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Journal/Book Title

Year

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Descripton Notes

Background

Analysis of a Binghamton Soot Sample for Tetrachlorodibenzofurans and Tetrachlorodibenzo-p-dioxins

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B.L. Jelus-Tyror, K. Aldous

October 1, 1981

INTRODUCTION

A fire caused by a malfunctioning PCB-filled transformer in the Binghamton state office building on February 6, 1981 released an unknown amount of incomplete combustion products into the 18-story building. A sample of soot (Tox. No. 811711965) was collected from an unspecified area of the building using a vacuum cleaner. A portion of the homogenized soot, intended to be used for animal toxicology studies, was soxhlet extracted for 16 hrs in benzene and analyzed for TCDF's and TCDD's by capillary GC/High resolution mass spectrometry (HRMS).

PROCEDURE

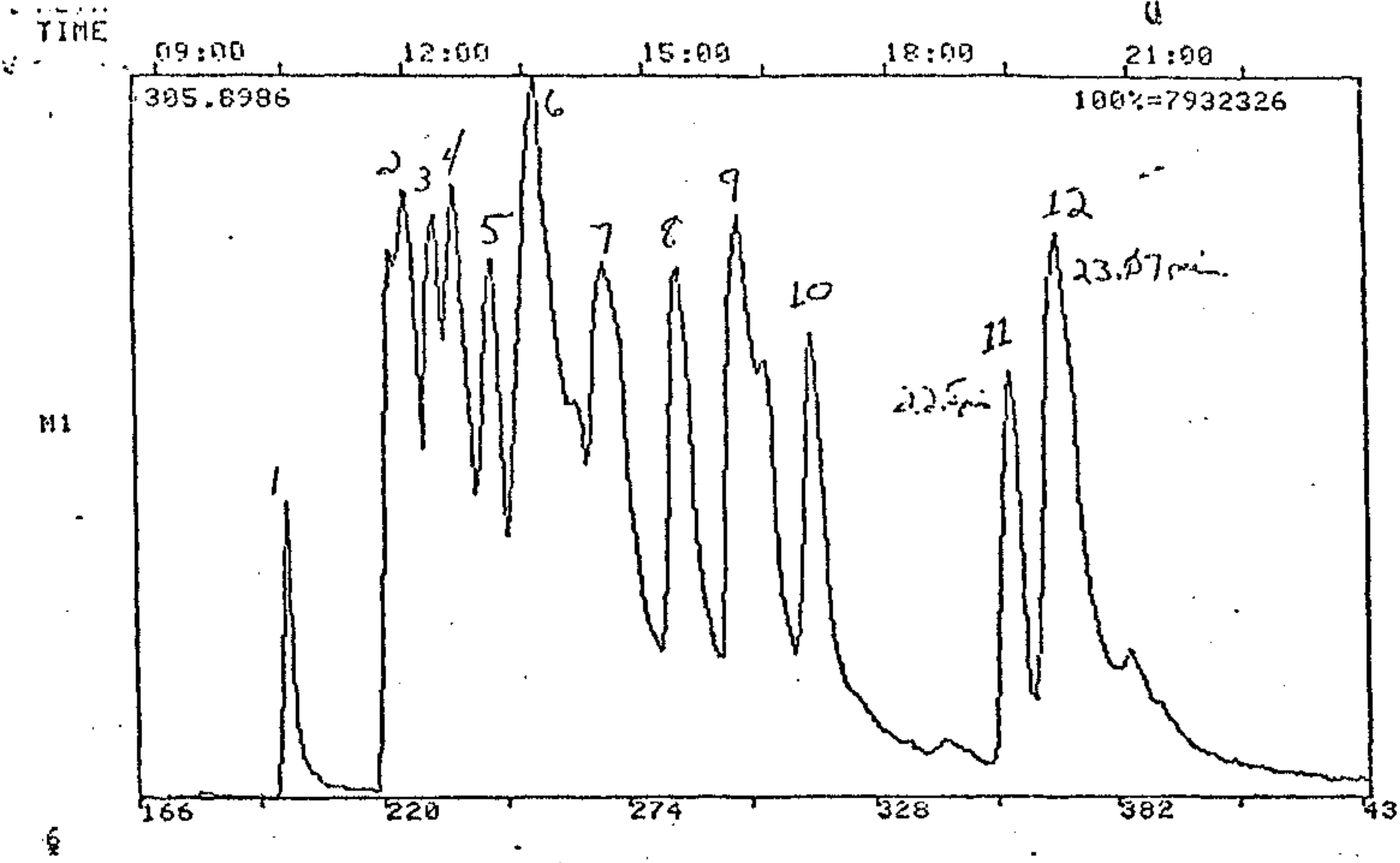
Fifty µl of the benzene extract (corresponding to 46 mg soot) was spiked with 6 ng of ^{13}C labelled 2,3,7,8-TCDD and cleaned-up prior to GC/HRMS injection using sequential liquid chromatographic columns containing PX-21 adsorptive carbon, 2% deactivated silica gel, and activated Florisil. An aliquot of the concentrated sample was then injected onto a 40 m x 3 mm OV275 coated soda glass GC capillary which is interfaced to the MS-50 HRMS through a jet separator. The temperature was appropriately programmed and mass profile data was accumulated for the m/e 306 (TCDF), 322,320 (TCDD) and 334 (^{13}C TCDD) ions. Standards (^{13}C 2,3,78-TCDD and unlabelled 2,3,7,8-TCDF) were run prior to sample injection. A control sample of Fisher activated coconut charcoal was similarly spiked and analyzed.

RESULTS AND DISCUSSION

The sample was found to contain a complex mixture of TCDFs as shown in the chromatogram in Figure 1. At least twelve distinct TCDF peaks are present. 2,3,7,8-TCDF eluted as peak No. 12 as determined by comparison with an injection of authentic 2,3,7,8-TCDF. The presence of amounts of tetrachlorodibenzo-p-dioxins in the sample are indicated by the M3 chromatogram in Figure 2. Closer inspection of the data revealed the presence of an interferent. However the data system allowed consideration of the intensity due to tetrachlorodioxin ions which were partially resolved from the interferents (Figure 3). The interferent appears at an m/e value very similar to that of the [M^{+}-Cl] fragment of heptachlorobiphenyl. Signal detected in the dioxin ion position in the m/e 321.8936 mass region which occurred at the same time in the chromatogram as the ^{13}C-2,3,7,8-TCDD were taken as being due to native 2,3,7,8-TCDD. This implies a relative retention time of 1.00 for native 2,3,7,8-TCDD.

The quantitative results of the analysis of the samples are summarized in Table I. The figures given in the table denote only "detectable" TCDF and TCDD. The sample clean-up procedure that was used requires the use of isotypically labelled standards to correct for low recovery. Presently, no labelled TCDF is available and the assumption was made that the recovery of all TCDF and TCDD isomers was the same as that of the ^{13}C labelled 2,3,7,8-TCDD internal standard based on preliminary TCDF recovery experiments. Although the capillary GC column gives a high degree of isomer separation, the analysis should not be considered completely 2,3,7,8-TCDD or TCDF isomer specific as other isomers may co-elute. The unexpectedly large amounts of TCDFs found in the sample exceeded the linear range of the HRMS, making a second injection using less sample necessary (Fig. 4) for proper quantitation (All calculations and several important mass profiles are included in the appendix). No TCDDs or TCDFs were found in the control carbon.

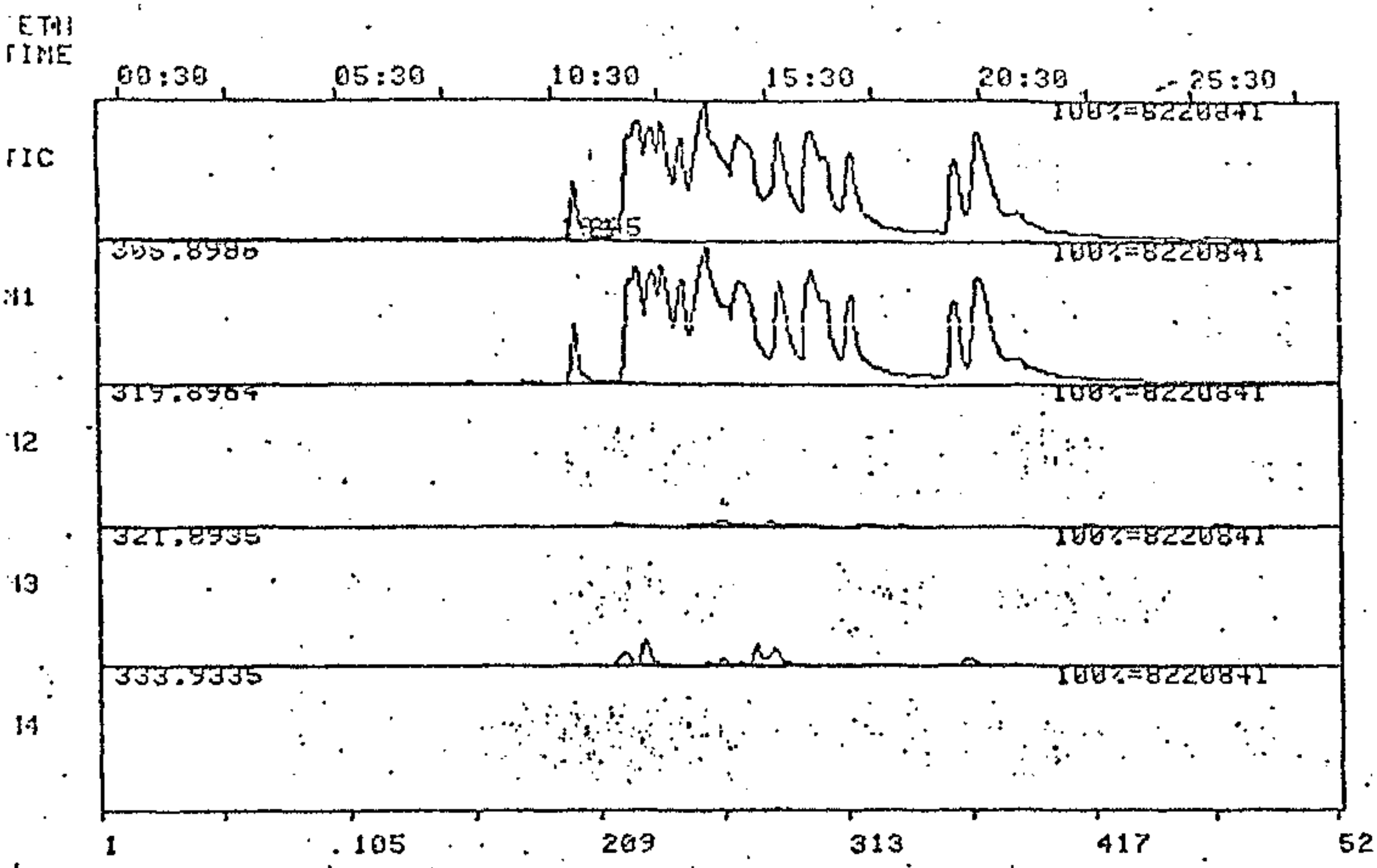
The results show that concentrations of TCDDs and TCDFs in this soot appear to be similar to those found in soot TOX No. 811710280 and air particulate sample Tox No. 811710977 previously taken from the Binghamton state office building.



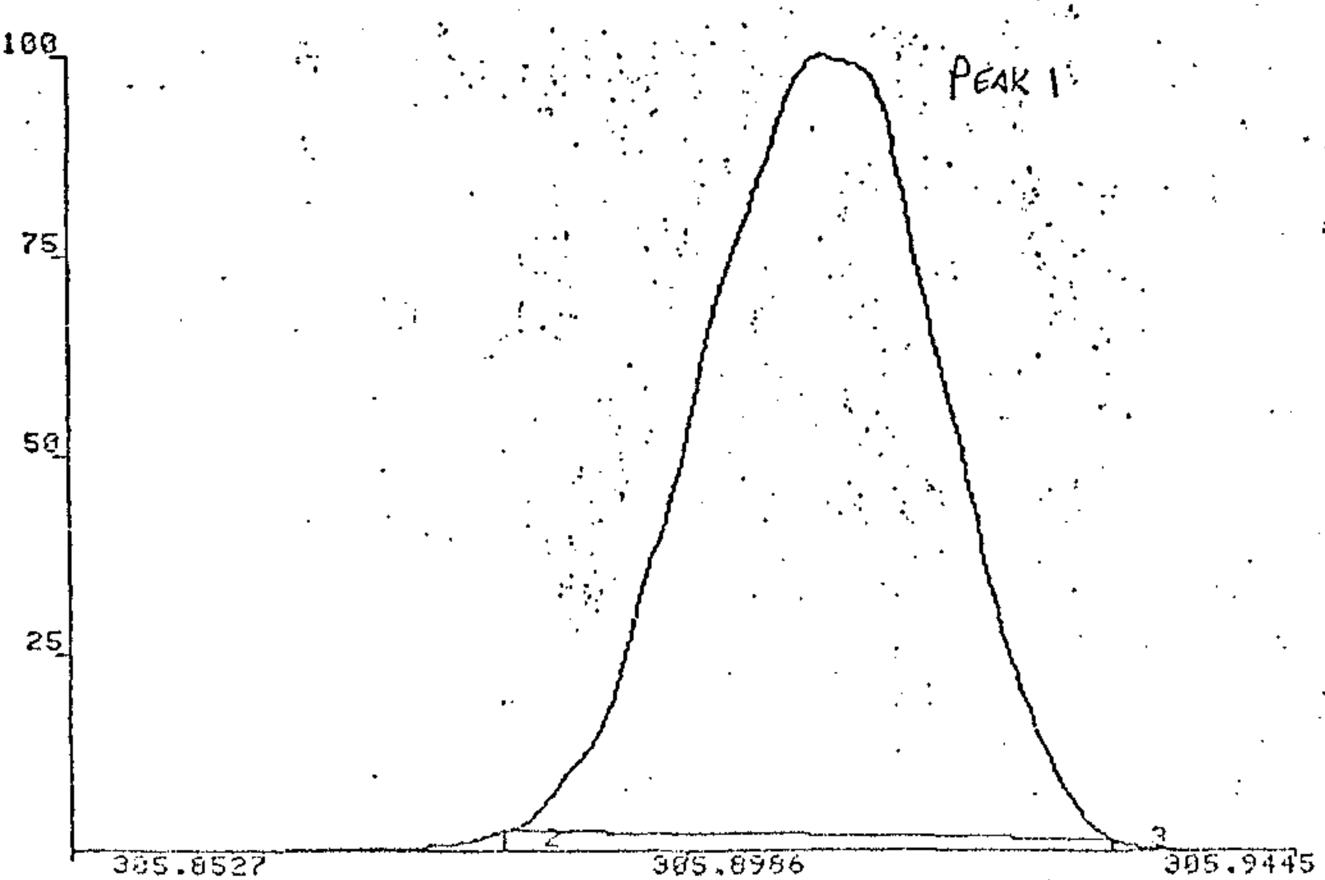
TIME
09:00
12:00
15:00
18:00
21:00
305.8986
100%=7932326
M1
1
2
3
4
5
6
7
8
9
10
11
12
22.5min
23.07min
166
220
274
328
382
43

2378 TCDD

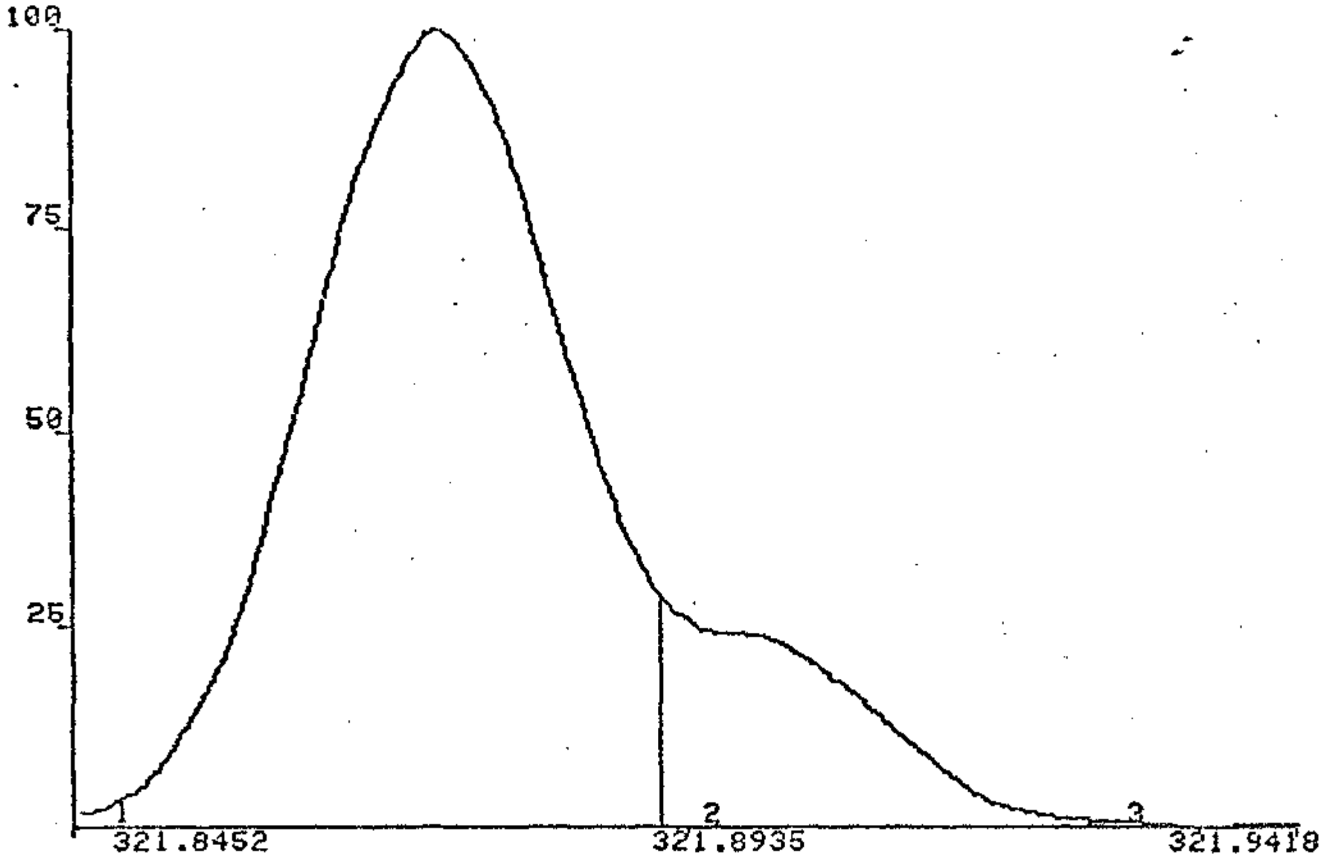
DS55 HIGH RESOLUTION MPM
RUNNAME FDHM8 DATE 7/10/81 TIME 21:11



RUNNAME FDHM8 DATE 7/10/81 TIME 21:11
MASS 305.8986 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 194-205 100% INTENSITY 148676



RUNNAME FDHM8 DATE 7/10/81 TIME 21:11
MASS 321.8935 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 149-438 100% INTENSITY 442547



DL HOW MANY AREAS?3

DS55 HIGH RESOLUTION MPM

PEAK SUMMATION REPORT

RUNNAME FDHM8 DATE 7/10/81 TIME 21:11

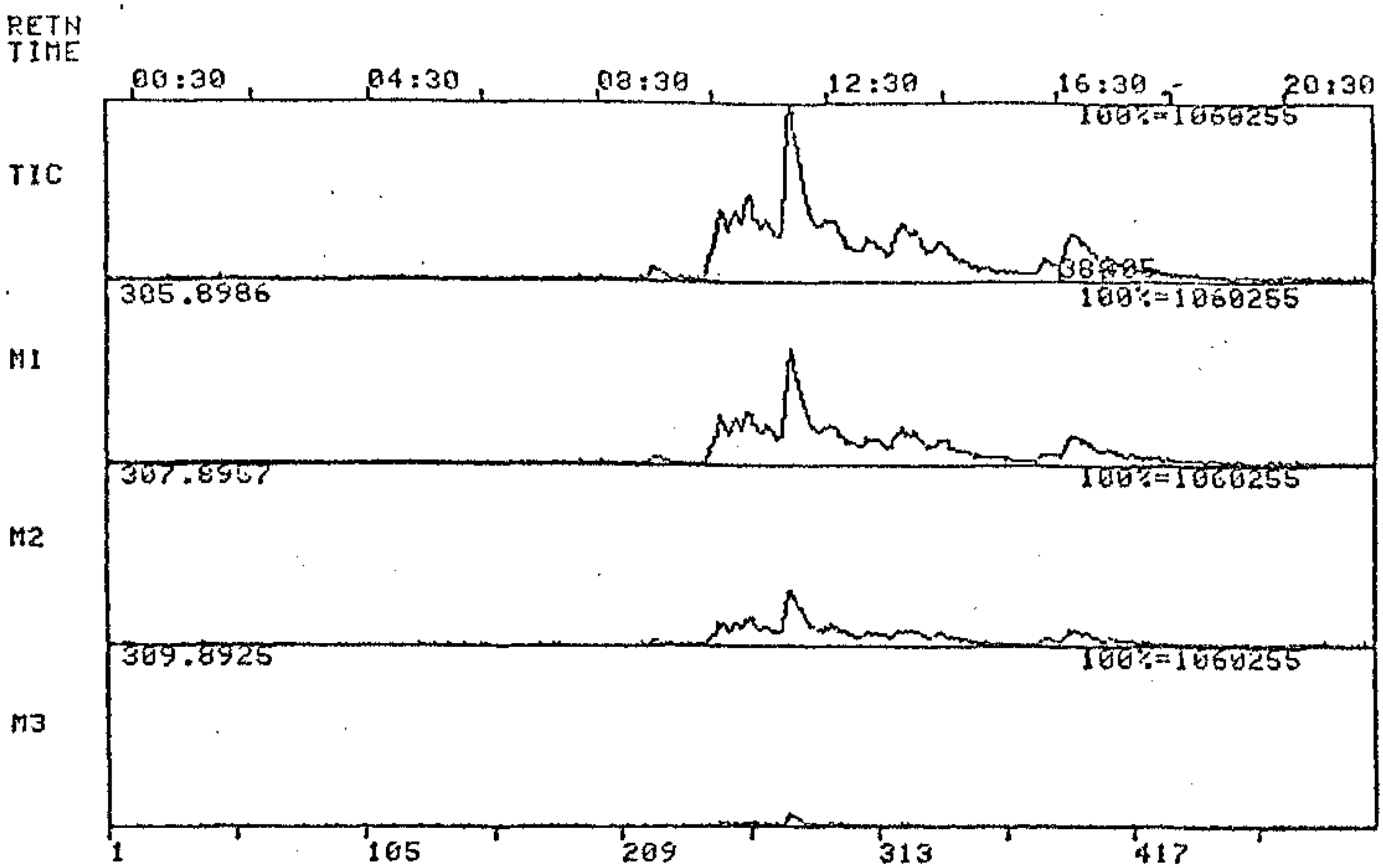
MASS	321.8935
SCAN WIDTH	300 PPM
SCAN TIME	0.3 SECS
SCAN NUMBERS	149- 438
STANDARD	0.0000
FACTOR	0

KAMINSKY'S BING. SOOT 2.66 OF 9.0UL

MASS CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SKIMMED	%TOTAL AREA	RELATIVE TO STANDARD
321.8789	TOTAL	32772100.	YES	NO	95.17	0.00
321.8733	1	27343700.	YES	NO	79.41	0.00
321.9021	2	5367326.	YES	NO	15.59	0.00
321.9331	3	61077.	YES	NO	0.18	0.00

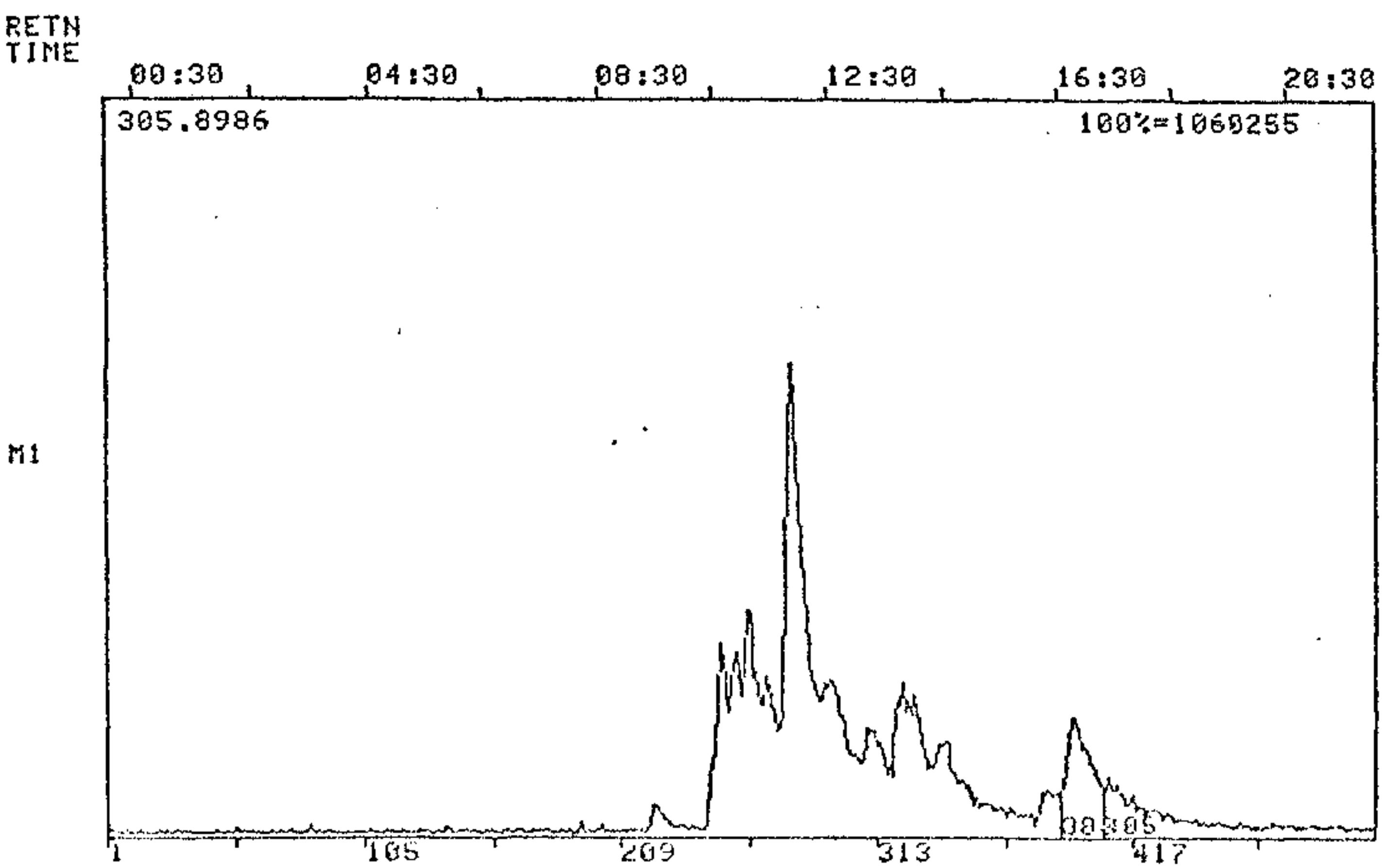
FIG. 4, SECOND INJECTION

720s DS55 HIGH RESOLUTION MPM
RUNNAME TDHM4 DATE 7/16/81 TIME 12:28



*DL *

DS55 HIGH RESOLUTION MPM
RUNNAME TDHM4 DATE 7/16/81 TIME 12:28



*DL *

Table I. Results for Sample 811711965*

Total Furan Concentration - 597 ppm (Detection Limit = 2.3 ppm)

2,3,7,8-Furan Concentration - 48 ppm (D.L. = .45 ppm)

Total Dioxin - 1.8 ppm (D.L. = .04 ppm) Ratio 320/322 = 0.87

2,3,7,8-Dioxin - 1.2 ppm (D.L. =.008 ppm) Ratio 320/322 = 0.86

Recovery - 4%

Amt. of ^{13}C-2,3,7,8-TCDD spike - 6000 pg

Weight of Sample - 46 mg

Conc. of Spike - .13 ppm

Relative Retention Times:

2,3,7,8-tetrachlorofuran -	Standard: 1.264	Sample: 1.269
2,3,7,8-tetrachlorodioxin -		Sample: 1.00

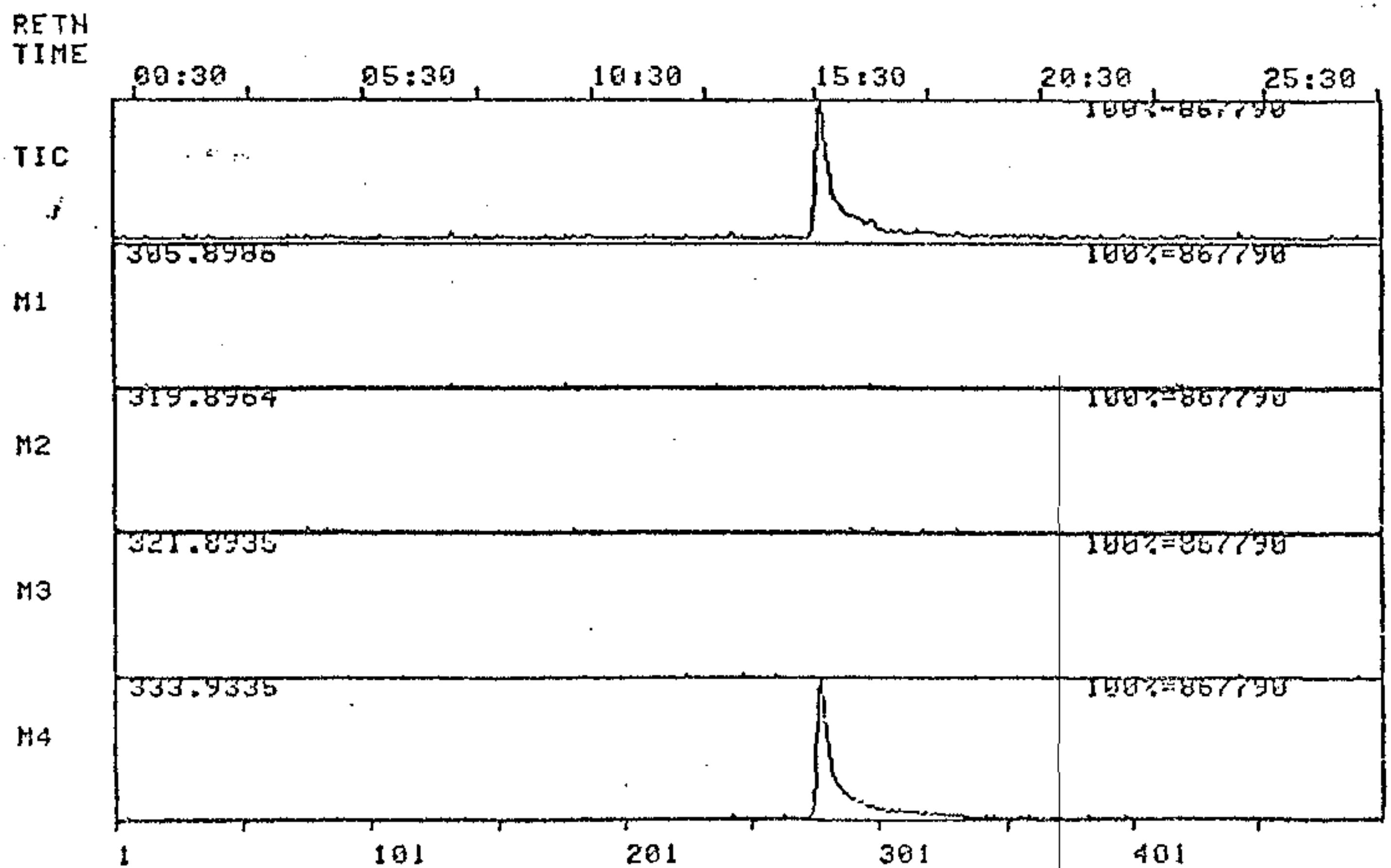
* No TCDF or TCDD was found in the control carbon sample

APPENDIX: Supplementary Data

1. Carbon blank
2. External standards
3. Mass profiles 1st injection-Runname FDHM8
4. Second injection data-Runname TDHM4
5. Calculations

Blank
Adsorptive Carbon

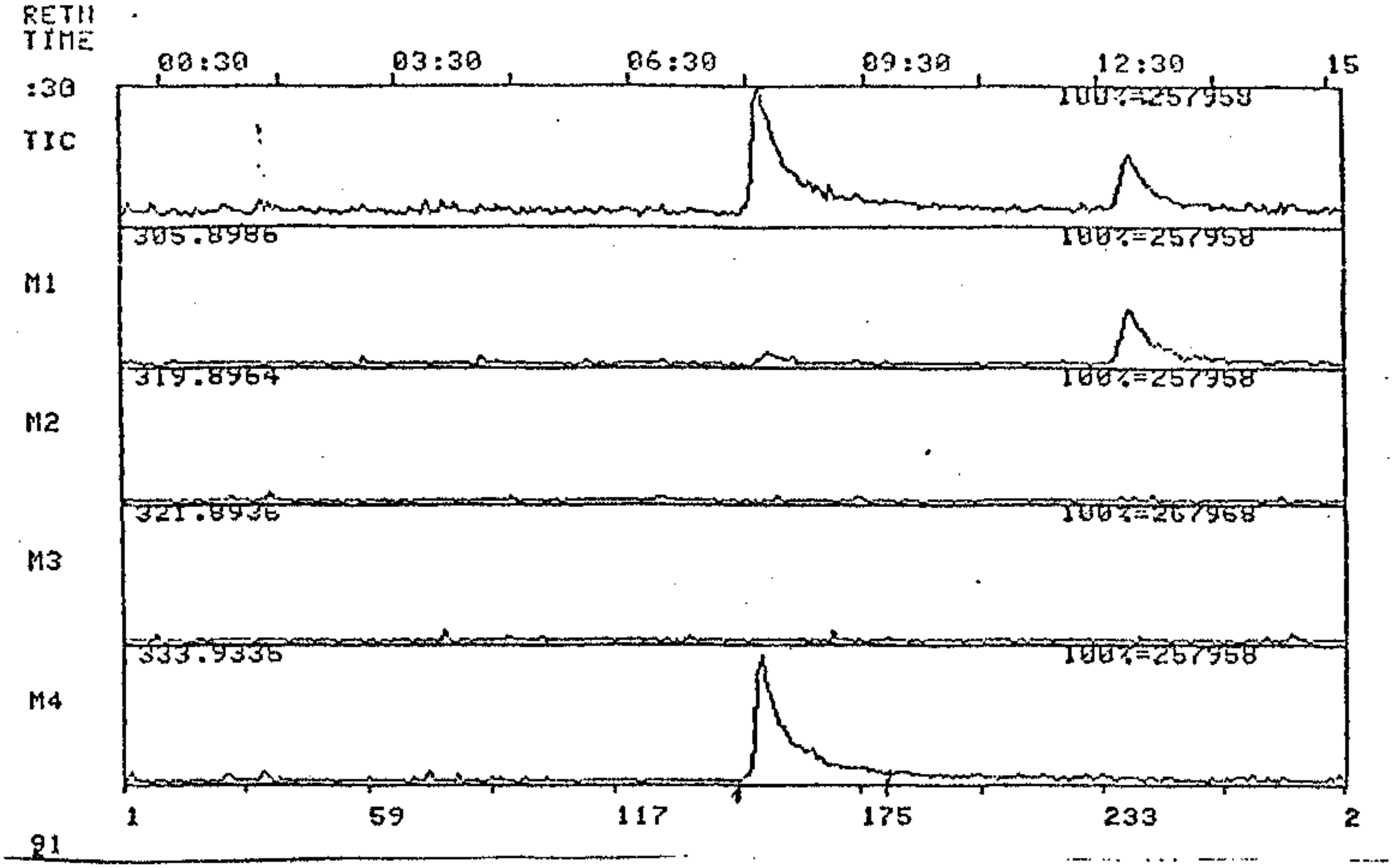
DS55 HIGH RESOLUTION MPM
RUNNAME FDHM7 DATE 7/10/81 TIME 20:26



*

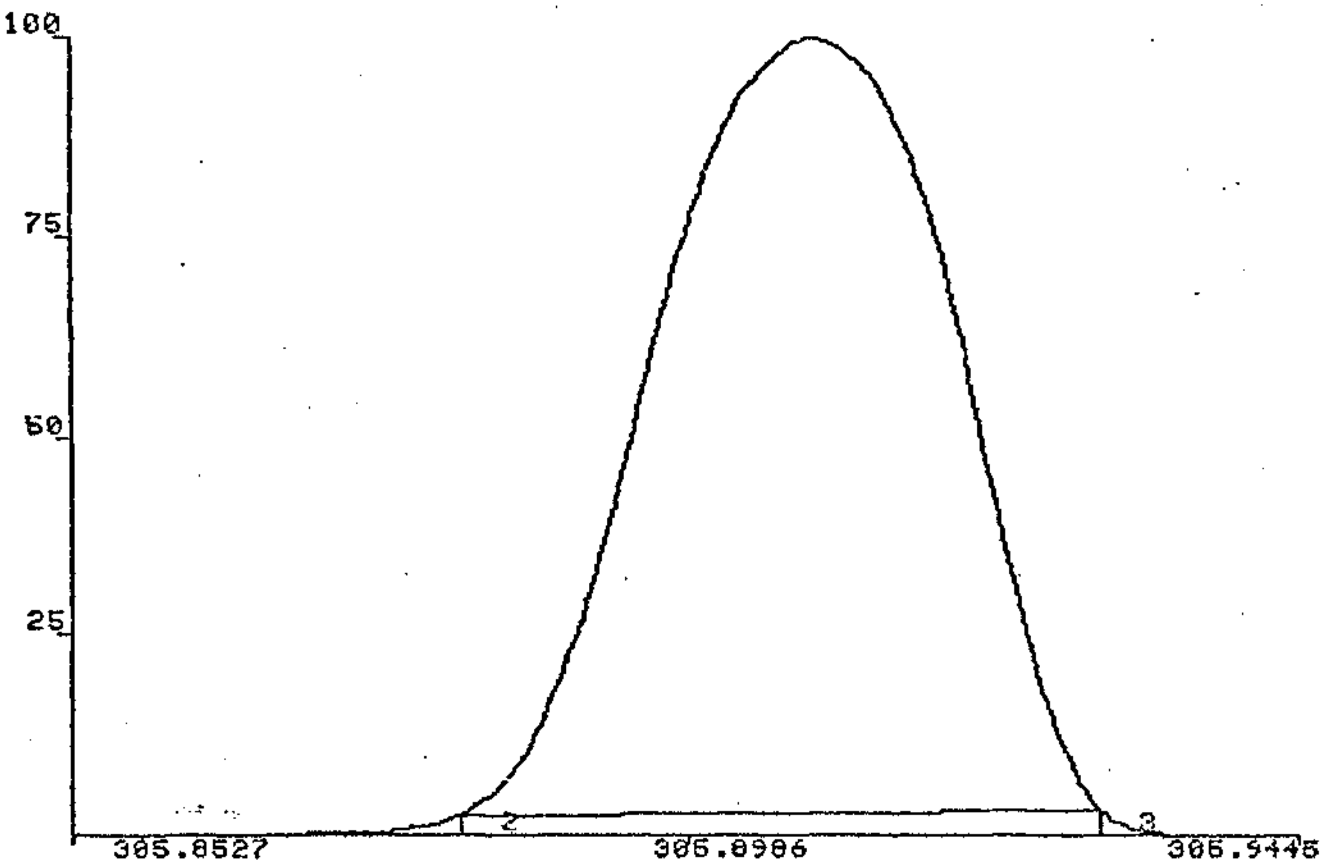
DSS5 HIGH RESOLUTION MPM
RUNNAME FDHM6 DATE 7/10/81 TIME 19:43

^{13}C 2378 TCDD and 2378 TCDF



TOTAL TCDF mass Profile
exceeds linear range in 1st injection

RUNNAME FDHM8 DATE 7/10/81 TIME 21:11
MASS 305.8986 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 149-438 100% INTENSITY 7971778



*SK AREA ID:2 *

DS55 HIGH RESOLUTION MPM

PEAK SUMMATION REPORT

RUNNAME FDHM8 DATE 7/10/81 TIME 21:11

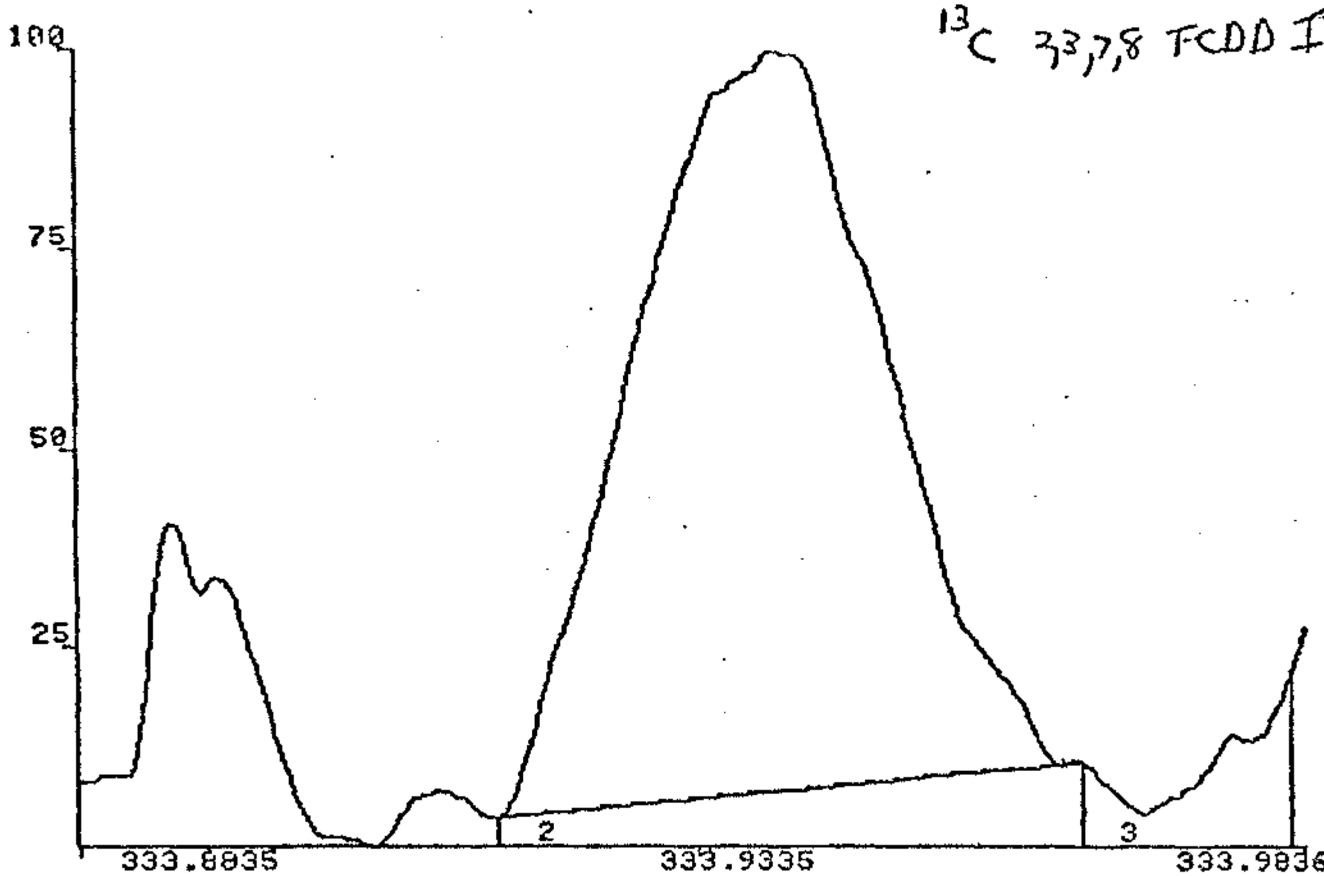
MASS	305.8987
SCAN WIDTH	300 PPM
SCAN TIME	0.3 SECS
SCAN NUMBERS	149- 438
STANDARD	0.0000
FACTOR	0

KAMINSKY'S BING. SOOT 2.55 OF 9.0UL

MASS CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SKIMMED	%TOTAL AREA	RELATIVE TO STANDARD
305.9072	TOTAL	585240300.	YES	NO	98.97	0.00
305.8716	1	1871699.	YES	NO	0.32	0.00
305.9072	2	551408100.	YES	YES	93.25	0.00
305.9333	3	1415924.	YES	NO	0.24	0.00

RUNNAME FDHM8 DATE 7/10/81 TIME 21:11
MASS 333.9336 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 279-307 100% INTENSITY 4589

^{13}C 2,3,7,8 TCDD Internal Std



DS55 HIGH RESOLUTION MPM

PEAK SUMMATION REPORT

RUNNAME FDHM8 DATE 7/10/81 TIME 21:11

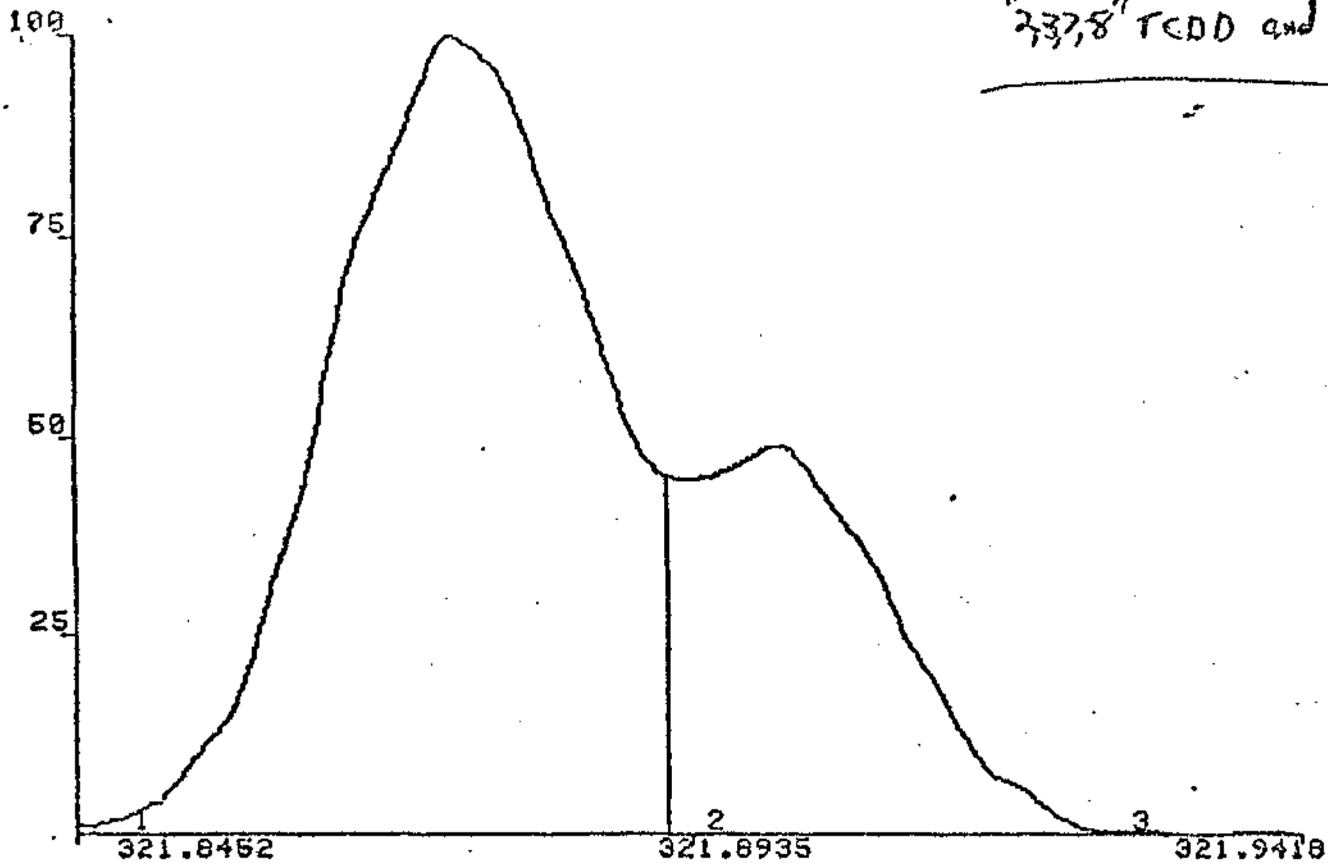
MASS	333.9336
SCAN WIDTH	300 PPM
SCAN TIME	0.3 SECS
SCAN NUMBERS	279- 307
STANDARD	0.0000
FACTOR	0

KAMINSKY'S BING. SOOT 2.55 OF 9.0UL

MASS CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SKIMMED	%TOTAL AREA	RELATIVE TO STANDARD
333.9351	TOTAL	319020.	YES	NO	66.54	0.00
333.8982	1	44037.	YES	NO	9.19	0.00
333.9402	2	223480.	YES	YES	46.61	0.00
333.9746	3	17729.	YES	NO	3.70	0.00

MASS 321.8935 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 279-307 100% INTENSITY 83676

"2,3,7,8" TCDD and Interferent



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DS55 HIGH RESOLUTION MPM

PEAK SUMMATION REPORT

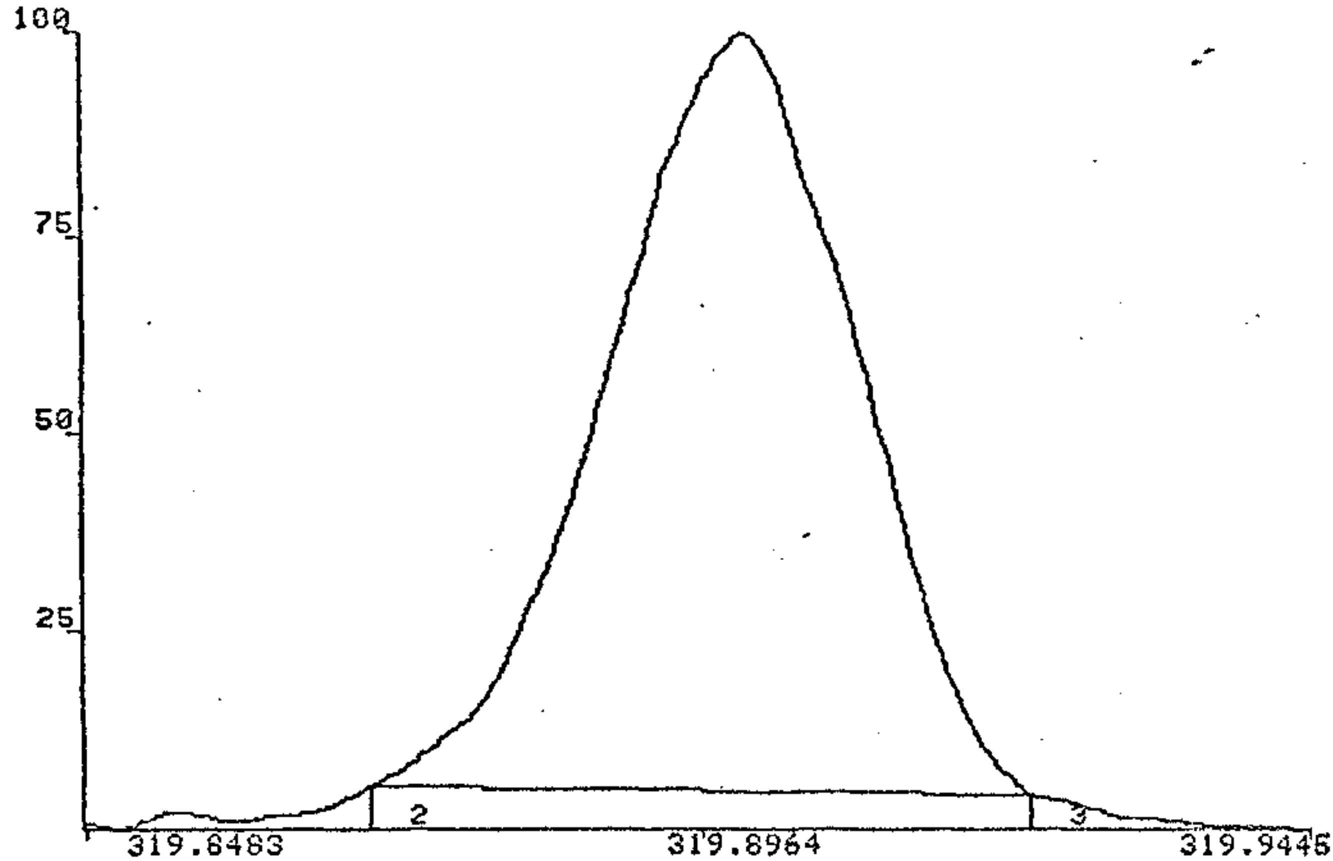
RUNNAME FDHM8 DATE 7/10/81 TIME 21:11

MASS 321.8935
SCAN WIDTH 300 PPM
SCAN TIME 0.3 SECS
SCAN NUMBERS 279- 307
STANDARD 0.0000
FACTOR 0

KAMINSKY'S BING. SOOT 2.55 OF 9.0UL

MASS CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SKIMMED	%TOTAL AREA	RELATIVE TO STANDARD
321.8828	TOTAL	7275879.	YES	NO	97.33	0.00
321.8748	1	5220057.	YES	NO	69.83	0.00
321.9023	2	2050417.	YES	NO	27.43	0.00
321.9319	3	5405.	YES	NO	0.07	0.00

RUNNAME FDHM8 DATE 7/10/81 TIME 21:11
MASS 319.8964 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 149-438 100% INTENSITY 89622



*SK AREA ID:2 *

DS55 HIGH RESOLUTION MPM

PEAK SUMMATION REPORT

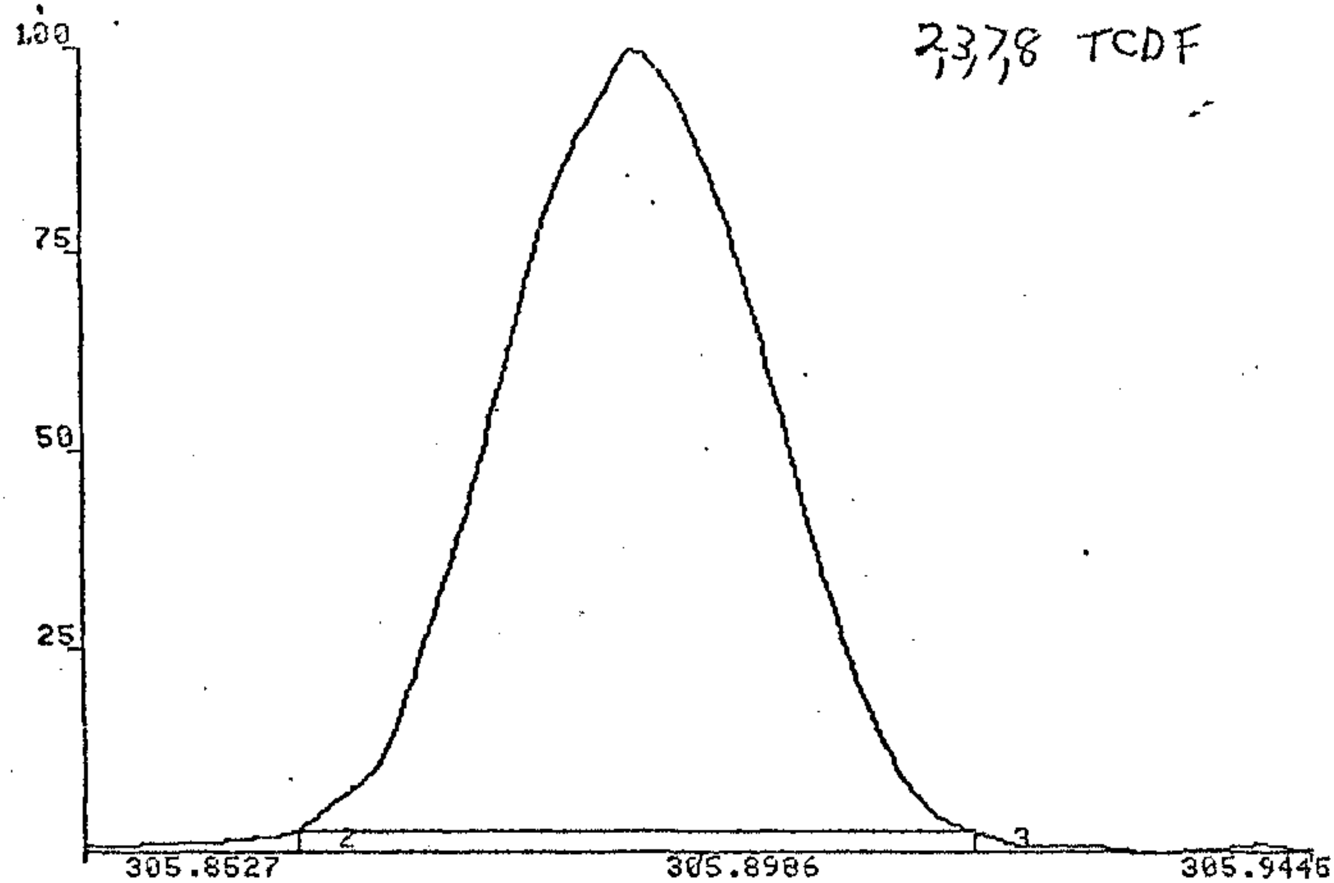
RUNNAME FDHM8 DATE 7/10/81 TIME 21:11

MASS 319.8965
SCAN WIDTH 300 PPM
SCAN TIME 0.3 SECS
SCAN NUMBERS 149- 438
STANDARD 0.0000
FACTOR 0

KAMINSKY'S BING. SOOT 2.65 OF 9.0UL

MASS CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SKIMMED	%TOTAL AREA	RELATIVE TO STANDARD
319.8972	TOTAL	6364537.	YES	NO	72.82	0.00
319.8596	1	79597.	YES	NO	1.08	0.00
319.8980	2	4685357.	YES	YES	63.60	0.00
319.9319	3	66501.	YES	NO	0.90	0.00

.MASS 305.8986 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 388-406 100% INTENSITY 31138



DS55 HIGH RESOLUTION MPM

PEAK SUMMATION REPORT

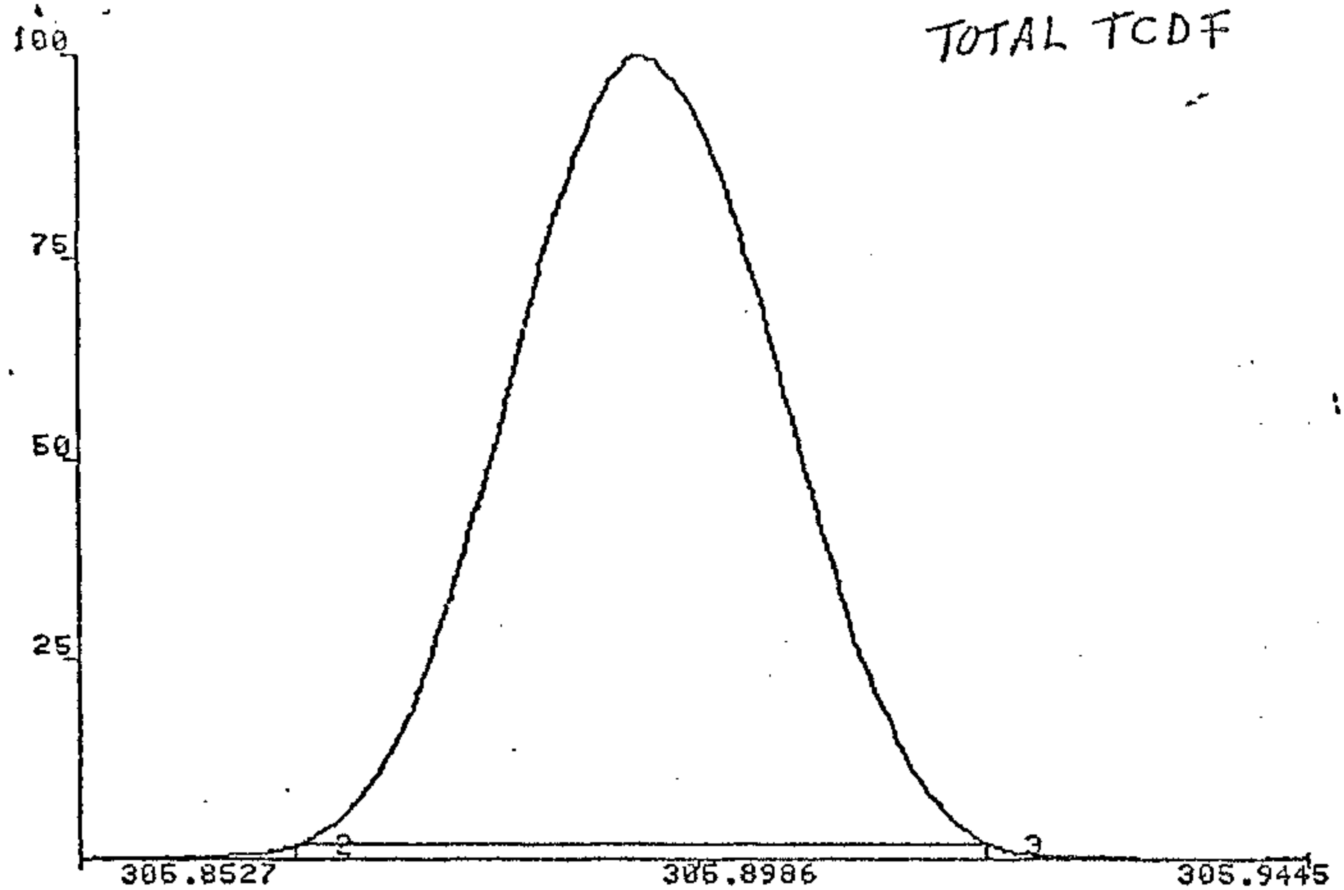
RUNNAME TDHM4 DATE 7/16/81 TIME 12:28

MASS	305.8987
SCAN WIDTH	300 PPM
SCAN TIME	0.3 SECS
SCAN NUMBERS	388- 406
STANDARD	0.0000
FACTOR	0

1.0UL DILUTION OF KAMINSKY'S SOOT

MASS CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SKIMMED	%TOTAL AREA	RELATIVE TO STANDARD
305.8938	TOTAL	2050185.	YES	NO	95.36	0.00
305.8613	1	14863.	YES	NO	0.69	0.00
305.8938	2	1917649.	YES	YES	89.20	0.00
305.9302	3	11737.	YES	NO	0.55	0.00

MASS 305.8986 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 214-478 100% INTENSITY 379262



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DS55 HIGH RESOLUTION MPM

PEAK SUMMATION REPORT

RUNNAME TDHM4 DATE 7/16/81 TIME 12:28

MASS	305.8987
SCAN WIDTH	300 PPM
SCAN TIME	0.3 SECS
SCAN NUMBERS	214- 478
STANDARD	0.0000
FACTOR	0

1.0UL DILUTION OF KAMINSKY'S SOOT

MASS CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SKIMMED	%TOTAL AREA	RELATIVE TO STANDARD
305.8948	TOTAL	25127260.	YES	NO	92.56	0.00
305.8611	1	64216.	YES	NO	0.24	0.00
305.8948	2	24077630.	YES	YES	88.70	0.00
305.9309	3	73307.	YES	NO	0.27	0.00

Calculation of Response Factor of Furan to Dioxin

Amt of TCDF injected = 1.2 μL of 150 pg/μL

Int of TCDF con = 677482

Sensitivity = 677482/180 = 3764 counts/pg

Amt of ^{13}C TCDD injected = 1.0 μL of 600 pg/μL

Int. of TCDD ion = 1949179

Sensitivity = 1949179/600 = 3249 counts/pg.

Response Factor of Furan is 3764/3249 = 1.16

For equal amounts of material, the response of TCDF is 1.16 times ^{13}C TCDD.

Calculation of Furan in peak number 1 (this peak was used as internal furan standard for the second injection)

$Amt_{Furan} = I_{305} \times (Amt\ ^{13}C/I_{334}) \times R.F.$

I_{305} = intensity of m/z 305 ion for peak no. 1 (the small peak delimited which has not saturated the amplifier)

= 8596844

$Amt_{^{13}C}$ = Amt of ^{12}C-TCDD spike (internal std.) added to sample

= 6 ng

I_{334} = intensity of m/z 334 ion (int. std.) = 223480

R.F. = response of 2,3,7,8-TCDF compared to ^{13}C 2,3,7,8-TCDD = 1.16

Amt_{Furan} = 8.597 x (6 ng/.223480) x 1.16

= 268 ng

Calculation of 2,3,7,8-TCDF

$Amt_{2378} = I_{2378} \times (Amt_{P1}/I_{P1})$

Amt_{2378} = amt of 2,3,7,8-TCDF

I_{2378} = intensity of 2,3,7,8-TCDF ions = 1917649

Amt_{P1} = amt of furan in peak 1 = 268 ng

I_{P1} = intensity of furan in peak 1 = 235188

$= 1.918 \times (268/235)$

= 2187 ng

$Conc_{2378}$ = 2187 ng/46 mg

= 48 ppm

Calculation of Total TCDF

$Amt_{TOT} = I_{TOT} \times (Amt/I)$

$= 24.-78 \times (268/.235)$

= 27459 ng

$Conc_{TOT}$ = (27459 ng/46 mg)

= 597 ppm

Calculation of 2,3,7,8-TCDD (scans 279-307)

$$Amt_{2378} = I_{2378} \times (Amt\ ^{13}C/I_{^{13}C})$$

$$= 2.050417 \times (6/.223480)$$

$$= 55.04 \text{ ng}$$

$$Conc_{2378} = 55.0 \text{ ng}/46 \text{ mg}$$

$$= 1.2 \text{ ppm}$$

Calcualtion of Total TCDD (scans 149-438)

$$Amt_{TOT} = I_{TOT} \times (Amt\ ^{13}C/I_{^{13}C})$$

$$= 5.367 \times (6/.395528)$$

$$= 80.4 \text{ ng}$$

$$Conc_{2378} = 80.4 \text{ ng}/46 \text{ mg}$$

$$= 1.8 \text{ ppm}$$