

# Optimisation of the Connection Between Thermal Analysis Systems and Quadrupole Mass Spectrometer Systems Together with Improved Data Interpretation for TA-MS Applications.

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# Topics



- ◆ Introduction

  - Why connect thermal analysis equipment to a mass spectrometer?

- ◆ The TA-MS hardware interface

  - How is the connection made?

  - How is the connection optimised?

- ◆ The software interface

  - How can TA and MS systems be controlled simultaneously?

- ◆ Data interpretation

  - Techniques for MS data interpretation

# Introduction-

## Why connect TA equipment to a mass spectrometer?

Data from thermal analysis equipment and mass spectrometry are complimentary.

The strengths of **Thermal Analysis** are:

- ◆ Sample environment control. Pressure, temperature, gas, vapour.
- ◆ Accurate weight measurement for uptake, and decomposition.

**MS compliments TA** techniques with speciation as a function of time and / or temperature.

- ◆ The combined TA-MS data is used to characterise materials



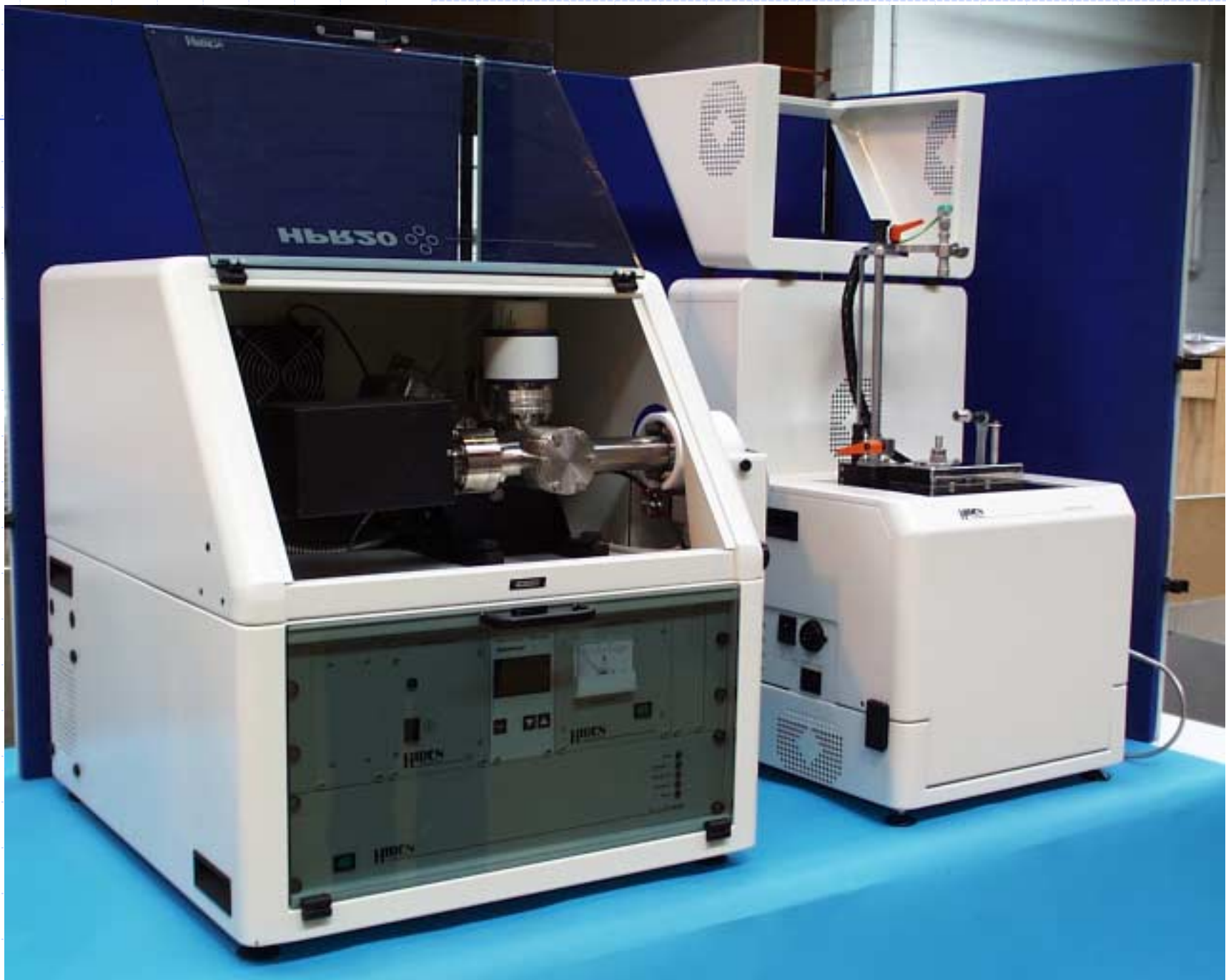
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# The TA-MS Interface

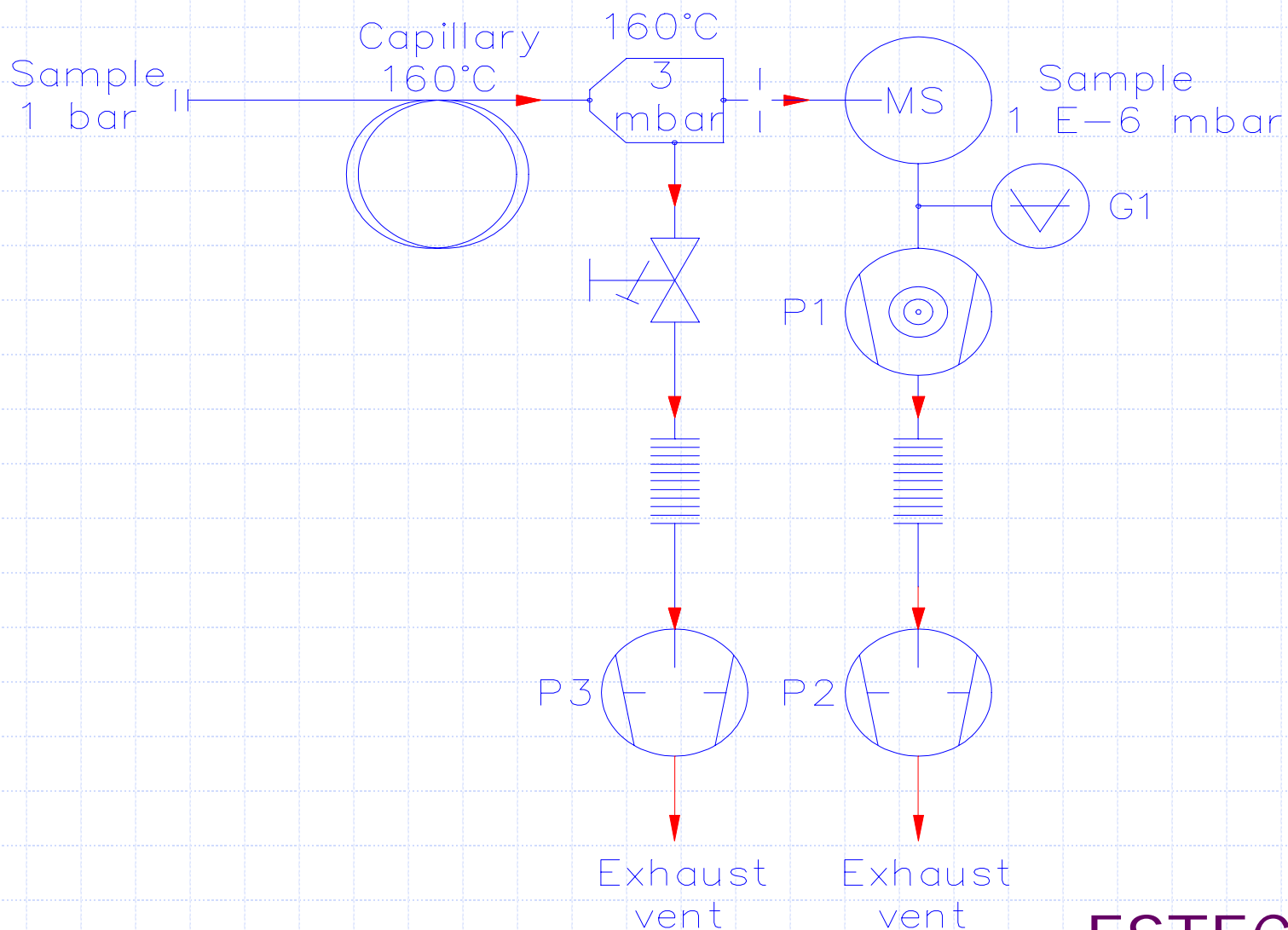


- ◆ Thermal analysis equipment typically operates at near atmospheric pressure.
- ◆ Specialized systems operate from high vacuum to high pressure.
- ◆ Mass spectrometers operate at high vacuum.
- ◆ The mass spectrometer interface provides for gas/vapour sampled from directly above the sample within the thermal analysis equipment to be analysed in near real time by the mass spectrometer.
- ◆ Where internal sampling is not practical the mass spectrometer can be connected to an external exhaust of the thermal analysis equipment.

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# Q/C – 20 overview



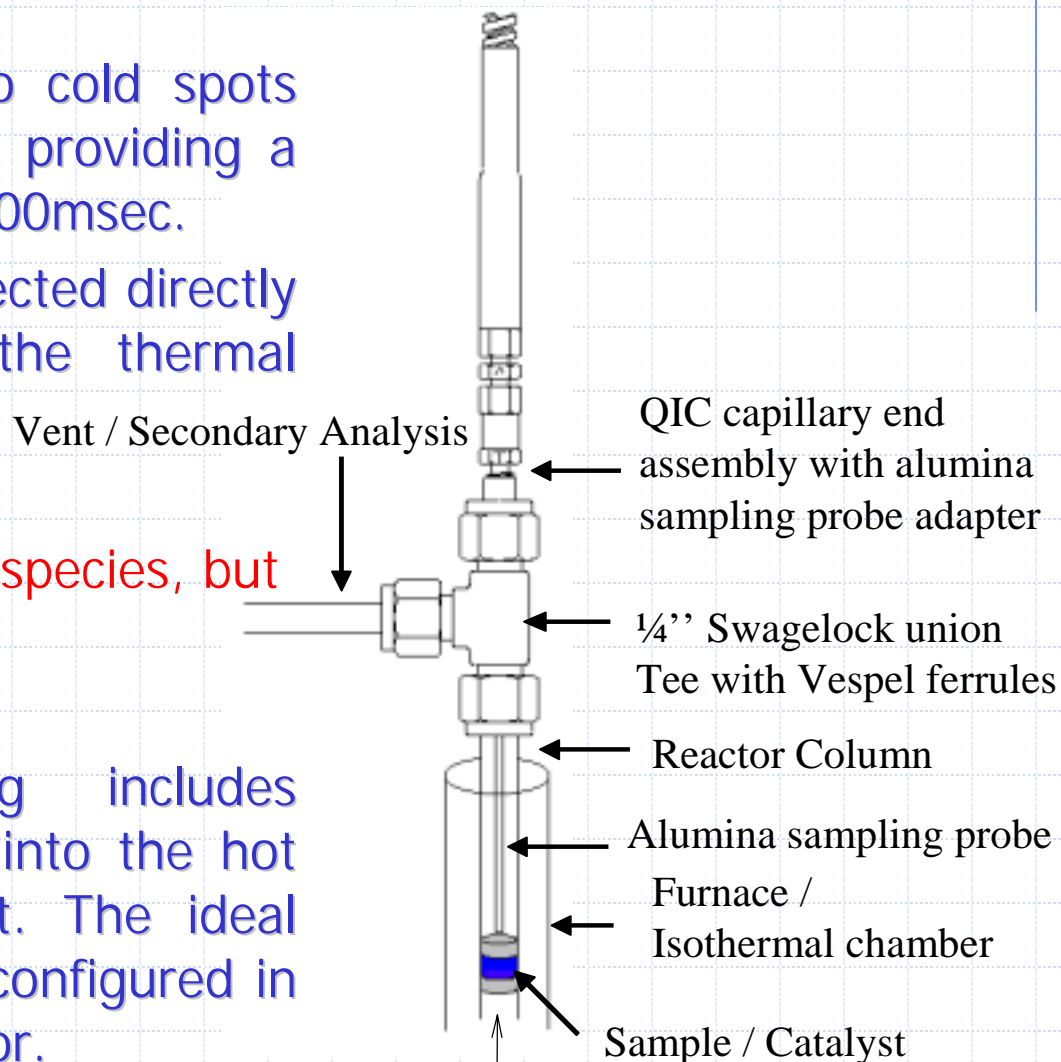
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# The TA-MS coupling

- ◆ The QIC capillary has no cold spots and minimum dead volume providing a response time of less than 500msec.
- ◆ Can the capillary be connected directly to the exhaust port of the thermal analysis equipment?

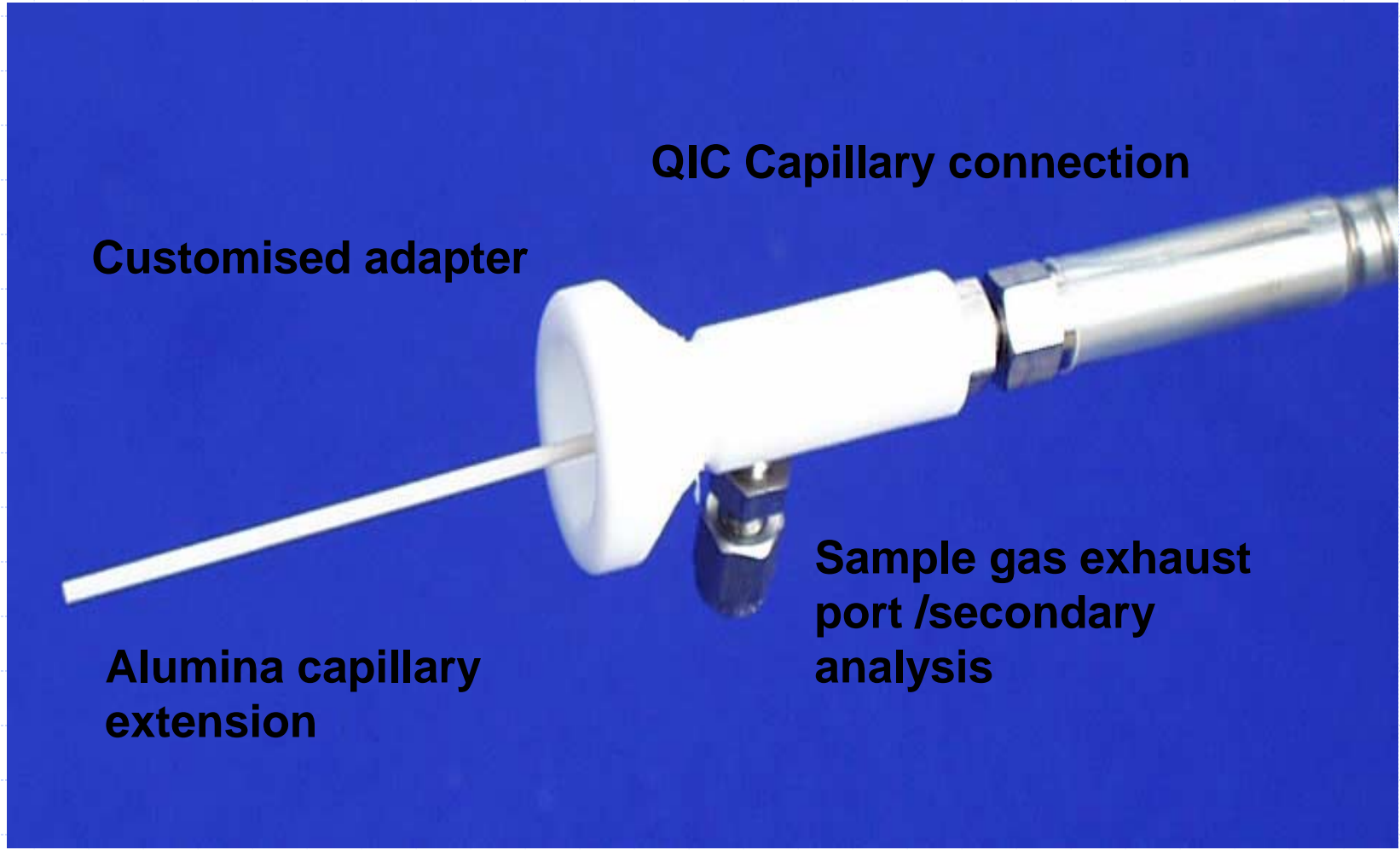
Yes, OK for non-condensing species, but expect peak broadening.

- ◆ An optimised coupling includes integration of the capillary into the hot zone of the TA equipment. The ideal inlet is shown opposite, as configured in Hiden's CATLAB micro-reactor.



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# Hidden Hot Zone Sampling Inlet



**Customised adapter**

**QIC Capillary connection**

**Alumina capillary extension**

**Sample gas exhaust port /secondary analysis**

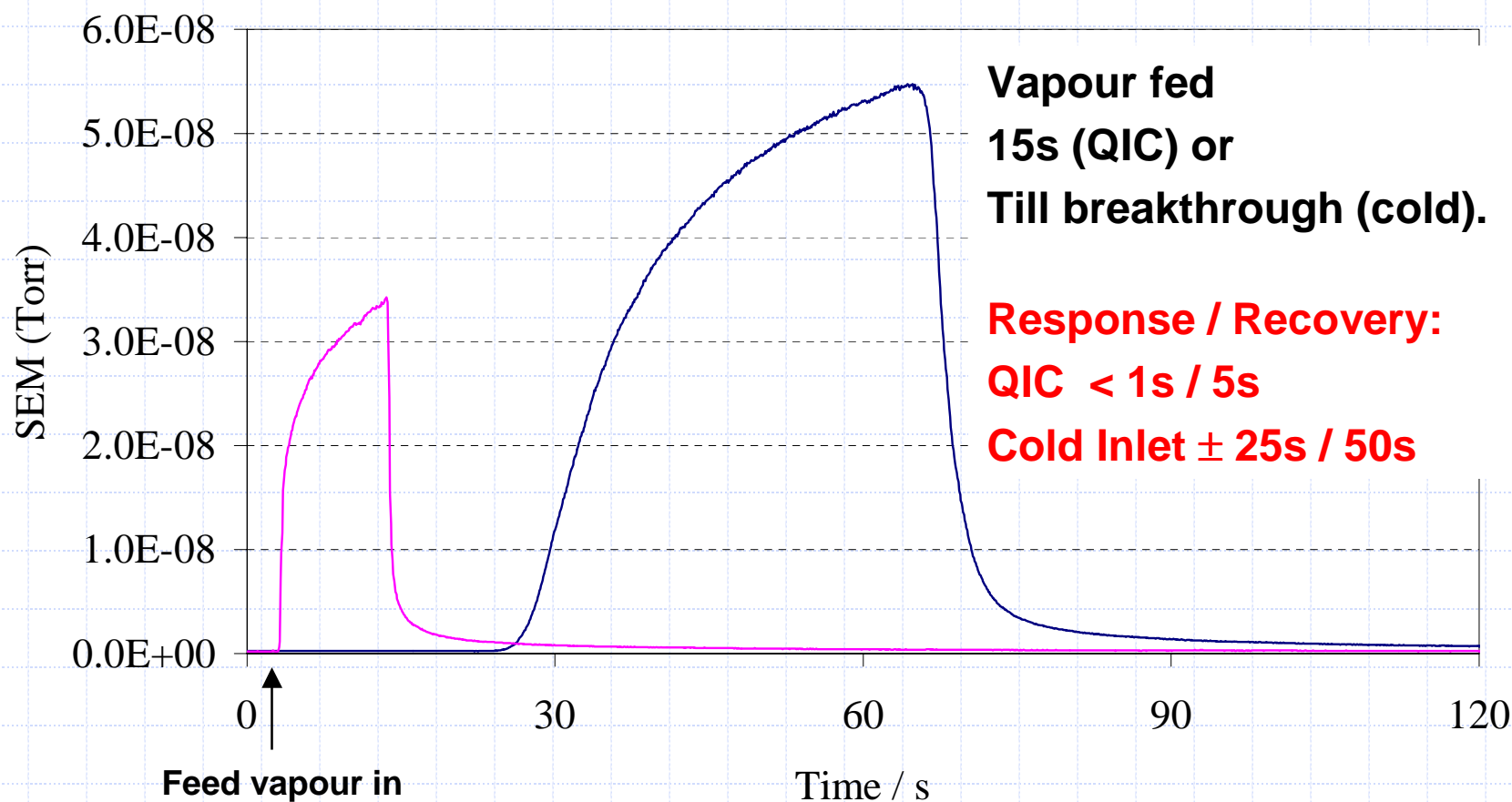
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# Effect of Cold Spot



## Effect of Cold Spot on Capillary Response - iPA



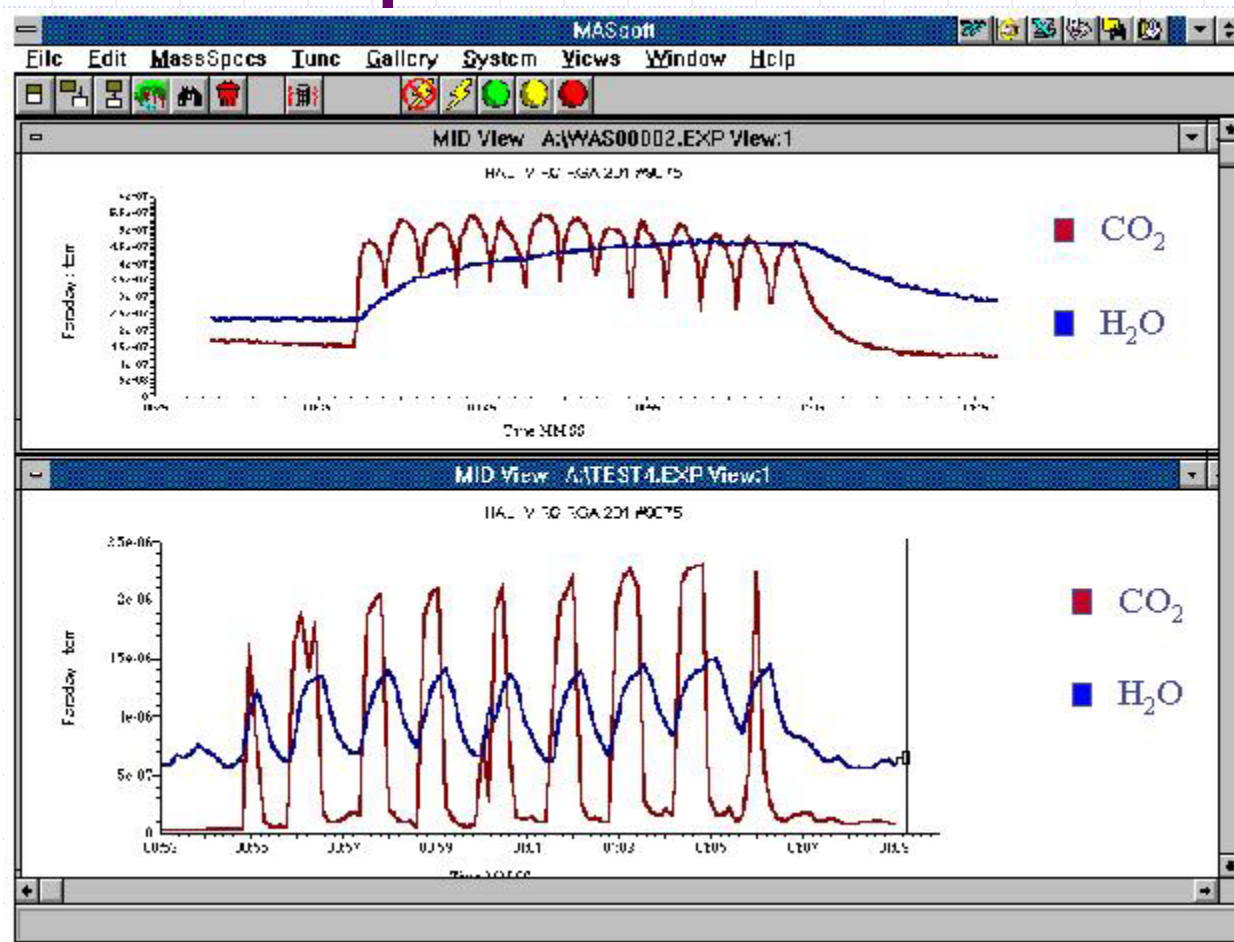
Vapour fed  
15s (QIC) or  
Till breakthrough (cold).

Response / Recovery:  
QIC < 1s / 5s  
Cold Inlet ± 25s / 50s

— Cold — QIC

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# Fast response to gases and vapours

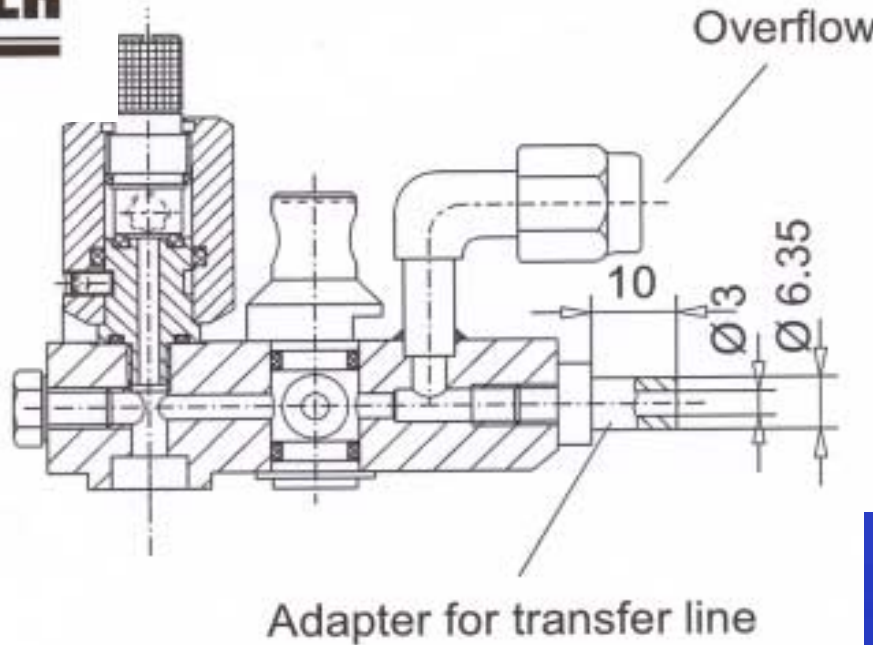


Conventional capillary inlet

QIC inlet

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# TA-MS adaptors - example



- TA Instruments
- Dupont
- Cahn
- Setaram

- Netzsch
- Hiden IGA
- Mettler Toledo
- Seiko



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# Software Interface



TA equipment can control the mass spectrometer and reads the mass spectrometer data through an RS232 connection.

Or

The mass spectrometer can read the TA equipment data, sample temperature and weight loss for example.

For detailed mass spectrometer studies it is recommended to read the TA equipment data into the mass spectrometer. This allows the user complete mass spectrometer control for complex studies. Ioniser electron energy for example.

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# Software Interface Cont.



Hiden's mass spectrometer systems can read data from TA equipment.

The system includes up to 16 analog input channels for reading data from devices, e.g. Temperature and weight.

The signals from the TA equipment are conditioned to be linear 0 – 10V f.s.d. and can be displayed with mass spectrometer data.

The MS system is started simultaneously with the TA equipment using Transistor Threshold Level (TTL) logic control.

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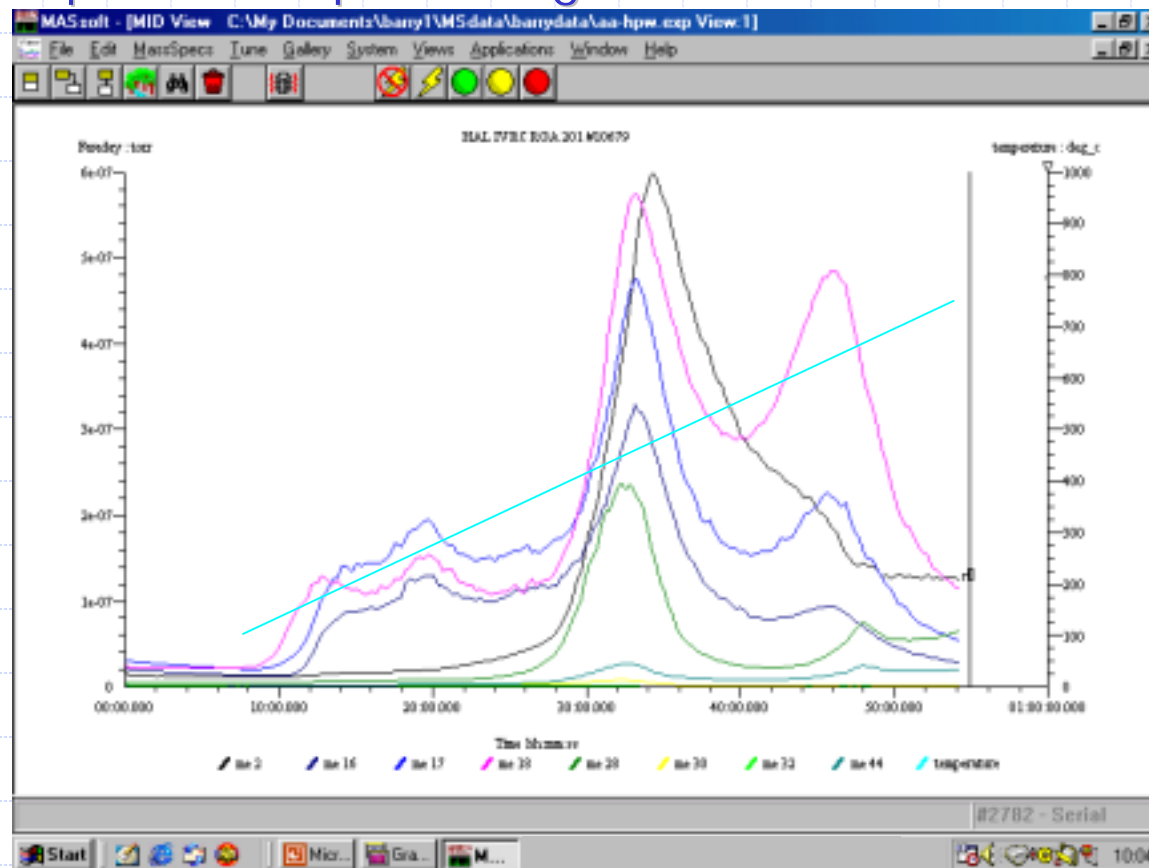
# Example TA-MS



TP-Decomposition of  $(\text{H}_3\text{PW}_{12}\text{O}_{40}) \cdot (\text{NH}_2(\text{CH}_2)_6\text{NH}_2)_{1.5}$ .

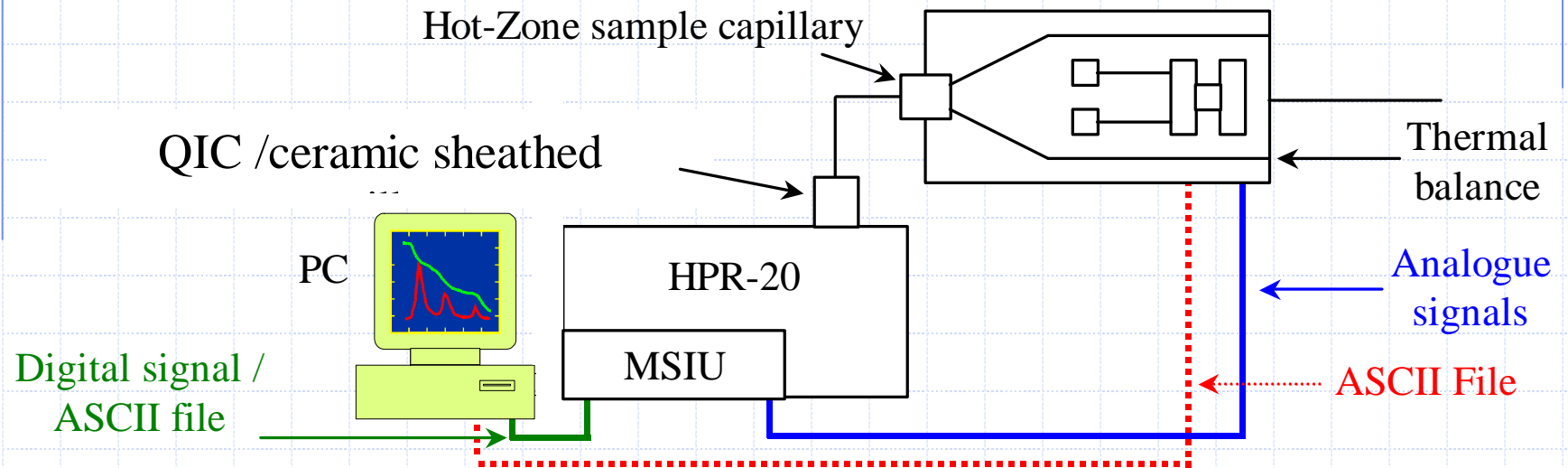
Simultaneous acquisition of Temperature.

Data shows optimum response of gases and water with Hot-Zone / QIC



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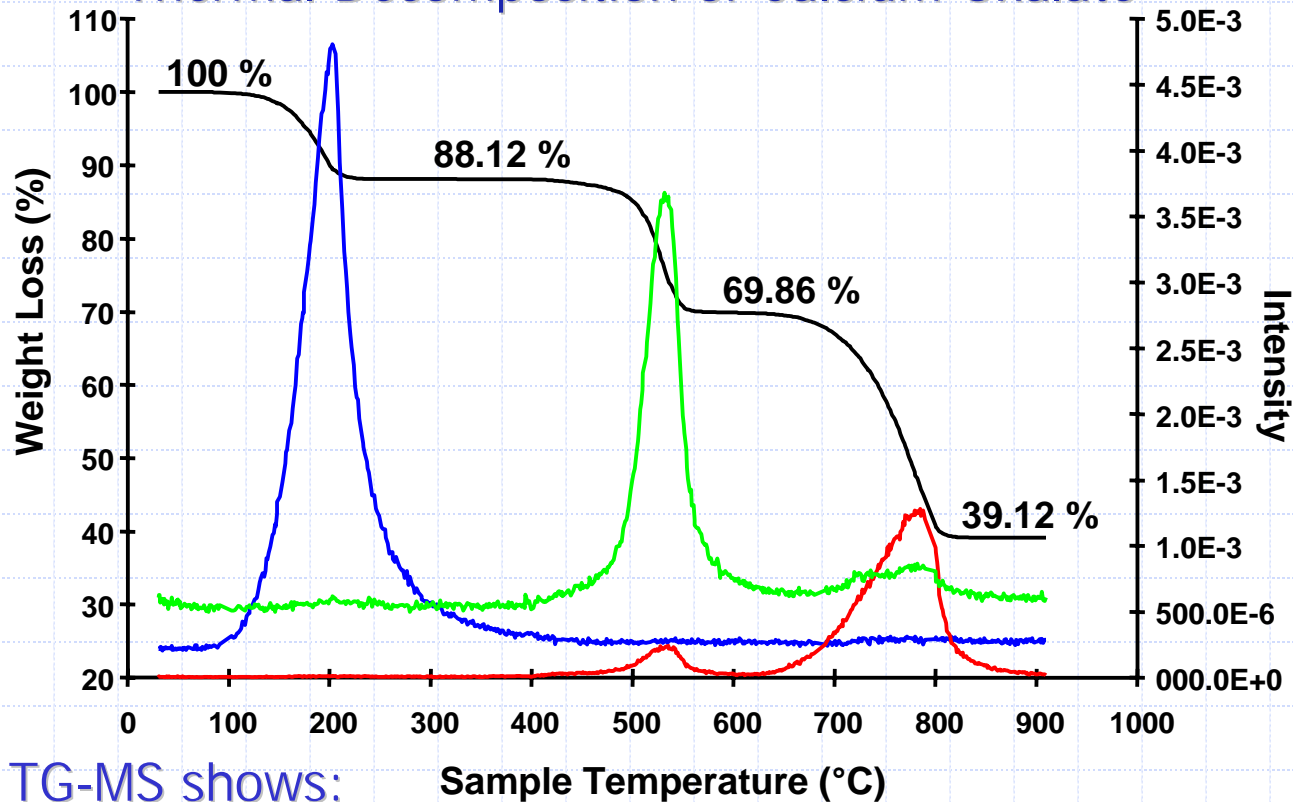
# Idealised TA-MS set-up



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# TGA-MS Example

## Thermal Decomposition of Calcium Oxalate



Coupled TG-MS shows:

- i) water desorption
- ii) partial oxalate decomposition with CO / CO<sub>2</sub> evolution
- iii) full decomposition of oxalate with CO<sub>2</sub> evolution.

One can also see the perfect correlation between mass loss and MS signals.

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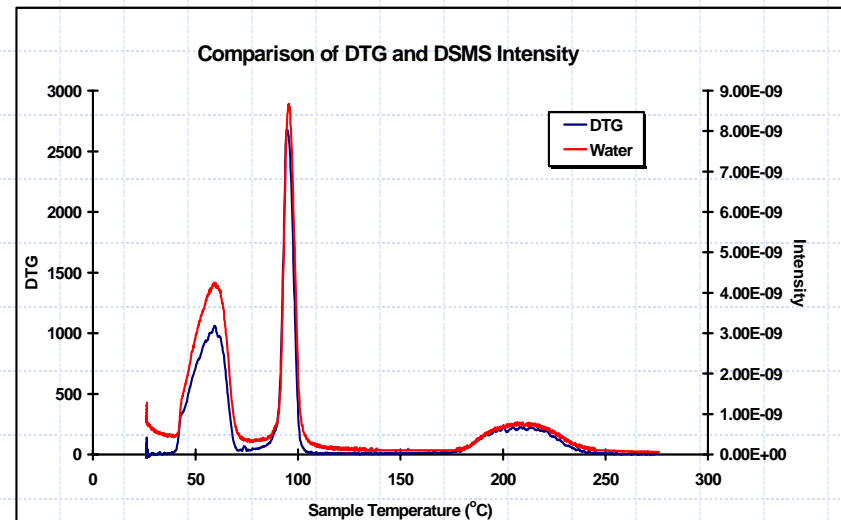
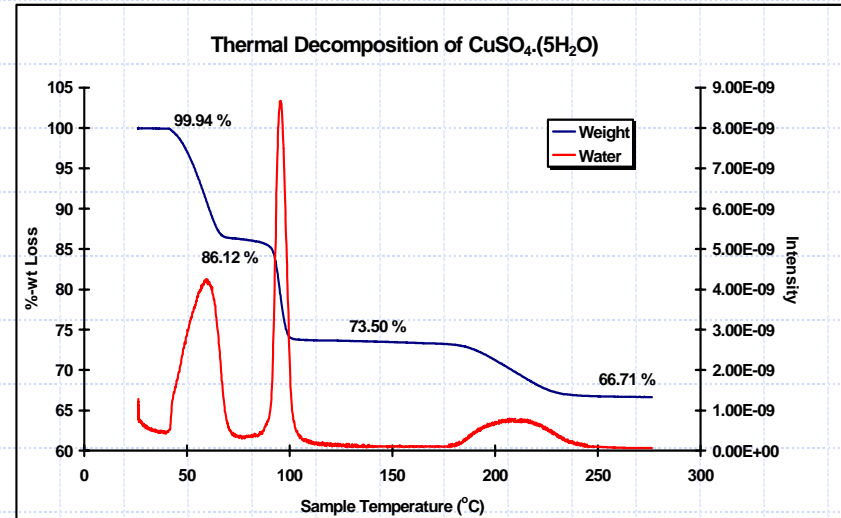


# TGA-MS Example



## Thermal Decomposition of $\text{CuSO}_4$

Coupled TGA/DTA-MS of this sample showed good agreement with expected values and again reflected exact correlation between mass loss and MS signals.



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# Data Interpretation 1.1



The previous examples of TA-MS illustrate excellent coupling between the TA equipment and the Hiden mass spectrometer. This data can be viewed as 'calibration data' proving that the sampling connection is optimised.

Data from unknown samples requires interpretation. Interpretation identifies:

- **The evolved species**
- **The temperature of evolution**
- **The abundance of evolved species.**

For catalysts Hiden systems include specific experimental methods and data interpretation software for the quantitative determination of catalyst characteristics e.g. active / metal surface areas, acid site concentration / strength determination etc.

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# Data Interpretation 1.2



NIST MS Search 2.0 - [Name search]

File Search View Tools Window Help

ALCOHOLDEHYDRATED Clear m:z mainlib From MAINLIB

Alcophenac  
Alcobam 2M  
Alcoban  
Alcolenac di-methyl derivative  
Alcolenac methyl derivative  
Alcohol  
Alcohol anhydrous  
Alcohol C10  
Alcohol C11  
Alcohol C12  
Alcohol C16  
Alcohol C8  
Alcohol C9  
**Alcohol, dehydrated**  
Alcohol, diluted  
Alcohol, rubbing  
Alcohols  
Alcold  
Alcofl  
Alcola  
Alcolalico  
Alcolalyque  
Alcolamilco  
Alcolamylique  
Alcolbutylique  
Alcolbutylique secondaire  
Alcolbutylique tertiaire  
Alcolethylque  
Alcoletilco  
Alcolisoamylique  
Alcolisobutylique  
Alcolisopropilco  
Alcolisopropylique  
Alcolmethylamylique  
Alcolmethylque  
Alcolmellitico  
Alcolpropilico

(mainlib) Ethanol

Name: Ethanol  
Formula: C<sub>2</sub>H<sub>6</sub>O  
MW: 46 CAS#: 64-17-5 NIST#: 118507 ID#: 1076 DB: mainlib  
Other DBs: TSCA, RTECS, EPA, USP, HODOC, NIH, EINECS, IRDB  
Contributor: NIST Mass Spectrometry Data Center, 1990  
10 largest peaks:  
31 999 | 45 514 | 29 298 | 27 224 | 46 216 |  
43 114 | 26 98 | 30 81 | 15 66 | 42 47 |

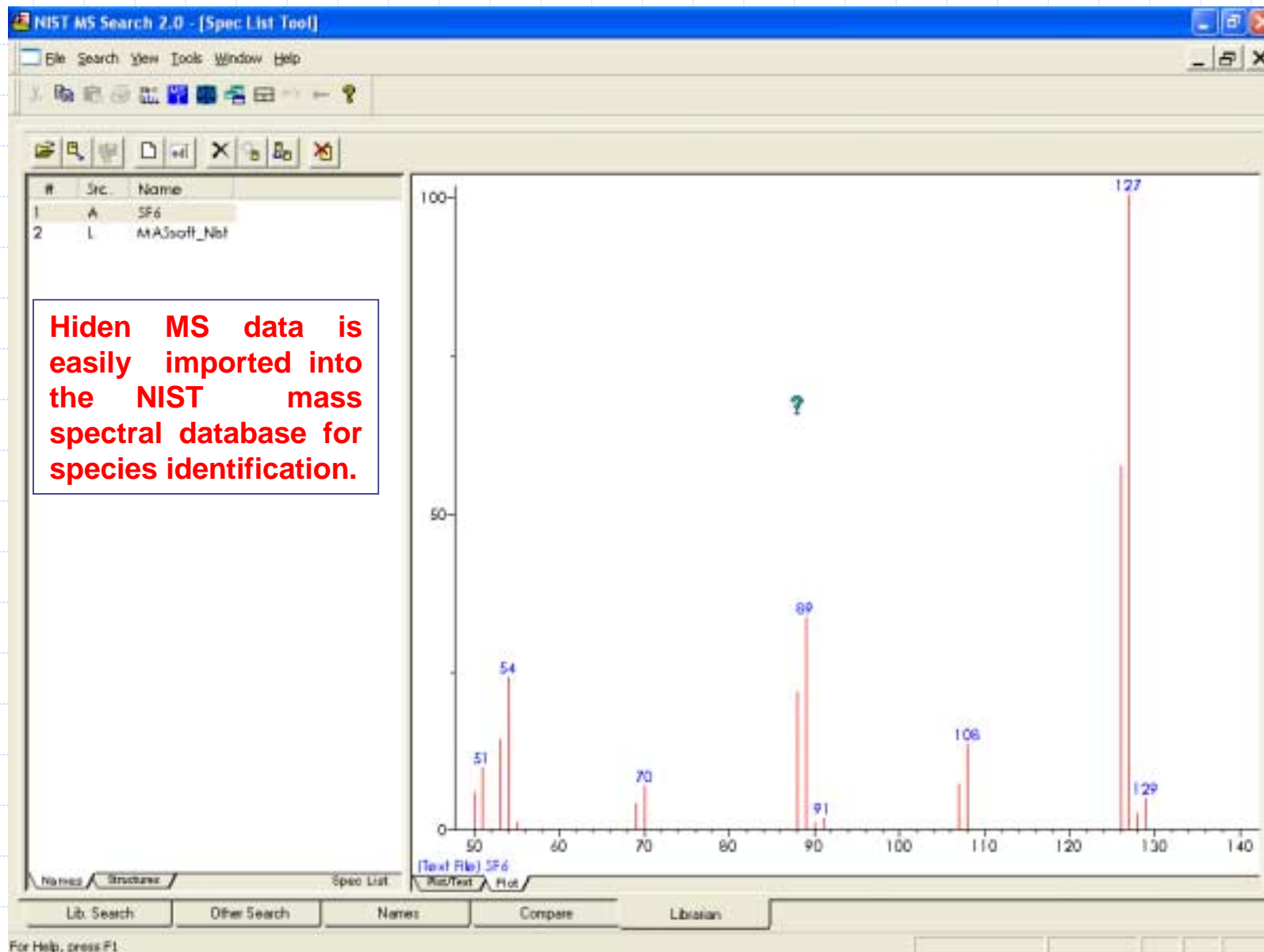
Synonyms:  
1 Ethyl alcohol  
2 Alcohol  
3 Alcohol anhydrous  
4 Algrain  
5 Anhydrol  
6 Dehydrated ethanol  
7 Ethyl hydrate  
8 Ethyl hydroxide  
9 Jaysol  
10 Jaysol S

Names Structures  
Lib. Search Other Search Names Compare Librarian

For Help, press F1

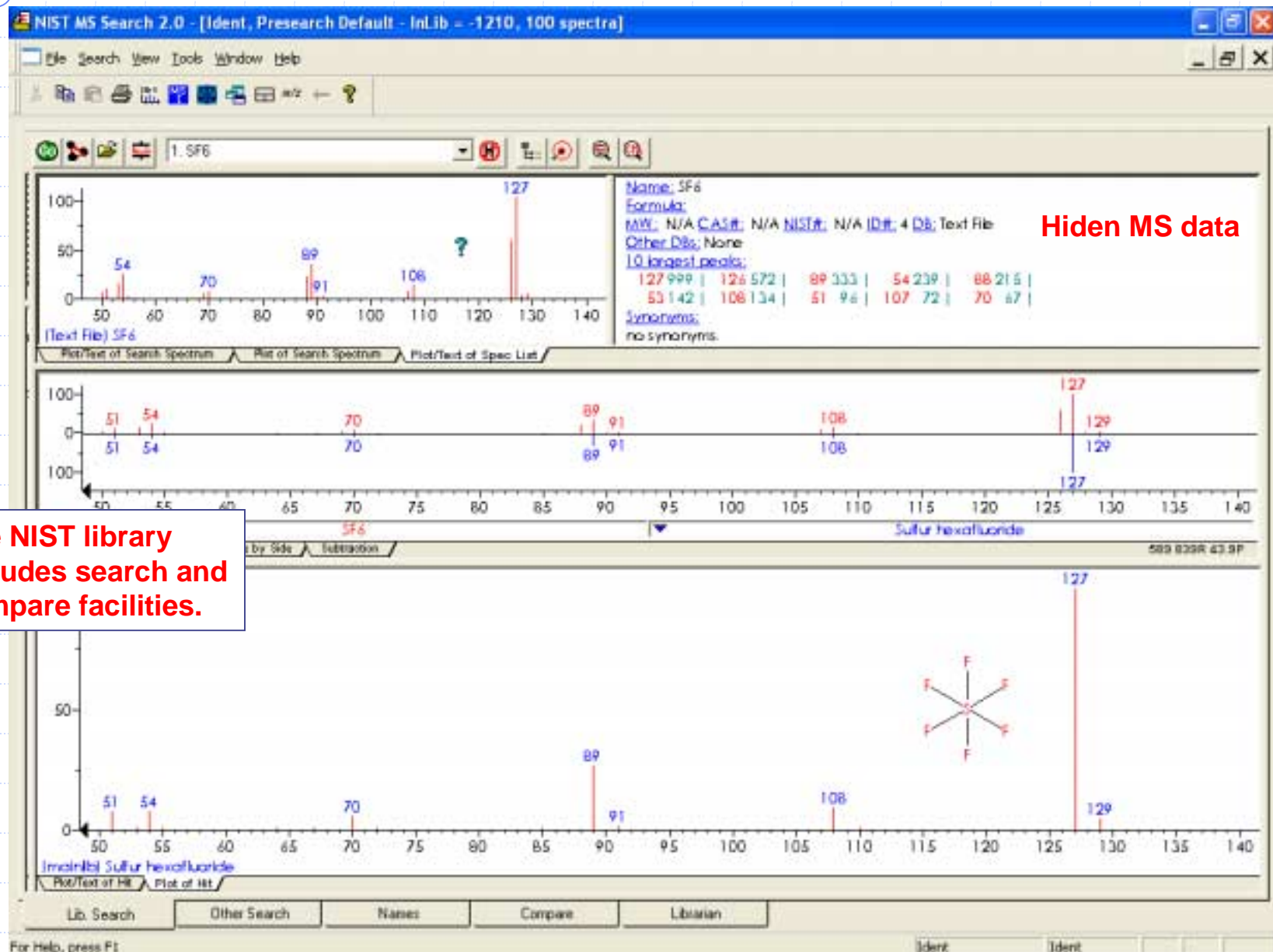
The NIST Mass Spectral Library contains 129,136 EI Spectra of 107,886 compounds

# Data Interpretation



**Hidden MS data is easily imported into the NIST mass spectral database for species identification.**

# Data Interpretation

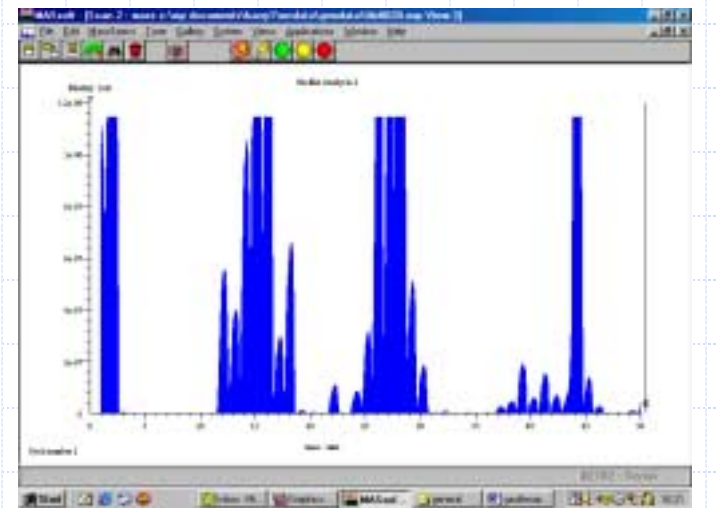
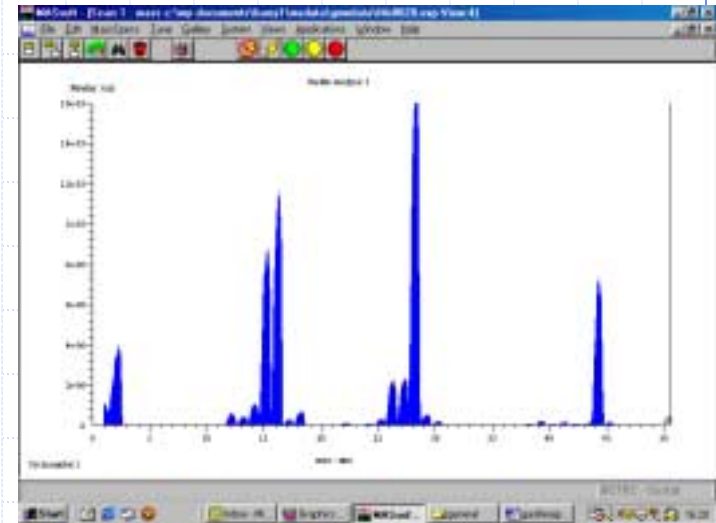


Hidden MS data

The NIST library includes search and compare facilities.

# Data Interpretation 1.2

- 1) Identify peaks due to known components.
- 2) Identify all **Molecular Ions** / significant peaks using ms library.
- 3) Assign remaining peaks noting the general appearance of the spectrum, checking for peak cluster from Isotope patterns and low-mass neutral fragment loss e.g.  $\text{CH}_2$
- 4) Compare to reference spectra on NIST98 database (available from Hiden Analytical).
- 5) Use Matrix Inversion routine or apply linear equations to calculate the gas composition.



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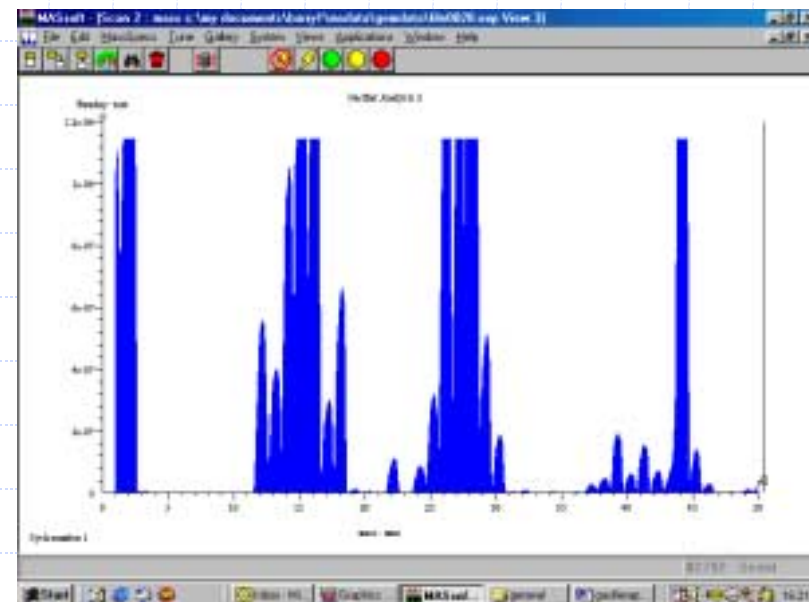
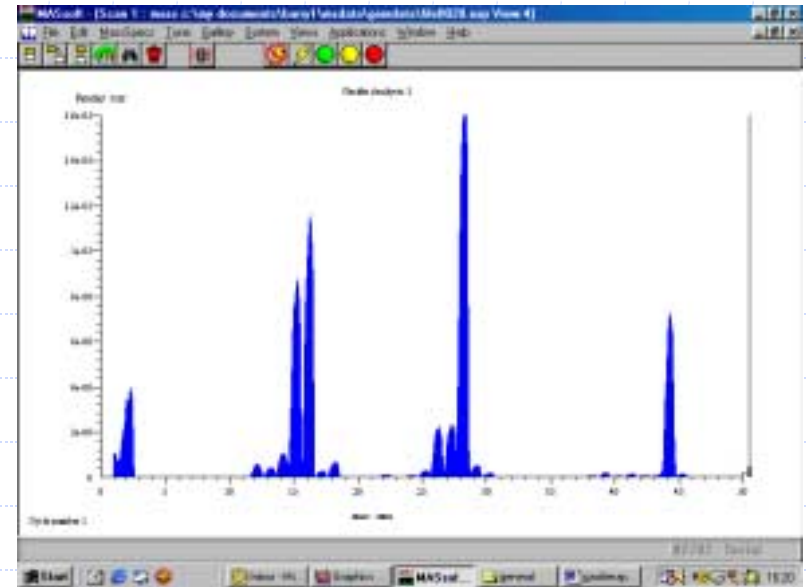
# Data Interpretation 1.3

## Analysis of the Pyrolysis of Landfill Solids



Once the identities of the various species have been compared the next step of the process is to construct the sets of equations necessary to determine the individual contributions at any given  $m/e$ .

However for some  $m/e$  values e.g.  $m/e$  28 which encompasses  $N_2$ ,  $CO$ , and all linear and iso alkanes and alkenes, the sheer complexity of contributions are such that standard Matrix Inversion Methods are required (available from Hiden Analytical).



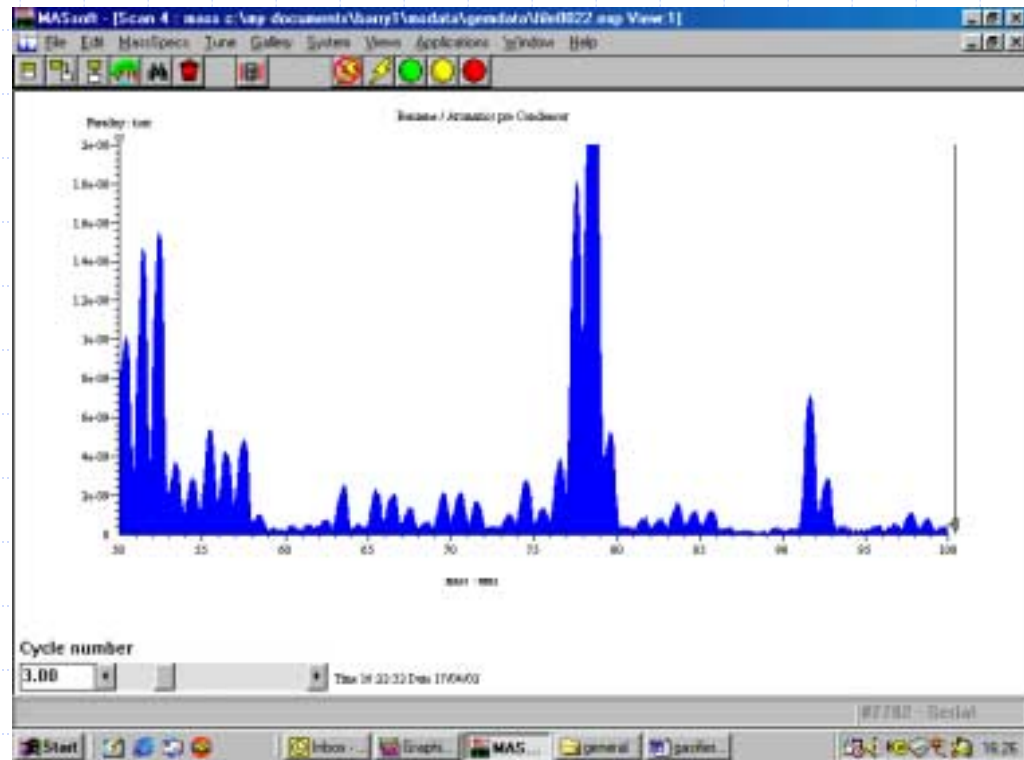
# Data Interpretation 1.4

## Analysis of the Pyrolysis of Landfill Solids



However Matrix Inversion requires both knowledge of the identity of all possible components present and the calibration of their individual contributions in a mixture which in this case would prove extremely time and labour intensive.

In this case the analysis can use a simpler linear combination approach to determine the individual contributions, these values are then incorporated into a set of equations to establish the gas composition.



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# Data Interpretation 1.5

## Analysis of the Pyrolysis of Landfill Solids



*Example 1:* At m/e 17 the peak appears as a result of both H<sub>2</sub>O (23% of the peak at m/e 18) + NH<sub>3</sub>. Hence:

$$\text{NH}_3 = (\text{m/e } 17 - (0.23 * \text{m/e } 18)) / 1.3$$

where 1.3 is the Relative Sensitivity of NH<sub>3</sub> cf. N<sub>2</sub>

*Example 2:* To calculate the N<sub>2</sub> concentration we cannot use the main peak at m/e 28 as indicated. Hence we derive the N<sub>2</sub> concentration from the m/e 14 N<sub>2</sub> daughter peak, corrected for the Methane overlap:

$$\text{N}_2 = (\text{m/e } 14 - (0.204 * \text{CH}_4)) * 20$$

NB. Methane concentration is itself derived from:

$$\text{CH}_4 = \text{m/e } 16 / 1.6 - (0.80 * \text{NH}_3) - ((0.218 * \text{m/e } 32) / 0.86)$$

where 1.3 is the Relative Sensitivity of CH<sub>4</sub>, 1.6 is the Relative Sensitivity of CH<sub>4</sub> and 0.86 is the Relative Sensitivity of O<sub>2</sub>

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# Data Interpretation 1.6



## Analysis of the Pyrolysis of Landfill Solids

*Example 3:* At m/e 12 the peak is a result of CO (5% of the CO at m/e 28) + Ethane (1.2% of total Ethane concentration) + Ethene (0.4% of total) + Propane (0.6% of total) + Propene (2.0% of total) + Butane (0.3% of total) + Butene (0.8% of total). NIST shows no contribution from CO<sub>2</sub> and contributions from C<sub>5</sub> + hydrocarbons are ca. 0.1%, which given their low concentrations are ignored. Hence:

$$\text{CO} = (20/1.05) * ((m/e 12 - (0.012 * \text{Ethane}) - (0.004 * \text{Ethene}) - (0.006 * \text{Propane}) - (0.02 * \text{Propene}) - (0.003 * \text{Butane}) - (0.008 * \text{Butene})))$$

Where 1.05 is the Relative Sensitivity of CO cf. N<sub>2</sub>

NB. It was necessary to account for contributions from homologous species e.g. all n and iso-alkanes or aromatics. This is necessary as it can be difficult to make specific assignments to fragments as members of the series display similar fragmentation patterns / contributions e.g. m/e 26 from all non-methane hydrocarbons. To account this a 'lumped' analysis was performed. Fortunately the similarity which makes this analysis necessary also validates it, as the lumped components are highly similar chemically and calorifically.

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# Data Interpretation 1.7 Results

## Analysis of the Pyrolysis of Landfill Solids



Species	%	Species	%	Species	%
H <sub>2</sub>	26.76	Propane/ Propene	0.426	HC / xylene	0.174
CO	27.16	Ethane	0.937	HC fragment	0.127
N <sub>2</sub>	3.707	O <sub>2</sub>	0.164	HC fragment	0.017
CH <sub>4</sub>	11.84	H <sub>2</sub> S	0.072	Pentene	0.021
NH <sub>3</sub>	0.420	Cl	0.158	iso-alkenes	0.021
H <sub>2</sub> O	4.521	Benzene / K	0.090	iso-Octane	0.023
Na	0.045	Argon	0.170	C <sub>6</sub>	0.008
HC (C <sub>2</sub> s +)	2.796	n-alkenes	0.130	C <sub>7</sub>	0.008
HC (C <sub>2</sub> s +)	2.696	Octane	0.096	Benzene	0.023
Ethane / Ethene	2.240	CO <sub>2</sub>	15.15	Xylene	0.013

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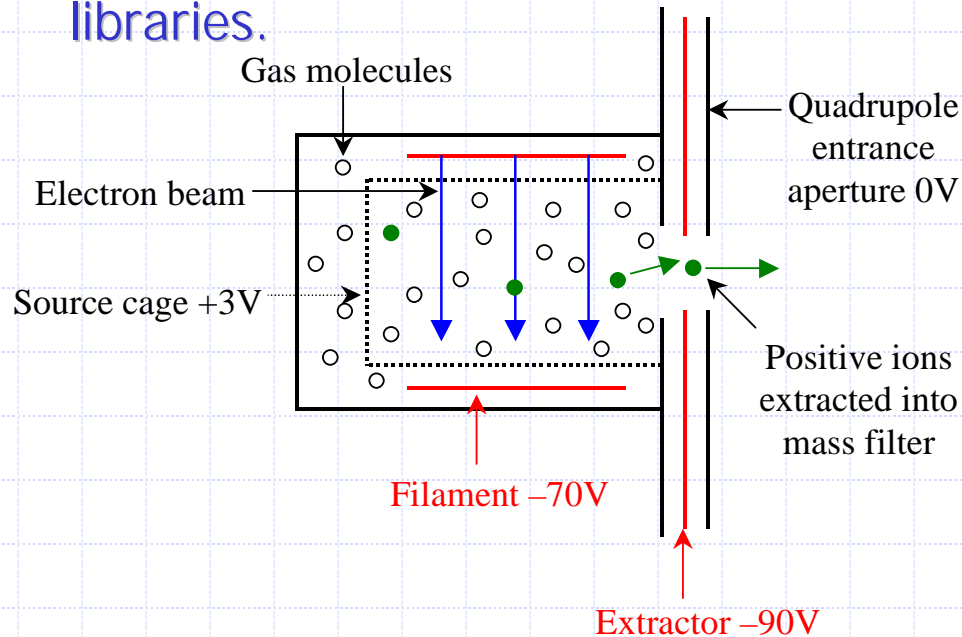
# Data Interpretation 2.1

## Soft Ionisation

Hiden quadrupole mass spectrometers can simplify the analysis of otherwise complex cracking patterns from multi-component gas / vapour mixtures via the method the 'Soft Ionisation'.

- **What is Soft Ionisation?**

Mass Spectrometers use a standard ionisation energy setting (70eV) to enable identification of species using standard mass spectral libraries.



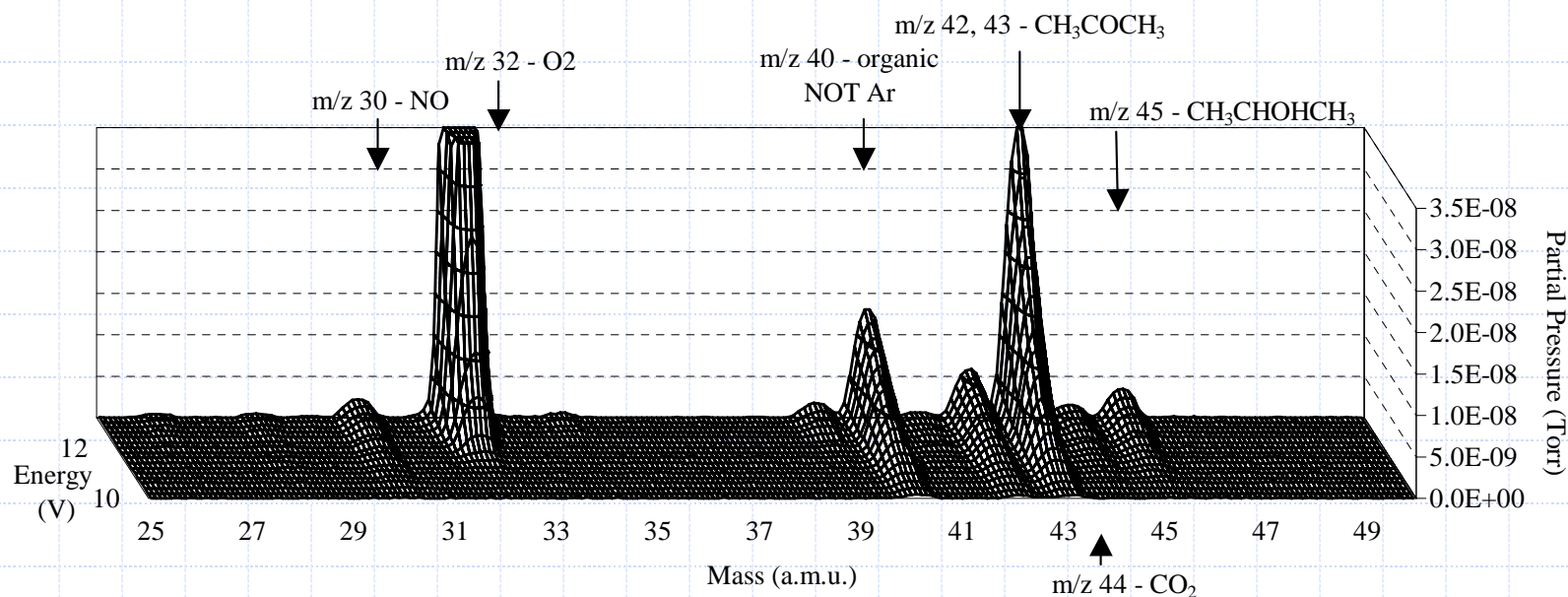
**Soft ionisation is the use of ionising electron energy at < 70eV to preferentially ionise the parent molecule with reduced fragmentation.**

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# Data Interpretation 2.2

## Soft Ionisation- How Does It Work?

This technique involves user-controlled variation of the ionising electron energy of the electrons from the ioniser filament through the normal scan tree set-up of the MASsoft program. This is made possible through the specific design of the Hiden ioniser and the precise ion source control provided by MASsoft.



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# Data Interpretation 2.3

*Table 1 – Ionisation Energies of Simple Inorganic and Organic Molecules*

	N <sub>2</sub> Nitrogen	O <sub>2</sub> Oxygen	Ar Argon	CO Carbon monoxide	CO <sub>2</sub> Carbon dioxide	NH <sub>3</sub> Ammonia	NO Nitric oxide	CH <sub>4</sub> Methane
I.E. / eV	15.58	12.07	15.76	14.01	13.77	10.07	9.26	12.61
	C <sub>2</sub> H <sub>2</sub> Ethyne	C <sub>2</sub> H <sub>4</sub> Ethene	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> Acetic acid	C <sub>2</sub> H <sub>6</sub> Ethane	C <sub>2</sub> H <sub>5</sub> OH Ethanol	C <sub>3</sub> H <sub>6</sub> O Propanal	C <sub>3</sub> H <sub>6</sub> O Acetone	C <sub>3</sub> H <sub>8</sub> O IPA
I.E. / eV	11.40	10.51	10.65	11.56	10.43	9.96	9.70	10.17
	C <sub>2</sub> H <sub>6</sub> O DME	C <sub>6</sub> H <sub>6</sub> Benzene	C <sub>6</sub> H <sub>14</sub> Hexane (n)	C <sub>6</sub> H <sub>12</sub> Cyclo- hexane	CH <sub>3</sub> OH Methanol	CH <sub>2</sub> O <sub>2</sub> Formic acid	CH <sub>2</sub> O Formalde- hyde	CCl <sub>4</sub> Carbon Tet.
I.E. / eV	9.72	9.24	10.13	9.86	10.85	11.33	10.88	11.47

The minimum electron energy required for ionisation is related to the electronic nature of the elements and strength of the bonds formed.

# Data Interpretation 2.4

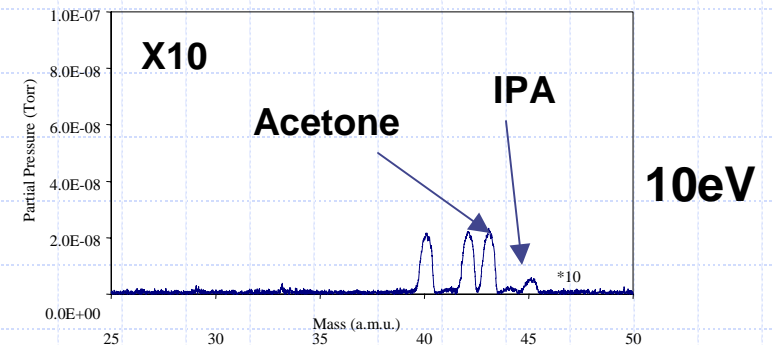
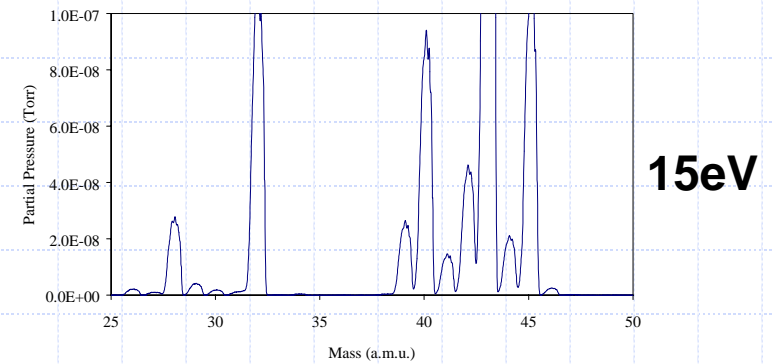
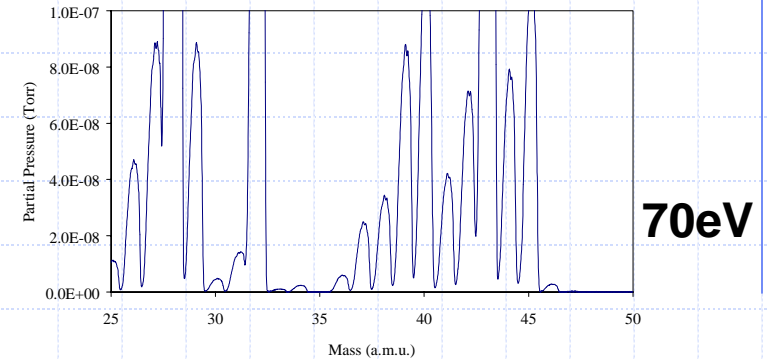


Analysis of IPA impurities in acetone is difficult due to the similarity in molecular weights, volatility and cracking characteristics.

The presence of air gases ( $N_2$ ,  $O_2$ , Ar,  $CO_2$ ) complicates the analysis.

The data shows the mass spectrum of the vapour at the standard electron ionisation potential of 70eV. A cursory analysis of this figure shows the presence of > 20 peaks from parent ions / fragments, the deconvolution of which is not trivial.

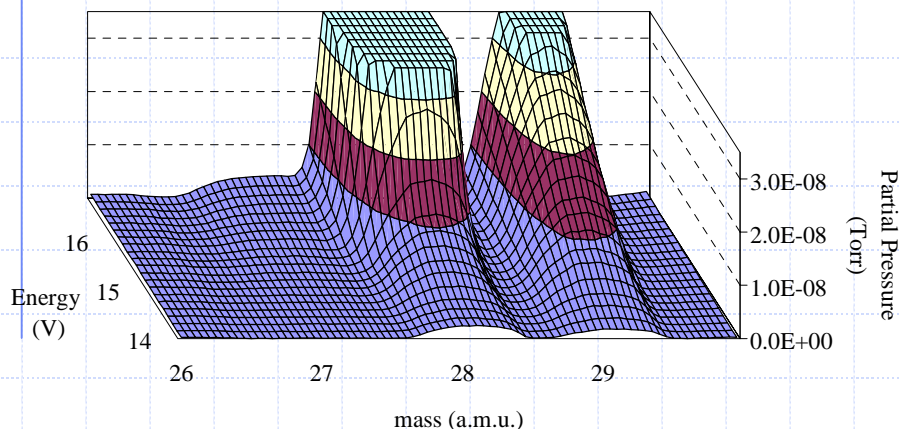
The spectra at 15eV and 10eV illustrate the spectral simplification obtained with soft ionisation.



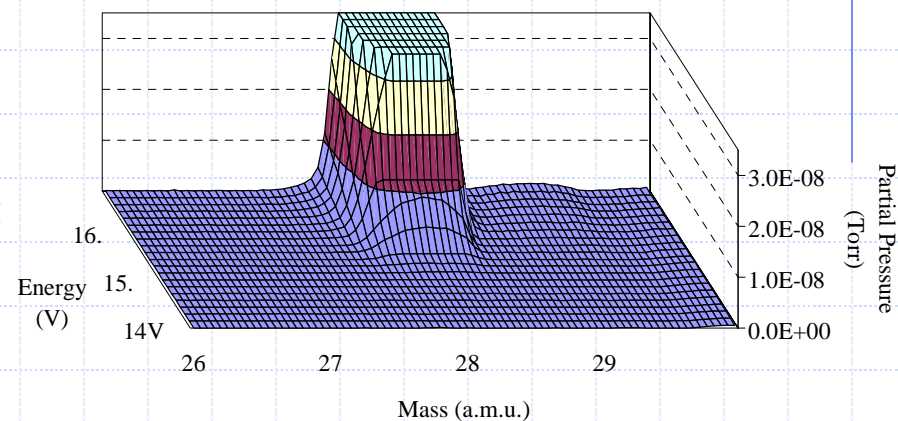
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# Data Interpretation 2.5

Effect of Electron Energy (14-18V) on MS of C6 Isomers in Air



Effect of Electron Energy (14-18V) on MS of Air



## Conclusions.

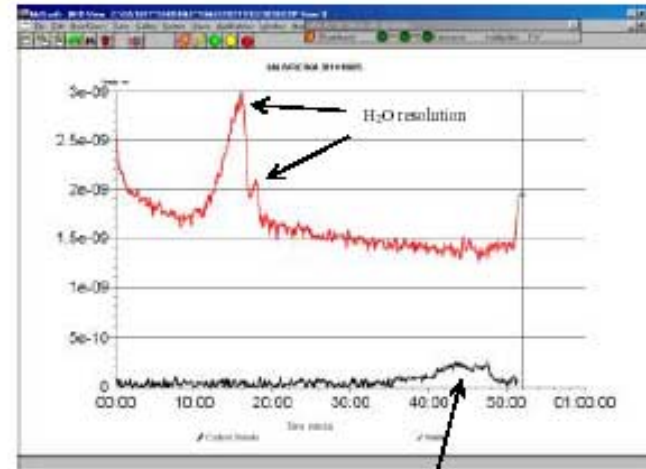
**Soft Ionisation is a simple and very useful method for the simplification of the analysis of complex mixtures with component concentrations from ca. 0.1 to 100% specifically where the 1<sup>st</sup> ionisation potential of the species vary by at least ~ 0.5 eV.**



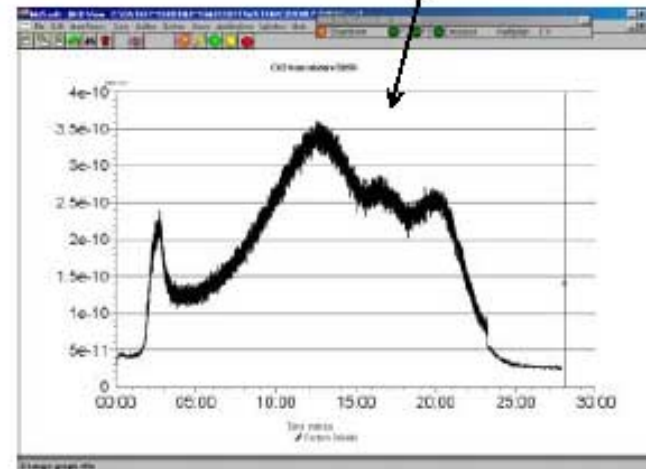
# The Final Word



TA-MS data from 50:50 CaOx : SrOx showing high resolution and response of the *Hiden TA-MS* coupling with a response to the minor differences in dehydroxylation temperatures / H<sub>2</sub>O evolution being clearly visible.



Detail of CO<sub>2</sub> response at ppm levels.

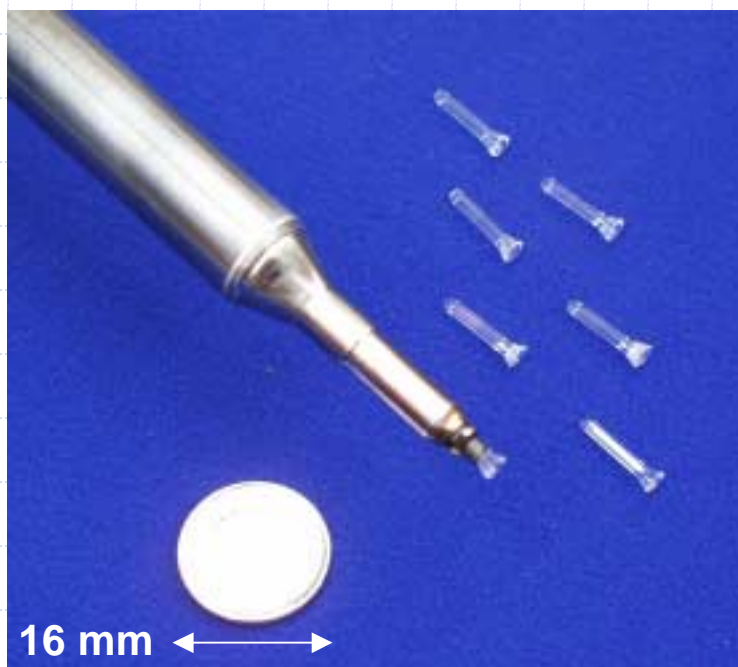


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# The Final, Final Word



Hiden are pleased to announce the development of an integrated High Temperature Solid Insertion Probe–mass spectrometer system, for in-situ TA-MS studies in collaboration with Professor Phil Barnes of the Centre for Applied Catalysis, University of Huddersfield.



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# The Final, Final Word



HPR-20 with Direct, High Temperature Solid Insertion Probe

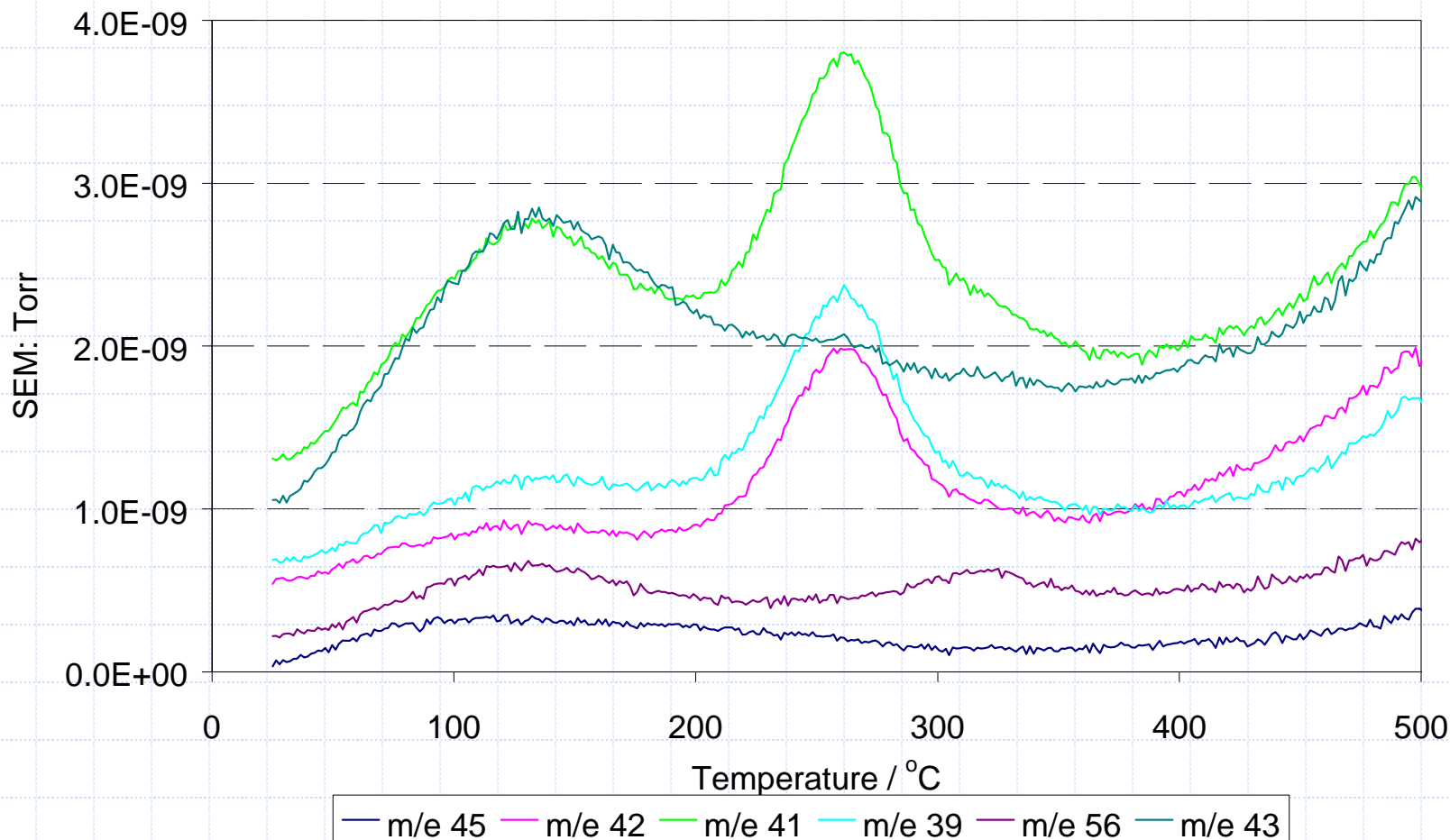


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# The Final, Final Word



Dehydration and Dimerisation of IPA over  $\gamma\text{-Al}_2\text{O}_3$  using the SIP



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# Conclusions



## To optimise TA-MS equipment:

- New equipment can be configured with optimum connections.
- Existing systems should be connected through customised couplings.
- Novel methods are available e.g. the direct solid insertion probe.

## Data interpretation and methods:

- Library search, linear combination, matrix inversion and soft ionisation techniques can be applied to identify and quantify species.
- Data interpretation provides catalyst characteristics, metal surface area for example

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