

**CURIE-POINT PYROLYSIS / GAS CHROMATOGRAPHY / MASS
SPECTROMETRY OF STANDARD DIPEPTIDES IN THE PRESENCE OF
TETRAMETHYLAMMONIUM HYDROXIDE**

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Nitrogen-containing organic compounds represent the second most abundant reservoir of nitrogen on earth. Despite the important implication of nitrogen in environmental processes, its chemical structure and origin remain widely unknown likely due to the refractory nature of its source macromolecules (30 to 50% of total nitrogen in humic substances) (Schulten & Schnitzer, 1998). Recent studies (del Rio *et al.*, 2004; Knicker & Hatcher, 2001), using ^{15}N NMR spectroscopy, pointed to the dominance of amide functions in natural environments, thus suggesting that N is engaged in polar building blocks. Pyrolysis in the presence of tetramethyl ammonium hydroxide (TMAH) has appeared as a powerful tool for the study of nitrogen-containing moieties.

For a few years, TMAH-Py/GC/MS has been applied to the study of refractory OM from different sources, and focused on nitrogen-containing macromolecules. For a better understanding of the pyrolysis results of these materials, the pyrolytic behaviour of model compounds has been investigated (Hendricker & Voorhees, 1998; Zang *et al.*, 2001). Thus the twenty protein amino acids have been pyrolysed in the presence of TMAH and a data base has been constituted (Gallois *et al.*, submitted).

As nitrogen mainly occurs in higher molecular weight structures and not as free amino acids, the influence of the peptidic linkage on the pyrolytic behaviour of amino acids has been investigated and eighteen dipeptides have been studied. TMAH-pyrolysis of dipeptides revealed that they do not behave as the mixture of the corresponding amino acids. In the pyrochromatogram of dipeptides the major pyrolysis products of free amino acids are generally only detected at low levels, except for the aromatic derivatives of the aromatic amino acids which remain very important. The most abundant compounds correspond to higher molecular weight derivatives, thus, methylated diketopiperazines as well as methylated derivatives of the dipeptides have been regularly identified at the end of the chromatograms. A good example of this is given by the pyrolysis of Ala-Tyr, presented in fig. 1.

Moreover, to precise the role of the peptidic bond on the pyrolytic behaviour of the amino acids, pyrolyses of symmetrical pairs of dipeptides were performed. They demonstrated the importance of the functional group involved in the peptidic bond. Compared

to high molecular weight derivatives the amount of pyrolysis products from one amino acid is enhanced when the amino acid is C-terminal.

So, as far as we can conclude, the pyrolysis of dipeptides in the presence of TMAH yields mainly stable cyclic structures (DKP and aromatics for corresponding amino acids) and also releases methylated derivatives of dipeptides in relatively important amounts.

Further work on higher molecular weight peptides and proteinaceous material will now take advantage of the amino acids data base and these considerations on dipeptides.

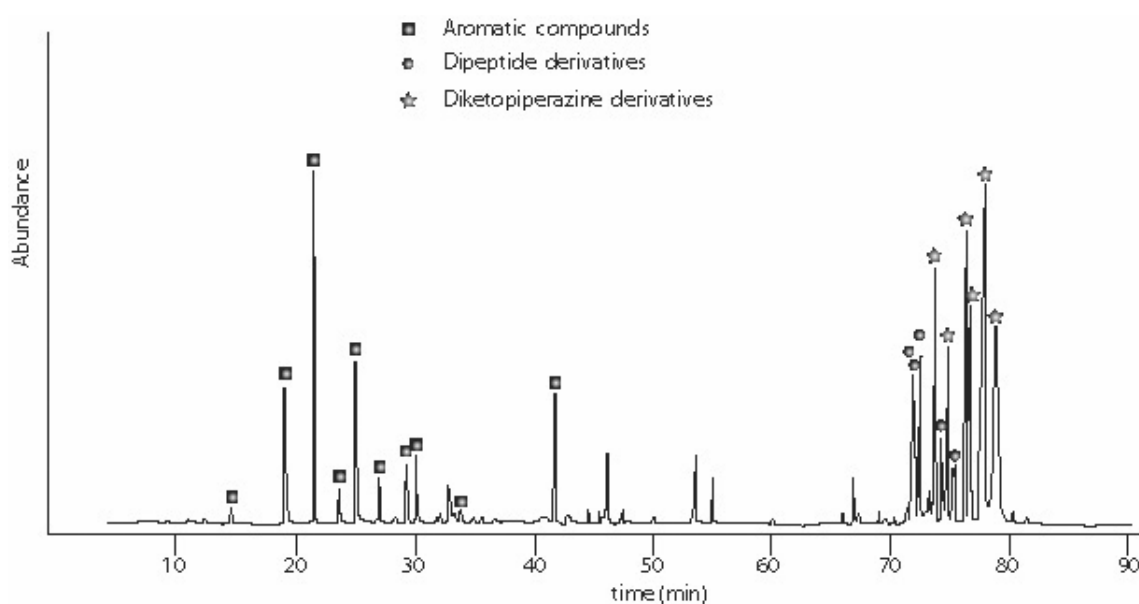


Figure 1. TIC chromatogram of the TMAH pyrochemolysis products released from Ala-Tyr.

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