Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 83–92

OPTIMISATION OF THE CONNECTION BETWEEN TA-MS SYSTEMS TOGETHER WITH IMPROVED DATA INTERPRETATION FOR TA-MS APPLICATIONS

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Abstract

TA-MS provides chemical and thermal response information. In order for this information to be meaningful sampling must be performed with minimum dead volume and without cold spots. Dead volume leads to response lag and peak broadening. Cold spots result in sample condensation, leading to inaccurate data and potentially inlet blockage. This paper describes a hot zone inlet system and 'in-situ' probe both of which provide fast response, zero dead volume sampling directly to the MS. The paper also discusses data interpretation methodologies and introduces 'soft ionisation' as a means of providing simplified analysis of complex mixtures.

Keywords: data analysis, inlet optimisation, thermal analysis–mass spectrometry

Introduction

Data obtained from thermal analysis equipment provides great insight into thermodynamic and mechanistic aspects of the thermal behaviour of materials and their interactions with probe molecules. Mass spectrometry may be employed in conjunction with thermal analysis to provide speciation of evolved species as function of temperature/time etc. to provide an extremely powerful technique for the characterisation of materials and their interactions and reactions with their environment. However, in order to obtain the full benefits from this technique one must take great care to optimise the coupling between the thermal analysis unit and the mass spectrometer.

There are several potential issues to be addressed which arise from the potentially conflicting modes of operation of the instruments. For example, thermal analysers typically operate at near atmospheric pressure although specialised systems do operate from high vacuum to high pressure. In contrast, the quadrupole filter of the MS requires high vacuum for operation. Moreover thermal analysers are primarily configured for optimum response to temperature, energy or mass changes rather than the provision for evolved gas analysis and so the placement or configuration of the mass spectrometer inlet assembly may not be ideal and may introduce dead volumes or 'cold' spots both of which can compromise the performance of the mass spectrometer system.

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

This paper will address these issues and also examine experimental and numerical methods to improve data analysis and interpretation for the TA-MS user.

Experimental

The mass spectrometer systems employed in these studies were based upon the standard Hiden HPR20-QIC mass spectrometer operating under the Hiden MASsoft operating system. The systems were variously configured with a standard heated QIC (Quartz Inert Capillary inlet), a coupled Hot-Zone sample inlet-QIC assembly and a Solid Insertion Probe (SIP) for the direct analysis of evolved species as a function of temperature under vacuum conditions within the mass spectrometer manifold. In all cases the systems included 2 standard 2.5 $m^3 h^{-1}$ oil sealed rotary pumps, 1 for dedicated sample pumping through the QIC to provide enhanced pump for light gases, specifically hydrogen and helium.

Results and discussion

Factors for consideration in placement of the MS inlet

An optimal solution to the connection of the thermal analyser to the mass spectrometer is to employ a high-temperature sampling probe situated directly above the sample pan within the thermal analyser. This configuration allows the direct sampling of all evolved gas/vapour species and their subsequent analysis in near real time by the mass spectrometer. An example of this direct sampling is provided by the Hiden Hot-Zone QIC, illustrated in Fig. 1 with a typical data example for the temperature programmed decomposition of a heteropoly acid (12-tungsto-phosphoric acid)–hexadiamine adduct shown in Fig. 2. The data show a large decomposition phenomenon with a peak response at ca. 450°C. This is ascribed to the oxidative decomposition of the hexadiamine species which act as a cross-linking tethers between the Keggin units of the heteropoly acid to form the three dimensional structure. The ability of the inlet system to monitor this decomposition phenomena reflects both the high sensitivity and fast response of the Hiden MS Hot-Zone QIC inlet with the observation of simultaneous responses of permanent gases and vapours, as evidenced by the coincident peaks of evolved decomposition products and oxidised species including ammonia, water, nitrogen, carbon dioxide and nitric oxide. This optimal response is ascribed to the minimal dead volume and non-interacting nature of the inlet system.

However, direct sampling is not always practical and the user may have to connect the MS inlet to the external exhaust of the thermal analyser. Again care must be taken to avoid introducing dead volume and cold spots into the inlet system which can severely compromise MS performance. Examples of the potential problems that non-ideal coupling can introduce are shown in Figs 3 and 4. Figure 3 shows the MS response and recovery in the analysis of condensable volatile organic compounds (VOCs), in this case isopropyl alcohol, into the standard QIC inlet and an inlet modified by inclusion of a 5 cm unheated ¼” SS tube to simulate a cold spot. Both inlets

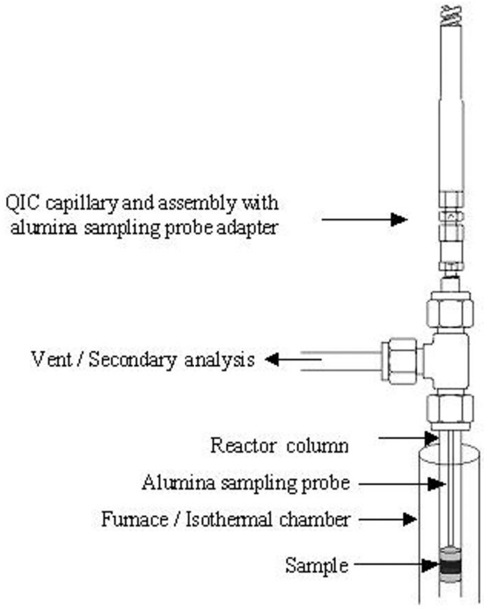

Fig. 1 The Hiden Hot-Zone-QIC inlet assembly

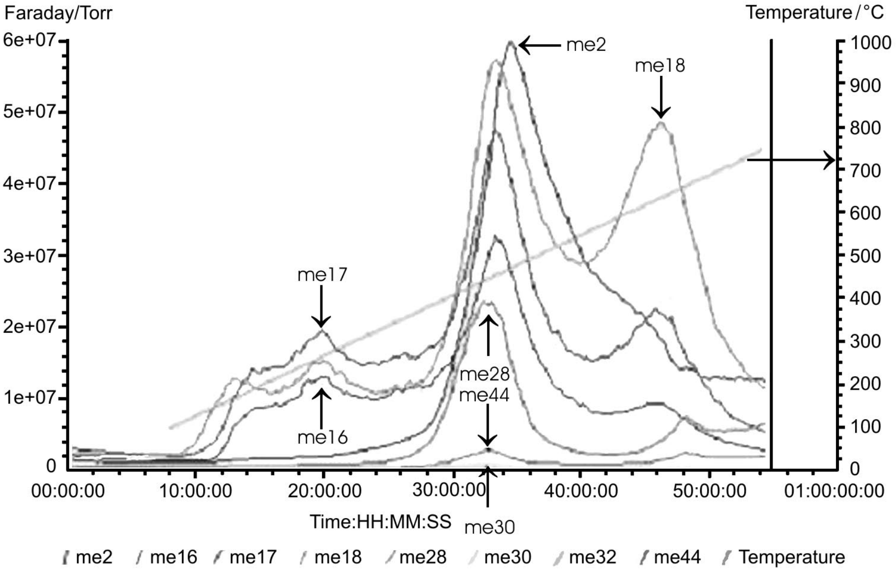

Fig. 2 TP-decomposition of $(H_3PW_{12}O_{40})\cdot(NH_2(CH_2)_6NH_2)_{1.5}$

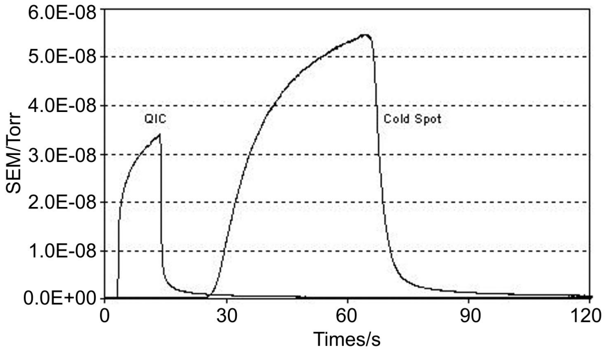

Fig. 3 MS response and recovery in the analysis of VOC's

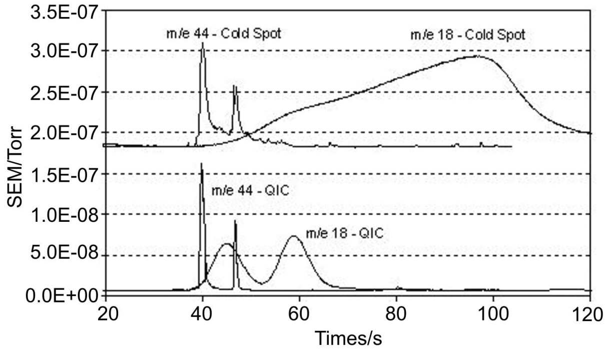

Fig. 4 MS response and recovery in the analysis of human breath

were exposed to IPA vapour, 15 s for the QIC and 25 s for the 'cold spot/QIC' i.e. until the IPA breakthrough. Notwithstanding the longer exposure of VOC in the latter case it is immediately apparent that the QIC provides significant improvements in both responses, <1 s cf. 25 s, and recovery, <10 s cf. >1 min for the 'cold spot'. Moreover the presence of cold spots and dead volume can also affect the analysis of permanent gases. Figure 4 contrasts the performance of the QIC with a system containing a cold dead volume. These data again reflect the adverse impact of the cold spot on the analysis of the condensable; in this case the moisture in human breath, but also examination of the response of the 'cold volume' inlet to CO_2 shows not only a response lag of ca. 1 s cf. the QIC but also the onset of peak broadening which under the conditions employed in thermal analysis can seriously compromise MS sensitivity for the detection of low levels evolved species or trace consumption of a reagent in a flowing stream e.g. H_2 consumption in temperature programmed reduction studies.

Direct solid insertion probe

A further alternative method to obtain immediate optimised MS response in temperature programmed studies is to perform the analysis 'in-situ' within the MS manifold. Such experiments are possible by the use of a direct Solid Insertion Probe (SIP), as illustrated in Fig. 5. This system allows the user to place the sample within a heatable assembly (T_{max} 800°C) and transfer the sample from atmosphere into a pre-dosing/degassing chamber and thence directly into the UHV quadrupole manifold. This configuration provides maximum concentration of all evolved species directly at the ioniser source and affords optimal detection of trace components from even very small masses of sample as well zero dead volume response. An example of the use of the SIP is shown in Fig. 6 which addresses the Temperature Programmed Reaction of iso-propyl alcohol over a commercial γ-Al_2O_3 catalyst. The study was performed using ca. 2 mg of catalyst which was pre-dosed with 25 mL of IPA vapour in air followed by evacuation for 1 h prior to transfer to the ioniser chamber and subsequent analysis at a ramp of 10°C min^{-1}. These data illustrate the high response afforded by the SIP configuration even when using extremely small samples. The data shows 2 main lower temperature phenomena centred at 140 and 265°C. The former compromises a mixture of loosely bound propene, hexane and IPA (1) and is ascribed to a combination of dehydration and dehydration – dimerisation of the IPA. The latter set of peaks is due to propene again derived from dehydration of the feed but adsorbed on stronger acid sites of the Al_2O_3. At higher temperatures the onset of more extensive reactions are evident including the dehydration of the Al_2O_3 itself (data not shown for clarity).

Data analysis and interpretation

A further consideration for the application of TA-MS methods, even in the case of optimised coupling of the units, is the analysis and interpretation of the data obtained. To successfully interpret data from an unknown one requires detection of all peaks from the evolved species, identification of temperature of evolution and the abundance of evolved species. The HPR20-QIC addresses all of these aspects. The high sensitivity of the quadrupole provides identification of all peaks and abundance determination and the facility for direct export and analysis in the NIST mass spectral database for the identification of simple spectra (NIST) or processing by the Hiden MatrixIn Matrix Inversion Method package or by linear equation combination method (see below). In addition temperature can be directly exported with MS data to provide full speciation and temperature phenomena determination.

An example of the linear combination method is found in the study of off gases from a pyrolysis gasifier unit. These units convert landfill solids e.g. domestic waste, via pyrolytic decomposition to provide an environmentally benign fuel for gas turbines. The process involves the anaerobic conversion of solid into the fuel gas via indirect heating to 400–800°C. The products of this process typically comprise gases, (vaporised) liquids and solid chars (which are subsequently filtered) of comparatively high *CV* (typically 15–30 MJ Nm^{-3}). Typically speciation of this mixture has been performed by off-line GC methods. However, these analyses have yielded wide variations in the concentrations of the fuel components, especially H_2, and consistently failed to provide full mass balance with % levels of unknown components, a particu-

Fig. 5 The Hiden HPR20-QIC mass spectrometer with solid insertion probe

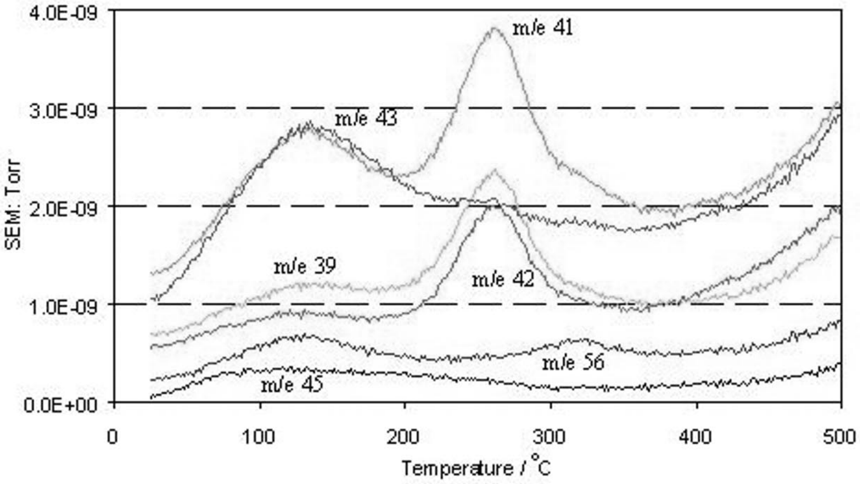

Fig. 6 Dehydration and dimerisation of IPA over γ-Al_2O_3 using the SIP

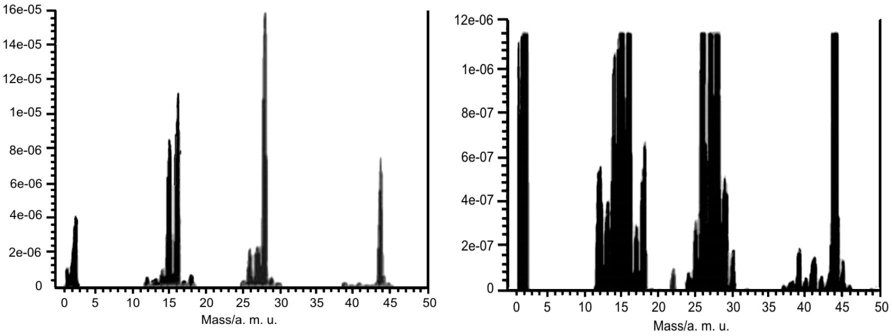

Fig. 7 Raw MS profiles of pyrolysis gasifier off-gas

lar concern given their contribution to the overall *CV* and combustion characteristics of the fuel gas.

On-line MS using the Hiden HPR20 QIC highlighted the complexity of the mixture confirming the presence of H_2, CO, N_2, CH_4, H_2O, C_2 & C_3 hydrocarbons, argon, CO_2, longer chain HCs, benzene and xylene amongst others (Fig. 7). Clearly the complexity of the MS profile renders a simple analysis impossible. Therefore in order to quantify the components in the mixture the follow steps were taken:

1) Identify all molecular ions/significant peaks.
2) Identify peaks due to known components
3) Assign remaining peaks noting the general appearance of the spectrum, checking for peak clusters from isotope patterns and low-mass neutral fragment loss e.g. CH_2
4) Compare to reference spectra on the MS database [1].

Once the identities of the various species have been established the next step 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 shear complexity is such that Matrix Inversion Methods are required. 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. Thus the analysis employed the simpler linear combination approach to determine individual contributions, these values then being incorporated into the full set of equations where appropriate to establish the full species profile.

At *m*/*e* 17 the peak is a result of both H_2O (23% of the peak at *m*/*e* 18)+NH_3. Hence:

$$NH_3 = (m/e\ 17 - (0.23 m/e\ 18))/1.3) \qquad (1)$$

where 1.3 is the relative sensitivity of NH_3 cf. N_2.

To calculate the N_2 concentration we cannot use the main peak at m/e 28 as indicated. Hence we derive the N_2 from the m/e 14 N_2 daughter peak, corrected for the methane overlap:

$$N_2 = 20(m/e\ 14 - (0.204CH_4)) \tag{2}$$

NB. Methane concentration is itself derived from:

$$CH_4 = m/e\ 16/1.6 - (0.80NH_3) - ((0.218m/e\ 32)/0.86) \tag{3}$$

where 1.3 is the relative sensitivity of CH_4 cf. N_2, where 1.6 is the relative sensitivity of CH_4 cf. N_2 and 0.86 is the relative sensitivity of O_2 cf. N_2.

Table 1 Fuel gas analysis (%) by linear combination method at 3 sample points

Species	S3	S2	S1	Species	S3	S2	S1
H_2	26.76	26.32	26.72	Argon	0.170	0.137	0.181
CO	27.16	27.23	26.28	*n*-Alkenes	0.130	0.120	0.152
N_2	3.707	3.713	3.554	Octane	0.096	0.107	0.160
CH_4	11.84	12.20	11.76	CO_2	15.15	15.61	15.06
NH_3	0.420	0.400	0.385	HC(C_2s+)	2.696	3.030	2.706
H_2O	4.521	3.295	5.008	HC/xylene	0.174	0.139	0.152
Na	0.045	0.033	0.119	HC fragment	0.127	0.072	0.099
HC(C_2s+)	2.796	3.102	2.803	HC fragment	0.017	0.120	0.132
HC(C_2s+)	2.696	3.030	2.706	Pentene	0.021	0.026	0.036
Ethane/ethene	2.240	2.771	2.529	*iso*-Alkenes	0.021	0.039	0.045
Propane/propene	0.426	0.403	0.388	*iso*-Octane	0.023	0.028	0.036
Ethane	0.937	0.570	0.885	C6	0.008	0.011	0.015
O_2	0.164	0.045	0.180	C7	0.008	0.011	0.016
H_2S	0.072	0.030	0.027	Benzene	0.023	0.198	0.213
Cl	0.158	0.049	0.138	Xylene	0.013	0.021	0.024
Benzene	0.090	0.177	0.198				

The results from this approach are shown in Table 1 and were found to be generally consistent both within different analysis runs and different analysis points but also in-line with estimates derived from on-line GC.

Soft ionisation for the analysis of complex mixtures

Quadrupole mass spectrometers generally employ Electron Ionisation (E.I.) to generate the ions which undergo mass filtration and detection. Conventionally the energy of the excited electrons employed is 70 eV. However, these energies provide little molecular discrimination in ionisation and result in extensive fragmentation of the ions produced, particularly for VOCs, which yield the characteristic but complex cracking patterns recorded (e.g. Fig. 7). Moreover the degree of spectral overlap and presence of unknown fragments can make deconvolution or matrix inversion methods impossible. An example of this is the analysis of exit gases from thermal analysers or chemical/catalytic reactors which may contain complex mixtures of organics, permanent gases, vapours and oxidation/decomposition/reaction products in a large excess of carrier e.g. N_2.

However it is possible to reduce or even avoid this excessive fragmentation by the application of the Soft Ionisation (S.I.) method [2]. This involves manipulation of the emission current and energy of the ionising electrons from the ioniser filaments to both reduce fragmentation and also achieve selective ionisation of individual components. The latter is possible as the energies required to produce the ions detected by the MS are a function of the electronic properties of the species under study and reflect the ease of removal of the most loosely bound electron i.e. the First Ionisation Energy. For example Figs 8a–c illustrate an analysis of IPA impurities in acetone, these scans are collated in Fig. 9 to create an ionisation surface i.e. the emergence potentials of molecular species. Normally the similar molecular weights, volatility and cracking characteristics of IPA and acetone would make this analysis highly difficult. Moreover the presence of permanent gases from air (N_2, O_2, Ar, CO_2) further complicate the analysis. This complexity is reflected in Fig. 8a which shows a typical mass spectrum at an electron ionisation poten-

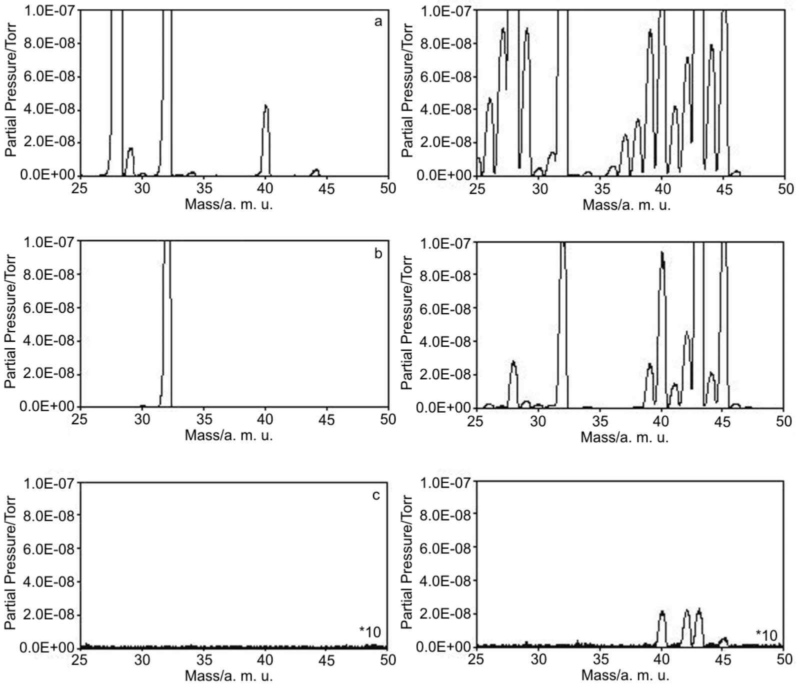

Fig. 8 MS profiles of air *vs*. acetone/IPA/air at electron energies of 70, 15, 10 V

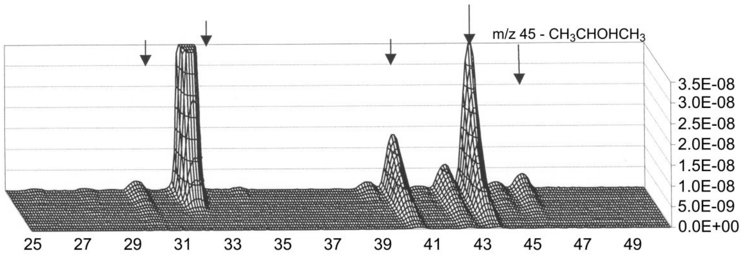

Fig. 9 MS surface of an acetone /IPA/air vapour at electron energies of 10–13 V

tial of 70 V. Cursory analysis of this data shows >20 peaks from parent ions/fragments the deconvolution of which would not be trivial.

However by utilisation of S.I. it is possible to control this ionisation and fragmentation to greatly simplify the MS spectra. Hence by reduction of the Electron Energy to 15 and 10 V (Figs 8b and 8c resp.) the ionisation of N_2, O_2 and CO_2 are reduced and removed. Interestingly, even at lower ionisation energies a peak at *m*/*e* 40 is present. This is not consistent with the ionisation Ar of 15.76 EV [2, 3] and indicated the presence of an unknown in the mixture which would not have been detected under conventional conditions. Comparison with standards indicated the formation of a condensation product inside the MS with a parent ion at *m*/*e* 84 and multiple daughter fragments. However, by again using S.I. fragmentation of the organic fractions was markedly reduced and suggested the presence of either allyl vinyl ether or 3-penten-2-one (1). Finally at 10 V the preferential ionisation of acetone (*m*/*e* 42, 43) *vs*. IPA (*m*/*e* 45) was also evident (Fig. 8c). A further example of the power of the S.I. technique may be found in discrimination of isomeric mixtures wherein control of the electron energy permits discrimination of *n* and cyclohexane [3].

Conclusions

TA-MS can provide a wealth of important information to the user provided appropriate consideration is made with regards to the mechanism of linking the instruments. A wide variety of potential solutions to this challenge are available to fulfil widely varying applications. Similarly, a range of analytical and mathematical methods have been developed to both simplify the nature of acquired data and to assist in the interpretation of the sometimes complex mass spectral cracking patterns obtained.

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