Transportable Miniature FTMS for Analysis of Corrosives and Chemical Warfare Agents

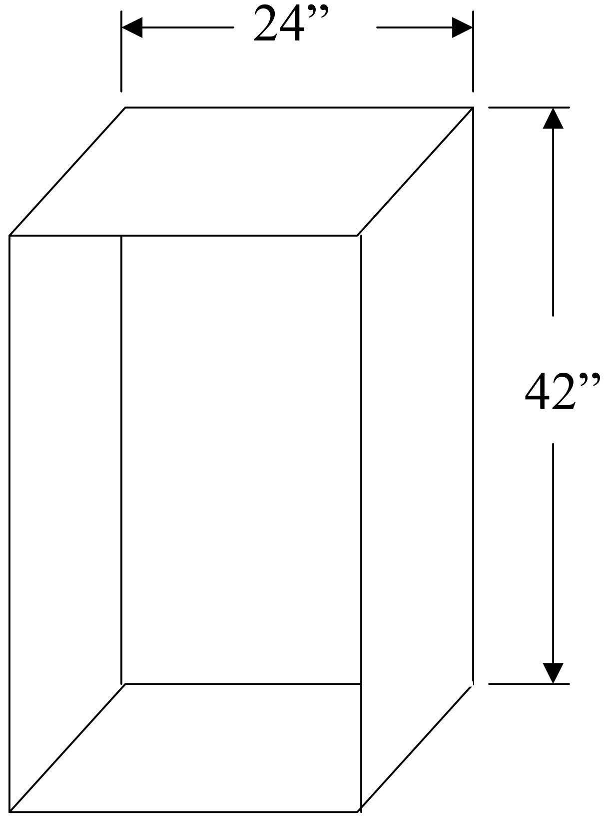
Wayne V. Rimkus, Dean V. Davis, Kenneth Gallaher

Siemens Applied Automation, 500 West Highway 60,
Bartlesville, OK 74003

Introducing the Quantra

- Rugged
- Transportable
- Accurate
- Fast
- Cheap
- Small (by FTMS standards!)
- 1 torr to 2 Atmosphere sampling
- Self contained

The relative size, absence of external pumping requirements and full battery backup of critical systems lead to the portability of the system. This translates to “field-ability” .



Miniature FTMS
Quantra

SIEMENS

Transportable

The author transporting the FTMS system – a small truck with a ramp was used. The Quantra is on wheels and is in the crate.

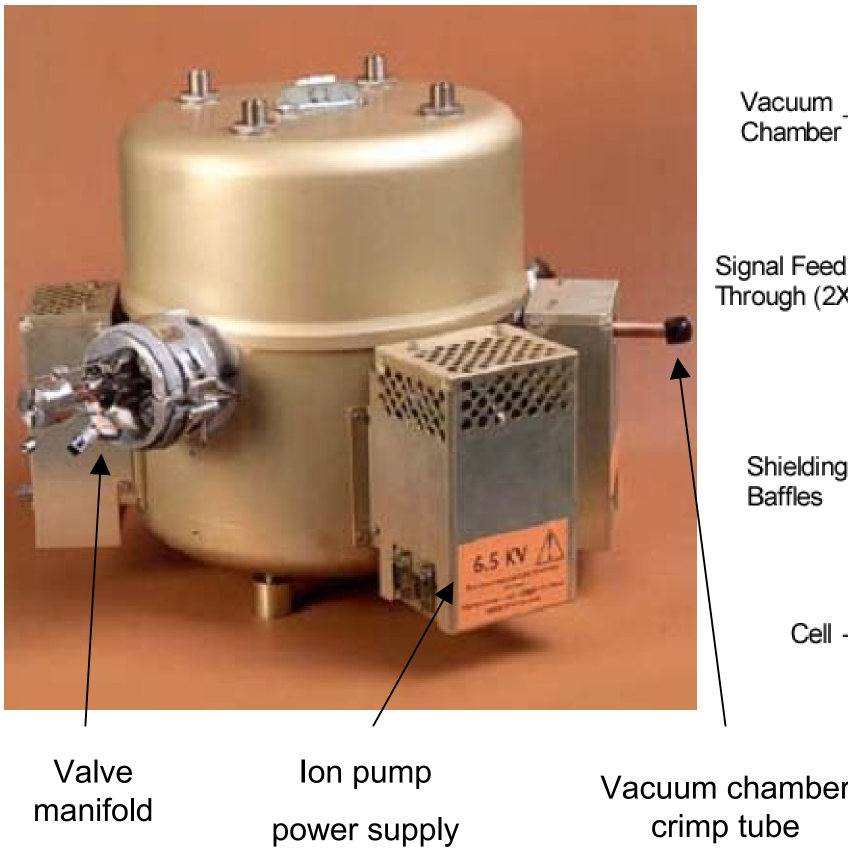
System was setup in a hotel room. Elapsed time - truck to 20,000 resolution – 15 minutes.

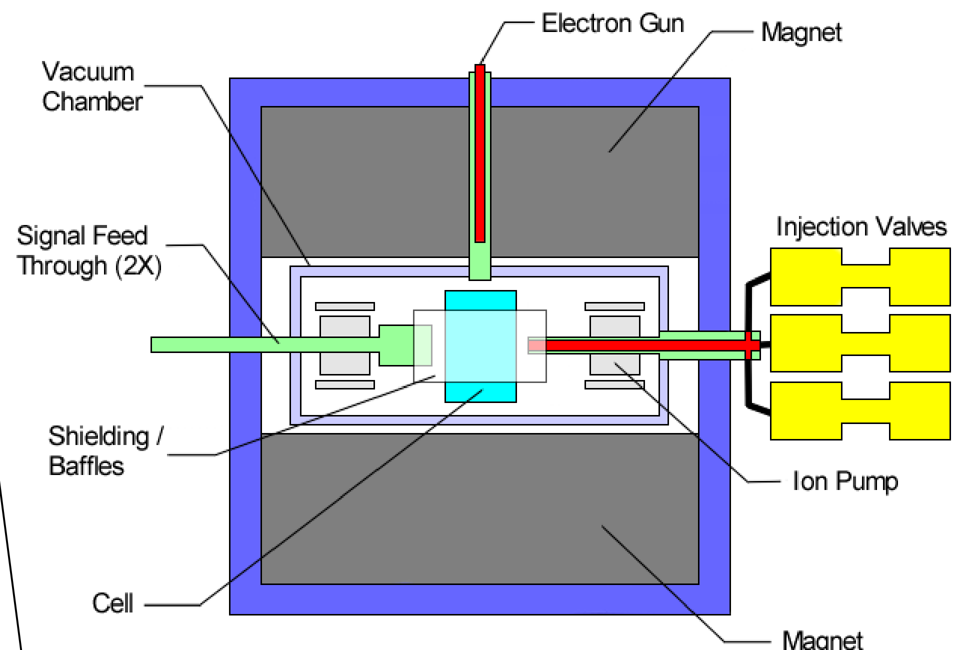
Unique Design Features

- Permanent Magnet (1 tesla)
- Ion Getter Pump (10^{-10} torr)
- Pulsed Valve – picoliter sampling
- Filament current in Nanoamps
- Battery Backup – All Critical Systems
- LOD 10 ppm, with trapping < 10 ppb (ppt?)
- Resolution at m/z 131 is 20,000
- Ion Manipulation
  - Ion Ejection
  - MS/MS
  - Chemical Ionization
  - Negative Ion Detection

Measurement Chamber

Sensor





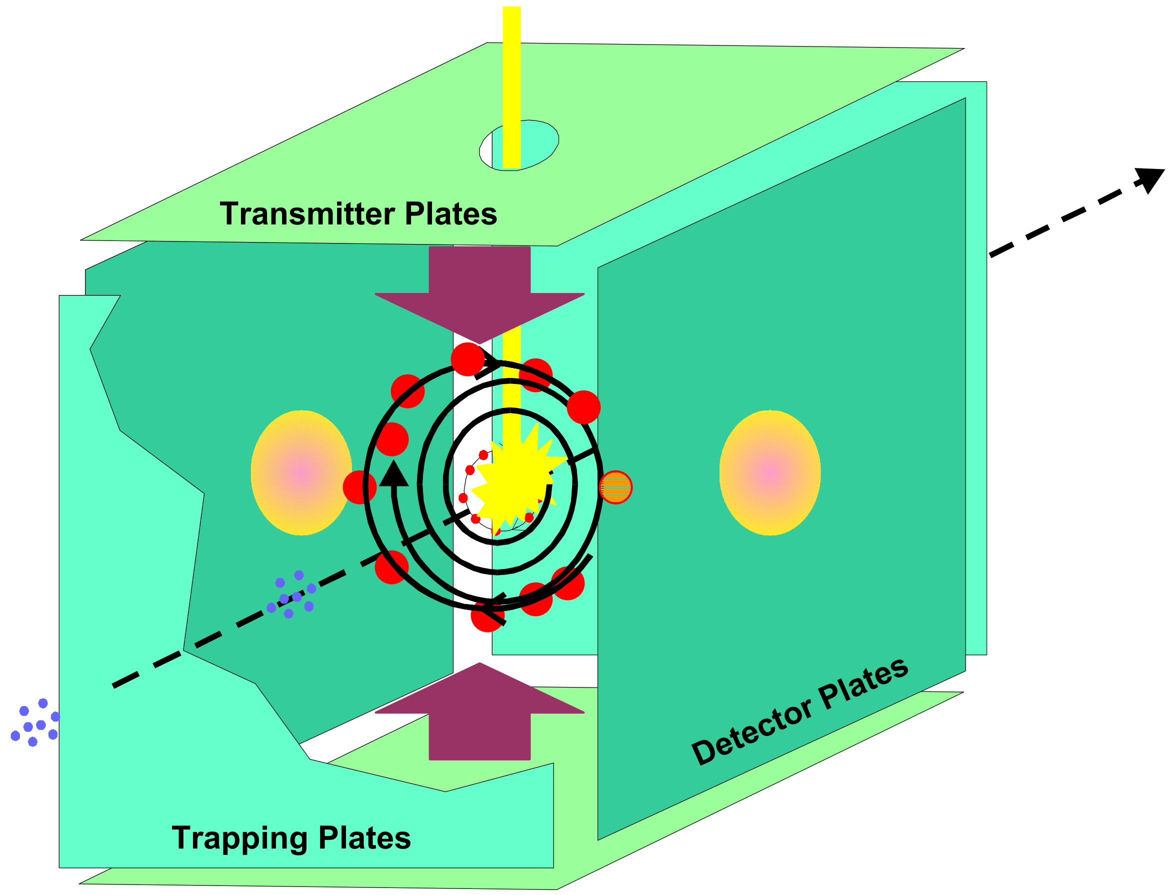
Quantra Valves

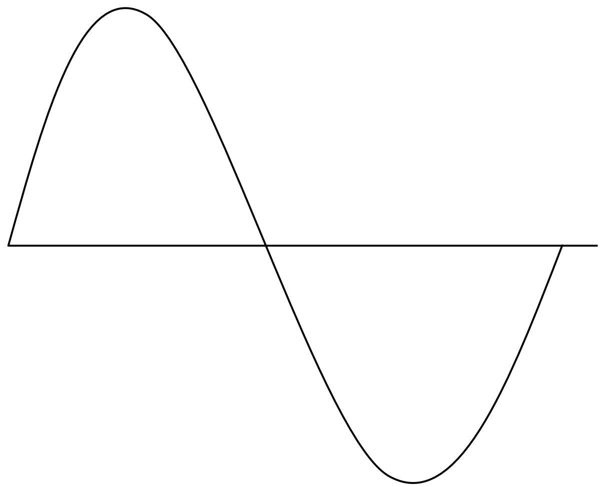
SIEMENS

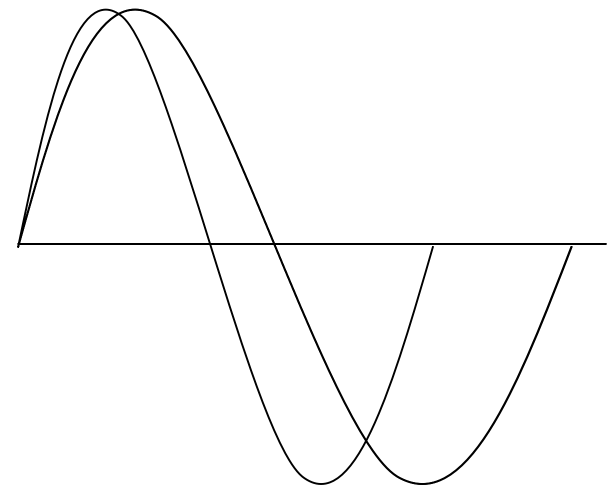
Theory of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

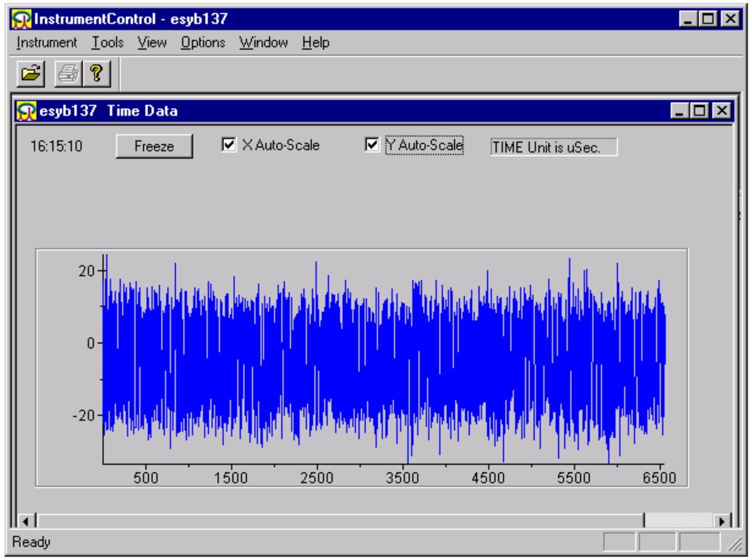
FTICR or FTMS

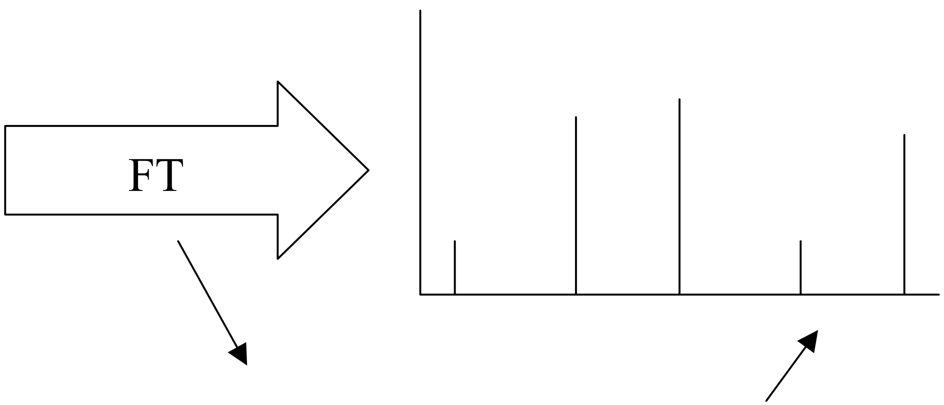
The FT-ICR Measurement Cell









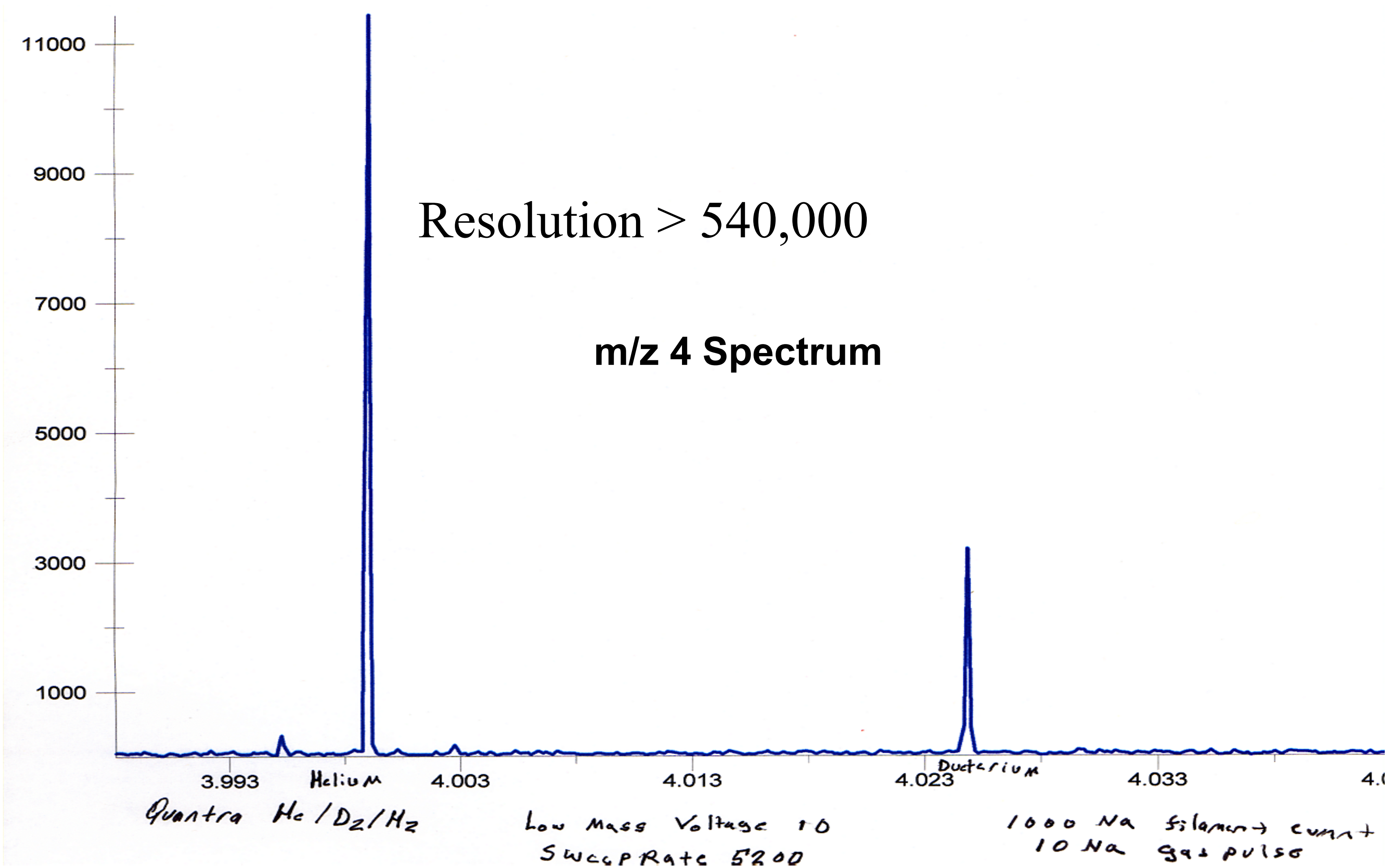


The FT produces a Frequency Domain

Time Domain

Subsequent non linear inversion yields Mass/Charge

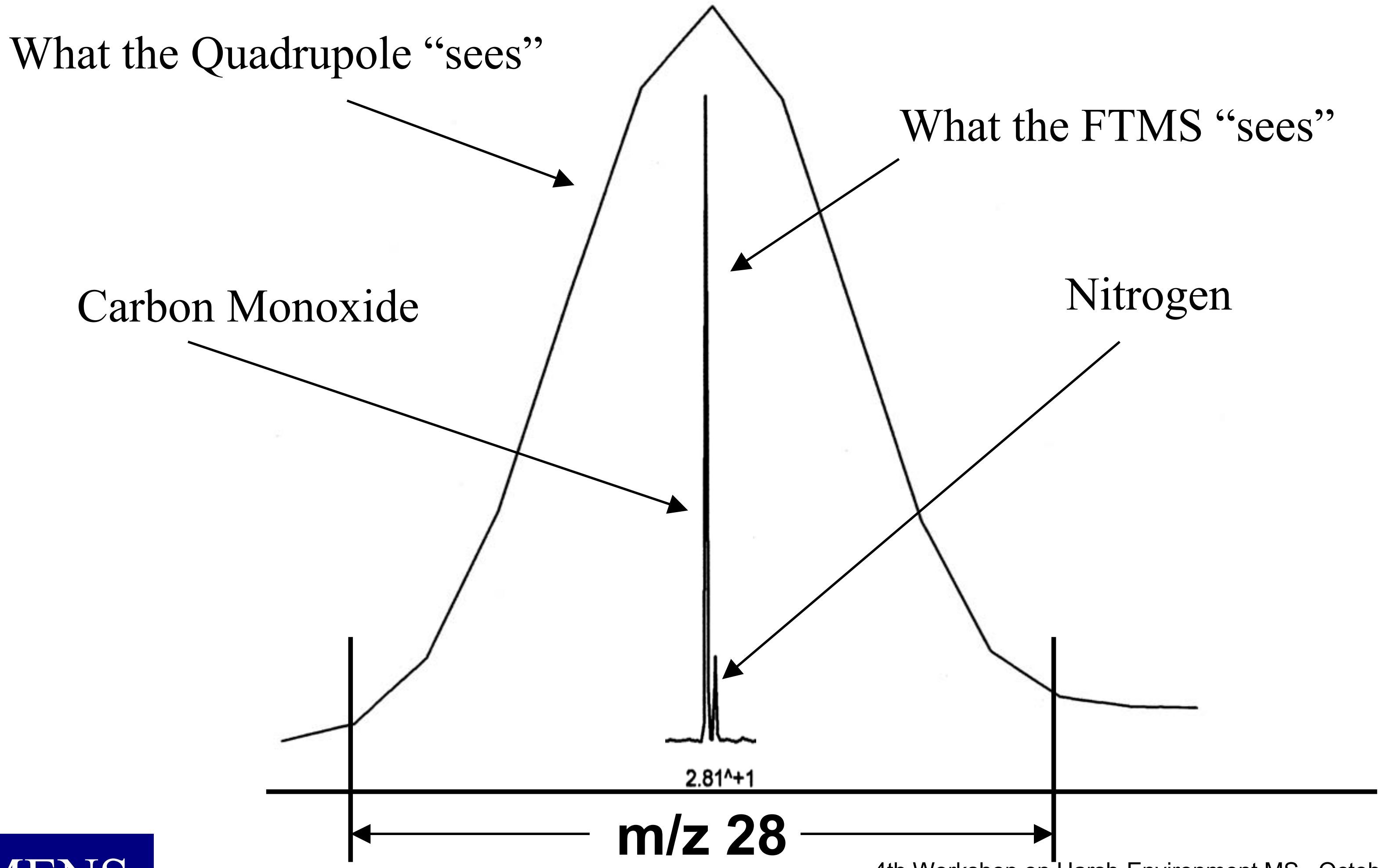
Mixed Hydrogen, Helium, Deuterium sample



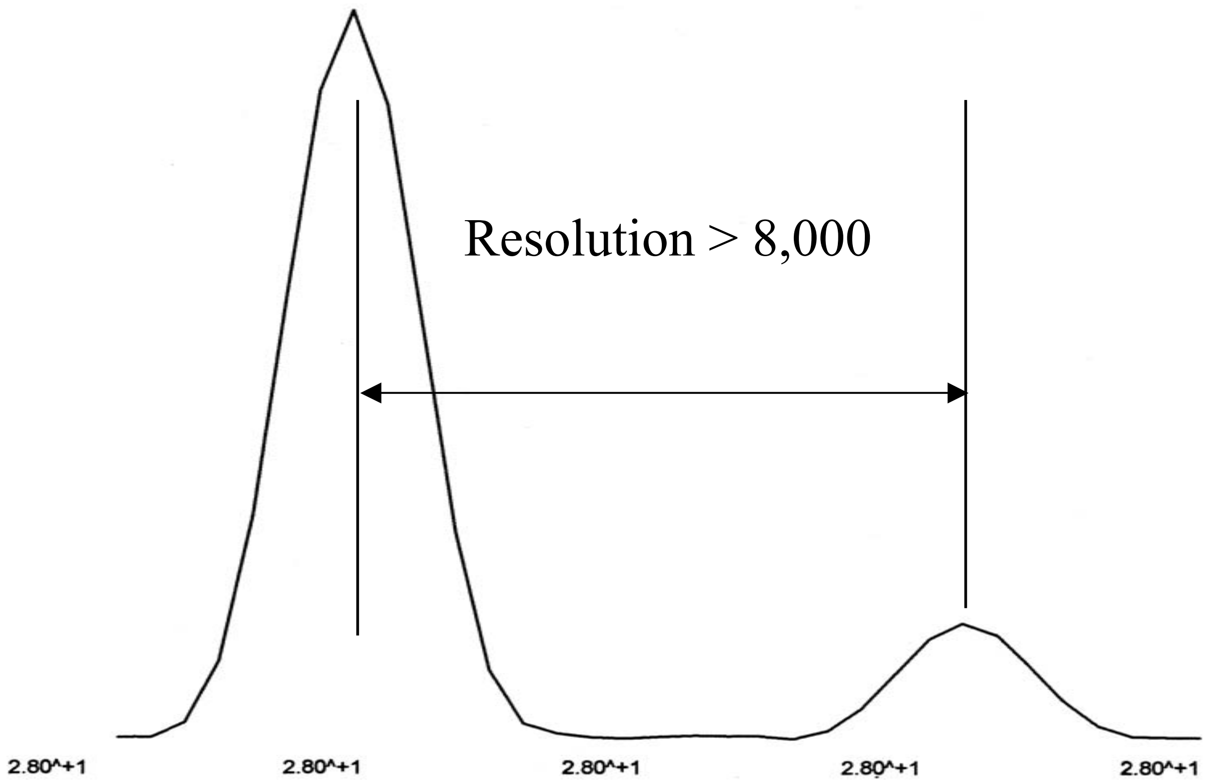
SIEMENS

Resolving Power

FTMS vs Quadrupoles



Resolution Zoom



Quantra exhibits very high resolving power

SIEMENS

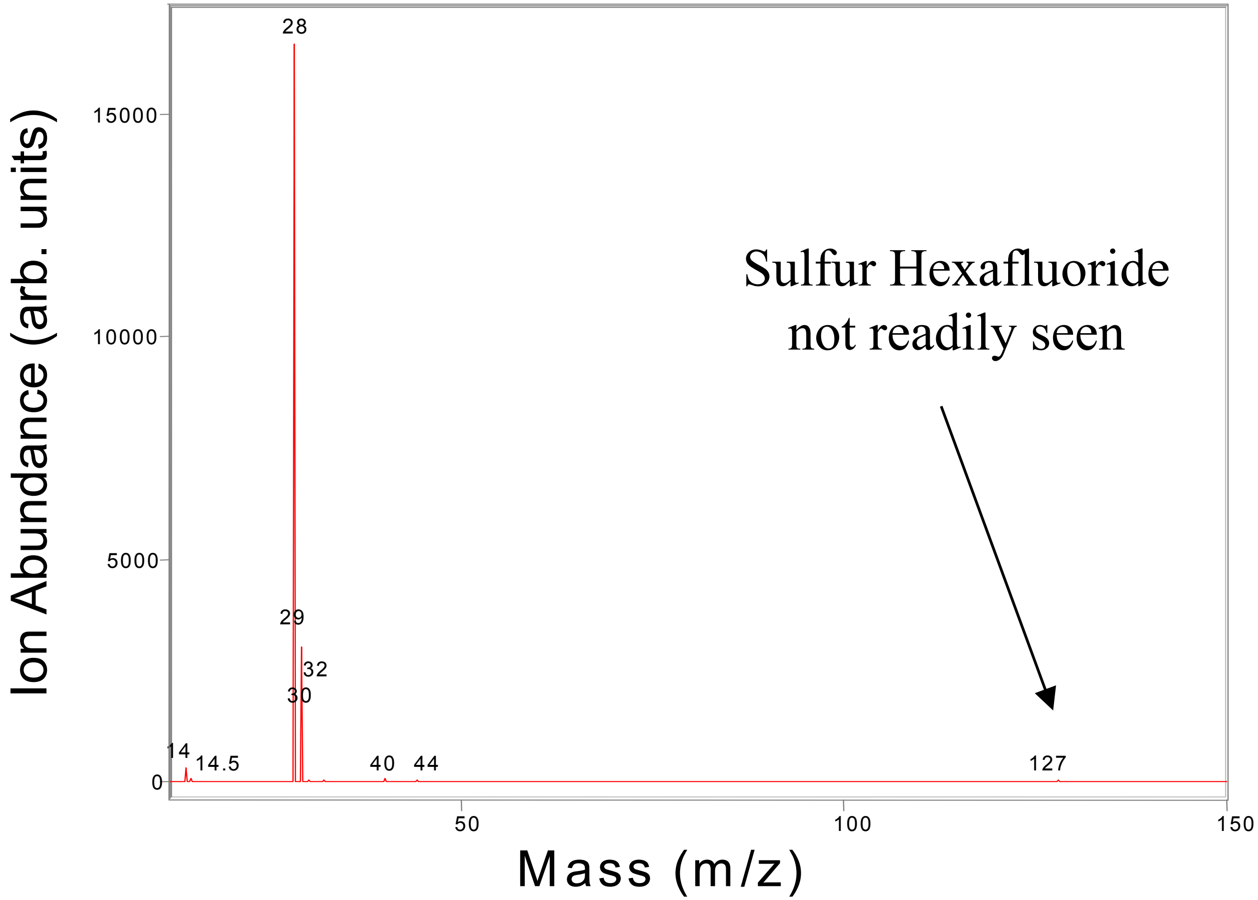
Quantra Instrument
Sensor and Electronics

Example Applications

- Trace organics in bulk gases
- Identification of materials during catalysis
- Headspace and Solids analysis
- Residual Solvents
- Ambient air monitoring
- Characterization of semi-conductor reaction mixtures
- Incinerator monitoring
- Chemical Threat

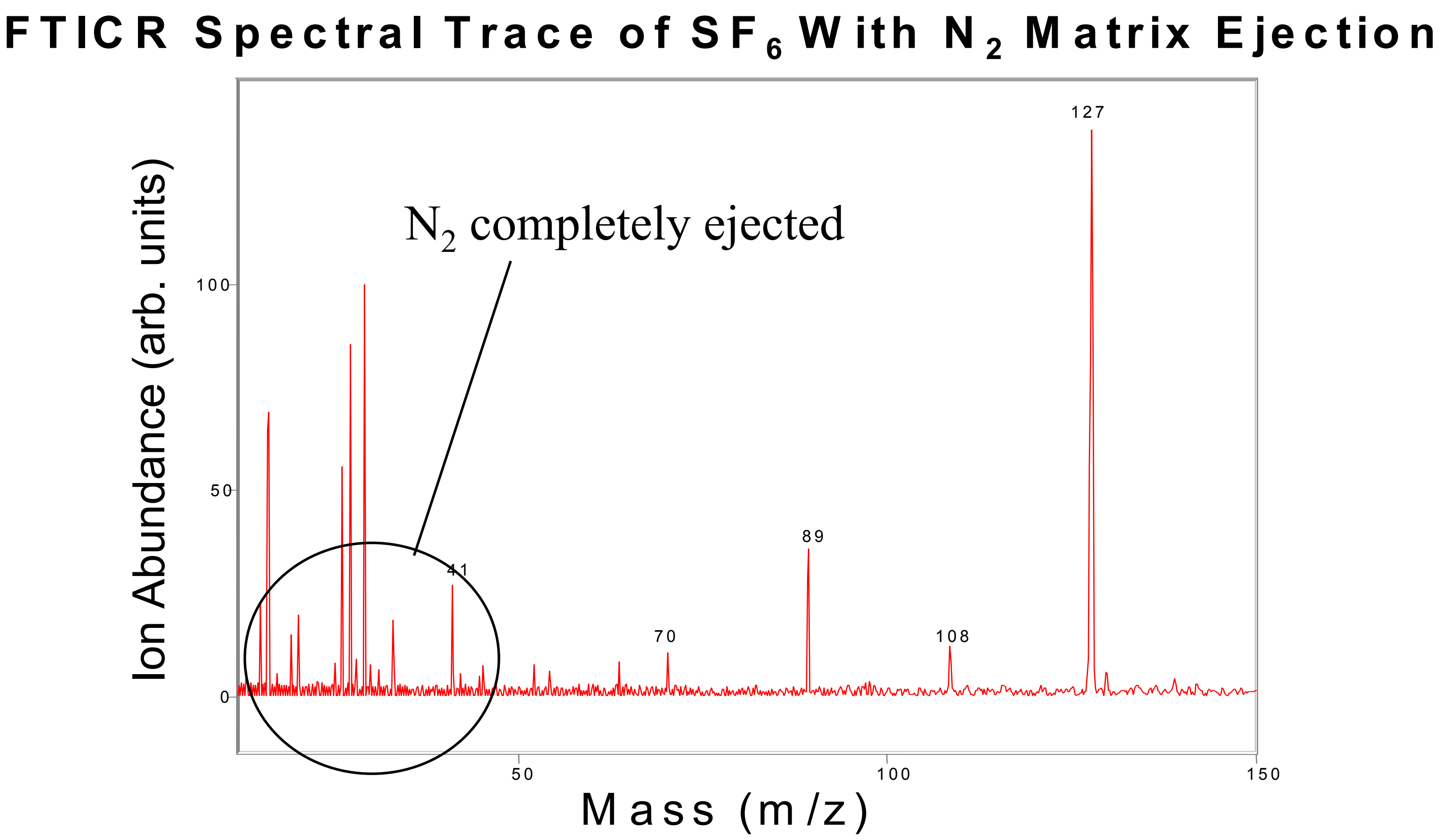
MS/MS in Direct effluent analysis

FTICR Spectral Trace of SF_6 Without N_2 Matrix Ejection

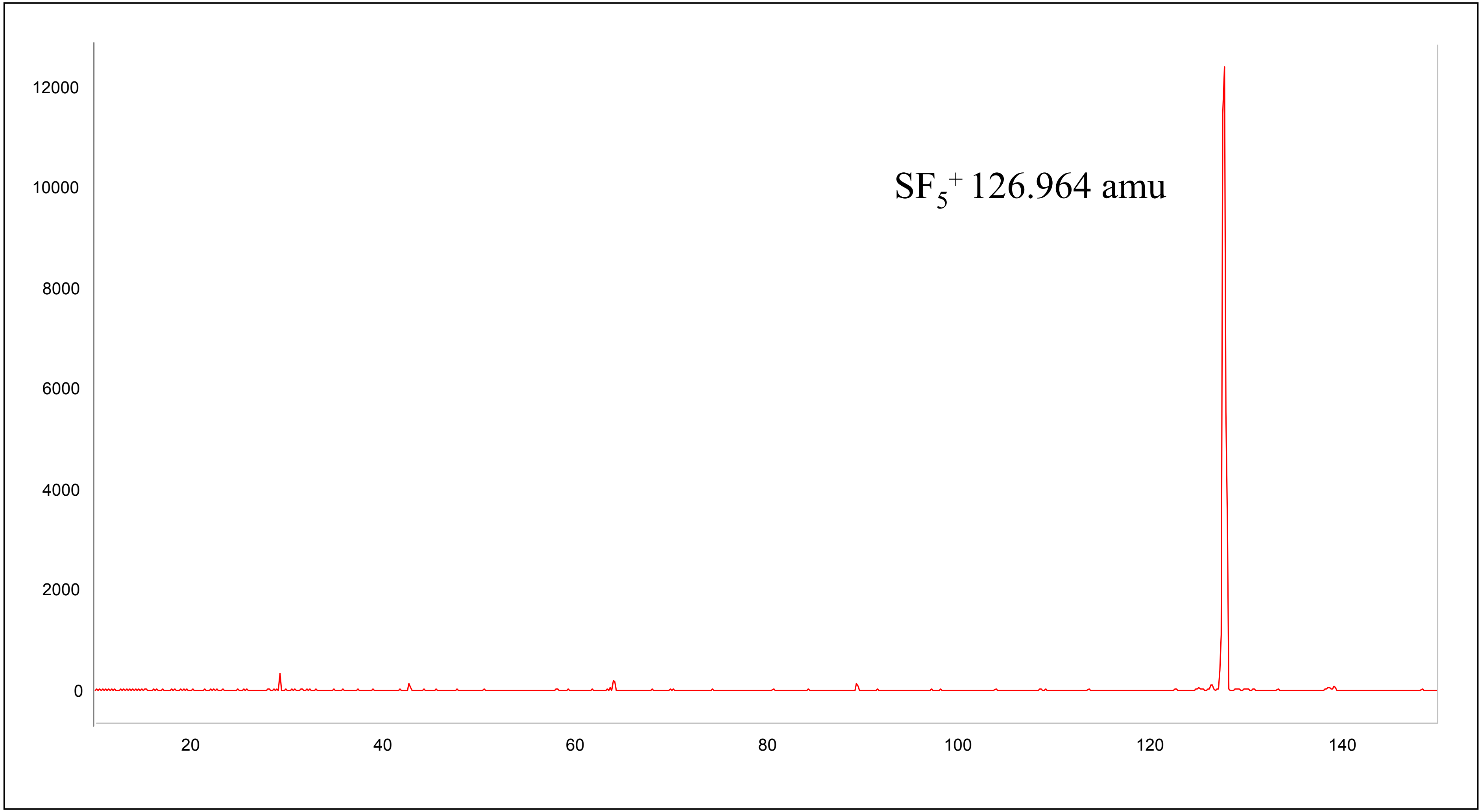


SIEMENS

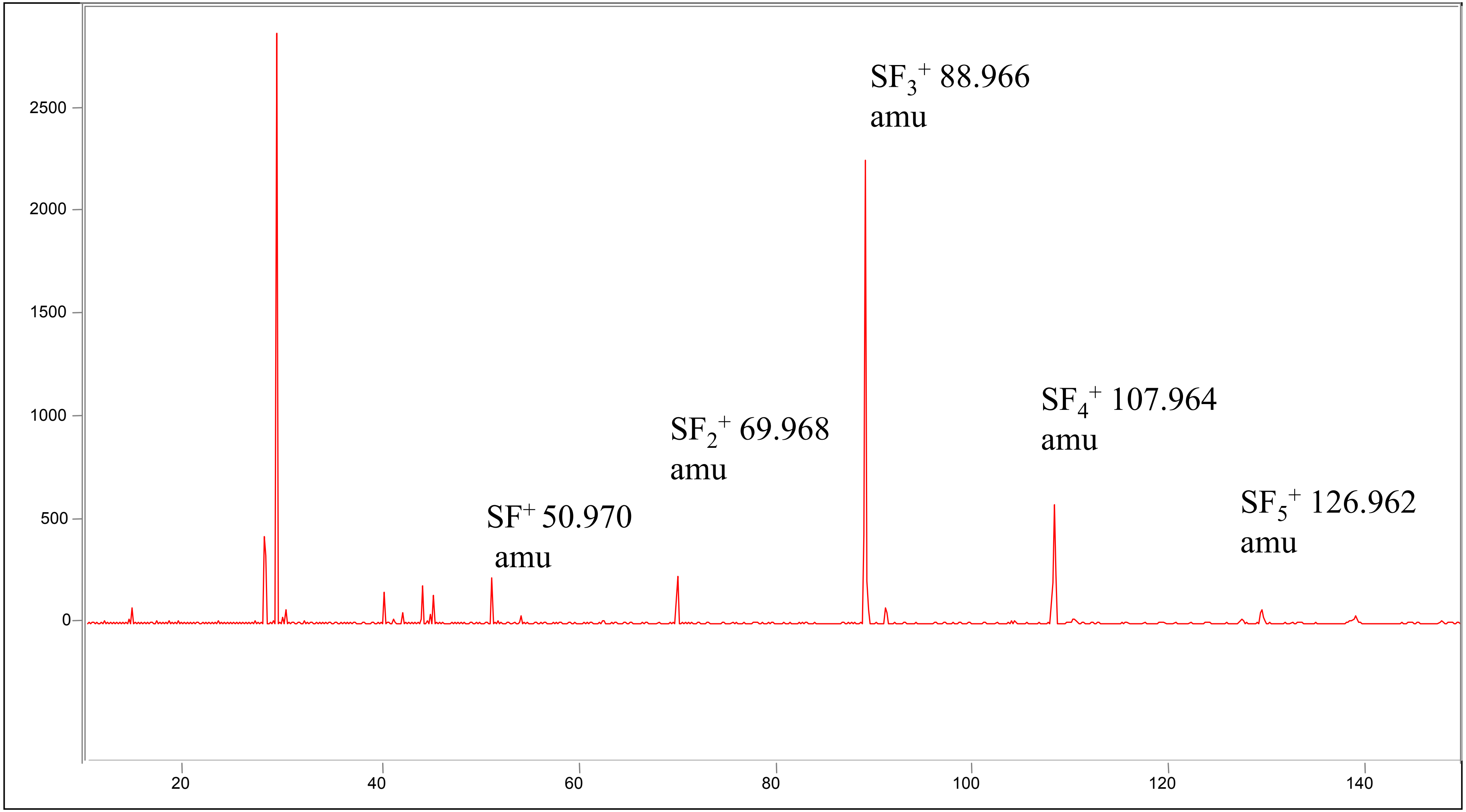
Study of process effluent with Nitrogen ejection



Isolated SF_5^+ Ion for MS/MS

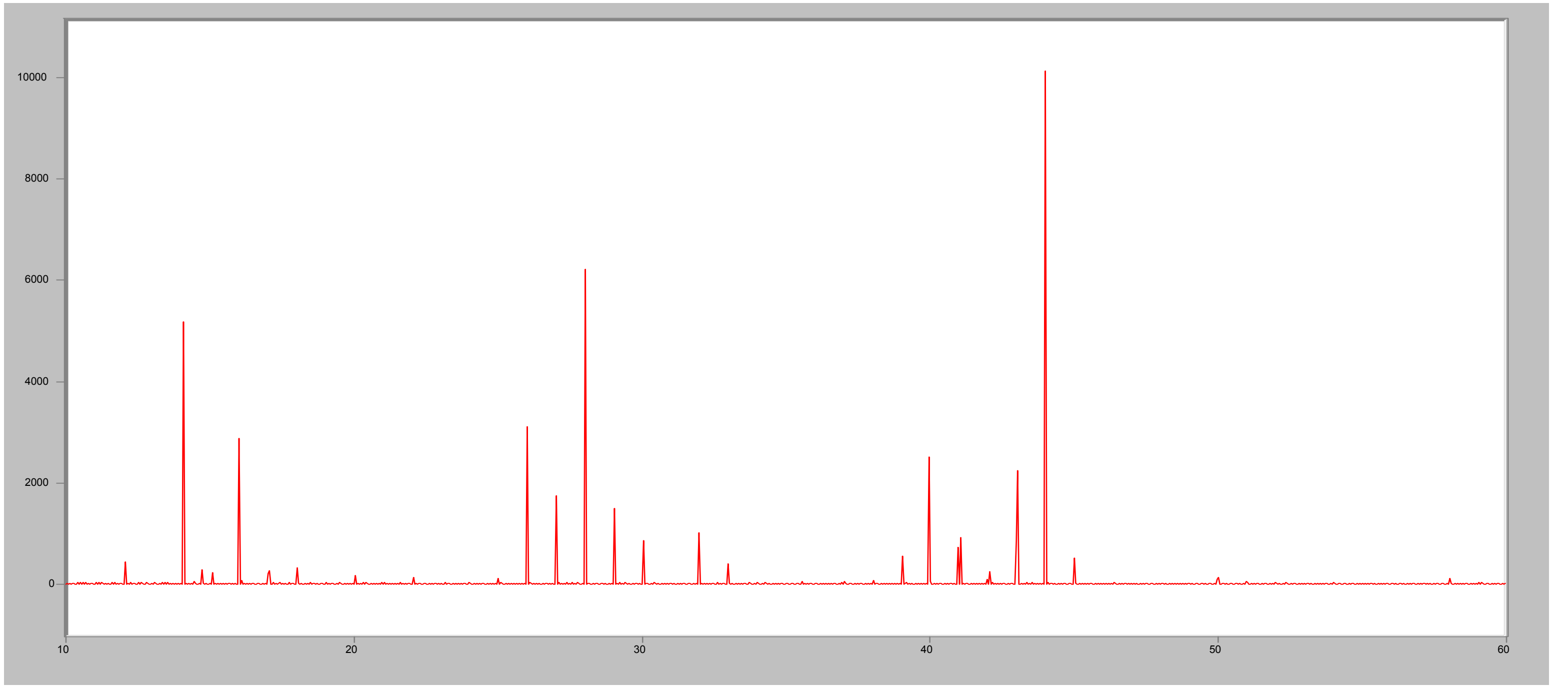


MS/MS Spectrum of SF_5^+



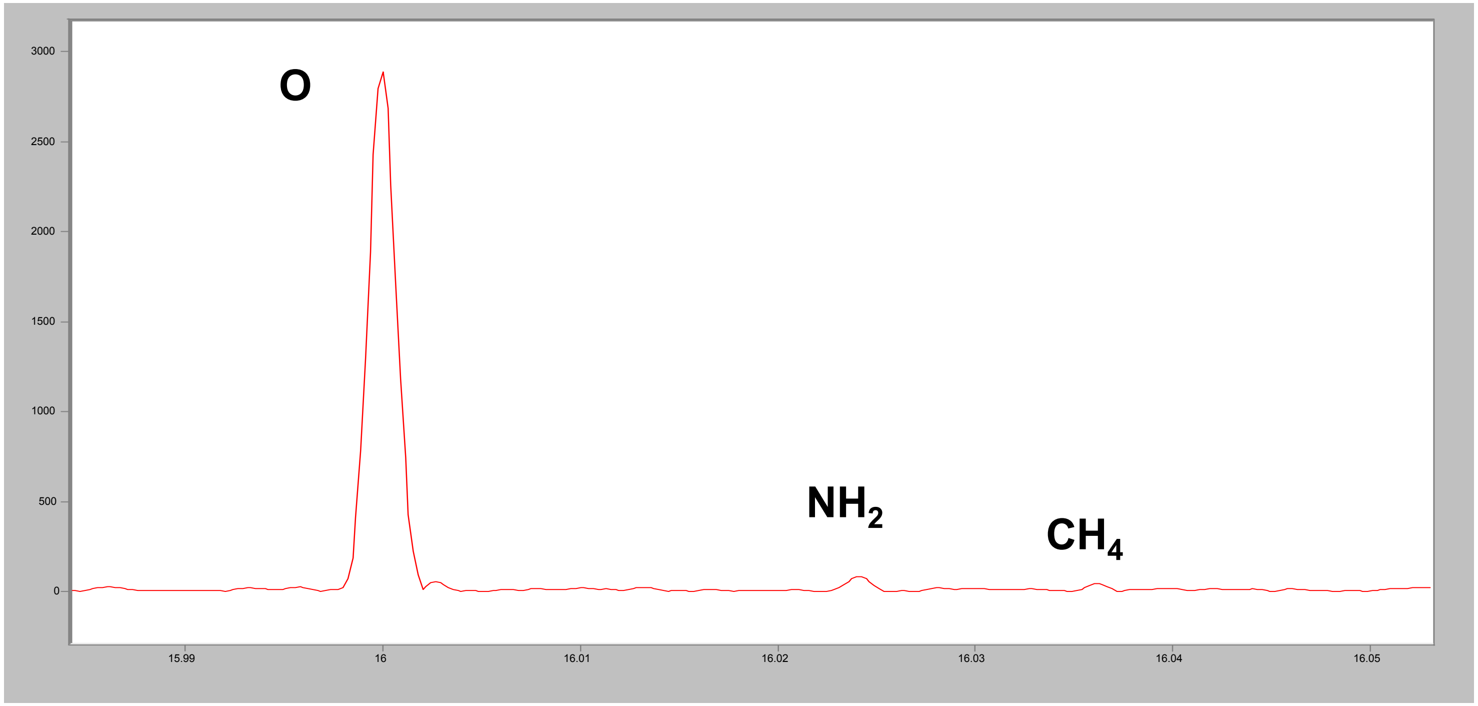
Fermenters

Fermenter 1
Headspace Spectrum



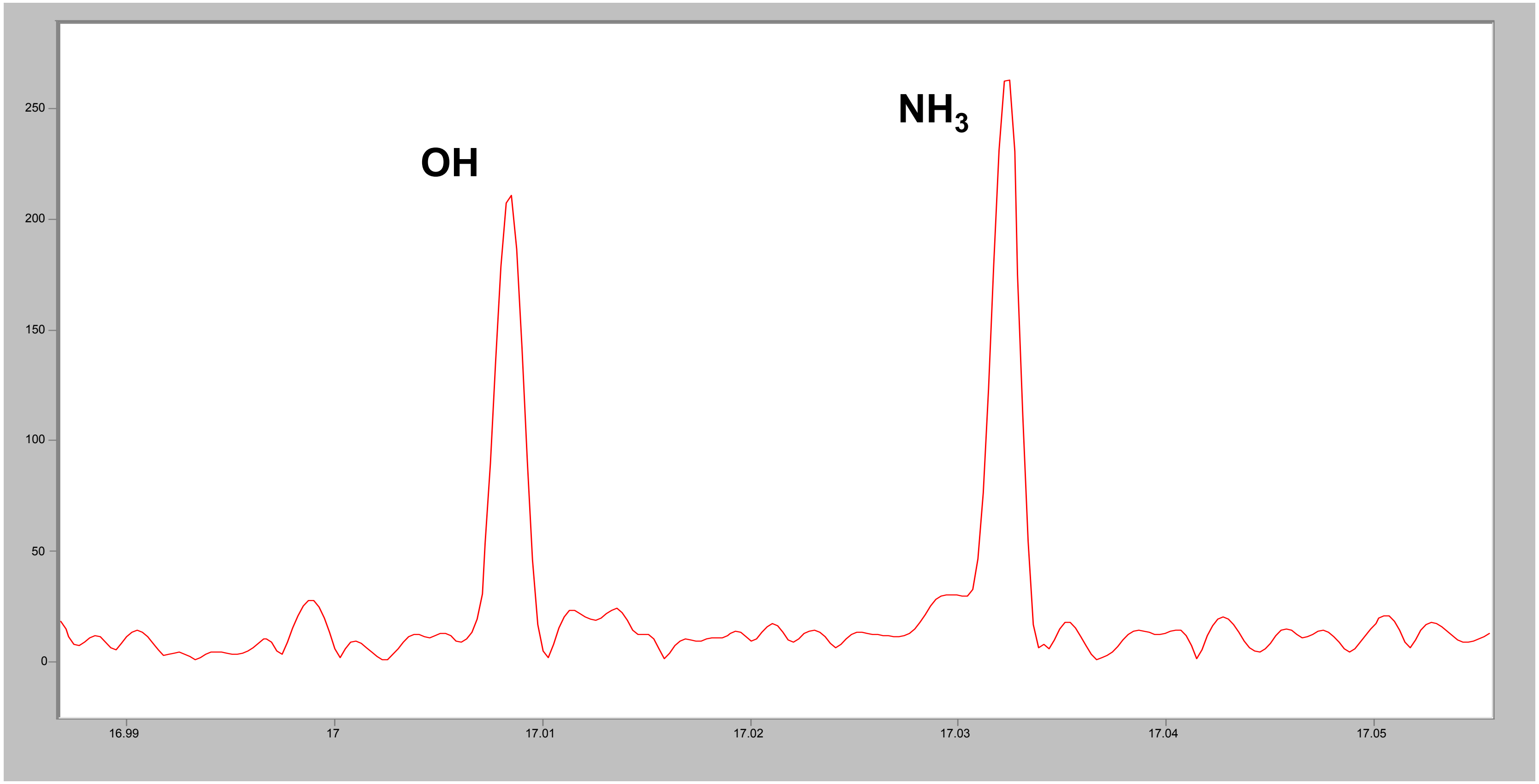
- 10 sets of “Mass Doublets” – Isobars
- 1 Triplet (Nominal mass 16 – O, CH_4, NH_2)

Mass 16



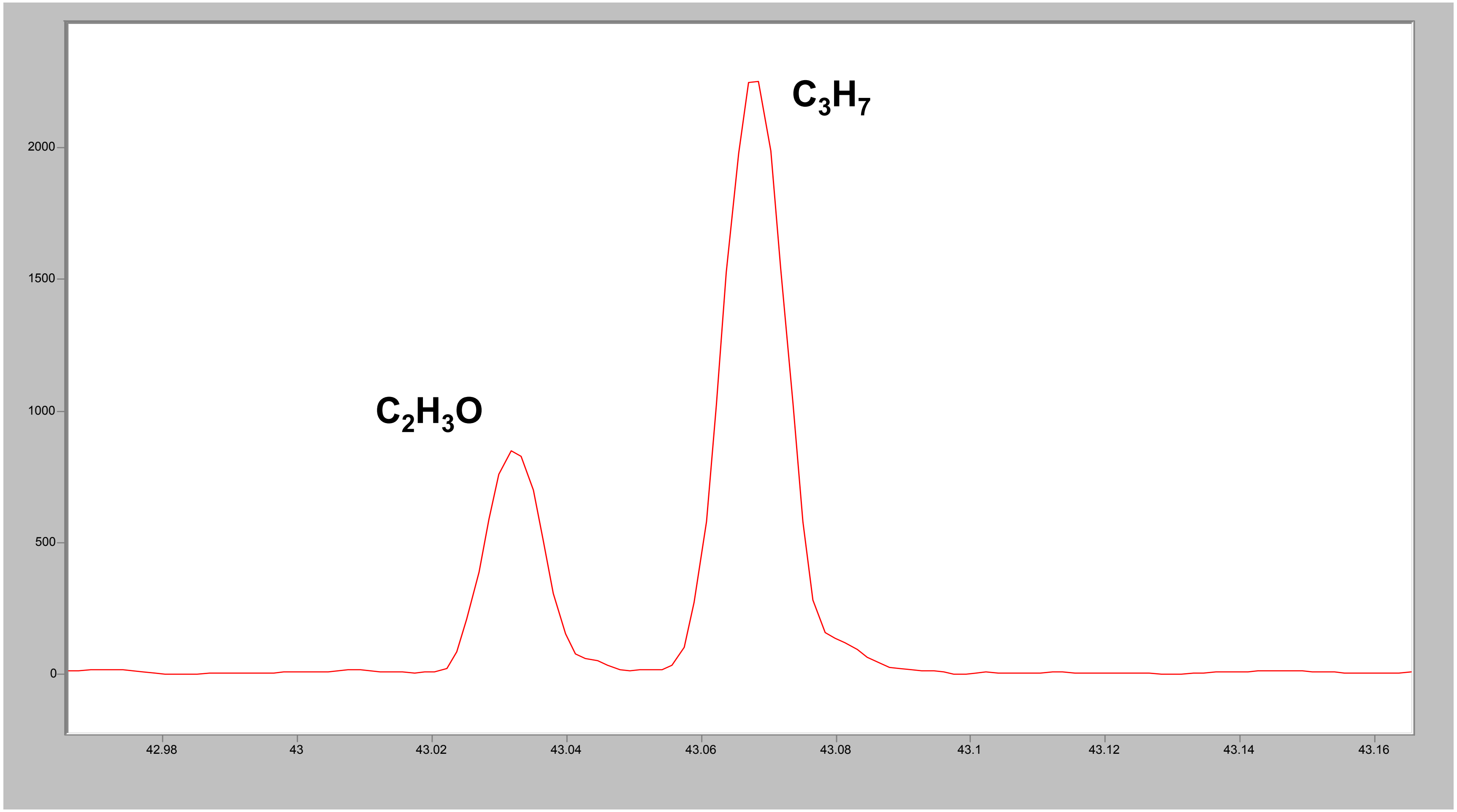
SIEMENS

Mass 17



SIEMENS

Mass 43



C3H7
C2H3O
2000
1500
1000
500
0
42.98
43
43.02
43.04
43.06
43.08
43.1
43.12
43.14
43.16

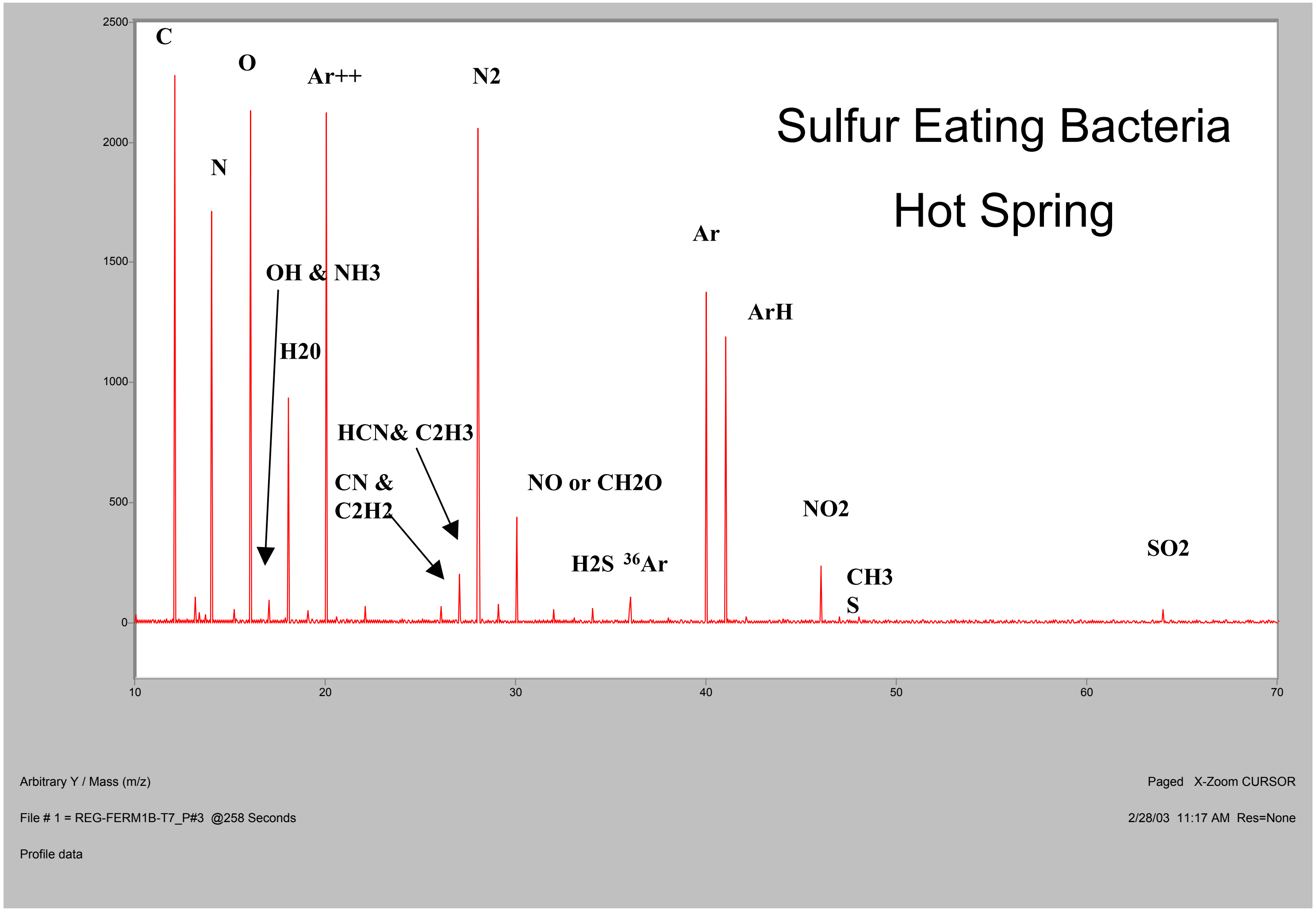
Summary Of Components Detected

Peak Number	Observed mass	Fragment	Assignment	Theory	Corrected obs	Corrected Delta
1	12.0029	C	C	12.0000	11.9989	-0.0011
2	**14.0069**	N	N	14.0037	14.0023	-0.0014
3	**14.0226**	CH2	CH2	14.0156	14.0180	0.0024
4	14.7103	noise?	noise		14.7055	
5	15.0281	CH3	e/butane/propane	15.0234	15.0232	-0.0002
6	**15.99996**	O	H2O	15.9949	15.9948	-0.0001
7	**16.0239**	NH2	NH3	16.0187	16.0187	0.0000
8	**16.0362**	CH4	CH4 trace	16.0312	16.0310	-0.0002
9	**17.0084**	OH	H2O	17.0027	17.0029	0.0002
10	**17.0322**	NH3	NH3	17.0265	17.0267	0.0002
11	18.0167	H2O	H2O	18.0106	18.0109	0.0003
12	19.9884	Ar^{+2}	Ar^{+2}	19.9812	19.9820	0.0008
14	25.0149	C2H	butane/propane	25.0078	25.0070	-0.0008
15	**26.0235**	C2H2	butane/propane	26.0157	26.0153	-0.0004
16	**26.0121**	CN	HCN	26.0031	26.0039	0.0008
17	**27.0195**	HCN	HCN	27.0109	27.0110	0.0001
18	**27.0313**	C2H3	butane	27.0235	27.0228	-0.0007
19	28.0058	CO	CO	27.9949	27.9970	0.0021
20	**29.0117**	CHO	acid?	29.0027	29.0026	-0.0001
21	**29.0224**	HN2	HN2	29.0140	29.0133	-0.0007
22	30.0067	NO	NO	29.9980	29.9973	-0.0007
23	32.0002	O2	O2	31.9898	31.9902	0.0004
27	39.0352	C3H3	propane	39.0235	39.0231	-0.0004
29	**39.9747**	Ar	Ar	39.9624	39.9623	-0.0001
32	**41.051**	C3H5	propane	41.0391	41.0383	-0.0008
33	**42.0224**	C2H2O	acetone	42.0106	42.0094	-0.0012
34	**42.0598**	C3H6	butane	42.0469	42.0468	-0.0001
35	**43.0327**	C2H3O	acetone	43.0184	43.0194	0.0010
36	**43.0677**	C3H7	butane &?	43.0548	43.0544	-0.0004
37	**44.0006**	CO2	CO2	43.9898	43.9870	-0.0028
38	**44.0145**	N 2O	N2O	44.0010	44.0009	-0.0001
39	45.0117	COOH	acid?	44.9977	44.9978	0.0001
40	50.0291	C4H2	butane	50.0157	50.0137	-0.0020
42	**58.0619**	C3H6O	acetone	58.0419	58.0441	0.0022
43	**58.0949**	C4H10	butane	58.0782	58.0771	-0.0011

Average delta

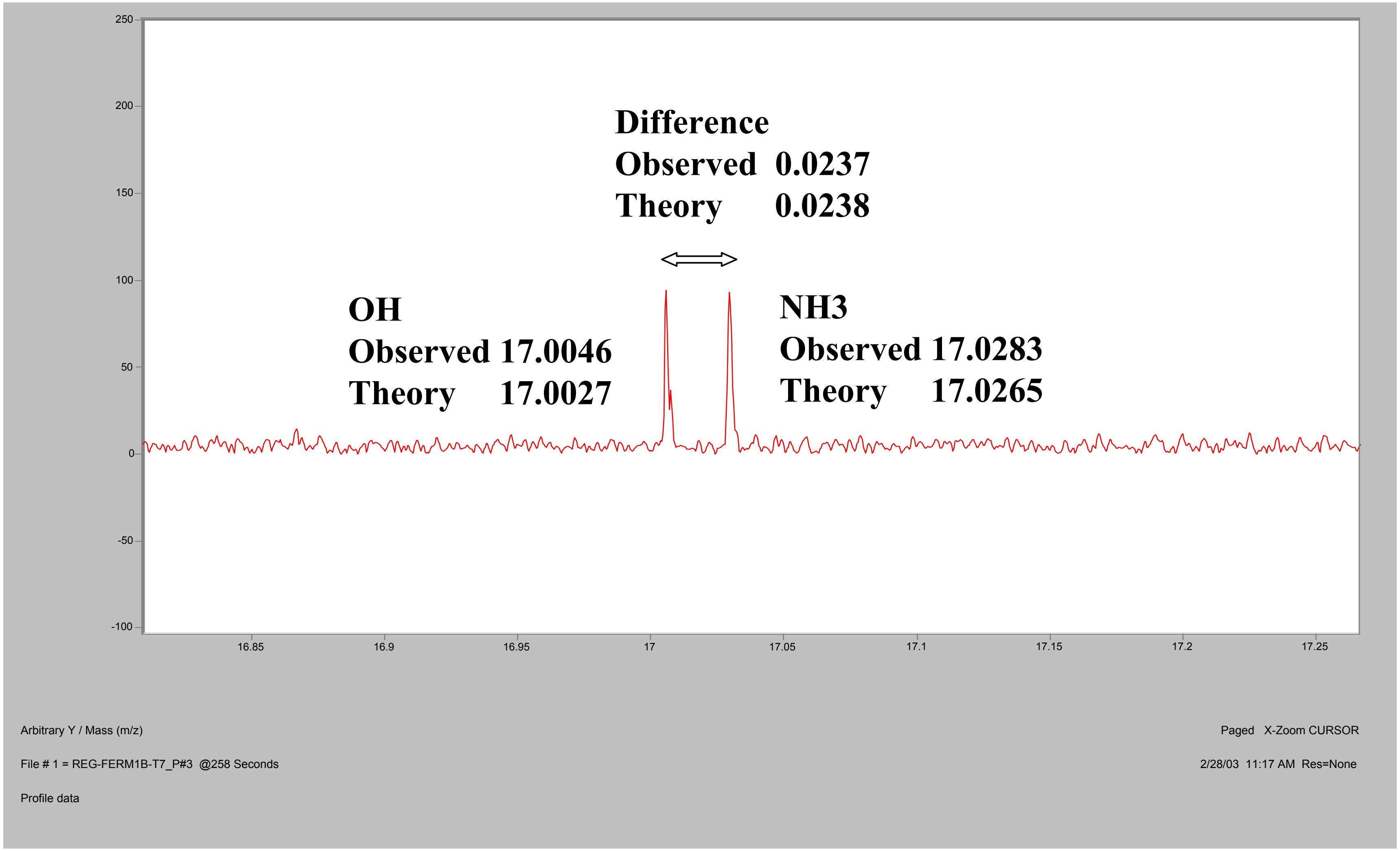
0.00015 AMU

Fermenter 2
N_2, Ar, and CO_2 Ejection



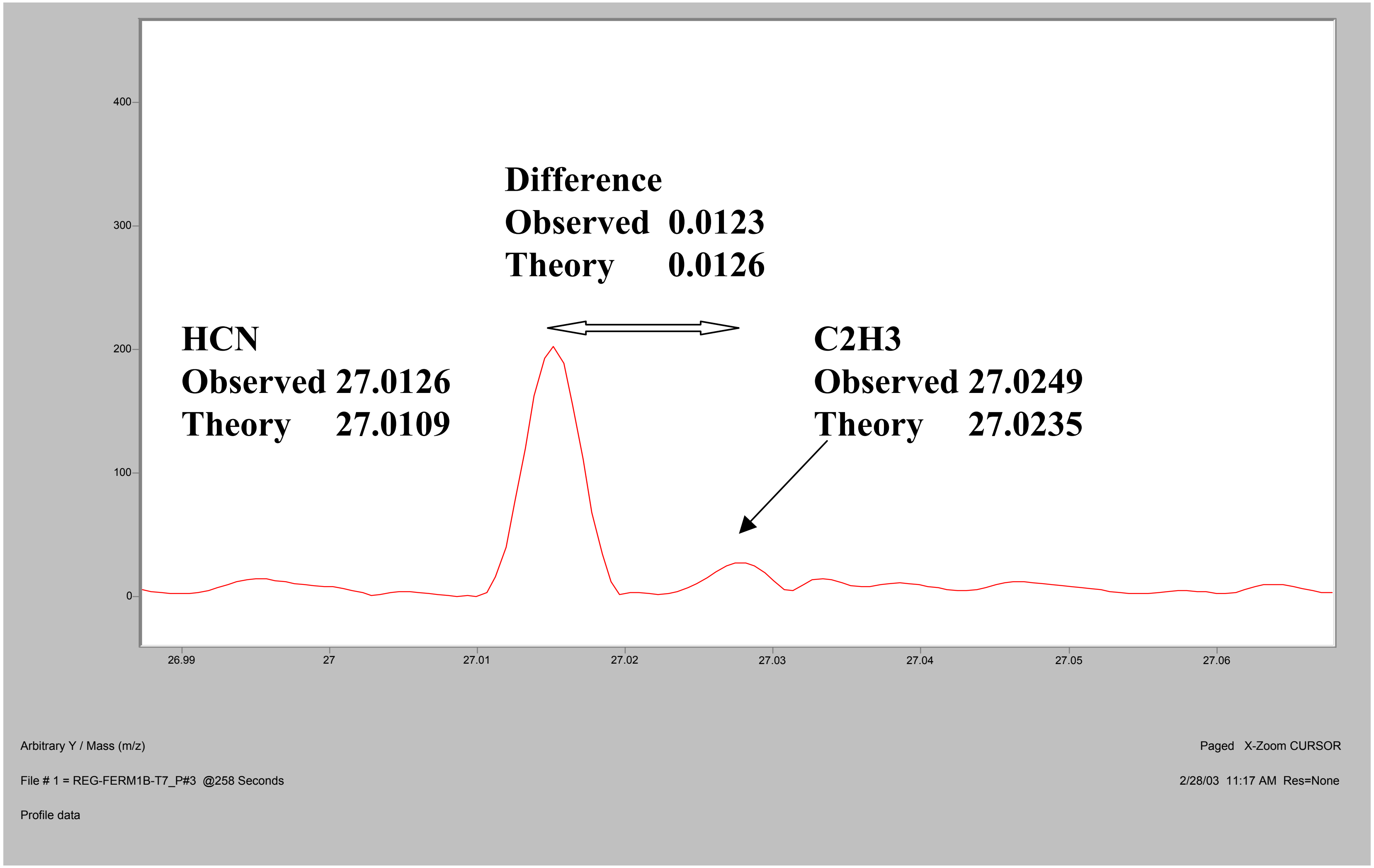
SIEMENS

Fermenter 2
m/z 17



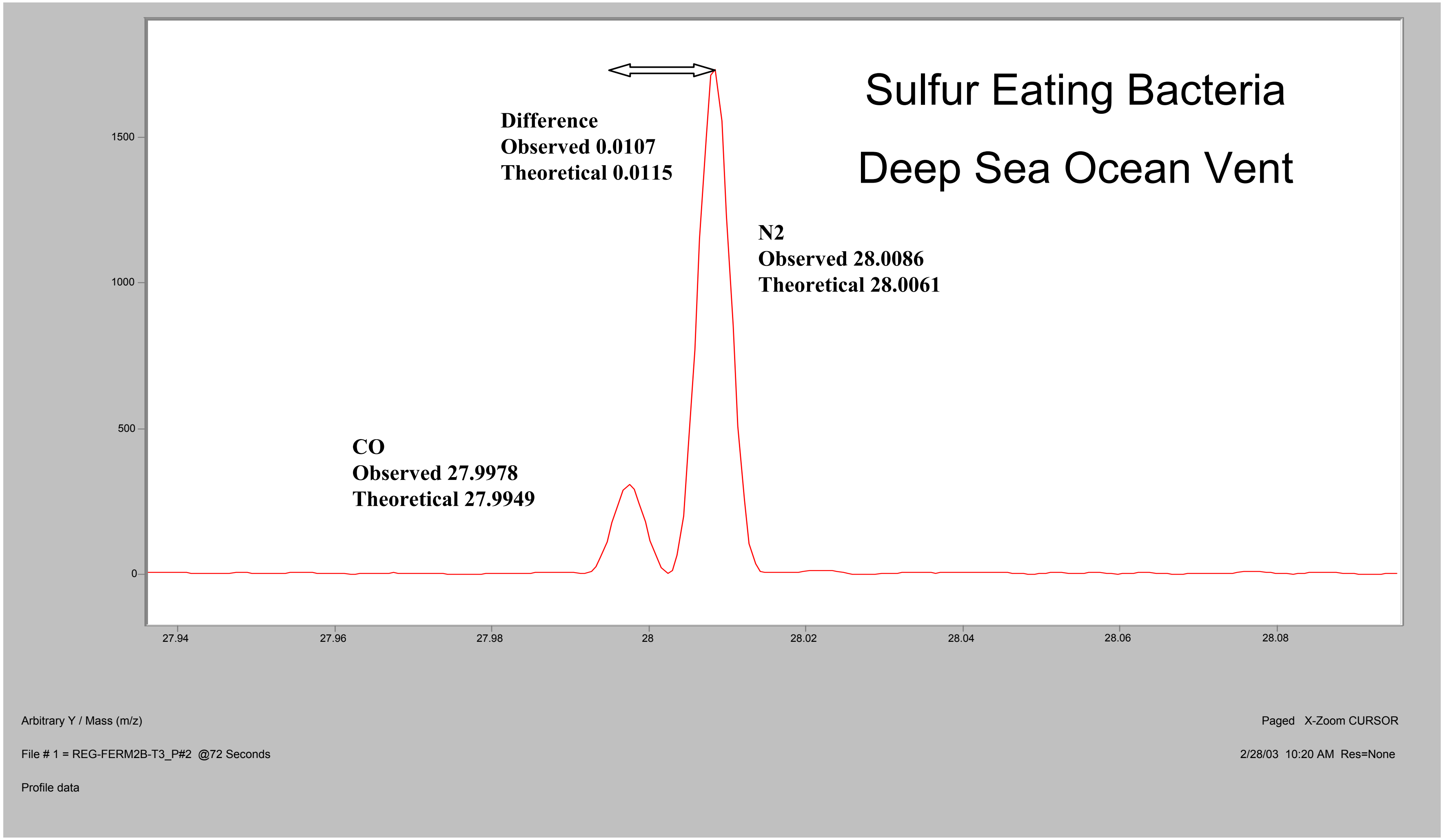
Fermenter 2

m/z 27



Fermenter 3

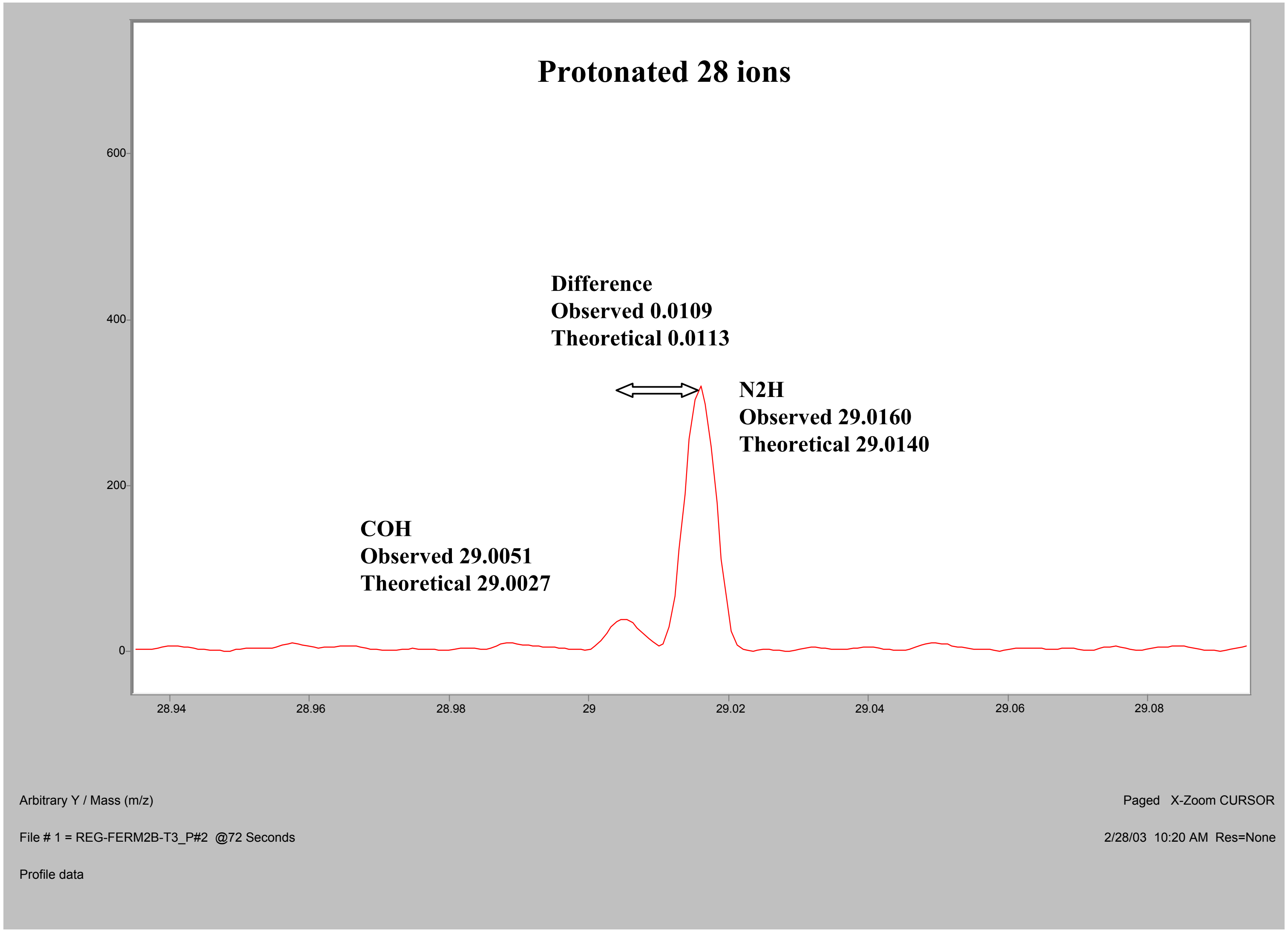
m/z 28



SIEMENS

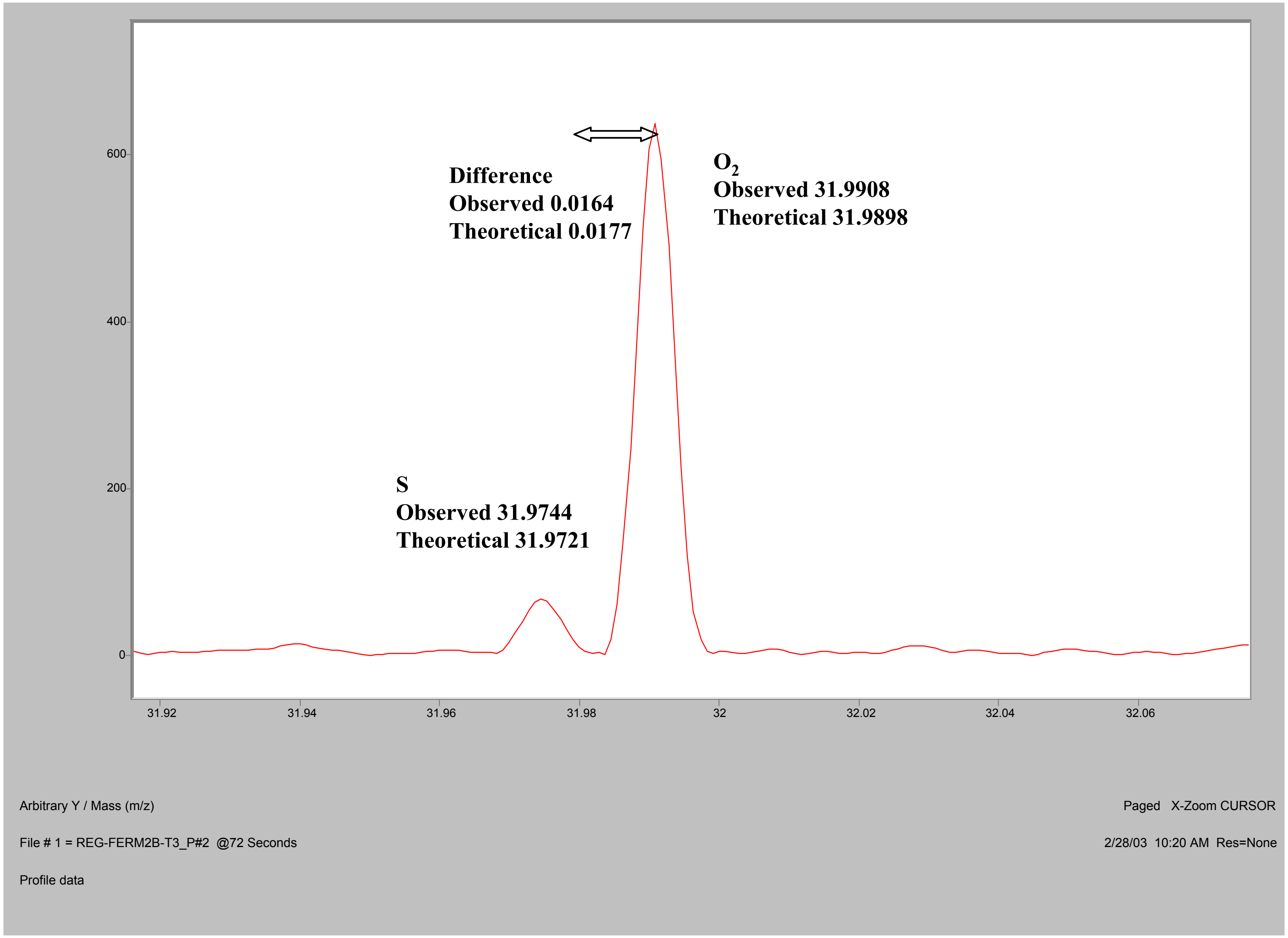
Fermenter 3

29 AMU



Fermenter 3

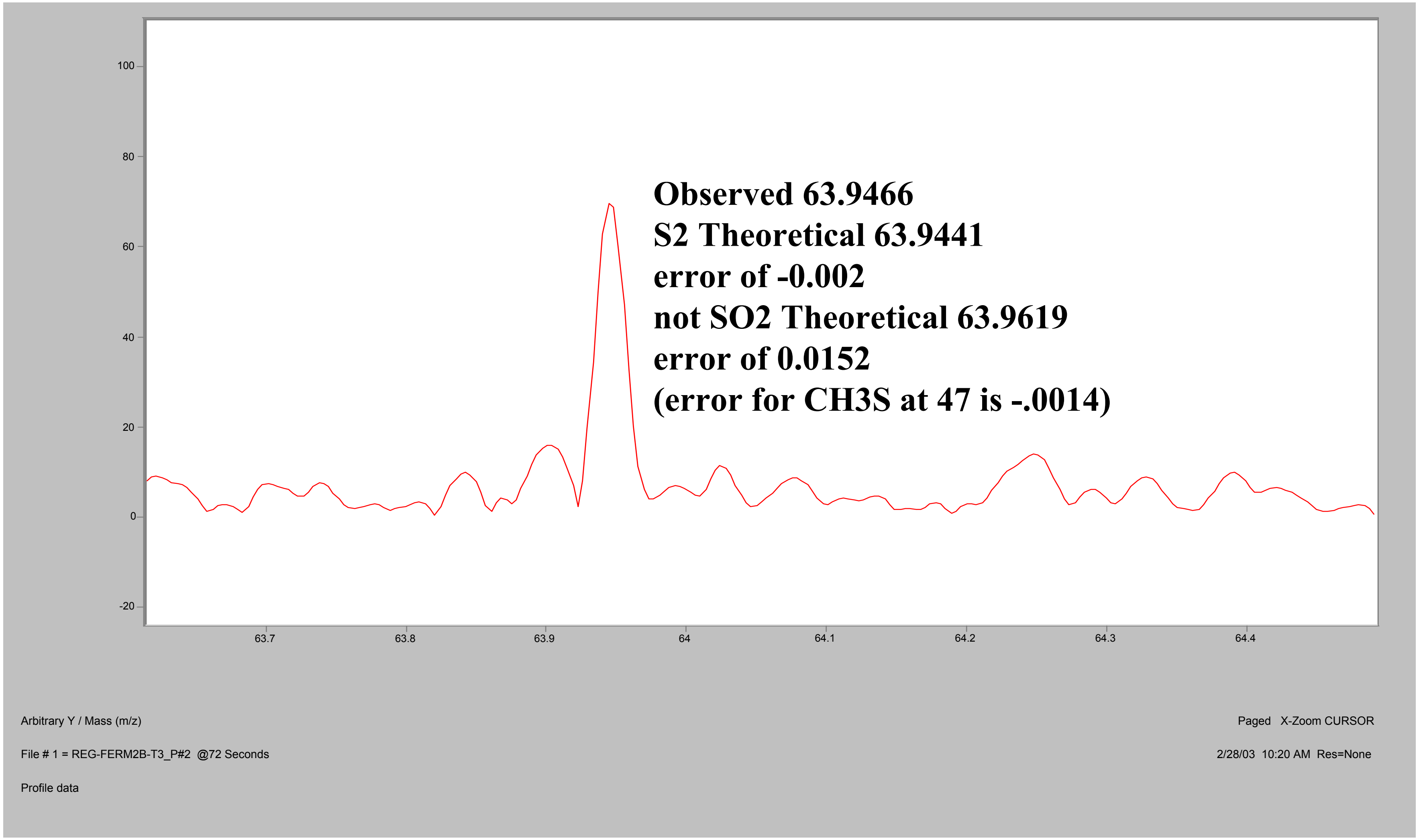
32 AMU



SIEMENS

Fermenter 3

m/z 64



observed	theory	Adjusted Diff.	fragment	assignment
14.0171	14.0031	0.0014	N	N2
15.0414	15.0235	-0.0024	CH3	
16.0137	15.9949	-0.0018	O	O2
16.0489	16.0313	-0.0006	CH4	CH4
17.0228	17.0027	-0.0015	OH	H2O
18.0319	18.0106	-0.0010	H20	H2O
19.0429			?	
20.0061	19.9812	-0.0011	Ar++	Ar
26.0536	26.0157	-0.0021	C2H2	Ethane
27.0517	27.0189	0.0052	HCN	HCN
27.0634	27.0234	-0.0020	C2H3	Ethane
28.0436	27.9949	0.0027	CO	CO
28.0504	28.0061	-0.0153	N2	N2
29.0492	29.0027	-0.0040	COH	COH
29.0594	29.014	-0.0028	N2H	N2H
30.0456	29.998	-0.0027	NO	NO
32.0428	31.9898	-0.0032	O2	O2
39.095	39.0234	-0.0027	C3H3	
40.0369	39.9624	-0.0028	Ar	
41.1163	41.0391	-0.0022	C3H5	
42.1271	42.047	-0.0020	C3H6	
43.1023	43.01839	-0.0028	CH3O	
44.0795	43.9898	-0.0055	CO2	
45.0866	44.9977	-0.0014	CHO2	
53.1565	53.0391	-0.0017	C4H5	
55.1796	55.0548	-0.0014	C4H7	
56.1913	56.0626	-0.0014	C4H8	
58.179	58.0418	-0.0020	C3H6O	acetone
65.2052	65.0391	-0.0013	C5H5	benzene
67.2285	67.0547	0.0001	C5H7	
68.2394	68.0626	0.0017	C5H8	
70.2652	70.0783	0.0011	C5H10	cyclopentane?
78.2719	78.047	0.0027	C6H6	Benzene
91.3506	91.0548	0.0045	C7H7	Toluene
92.3709	92.0626	-0.0019	C7H8	Toluene
		0.00037	**4/10 of a millimass unit**	

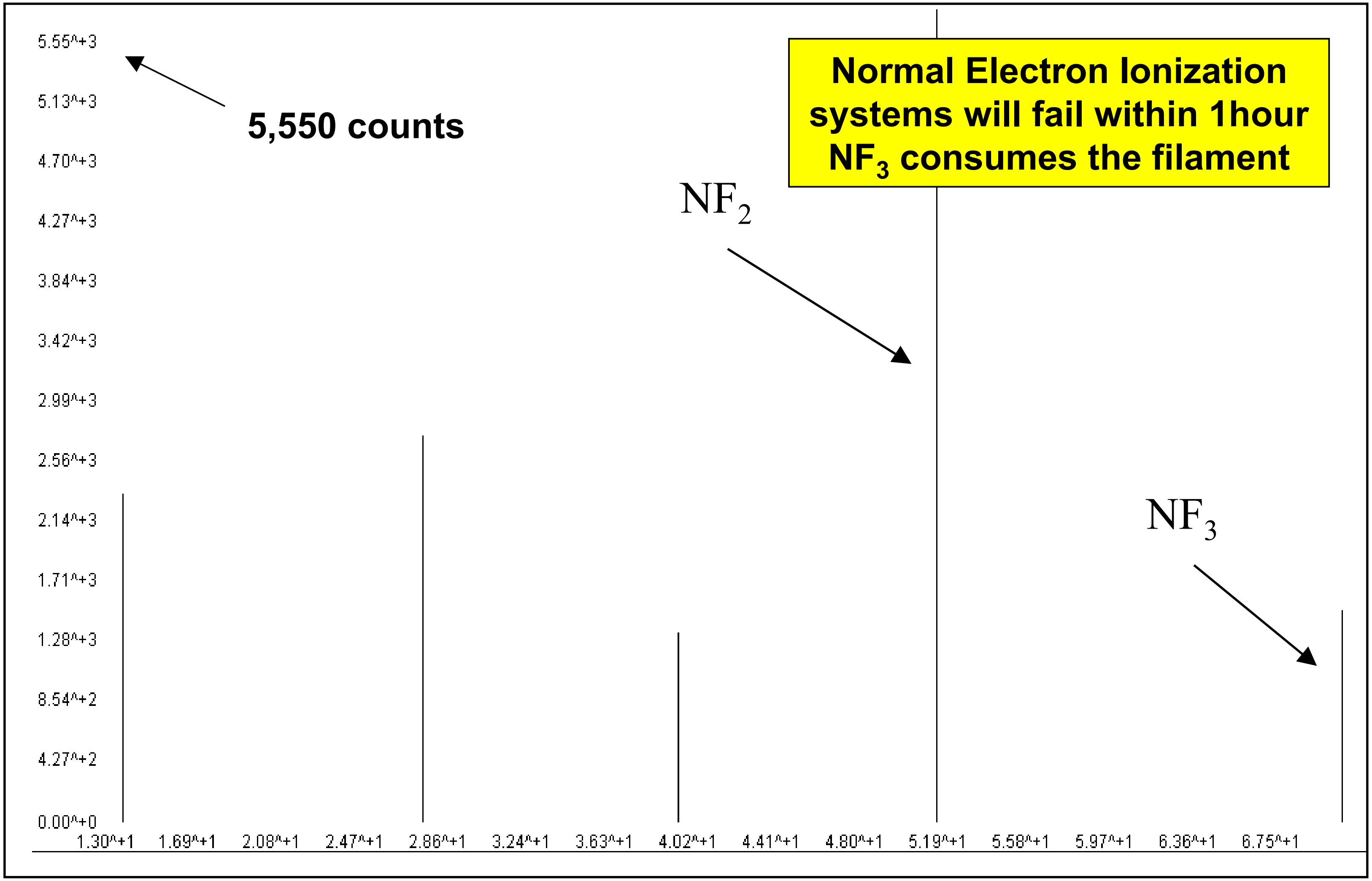
Data from a Cigarette “smoked” via an aspirator

35 ml volume

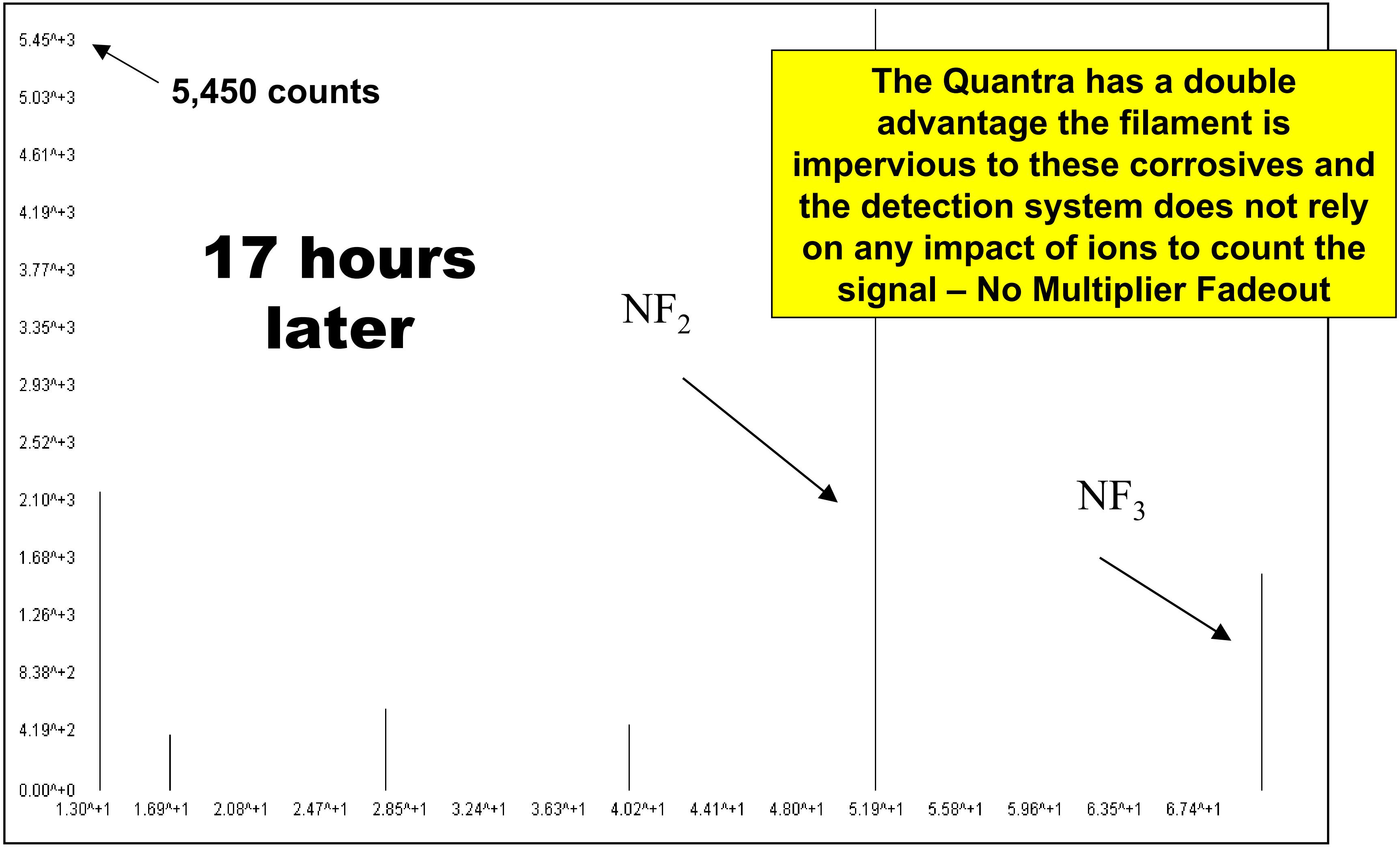
Average difference
0.4 Millimass Unit

Corrosives

Spectrum #1 - NF_3



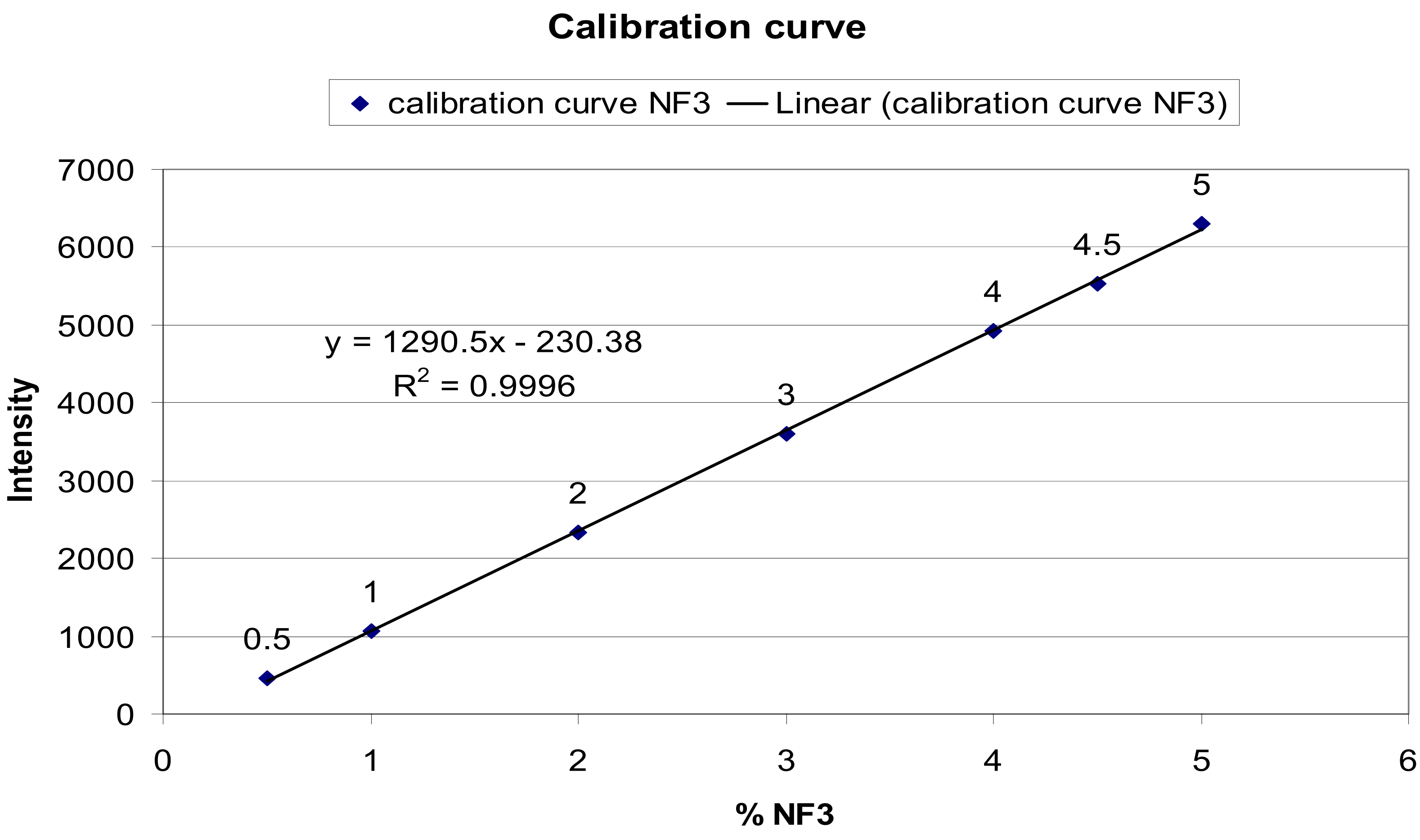
Spectrum #2000 - NF_3



SIEMENS

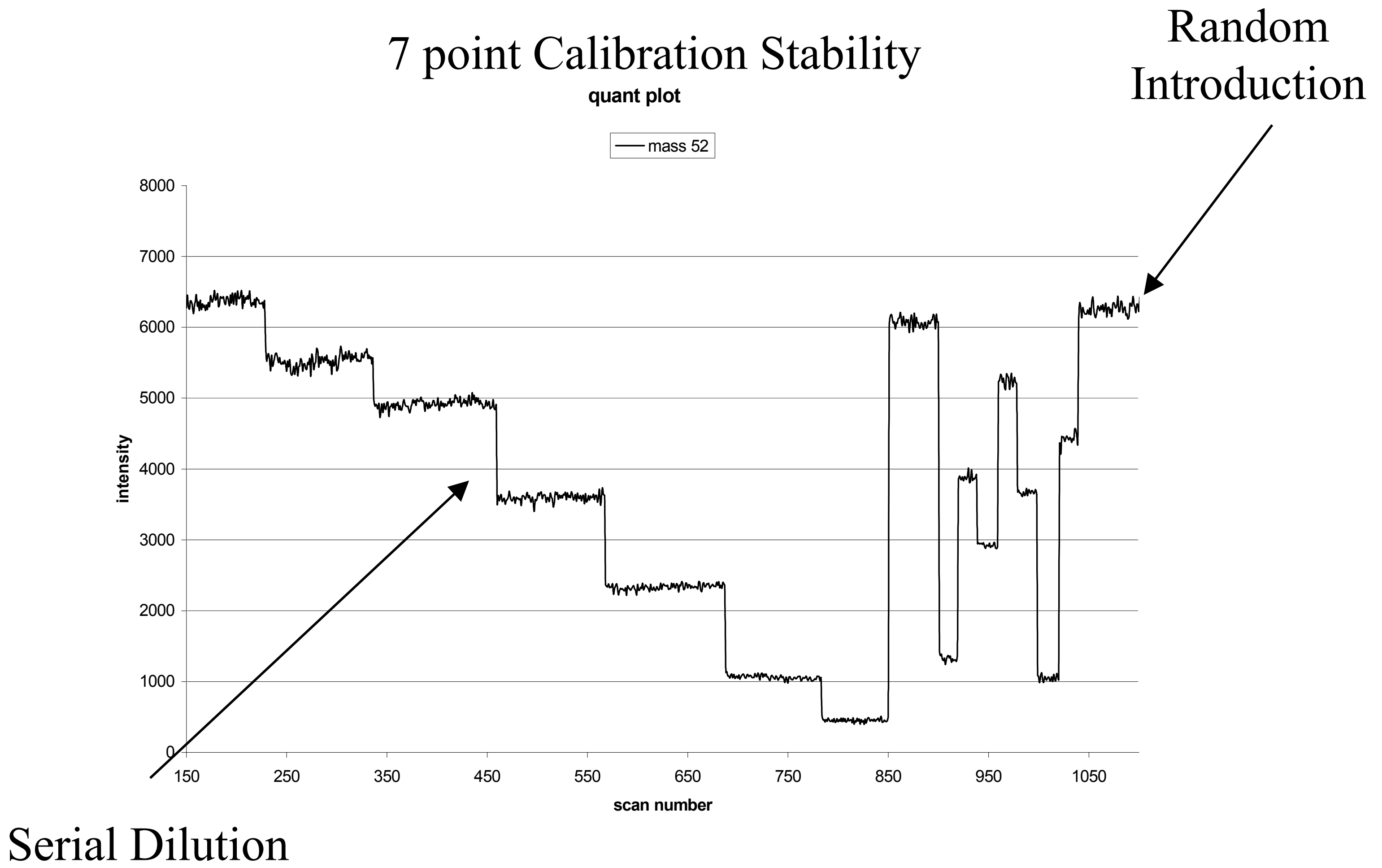
NF_3 in Nitrogen calibration

m/z 52 peak



SIEMENS

m/z 52 Peak from NF_3



Random validation points

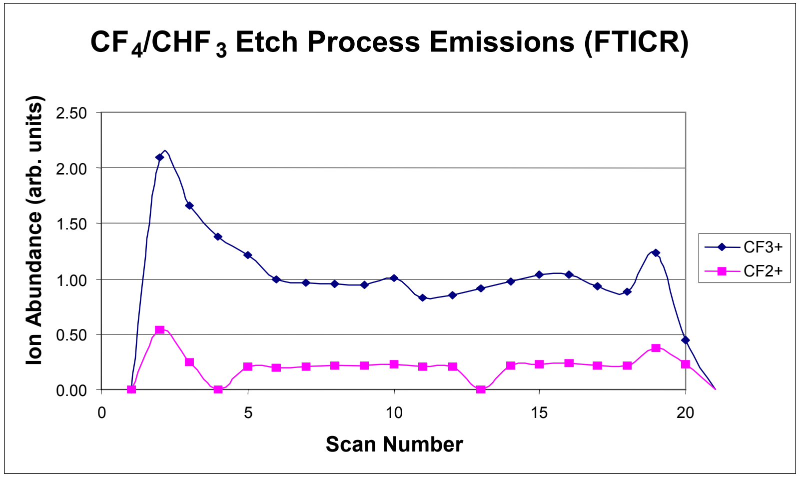
actual	calc	95% confidence		
% NF3	%NF3	Conc		RSD
1.25	1.21	1.28	1.14	3.51
3.33	3.19	3.26	3.11	1.33
2.56	2.45	2.49	2.40	0.91
4.38	4.24	4.35	4.13	1.35
3.15	3.02	3.07	2.97	0.85
1.01	0.99	1.05	0.93	3.76
3.70	3.61	3.73	3.49	1.73
5.00	5.01	5.13	4.89	1.28

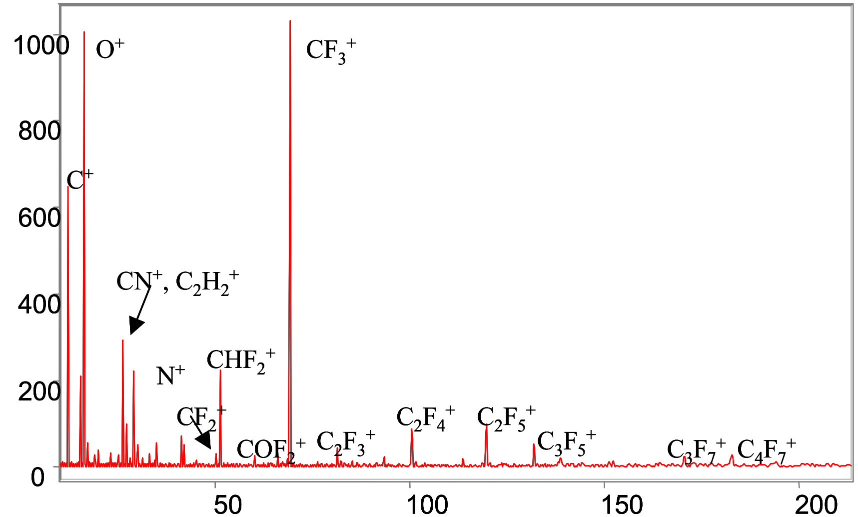
1 – 4% RSD

Semiconductor Gas Sampling

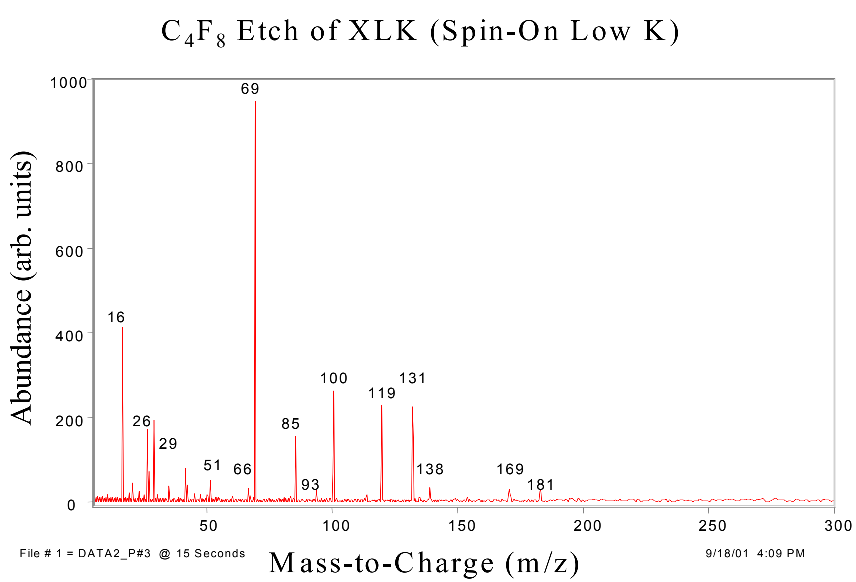
Semiconductor applications (Etch process and abatement) involving highly corrosive fluorocarbon species were readily analyzed with the Quantra Mini FTMS. Response times are similar to FTIR (data presented in part at 50th ASMS - 2002).

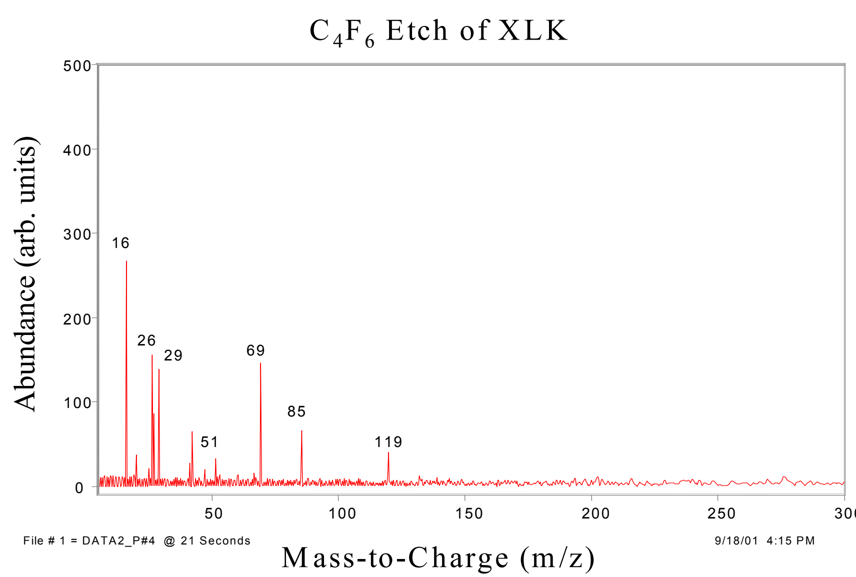
Once again the design features of this miniature FTMS allow aggressive and corrosive species to be directly sampled with no ill effects to the mass spectrometer. Placement of the filament, very low filament current, very high vacuum, extremely small sample volume and fast pumping are equally important in this design scheme and yield an extremely rugged system.



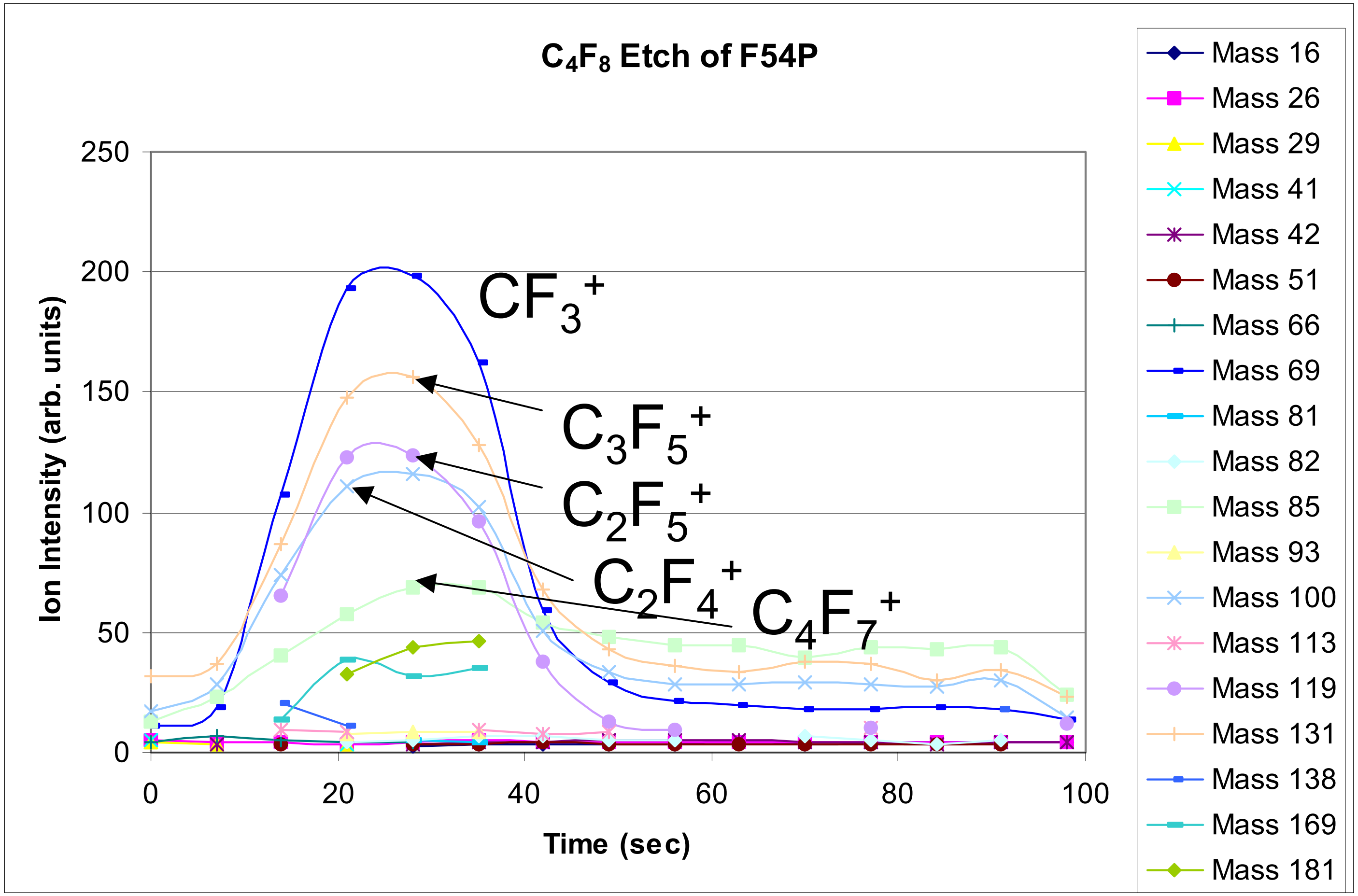


FTMS Spectrum During $CF_4/CHF_3/Ar$ Etch Process

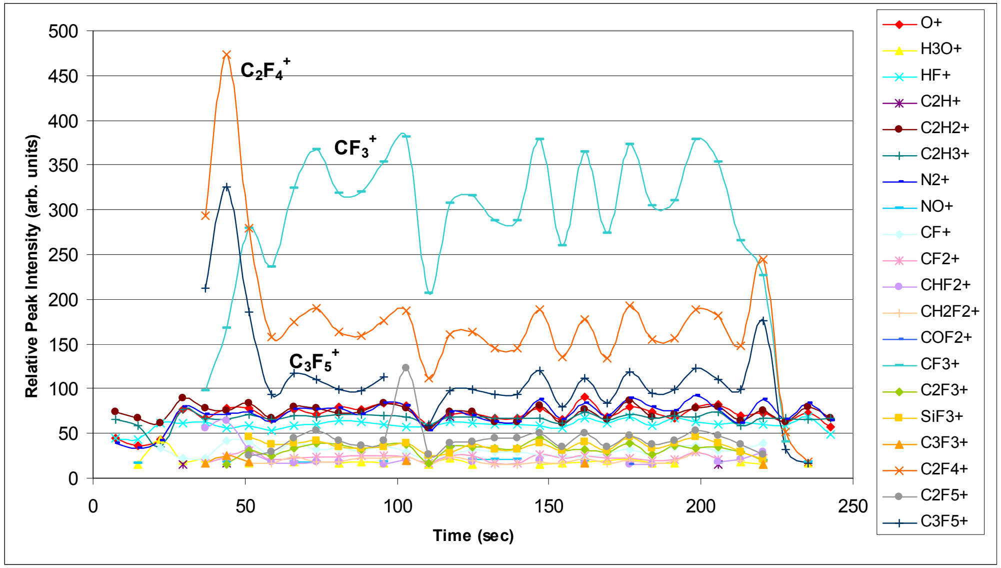




Process Monitoring During High-Density Plasma Etch

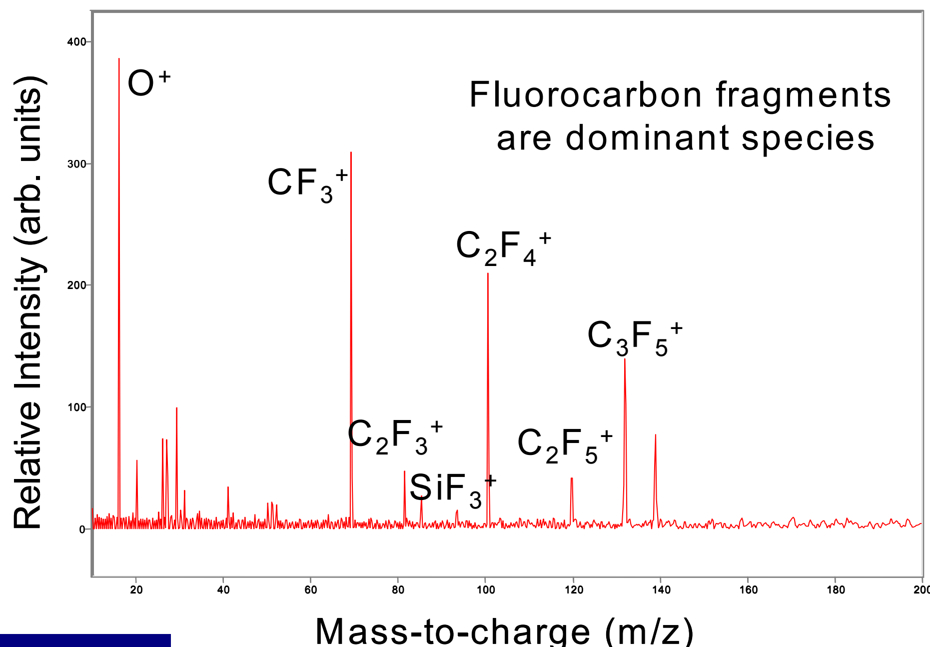


Portability and effective sample introduction make the Quantra a particularly useful instrument for process monitoring. Generally it is impervious to aggressive species that will damage filaments or electron multipliers.



Emission Trend Plot During an Etch Process

Very corrosive Fluorocarbon species – analyzed with no adverse affects to mass spectrometer performance



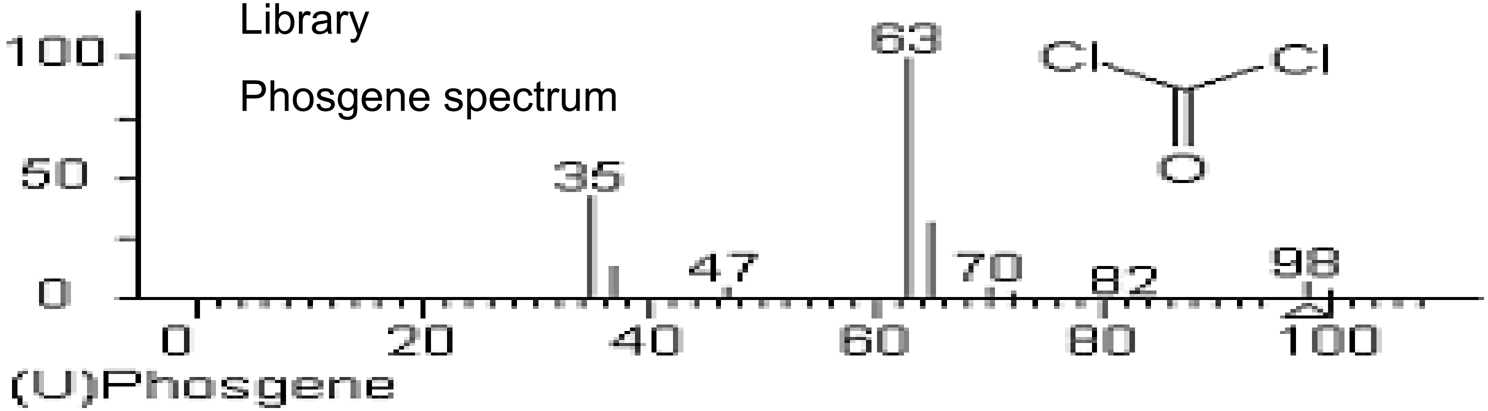
Predominance of Fluorocarbon species here indicated a plasma instability – this was corroborated by FTIR

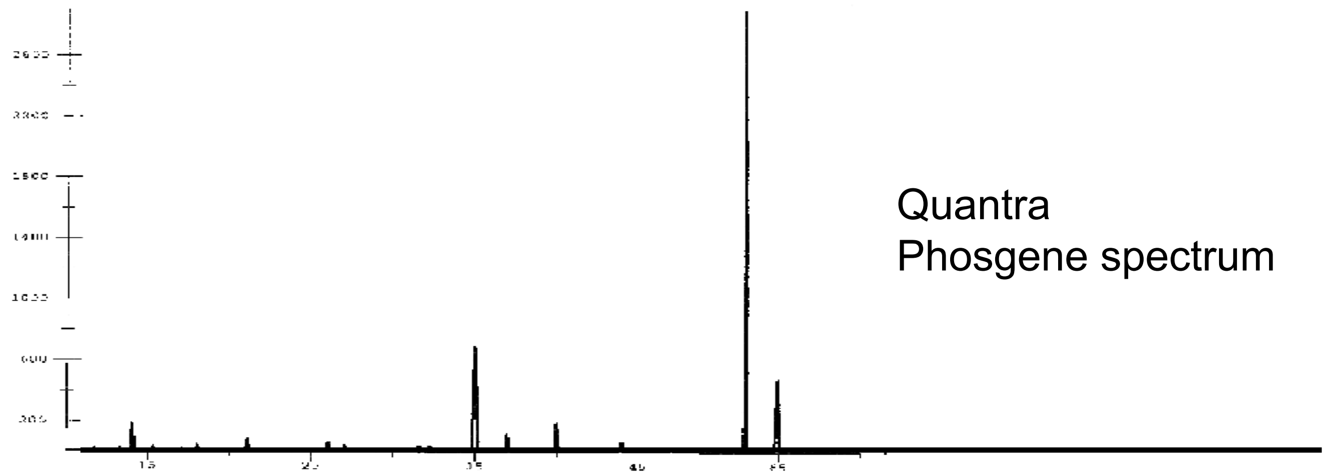
SIEMENS

Courtesy of Motorola APRDL – Austin Texas

Phosgene Measurement

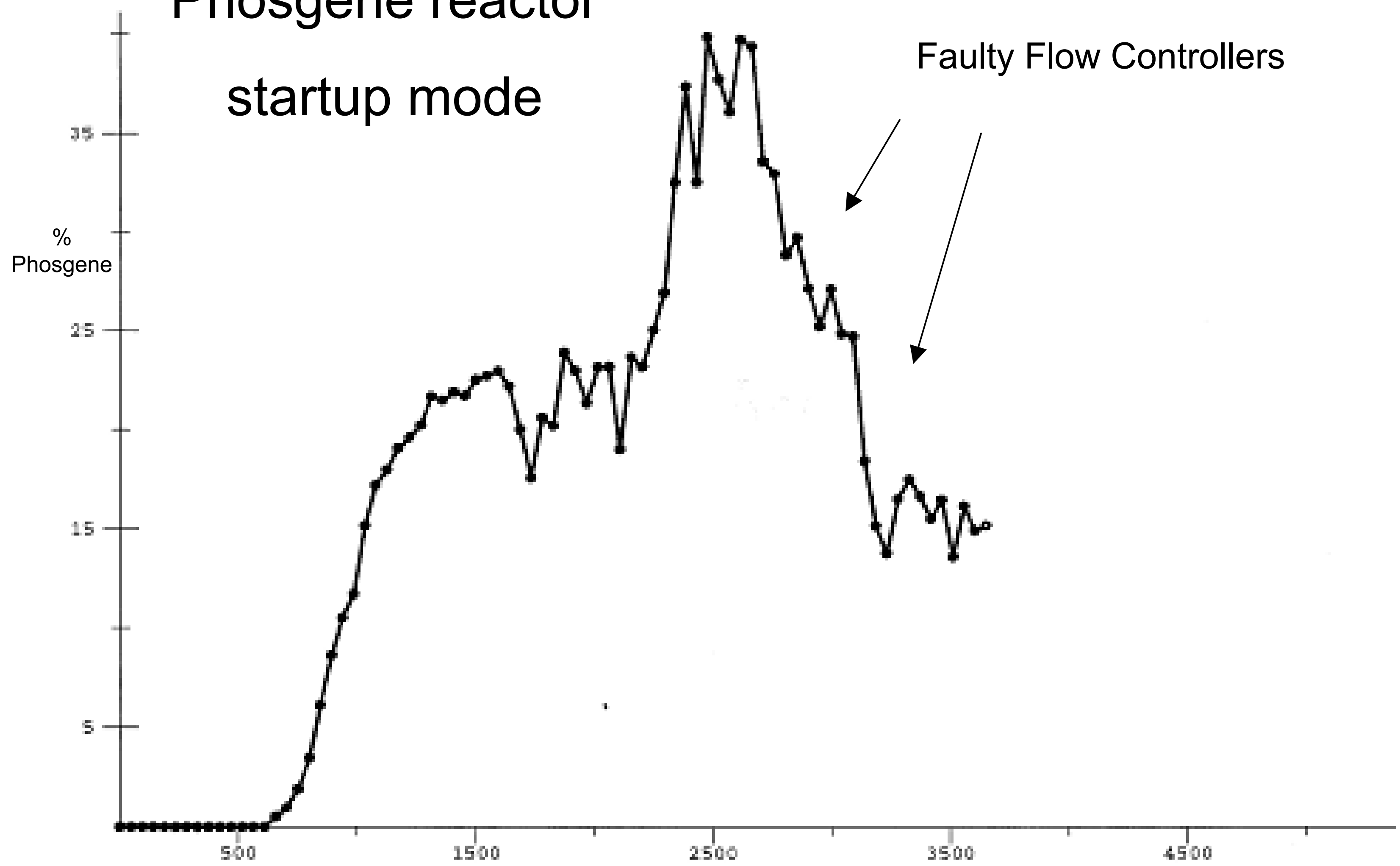
Phosgene



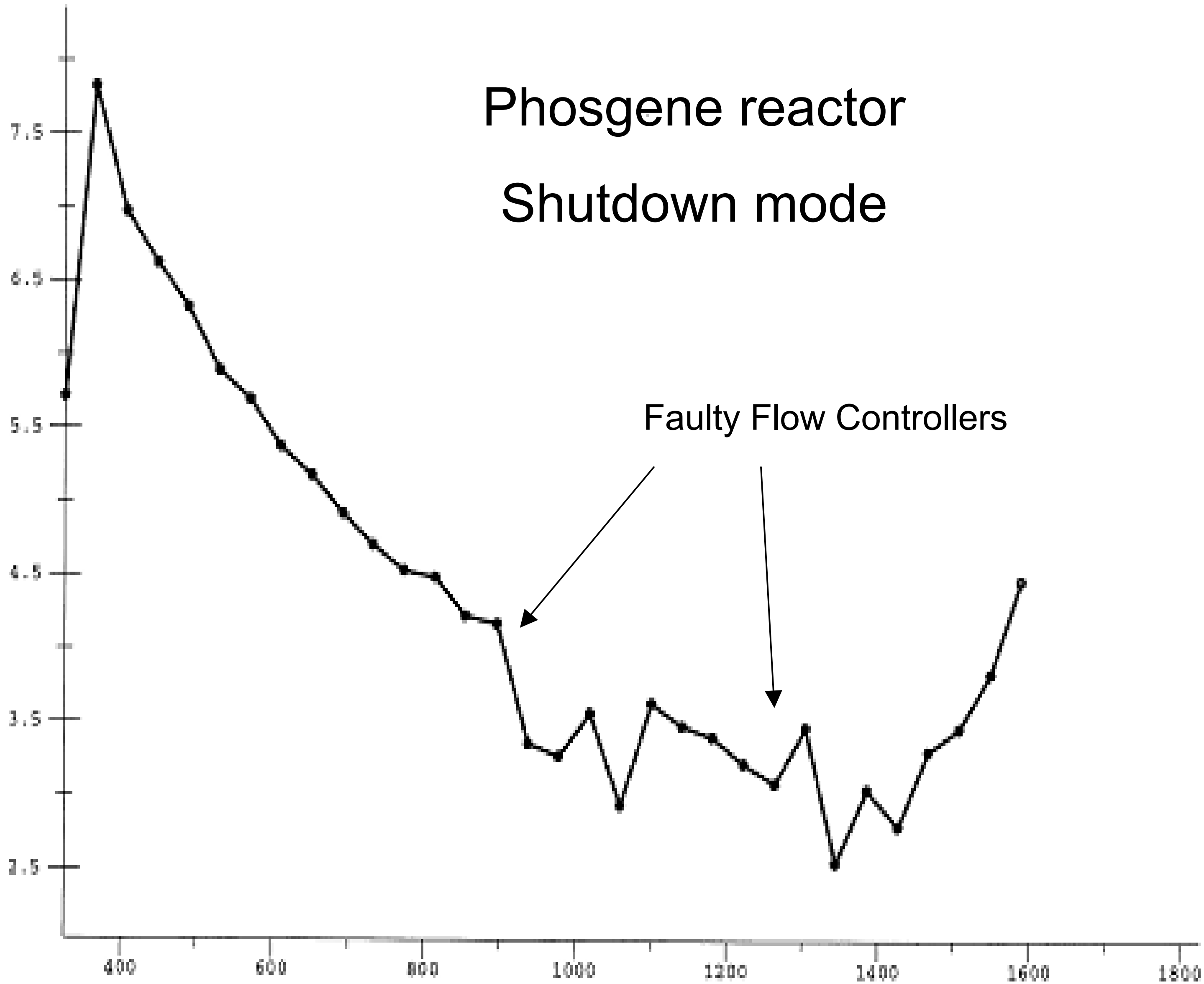


Library match of the low resolution Quantra spectrum was quite good.

Phosgene reactor startup mode



SIEMENS



Phosgene reactor
Shutdown mode
Faulty Flow Controllers
7.5
6.5
5.5
4.5
3.5
2.5
400
600
800
1000
1200
1400
1600
1800

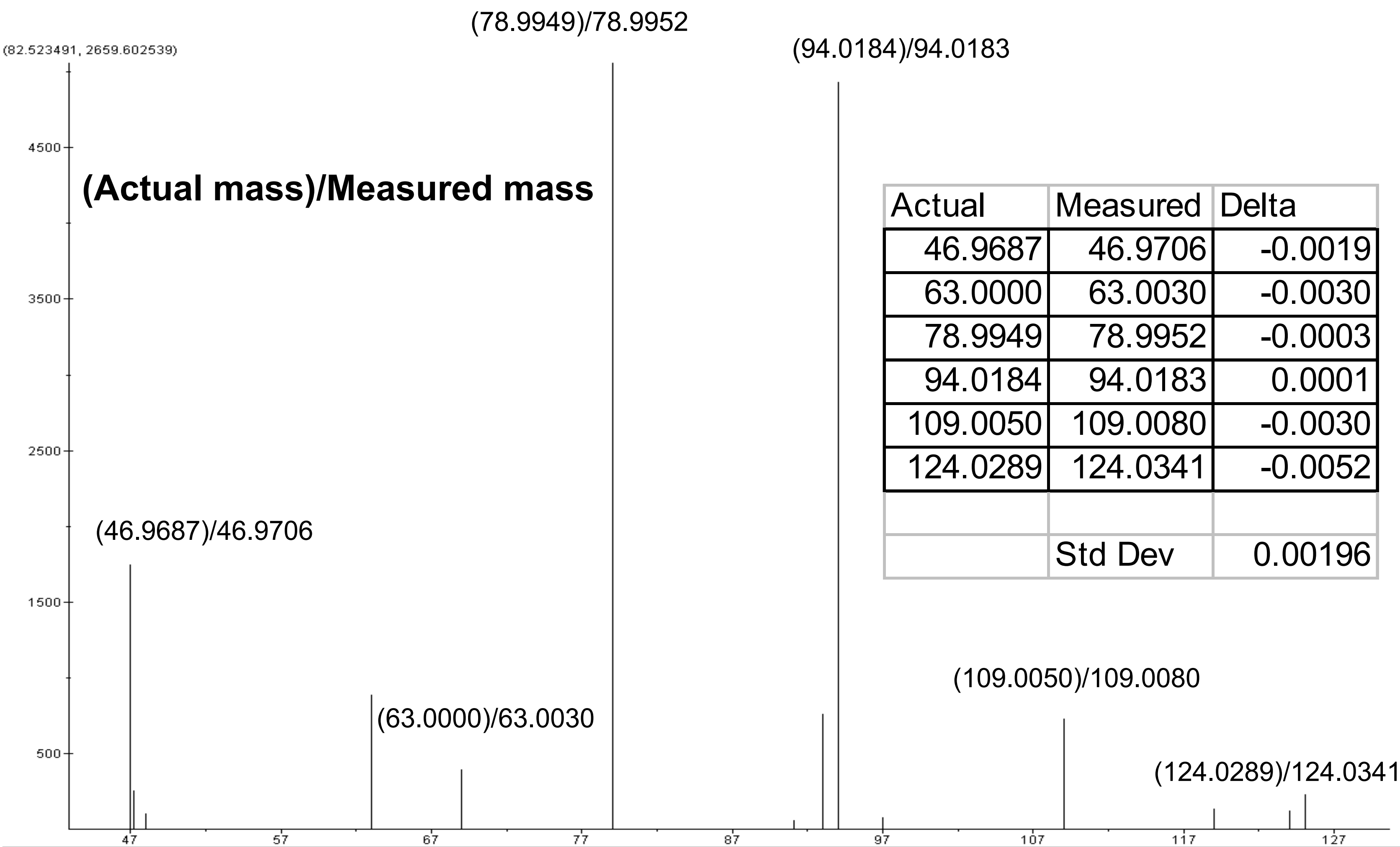
SIEMENS

Chemical Warfare Surrogates

DMMP, DBBP

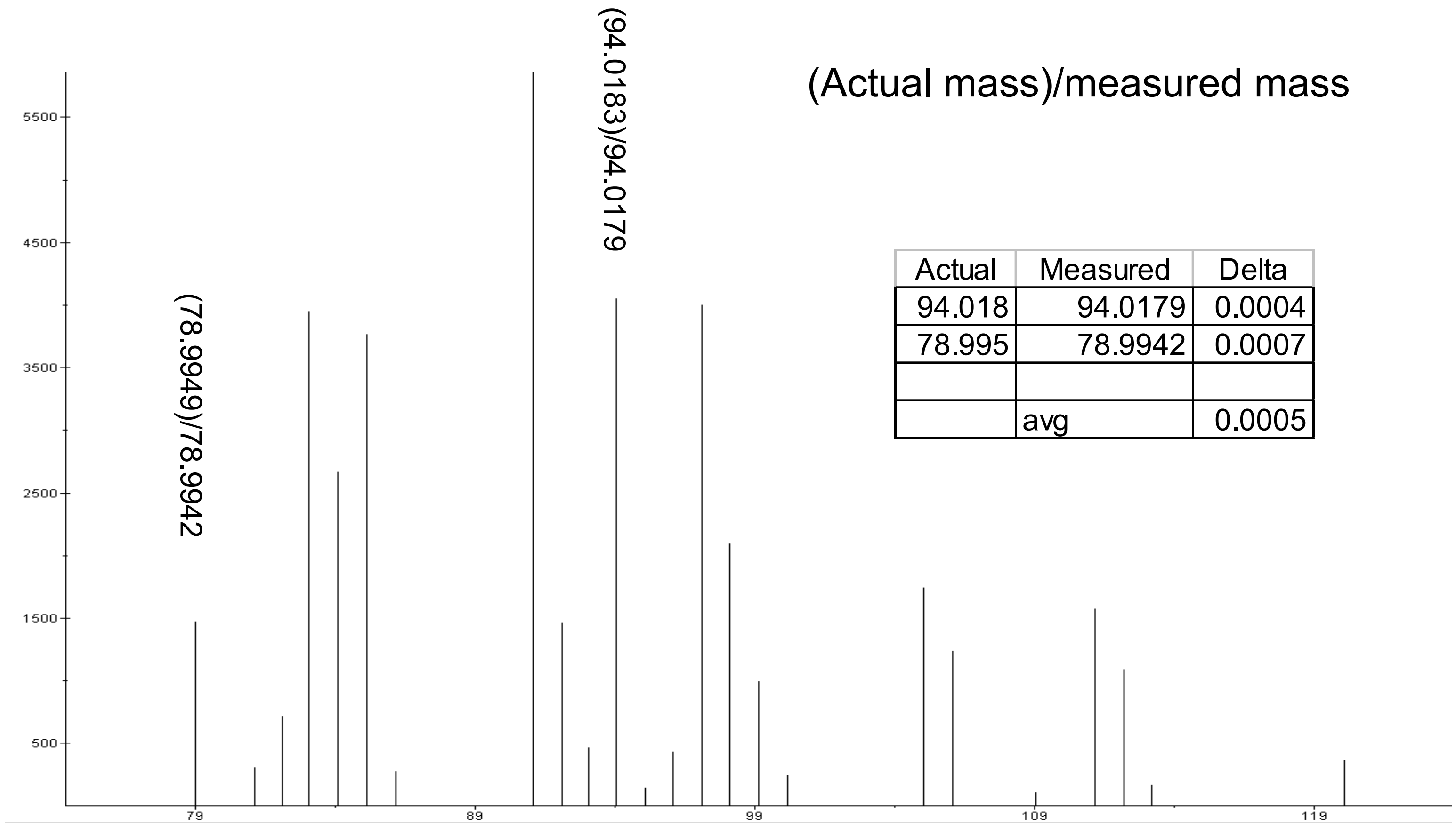
Chemical Warfare surrogates were obtained from Aldrich. Samples of DMMP (Dimethylmethylphosphonate $C_3H_9PO_3$) and DBBP (Dibutylbutylphosphonate $C_{12}H_{27}PO_3$) were analyzed using a direct liquid inlet. The samples were dissolved in methanol and a few microliters were injected into the mass spectrometer. Additional methanol laced DMMP and DBBP samples were added to a gasoline matrix. The aim of this experiment was two fold: 1. Determine what accuracy of mass measurement could be obtained on these compounds, and 2. Determine whether that accuracy would be sufficiently high enough to "target" these surrogates using their exact mass in a complex matrix.

DMMP Dimethylmethylphosphonate $C_3H_9PO_3$ spectrum



Actual	Measured	Delta
46.9687	46.9706	-0.0019
63.0000	63.0030	-0.0030
78.9949	78.9952	-0.0003
94.0184	94.0183	0.0001
109.0050	109.0080	-0.0030
124.0289	124.0341	-0.0052
	Std Dev	0.00196

DMMP in a Gasoline Matrix

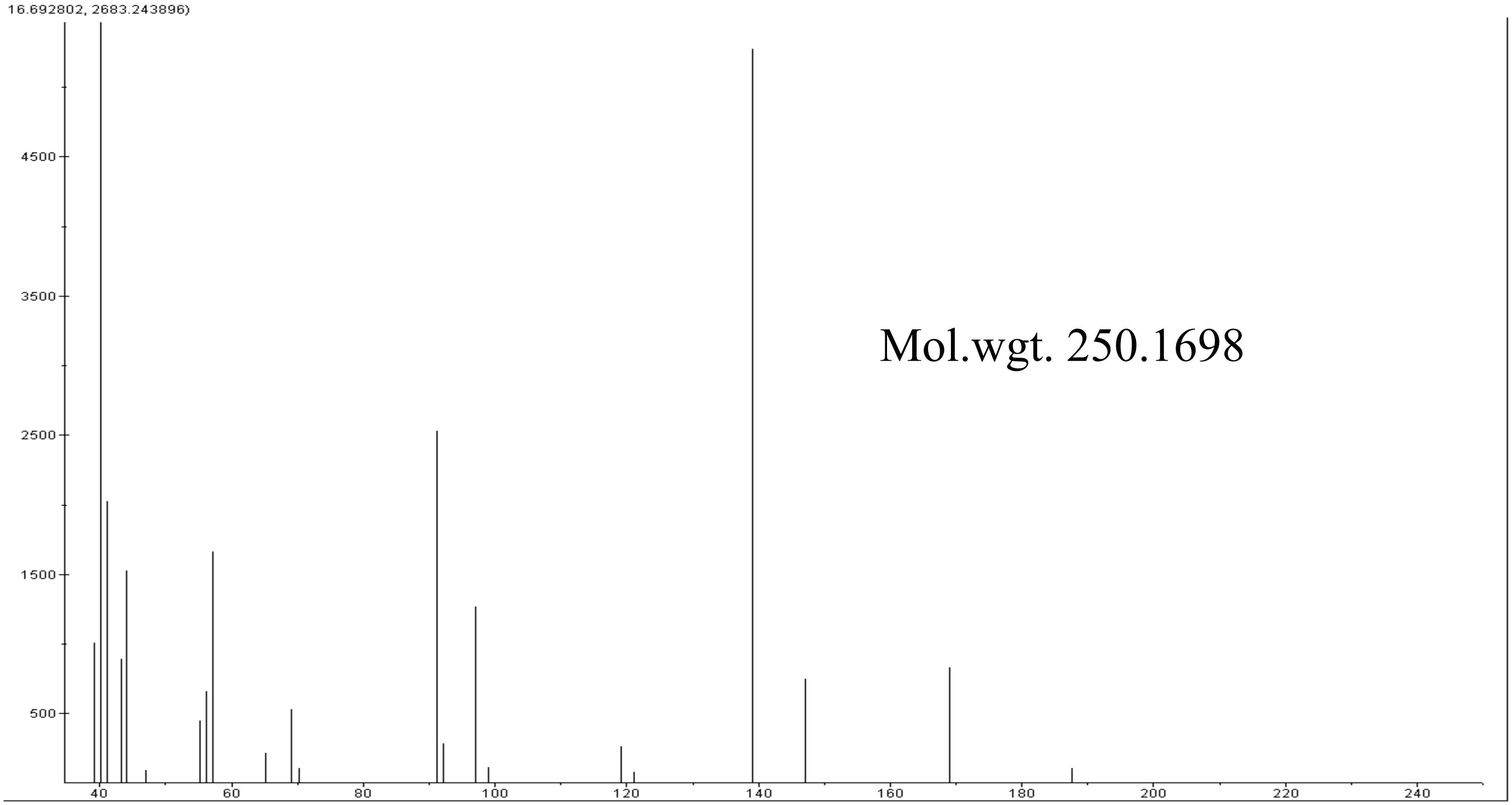


(Actual mass)/measured mass

Actual	Measured	Delta
94.018	94.0179	0.0004
78.995	78.9942	0.0007
	avg	0.0005

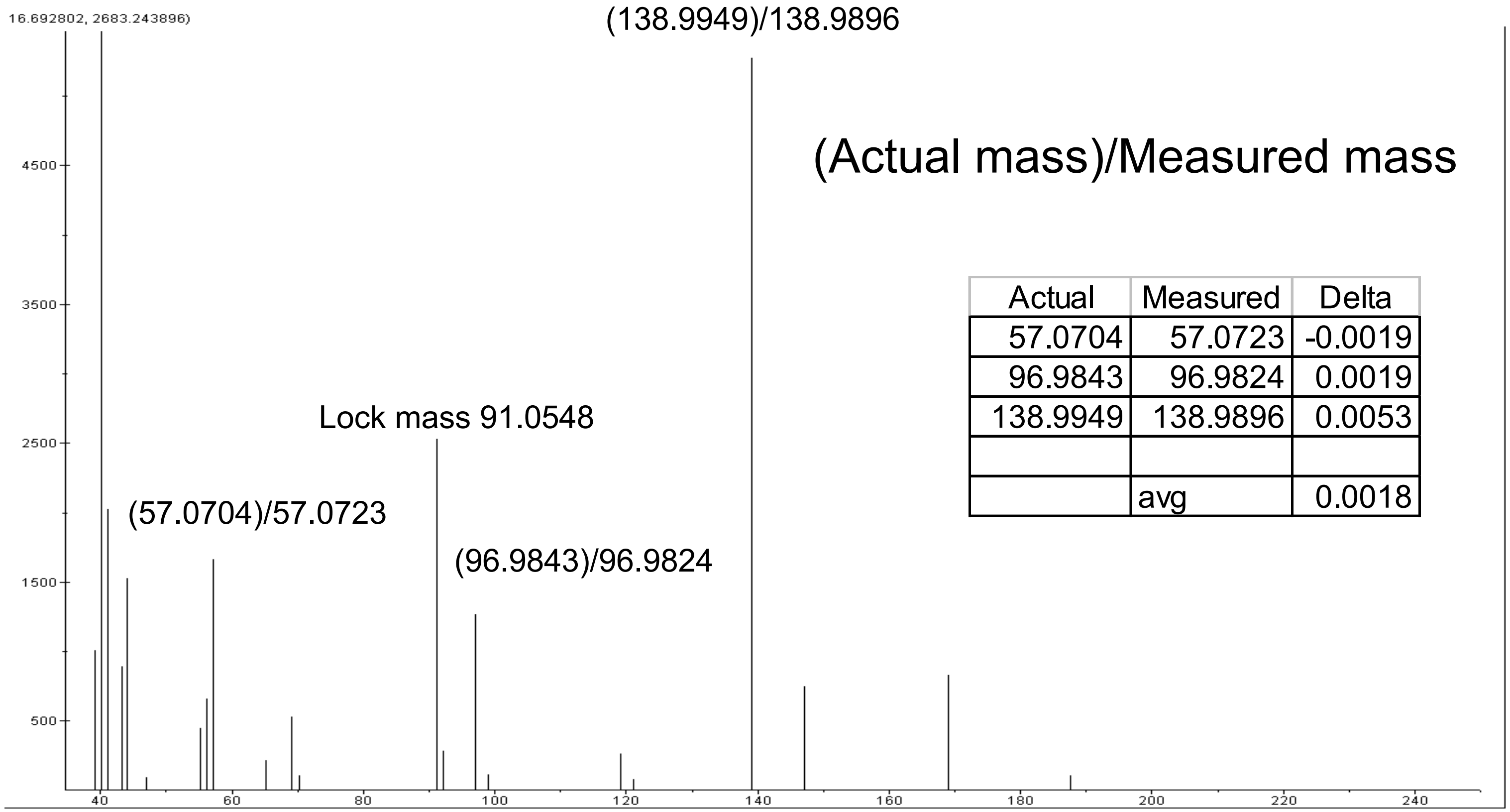
SIEMENS

DBBP Dibutylbutylphosphonate $C_{12}H_{27}PO_3$ Spectrum



DBBP Dibutylbutylphosphonate $C_{12}H_{27}PO_3$ Spectrum

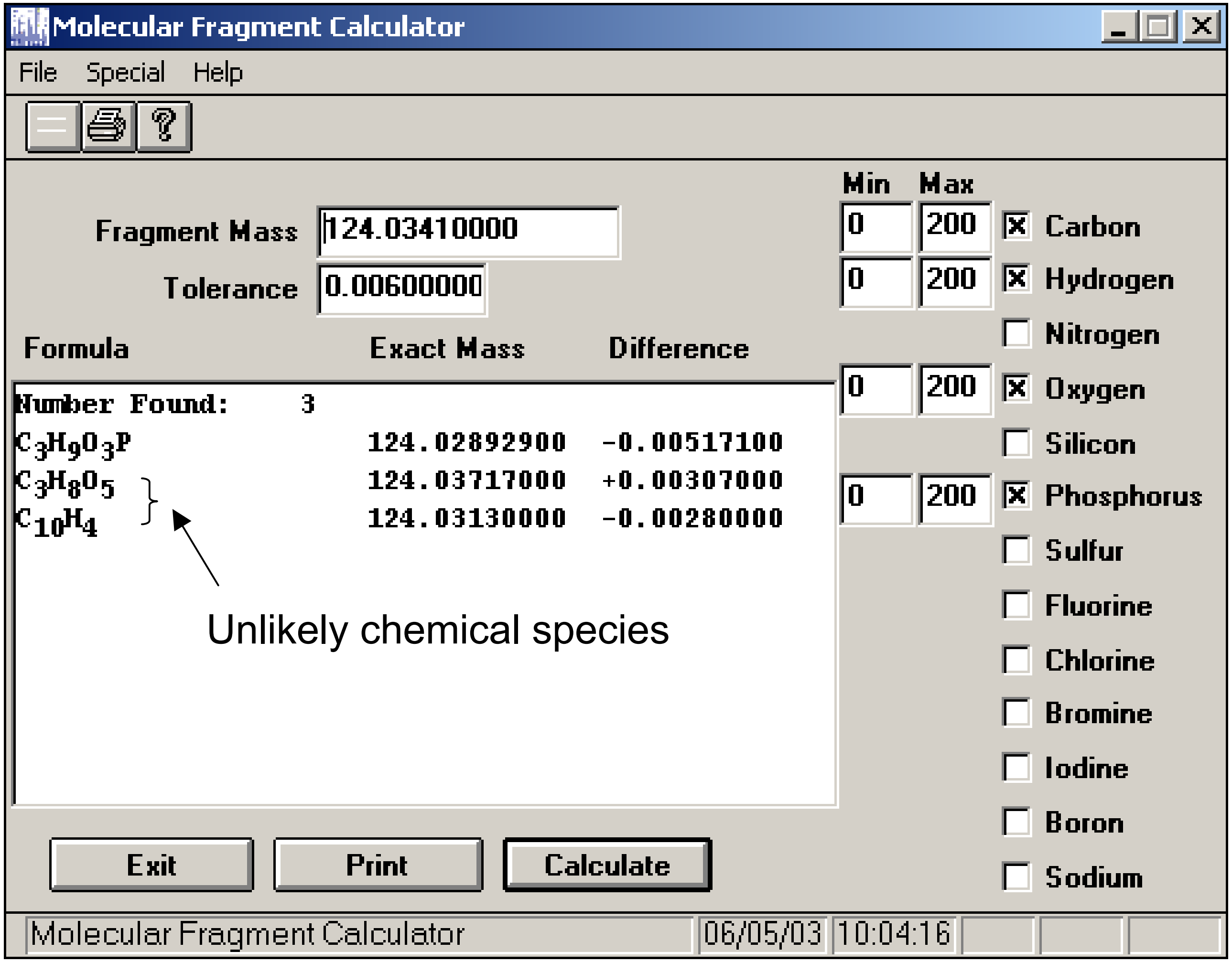
Hydrocarbon Matrix



Actual	Measured	Delta
57.0704	57.0723	-0.0019
96.9843	96.9824	0.0019
138.9949	138.9896	0.0053
	avg	0.0018

SIEMENS

DMMP



As can be seen from this typical exact mass fragment calculator, it is possible to "target" a compound such as DMMP, using a few millimass unit tolerance, thus drastically reducing the possible "hits" at any given mass. The mass accuracy provided by this mini FTMS is more than adequate for this type of an analysis.

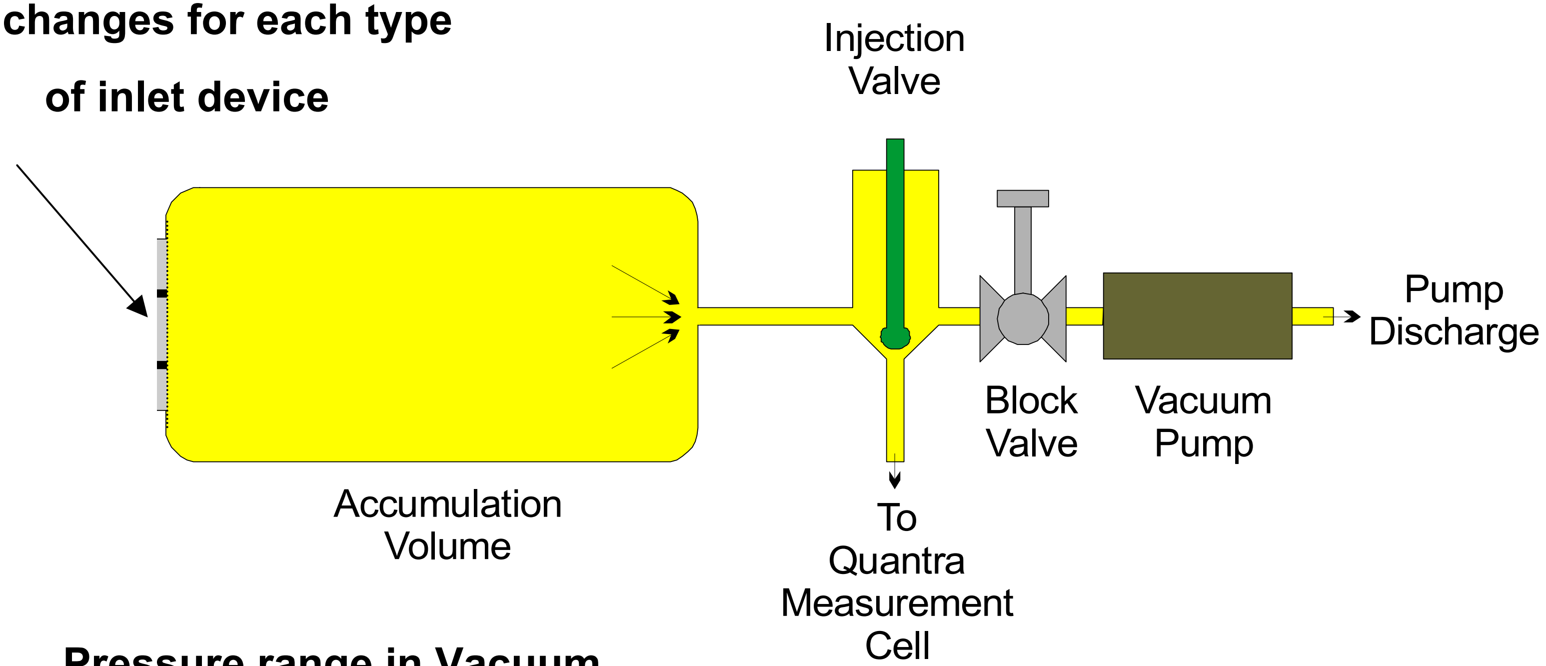
Vacuum inlet

- Adsorption/Desorption
- Membrane Probe
- Direct Exposure Probe
- Solids Probe
- Liquid Injection
- High Temperature Nozzle Inlet
- Cryo Trapping

Standard assembly for the Vacuum inlet System

- Accumulation volume with heater and controller
- Metering or block Valve
- Small Vacuum pump and Vacuum gauge system

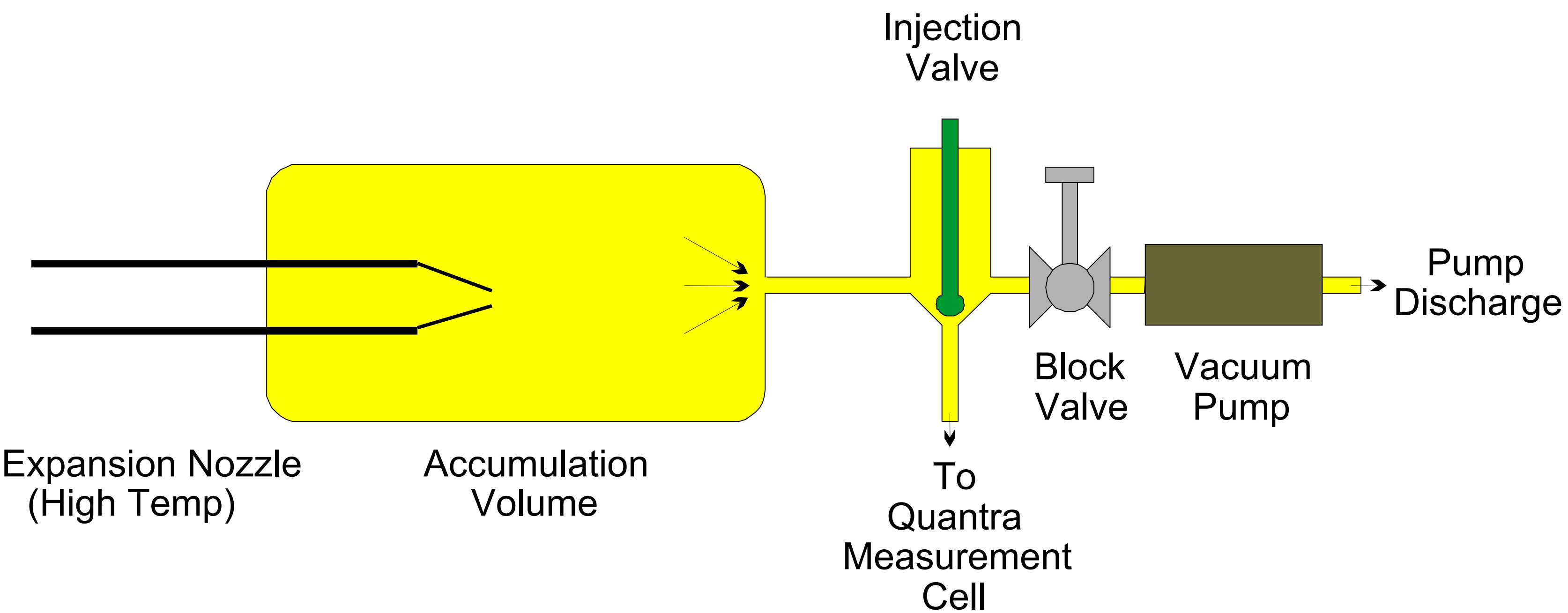
End changes for each type of inlet device



Pressure range in Vacuum inlet 1 – 10 torr

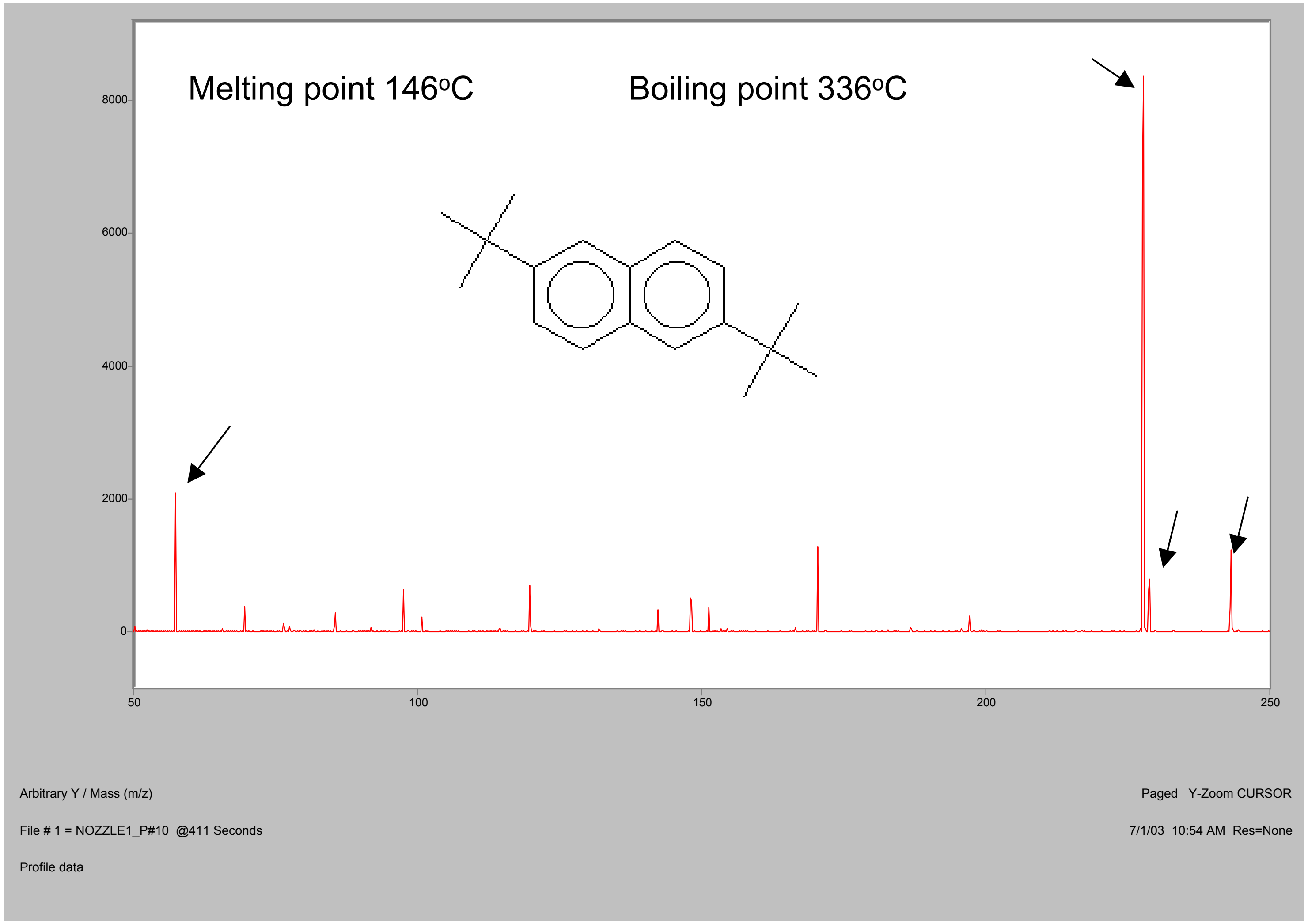
High Temperature Expansion Nozzle

(Molecular Leak)

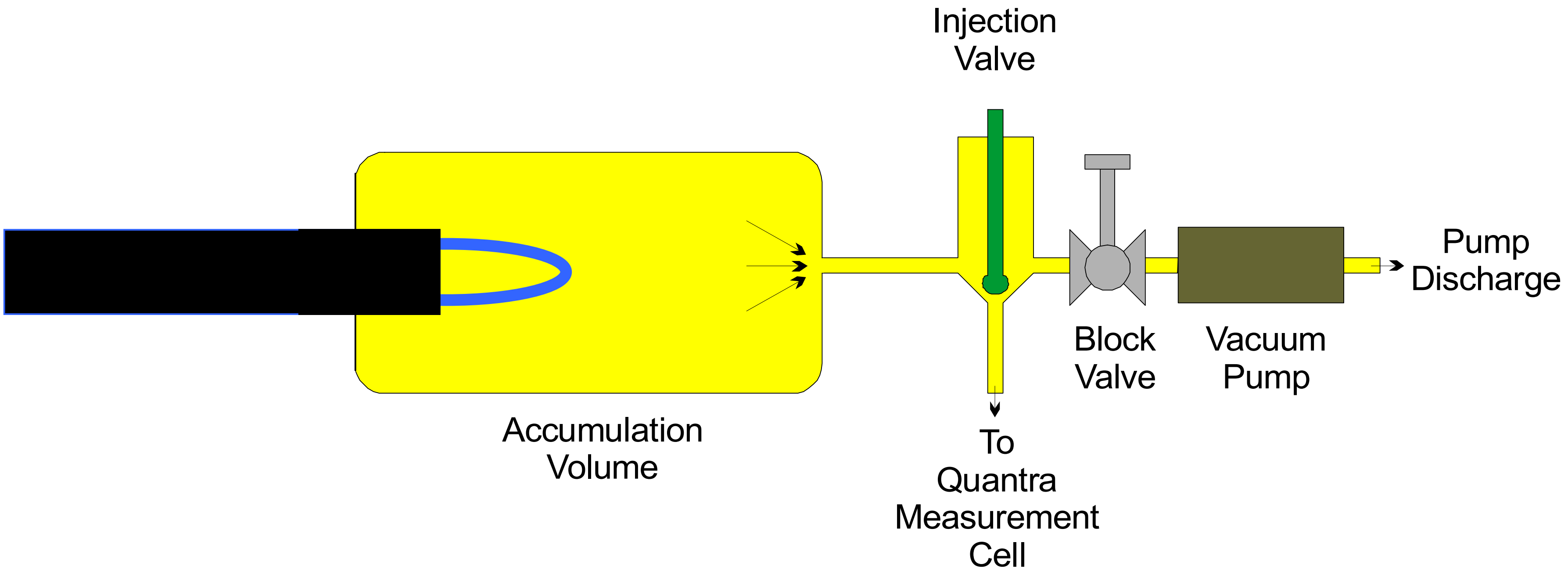


SIEMENS

2,6 di-tert-butylnapthalene
Using expansion nozzle



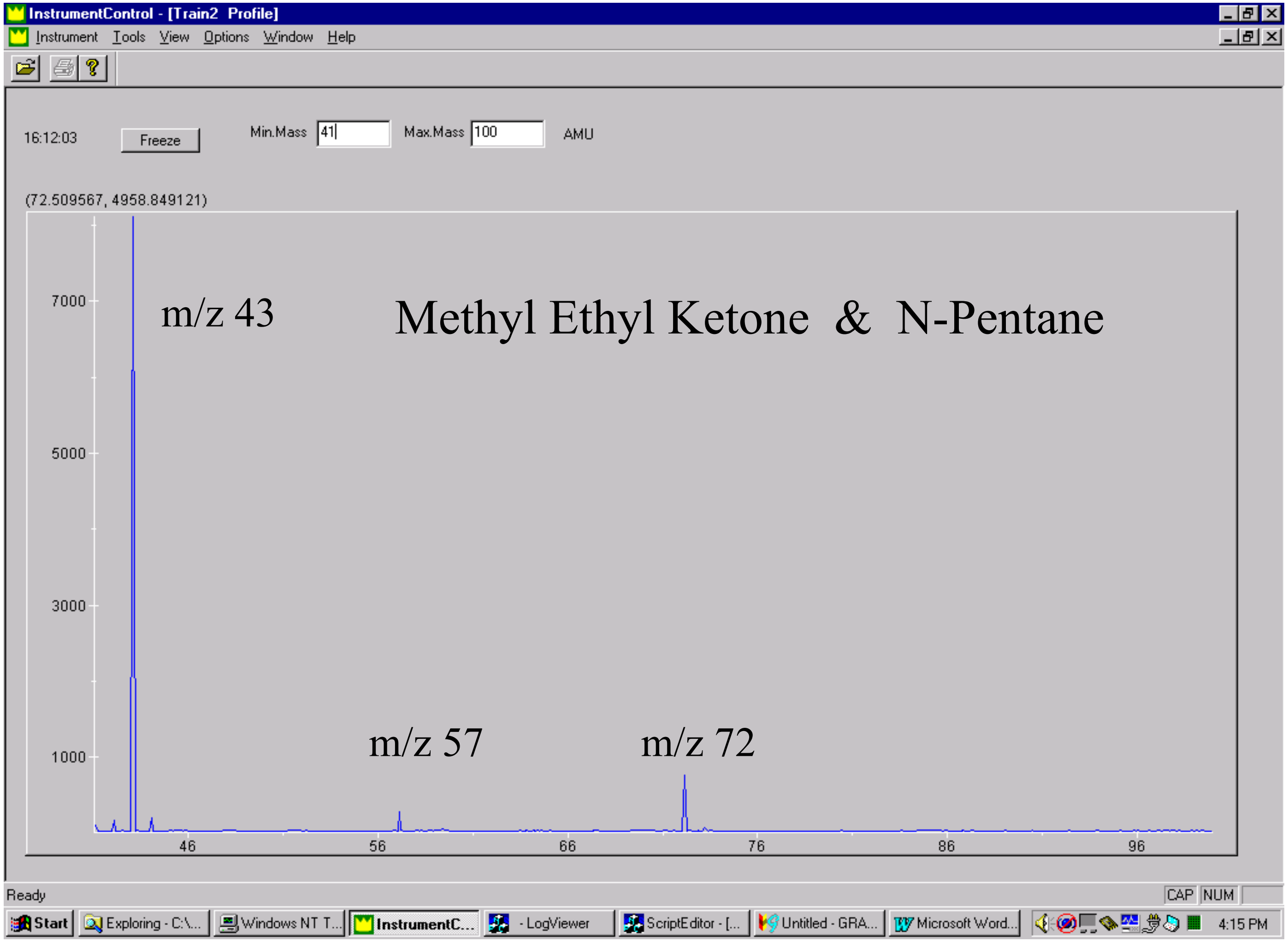
Vacuum inlet – MIMS Probe



SIEMENS

MIMS/HR-FTMS

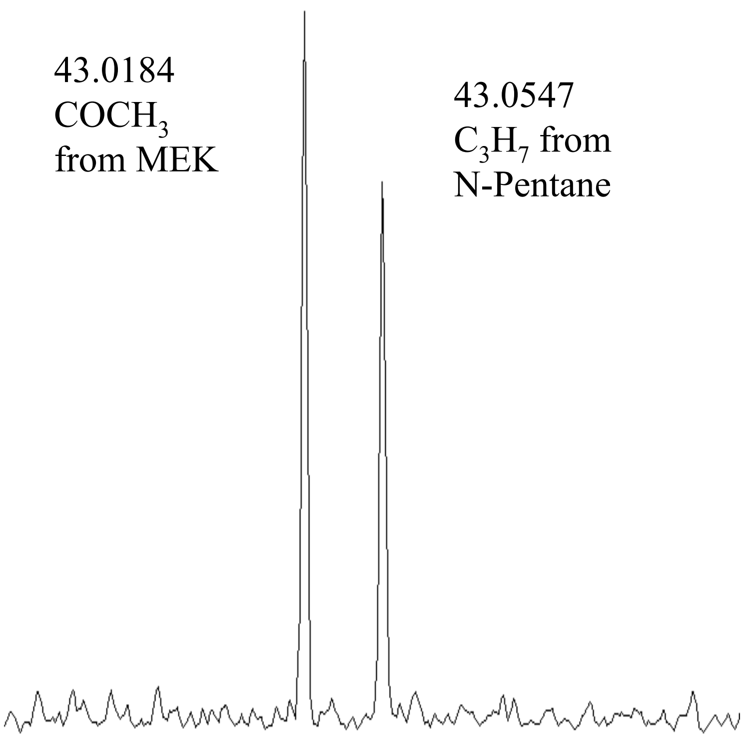
Typical Isobaric Interferences – aliphatic ketone vs alkane

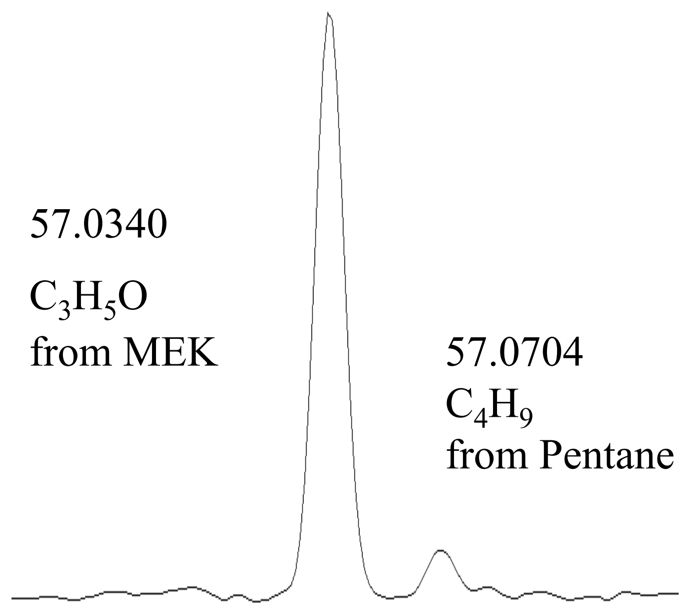


SIEMENS

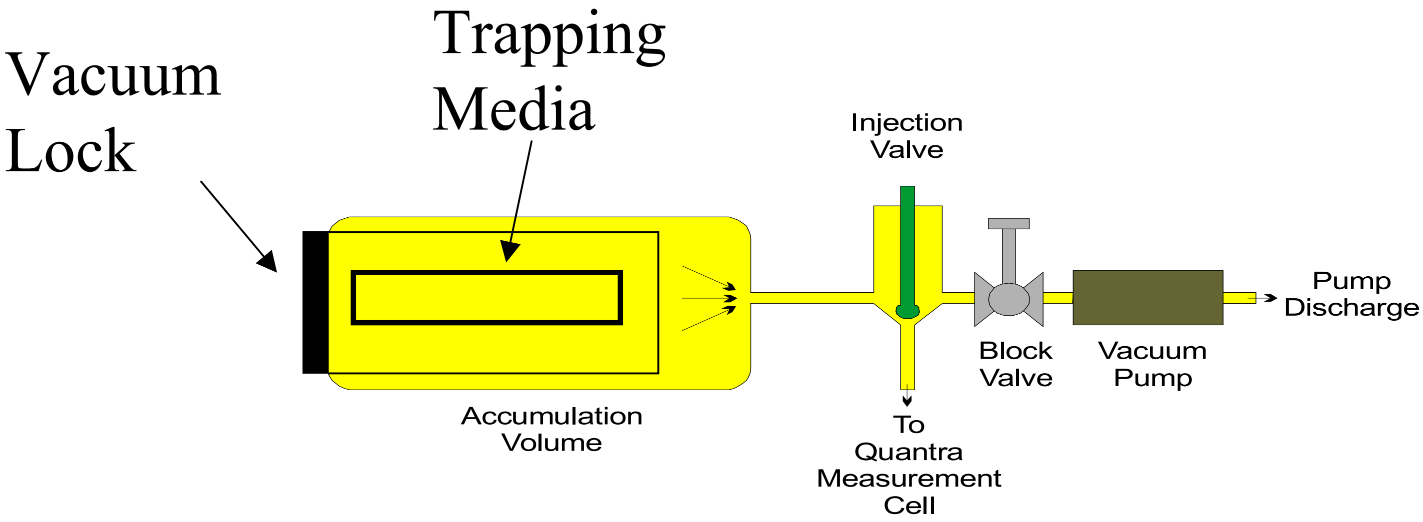
MIMS/HR-FTMS

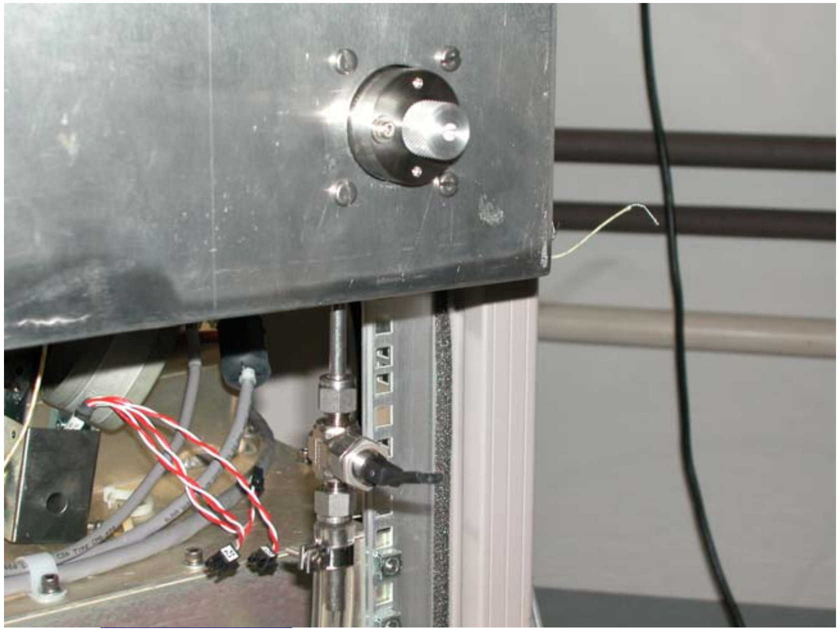
m/z 43 and 57 doublets

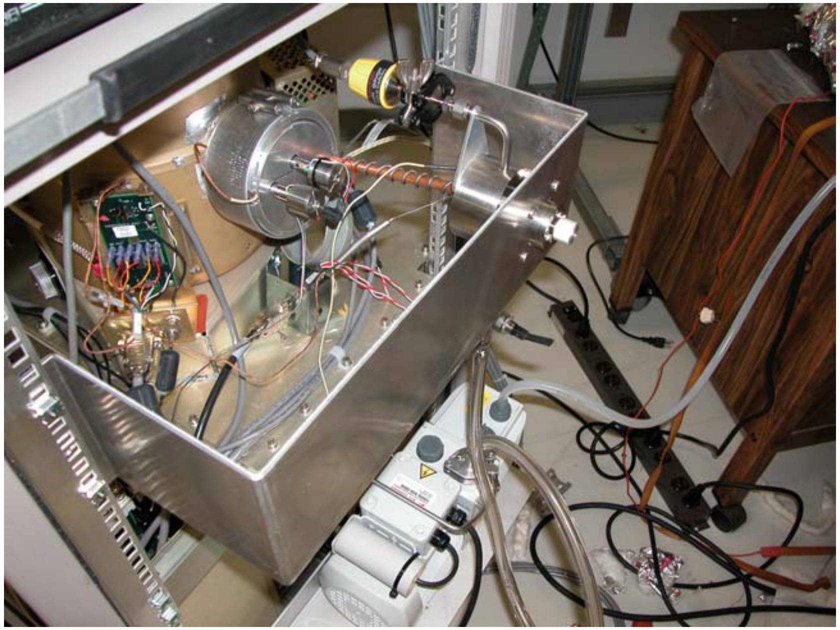




Vacuum inlet Adsorption/Desorption

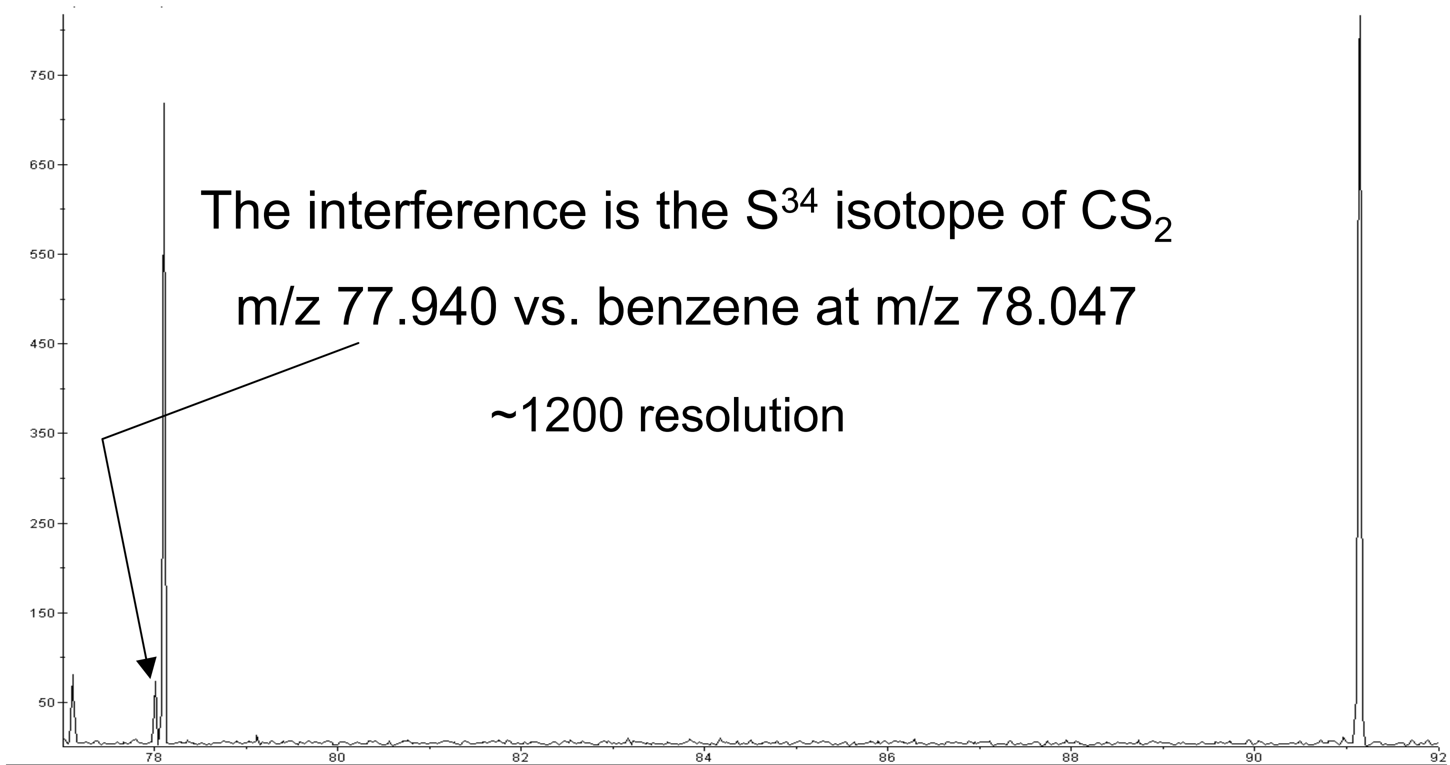






1 ppm Benzene and Toluene 8 ml/min for 5 minutes

(carboxen 563)

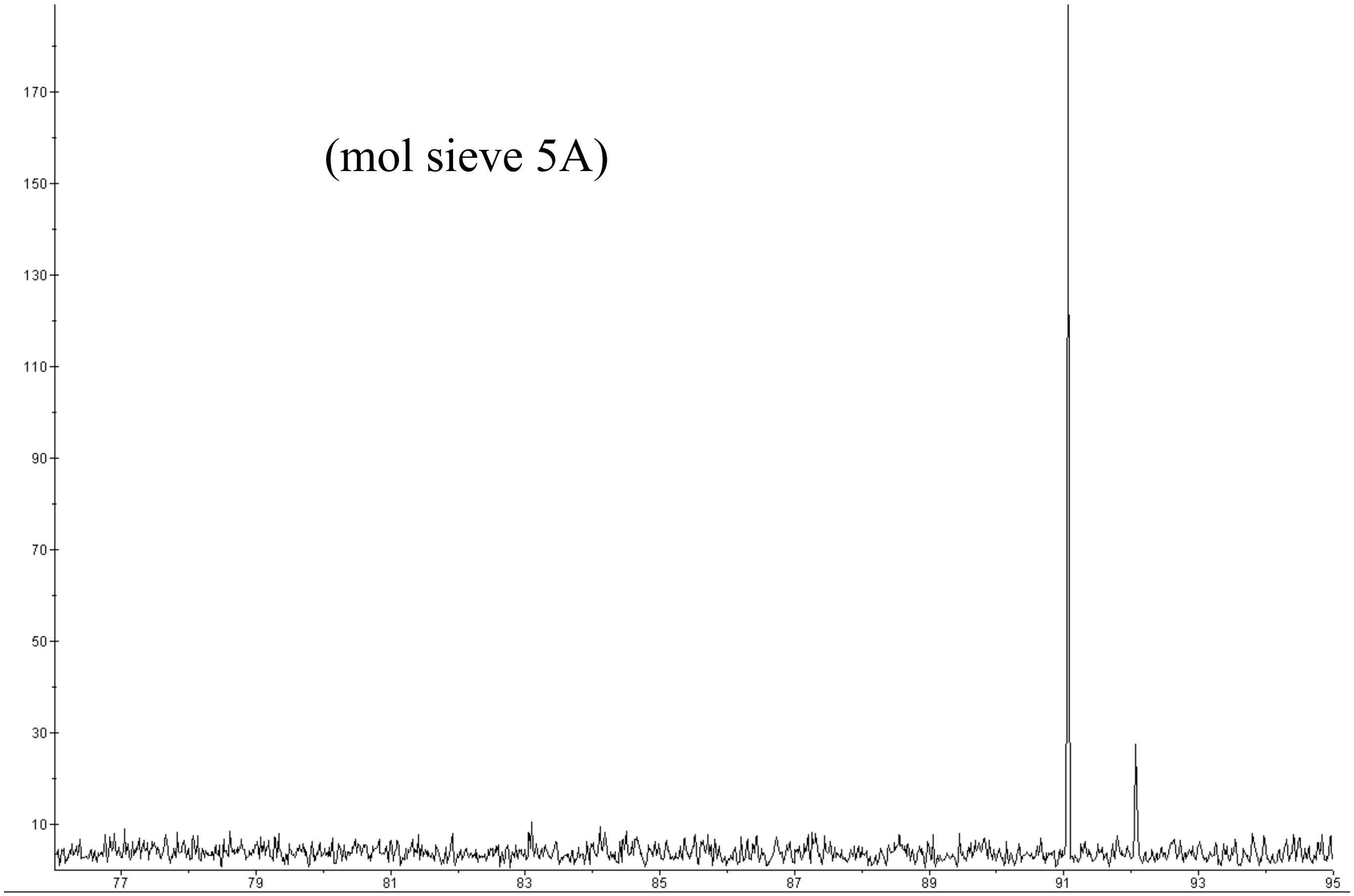


The interference is the S^{34} isotope of CS_2

m/z 77.940 vs. benzene at m/z 78.047

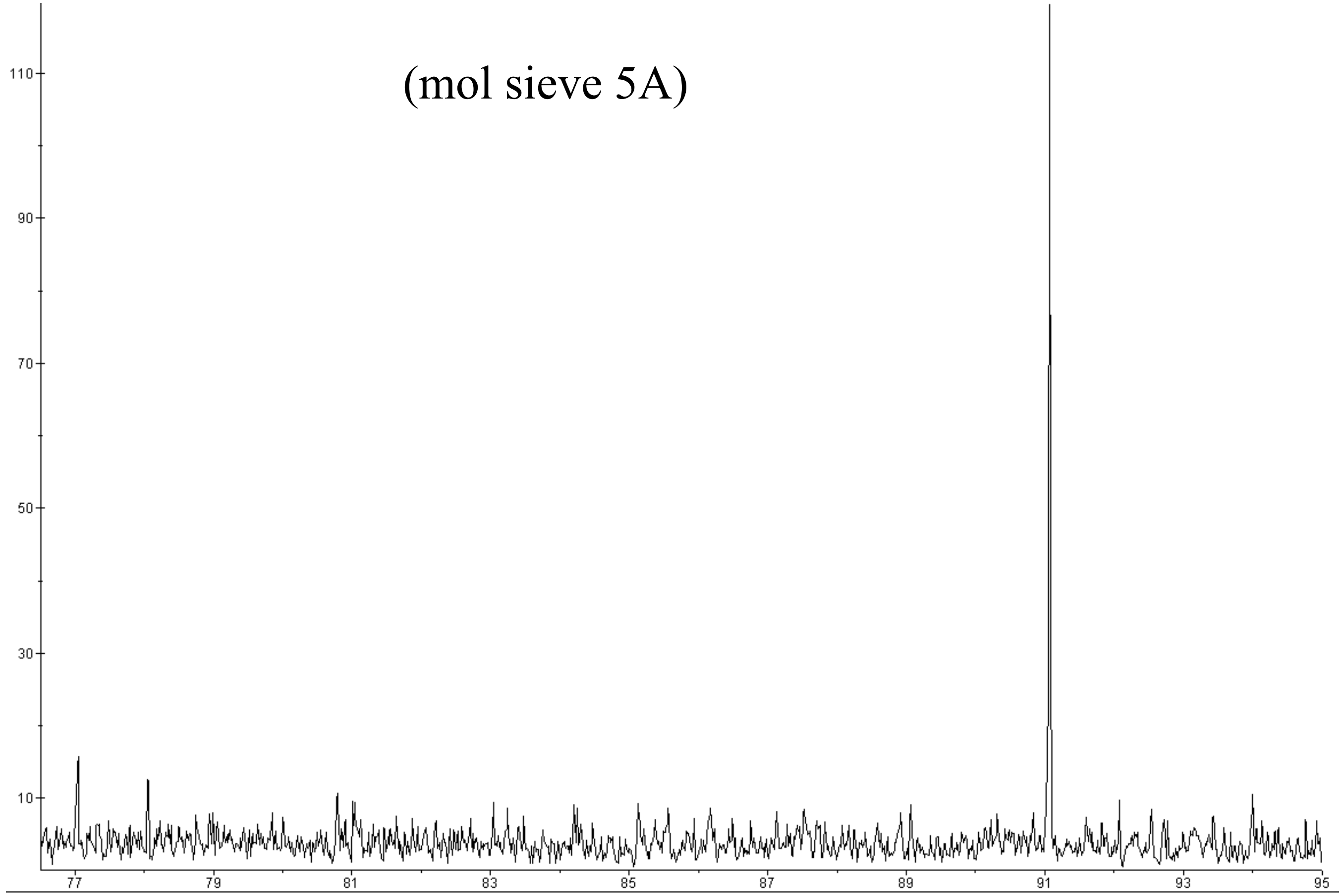
~1200 resolution

100 ppb Benzene and Toluene
8 ml/min for 1 minute



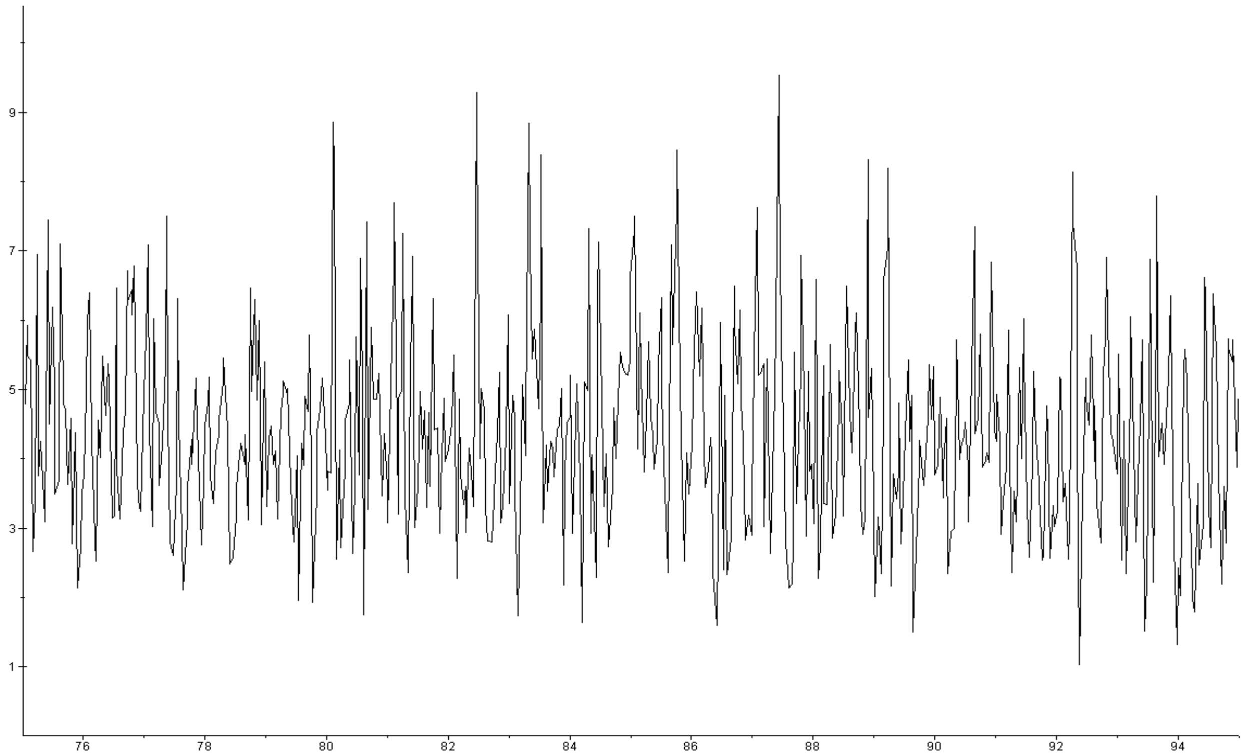
SIEMENS

10 ppb Benzene and Toluene
20 ml/min for 15 minutes



SIEMENS

Blank



SIEMENS

Quantra as a field unit

At ambient temperature the Quantra will draw 300 watts, with heaters on approximately 700 watts, runs from a generator or a voltage inverter, and typically uses a laptop

Conclusion:

Adverse effects from corrosive and aggressive species are minimized due to design features of a new miniature FTMS.

The system is capable of process analysis as well as transportable field analysis of species ranging from phosgene gas and various fluorocarbons to NF3 and chemical weapons surrogates with little or no detriment to the mass spectrometer.

While pure elemental analysis, requiring 5 ppm or less mass accuracy is not readily seen above m/z 100 with this instrument, targeting species by their exact mass with subsequent identification – even in a complex background is definitely possible.

The system works very well in the field!

Acknowledgements:

Victor Vartanian, Brian Goolsby,

Motorola – Austin, Texas

Steve Beu

Beu Consulting – Austin, Texas

Dean Davis, Lonnie O'bannion

Siemens Applied Automation – Bartlesville, OK

Questions?

wayne.rimkus@siemens.com

918 519 3071 Cell

http://www.sea.siemens.com/ia/product/aiquantra.html

Applications

Budget Quote

Specifications