Thermal Analysis and Soft Ionization Mass Spectrometry

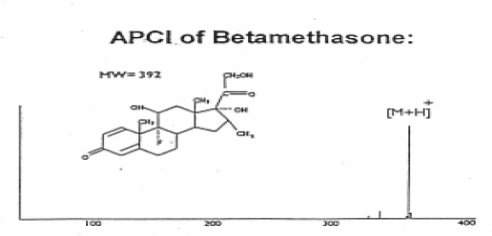
Ennio Cantergiani and Pascal Fuchsmann

Fayrouz Manufacturing & Technology Centre
case postale 381 – ZI Le PLanchy
1630 Bulle, Switzerland
Tel: +41 26 919 10 21, Fax: +41 26 919 10 20 , Email: ecantergiani@fayrouz.com

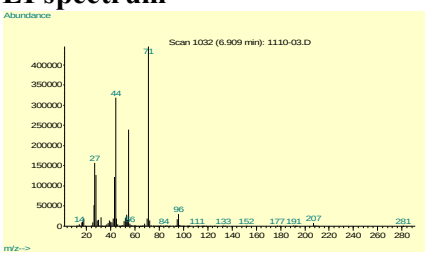
Abstract:

Thermal analysis is a very common analytical technique producing gaseous and volatile compounds. The qualitative analysis of evolved gases from a thermal analyzer is normally performed using a FT-IR and/or a Mass Spectrometer. The actual commercial mass spectrometers used in thermal analysis are based on Electron Impact (EI) as ionization source and quadrupole as mass analyzer. This combination is, of course, the cheapest one, but in particular cases, it becomes a limitation. The correct combination between ion source and mass analyzer could improve selectivity and sensitivity of the analysis of evolved gases, especially when organic volatile compounds are investigated. Investigations of low molecular weight gases such as H_2, CO_2, $H_2O(g)$, etc. is well performed by the actual commercial instruments, but flavour molecules, process flavours, degradation products or contaminants could be present in so low amounts and with so many other molecules that EI is not the suitable ionization source for this kind of analysis.

APCI spectrum



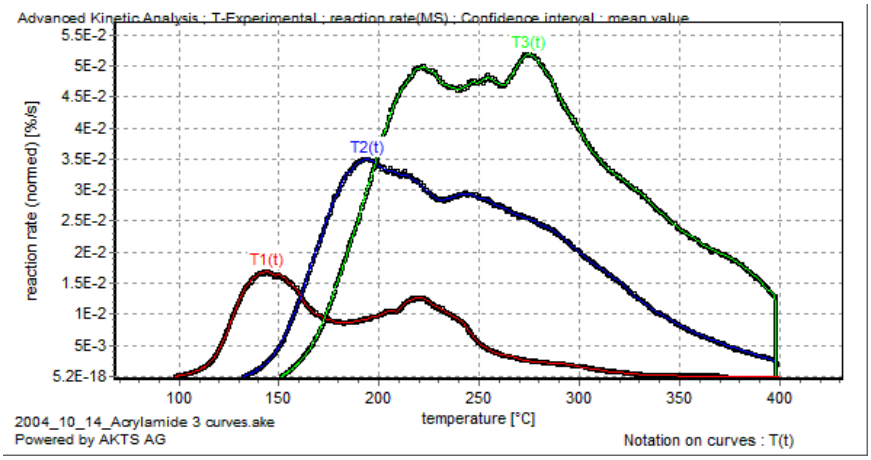
EI spectrum



The present work shows how a modified Atmospheric Pressure Chemical Ionization (APCI) could be used in association with a thermal analyzer (DSC 7, Perkin-Elmer) to analyze special organic volatile compounds. APCI is normally used in liquid chromatography environment, but it is also suitable for analysis in gaseous phase. The main advantage of soft ionization compared to EI is the low fragmentation of the molecular ion. More than 900 organic volatile compounds were identified in roasted coffee. It is easy to imagine in the case of real-time analysis of coffee roasting that fragmentation using EI will not help the interpretation of the MS data. Soft ionization will give protonated molecular ions which will be much more useful than fragments of molecular ions. Maillard reaction and Strecker degradation occur during thermal processes of food preparations. High sensitivity soft ionization allows the detection, in real-time, of intermediate products such as Schiff's base or undesired molecules such as

contaminatns or off-flavours. An example is the production of Acrylamide using the well known reaction model between Asparagine and Fructose in acidic condition.

Graph 2: monitoring of acrylamide protonated molecular ion as a function of temperature



A thermokinetic calculation has been performed in order to predict the evolution of acrylamide reaction rate as a function of time and temperature. Examples on evolution of flavour molecules during coffee roasting, tobacco burning, polymer and drug degradation have been performed. Quantitative data can also be performed using standard solutions.

Conclusions

A suitable ionization source (APCI in the present work) is necessary when low concentration of organic volatile compounds is investigated in association with thermal analyzer. Real-time analysis of flavours, contaminants, degradation products can be realized and further analysis such as thermokinetics is also possible. The challenge is now to build a commercial instrument based on thermal analysis and soft ionization mass spectrometry.

References:

1. Taylor, A.J. and D.D. Roberts, eds. *Flavor perception*. 2004, Blackwell publishing Ltd: Oxford.
2. Taylor, A.J., et al., Atmospheric pressure chemical ionisation mass spectrometry for in vivo analysis of volatile flavour release. Food Chemistry, 2000. **71**(3): p. 327-338.
3. Lindinger, W., A. Hansel, and A. Jordan, On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) - Medical applications, food control and environmental research. International Journal of Mass Spectrometry, 1998. **173**(3): p. 191-241.
4. Jost, C., et al., Atmospheric pressure chemical ionization mass spectrometry for the detection of tropospheric trace gases: the influence of clustering on sensitivity and precision. International Journal of Mass Spectrometry, 2003. **223-224**: p. 771-782.