The Portable Horiba–Kore Mass Spectrometer MS-200 (Membrane Inlet Time of Flight MS)

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Figure 1

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Abstract

The MS-200 is a battery operated portable membrane inlet time of flight mass spectrometer. This technique allows semi continuous real time in-situ analysis of VOCs in gaseous samples.

The talk will describe some of the features and design considerations, working principles of the inlet system and the mixture analysis software. Application data and limitations of the technology will be discussed.

If you have any further questions that might not have been addressed in this presentation, please visit our web site at:

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1   Design Considerations

1.1   Advantages of In-situ Analysis

Traditional environmental analysis is done by sampling the soil, air or water and transports it back to the laboratory for analysis. Other techniques extracted the analyte from the sample matrix (adsorption onto an adsorbent) followed by transport and laboratory analysis of this "representative" adsorbent.

The top circle of Figure 2: Advantages of In Situ Analysis" shows the difficulties and inflexibility of this "classic" approach for environmental analysis. In addition, the change of the sample during the sampling process and the transport to the laboratory is questionable.

In opposite, in situ analysis normally combines the sampling and analysis and produces an analytical result almost instantly. This simplifies the sampling strategy. It also allows a flexible sampling strategy that adapts onto the knowledge gained from the last data point collected.
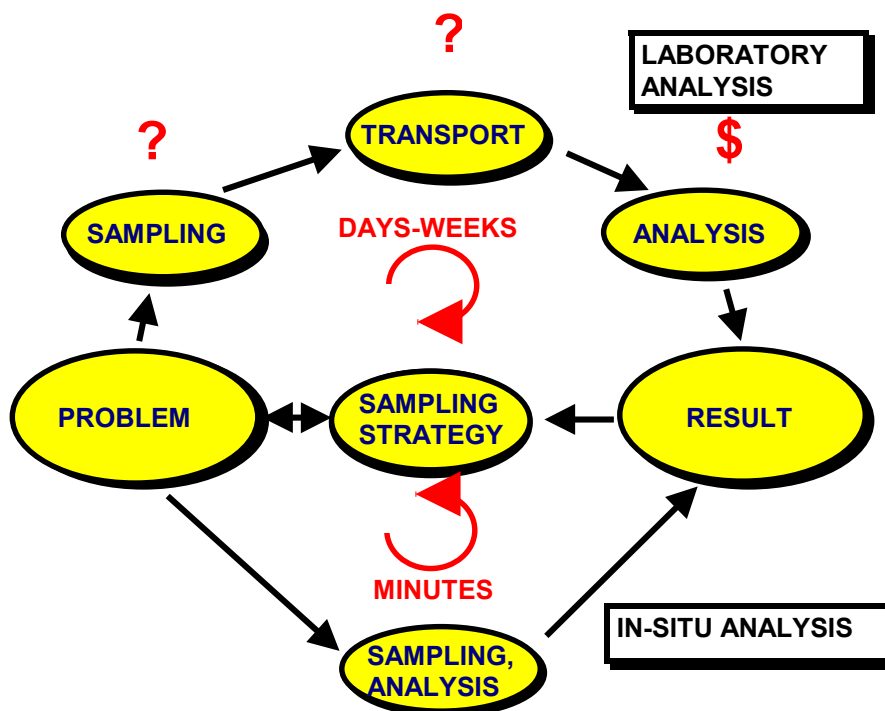

Figure 2: Advantages of In Situ Analysis

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1.2 Requirements on Portable Instrumentation

- When designing a portable analytical instrument to allow in situ analysis one starts with a black box and a list of requirements.

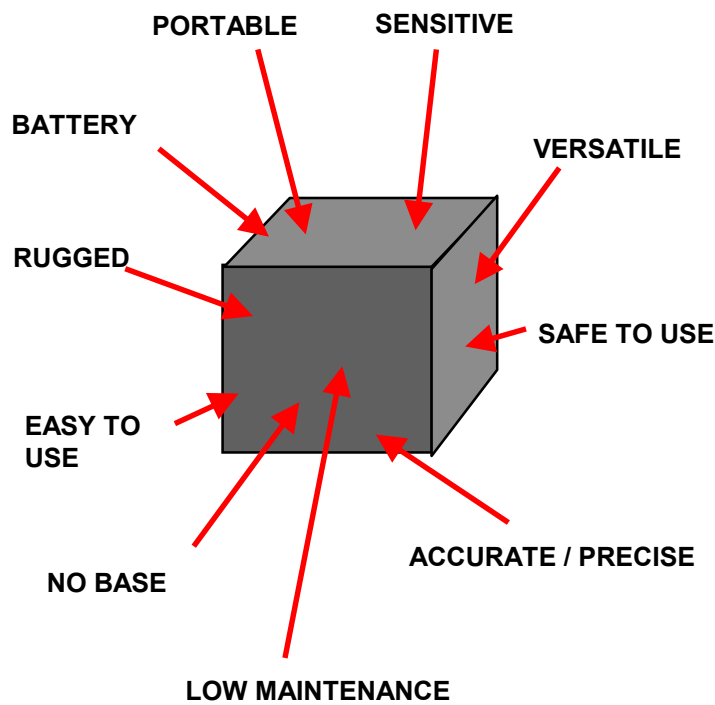- This initial thinking process is illustrated in Figure 3 - Requirements.

Figure 3 - Requirements

1.3 How to Achieve the Design Considerations

- **Mass spectrometer**

  MS offers chemical information about the sample and the potential of identification of unknown components

- **No GC-interface**

  GC column sensitive to contamination, requires carrier gas, delay / waiting time

- **No mechanical vacuum pumps**

  Power thirsty; shock / vibration sensitive

The answer for us was to built a:

→ **Membrane inlet time of flight mass spectrometer**

  Full mass spectrum information in every experiment (no scanning); high sensitivity (low leak rate, small pumps); semi continuous measurement; no consumables (other than electricity); relatively rugged; versatile; flexible.

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2   Working Principles of the MS-200

This figure shows a schematic cross sectional few of the patented Kore TOF flight chamber.

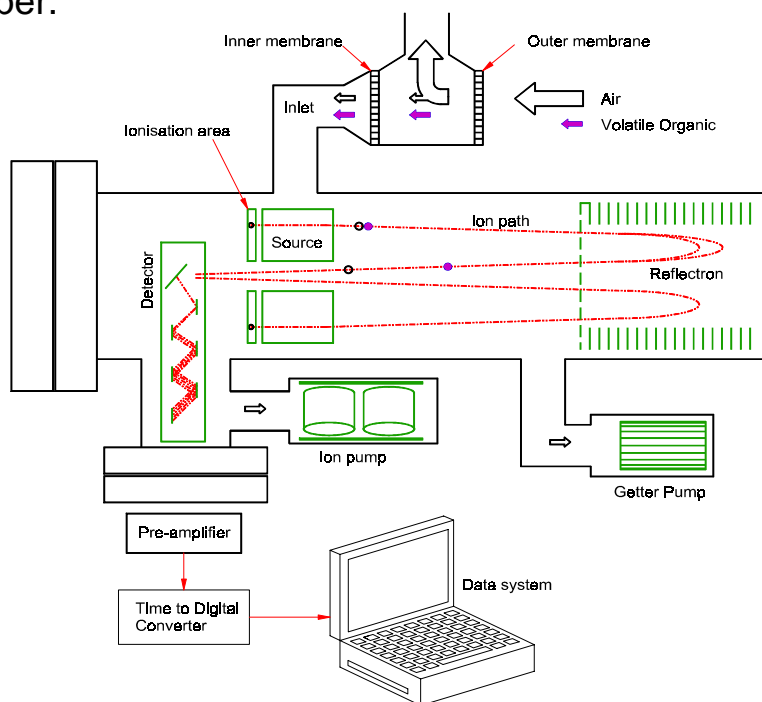- This figure shows the membrane inlet system where the volatile organic compounds in the gaseous sample are concentrated and introduced into the vacuum of the mass spectrometer.

- The molecules of the sample are ionised by the electron-emitting filament and the produced ions are accelerated into the spectrometer.

- To extend the flight path and to compensate for different start energies of molecules of the same mass, the ions are reflected in a reflectron (sloping electrical field). The ion beam is slightly tilted so that it "collapses" in a "parabolic" path to a single point where it hits the detector.

- The detector that reports the hits to the time to digital converter (TDC) that builds up a histogram of the arrival times of the ions.

- This histogram is sent to the laptop computer where the time spectrum is calculated into a mass spectrum and displayed.

- To maintain the vacuum in the analyser chamber the remaining gas molecules are pumped away by the ion and the getter pump.

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2.1 Working Principle of Membrane Inlet

- How does this double membrane inlet work? The molecules of the sample gas go into solution into the poly-dimethyl-siloxane (PDMS) membrane and due to the difference in partial pressure permeate through.

second membrane   first membrane

analyser vacuum   intermediate   atmosphere
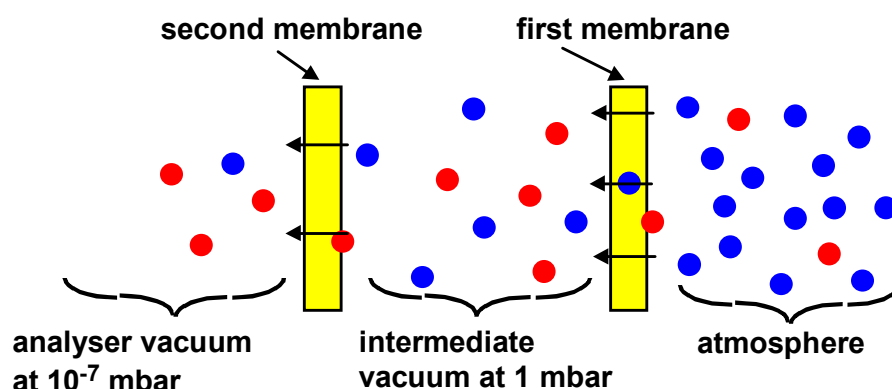at 10^{-7} mbar   vacuum at 1 mbar

Figure 5 – Membrane Concentrator

- The partition coefficient and the solubility of different chemicals in the PDMS are different, and therefore the membrane is a selective barrier to the sample.

- Looking at the intermediate vacuum step at 1 mbar, there are 1/1000 of the molecules than at atmosphere. However, due to the selectivity of the membrane the relative concentration for VOCs has changed (enrichment for benzene is approximately 100 times compared to the nitrogen background).

- The same selective permeation happens on the second membrane with a pressure step from 1 down to 10^{-7} mbar. This results in an overall concentration factor for benzene of 10,000.

- Using this membrane inlet, the leak rate into the spectrometer is approximately 0.2 µl/sec (≈ 10nMol/sec). This low leak rate together with the high sensitivity of the spectrometer is key to using non-mechanical vacuum pumps to maintain the vacuum in the spectrometer.

2.2 Mixture Analysis

What are the problems associated with using a membrane inlet mass spectrometer (MIMS) instead of a GC/MS?

- Using MIMS instead of gas chromatographic inlet, the pre separation of the sample into different fractions of pure components is not provided. This result in the mass spectrum obtained being a linear superposition of the spectra of all the components in the sample.

MIMS → **linear superposition of single mass spectra of all components in the sample**

| Spectrum of pure component A | Spectrum of pure component B | Resulting Spectrum of mixture |

Figure 6 – Mixture analysis

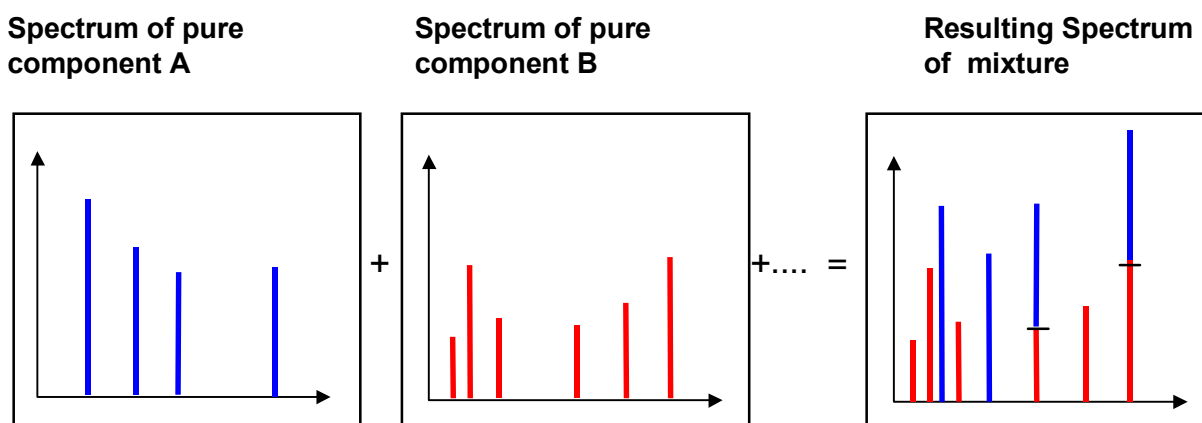- Each chemical has it's unique (almost if we are neglecting isomers that have very similar) mass fragmentation pattern. This pattern can be seen as a fingerprint, identifying chemical it origins from.

- This typical fingerprint allows the mixture analysis software to perform a least square fit of library data to the obtained mass spectrum and calculates the quantities of the components of interest.

3 Performance

3.1 Example Response to Xylene

To test the performance of the MS-200 and the mixture analysis software different concentrations of a mixture of gases were supplied. The result of the mixture analysis was recorded.

Figure 7 – Linearity of Response

- Using a gas divider, different fractions of a standard containing 400 ppb of xylene were supplied to the spectrometer. The MS-200 took a data point every minute.

- At the beginning clean nitrogen was supplied to the instrument, after five minutes it was changed to 100% of the sample. Than every five minutes the concentration was changed to 0% than 20%; 40%; 60% 80%; 100% and than down again followed by another full concentration check.

- Figure 7 shows the delay time of the MS-200 inlet to respond to a step change in the inlet. It also shows the repeatability of the analysis.

- Linearity of the response in the case of xylene is within ±6% in this experiment.

- Xylene was one from 8 components in nitrogen (including toluene)

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3.2 Detection Limit for Some Components

- The detection limit of the mass spectrometer is determined by calibrating the spectrometer to the component of interest. Than 31 background samples are analysed and the standard deviation of the mixture analysis result is calculated.

Component	σ	Component	σ
Benzene	> 5 ppb		
Xylene	> 5 ppb	Toluene	> 5 ppb
Dichloromethane	> 10 ppb	Trichloroethane	> 5 ppb
Ethylacetate	> 30 ppb	Methanol	$\approx$ 1 ppm
n-Hexane	> 10 ppb	2-Propanol	$\approx$ 1 ppm

Table 1 – Detection Limits

- The sensitivity to benzene is around 15 $^{counts}/_{(ppb \, second)}$ In the 78 amu peak.

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4 Applications

4.1 Air Monitoring on the International Space Station

- The MS-200 was evaluated for it's suitability as a VOC analyser on the International Space Station (ISS)

- The MS-200 was calibrated for the first nine chemicals in the following table. Those components where chosen as representatives for the air in the ISS.

- After the calibration of the instrument two challenge mixes where analysed. This mixes where produced and analysed by scientists at NASA. Additional (to us unknown) chemicals where added. This was done to assess interference with other chemicals that are present in a typical environment.

- The turquoise column represents the concentrations as analysed and reported at NASA by GC/MS. The yellow column includes the results we reported. The grey column reports the difference in reported concentrations.

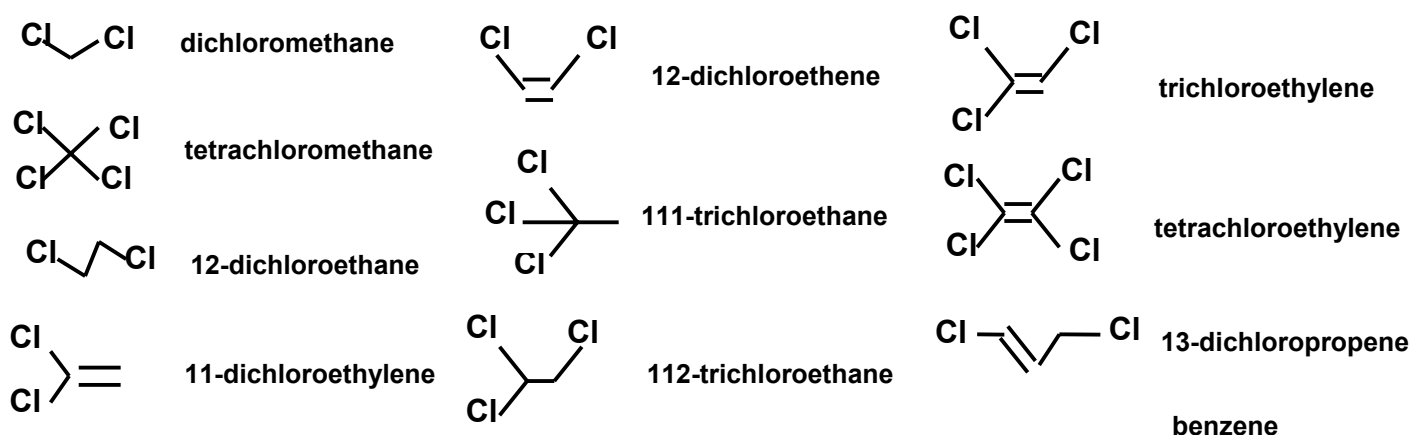| COMPONENT	Challenge Mix 1				Challenge Mix 2		
	NASA	Kore	Differ		NASA	Kore	differ
	Ppb	ppb	Ppb		ppb	ppb	ppb
Methanol	100	BQL			330	BQL	
Ethyl Acetate	40	X			120	X	
Isopropanol	700	BQL			94	BQL	
Acetaldehyde (Ethanal)	220	X			150	X	
m-Xylene	100	135	35		310	268	-42
Toluene	370	479	109		40	0	-40
Methylene Chloride	45	89	44		190	173	-17
1,1,1 trichloroethane	130	78	-52		28	75	47
Hexane	280	319	39		40	136	96
Acetone	140				270		
Ethanol	380				900		
Benzene	20				29		
Octamethylcyclotetrasiloxane	600				700		
Methane	101000				298000		
Carbon Dioxide	0				8986000		
Humidity	47%	43%			71%	42%	

Table 2 – NASA Challenge Mix

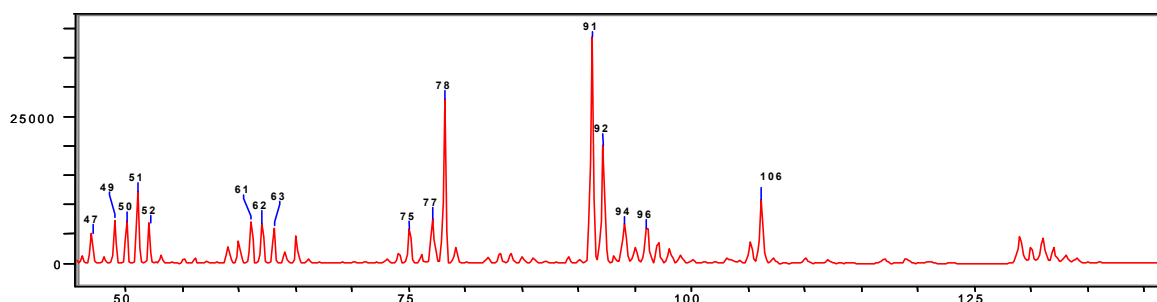BQL = Below Quantification Limit

- The x indicates difficulties due to the calibration standard used.

- The mixture analysis software pointed out that there are additional peaks that can not be assigned to the calibrated chemicals. Some of those peaks could be matched to the octametylcyclotetrasiloxane indicating the possibility of the identification of unknowns.

4.2   11 Hydrocarbons in Soil (1ppm simulation)

- The idea is to purge chlorinated hydrocarbons from the soil and analysing the headspace.

- This application shows that the mixture analysis software is capable to de-convolute complex mixtures of very similar chemical components in a gas mix.

This figure shows the resulting mass spectrum from the above chlorinated hydrocarbon mix.

- With such a complex mixture, one expects to face some problems. The spectra patterns of 11-dichloroethylene and12-dichloroethene are very similar, so are the mass spectra of the two isomers 111-trichloroethane and 112-trichloroethane.

- Table 3 shows the recorded counts for the components in the mixture analysis. Additionally with the counts (concentration), the mixture analysis reports a number representing the confidence calculated when matching library spectra to the real sample.

- The confidence number indicates to the user that the software is struggling to assign peaks. By simply removing the component that reports poor fitting from the library, the interfering chemicals can be identified.

- In the first example 11-dichloroethylene is removed, as a result of this almost all the counts originally assigned to 11-dichloroethylene are given to 12-dichloroethene. Additionally the reported confidence for 12-dichloroethene improves.

- A similar test was performed with the two isomers 111-trichloroethane and 112-trichloroethane.

Comp. name	All 11 mix		11-dichloroethylene removed				111-trichloroethane removed			
	counts	Conf %	Counts	Conf %	Counts change	% change	Counts	Conf %	counts change	% change
Dichloromethane	15016	1.46	15121	1.45	105.5	0.7	15032	1.46	16	0.1
Tetrachloromethane	15097	1.09	15115	1.09	17.5	0.1	15025	1.02	-73	-0.5
12-dichloroethane	46912	0.68	46831	0.68	-81.3	-0.2	46920	0.68	8	0.0
11-dichloroethylene	-5314	14.84	0	0.00	5314.0	-100.0	-5314	14.84	0	0.0
12-dichloroethene	72697	1.33	67011	0.70	-5686.0	-7.8	72705	1.33	8	0.0
111-trichloroethane	-432	82.63	-432	82.76	0.7	-0.2	0	0.00	432	-100.0
112-trichloroethane	46391	1.09	46074	1.09	-317.2	-0.7	46009	0.86	-382	-0.8
Trichloroethylene	62590	0.51	62708	0.50	118.1	0.2	62540	0.50	-49	-0.1
Tetrachloroethylene	216621	0.23	216438	0.23	-183.0	-0.1	216643	0.23	22	0.0
13dichloropropene	60328	0.58	60478	0.58	150.4	0.2	60340	0.58	13	0.0
Benzene	243492	0.26	243620	0.26	128.0	0.1	243486	0.26	-6	0.0
AR	64028	1.82	64053	1.82	25.0	0.0	64026	1.82	-1	0.0
H	19284	2.05	19284	2.05	0.0	0.0	19284	2.05	0	0.0
N2	11672	9.95	11602	10.01	-69.9	-0.6	11679	9.94	7	0.1
CO2	60605	0.66	60695	0.66	90.4	0.1	60602	0.66	-3	0.0
H2O	105966	0.43	105966	0.43	0.0	0.0	105966	0.43	0	0.0
O2	11800	2.29	11775	2.29	-25.3	-0.2	11803	2.29	3	0.0

Table 3: Mixture Analysis Report

- In such situations, the concentration of the two components that conflict can be only given as a total (assuming similar sensitivity of the individual components).

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4.3 Investigation into Arson

- The fact that our TOF instrument always produces a complete mass spectrum of the sample can be used in qualitative applications, where the actual concentration of a chemical is of secondary interest.

- In cases of arson, analysing the air on a suspected site in situ might reveal typical fingerprints of commonly used accelerants.

- The following figure shows the different mass spectra from petrol, methylated spirit and a paint thinner.

- Analysis of a real carpet sample, that was lighted using petrol, has shown little interference of the spectra by other components released during the combustion process of the carped.
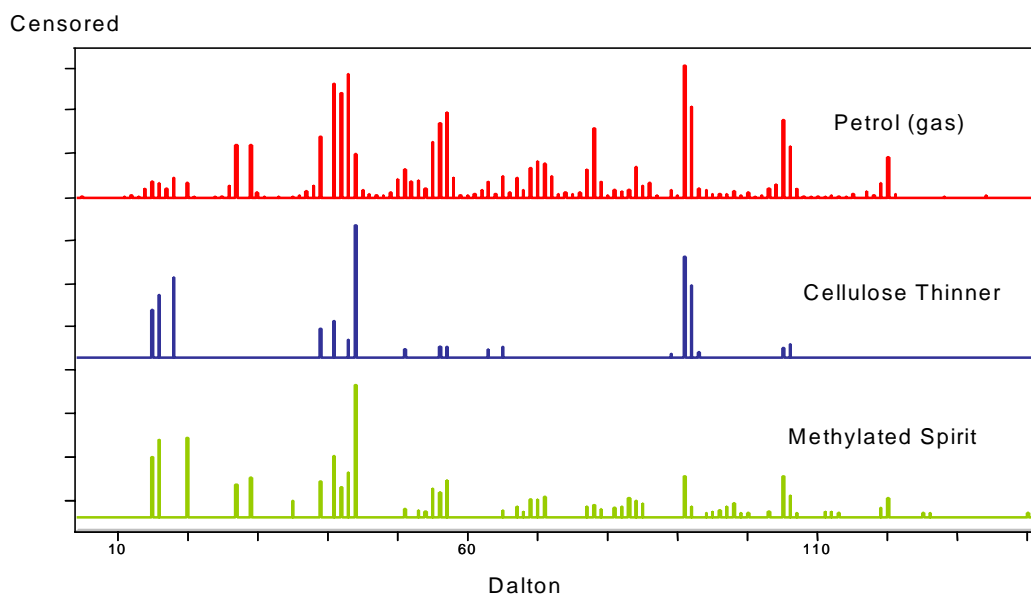

Figure 8 – Different accelerants

5   Conclusions

- It is possible to built a portable mains independent mass spectrometer on a commercial basis

- Double membrane inlet allows continuous semi real time analysis of mixtures of gases with the potential of high sensitivity (no further pre-concentration required).

- MS-200 has proven analytical performance

- TOF offers possible identification of unknowns

- Different membrane options to be investigated for more polar components (alcohols) and faster response times.

- Current instrument is flexible but might have to be adapted to suit specific applications

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Appendix

Weight of Individual Components

MS200 components break down	Individual weights	
Carrying case	4.75	
Sheet metal work	2.75	Kg
Time to digital converter	1.00	
High voltage power supplies	0.90	Kg
Ancillary equipment	0.20	
Lead acid Battery	4.03	Kg
Peristaltic pump	1.18	Kg
Analyser (Including. inlet system and pumps)	6.08	Kg
Total instrument weight	20.79	Kg

Table 4 – Break Down of the Weight

Power Consumption

Consumer	Power	
Ion Pump	1.1	Watt
Filament	8	Watt
Sample Pump	0.27	Watt
Inlet Pump	3.2	Watt
Inlet Valve	4.2	Watt
TDC + HV (standby)	10	Watt
TDC + HV (acquire data)	24	Watt

Table 5 – Break Down of Power Consumption

- Instrument switched off (ion pump only)   1.1 W

- Instrument ready for analysis   16.77 W

- Peak power, instrument acquiring data   40.77 W

- Average   (1 data point every 1 minute)   21 W
                   (1 data point every 5 minutes)   18 W

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Comparison between MS-200 and NIST Spectra

- Here we show that the spectra produced by the MS-200 can be easily compared to spectral databases like NIST.

- This is an essential requirement to allow the identification of unknowns.

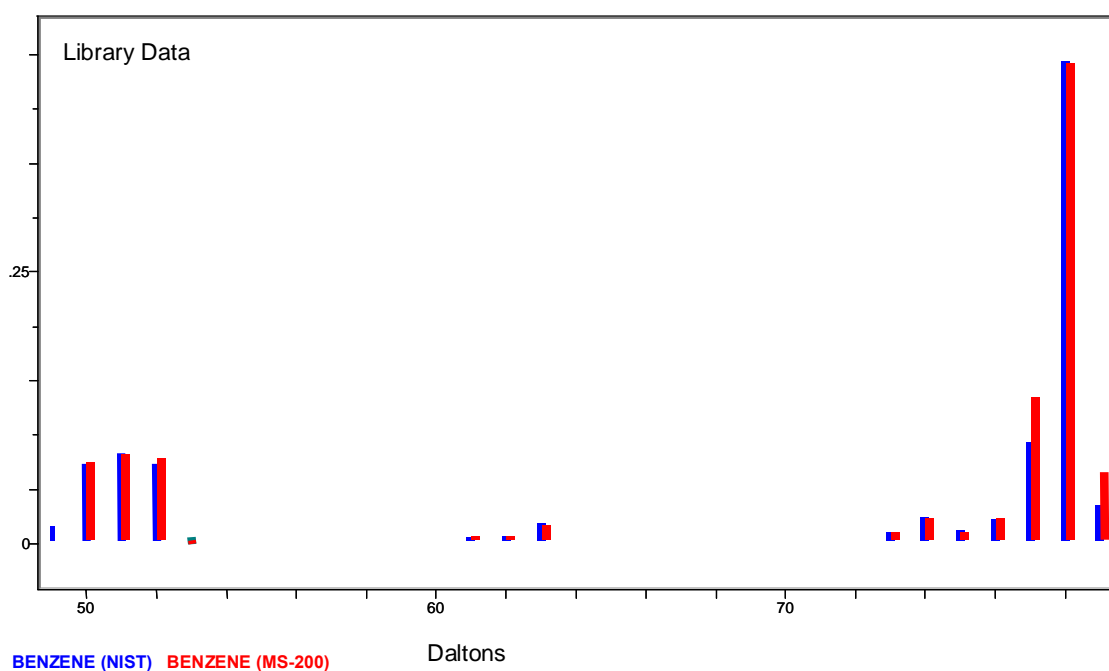- Identification of unknowns will require an experienced user with a good understanding of the environment in which the measurement was taken.

Figure 9 – Comparison of NIST to MS-200 Spectra

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