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Niacinamide in Canned Tomato Sauce

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Routine surveillance/compliance samples of high-production raw agricultural commodities and processed foods are analyzed in our pesticide monitoring program via multiresidue procedures (Luke et al. 1975, 1981). Unknown analytical responses (UARs) are often encountered. Considerable interest is usually focussed on those cases where the Hall electrolytic conductivity detector (HECD) has indicated the presence of organohalogen, organonitrogen or organosulphur. Such incidences are then analytically approached by gas chromatography mass spectrometry (GCMS). The potential of mass spectrometry in successfully identifying UARs at low concentration levels and unambiguously confirming suspected industrial chemical residues has been illustrated (Cairns et al. 1983). However, it is the knowledgeable interplay between the various ionization techniques and reagent gases, origin of sample, and the availability of a reliable compilation of reference spectra (Cairns, Siegmund & Jacobson 1983) that can provide a powerful tripartite union in solving difficult problems.

This paper describes a recent incidence of a nitrogen-containing UAR in an extract of canned tomato sauce, which was later identified by GCMS as niacinamide (3-pyridinecarboxylic acid amide) [also referred to as Vitamin B_3] occurring at the 3-4 ppm level. In pesticide screening of fresh tomatoes over the last decade in this laboratory, residues at this retention zone have been observed from time to time, but at such low signal strengths not to warrant further investigation. Speculation as to the sudden occurrence of niacinamide is presented.

MATERIALS AND METHODS

All chromatographic data were obtained on a Tracor Model 560 gas chromatgraph equipped with a Hall Model 700A electrolytic conductivity detector in the nitrogen mode; operating conditions:

75 cm x 2 mm i.d. glass column packed with 2% DEGS on 80/100 mesh Chromosorb W.A.W., carrier gas 50 mL H_2/min.; column inlet 200°C; column temperature 160°C, isothermal; 120 cm x 2 mm i.d. glass column packed with 3% OV-17 on 80/100 Chromosorb W.H.P.; carrier gas, 15 mL H_2/min; column inlet 200°C; column temperature 180°C, isothermal; detector parameters were as described in Luke et al. (1981).

All spectra were obtained on a Finnigan Model 3300 quadrupole mass spectrometer equipped with a CI source and INCOS Data System; operating conditions: 45 cm x 2 mm i.d. glass column packed with 2% DEGS on 80/100 mesh Chromosorb W; carrier gas and reagent gas for chemical ionization, 30 mL methane/min; column inlet, 250°C; column temperature, 160°C, isothermal.

Sample was extracted by the Luke procedure (Luke et al. 1981) and 4 mg (extract equivalents) were injected onto the GC. For identification by GCMS, the sample extract was further cleaned up by elution through carbon (Luke & Doose 1983) and concentrated to 0.1 mL using a stream of dry nitrogen. 1 uL of this extract representing 0.1 g of sample was then used for analysis.

RESULTS AND DISCUSSION

The sample extract was first examined by HECD and found to contain an unknown organonitrogen compound at RR_t = 0.51 (on OV-17) and 2.22 (on DEGS) [both relative to chlorpyrifos]. On 3% OV-17 the elution profile was decidedly non-gaussian and tailed badly. At 200°C (our standard reporting temperature of Rts), the peak was obscured by the solvent front. However, on 2% DEGS the peak shape was acceptable for quantitative purposes. Lack of comparison GC retention data from our extensive data base (Pesticide Analytical Manual 1982) prompted immediate investigation by GCMS.

The sample extract was then re-examined by both chemical ionization (CI) and electron impact (EI) mass spectrometry (Figure 1). Recognition of the protonated molecular ion at m/z 123 (Figure 1A) under CI conditions is paramount to an in-house architectural approach that relies heavily on the availability of a large collection of reference data (Cairns, Siegmund & Jacobson 1983).

The only compounds in this data base listing of over 2300 pesticides and industrial chemicals with a molecular weight of 122 were L-cysteine and m-xylenol (no nitrogen content anyway). Comparative GC retention data eliminated them as potential candidates. Although recognition of the molecular weight of the compound of interest is invaluable in assisting with identification, the often lack of fragmentation under CI can quickly become

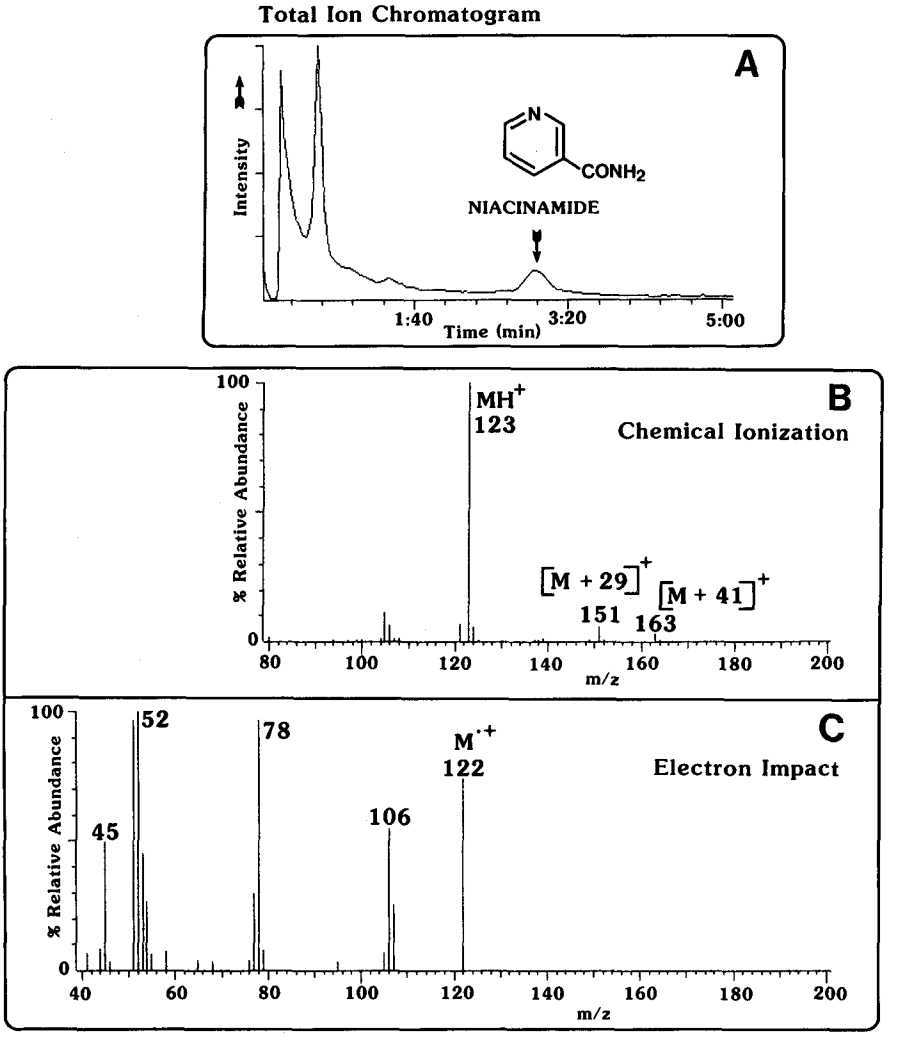

Figure 1. Total ion chromatogram (**A**) of extract of canned tomatoes recorded under GCMS conditions with mass spectral data of the peak as follows: (**B**) chemical ionization with methane as reagent gas, and (**C**) electron impact.

a liabilty if further structural elucidation is required. To solve this dilemna, the extract was also examined under EI conditions (Figure 1B). In this case, the presence of an ion at m/z 122 confirmed the previous conclusion that the molecular

weight was indeed 122. Appearance of ions at m/z 106 and m/z 78 indicated possible loss of NH_2 and CO respectively, while the ion at m/z 78 probably represented a pyridine ring. With these basic assumptions, a computer library search of the EPA/NIH Mass Spectral Data Base (Heller & Milne 1982) was conducted. A strong possibility emerged, niacinamide. Subsequent examination of a reference standard provided confirmation. It is a rare occasion when a suspected UAR is identified by the computer search. This case history has encouraged the inclusion of vitamins in the master pesticide listing. Recovery studies were performed (approx. 35%) and quantitation carried out on the sample (3-4 ppm). The occurrence of niacinamide in canned tomato sauce deserves speculative comments. Previous studies on raw agricultural lots of tomatoes by this laboratory over the past decade have indicated the presence of a very weak response (just noticeable above background) in the expected region for niacinamide. Why should niacinamide suddenly appear in our chromatograms as a distinct peak? Several answers could be advanced to explain this incidence. While the fresh tomatoes collected for analyses are not considered at the peak of their ripeness, niacinamide may only develop to the noticeable level in tomatoes at full maturity used in the canning industry. Another explanation might be the fact that the preparation of a sauce concentrates the ambient lower levels of niacinamide (i.e. below 1 ppm) in fresh tomatoes. On the other hand, the niacinamide might well be a minor constituent of one of the other ingredients added to make the sauce. Whatsoever the source of niacinamide, its presence in canned tomato sauce should be brought to the attention of other workers in the field of pesticide residues should they encounter it in their surveillance studies. Further investigations are planned to determine the incidences and sources of niacinamide in tomato sauce.

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