



HPR-20

Analysis of Complex gas / vapour mixtures from a Pyrolysis Gasifier

Summary

Hiden quadrupole mass-spectrometers have been applied to the analysis of the complex gas / vapour fuel mixture produced by the pyrolytic decomposition of landfill solids. This application note describes measurements made on this complex gas / vapour mixture using the Hiden HPR-20 QIC followed by analysis and deconvolution of the data to provide determination of the concentrations of fuel and ballast components and contaminants in the gas. The data highlight the ability of the HPR series QMS to perform analyses relevant to real-world scenarios typically considered intractable.

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Complex Mixtures Analysis

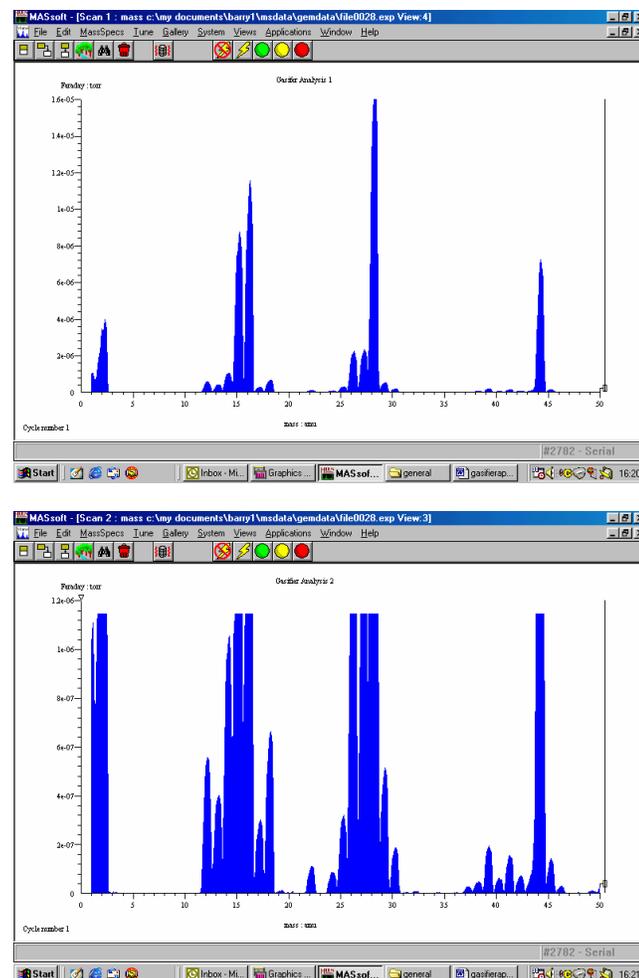
Hidden mass spectrometers afford the researcher a means for real-time, on-line analysis of gas /vapour mixtures not provided by conventional off-line methods e.g. gas chromatography. However, two of the main issues encountered in the application of MS analysis to real, and generally complex, mixtures arise from spectral interference and the extensive fragmentation of the ions produced, particularly for organic species, which result in their characteristic but complex cracking patterns.

Generally these issues may be addressed by selection of non-interfering peaks, however in certain cases this is not possible. For example the exit gases / vapours from a process may contain complex mixtures of organic feeds / products and entrained permanent gases. Similarly, the differentiation of hydrocarbon fractions, which can exhibit similar cracking patterns under conventional conditions, can be problematic to even the experienced mass spectrometrists.

An example of such a complex analysis is found in the study of off gases from a pyrolysis gasifier unit (Example shown in Figure 1.). These units convert landfill solids e.g. domestic waste, via pyrolytic decomposition to provide an environmentally benign fuel for gas turbines. The pyrolysis process involves the anaerobic conversion of solid matter into the fuel gas via indirect heating at temperatures 400 – 800 °C. The resultant products of this process typically comprise gases, (vaporised) liquids and solid chars (which are subsequently filtered) of comparatively high CV (typically 15 - 30 MJ/Nm³). Typically speciation of this complex mixture has been performed by off-line GC methods. However, these analyses have yielded wide variations in the

concentrations of the fuel components, especially H₂, and consistently failed to provide full mass balance with % levels of unknown components, a particular concern given their contribution to the overall CV and combustion characteristics of the fuel gas.

Figure 1a/b Raw MS profiles of Gasifier off-Gas

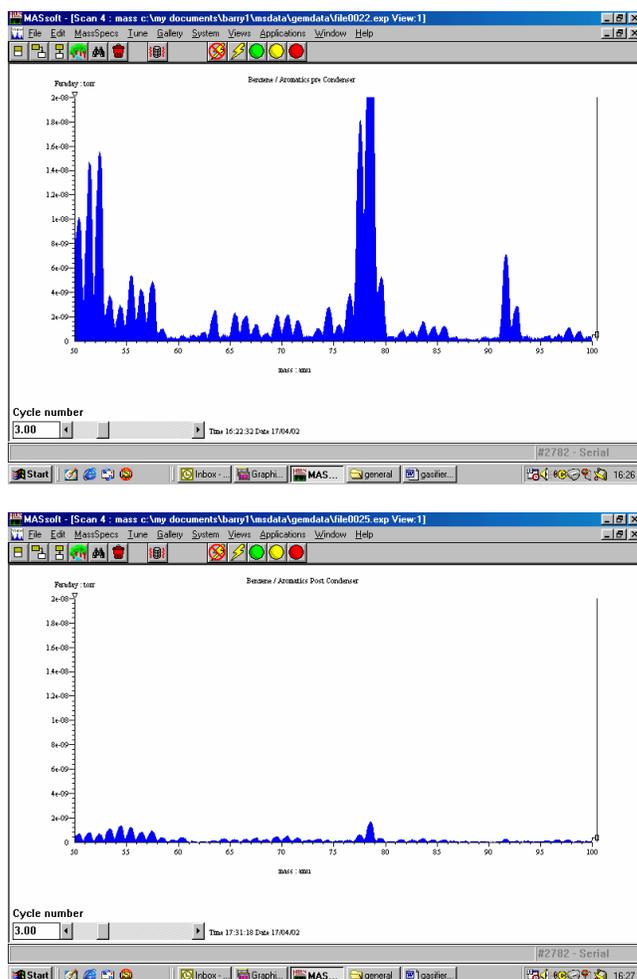


On-line MS using the Hidden HPR20 QIC (above) highlighted the complexity of the mixture confirming the presence of H₂, CO, N₂, CH₄, H₂O, C₂ & C₃ hydrocarbons, Argon, CO₂, longer chain HCs, Benzene and xylene amongst others. Clearly this degree of complexity renders a simple analysis impossible. Therefore in order to quantify the individual 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. CH₂
- 4) Compare to reference spectra on the NIST98 database (available from Hiden Analytical).

Figure 2. MS Profiles of Heavy Ends Pre / Post Condenser Unit



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 N₂, 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). 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.

e.g.1/ at m/e 17 the peak appears as a result of both H₂O (23% of the peak at m/e 18) + NH₃. Hence:

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

where 1.3 is the Relative Sensitivity of NH₃ cf. N₂

e.g.2/ To calculate the N₂ concentration we cannot use the main peak at m/e 28 as indicated. Hence we derive the N₂ concentration from the m/e 14 N₂ daughter peak, corrected for the Methane overlap:

$$N_2 = (m/e\ 14 - (0.204 * CH_4)) * 20$$

NB. Methane concentration is itself derived from:

$$CH_4 = \frac{m/e\ 16 / 1.6 - (0.80 * NH_3) - ((0.218 * m/e\ 32) / 0.86)}{1}$$

Where 1.3 is the Relative Sensitivity of

CH₄ cf. N₂ Where 1.6 is the Relative Sensitivity of CH₄ cf. N₂ and 0.86 is the Relative Sensitivity of O₂ cf. N₂

e.g.3/ at m/e 12 a 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 CO₂ and contributions from C₅ + hydrocarbons are ca. 0.1%, which given their low concentrations are ignored. Hence:

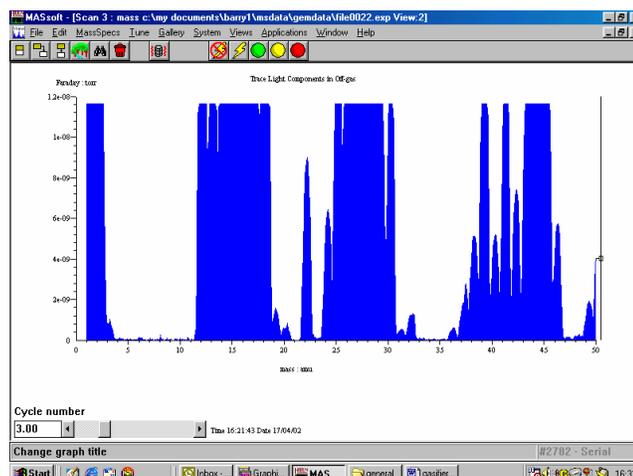
$$\text{CO} = (20/1.05) * ((m/e \ 12 - (0.012 * \text{Ethane}) - (0.004 * \text{Ethene}) - (0.006 * \text{Propane}) - (0.02 * \text{Propene}) - (0.003 * \text{Butane}) - (0.008 * \text{Butene}))$$

Where 1.05 is the Relative Sensitivity of CO cf. N₂

In addition to this method it was necessary to make provision for contributions for homologous series species e.g. all n and iso-alkanes or aromatics. This is necessary as it can be particularly difficult to make specific assignments to fragments as members of the series display similar fragmentation patterns and contributions e.g. m/e 26 which encompasses contributions from all non-methane hydrocarbons. To account cases where no specific assignment could be made 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.

The raw spectra used and some results derived from this analysis approach are shown in Figures 1a, 1b, 2a, 2b, 3 and Table 1.

Figure 3. MS Profile of Trace Light Fractions



Analysis was performed at 3 sampling points to ensure representative speciation over the pyrolysis unit and also to examine the scrubbing system used to condense aromatics prior to the gas turbine (point S3). In each case 40 profile scans were taken, 30 over 1– 50 amu at increasing amplification and 10 over the range 50 - 100 amu for analysis of aromatics and long chain HCs. The data obtained showed a high reproducibility (\pm 0.4% of absolute signal) and good agreement over the 3 sampling points. The major differences outside of this error range were recorded for Benzene, Xylene and longer chain HCs and are ascribed to the condensation of these components. In addition the data reveal the presence of a range of contaminants including NH₃, H₂S, O₂ as well as trace levels of alkali metals and Chlorine.

Table 1 – % Fuel Gas Analysis at 3 Sample Points

Species	S3	S2	S1
H ₂	26.76	26.32	26.72
CO	27.16	27.23	26.28
N ₂	3.707	3.713	3.554
CH ₄	11.84	12.20	11.76
NH ₃	0.420	0.400	0.385
H ₂ O	4.521	3.295	5.008
Na	0.045	0.033	0.119
HC (C ₂ S +)	2.796	3.102	2.803
HC (C ₂ S +)	2.696	3.030	2.706
Ethane / Ethene	2.240	2.771	2.529
Propane/ Propene	0.426	0.403	0.388
Ethane	0.937	0.570	0.885
O ₂	0.164	0.045	0.180
H ₂ S	0.072	0.030	0.027
Cl	0.158	0.049	0.138
Benzene / K	0.090	0.177	0.198
Argon	0.170	0.137	0.181
n-alkenes	0.130	0.120	0.152
Octane	0.096	0.107	0.160
CO ₂	15.15	15.61	15.06
HC/xylene	0.174	0.139	0.152
HC fragment	0.127	0.072	0.099
HC fragment	0.017	0.120	0.132
Pentene	0.021	0.026	0.036
iso-alkenes	0.021	0.039	0.045
iso-Octane	0.023	0.028	0.036
C ₆	0.008	0.011	0.015
C ₇	0.008	0.011	0.016
Benzene	0.023	0.198	0.213
Xylene	0.013	0.021	0.024

The presence of residual trace levels

of oxygen is of some interest, particularly in the context of the high levels of CO₂ recorded. These observations suggest an appreciable level of O₂ is fed into the pyrolysis unit which in turn facilitates combustion of significant levels of the fuel components. This combustion process will both modify the compositional characteristics in-situ, which may markedly change the nature of the reactions occurring within the unit, but will also change the thermal profile of the pyrolysis unit and affect the final calorific value of the fuel gas produced.

Conclusions

The MS analysis of fuel gas produced from pyrolysis of landfill solids has been performed and has enabled on-line, real-time speciation of all fuel, ballast and contaminant components. This has been made possible by mathematical deconvolution of the various spectral interferences present by construction of a set of linear equations.