



Rapid Screening Method for Carbamates in Orange Oil

Using an Ultra Carbamate HPLC Column

Julie Kowalski, Ph.D., Innovations Chemist

- Fast analysis times, for increased sample throughput.
- Simple methodology saves time—no sample preparation.
- Accurate mass identification, for definitive results.

Concern over the presence of pesticides in food products, particularly citrus, is growing, resulting in an increasing number of countries regulating insecticides such as carbamates. EPA Method 531.1 describes a method for the analysis of carbamates in water, but not in other commodities. Matrices like citrus oil contain numerous interferences and often require time-consuming sample preparation. However, the method described here requires no sample preparation and provides fast analysis times, significantly increasing sample throughput.

Carbamates are most easily determined via HPLC analysis because derivatization is required for GC analysis. The rapid screening method shown here uses the Ultra Carbamate HPLC column, which is designed specifically for analyzing carbamates and is compatible with both traditional detectors and mass spectrometry. This column works well with mass spectrometry amenable buffers and allows an initial mobile phase composition of 20% organic, which promotes complete ionization at the electrospray source.

Orange oil was spiked at 10ppm with a carbamate mix and analyzed (Figures 1-2). The monoisotopic masses and retention times were compared to an injected standard and found to match closely (Table I). The high mass accuracy of the Leco Unique TOF-MS allowed positive analyte identification, even in a complex mixture containing compounds with the same nominal mass (within 1 amu) as the target carbamate. By using the Ultra Carbamate column in conjunction with the Leco Unique TOF-MS, we were able to develop a quick, easy, and accurate screening method for carbamates in a complex matrix such as orange oil.

References:

B. Mayer-Helm, L. Hofbauer, J. Muller. Rapid Communications in Mass Spectrometry, 20 (2006), page 529-536

Ultra Carbamate Column

3 μ m Column, 2.1mm cat. #
50mm 9177352

Figure 1 Reference standard carbamates resolve quickly on an Ultra Carbamate HPLC column. (extracted ion chromatograms)

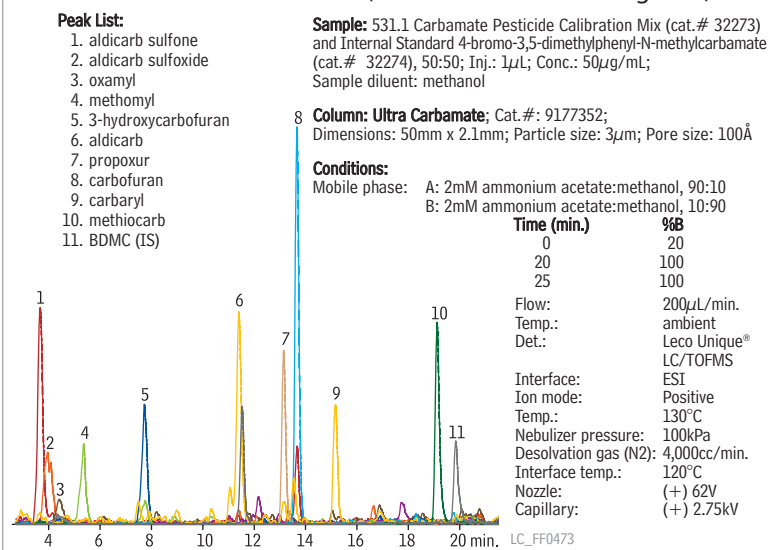


Figure 2 Positive identification of carbamates in orange oil injected with no sample preparation. (extracted ion chromatograms)

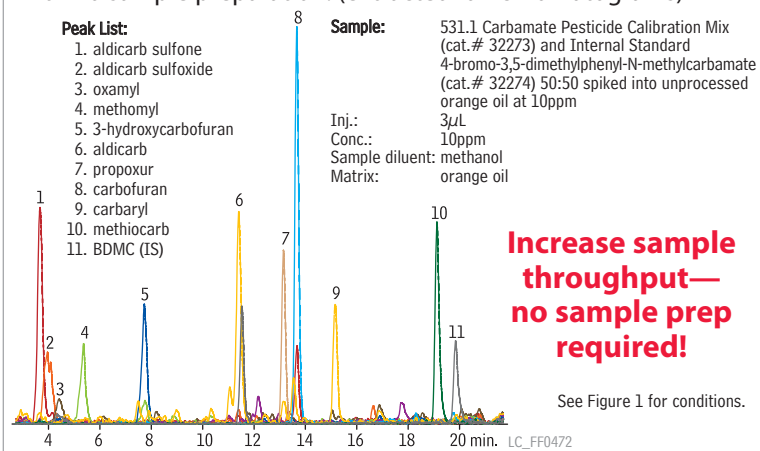


Table I Carbamates were positively identified in matrix using both retention time and mass.

| | | calculated ion monoisotopic mass | standard ion monoisotopic mass | standard retention time (min.) | orange oil ion monoisotopic mass | orange oil retention time (min.) |
|---------------------|-----------------------------------|----------------------------------|--------------------------------|--------------------------------|----------------------------------|----------------------------------|
| aldicarb sulfone | [M+H] ⁺ | 223.075 | 223.099 | 3.81 | 223.142 | 3.67 |
| aldicarb sulfoxide | [M+H] ⁺ | 207.080 | 207.103 | 4.31 | 207.122 | 4.09 |
| oxamyl | [M+NH ₄] ⁺ | 237.102 | 237.085 | 4.97 | 237.110 | 4.41 |
| methomyl | [M+H] ⁺ | 163.054 | 163.074 | 5.84 | 163.086 | 5.36 |
| 3-hydroxycarbofuran | [M+H] ⁺ | 238.108 | 238.121 | 8.32 | 238.128 | 7.73 |
| aldicarb | [M+H] ⁺ | 191.085 | 191.0728 116.0751* | 11.92 | 116.052* | 11.53 |
| propoxur | [M+H] ⁺ | 210.113 | 210.152 | 13.53 | 210.153 | 13.14 |
| carbofuran | [M+H] ⁺ | 222.113 | 222.140 | 13.98 | 222.120 | 13.66 |
| carbaryl | [M+H] ⁺ | 202.087 | 202.084 | 15.48 | 202.101 | 15.17 |
| methiocarb | [M+H] ⁺ | 226.090 | 226.097 | 19.22 | 226.060 | 19.12 |
| BDMC | [M+H] ⁺ | 258.013 | 258.042 | 19.89 | 258.005 | 19.84 |

* m/z 116.052 is a fragment ion with higher intensity than the [M+H]⁺ ion and was used for identification in orange oil