

Methods for characterizing coal-derived tars and liquids

Alan Herod

Chemical Engineering, Department
Imperial College London

London SW7 2AZ

Introduction

The work described has come from Prof. Kandiyoti's group, with numerous students over two decades at least.

Detailed summaries can be found in two references:

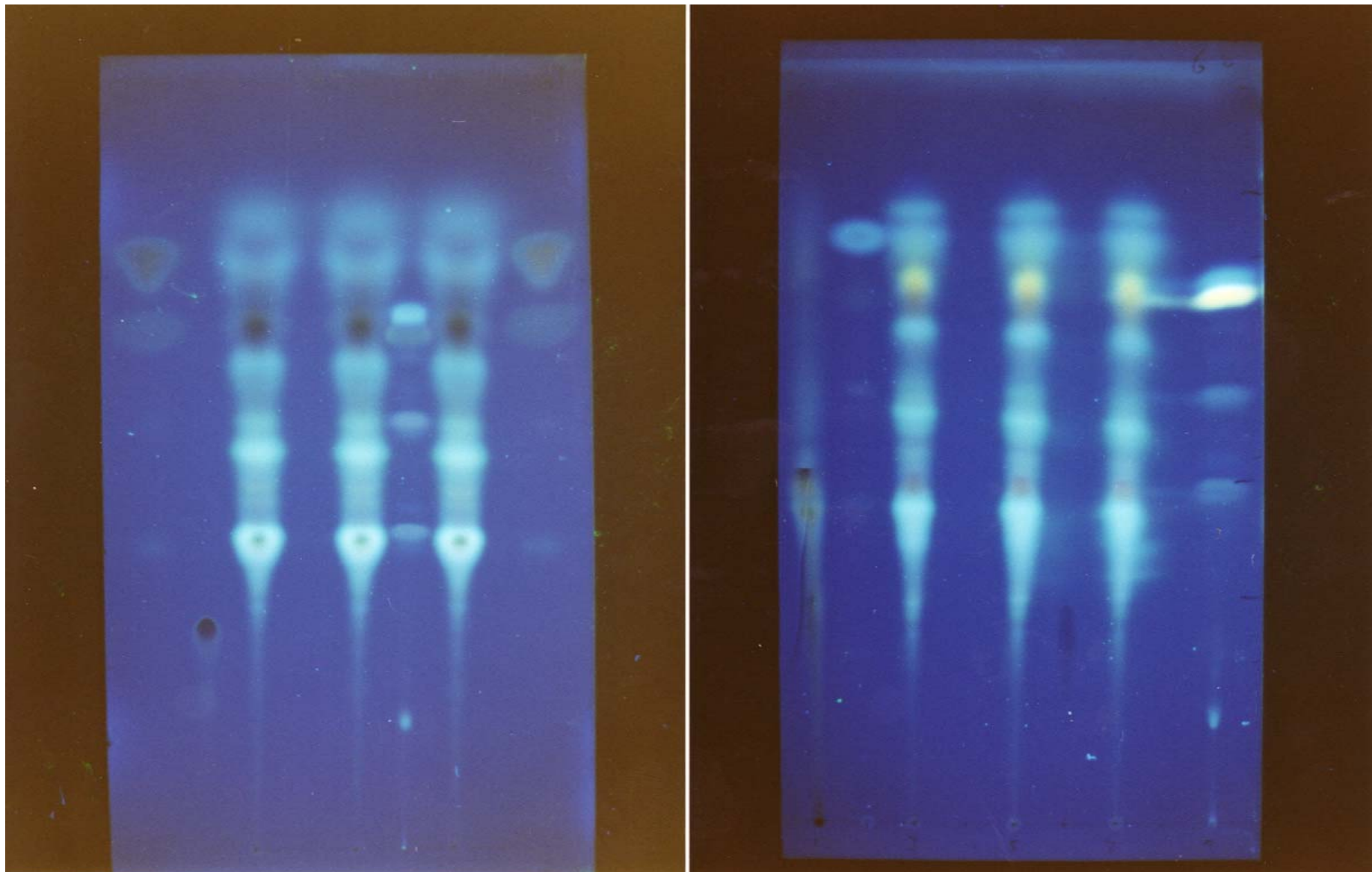
R. Kandiyoti, A.A. Herod, K.D. Bartle. *Solid Fuels and Heavy Hydrocarbon Liquids: Thermal Characterisation and Analysis*. Elsevier 2006, ISBN: 0-08-044486-5.

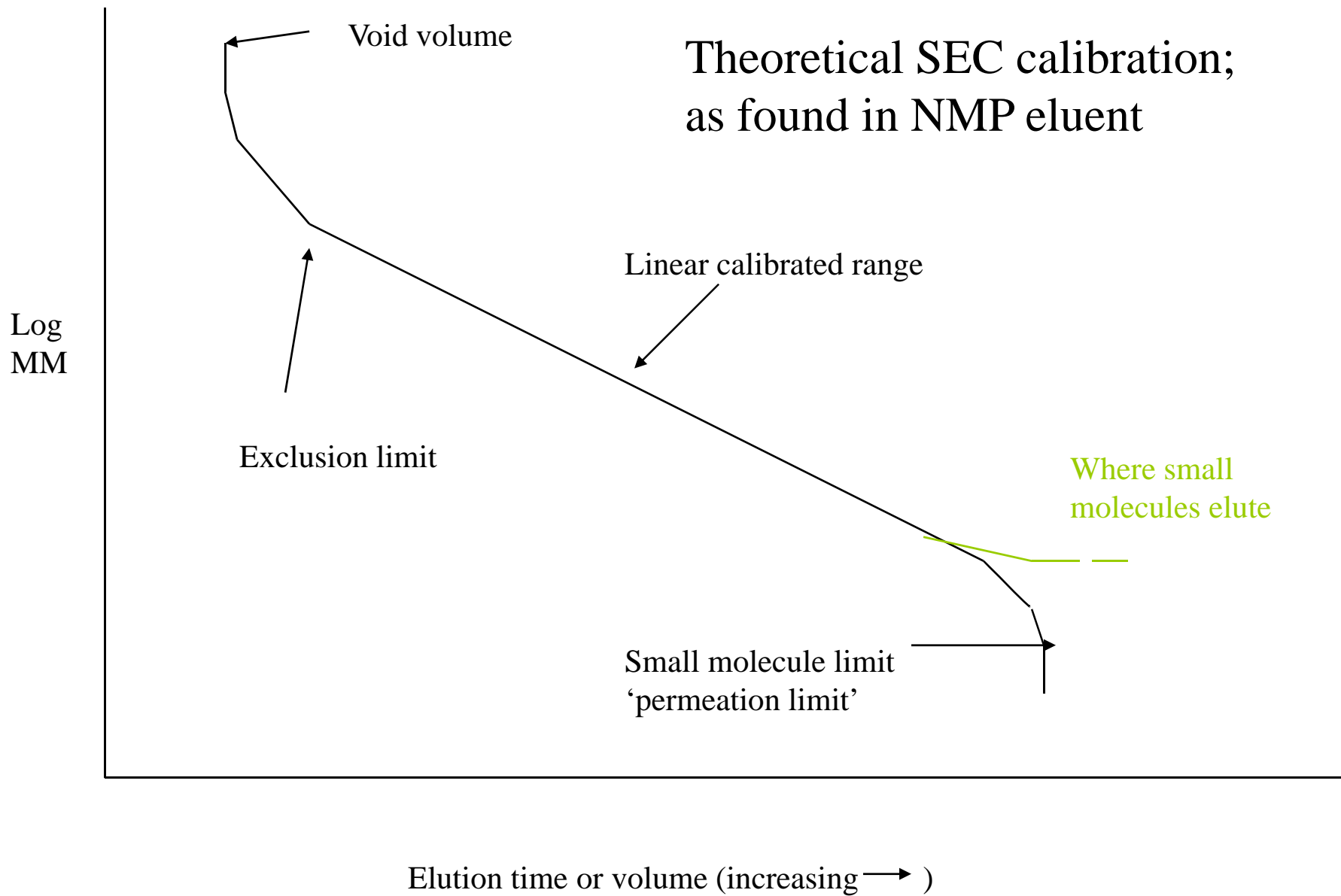
Alan A. Herod, Keith D. Bartle and Rafael Kandiyoti. The characterization of heavy hydrocarbons by chromatographic and mass spectrometric methods: an overview. *Energy & Fuels*, 2007 21, 2176-2203

We have developed methods to detect and characterize the large molecules in coal tars such as size exclusion chromatography (SEC), UV-fluorescence (UVF), mass spectrometric methods (LD-MS and MALDI-MS) having realised that GC-MS could only detect small molecules, $< m/z$ 300 with probe-MS reaching perhaps m/z 500-600.

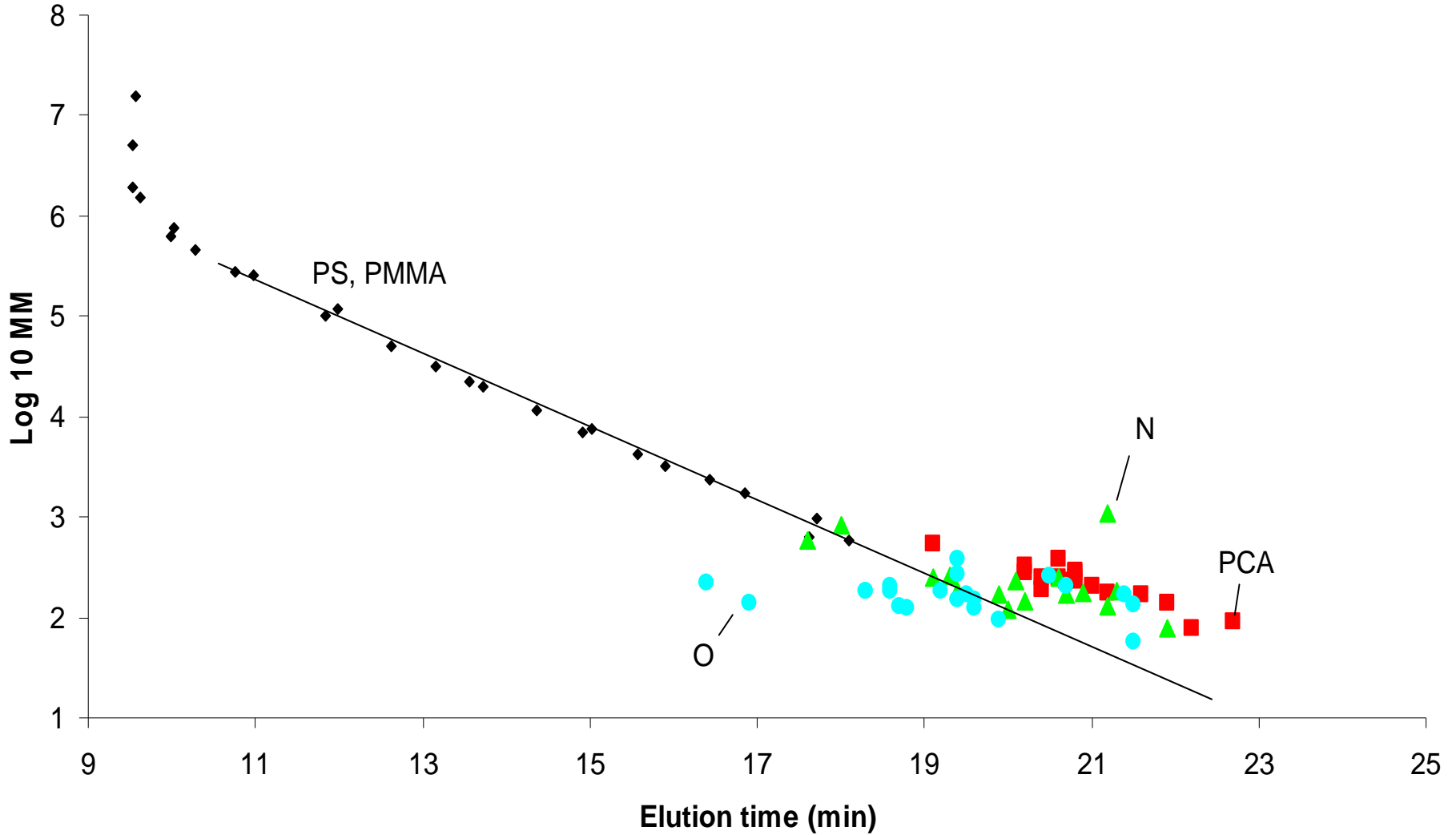
The work started with TLC since the intractable material stayed where put initially.

TLC of pitch, 3 spots, 2 UV wavelengths [254 and 366 nm]

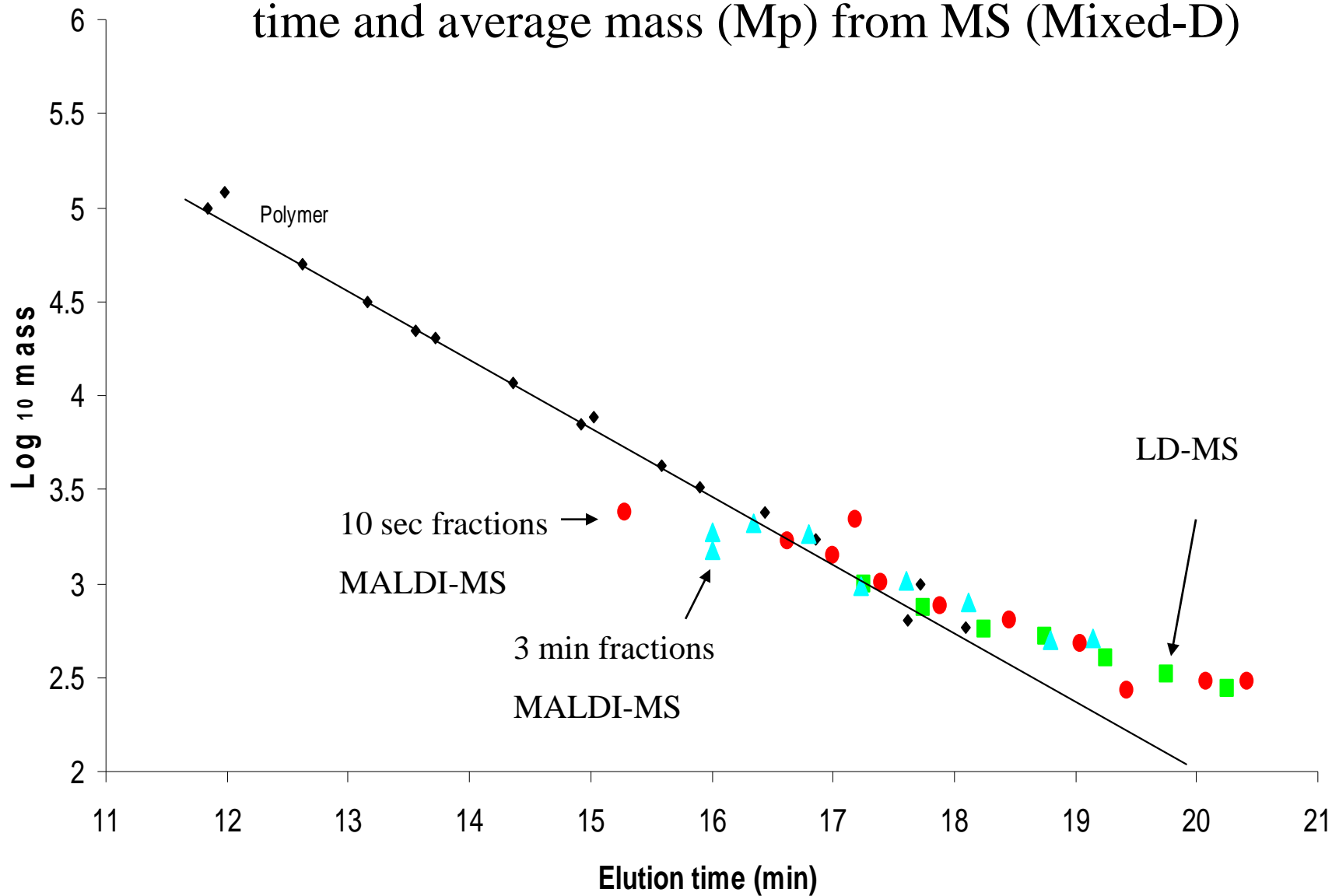




We have used Polymer Labs Mixed-Bed columns (A, D and E) and here we will show only the Mixed-D calibration data.



Pitch fractions from SEC – analytical SEC elution time and average mass (Mp) from MS (Mixed-D)



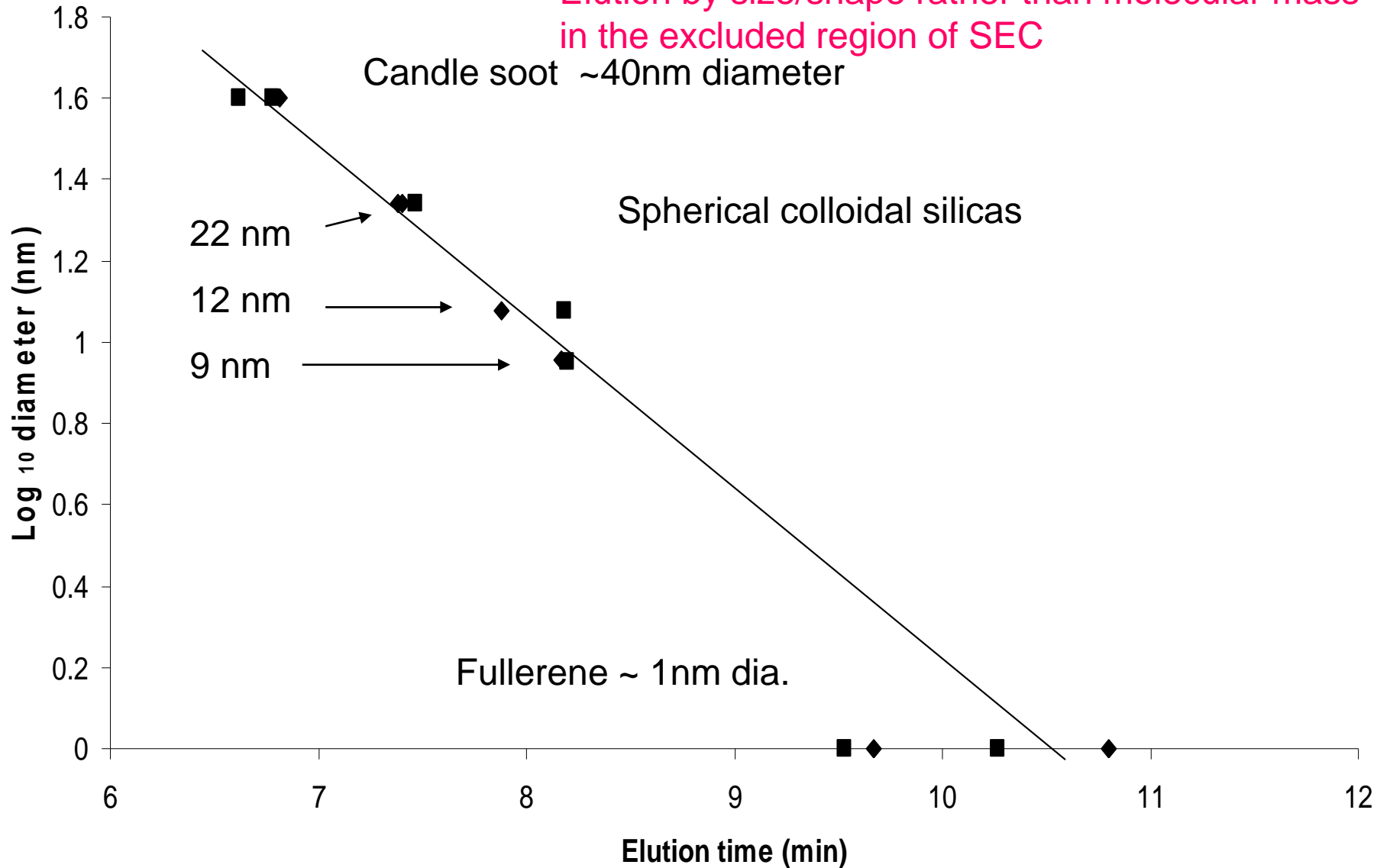
Spherical standards Mixed-D

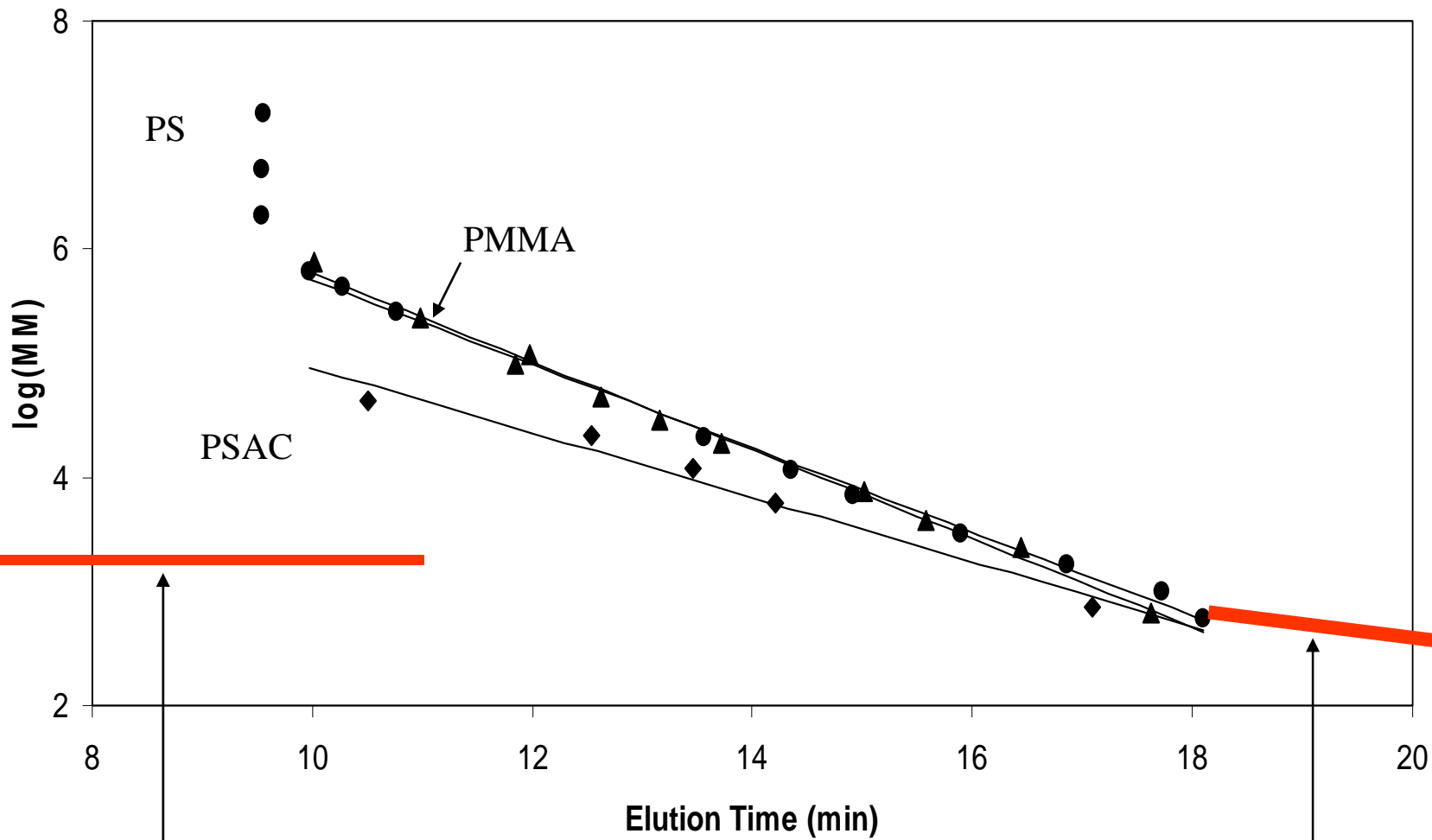
Elution by size/shape rather than molecular mass
in the excluded region of SEC

Candle soot ~40nm diameter

Spherical colloidal silicas

Fullerene ~ 1nm dia.





PS

PMMA

PSAC

Spherical standards
from 6.5 min

Mixed-D calibration

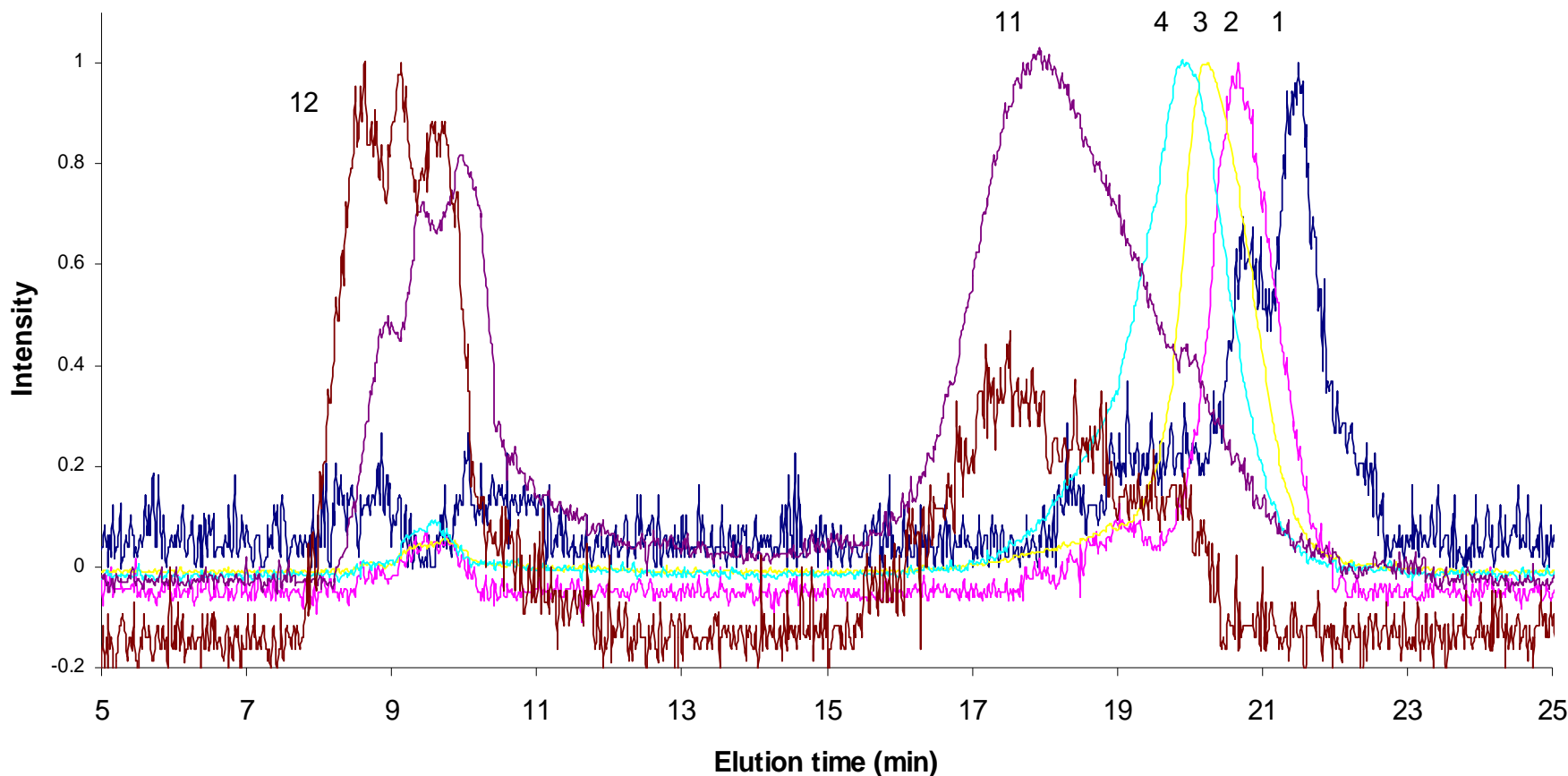
Small molecules to 23 m

SEC of coal-liquids always show bimodal distributions, even fractions from solvent solubility, column chromatography, planar chromatography. Some examples are shown next. In each case of fractionation, the lower-size peak shifts to shorter elution times as the solvent used increases in polarity or solvent power (e.g. from pentane to acetonitrile, to pyridine, to NMP) (larger mass) while the relative intensity of the excluded peak increases.

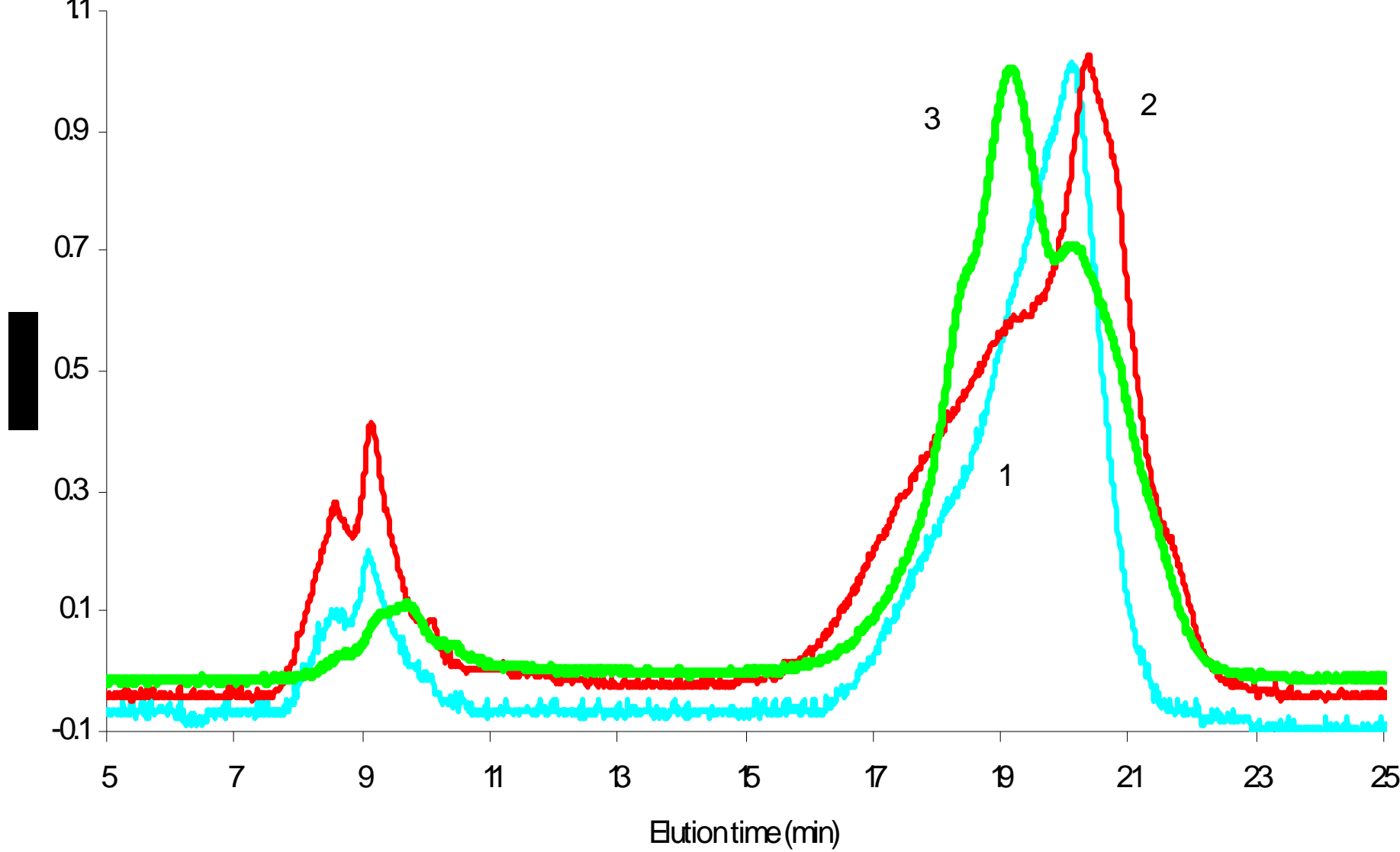
Hydrogenation attacks the excluded peak first but does not reduce it to small molecules; liquefaction extracts always contain some excluded material and the proportion reduces with severity of conditions of liquefaction [Flowing solvent > microbomb extract > PoA digest].

Planar chromatography of pitch followed by SEC in NMP [W. Li, T.J Morgan, A.A. Herod and R. Kandiyoti. TLC of pitch and a petroleum vacuum residue - relation between mobility and molecular size shown by SEC. J. Chrom A 2004; 1024, 227-243.] did show regular size increases with increasing TLC immobility. Some fractions are shown here.

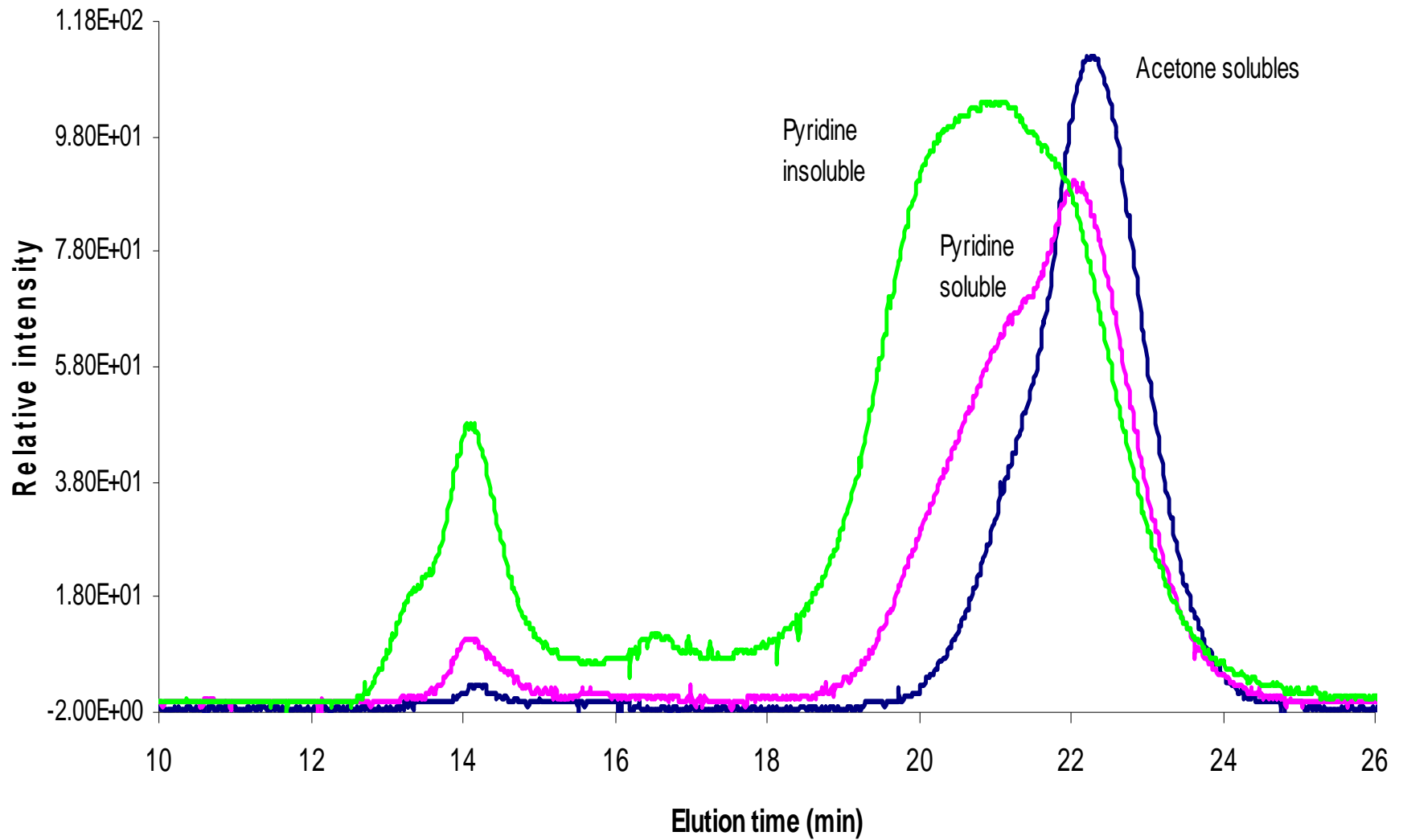
Pitch fracs from TLC by SEC in NMP



SEC of coal tar pitch (1), PoA coal digest (2), low temperature tar (3) 350 nm Mixed-D column

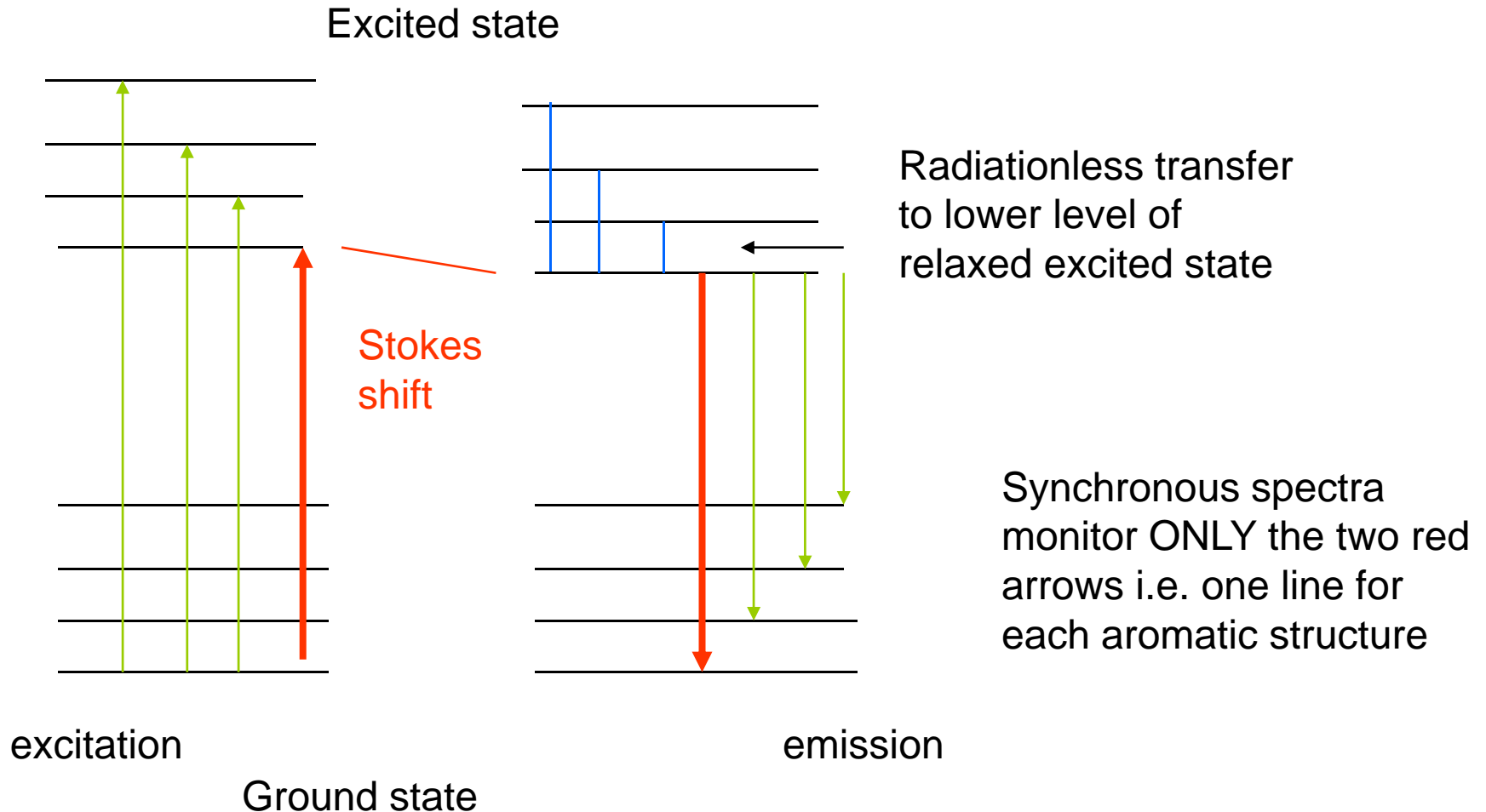


Pitch fractions on Mixed-A column, UV-A 350nm

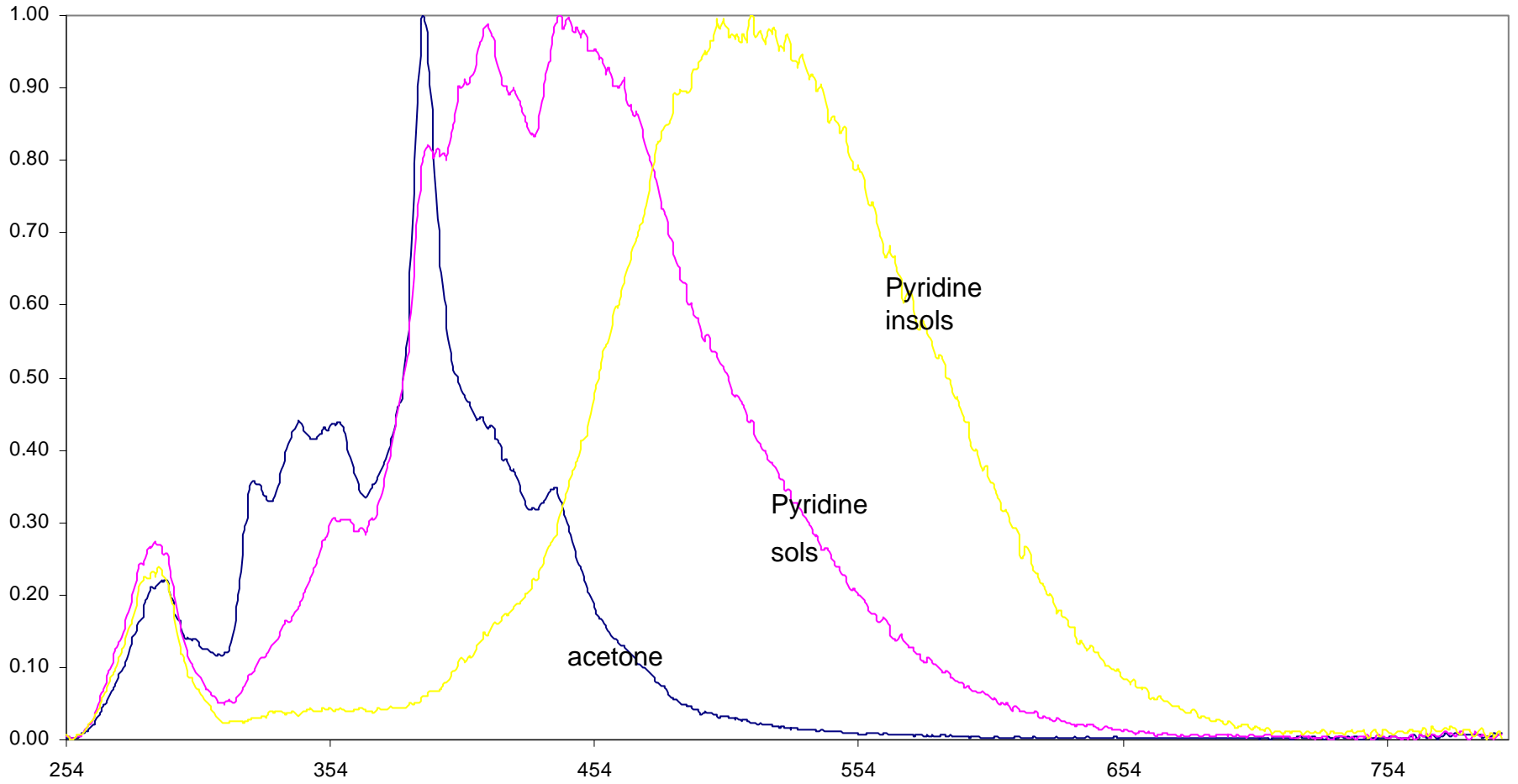


UV-fluorescence spectroscopy

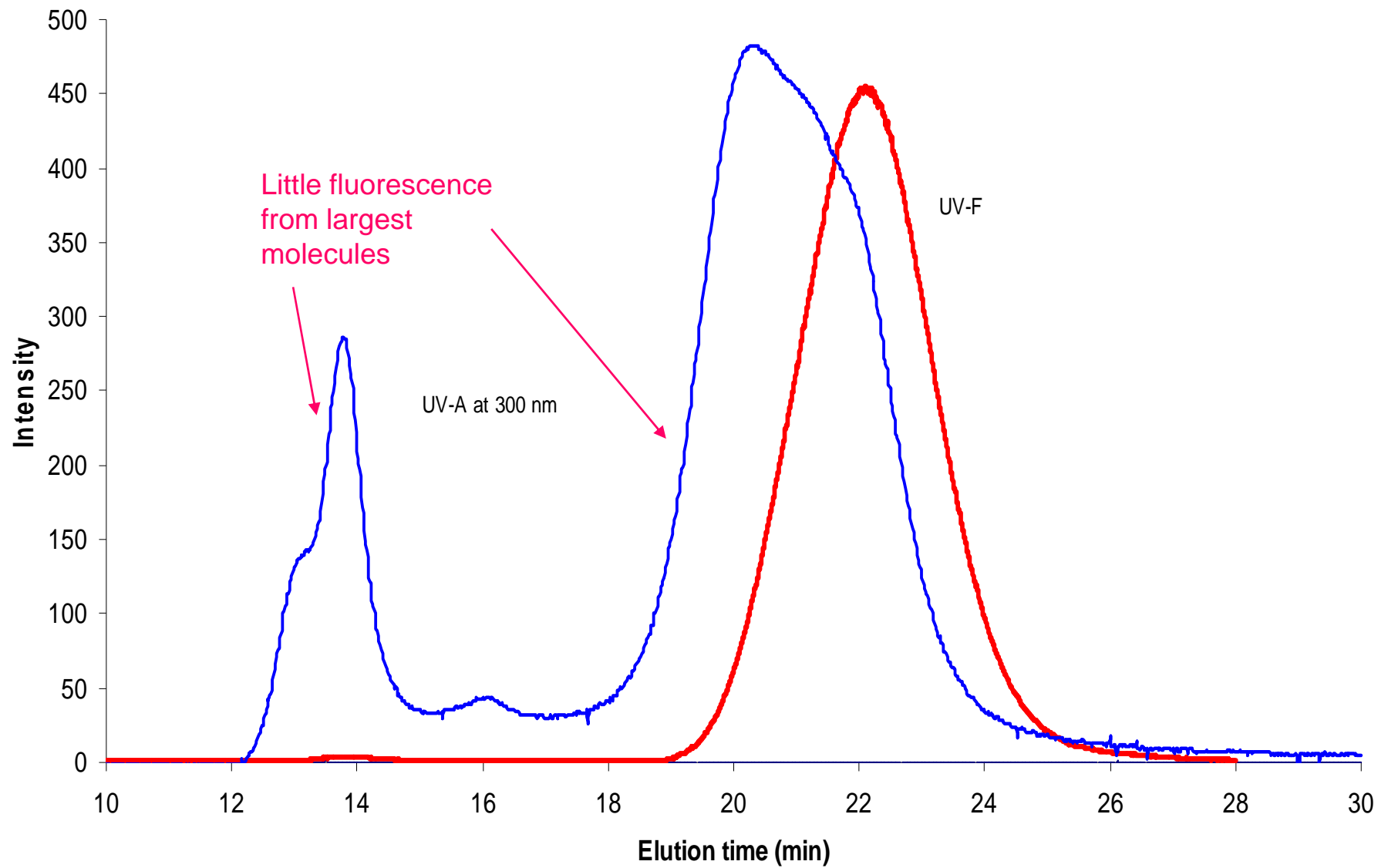
Static UV-fluorescence can be done in NMP solution, with spectra obtained in excitation mode, emission mode or in synchronous mode. The following examples show only synchronous mode spectra.



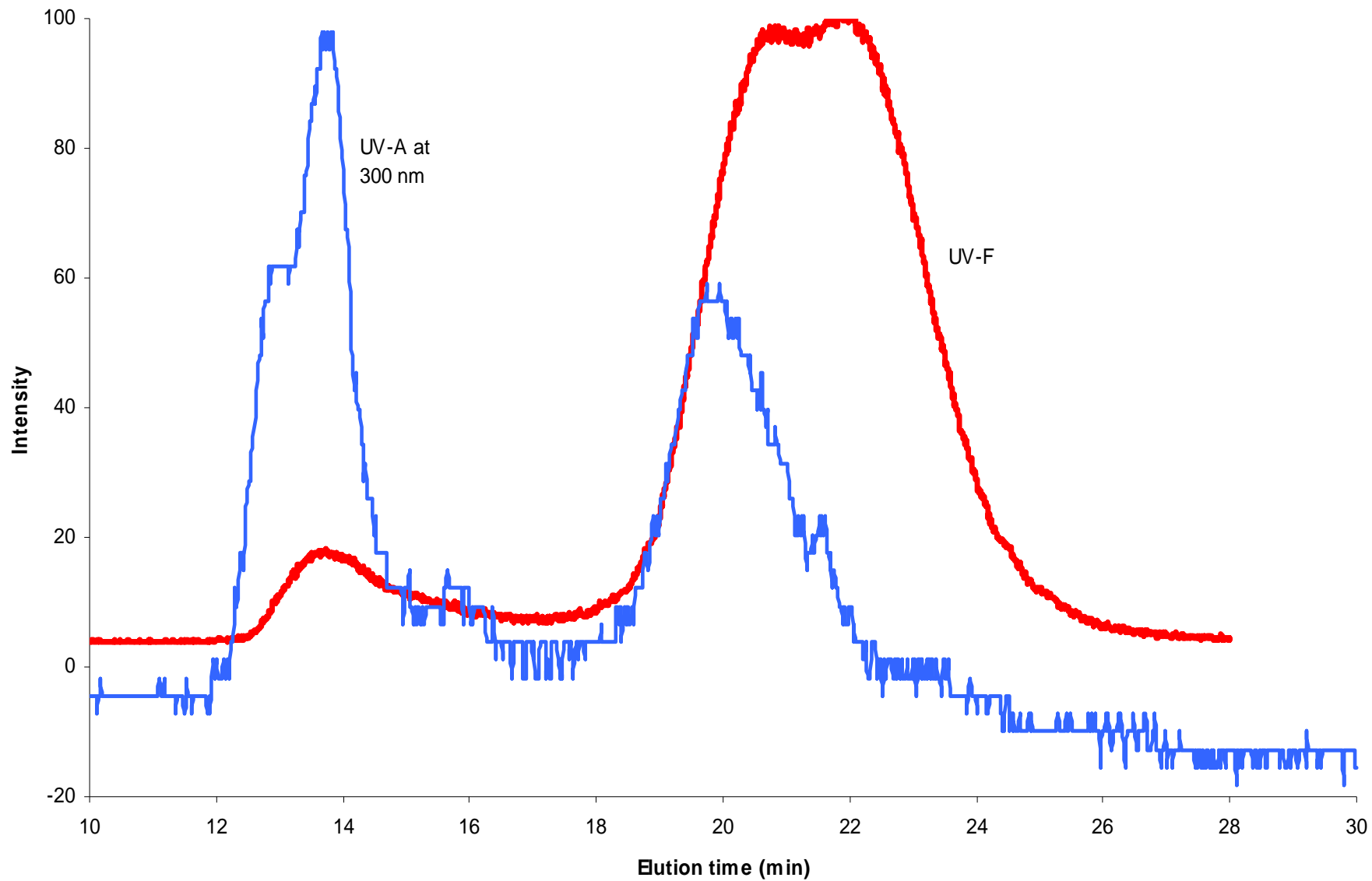
Acetone Pitch Fracs in NMP - Peak Norm



UV-A and UV-F of pitch pyridine insolubles, Mixed-A column



PoA digest nmp sols UVAF Mixed A



Mass spectrometry has the problem of discrimination against high-mass molecule ions in a polydisperse sample. In GC-MS, the upper mass limit is $\sim m/z$ 300 and only $\sim m/z$ 1200 for ionisation methods requiring volatility of molecules. Even ESI-MS does not go higher in mass in such samples. Our SEC calibration reached m/z 3000.

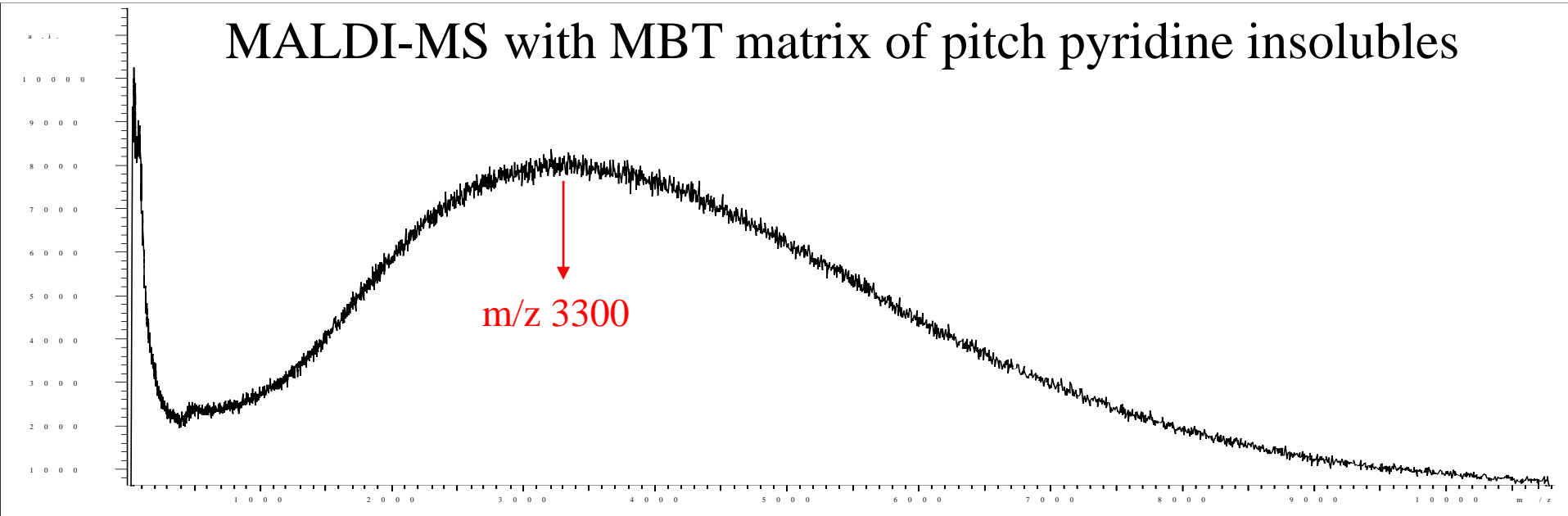
In MALDI- and LD-MS, higher mass ions can be generated and we have reached m/z 200,000 in petroleum asphaltenes and a few examples follow. Bimodal distributions are now suspect and we consider signal $>10k$ as cluster ions rather than separate species – caused by having a thick sample layer on the target.

First work with Cambridge Mass Spectrometry LIMA 401 L TOF MS with Nd/YAG laser at Heriot-Watt Uni in 1988- 1993.

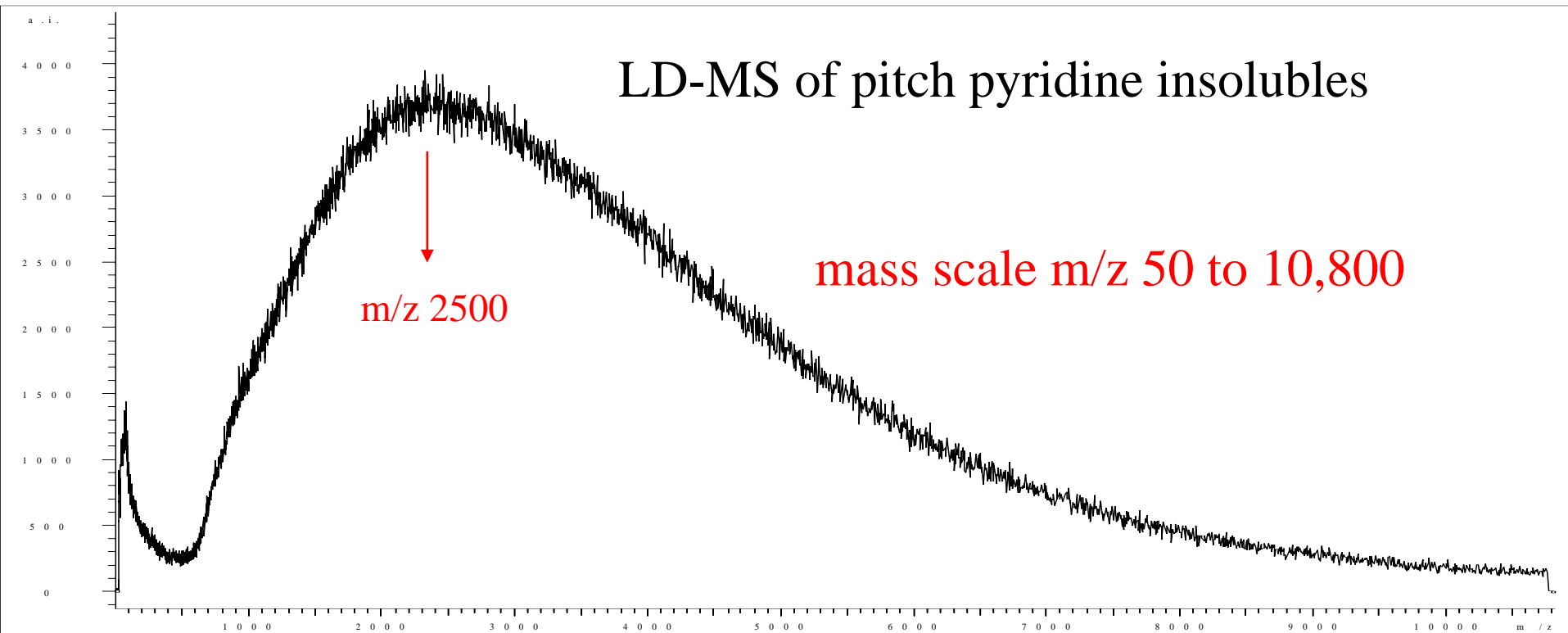
Later with Kratos instruments, then Fisons VG TOFSPEC at School of Pharmacy, London.

Finally with Bruker Daltonics Reflex IV MALDI-TOF instrument at Imperial.

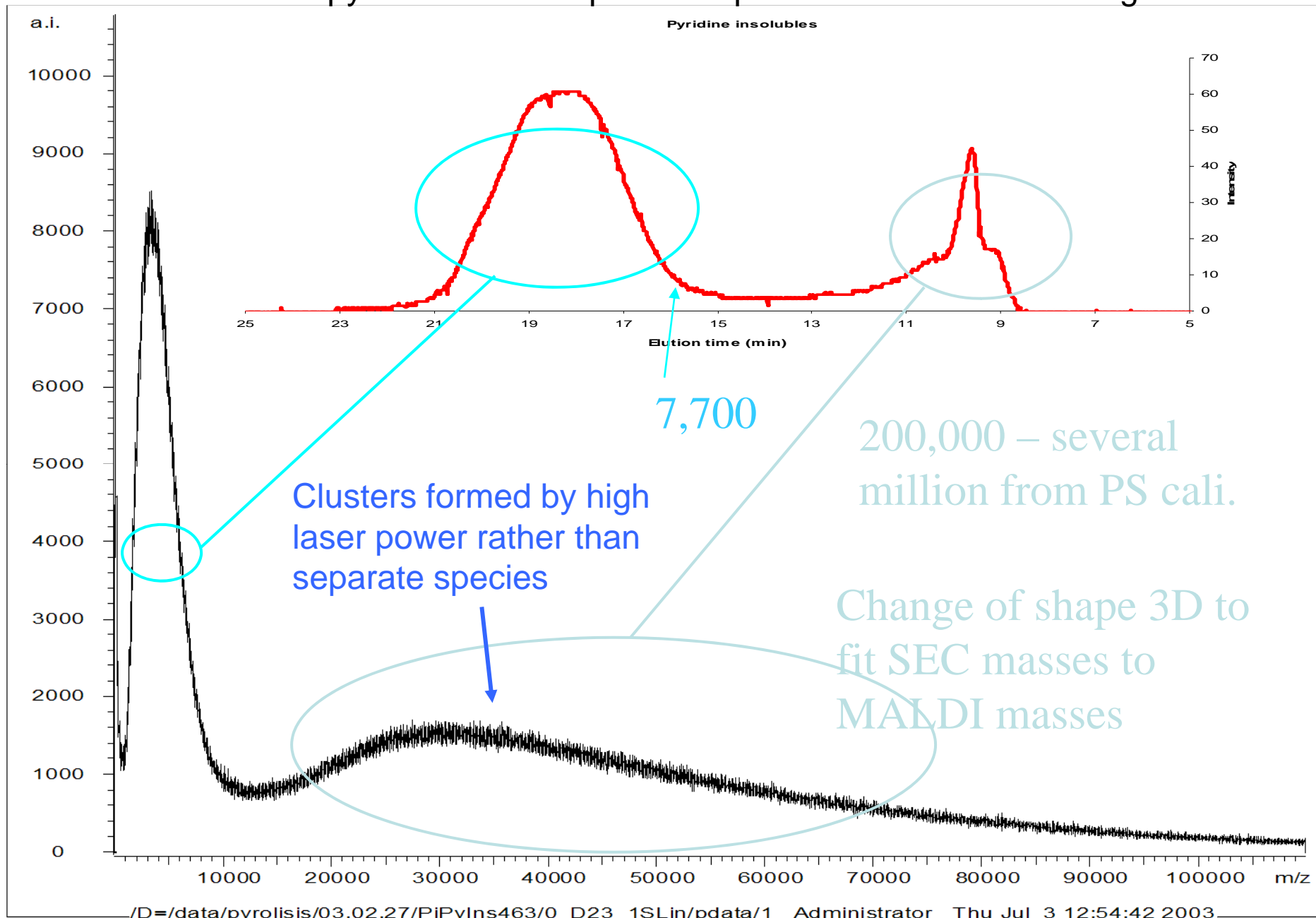
MALDI-MS with MBT matrix of pitch pyridine insolubles



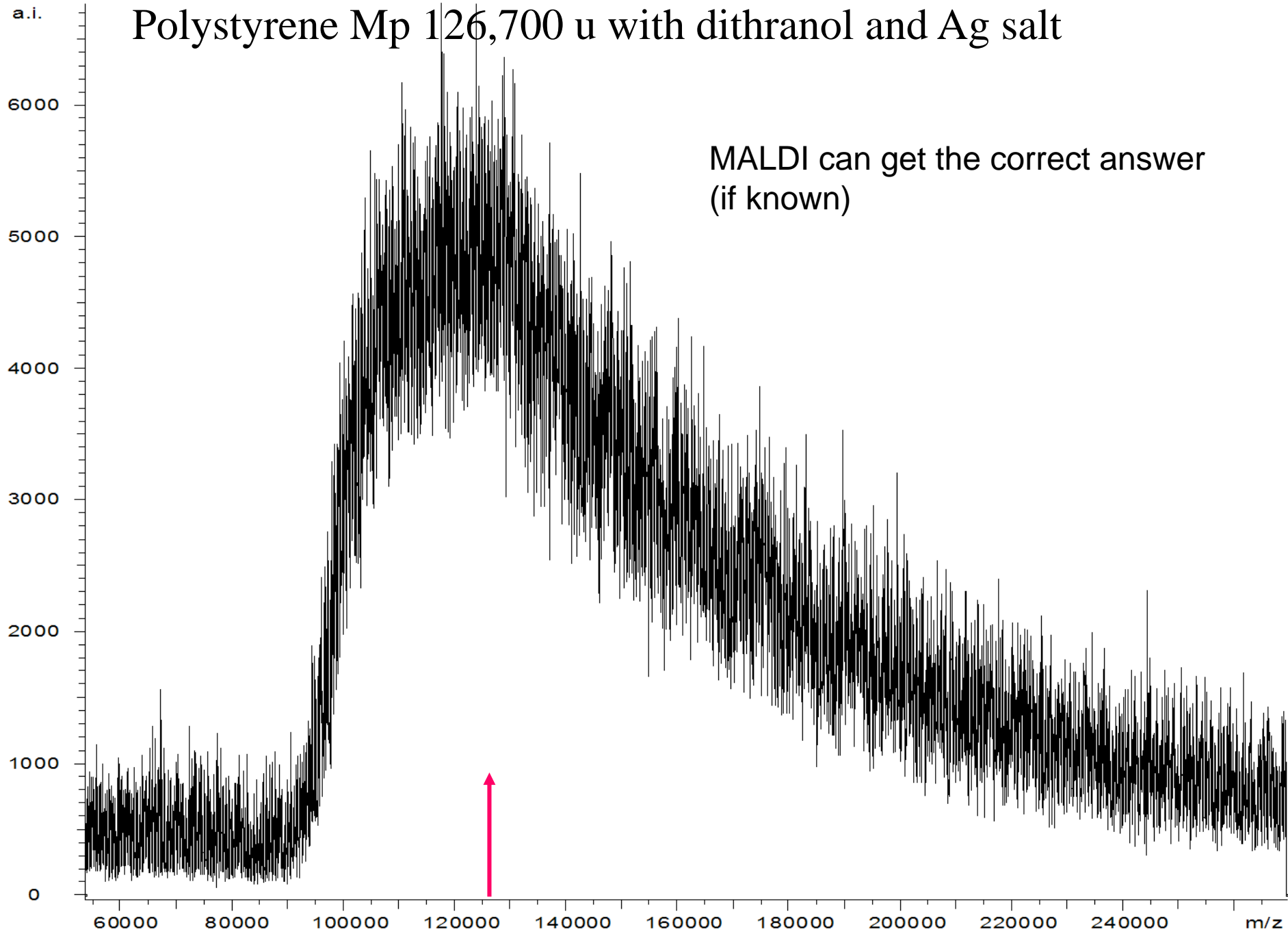
LD-MS of pitch pyridine insolubles



LD-MS of pyridine insols of pitch compared with SEC chromatogram



Polystyrene Mp 126,700 u with dithranol and Ag salt



MALDI can get the correct answer
(if known)

The new approach to LD-MS of these complex materials relies on fractionating the sample by TLC using flexible-backed plates. After development, the appropriate section of the plate is cut out, stuck to the LD-MS target plate with sticky-tape and inserted directly into the mass spectrometer.

LD-MS show that the smallest molecules are the most mobile on the plate, while the least mobile are the largest sized-molecules. Use of too high laser power can produce cluster ions (rather than molecular ions) that can obscure the ions from the larger (less-mobile) molecules if no fractionation has been done. There is no doubt that molecules up to m/z 10,000 can be detected by this method, with a peak intensity of around m/z 3-4,000. It is important to reduce the polydispersity of samples before acquiring their mass spectra.

These LD-MS data are supported by the SEC chromatograms of the same fractions recovered from the TLC plate. UV-fluorescence spectra indicate that the less mobile fractions from the plate contain larger aromatic chromophores than the small molecules, indicating that these are true molecules and not aggregates in solution.

CONCLUSIONS

MALDI-MS and LD-MS give similar mass distributions for the retained material of SEC as the polymer calibration of SEC. So mass ranges up to m/z 10,000 in most coal-derived residue samples can be taken as established. **Structures unknown after GC-MS range.**

The bimodal mass distribution of LD-MS found by increasing laser power and reducing small-molecule intensity by voltage reduction or by delayed ion extraction appears to give artefacts (cluster ions) and the polydispersity of the sample must be reduced by fractionation. Also, the thickness of the sample layer must be small to avoid aggregate formation at high laser power.

The excluded material of SEC has not been characterized by LD-MS – it may be 3-dimensional and liable to form char on heating and could appear in the mass spectrum – needs more work.

Implications for processing of these unknown structures.

BUT have we reached the upper mass limits yet?