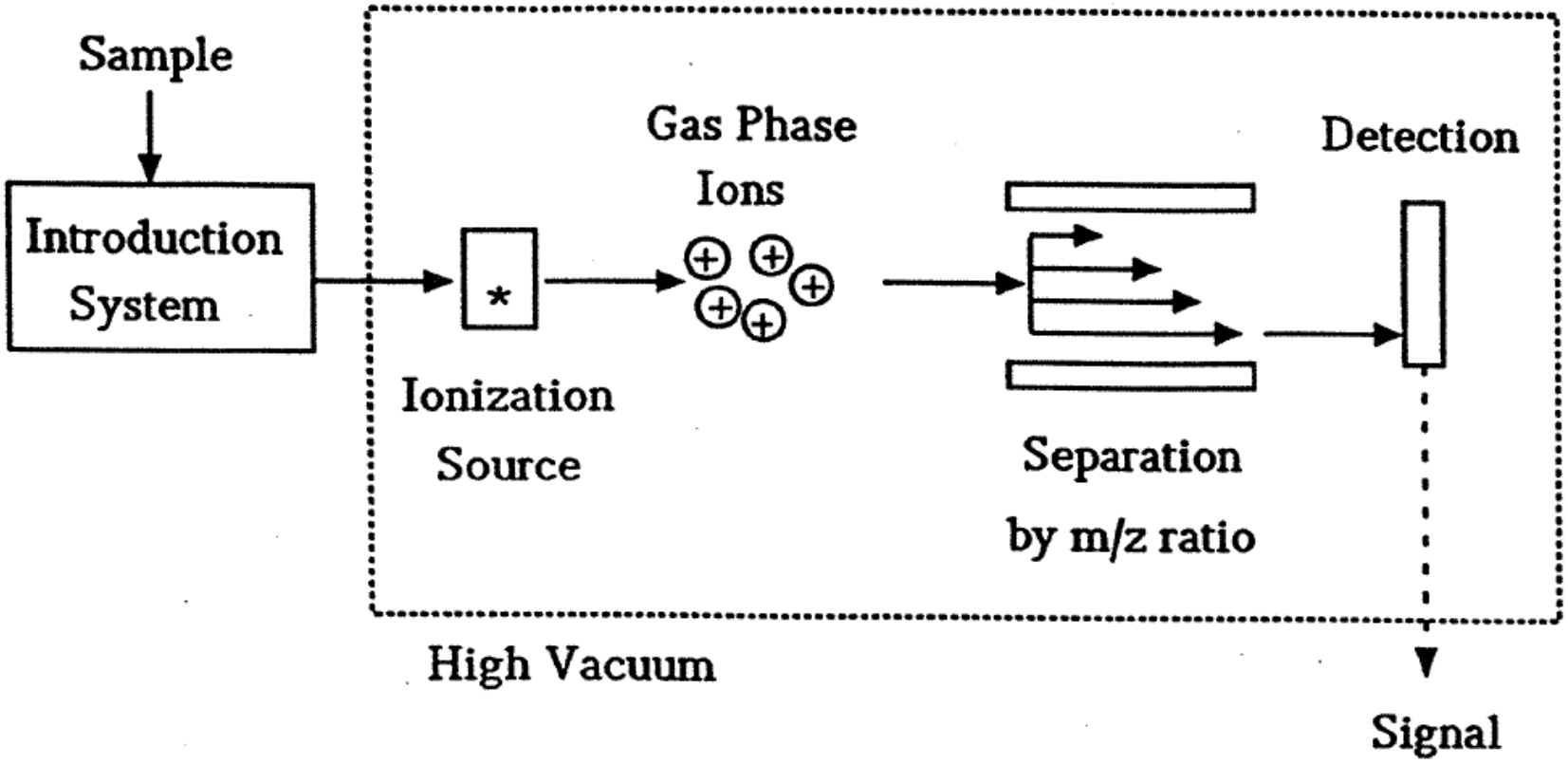
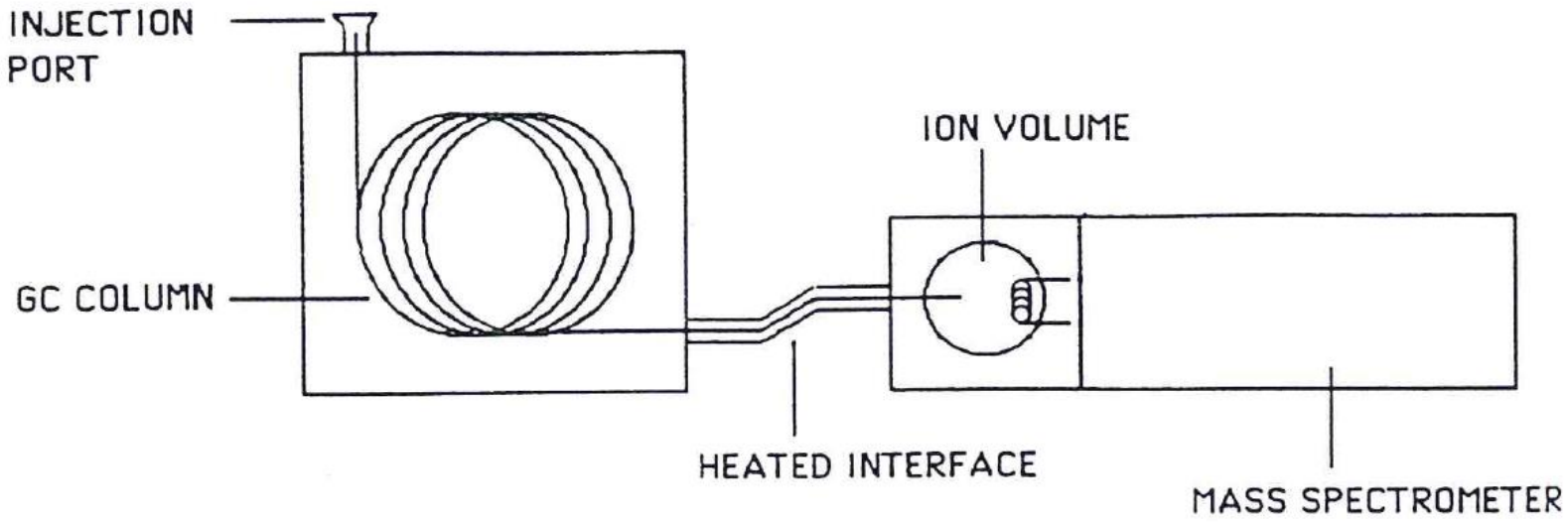
GC/MS

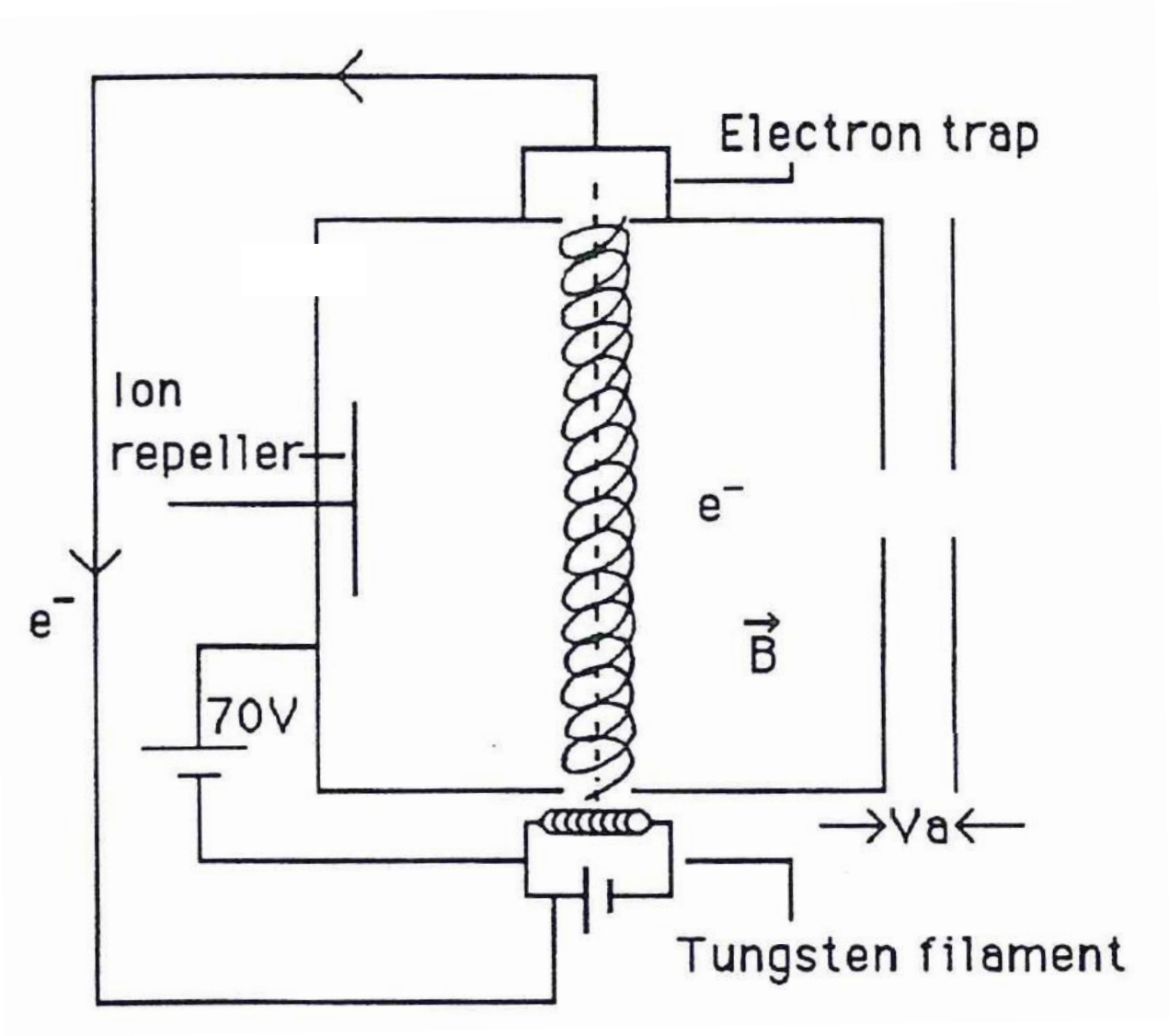
Mass spectrometry



Components of a GC/MS system



The electron impact ionization source

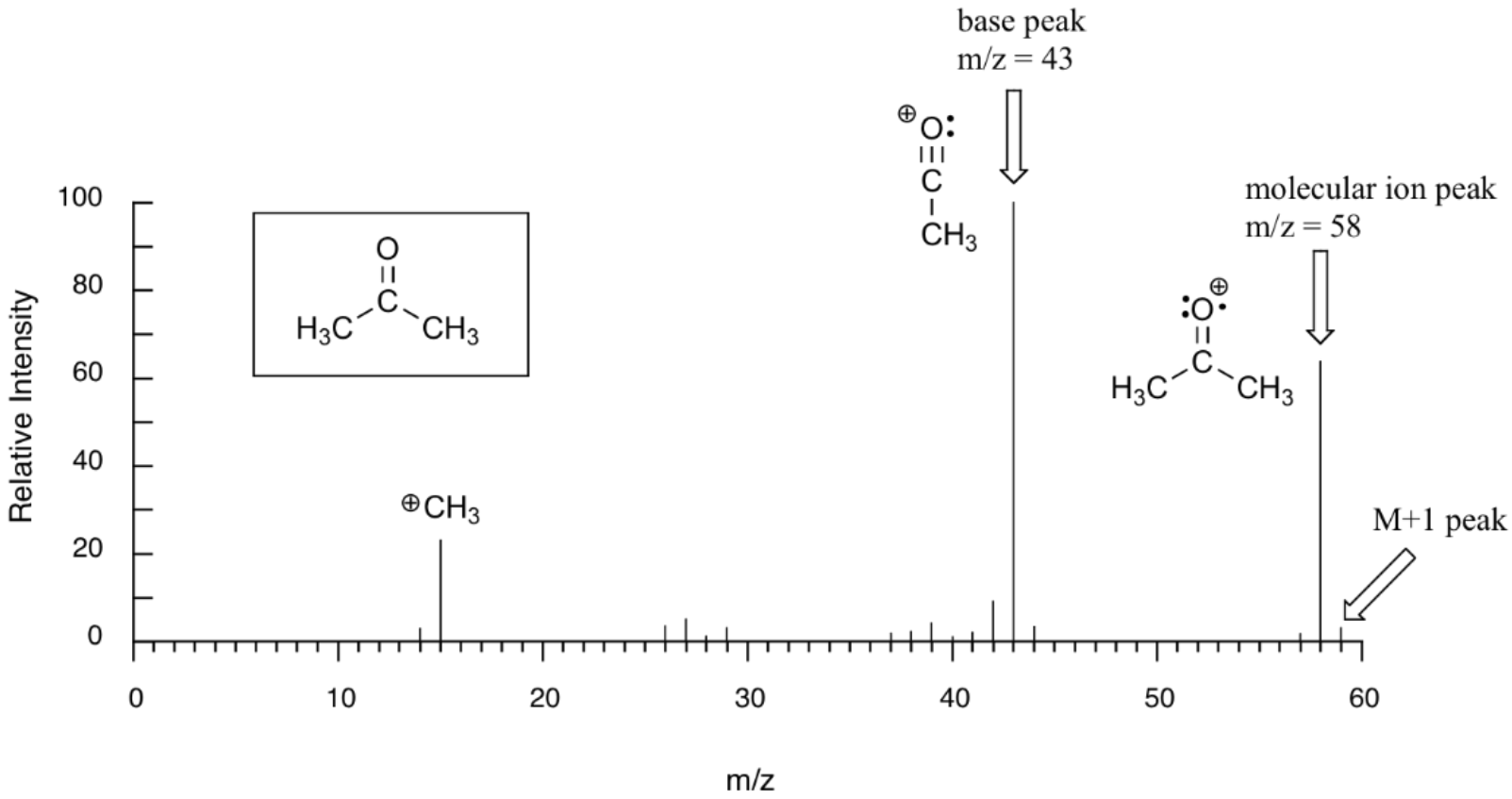


$M + e^- \rightarrow M^{\cdot +} + 2e^-$

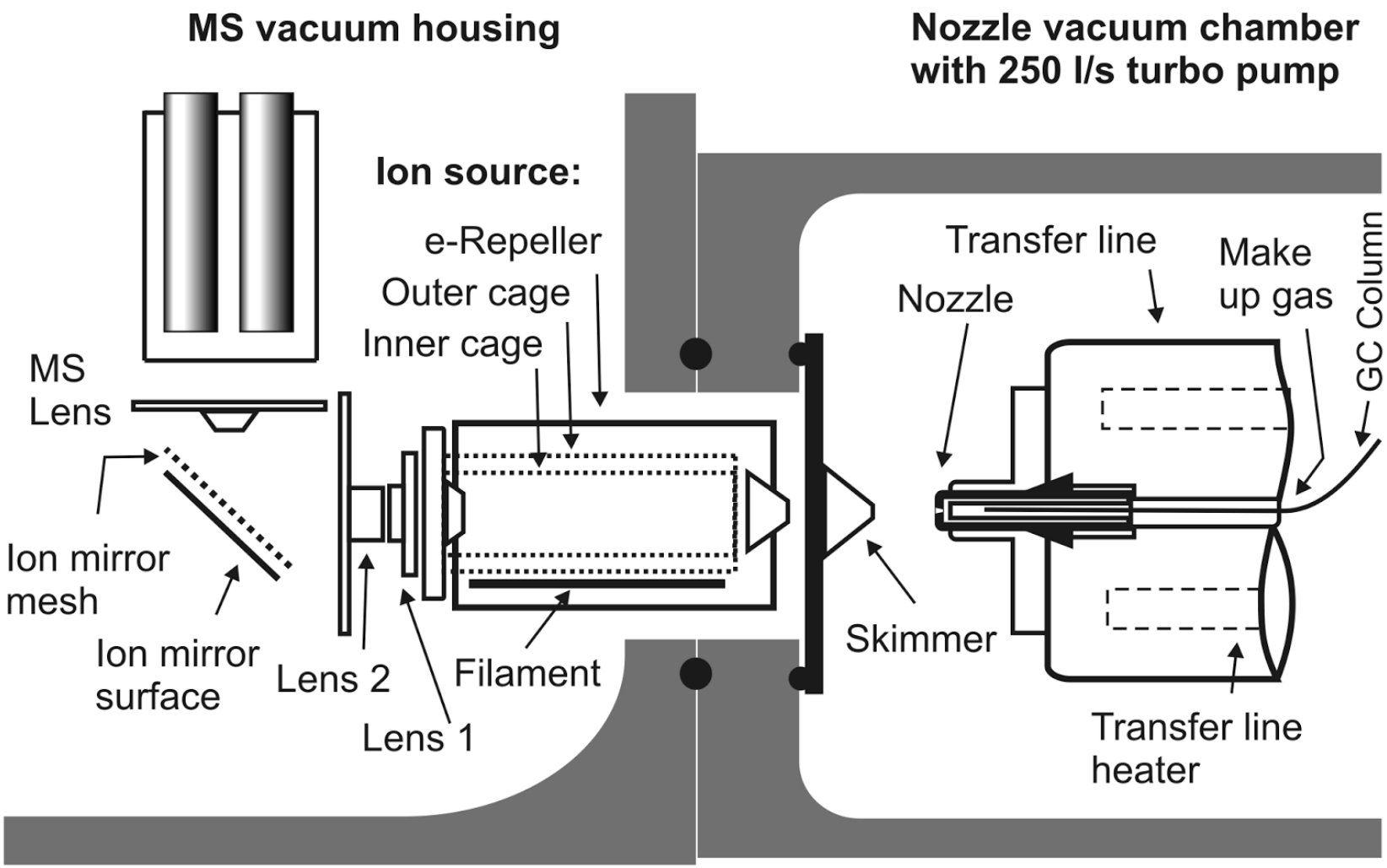
$M^{\cdot +} \rightarrow F^+ + N^{\cdot}$

-Sample evaporated in source from heated probe
-Sample introduced by GC
-Gas inlet

Typical EI mass spectrum: acetone

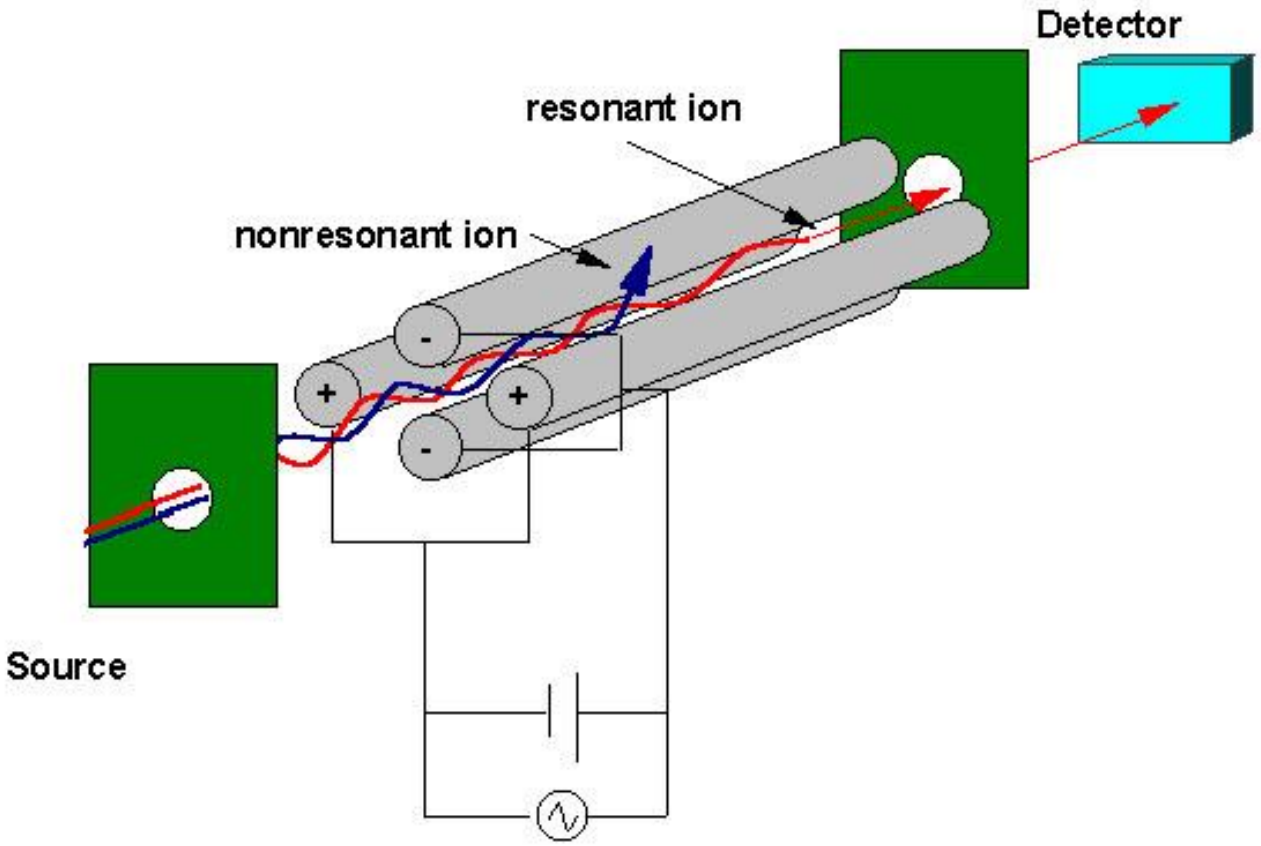


GC/MS interface



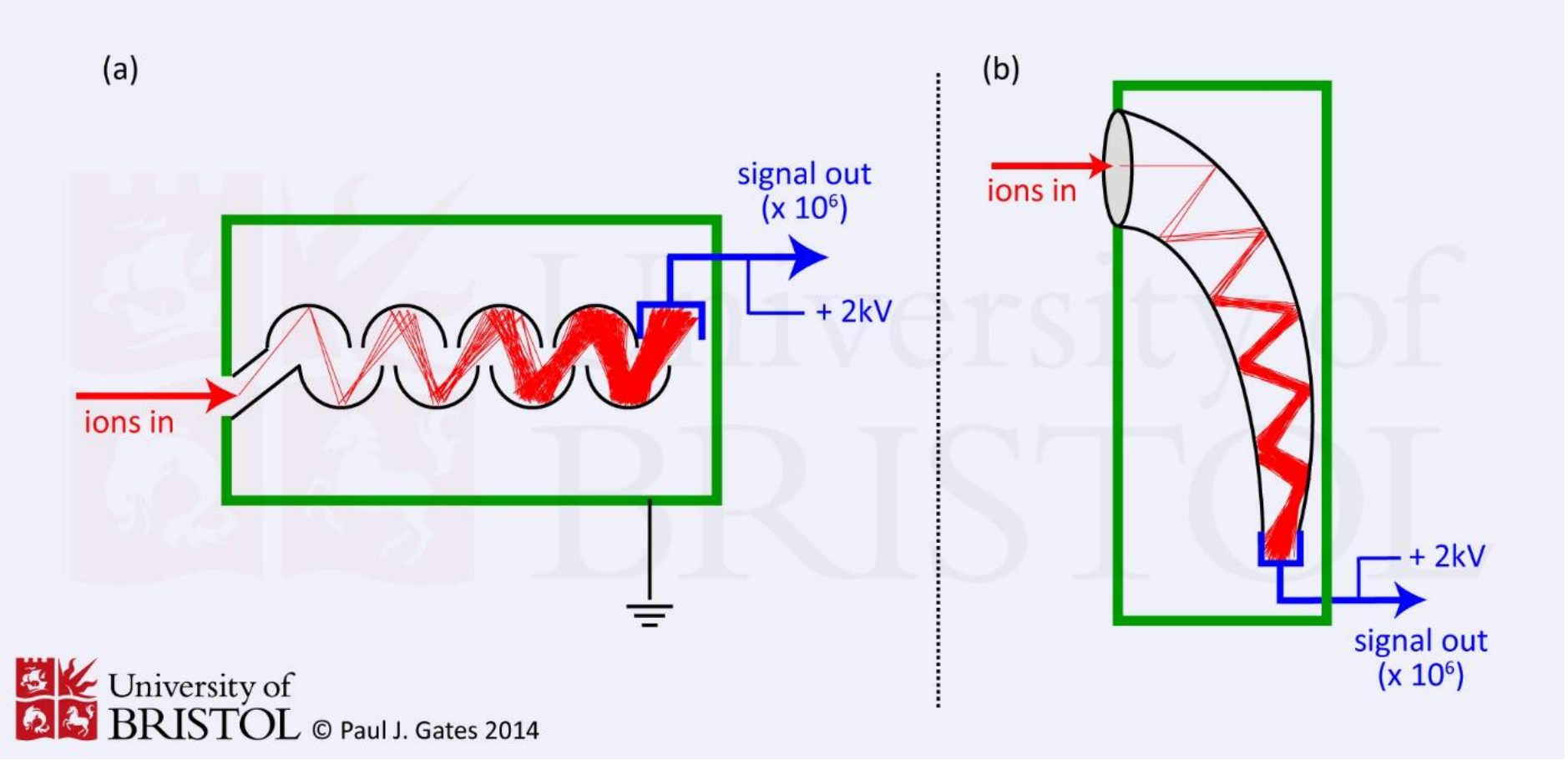
http://blog.avivanalytical.com/2013/06/what-can-be-improved-in-gc-ms-when.html

Quadrupole mass analyzer



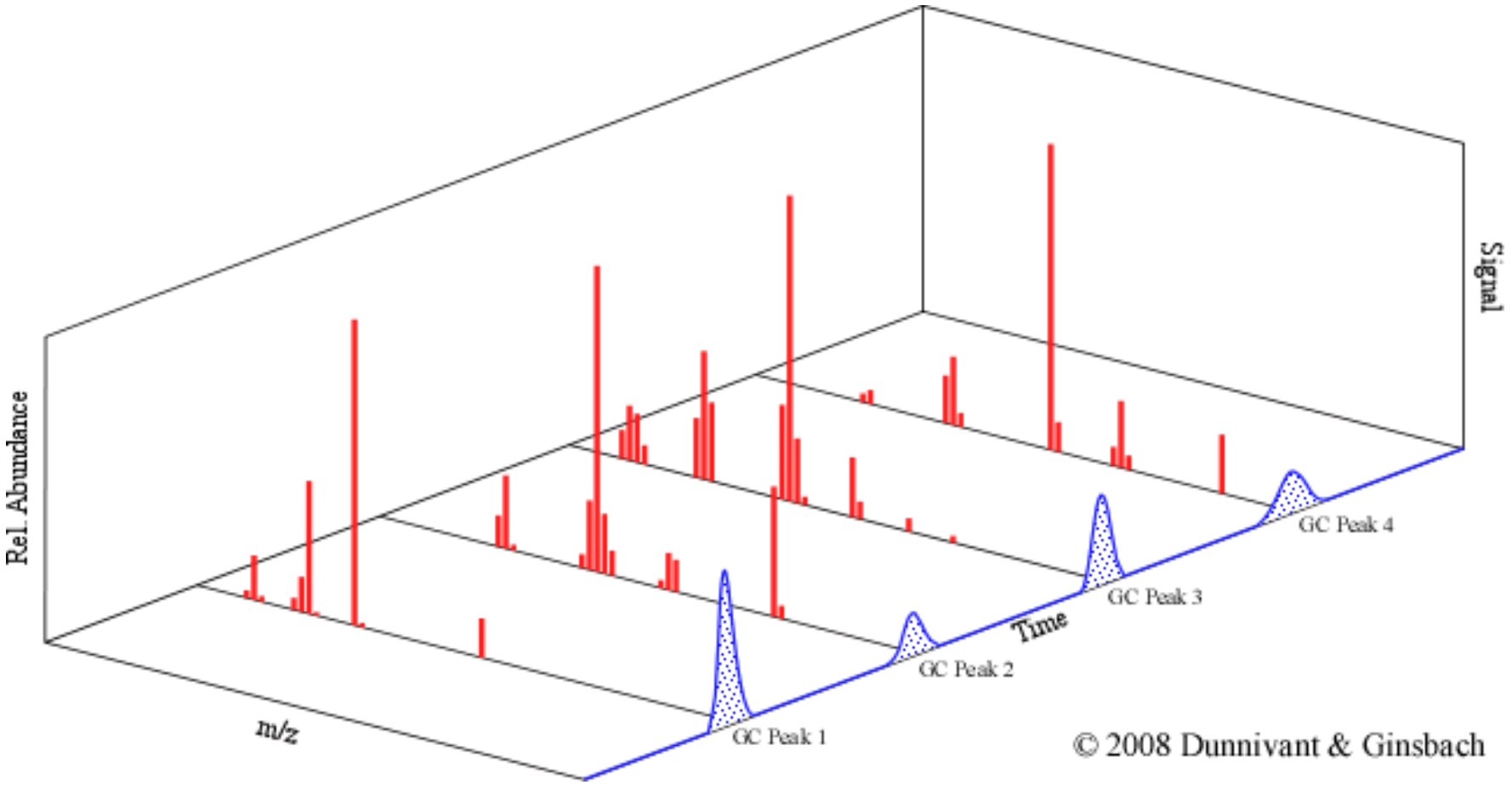
http://www.ivv.fraunhofer.de/en/leistungsangebot/stoerstoffanalyse/ms_pages/Introduction_into_mass_spectrometry/ms_intro_analyzers.html

Detector: electron multiplier

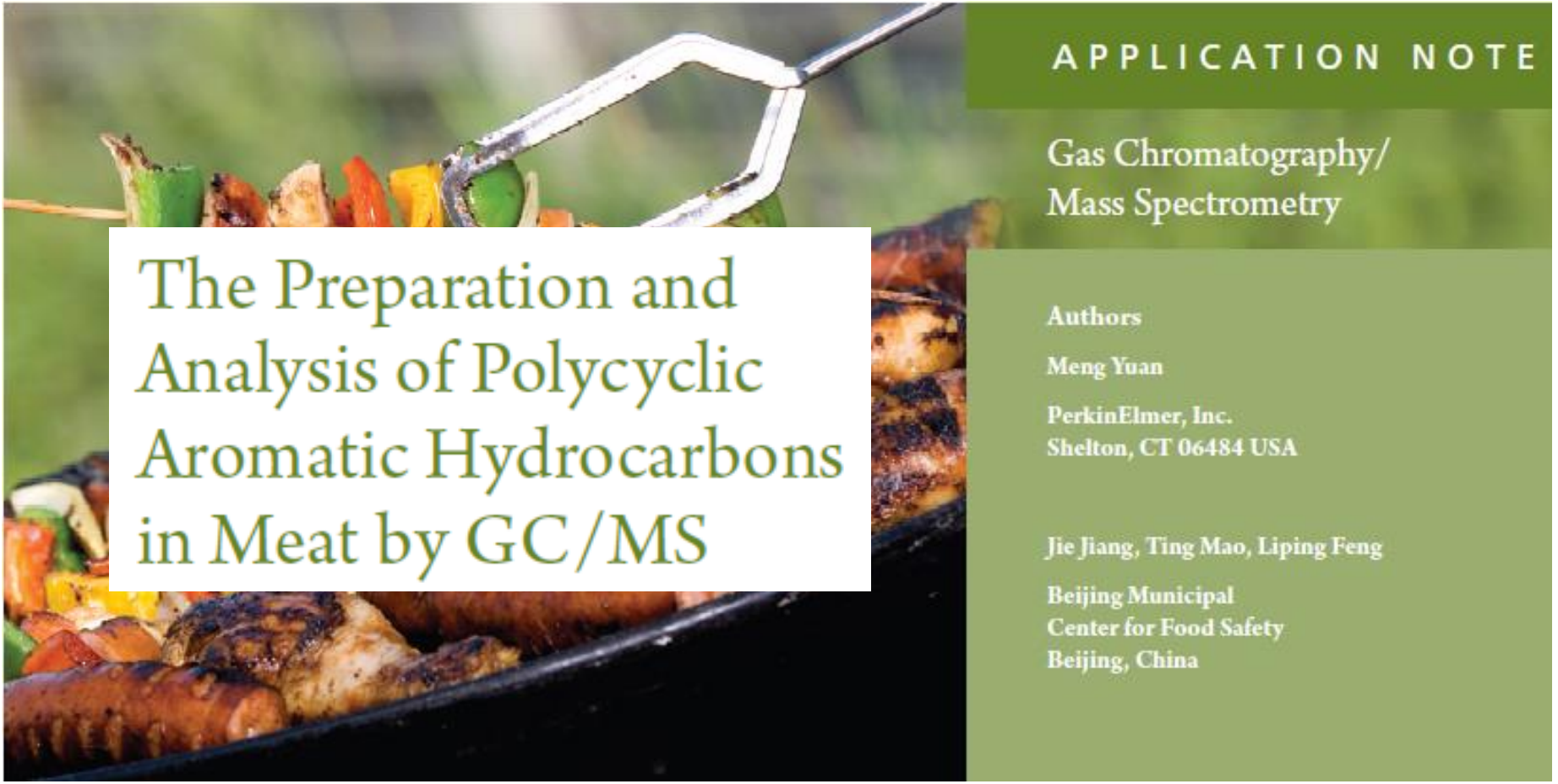


http://www.chm.bris.ac.uk/ms/detectors.xhtml

GC/MS output


Rel. Abundance
m/z
Time
Signal
GC Peak 1
GC Peak 2
GC Peak 3
GC Peak 4
© 2008 Dunnivant & Ginsbach

Application 1



http://www.perkinelmer.com/PDFs/downloads/APP_PAHinMeatbyGCMS.pdf

Purpose

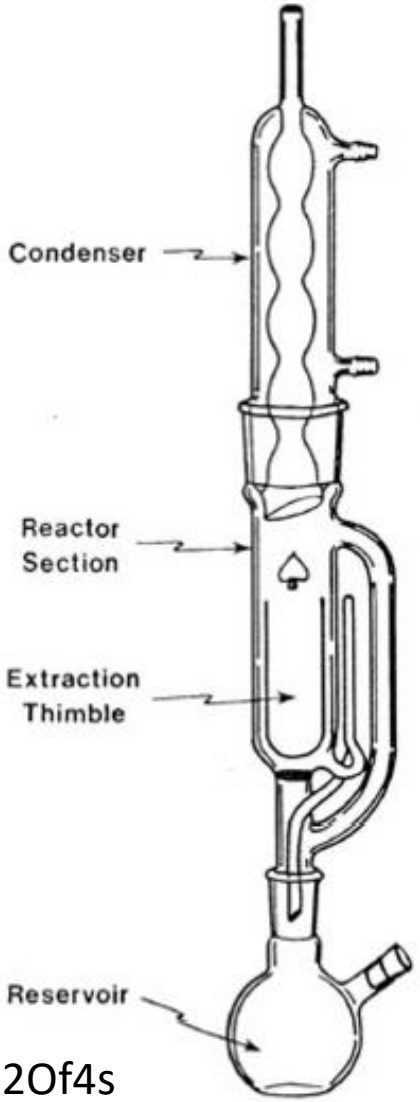
- This application note presents a method developed to measure 15 + 1 EU priority PAHs at low levels using gas chromatography mass spectrometry (GC/MS).
- It also describes a reliable procedure for extraction and purification of PAHs from meat samples.
- The sample preparation focuses on benzo[a]pyrene.
- In addition to method optimization and calibration, a variety of meat samples are analyzed and the amount of PAHs determined.

Experimental

1) Solvent Extraction

A solvent extractor was used to obtain PAHs from the meat samples.

Typically: Soxhlet extraction



https://www.youtube.com/watch?v=tUDdkU2Of4s

2) Gel permeation chromatography (GPC)

- Molecules are separated by size
- Small molecules enter pores of stationary phase (b), large molecules do not (a)
- Larger molecules elute first

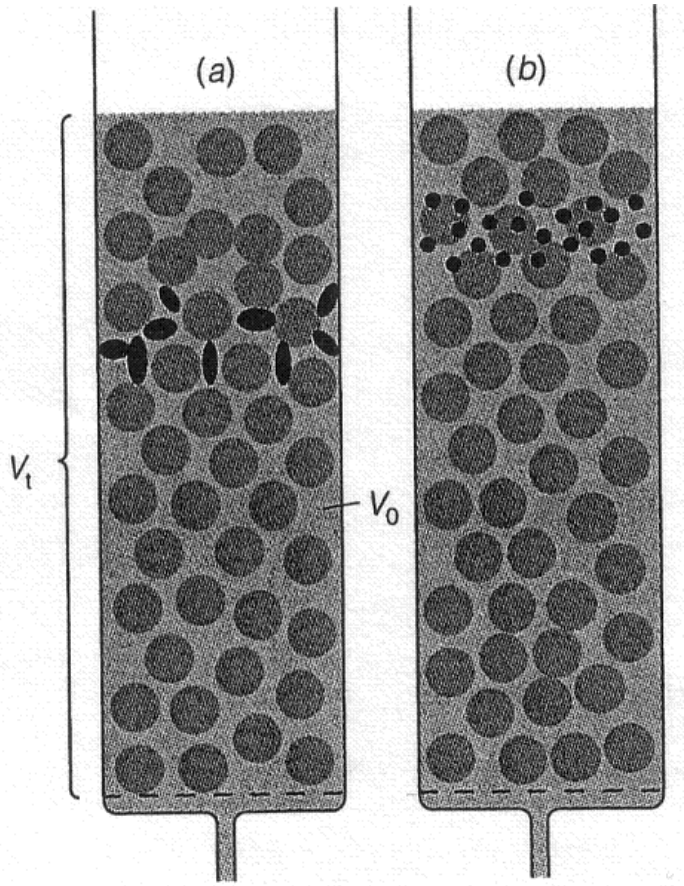
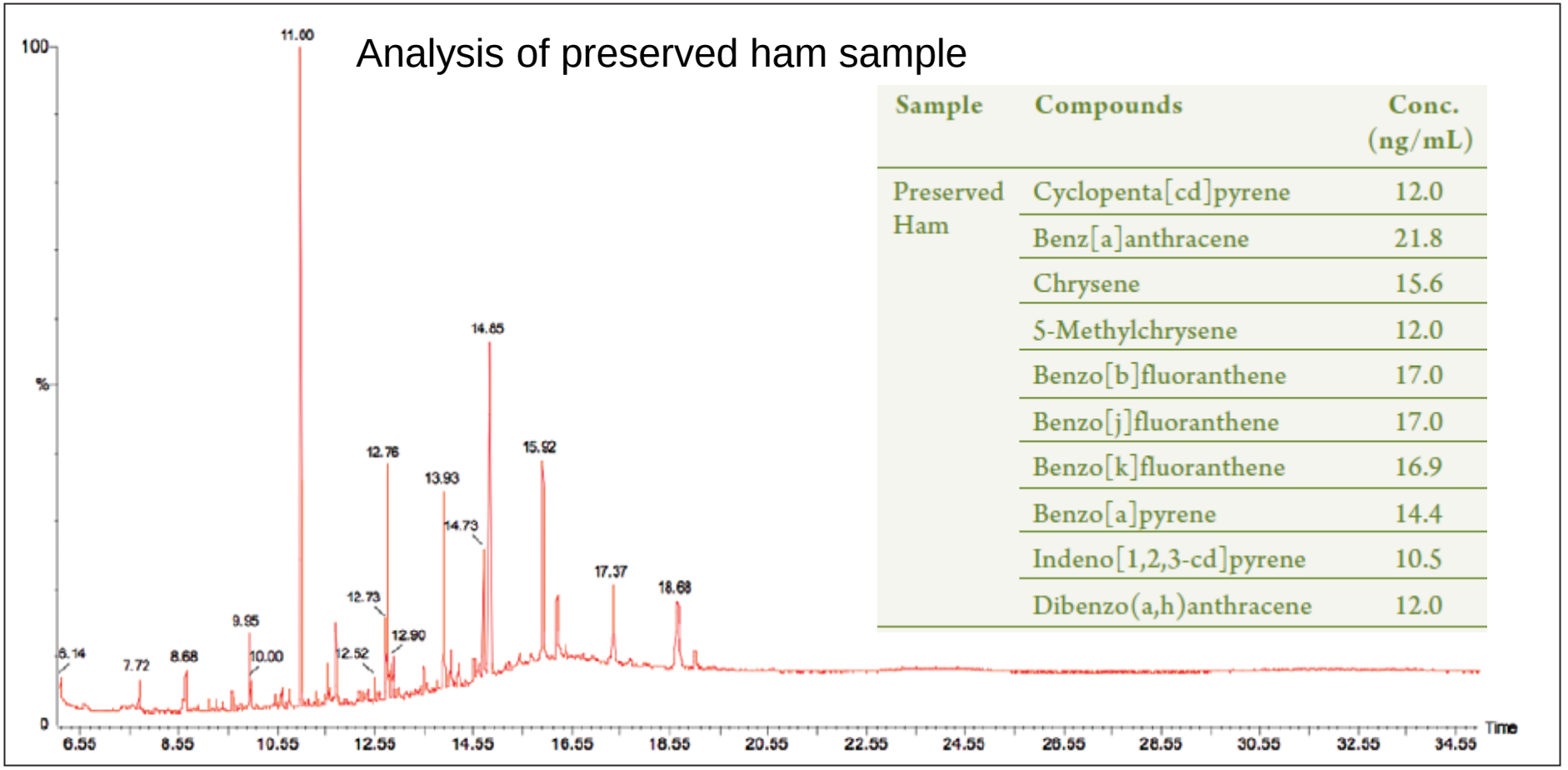


Table 2. **Instrumental Parameters.**

Gas Chromatograph	**PerkinElmer Clarus 680 GC**
Oven Program Initial Temperature	50 °C
Hold Time 1	2 min
Ramp 1	25 °C/min to 200 °C
Hold Time 2	0 min
Ramp 2	15 °C/min to 310 °C
Hold Time 3	19.67 min
Equilibration Time	0.2 min
Column	PerkinElmer – Elite™-5ms 30 m x 0.25 mm x 0.25 µm
Injector	Programmable Split/Splitless
Injection Mode	Splitless and Pressure Pulse
Injection Volume	1 µL
Inlet Temperature	280 °C
Carrier Gas	Helium
Carrier Gas Flow Rate	1 mL/min
Mass Spectrometer	**PerkinElmer Clarus 600 MS**
Mass Range	45-450 u
Solvent Delay Time	6 min
Scan Time	0.20 sec
Transfer Line Temperature	280 °C
Source Temperature	240 °C
SIM Mode	8 SIM groups
SIR Dwell Time	0.04 sec

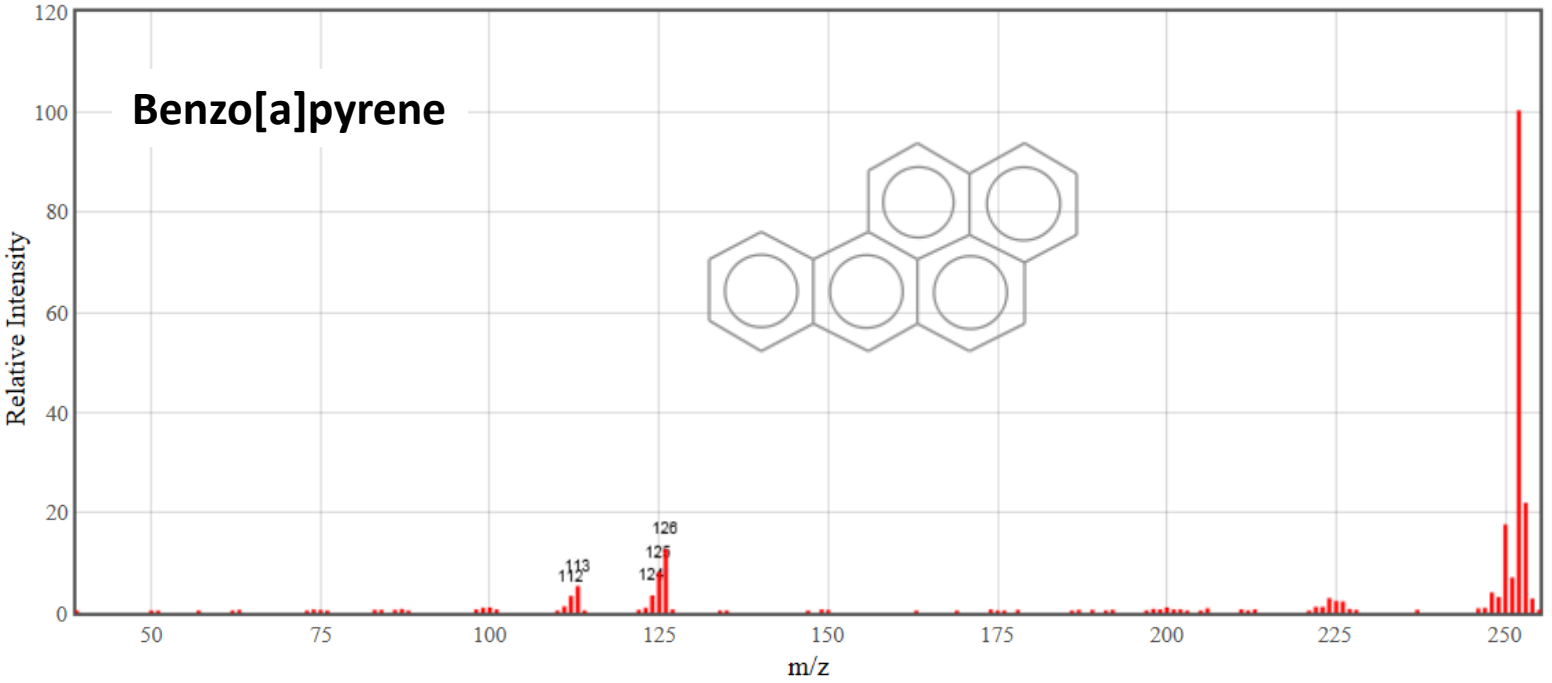
Following the calibration of the system, 5 g of bacon, preserved ham and sausage were analyzed and the PAH concentrations quantified.

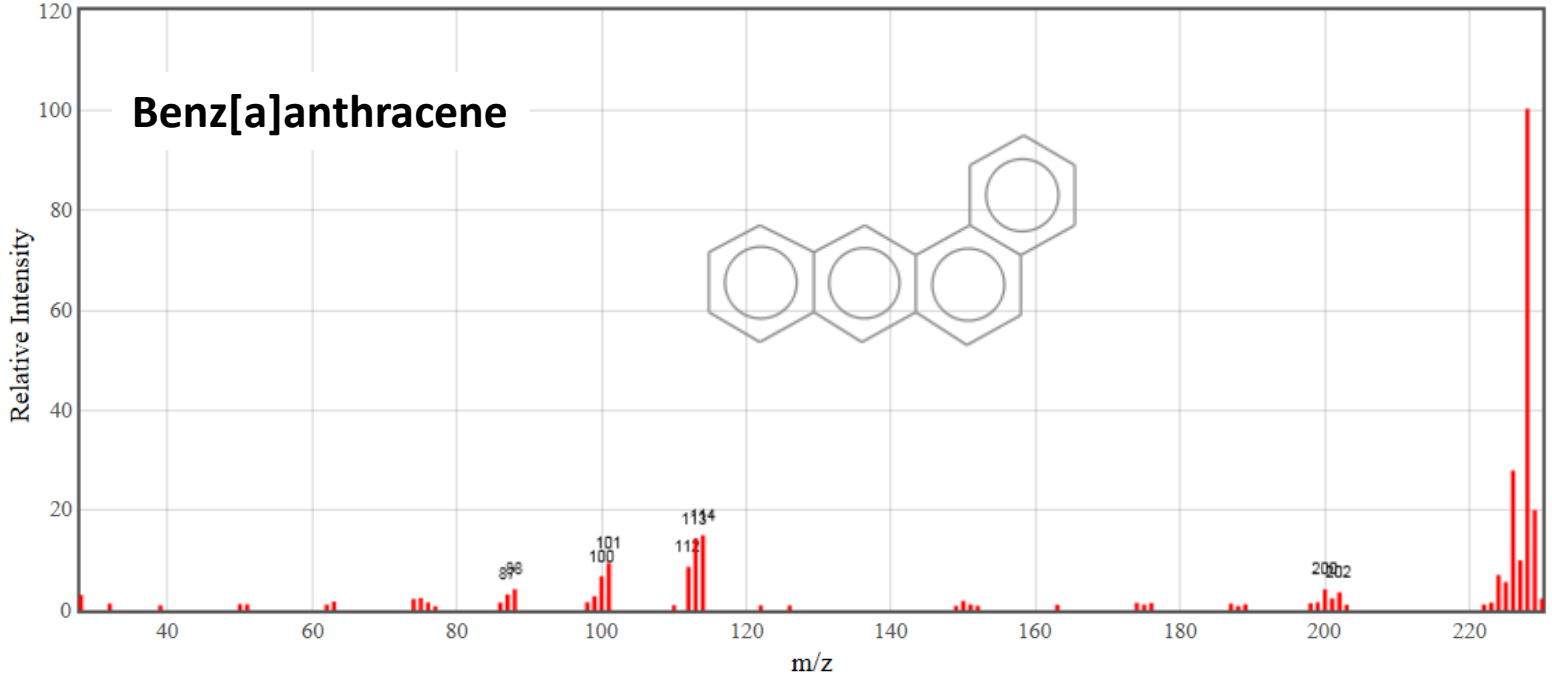


Sample	Compounds	Conc. (ng/mL)
Preserved Ham	Cyclopenta[cd]pyrene	12.0
	Benz[a]anthracene	21.8
	Chrysene	15.6
	5-Methylchrysene	12.0
	Benzo[b]fluoranthene	17.0
	Benzo[j]fluoranthene	17.0
	Benzo[k]fluoranthene	16.9
	Benzo[a]pyrene	14.4
	Indeno[1,2,3-cd]pyrene	10.5
	Dibenzo(a,h)anthracene	12.0

Figure 2. Total ion chromatogram (TIC) of the analysis of preserved ham sample.

Sample	Compounds	Conc. (ng/mL)
Bacon	Cyclopenta[cd]pyrene	9.3
	Benz[a]anthracene	22.1
	Chrysene	18.4
	5-Methylchrysene	9.5
	Benzo[b]fluoranthene	15.2
	Benzo[j]fluoranthene	15.2
	Benzo[k]fluoranthene	15.1
	Benzo[a]pyrene	14.2
	Indeno[1,2,3-cd]pyrene	11.7
	Dibenzo(a,h)anthracene	14.3
Sausage	Cyclopenta[cd]pyrene	7.8
	Benz[a]anthracene	21.6
	Chrysene	11.3
	5-Methylchrysene	6.3
	Benzo[b]fluoranthene	12.8
	Benzo[j]fluoranthene	12.8
	Benzo[k]fluoranthene	12.7
	Benzo[a]pyrene	12.0
	Indeno[1,2,3-cd]pyrene	11.6
	Dibenzo(a,h)anthracene	14.4



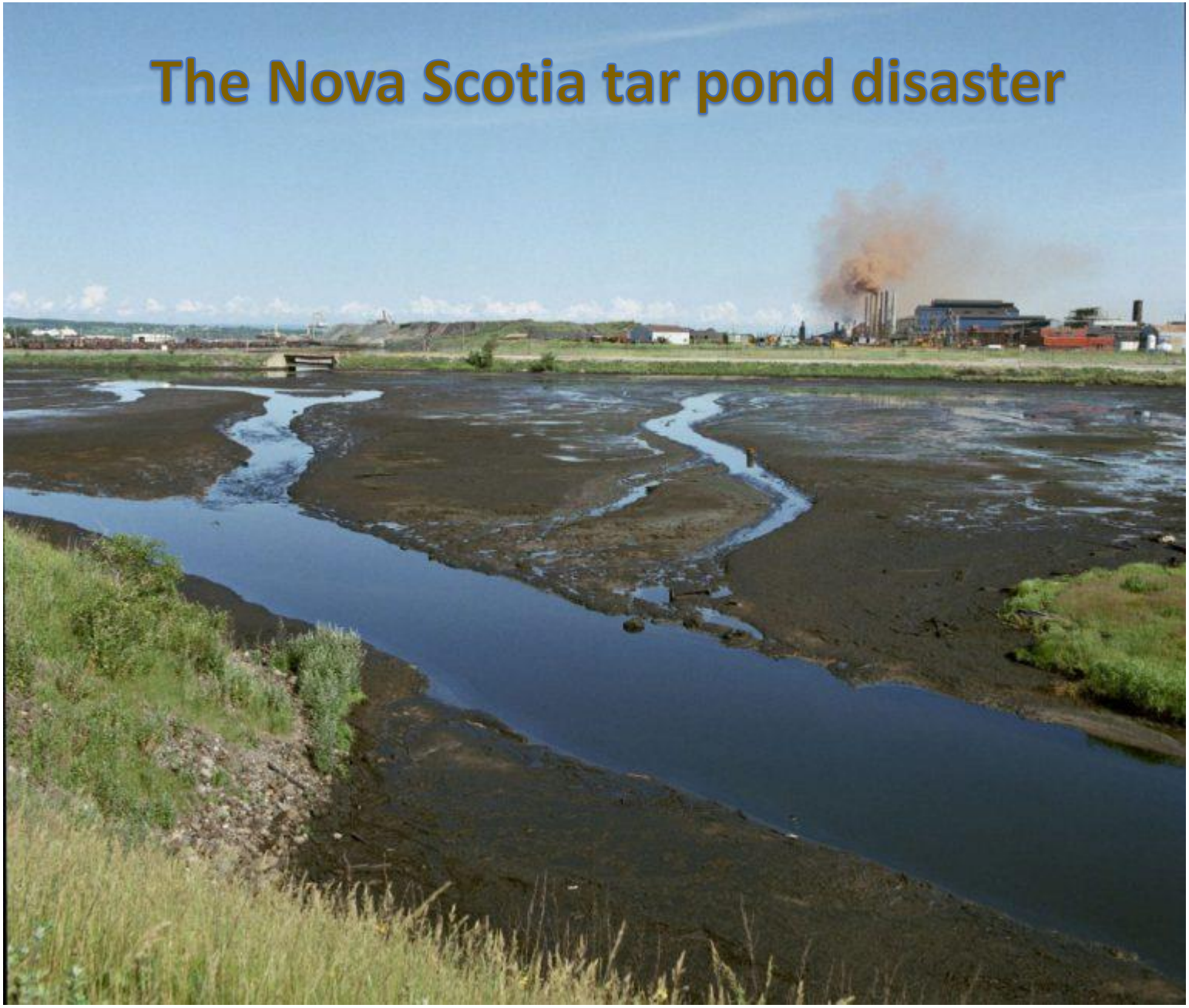


http://webbook.nist.gov/cgi/cbook.cgi?ID=C50328&Mask=200

Table 3. **Calibration Table for PAHs.**

Name	Retention Time	Quantifier Ion	Qualifier Ion 1	Qualifier Ion 2	%RSD of Peak Area (n=7) 100 ng/mL	r^2 (5 – 500 ppb)
Naphthalene-D8	7.28	136	137	108		
Phenanthrene-D10	10.79	188	189	80		
Cyclopenta[cd]pyrene	14.78	226	227	224	0.5	0.9999
Benz[a]anthracene	14.78	228	229	226	1.1	0.9996
Chrysene-D12	14.79	240	241	236		
Chrysene	14.83	228	229	226	3.0	0.9999
5-Methylchrysene	15.52	242	241	239	1.5	0.9997
Benzo[b]fluoranthene	16.56	252	253	250	0.3	0.9986
Benzo[j]fluoranthene	16.56	252	253	250	0.3	0.9986
Benzo[k]fluoranthene	16.56	252	253	250	0.3	0.9987
Benzo[a]pyrene	17.19	252	253	250	0.3	0.9981
Perylene-D12	17.29	264	265	260		
Indeno[1,2,3-cd]pyrene	19.89	276	277	138	0.4	0.9972
Dibenzo(a,h)anthracene	19.96	278	279	276	0.1	0.9965
Benzo[ghi]perylene	20.65	276	277	138	0.9	0.9997
Dibenzo[a,l]pyrene	25.09	302	151	150	0.3	0.9959
Dibenzo[a,e]pyrene	26.85	302	151	150	0.2	0.9942
Dibenzo[a,i]pyrene	27.56	302	151	150	0.2	0.9913
Dibenzo[a,h]pyrene	27.94	302	151	150	0.2	0.9926

Application 2

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Glace Bay
Baddeck
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Moncton
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Frédéricton
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Oromocto
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New Glasgow
Antigonish
Port
Hawkesbury
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Truro
Saint-John
Wolfville
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Sherbrooke
Saint-Andrews
Baie de Fundy
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NOUVELLE-ÉCOSSE
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Bridgewater
Lunenburg
101
Yarmouth
Shelburne
103


Atlantic Ocean
Sydney Harbour
North Tar Pond
South Tar Pond
Cooling Pond
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NO
TRESPASSING
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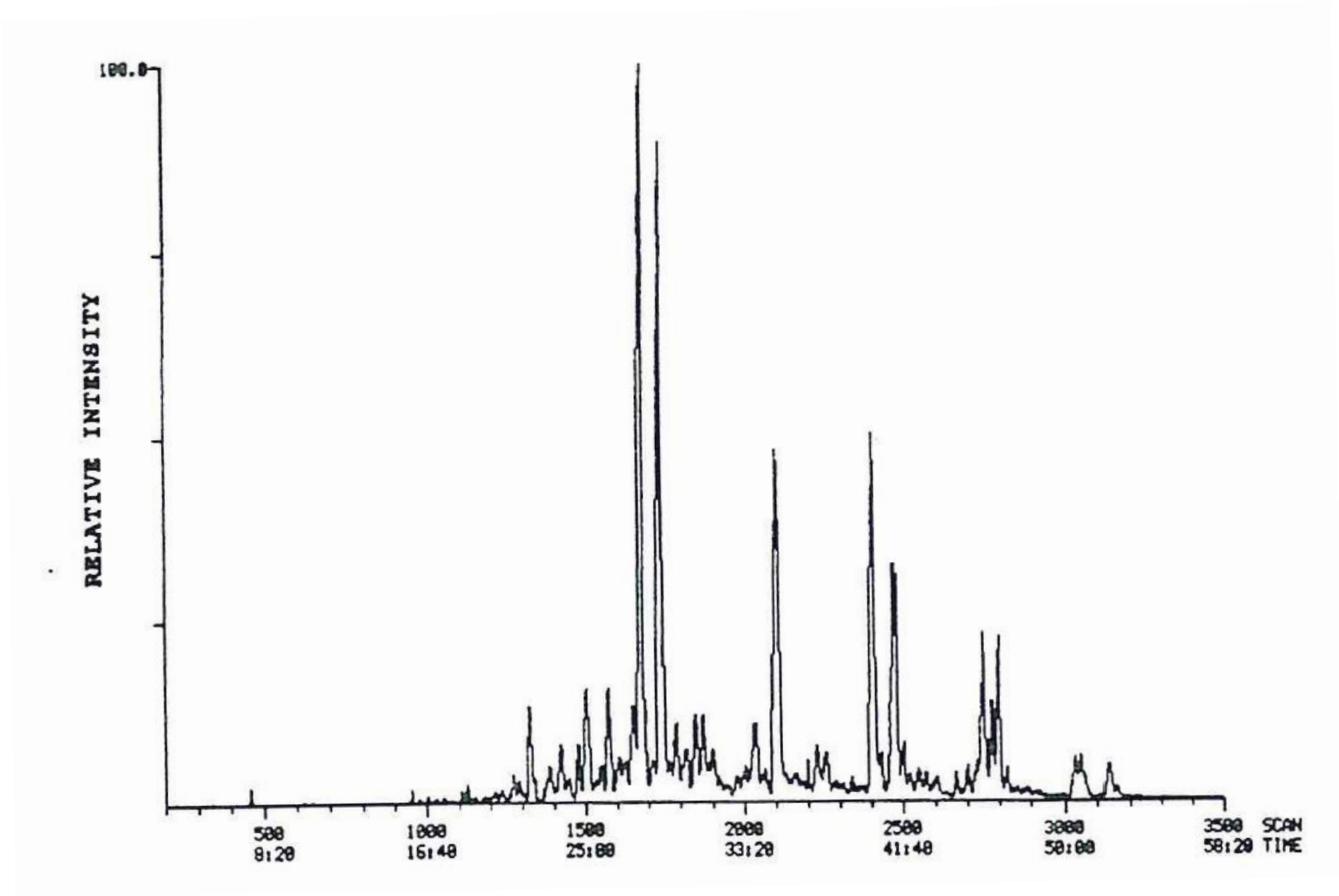
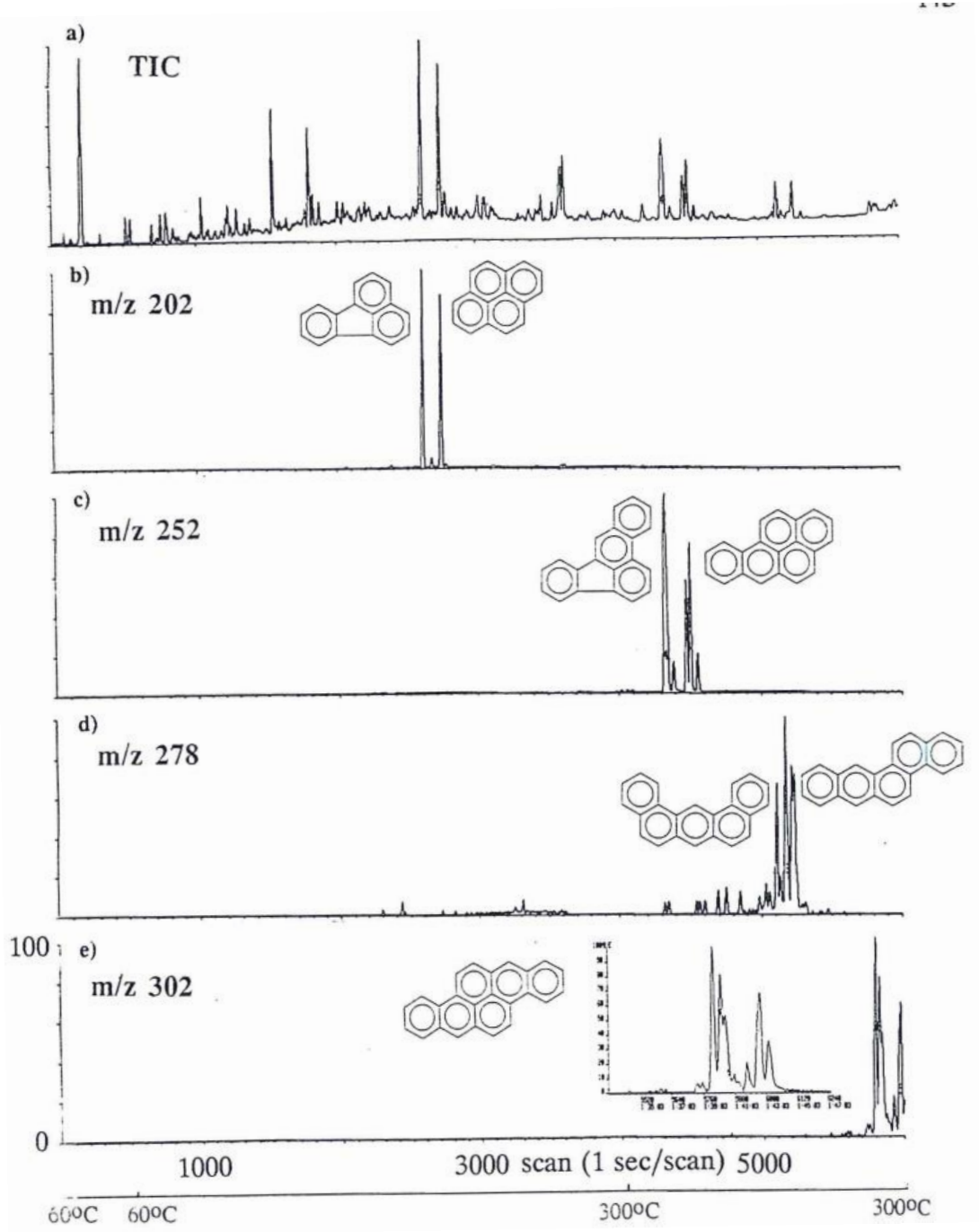
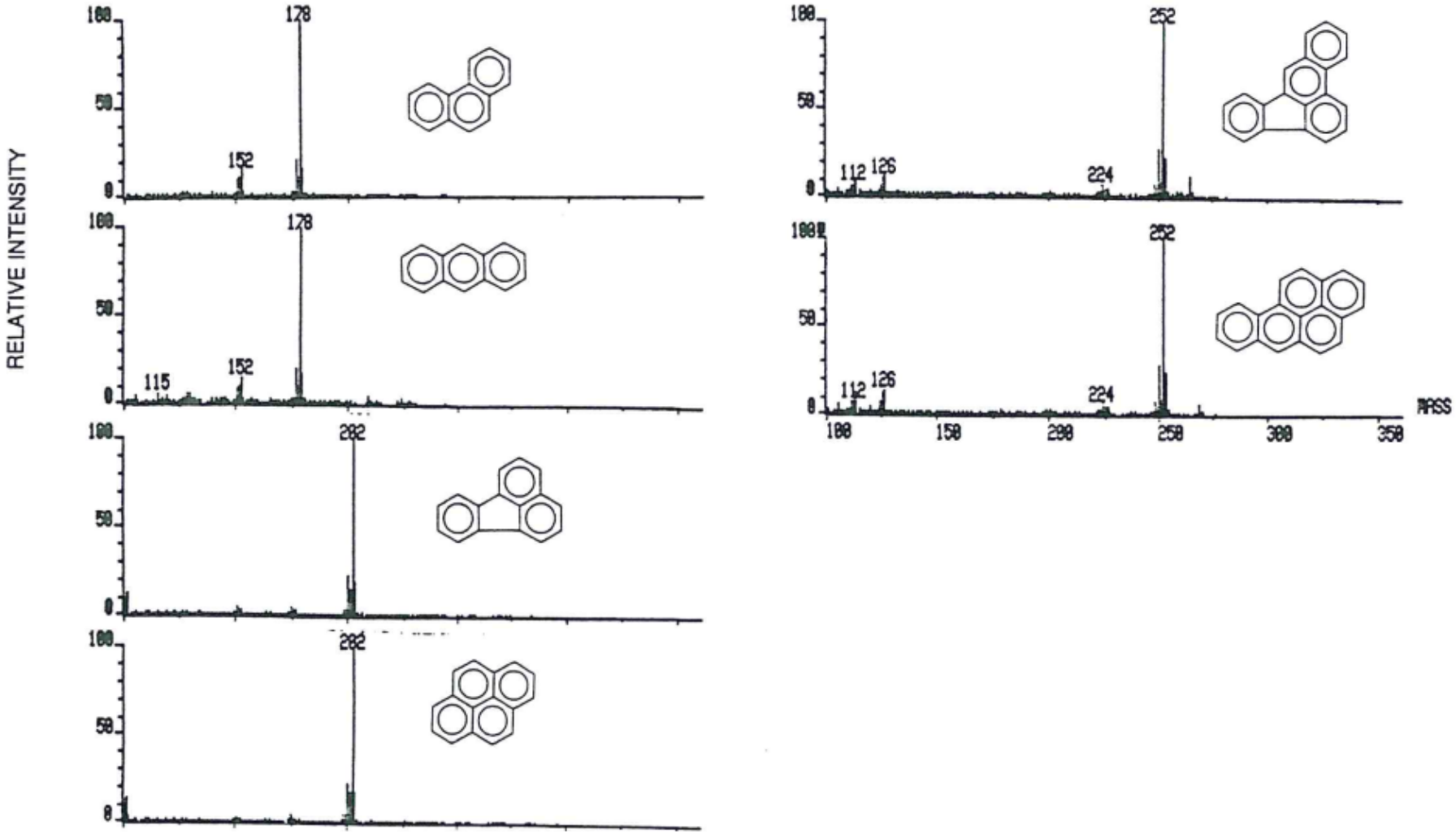
Sediment PAC fraction GC/MS TIC




a)
TIC
b)
m/z 202
c)
m/z 252
d)
m/z 278
100
e)
m/z 302
0
1000
3000 scan (1 sec/scan) 5000
60°C
60°C
300°C
300°C


RELATIVE INTENSITY
100
50
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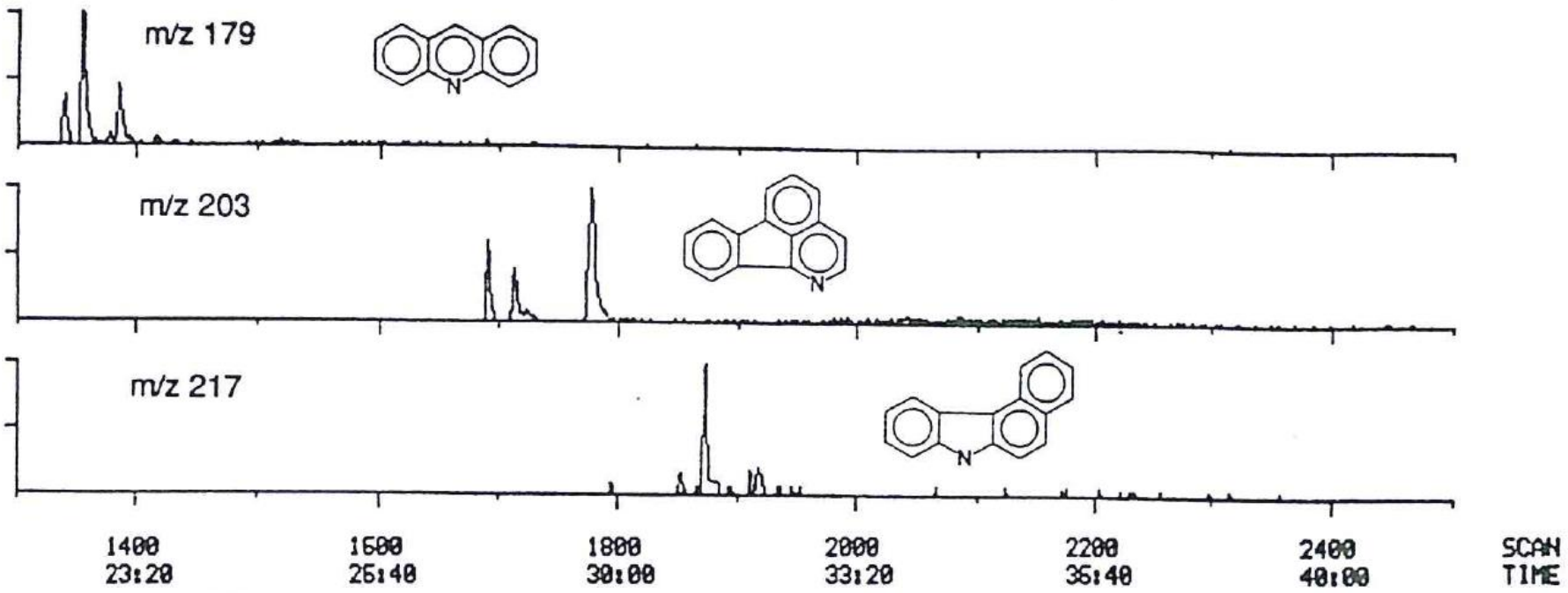
178
115
152
282
282
252
112
126
224
252
112
126
224
MASS
100
150
200
250
300
350

Selected ion chromatograms: PANHs



Remediated Sydney tar ponds unveiled as green space

Open Hearth Park is a 39-hectare green area featuring sports fields, walking trails, and a playground

The Canadian Press Posted: Aug 30, 2013 7:04 AM AT Last Updated: Aug 30, 2013 3:26 PM AT

Ways of targeting specific analytes in GC/MS:

- Selected ion chromatograms for $M^{\cdot+}$ or F^{+}
- Selected reaction monitoring
  ($\Delta m/z$ when $M^{\cdot+} \rightarrow F^{+}$)
- Constant neutral loss

GC/MS summary

- One of the most widely used analytical technique in all fields
- Combines the advantages of universal (TIC) and specific (SICs) detection
- Qualitative and quantitative
- Relatively low cost in the world of mass spectrometry
- Quadrupole and ion trap mass analyzers mostly used
- Used for volatile compounds and derivatization required for others
- Up to mass about 800-1000.

Questions

1: What is the difference between the total ion current and a selected ion current in gas chromatographymass spectrometry (GC/MS)?

2:
a) Explain, in a reaction, how ions are formed by electron impact ionization.
b) What types of molecules is this technique used for?

3: How does an electron capture detector create a signal when analyzing halogenated compounds by GC?