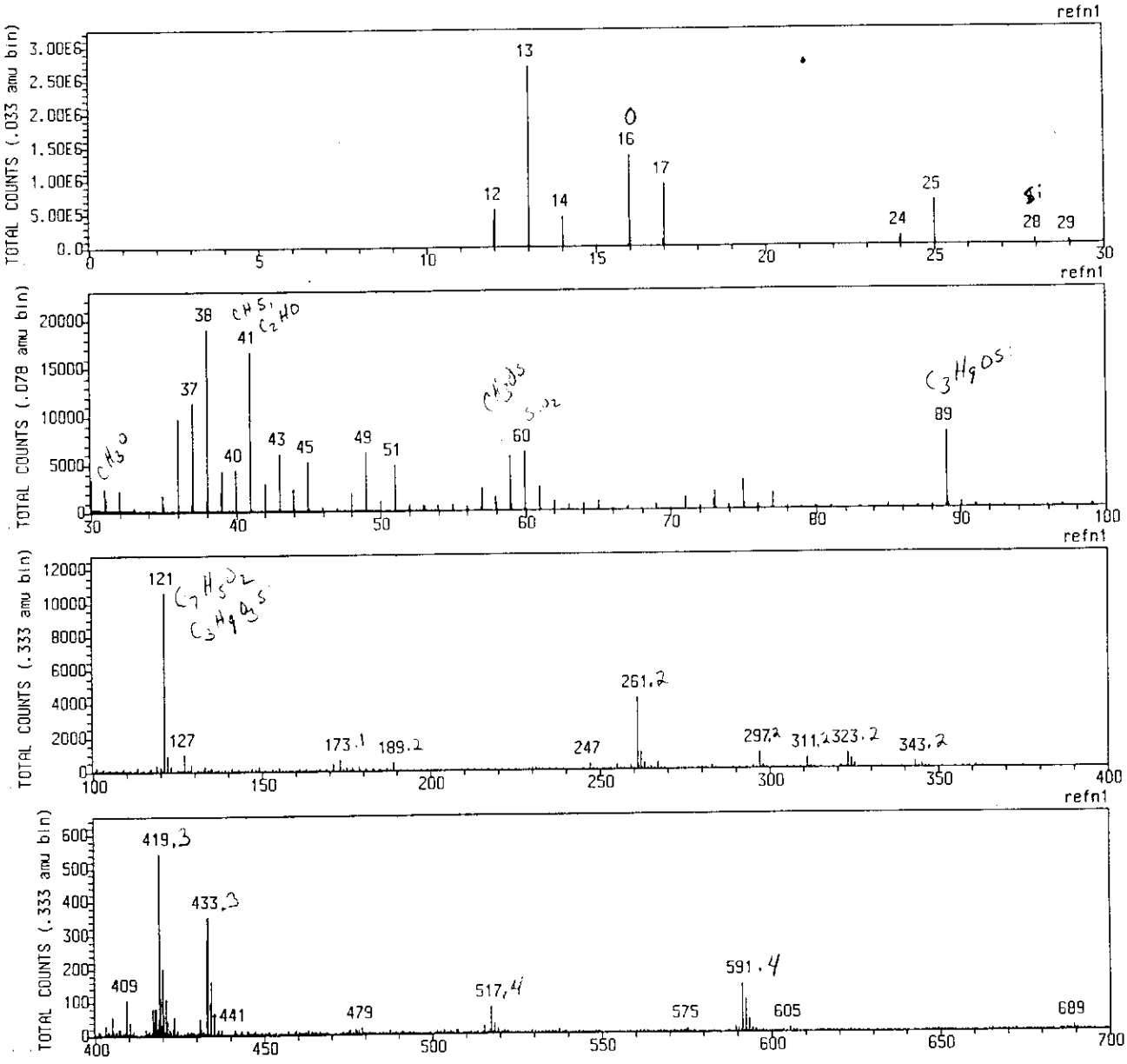

FILE NAME: refn1 DATE : 3 Oct 96 13:26 ACQUISITION TIME: 15.0 MIN. SPECTRUM INTEGRAL : 8760137
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DATA SET: 1 Spectra; 1 Image(s) RASTER SIZE: 81µm RASTER TYPE: 81

FIGURE 2

EVANS EAST
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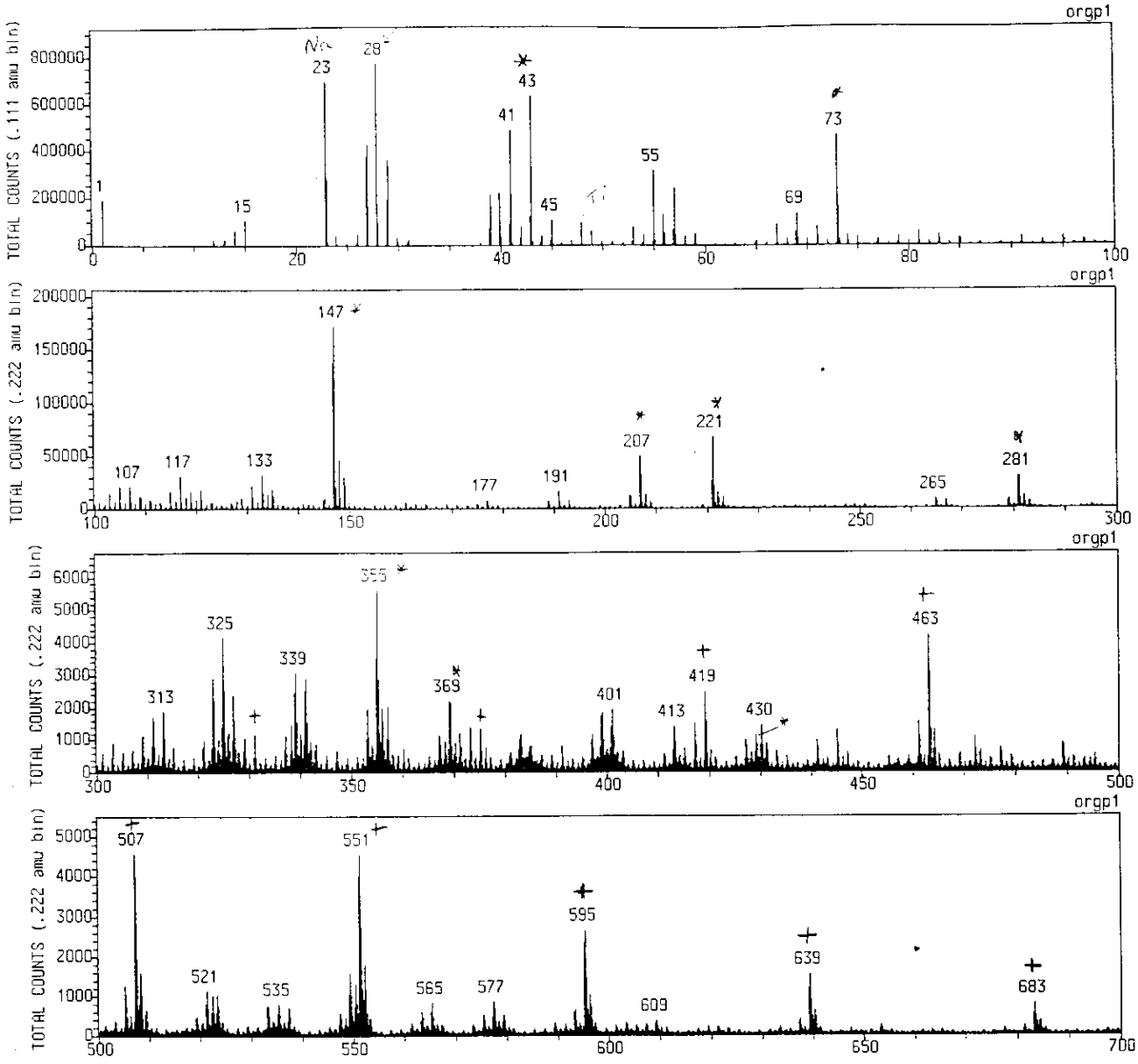
PDMS = *
PEG = +



FILE NAME: orgp1 DATE : 3 Oct 96 10:21 ACQUISITION TIME: 15.9 MIN. SPECTRUM INTEGRAL : 12078391
Origin (8.5 mm down from frame, 3 mm in); cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 9 Image(s) RASTER SIZE: 242um RASTER TYPE: 242

FIGURE 3

EVANS EAST
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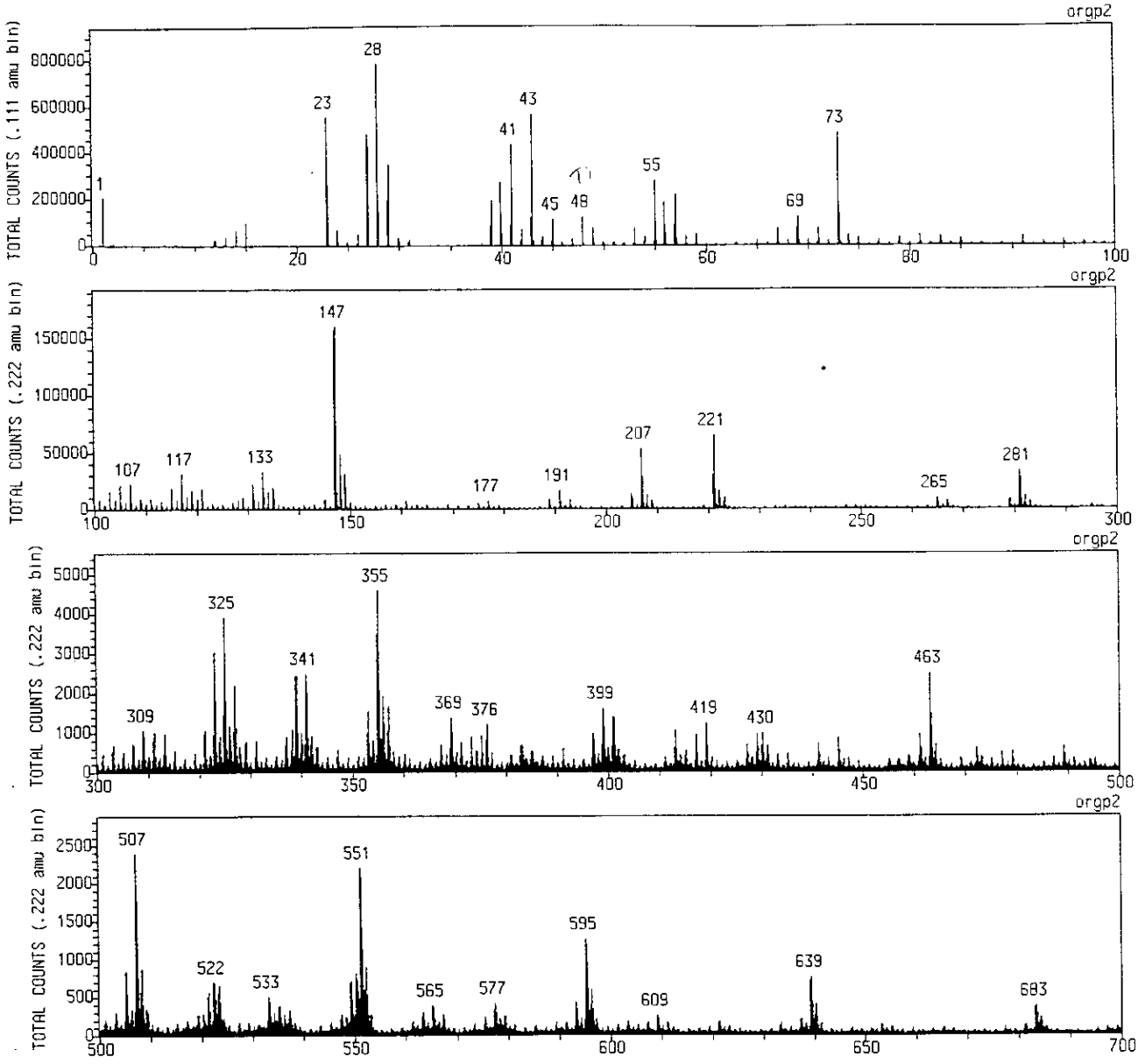

FILE NAME: orgp2 DATE : 3 Oct 96 10:50 ACQUISITION TIME: 15.0 MIN. SPECTRUM INTEGRAL : 11839259
Origin (8.5 mm down from frame, 5 mm in); cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 9 Image(s) RASTER SIZE: 242μm RASTER TYPE: 242

FIGURE 4

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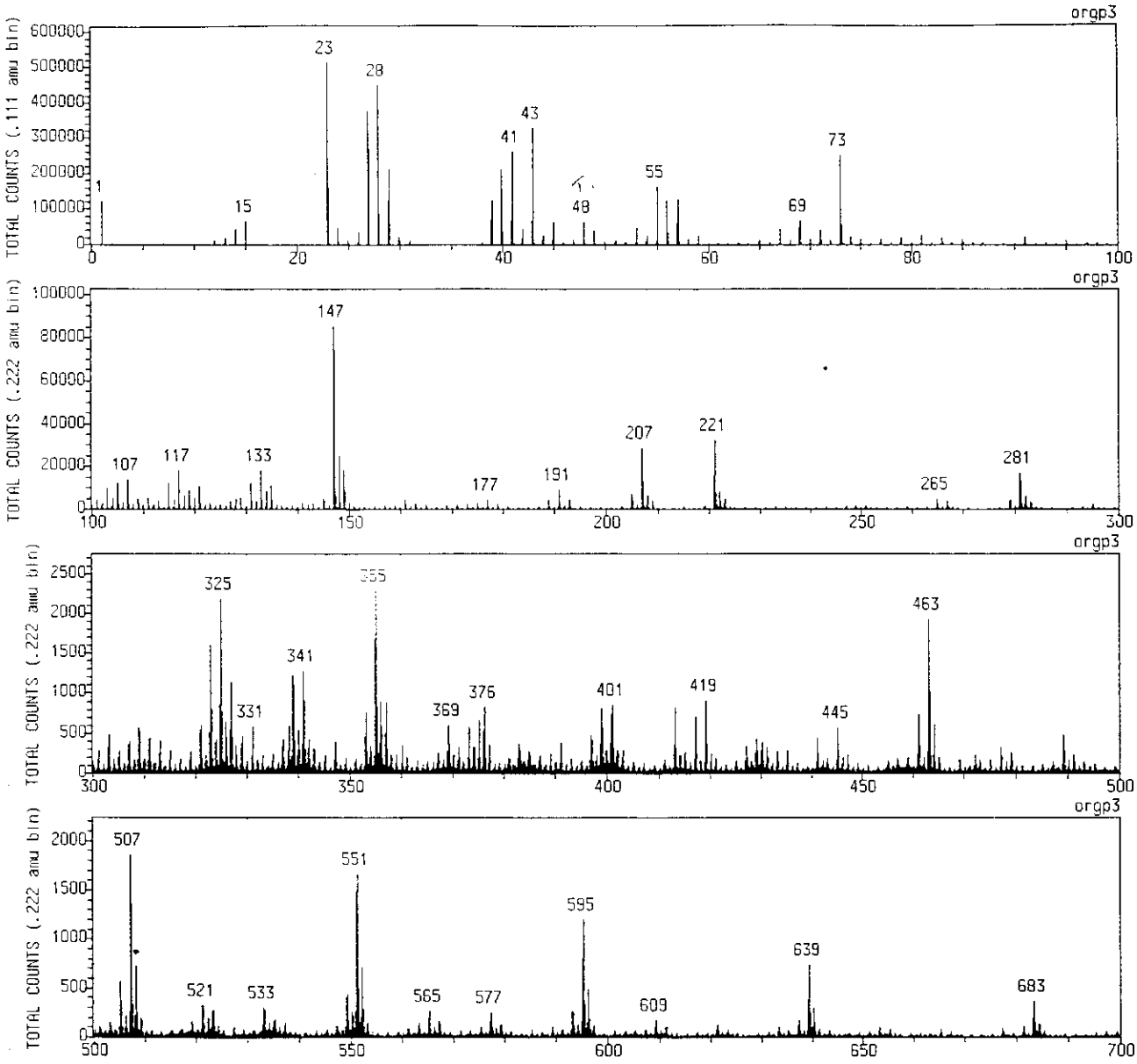

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Origin (8.5 mm down from frame, 7 mm in); cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra;10 Image(s) RASTER SIZE: 242um RASTER TYPE: 242

FIGURE 5

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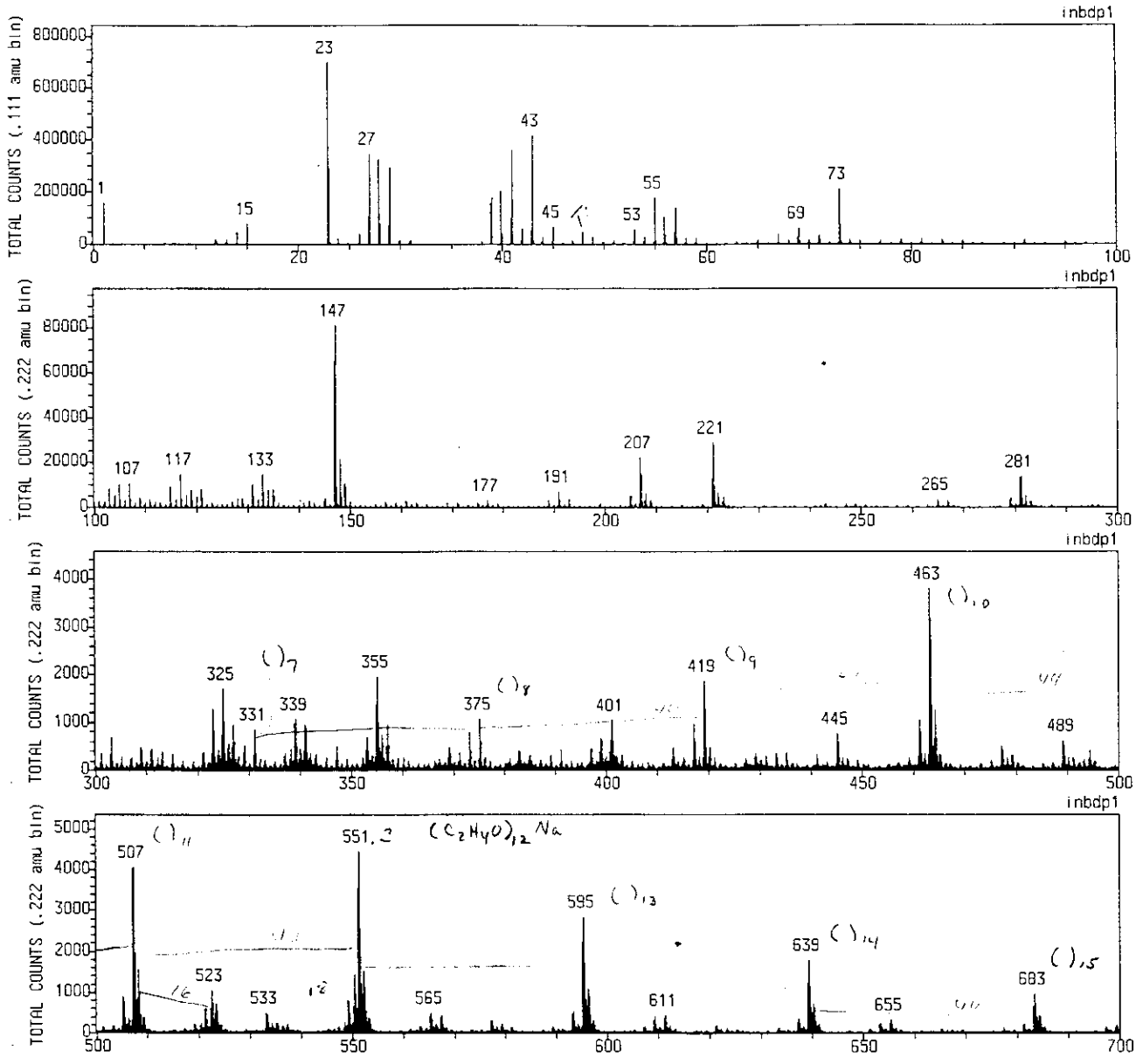

FILE NAME: inbdp1 DATE : 3 Oct 96 11:30 ACQUISITION TIME: 15.0 MIN. SPECTRUM INTEGRAL : 7474205
Inboard (30.5 mm inboard from origin, 5.3 mm forward from origin; cd0, ne es, ga2, pa8K, dv1500, 15b
+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 9 Image(s) RASTER SIZE: 242µm RASTER TYPE: 242

FIGURE 6

EVANS EAST
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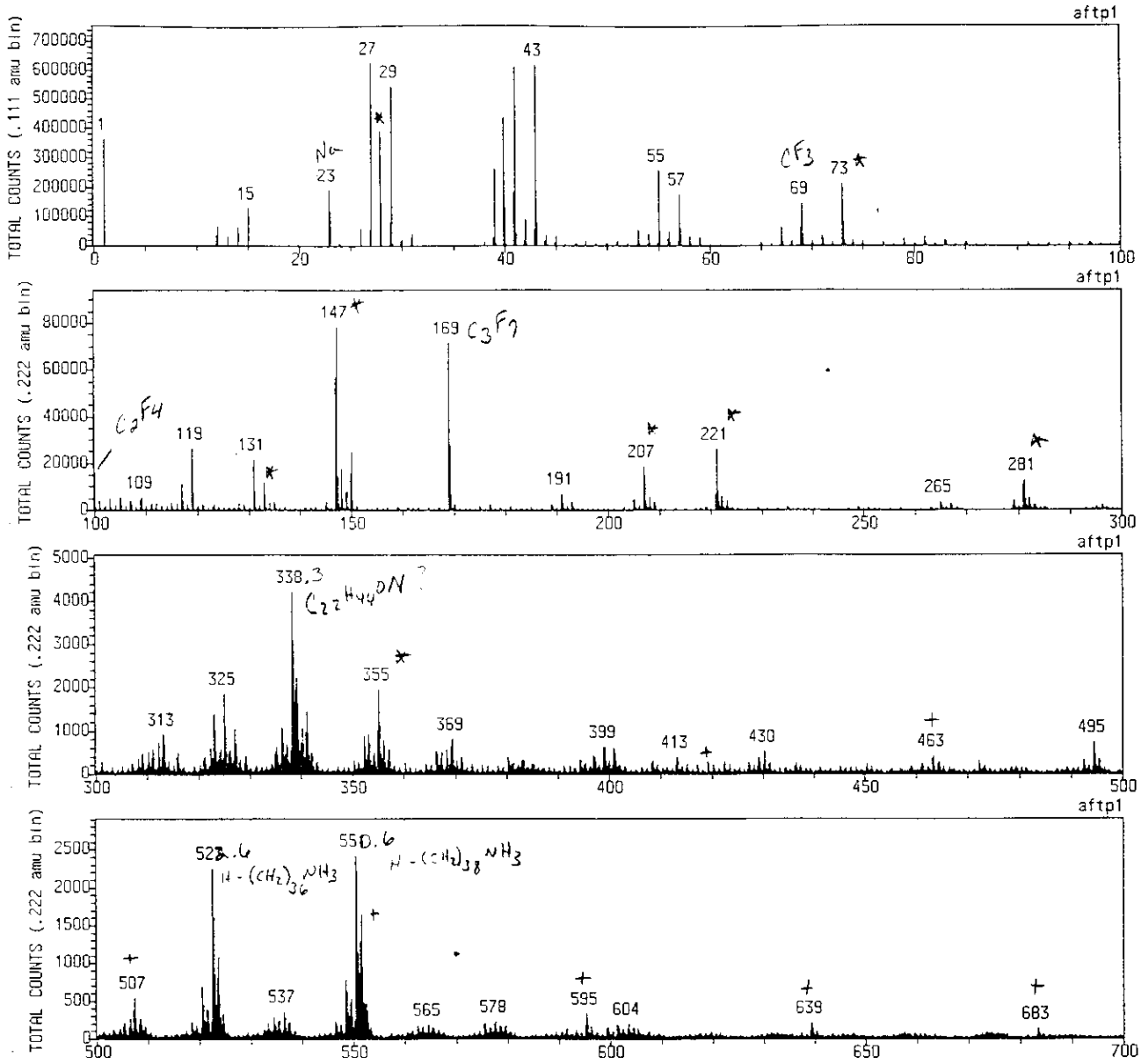
PDMS = *
PEG = +



FILE NAME: aftp1 DATE : 3 Oct 96 11:57 ACQUISITION TIME: 15.0 MIN. SPECTRUM INTEGRAL : 9135058
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DATA SET: 1 Spectra; 9 Image(s) RASTER SIZE: 242µm RASTER TYPE: 242

FIGURE 2

EVANS EAST
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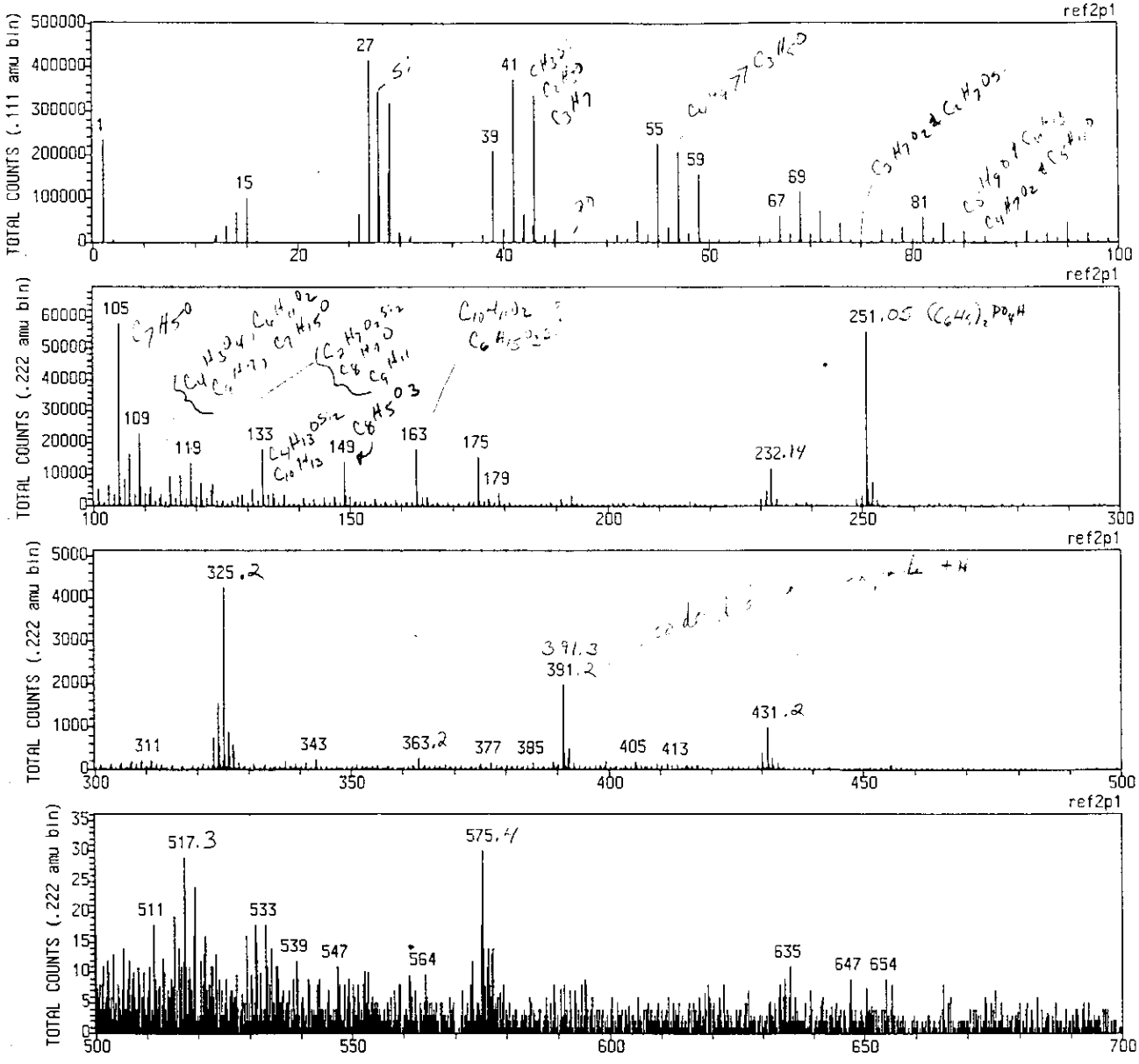

FILE NAME: ref2p1 DATE : 3 Oct 96 14:37 ACQUISITION TIME: 15.0 MIN. SPECTRUM INTEGRAL : 5439205
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+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 1 Image(s) RASTER SIZE: 81µm RASTER TYPE: 81

class 2 dye penetrant (New)

FIGURE 8

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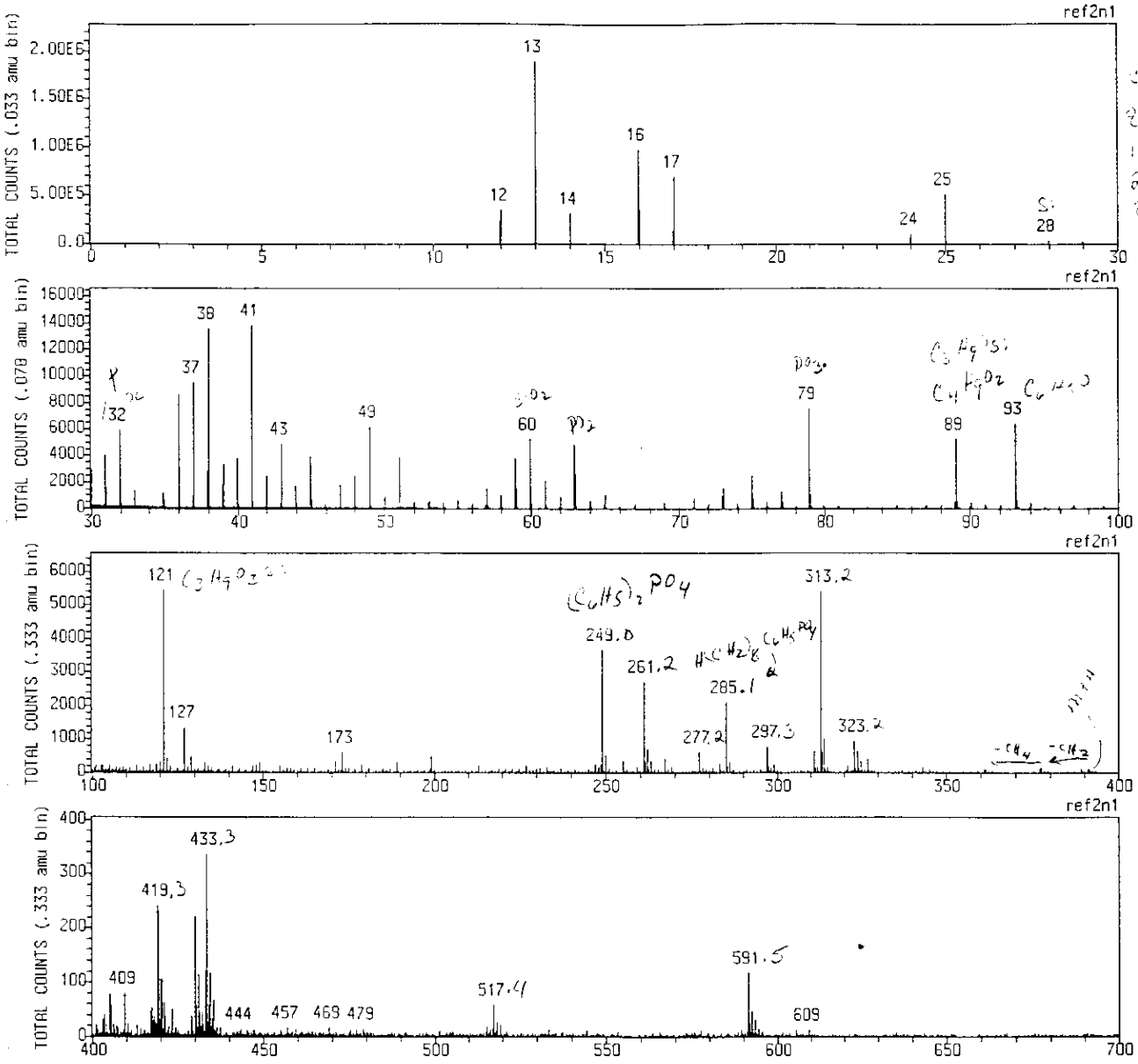

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- IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 1 Image(s) RASTER SIZE: 81µm RASTER TYPE: 81

FIGURE 9

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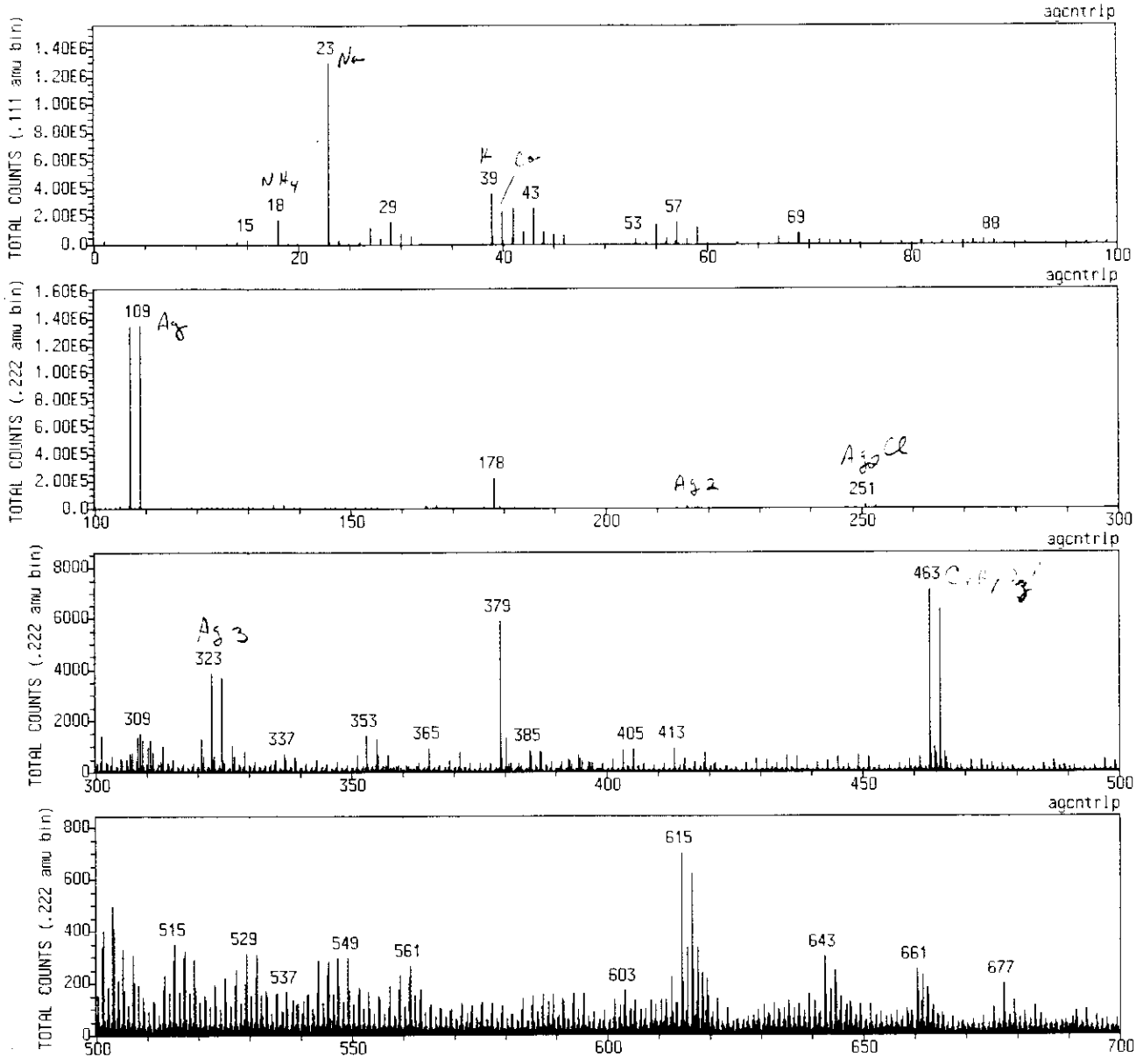

FILE NAME: agcntrlp DATE : 10 Oct 96 7:59 ACQUISITION TIME: 2.2 MIN. SPECTRUM INTEGRAL : 9509829
Control silver sheet,; cd0, no es, ga2, aw 4, dv8K, pa 8K
+ IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 0 Image(s) RASTER SIZE: 81µm RASTER TYPE: 81

FIGURE 18 (18)

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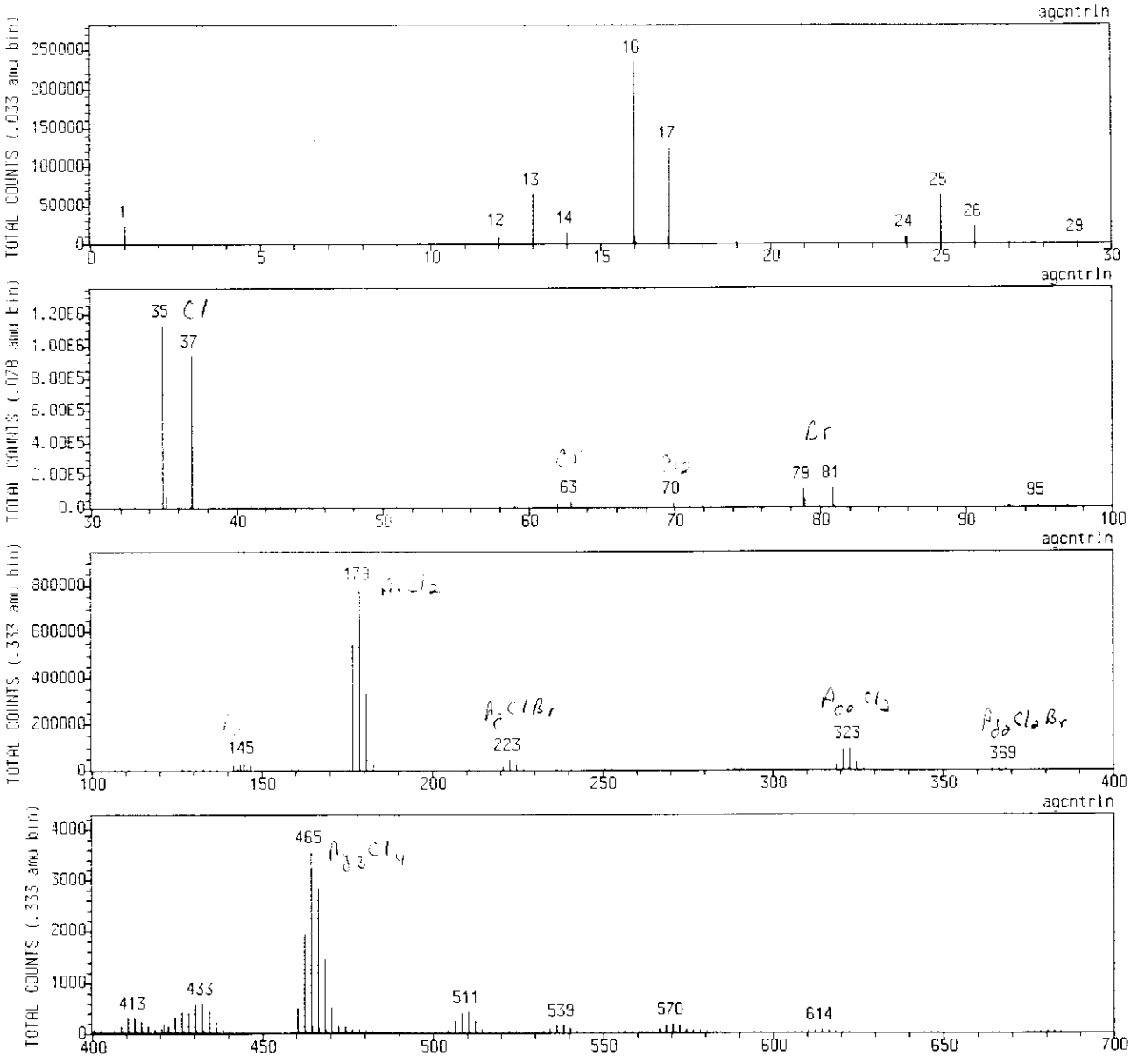

FILE NAME: agcntrln DATE : 10 Oct 96 8:07 ACQUISITION TIME: 2.1 MIN. SPECTRUM INTEGRAL : 6077509
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- IONS PRIMARY GUN: LMIG TIME RECORDER: Multi-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 138 ps
DATA SET: 1 Spectra; 0 Image(s) RASTER SIZE: 81µm RASTER TYPE: 81

FIGURE 11