



## Soft Ionisation for Analysis of Complex Gas / Vapour Mixtures

### Simplification of Real Time Gas Analysis

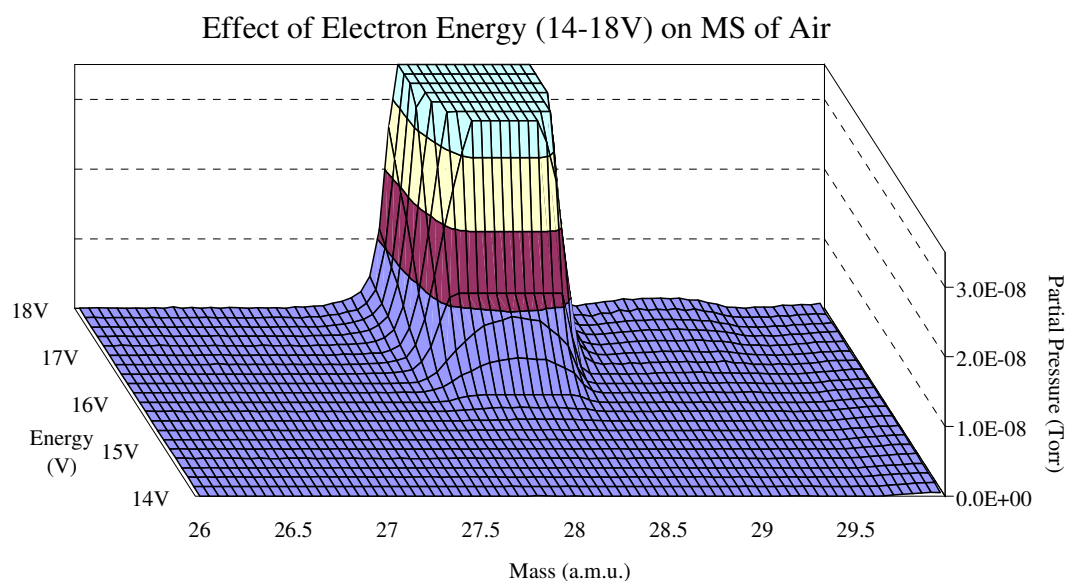
#### Soft Ionisation Overview

Hidden quadrupole mass-spectrometers can simplify the analysis of otherwise complex cracking patterns from multi-component gas / vapour mixtures via the method of 'Soft Ionisation'. This method provides user-defined ionisation to facilitate mass analysis and species discrimination / identification.

This application note describes measurements made on gas / vapour mixtures and isomeric mixtures using the Hidden HPR Series real time process gas analysers to analyse differing emergence potentials of organics, isomers and permanent gases. The two sets of data illustrate the performance of Soft Ionisation as a highly selective method for real-time analysis of mixtures and highlight the ability of Hidden QMS analysers to perform analyses not available to other systems.

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**Figure 1. Onset of  $N_2$  Ionisation at ~ 15.6 eV**

## Soft Ionisation

### Soft Ionisation of Molecules

In Hiden quadrupole mass spectrometers Electron Ionisation (E.I.) of the sample is utilised to generate the ions which undergo subsequent mass filtration and detection. In conventional E.I. the excited electrons typically have energies of the order of 70 eV. However, these high energies provide little molecular discrimination in the ionisation of the sample and also result in extensive fragmentation of the ions produced, particularly for organic species, which result in the characteristic but complex cracking patterns recorded.

In general usage these factors may be addressed quite simply, however in certain applications this is not the case. For example the exit gases from thermal analysers or chemical / catalytic reactors may contain complex mixtures of

organics, permanent gases and oxidation / decomposition products in a large excess of carrier e.g. air. Clearly the identification of these trace species is not trivial. Similarly the identification of isomeric fractions, which may well exhibit similar cracking patterns under conventional conditions can also be problematic to even the experienced mass spectrometrist.

To aid the MS user in these demanding applications Hiden have developed the method of Soft Ionisation (S.I.) (example for  $N_2$  shown in Figure 1 above). 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. Thus for example the analysis of IPA impurities in acetone would normally be highly difficult due to

the similar molecular weights, volatility and cracking characteristics of the two species. The presence of permanent gases from air (N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>) would also normally further complicate the analysis. This complexity is reflected in Figure 2b which shows a typical mass spectrum obtained by sampling solvent vapour which the typical high electron ionisation potential of 70V. A cursory analysis of this figure shows the presence of > 20 peaks from parent ions / fragments the deconvolution of which would not be trivial.

By utilisation of S.I. it is possible to control this ionisation and fragmentation.

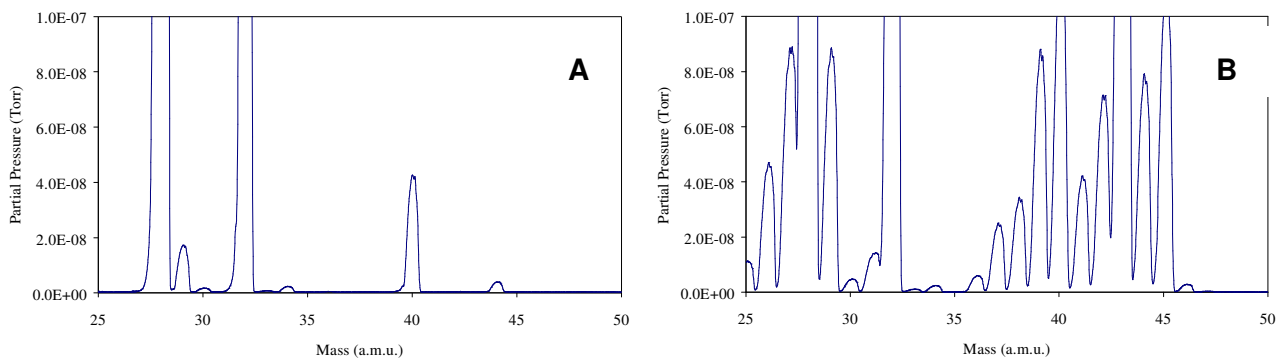
Hence by reduction of the Electron Energy to 15 and 10V (Figs. 3 and 4 *resp.*) the ionisation of N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> are reduced and then removed. Interestingly, even at low ionisation potential a peak at m/e 40 was recorded (3b and 4b). Initially this was ascribed to Ar, however comparison with air (Figs. 3a, 4a) contradicted this, consistent with the ionisation potential Ar of 15.76 EV (Table 1). This indicated the presence of an unknown in the mixture which would have been missed under normal conditions.

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

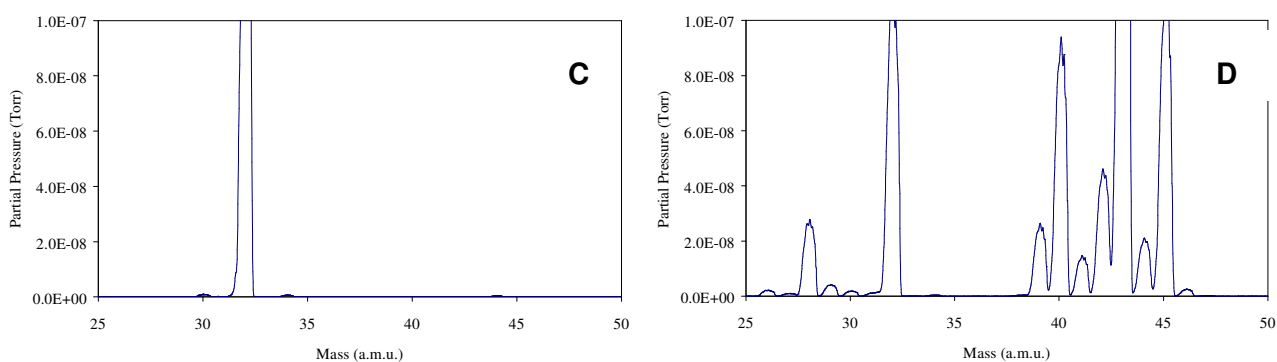
	N <sub>2</sub> Nitrogen	O <sub>2</sub> Oxygen	Ar Argon	CO Carbon monoxide	CO <sub>2</sub> Carbon dioxide	NH <sub>3</sub> Ammonia	NO Nitric oxide	CH <sub>4</sub> Methane
I.E. / eV	15.58	12.07	15.76	14.01	13.77	10.07	9.26	12.61
	C <sub>2</sub> H <sub>2</sub> Ethyne	C <sub>2</sub> H <sub>4</sub> Ethene	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> Cyclohexane	CH <sub>3</sub> OH Methanol	CH <sub>2</sub> O <sub>2</sub> Formic acid	CH <sub>2</sub> O Formaldehyde	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

Subsequent analysis and comparison against acetone vapour and IPA vapour showed the formation of a condensation product inside the MS chamber with a parent ion at m/e 84 with multiple fragments. However by again using S.I. fragmentation of the various organic fractions markedly reduced and suggested the presence of either allyl

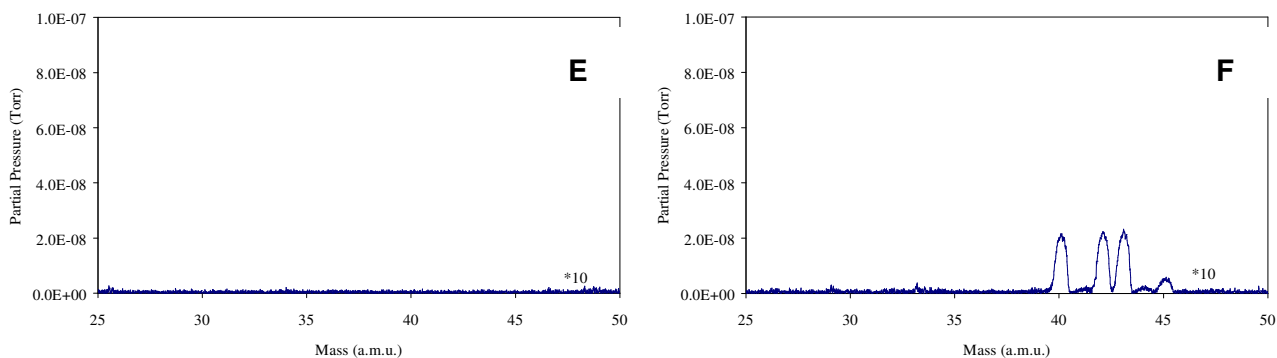
vinyl ether or 3-penten-2-one (source NIST98). Moreover in addition to at 10 V the preferential ionisation of acetone (m/e 42, 43) vs IPA (m/e 45) was evident (Fig. 4b / Fig. 5). Thus it is clear that S.I. greatly reduced the complexity of the MS trace in this application and also provided information not available without this facility.



**Figure 2. MS Profile of Air (a) and Acetone / Isopropyl Alcohol / Air vapour (b) at an Electron Energy of 70V**



**Figure 3. MS Profile of Air (c) and Acetone / Isopropyl Alcohol / Air vapour (d) at an Electron Energy of 15V**



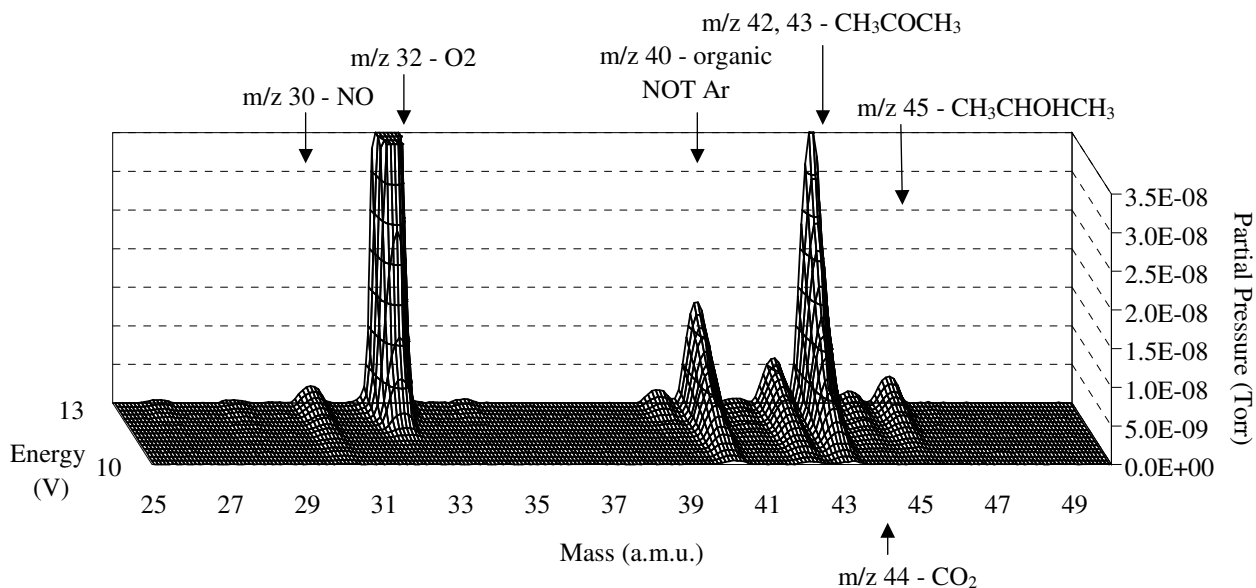
**Figure 4. MS Profile of Air (e) and Acetone / Isopropyl Alcohol / Air vapour (f) at an Electron Energy of 10V**

A further benefit of the SI technique is to collate the simple single energy profile scans in figures 2-4 via a co-variant scan of electron energy vs mass in the MASsoft software to create an ionisation surface i.e. the emergence potentials of molecular species. An example of such a surface for the acetone / IPA / air system is shown in Figure 5. Note that the ionisation energies required reflect the electronic properties of the species under study and are a measure of the ease of removal of the most loosely bound electron i.e. the First Ionisation Energy. To aid the user ionisation energies of various species are included in Table 1 (CRC Handbook of Chemistry and Physics 78<sup>th</sup> ed.)

## Soft Ionisation

### Conclusion

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.



**Figure 5. MS surface of an Acetone/I.P.A./Air vapour stream at electron energies of 10-13eV.**