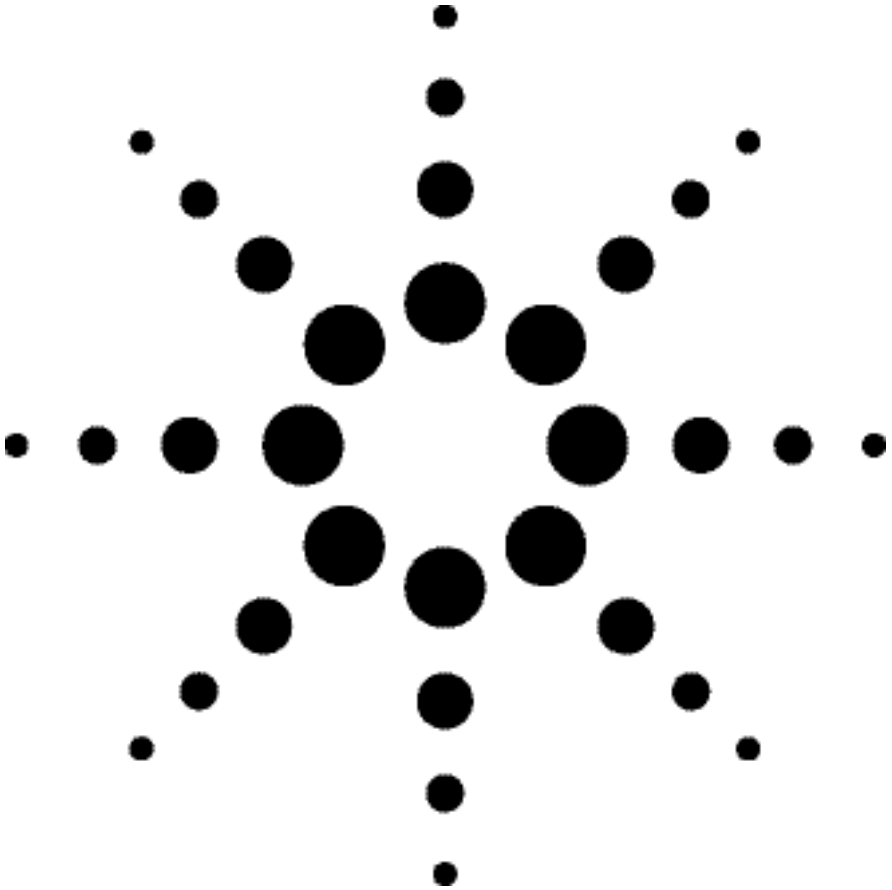
GC-MS Approaches to the Analysis of Acrylamide

PittCon 2003 Poster



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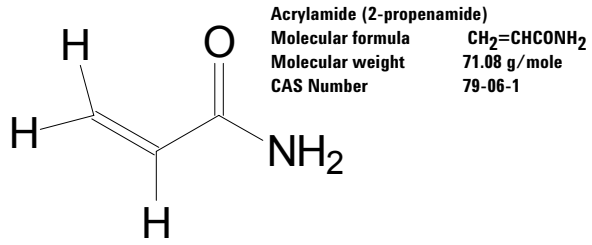
Introduction

The discovery announced in April 2002 by scientists at Sweden's National Food Administration of acrylamide (2-propenamide) in fried and baked foods at levels many times that allowed in water suggested a much higher exposure than previously estimated [1]. Acrylamide (Figure 1) is a known neurotoxin and considered a probable human carcinogen. The World Health Organization considers 0.5µg/L the maximum level for acrylamide in water, however foods such as french fries, baked potato chips, crisp breads were found to contain acrylamide between 100 and 1000 µg/kg. Acrylamide was not found in the raw foodstuffs and cooking by boiling produced no detectable levels. Recent work has suggested acrylamide forms via the Maillard reaction which occurs when amino acids and sugars (e.g. asparagine and sucrose) are heated together. The concern over these relatively high concentrations has lead to studies of the occurrence of acrylamide in a wide variety of foods.



Acrylamide (2-propenamide)

Molecular formula	$CH_2=CHCONH_2$
Molecular weight	**71.08 g/mole**
CAS Number	**79-06-1**

Figure 1.

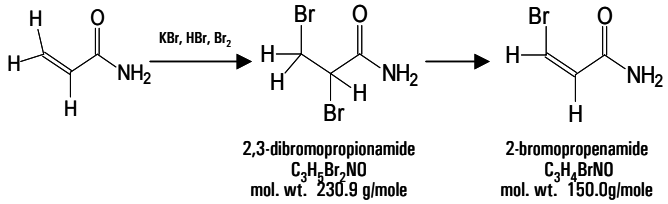
Acrylamide Analytical Methodologies

A wide variety of instrumental approaches have been applied to acrylamide. Liquid chromatography with tandem MS-MS detection has been used and shown itself useful to approximately 50 µg/kg (ppb) or better using the 71 to 55 m/z transition. Gas chromatographic methods using MS detection with electron impact ionization also suffer from the relatively small size of the molecule. This poster presents alternative GC-MS approaches using chemical ionization which improve this analysis.

Extraction from processed foods exploits the high aqueous solubility of acrylamide. A sample is homogenized and extracted with hot water. (Methacrylamide, CH2=C(CH3)2CONH2, is frequently used as an internal standard). Acrylamide can be determined directly or converted to the 2,3-dibromopropionamide by treatment with a brominating solution (equation 1). An option is to further treat this derivative to form a more stable analyte, the 2-bromopropenamide [2]. These three compounds comprise the most prevalent approaches to acrylamide via GC-MS and for completeness all three will be briefly considered here.

Experimental

Acrylamide was purchased from Sigma-Aldrich Chemicals (Milwaukee, WI). Injections were made into an Agilent 6890Plus GC - 5973N MSD with CI option. Several columns were used: DB-WAXter, DB-624 and DB-35ms.

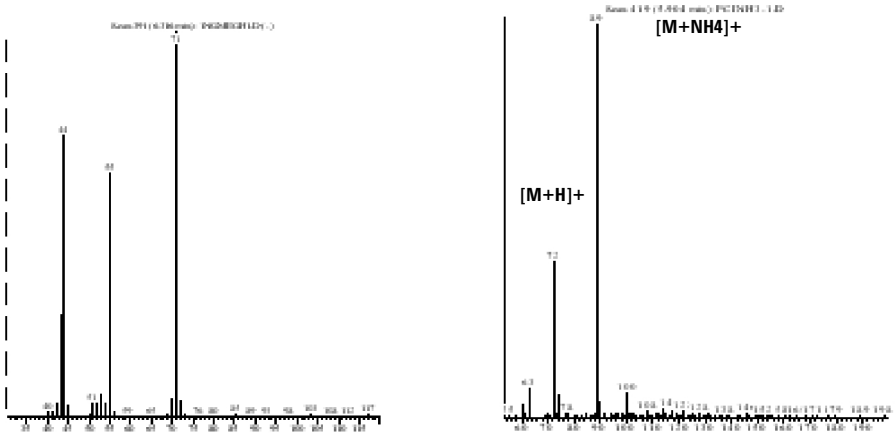


Equation. 1

Results and Discussion

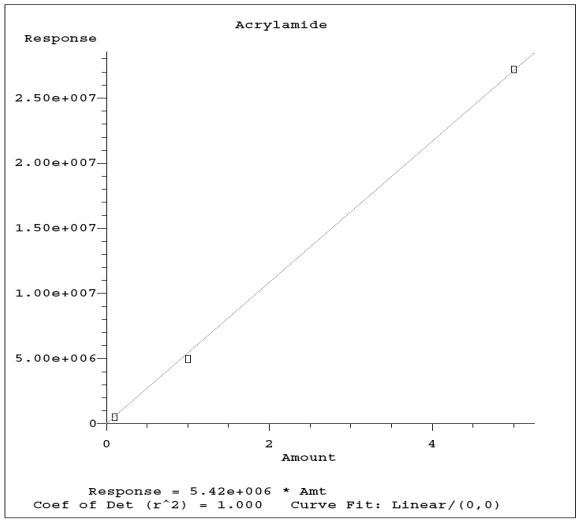
Electron impact (EI) mass spectrum for acrylamide reveals very low mass fragments; 71, 55, 41 m/z. Although there is good intensity at sub-ng levels, the ions are expected to be subject to interferences in food samples. The positive chemical ionization (PCI) spectra with ammonia provides more selective ionization which is of greater utility than EI in food matrices.

Mass spectra of acrylamide in EI (left) and PCI-ammonia (right)



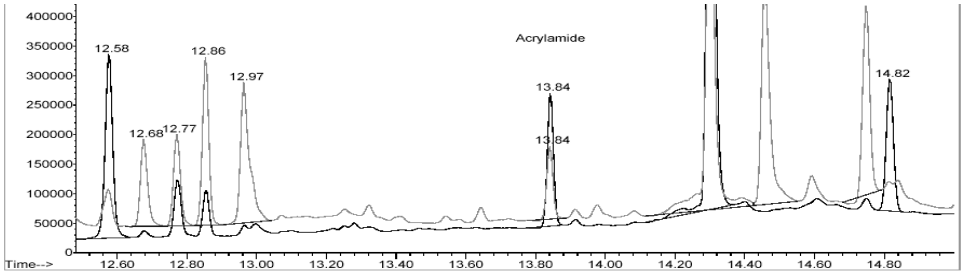
PCI-NH3 SIM calibration curve from 0.1 ppm to 5 ppm

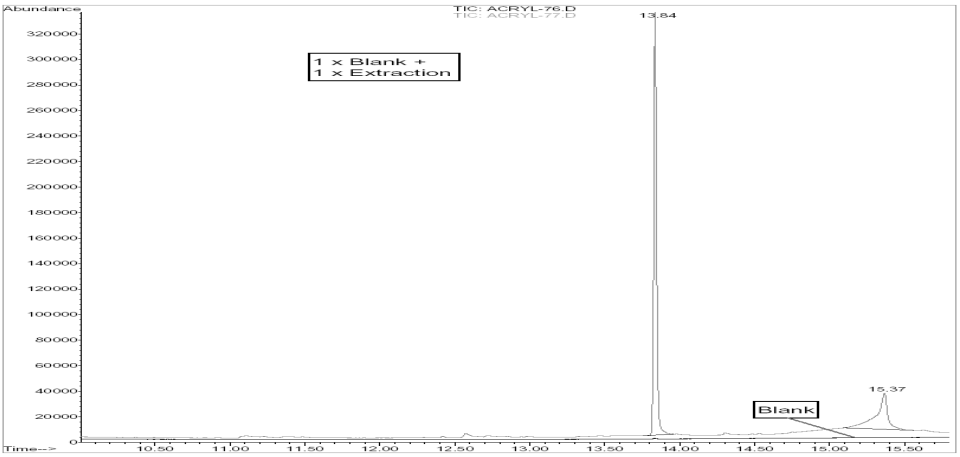
Ammonia PCI results in two ions; 72 m/z, the protonated molecule, [M+H]+ , and 89 m/z due to the adduct, [M+NH4]+. PCI provides good selectivity and sensitivity for acrylamide – picograms levels can be detected. At right, a calibration curve shows good linearity in PCI.



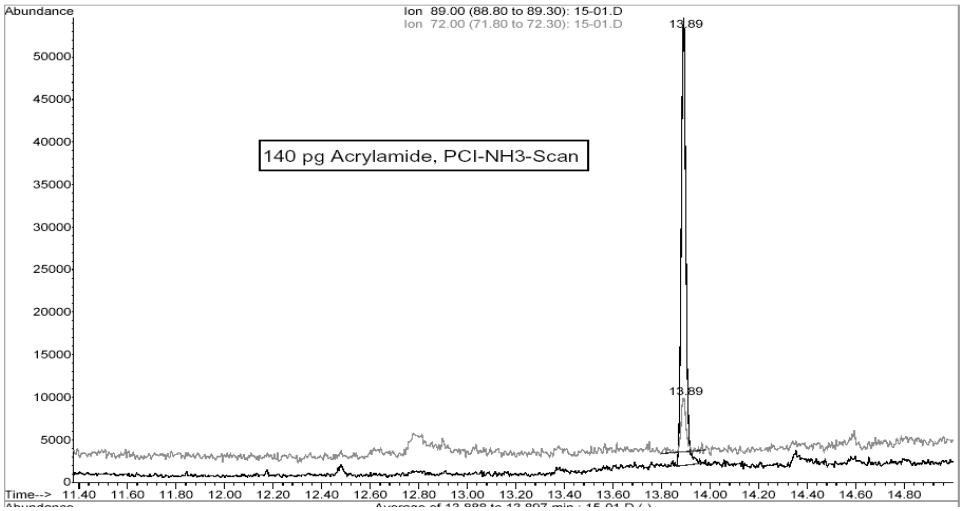
The figures below contrast the selectivity of EI-SIM (using ions m/z 55 and 71) and PCI-NH3-SIM (using ion m/z 89) for acrylamide in a typical matrix. The potential for interferences is reduced in PCI.

Acrylamide in crispbread at 1.75 ppm via EI-SIM (upper) and PCI-NH3 SIM (lower): effectively 0.7 ng injected





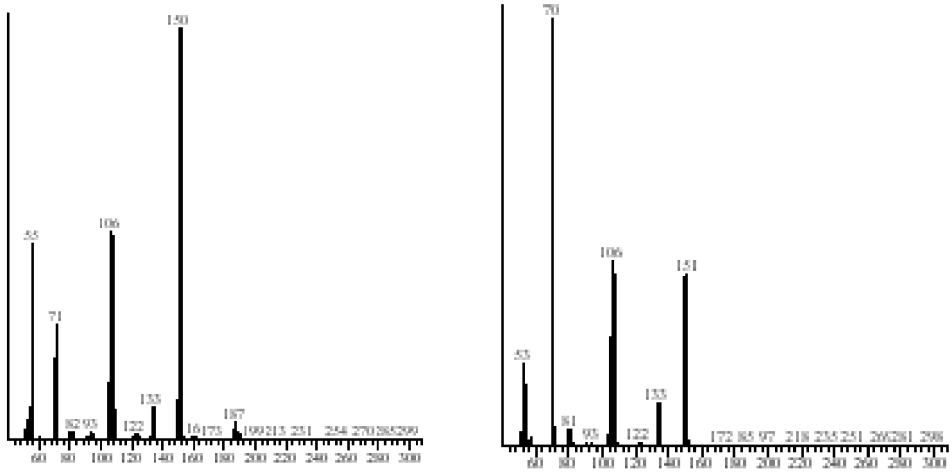
Acrylamide at 0.35 ppm in crispbread using PCI-NH3 scan: equivalent to 140 pg injected



Analysis via the brominated derivatives

The EI spectrum of the 2,3-dibromopropionamide shows intense ions at higher masses than the native acrylamide; specifically the ions at 150 and 152 m/z due to loss of Br. Similarly the 2-propenamide shows relatively intense molecular ions at 149 and 151 m/z.

The mass spectra in electron impact ionization of the brominated acrylamide derivatives, 2,3-dibromopropionamide (left) and 2-bromopropenamide (right)



Conclusions

Rapid and sensitive screening for acrylamide is possible using GC-MS-SIM with positive chemical ionization using ammonia reagent gas with detection on the order of picograms injected. This approach is only limited by the potential for interferences, which is reduced in PCI, and the single confirming ion.

The brominated derivatives offer the best approaches due to the higher mass fragments provided in EI with detection limits around picograms injected. However, the 2,3-dibromopropionamide undergoes break-down in splitless injection to form the 2-bromopropenamide. This approach requires use of labeled acrylamide (deuterated or 13C) in the analysis or conversion to the 2-bromopropenamide through bench chemistry. However care must be exercised with the 2-bromopropenamide since the 149 ion is subject to interferences from phthalates which are found in food packaging agents and are ubiquitous contaminants of solvents. This makes chromatographic separation even more important. Native acrylamide analysis appears best on the DB-WAXter and DB-624 columns while the brominated derivatives do well on the DB-35ms column.

References

1. Swedish researchers report acrylamide found in starchy foods, in Chemical & Engineering News. 2002. p. 38.

2.Castle, L., M.J. Campos, and J. Gilbert, Determination of acrylamide monomer in hydroponically grown tomato fruits by capillary gas chromatography - mass spectrometry. J-Sci-Food-Agric. 1991; 54(4): 549-555.

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