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Environmental Air Monitoring by TD/GC-TOF MS with Variable Energy Ionization

Nicola Watson, Ph.D.

Where we're going next in air?

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Challenges facing the 'Air' market

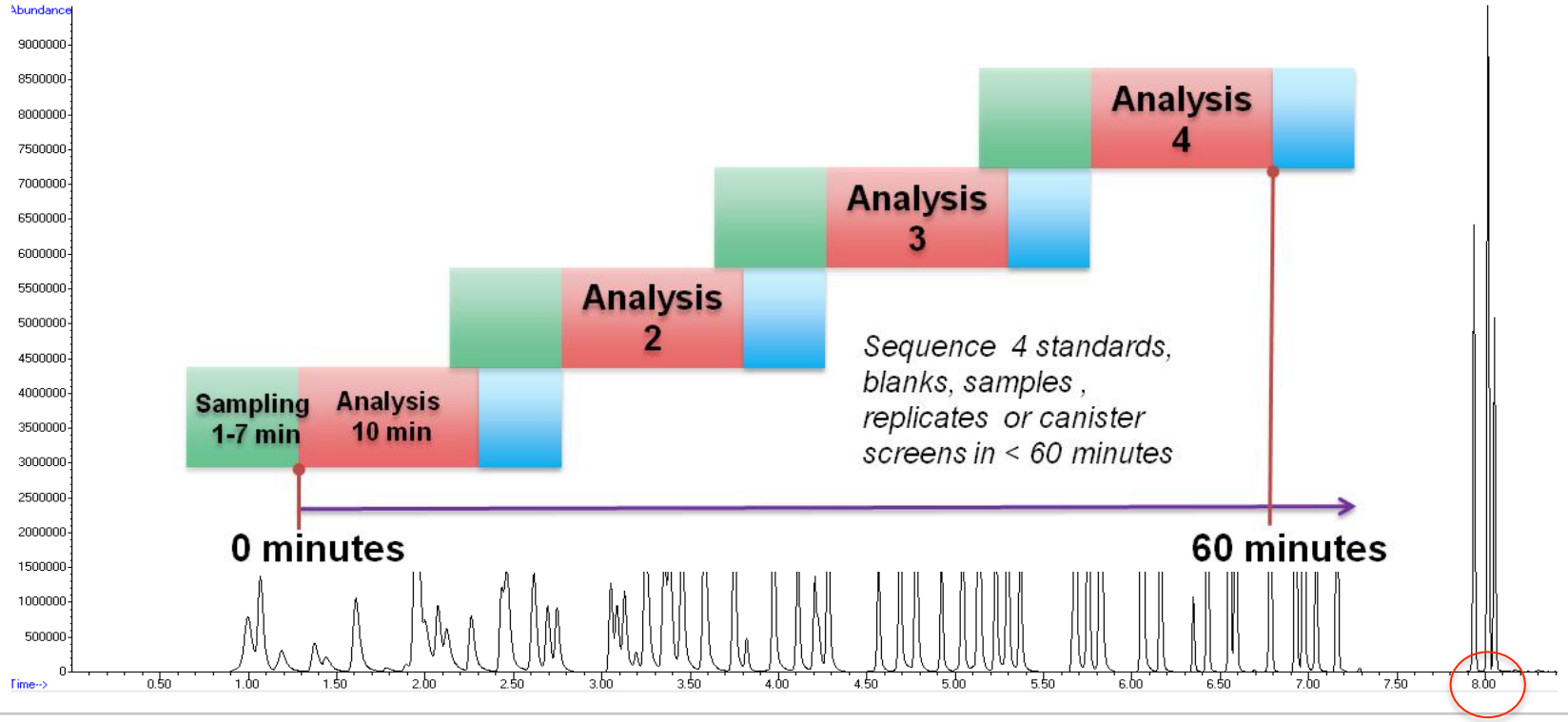
- Market at rock bottom price for standard TO-15 analysis
  - Tackle this by,
    - Increasing throughput
    - One analysis for all (e.g. combining TO-15 and PAMS)
- New/changes to existing method requirements
  - New compounds
  - New reporting limits required for different applications (e.g. Indoor Air)
  - IDLs, MDLs, PLQs, LOQs. Which is meaningful?
- Does variable energy ionization add another dimension to air analyzes?

TO-15 Fast GC = more runs per hour

Factors for increasing productivity include

- Time to prepare sample
- Analysis and cool down of GC-MS system

A 50 mL standard (100 ppb) run with a 100:1 split



8.5 Minute run for TO-15 analysis

MDLs for TO-15 Fast analysis

Method Detection Limits for TO-15

- MDLs are determined based on the performance of the method, there are a number of factors
  - Instrument/canister cleanliness/matrix
  - Detector performance
  - Pre-concentration sample volume limits
- All must be taken in to account when assessing a system/method suitability.

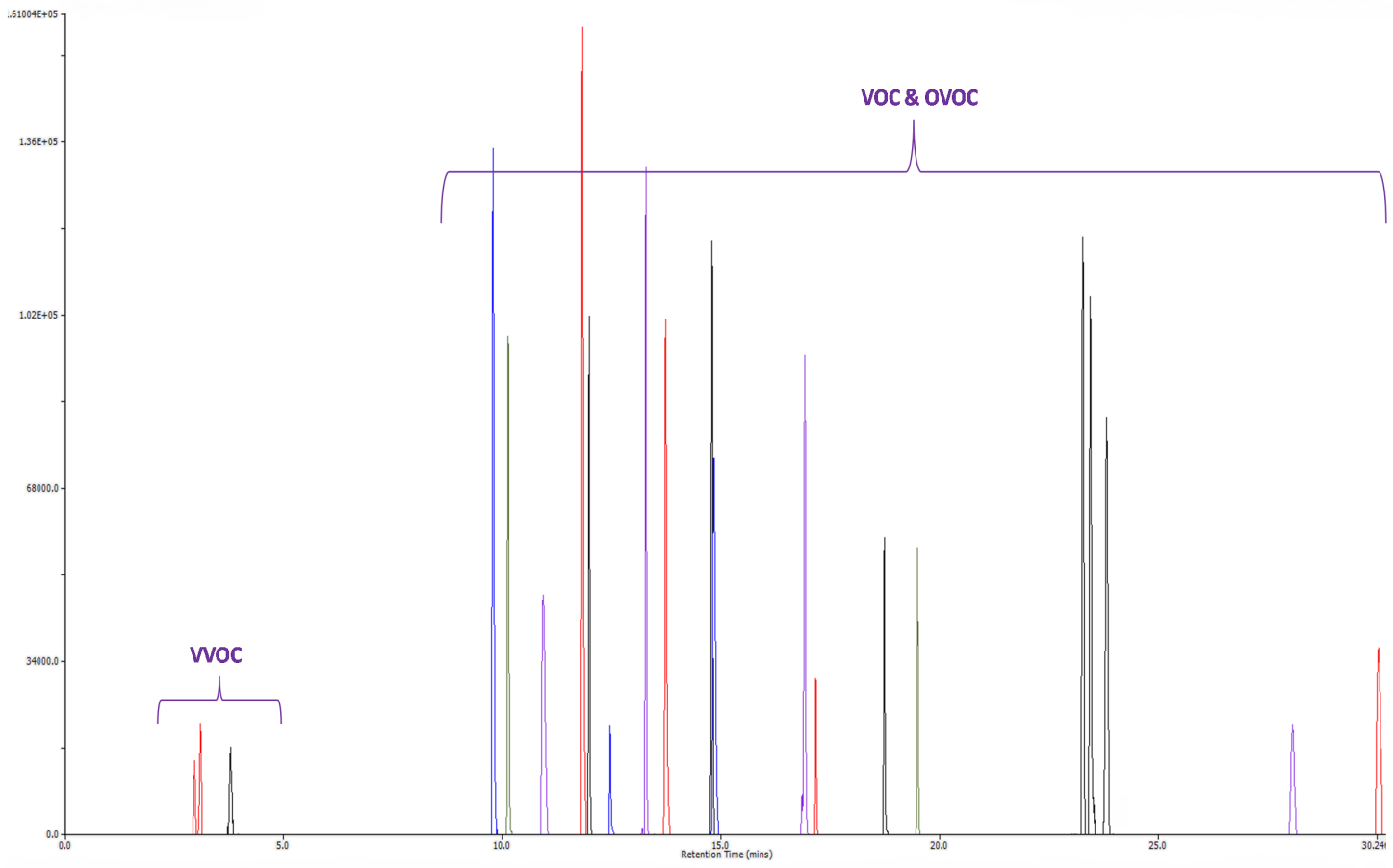
For a 500 mL sample split 20:1, MDL's range from 0.08 ppbv (1,3 butadiene, 0.18 µg/m^3) to 0.014 ppbv (naphthalene, 0.07 µg/m^3)

For a 1000 mL sample split 5:1, MDL range's from 0.01 ppbv (1,3 butadiene, 0.02 µg/m^3) to 0.002 ppbv (naphthalene, 0.009 µg/m^3)

Universal air monitoring

VVOC, VOC and polar VOCs with no dehydration or membrane drying

10 mL of a 4 ppb standard (5:1 split) 80 % RH



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IDLs for small sample volumes

45 mL sample volume (75% RH standard) split 2:1

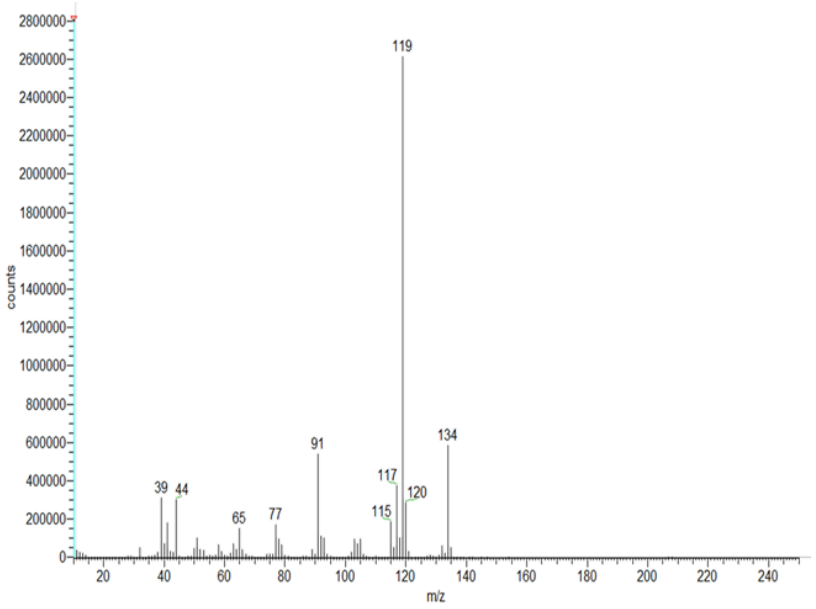
- IDLs are typically based on level/concentration of analyte required to produce a signal that is statistically different to the fluctuation of the background signal of the instrument (instrument noise).
- IDLs for the instrument set up using a 45 mL sample volume (split 2:1) are shown below.

Ion	Name	IDL (ppbV)	Ion	Name	IDL (ppbV)	Ion	Name	IDL (ppbV)
26	Ethylene	0.083	41	Propene	0.049	56	Acrolein	0.071
26	Acetylene	0.040	43	Isobutane	0.026	45	IPA	0.017
30/27	Ethane	0.060	43	Butane	0.012	43	Pentane	0.009
50	Chloromethane	0.011	45	Ethanol	0.061	41	n-Hexane	0.010
29	Propane	0.088	43	Isopentane	0.020	43	Heptane	0.013

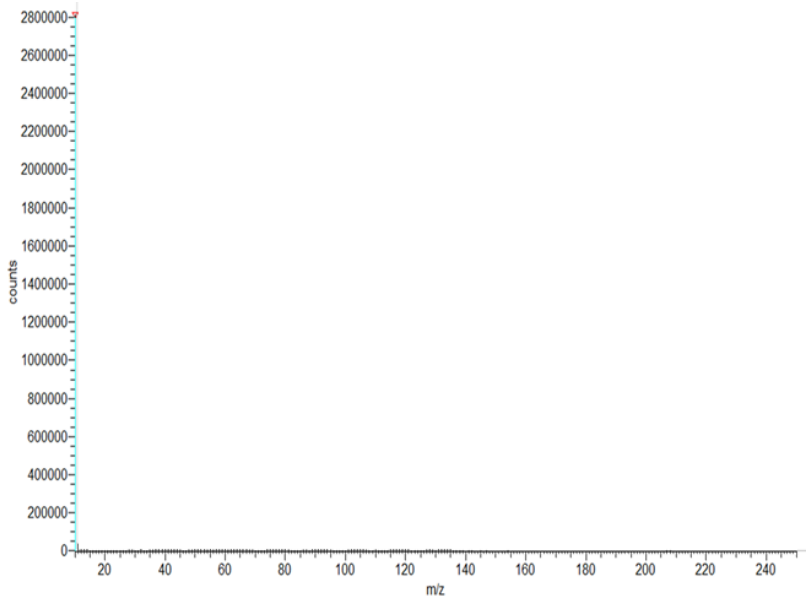
Variable-energy electron ionisation

Historically…

70 eV mass spectrum of p-cymene

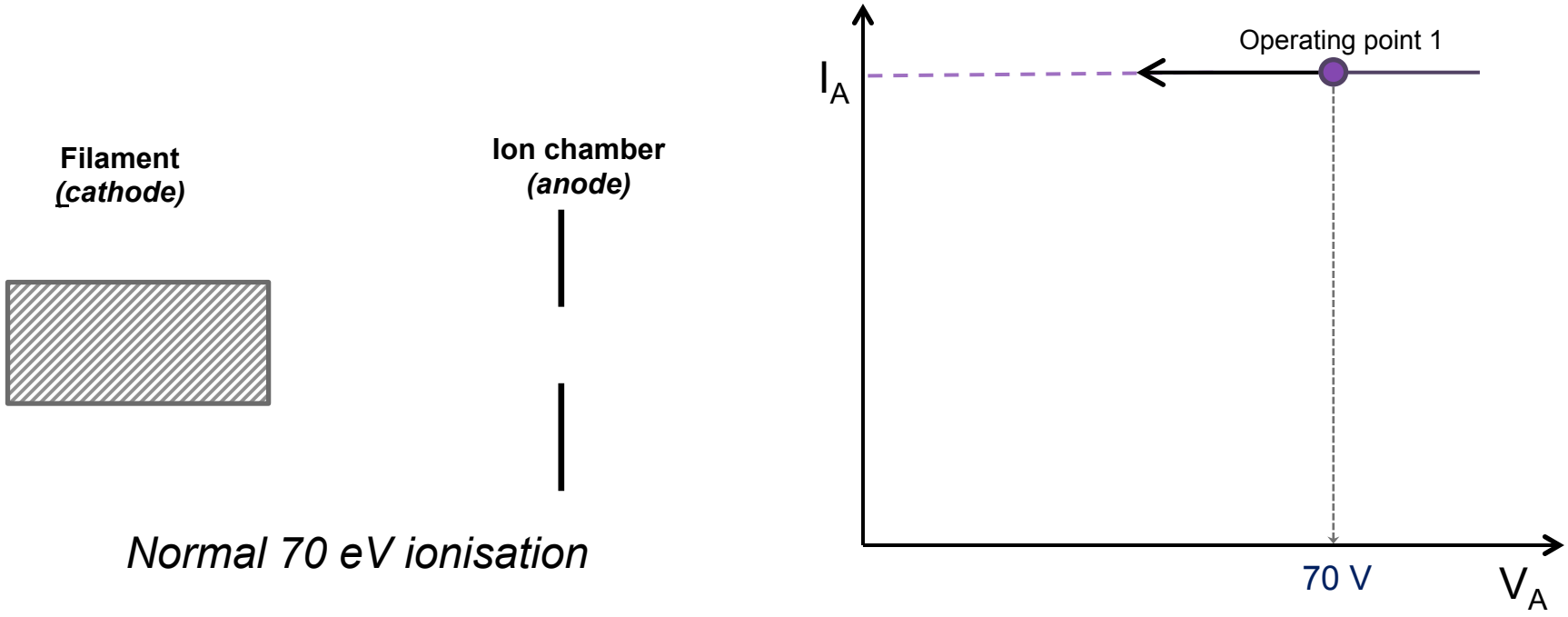


12 eV mass spectrum of p-cymene



Thermionic emissions

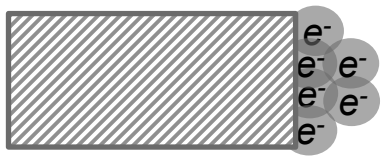
Emissions of electrons from hot cathode



Normal 70 eV ionisation

Thermionic emissions

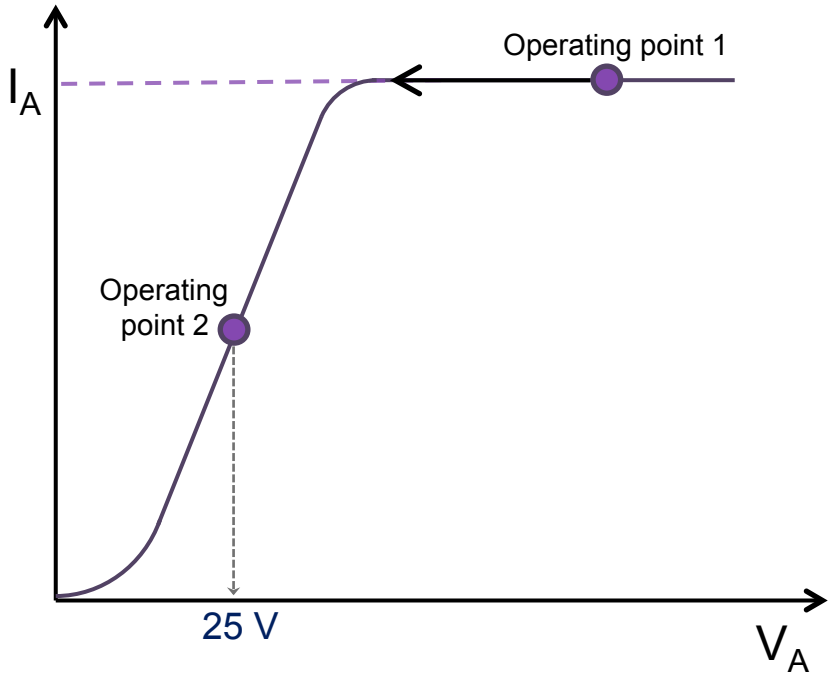
Emissions of electrons from hot cathode



Filament
(cathode)

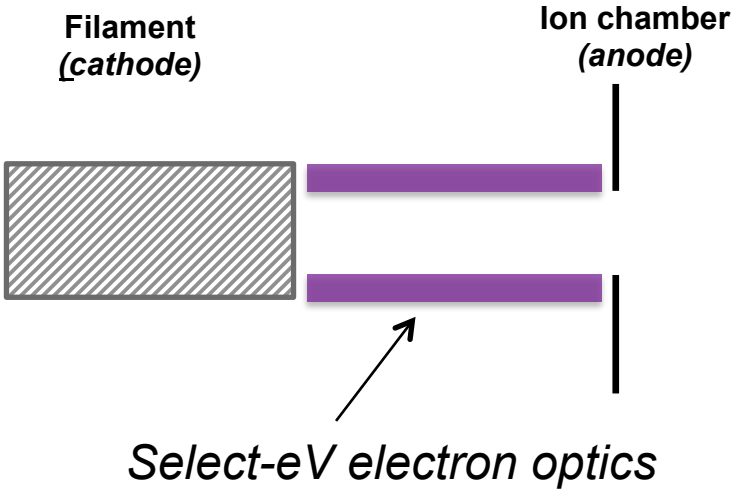
Ion chamber
(anode)

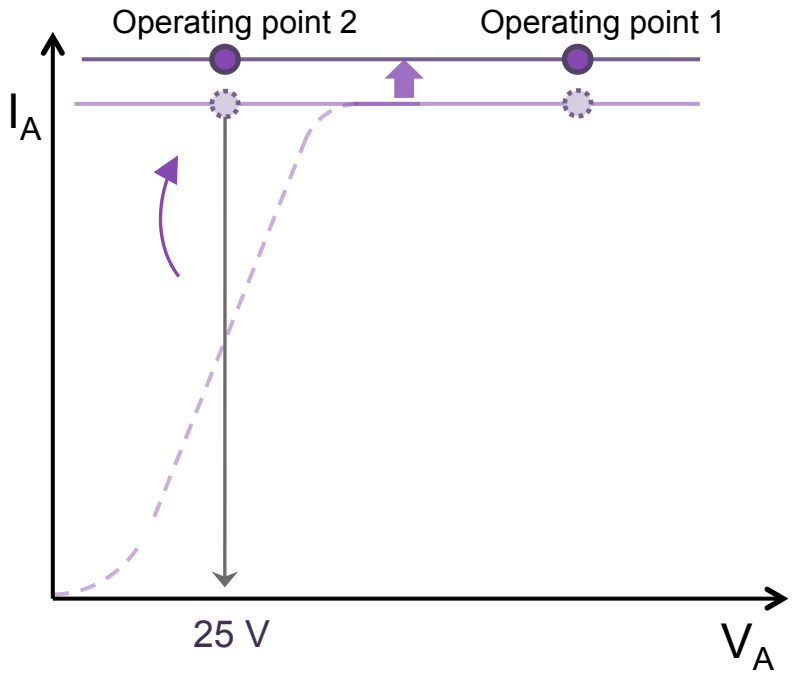
Space-charge limitation



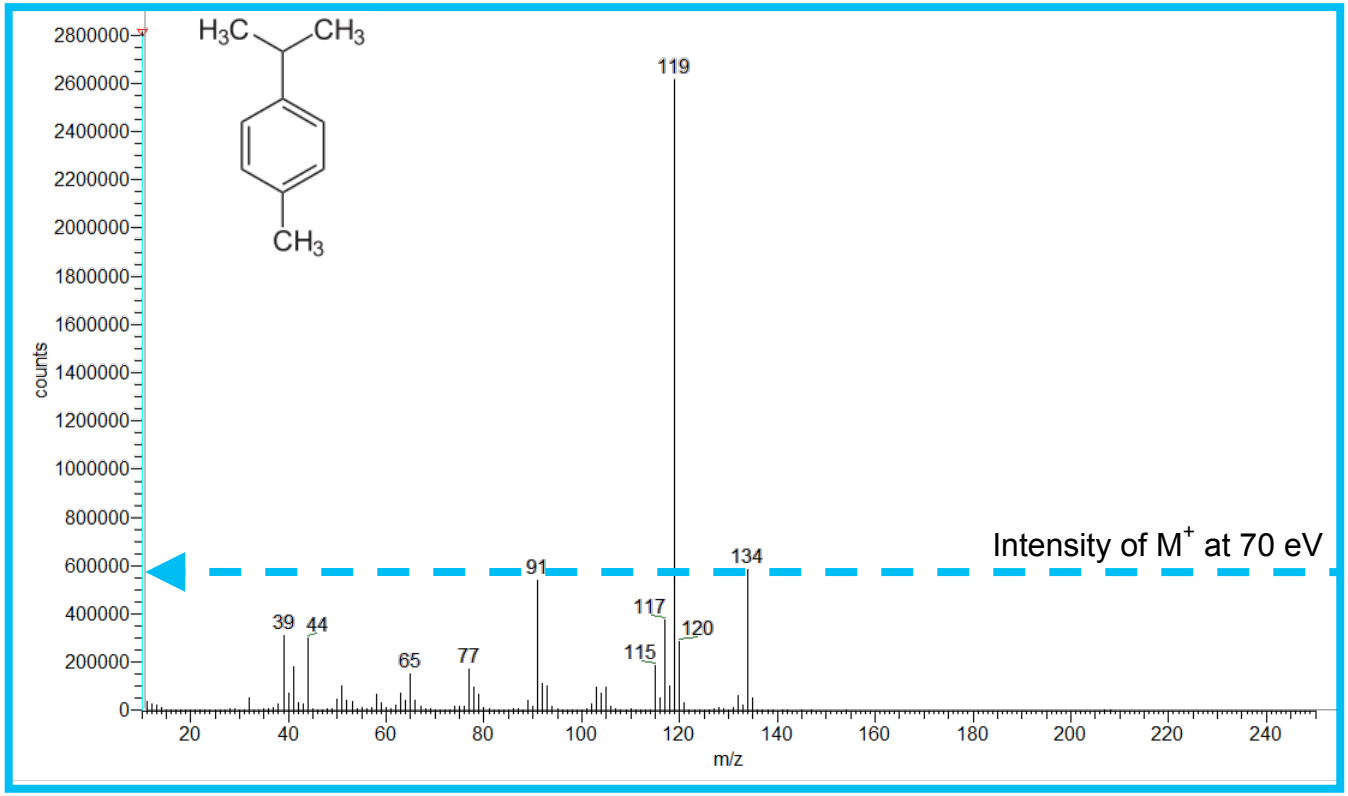
Select-eV technology

Variable-energy electron ionisation



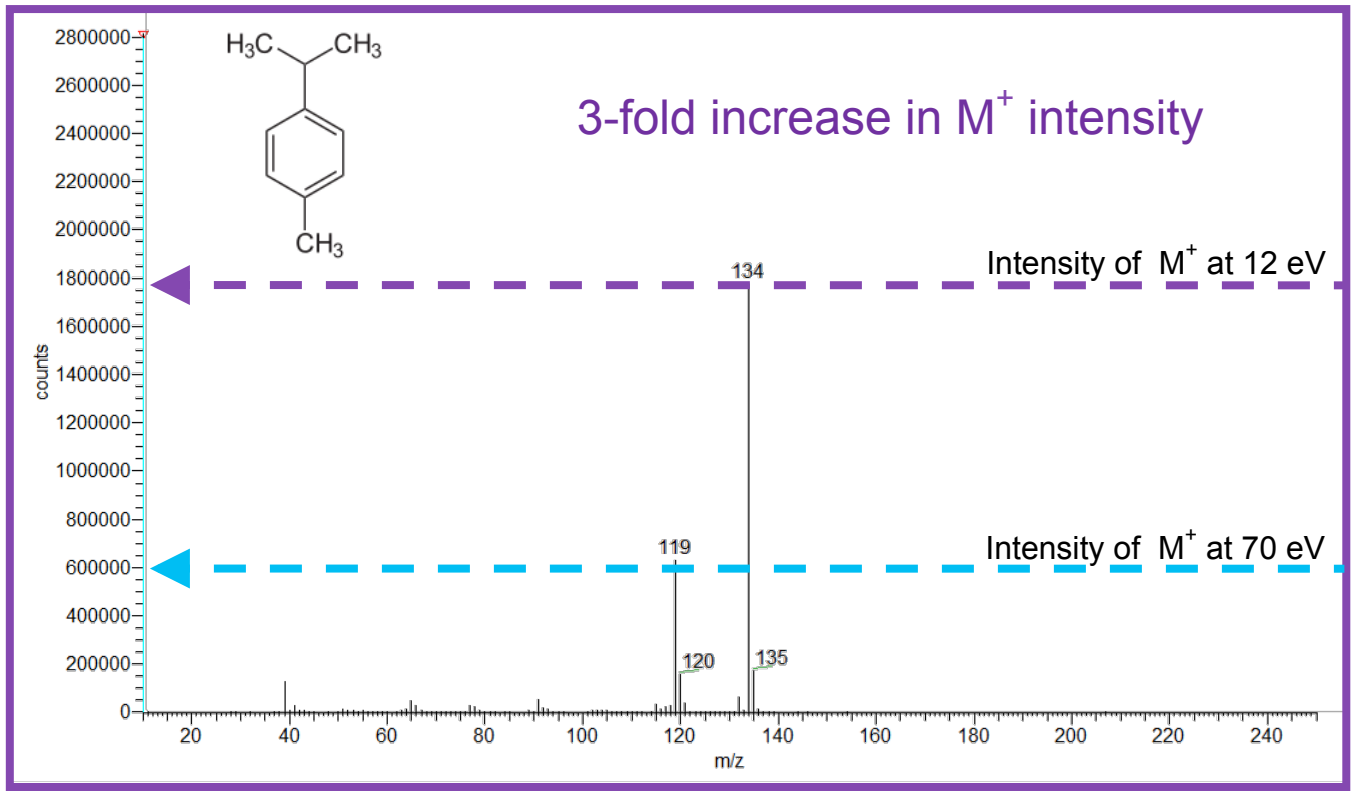


Select-eV: Proof of concept

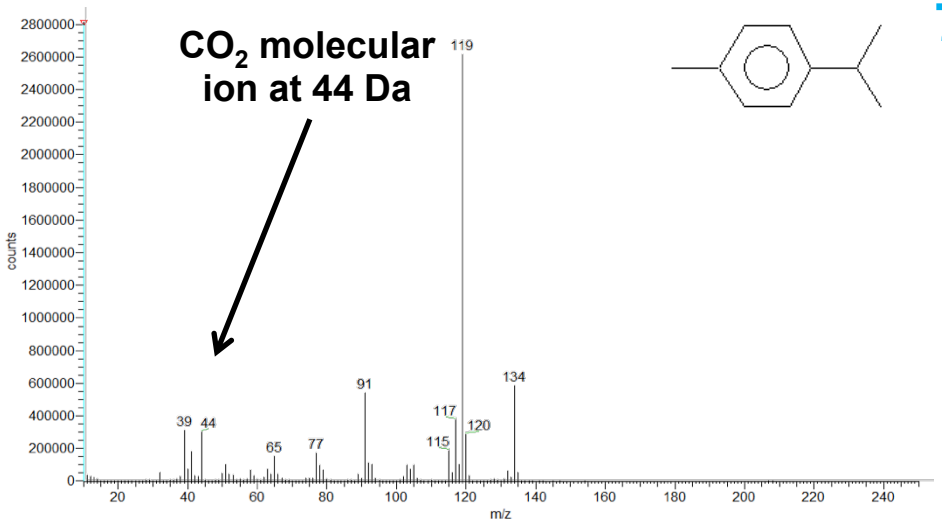


Select-eV: Proof of concept

Spectrum of *p*-cymene at **12 eV**



Selectivity enhancement at low eV



70 eV

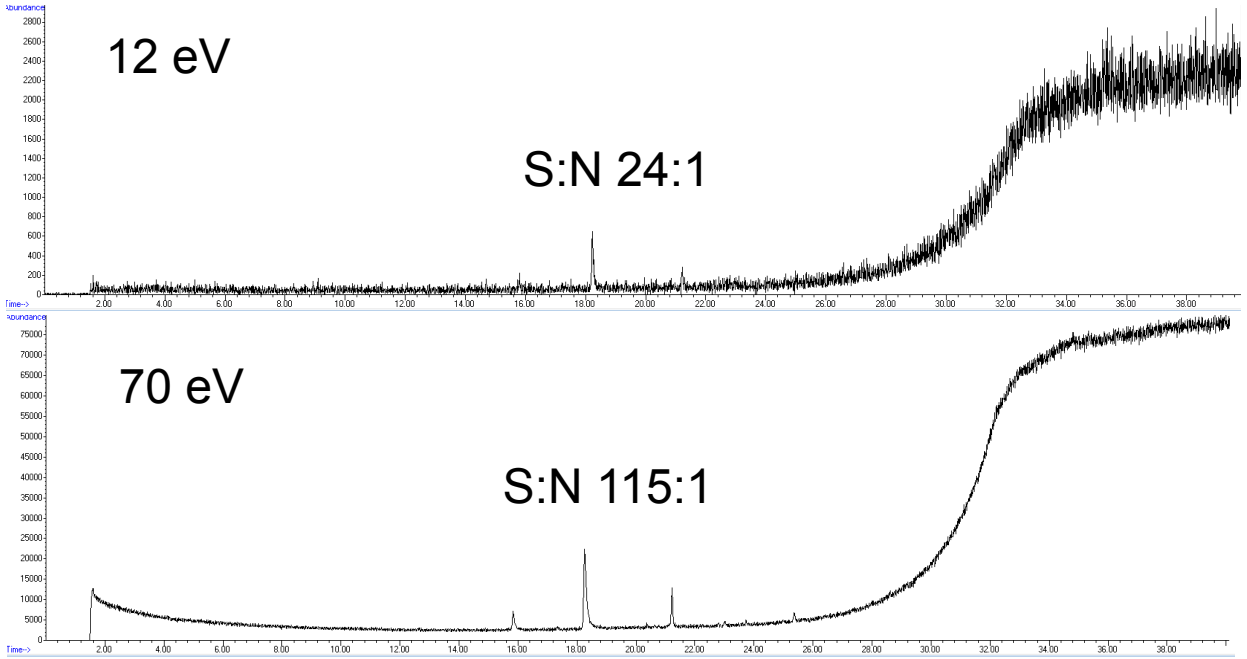
- Ionisation potential of common gases in GC–MS
  - CO_2: 13.8 eV
  - N_2: 15.6 eV
  - H_2: 15.4 eV
  - **He: 24.6 eV**

- Residual background gases are not ionised
- Carrier gas is not ionised
- Ion flux is composed solely of sample

Select-eV applied to TO-15

Theory states

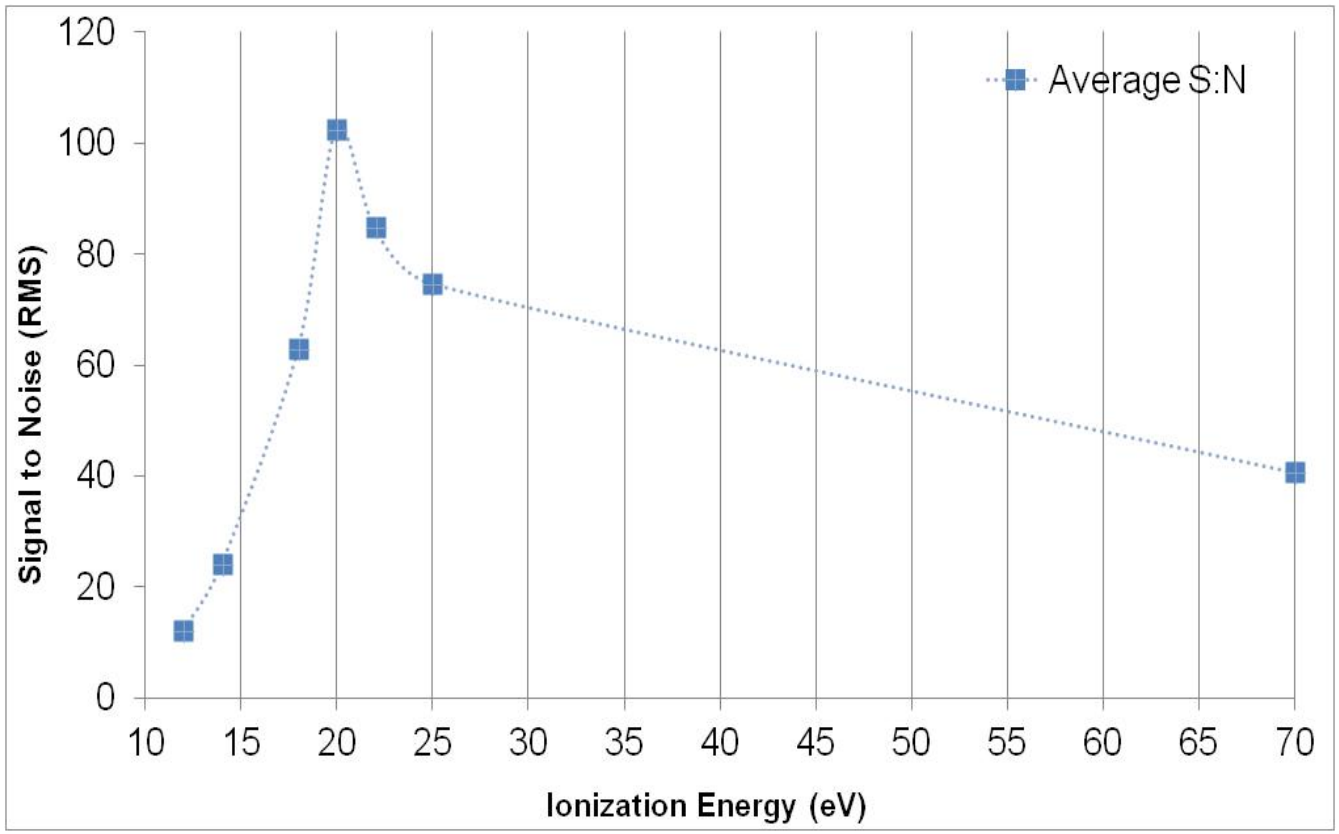
- Lowering the eV to below the background gases should help remove interference and aid identification of certain compounds e.g. using 12 eV should reduce ionization of background gases, like CO_2 (IP 13.77)
- Example of 2-propanol at 70 eV and 12 eV, shows reduction in background



Extracted Ion 45 shown

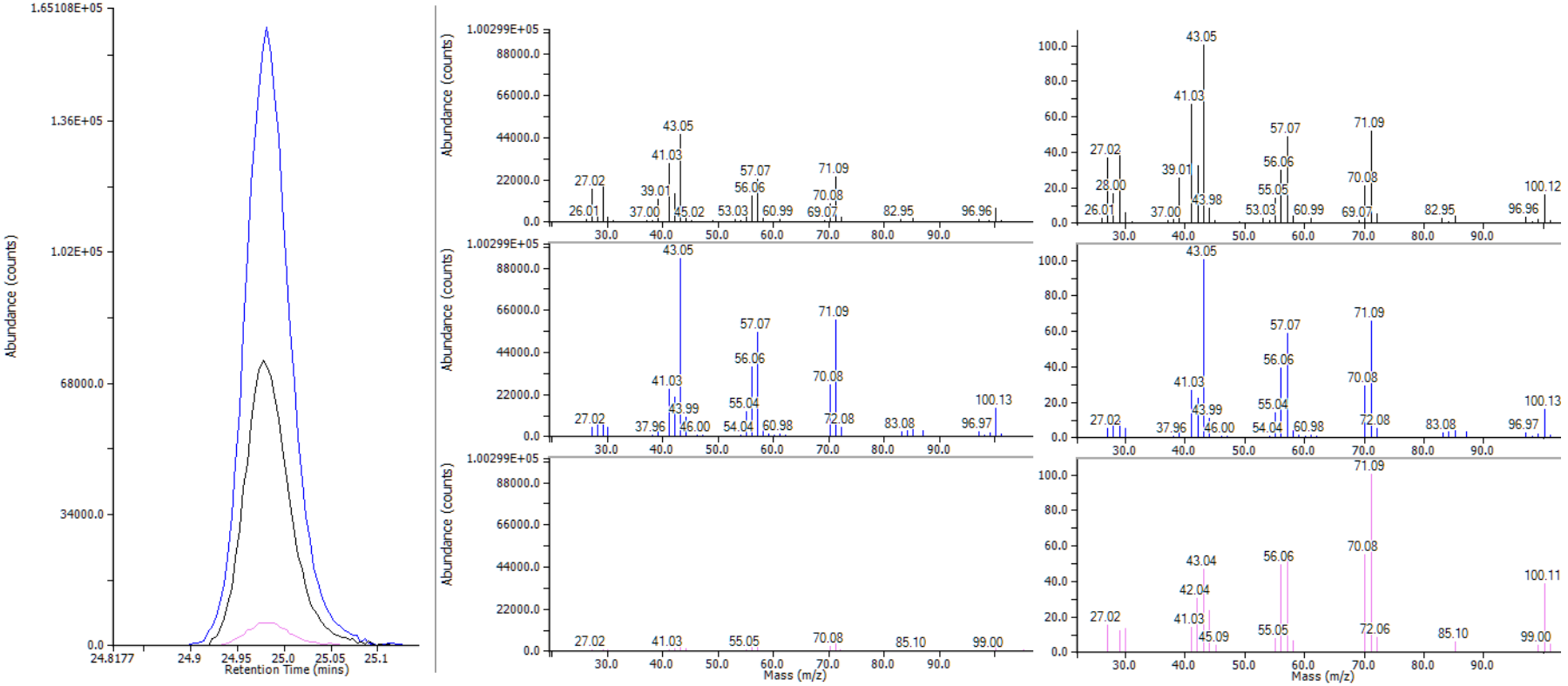
As always, there is a compromise…

- Average S:N for the TO-15 suite of compounds at a range of Ionisation energies.



Spectral comparison of a range of Select-eV values

- Comparison of chromatograms and mass spectra obtained at 70 eV (black), 20 eV (blue) and 14 eV (purple) for heptane in a 5 mL sample of a 100 ppb, split 68:1. The mass spectra on the left show absolute intensity, and relative intensity on the right.



IDLs for small sample volumes at 70 eV

45 mL sample volume (75% RH standard) split 2:1

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50	Chloromethane	0.011	45	Ethanol	0.061	41	n-Hexane	0.010
29	Propane	0.088	43	Isopentane	0.020	43	Heptane	0.013

IDLs for small sample volumes at 20 eV

45 mL sample volume (75% RH standard) split 2:1

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- IDLs for the instrument set up using a 45 mL sample volume (split 2:1) are shown below.

Ion	Name	IDL (ppbV)	Ion	Name	IDL (ppbV)	Ion	Name	IDL (ppbV)
26	Ethylene	0.035	41	Propene	0.019	56	Acrolein	0.025
26	Acetylene	0.030	43	Isobutane	0.018	45	IPA	0.006
30/27	Ethane	0.039	43	Butane	0.007	43	Pentane	0.003
50	Chloromethane	0.004	45	Ethanol	0.038	41	n-Hexane	0.006
29	Propane	0.049	43	Isopentane	0.013	43	Heptane	0.006

1.5 to 3 times the sensitivity of 70 eV IDLs from a 45 mL sample

Conclusions

- Fast –GC of TO-15 analysis is now becoming standard, labs are expecting higher throughput to be cost competitive in the market.
- More laboratories are moving to single analysis for multiple VOC lists, reducing overhead costs and also increasing throughput.
- Laboratories are also reducing downtime – use of more sensitive instruments, means smaller samples and cleaner systems
- Development of new technologies needs to be implemented in laboratories as standard. The full potential of Select-eV is becoming realised not only in VOC analyzes but branching out in to other Environmental areas like SVOCs – is there an application that can be run for indoor air monitoring of SVOCs ??

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Questions?

Acknowledge the work of the Markes Application Team, Dr David Wevill and Hannah Schwab