Uploaded to VFC Website
~ October 2012 ~

This Document has been provided to you courtesy of Veterans-For-Change!

Feel free to pass to any veteran who might be able to use this information!

For thousands more files like this and hundreds of links to useful information, and hundreds of "Frequently Asked Questions, please go to:

Veterans-For-Change

Veterans-For-Change is a 501(c)(3) Non-Profit Corporation
Tax ID #27-3820181

If Veteran's don't help Veteran's, who will?

We appreciate all donations to continue to provide information and services to Veterans and their families.

https://www.paypal.com/cgi-bin/webscr?cmd=_s-xclick&hosted_button_id=WGT2M5UTB9A78

Note: VFC is not liable for source information in this document, it is merely provided as a courtesy to our members.

Item ID Number	02224
Author	Smith, R.M.
Corporate Author	
Report/Article Title	Typescript: Determination of TCDFs and TCDDs in Air Samples from the Sixteenth Floor of the Binghamton State Office Building, March 16, 1983
Journal/Book Title	
Year	
Month/Day	
Color	☐
Number of Images	20
Descripton Notes	

Determination of TCDFs and TCDDs in Air Samples from the Sixteenth Floor of the Binghamton State Office Building

R.M. Smith, D. Hilker, P. O'Keefe, K. Aldous

Toxicology Institute

New York State Department of Health

March 16, 1983

INTRODUCTION

Prior to building cleanup, analysis of soot samples from ceiling panels on floors 1-17 of the chemically contaminated Binghamton State Office Building (1,2) showed that most samples contained PCBs (28-23000 ppm total) and a complex mixture of tetra- to octa- PCDF isomers (average concentration in ppm was: Cl_4=33, Cl_5=40, Cl_6=18, Cl_7=6, Cl_8 < 1-3). The PCDDs were not detected by the less sensitive full scan HRMS method used. 2,3,7, 8 TCDD was then determined in several samples by HPLC/GC SIM techniques and was present at concentrations of 0.26-2.2 ppm. This data corellated well with the results of a biologically based cell keratinization assay (CKA) which screens for "2,3,7,8 TCDD-like activity".

It was then necessary to analyze several air samples from a cleaned-up section of the building (16th floor was available first) and investigate the sensitive analytical methods necessary to determine PCDFs and PCDDs at low (e.g. pg/m^3) concentrations in air. The results would also show whether building clean-up efforts were proceeding satisfactorily for re-entry.

Approximately 50 m^3 of air were sampled and analyzed for total (gaseous and particulate) PCDF and PCDD using capillary GC/SIM high resolution mass spectrometry. Tetra-compounds were investigated first. Isomer specificity was provided solely by a SP-2330 capillary column which resolves many but not all of the TCDD and TCDF isomers. All 38 possible TCDF isomers have only recently been synthesized and identified (3) but are not yet unavailable to our laboratory. All 22 TCDD isomers however are available in our laboratory.

EXPERIMENTAL

Laboratory Volatilization and Trapping Studies

Experiments using ^{14}C radiolabeled 2,3,7,8-TCDD demonstrated that it can be volatilized (from 33% at 25° to 97.4% at 280°C), transported in an air stream and trapped by 8 g of 30-70 mesh silica gel. The apparatus is shown in Figure 1. At the high air flow rates required for sampling (e.g. 20 liter/min = 57.6 M^3/48 hrs) the trapping efficiency was found to be dependent on temperature and volume of air. Overall TCDD trapping and elution efficiency ranged from 70 to 100% depending on the experimental conditions employed. A three day laboratory study of TCDD breakthrough showed 78% was trapped and recovered from a 74.3 M^3 sample of air. Qualitative analysis by HPLC and GC identified the trapped material as 2,3,7,8 TCDD.

For field use, the glass "cartridge" containing silica gel was housed in a rugged teflon housing, sealed with fluoroelastomer Viton "o" rings and preceded by a glass microfiber air particulate filter (EPM 2000, 0.3μ) as shown in Figure 2. A similar "cartridge" design for collection of large volumes of semivolatiles has been described in the literature (4). Tests of the trapping efficiency of the field sampler by liquid scintillation counting showed a 70% recovery for 2,3,7,8-TCDD volatilized at 280°. This was identical to that found in the lab experiments.

Samples for Analysis

To investigate the variation of concentration with location, four sampling sites on the (cleaned, air uncirculated) 16th floor were chosen

for analysis. The first group of 4 samples consisted of 3 samples (duplicate for PCDF, 1 for CKA) from site A, the northeast corner of the floor, and 1 sample (for PCDF) from site B, the southeast corner. PCBs were simultaneously sampled for independent analysis. The second group of samples taken 1 week later consisted of 3 samples from site C, the NW corner, and 1 from site D, the SW corner. A solvent blank, a background air sample taken at Albany,, NY, and 2 TCDD and TCDF fortified air samples were also analyzed as part of normal quality control procedures.

Sampling Procedures

Prior to sampling, internal standards (10 µL mixed 190 pg/µL ^{37}Cl 2,3,7,8 TCDF, 17.1 pg/µL ^{13}C 2,3,7,8 TCDD and 714 pg/µL OCDD) in cyclohexane were deposited directly on the 140° activated silica gel trapping adsorbent contained in the pyrex thimble. No internal standard was added to the sampler for CKA. The thimble was plugged with glass wool, placed inside its teflon housing, and the entire apparatus was assembled as shown in Figure 2. To check for breakthrough during actual sampling, an additional silica gel adsorbent stage was added in series. It was spiked and analyzed separately.

The open ends of each sampling train were then secured with aluminum foil and the samplers were transported to the Binghamton sampling site.

The sampling was conducted by Versar. Each sampler was clamped in a vertical position and connected to a 1.5 CFM Gast vacuum pump (using rubber tubing) via a flowmeter which constantly monitored the air flow. The sampling rate was adjusted to 23 L/min. After approximately 50 M^3

had been sampled, the pumps were turned off, the samplers were wrapped in foil, and returned to the laboratory for clean-up and GC/HRMS analysis.

Extraction

The Pyrex thimble containing silica gel, internal standards, and adsorbed compounds was removed from each sampler and its exterior was washed with benzene to remove any handling residue. The corresponding glass fiber filter containing collected particles was then folded and placed inside the Pyrex thimble, thus combining the sections. The thimble was then placed in a Pyrex soxhlet apparatus charged with 75 ml distilled-in-glass benzene and continuously extracted for 16 hrs. Two of the background samples (NSA 1S, NSA 2S) were spiked with unlabeled TCDF and TCDD prior to extraction.

Sample Clean-up

The extracted sample was cleaned up prior to GC/MS to remove PCBs and non-planar aromatics and isolate the Cl_4 to Cl_8 PCDFs and PCDDs. Each sample was directly injected onto a pre-programmed automatic clean-up system that provides sequential multi-solvent chromatography on basic alumma, PX-21 adsorptive carbon, and neutral alumma (Figure 3). Only a single concentration step was needed i.e. to concentrate the sample to 10 µl prior to GC/MS injection.

Capillary GC/High Resolution Mass Spectrometry

A portion (typically < 2 µl) of the purified extract was injected onto a 60 meter capillary gas chromatography column (0.3 mm i.d.) coated

with 15% SP2330. The column oven was temperature programmed with a starting temperature of 80°C for 1 minute and then ramped at 12°C/min to 205°C. The final temperature, 205°C was held isothermally until after the analyte eluted. The column was interfaced to the source of the Kratos MS-50 mass spectrometer using an open split interface and deactivated fused silica transfer line. The interface was maintained at approx. 280°C.

Data were acquired from the Kratos MS-50 high resolution mass spectrometer operated in electron impact mode (70eV) at approx. 10,000RP (source temerature was 250°C) and stored by the Kratos DS-55 data system using a program called HRMPM (high resolution multiple peak monitoring). During the chromatographic run the m/e 303.9016, 305.8987, and 311.8898 masses corresponding to the native tetrachlorodibenzofuran (TCDF) molecular ion peaks and the tetra ^{37}Cl-labelled internal standard molecular ion peak (m/e 311.8898) were monitored. For the analysis of TCDD, samples were placed into the source of the mass spectrometer by direct introduction probe in order to obtain greater sensitivity. The probe tip was heated ballistically to approx. 200°C and held isothermally until the sample evaporated. In this case m/e 321.8936 and 333.9338, (native TCDD ion and ^{13}C labelled TCDD internal standard ion) were monitored.

The area under the mass peak profile for each of the three ions monitored was summed over the time period in which the TCDF eluted. The area of the internal standard peak was ratioed to the area of the native peak to compute the concentration of the native material. The ratio of the m/e 303.9016 to 305.8987 intensities (M^+, $M+2^+$) along with the coincidence of retention time on the gas chromatograph provided

additional data used in the verification of native TCDF. Data acquired for the analysis for TCDD were processed in the same manner, summing the mass peaks profiles over the time period in which the sample evaporated from the probe capillary.

Calculations

For increased accuracy, the concentration and detection limits of TCDDs and TCDFs in air were calculated using an isotope dilution internal standard method as shown below. The percent recovery of internal standard (versus external standard) does not enter into these calculations and is provided in table 1 for information purposes only.

$$C_1 = XC_2 A_1/A_2 \qquad \text{(eq. 1)}$$

Where C_1 = the calculated concentration of native TCDF (or TCDD) in pg/M^3

X = a theoretical mass spectral response factor that corrects for differences in isotope abundances (1 for ^{13}C TCDD, 2.5 for ^{37}Cl TCDF).

C_2 = the known concentration of added, isotopically labeled TCDF (or TCDD) in pg/M^3

A_1 = the measured area under the mass profile due to native TCDF at m/e 305.8987 (or TCDD at 322) in arbitrary counts.

A_2 = the measured area under the mass profile due to isotopically labeled TCDF at m/e 311.8898 (or TCDD at 334) in arbitrary counts

We have used the above calculation and made the assumption that the labeled standard, added to the silica gel adsorbent prior to sampling, is recovered through trapping and clean up identically to the TCDF or TCDD in air. Strictly however, one would expect to observe a slightly lower recovery of internal standard if the trapping efficiency is < 100% (experimentally 78%/74M[3]) because internal standard is applied at the beggining of the sampling period while trapped compounds are continuously accumulating over a 48 hr period. NSA 2 and NSA 3 samples fortified with native TCDF and TCDD at the end of the trapping period were corrected for this effect.

Detection limits were similarly calculated using equation 1, substituting for A_1 the average MS noise (30 millimass units each side of m/e 305.8987 for TCDFs) in arbitrary counts and incorporating a standard detection limit factor of 2.5.

The recovery of ^{37}Cl labeled TCDF or ^{13}C labeled TCDD was calculated as follows:

$$R = 100 \frac{A_2 r}{f t} \quad \text{(eq. 2)}$$

where R = percent recovery

A_2 = the measured area at m/e 311.8898 due to ^{37}Cl TCDF internal standard added prior to sampling.

r = the measured mass spectral response at m/e 311.8898 for an external ^{37}Cl TCDF standard in pg/area

f = the fraction sample injected

t = the total amount of ^{37}Cl TCDF internal standard added prior to sampling in pg.

RESULTS AND CONCLUSIONS

All 5 air samples taken from the 16th floor of the BSOB were found to contain small amounts of a complex mixture of TCDFs as shown by the typical high resolution ion chromatograms and mass profiles for sample A2 in figures 4-7. The total concentration of observed TCDF isomers (obtained by summing scans containing the proper response at both 303.9013 and 305.8986 TCDF masses) ranged from 52 to 102 pg/m^3 of air. (See Table 1 which is a summary of results, giving TCDF and TCDD concentrations, detection limits, ion ratios, GC retention times, recoveries, and results of blanks and fortified samples.) Near the detection limit of the instrumentation and using a highly selective SP2330 capillary GC column as the only means of TCDF isomer separation, (2 other TCDF isomers have been shown to have nearly the same GC retention time on this column (3)), the "2378" TCDF isomer was found to be a major TCDF component. 12-20% of "2378" TCDF was found in all samples. These "2378" TCDF concentrations ranged from 7.0 to 16 pg/m^3 of air. For quality control, 2 air samples taken from the Albany area and fortified to 6.6 and 5.5 pg/m^3 2378 TCDF were found to have concentrations of 8.1 and 5.4 pg/m^3 (+23% and -2% errors). Although particulate and/or gaseous compounds were trapped separately, they were combined prior to extraction and analysis. Therefore, all results represent a total of particulate + gaseous compounds.

Penta-CDF was detected at a concentration of 22 pg/m^3 (total) only in sample A2 as shown by the mass profiles in figure 8. Other samples had no detectable penta-CDF at a detection limit of ca 5 pg/m^3. It is important to note that quantitation for these heavier compounds was severely limited due to the lack of a labeled penta-CDF internal standard

and native standards from which to obtain experimental response factors and provide fortified quality control samples.

The TCDD analysis was accomplished using the direct insertion probe HRMS rather than capillary GC/HRMS because of the greater sensitivity that could be obtained. No TCDD was detected in any air sample at detection limits of < 1.3 pg/m^3. The MS signal due to internal ^{13}C 2378 TCDD standard in the samples (2.8 pg/m^3 spiking level) was clearly evident. Because of apparent chemical noise at these low levels, a slight response of signal at m/e 321.8935 was noted. However it did not meet the normal analytical criteria for TCDD.

An Albany air sample fortified to 6.4 pg/m^3 TCDD was similarly analyzed and found to have a concentration of 5.4 pg/m^3 (-16% error).

Future efforts will be directed towards improving our detecton limits for TCDD.

Table 1. HRMS Results for BSOB 16th Floor Air Samples

SAMPLE	"2378" TCDF[1]					Total TCDF			Total Penta-CDF
	Concentration of 2,3,7,8-TCDF (pg/M^3)	detection limit	304/306	relative retention time	^{37}Cl TCDF Recovery (%)	concentration (pg/M^3)	304/306	2378/Total (%)	concentration (pg/M^3)
A1 (NE corner)	16	6.1	.76	1.0	86	93	.83	17	-6
A2 (NE corner)	12	5.7	.90	1.0	50	102	.80	12	22[2]
B (SE corner)	13	4.2	.75	1.0	55	78	.68	17	ND(<5)
C2 (NW corner)	9.2	7.2	.76	1.0	69	55	.75	20	ND(<5)
D (SW corner)	7.0	3.5	.88	1.0	50	52	.74	16	ND(<5)
Solv. Blank[3]	ND	7.3	NA	NA	57				
NSA 1[4] (background)	ND	5.1	NA	NA	41				
NSA 2-S (TCDF=6.6, TCDD-7.7)	8.1 (+23%)	3.1	.79	1.0	35				
NSA 3-S (TCDF=5.5, TCDD=6.4)	5.4 (- 2%)	2.8	.79	1.0	61				
A2 (2nd)	ND	8.8	NA	NA					

[1] Analyzed by capillary GC/HRMS

[2] At least 2 isomers were detected. Detection limits were approximately 5 pg/M^3. Ratio of 342/340 was .53 and .76.

[3] Calculated for a theoretical 60 M^3 volume of air.

[4] NSA 1-3: New Scotland Avenue Samples - considered quality control.

[5] Analyzed by direct probe HRMS to obtain extra sensitivity.

[6] Entire sample used for PCDFs.

REFERENCES

1. Determination of Polychlorinated Dibenzofurans in Soot Samples from a Contaminated Office Building, R.M. Smith, D.R. Hilker, P.W. O'Keefe, S. Kumar, and K.M. Aldous. NYS Health Department, Toxicology Institute Report, March, 1982.

2. Comparisons of Chemical and Biological Data on Soot Samples from the Binghamton State Office Building, G. Eadon, K. Aldous, G. Frenkel, J. Gierthy, D. Hilker, L. Kaminsky, P. O'Keefe, J. Silkworth and R. Smith. NYS Health Department, Toxicology Institute Report, March, 1982.

3. Synthesis of the 38 Tetrachlorodibenzofuran Isomers and Identification by Capillary Column Gas Chromatography/Mass Spectrometry, T. Mazer, F. Hileman, R. Noble and J. Brooks. Anal. Chem. 55 (1983) 104-110.

4. Modification and Evaluation of a High-Volume Air Sampler for Pesticides and Semi Volatile Industrial Organic Chemicals, R. Lewis and M. Jackson, Anal. Chem. 54 (1982) 592-594.

Table 1 Continued

	TCDD[5]		
	TCDD	detection limit	^{13}C TCDD recovery
A1 (NE corner)	--[6]	--	--
A2 (NE corner)	<1.2	1.1	52
B (SE corner)	<1.3	0.55	64
C2 (NW corner)	<1.3	0.62	66
D (SW corner)	ND	1.0	32
Solv. Blank	ND	0.53	57
NSA 1 (background)	ND	0.72	64
NSA 2-S (TCDF=6.6, TCDD=7.7)	--[6]	--	--
NSA 3-S (TCDF=5.5, TCDD=6.4)	5.4 (-16%)	0.27	58

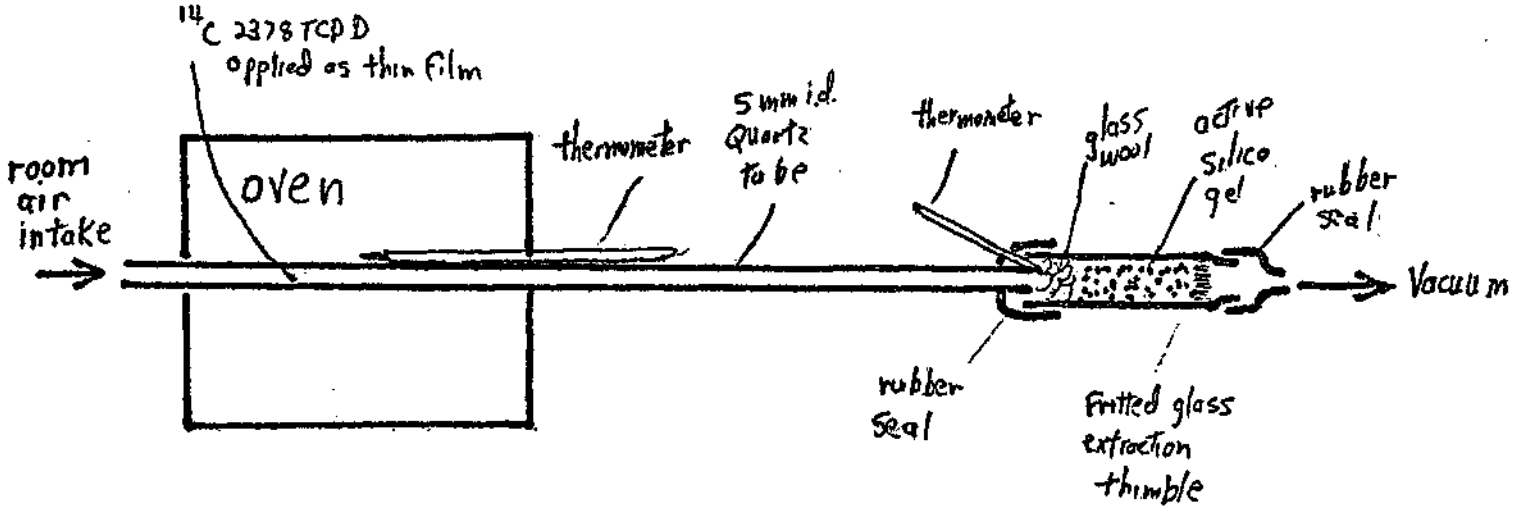


Figure 1. TCDD Volatilization and Trapping Apparatus

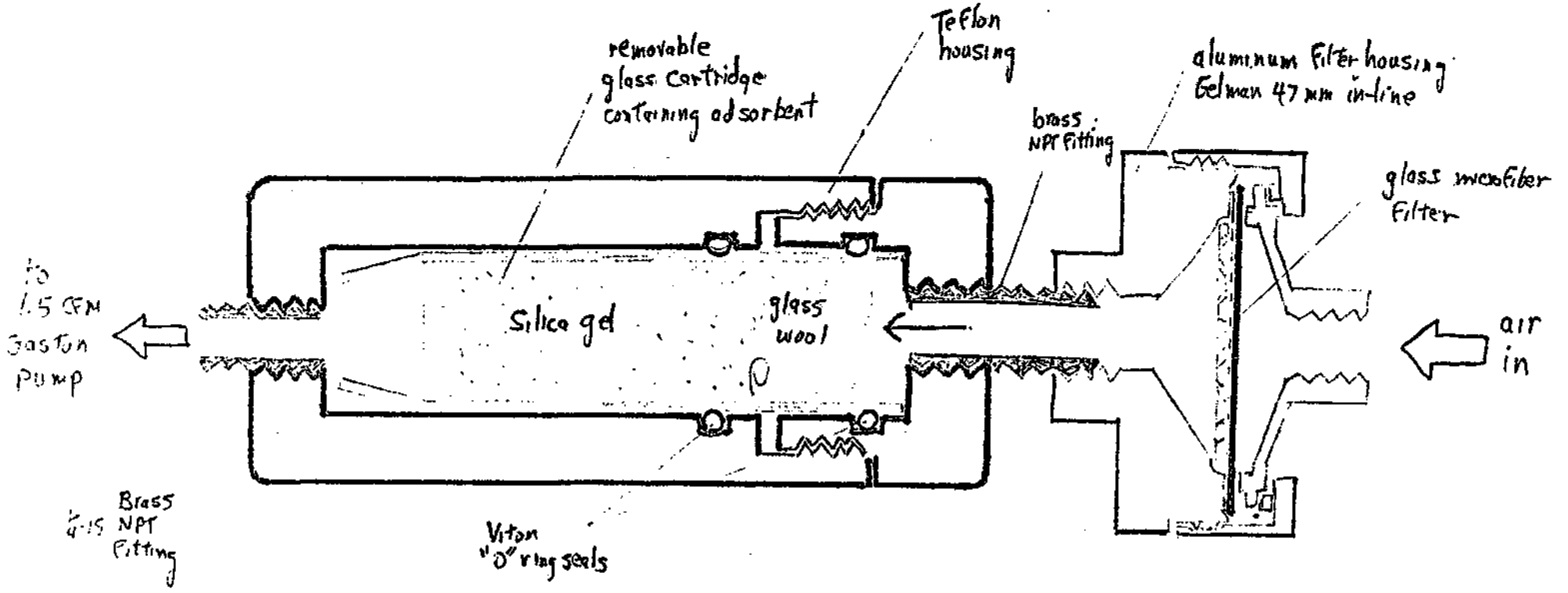


Figure 2 Two Stage Air Sampling Apparatus For PCDFs and PCDDs

(shown assembled)

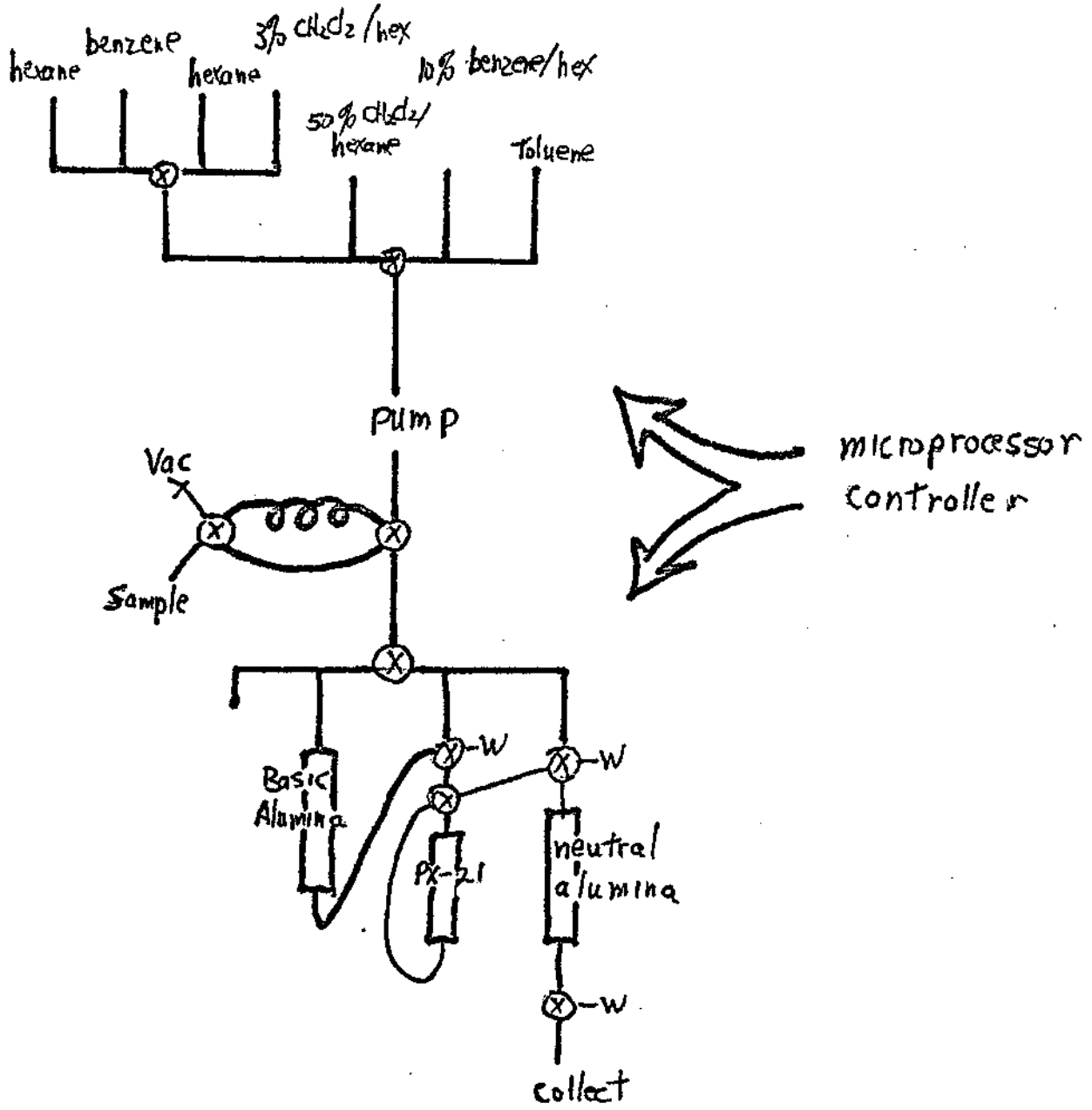


Figure 3. Automated Clean up System For Air Samples

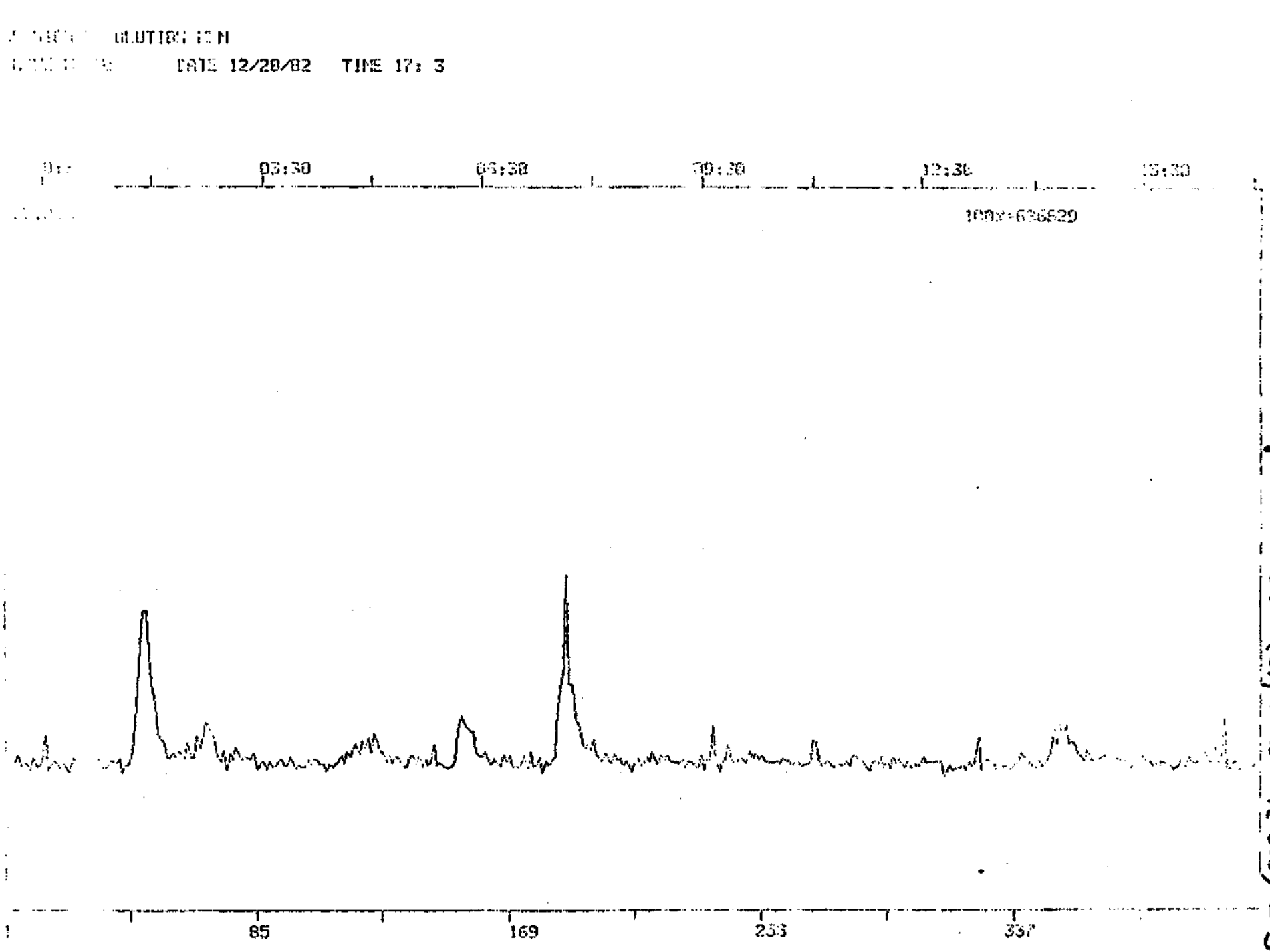


Fig. 7. ICU 3s (expanded m/e 365) of Sample A2

Fig. 5. Mass Chromatograms for TCDFs and ^{37}Cl-2378 TCDF - Sample A2

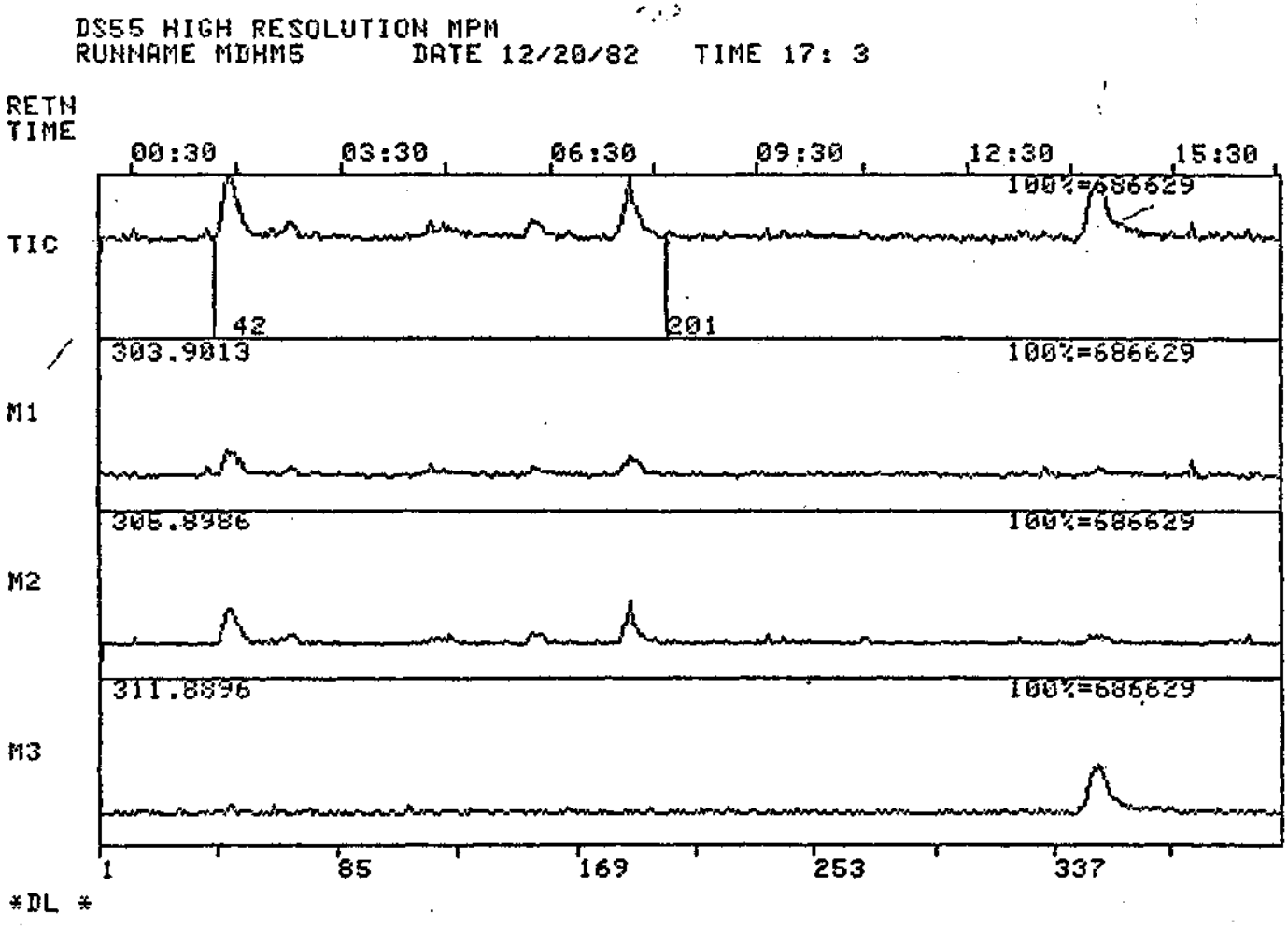
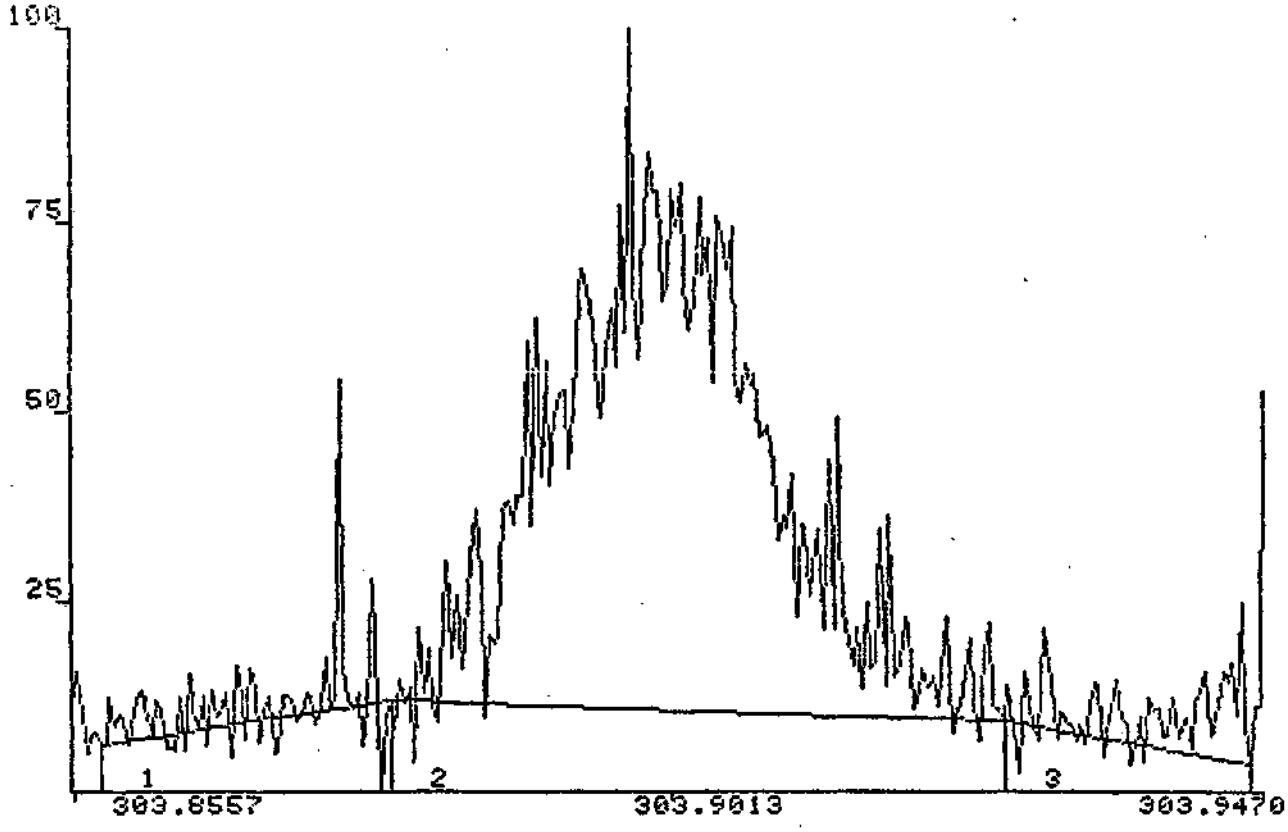


Fig. 6 Mass Profiles For TCDFs - Sample A2

RUNNAME MDHMS DATE 12/20/82 TIME 17: 3
MASS 303.9013 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 42-201 100% INTENSITY 139105



*

RUNNAME MDHMS DATE 12/20/82 TIME 17: 3
MASS 305.8986 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 42-201 100% INTENSITY 149793

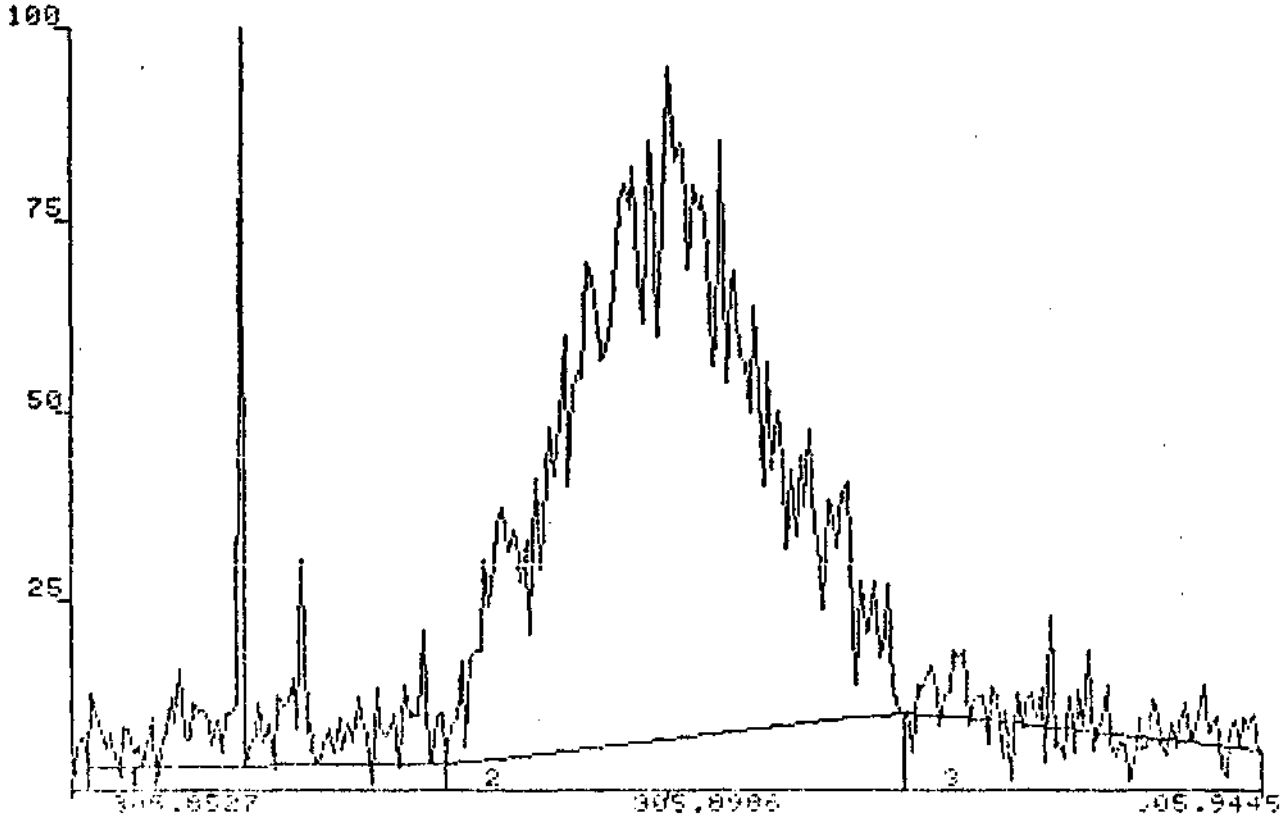
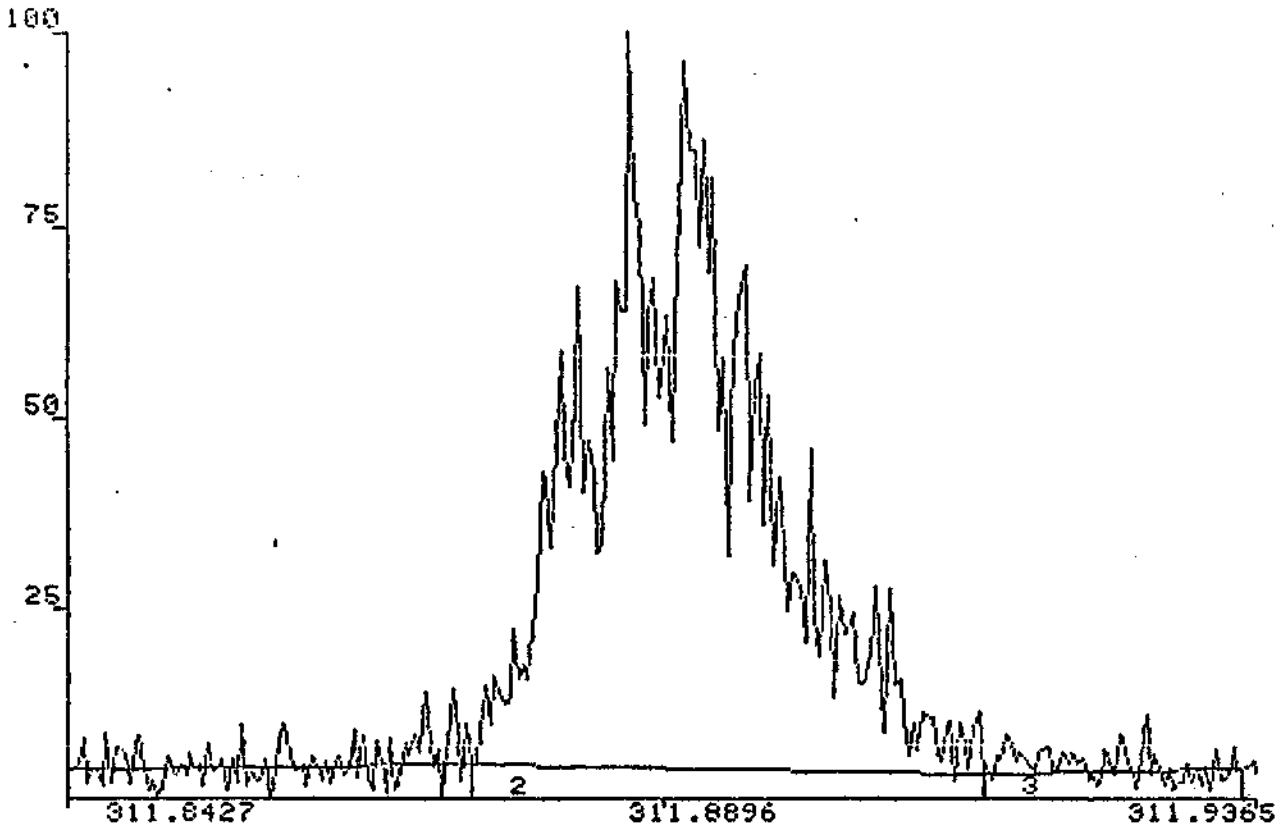


Fig 7. Mass Profile for Cl ICDF Internal Standard – Sample A2

RUNNAME MDHMS DATE 12/20/82 TIME 17: 3
MASS 311.8896 SWEEP 300 (PPM) SCANTIME 0.3 (SECS)
SCANS 342-355 100% INTENSITY 39325



*SK AREA ID:1 *

DS55 HIGH RESOLUTION MPM

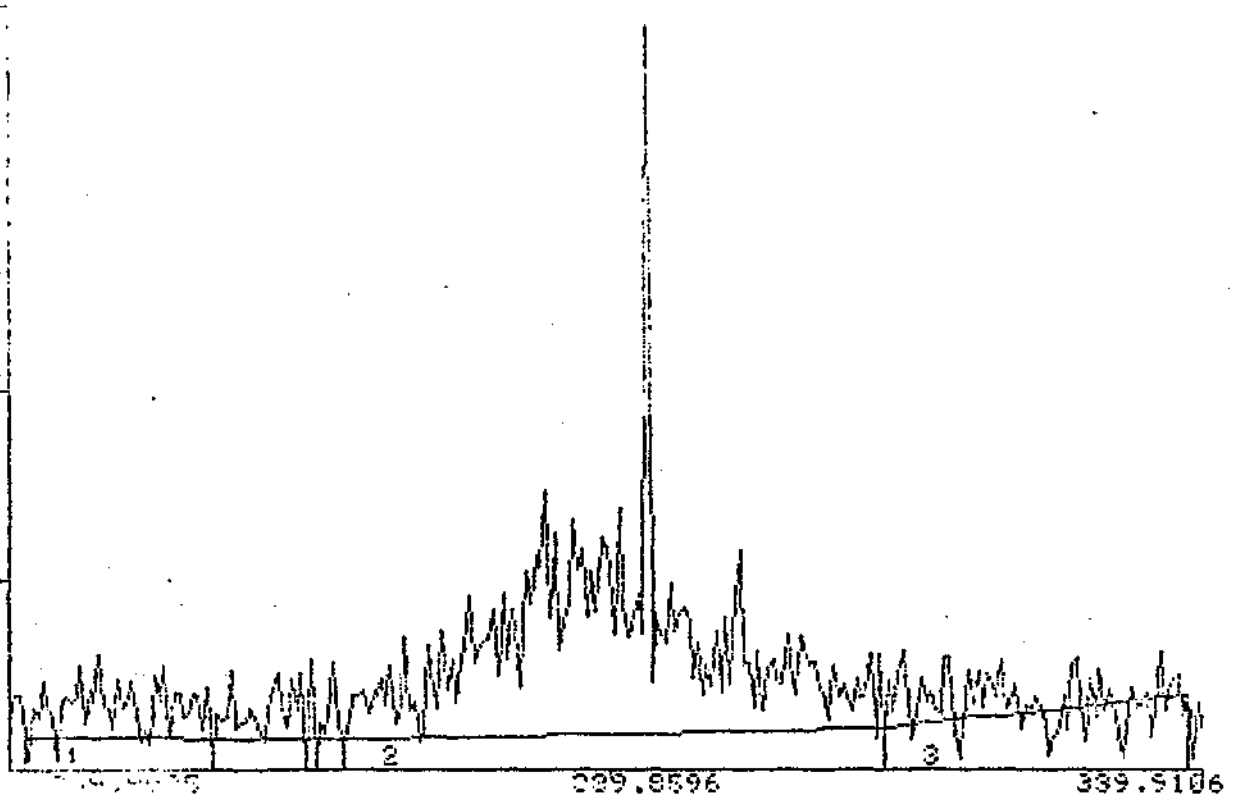
PEAK SUMMATION REPORT

RUNNAME MDHMS DATE 12/20/82 TIME 17: 3

MASS	311.8896
SCAN WIDTH	300 PPM
SCAN TIME	0.3 SECS
SCAN NUMBERS	342- 355
STANDARD	0.0000
FACTOR	0

1.4 UL OF 6 UL A2 (1ST + P)

MASS CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SKIMMED	%TOTAL AREA	RELATIVE TO STANDARD
311.8897	TOTAL	1528079.	YES	NO	49.99	0.00
311.8586	1	39753.	YES	YES	1.30	0.00
311.8926	2	1169929.	YES	YES	38.27	0.00
311.9251	3	22838.	YES	YES	0.75	0.00



ARG CENTROID	ITEM	AREA	BASELINE SUBTRACTED	BASELINE SMOOTHED		
19.0599	TOTAL	1103782.	YES	NO	21.[illegible]	[illegible]
[illegible].8830	1	103952.	YES	YES	3.03	0.00
39.8601	2	515569.	YES	YES	10.08	0.00
129.8962	3	56827.	YES	YES	1.11	0.00