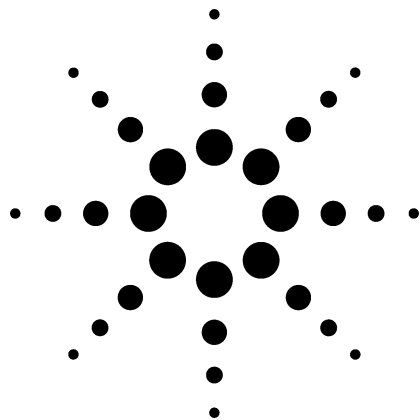


Identification of Unknown Reaction By-Products and Contaminants in Epoxyphenolic-Based Food Can Coatings by LC/TOF-MS



Application

Food Safety

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Abstract

This application illustrates how time-of-flight mass spectrometry can be used in the safety evaluation of new and existing can coatings used in the food industry. The accurate mass provides information for the parent compound and fragment ions greatly increase the confidence in the identification process.

Introduction

The internal surface of metal cans used to pack foodstuffs is often coated to form a barrier between the food and the metal of the can. The coating formulation may contain various components such as resins, crosslinking agents, catalysts, lubricants, wetting agents, and solvents. The potential exists for these ingredients, or by-products of reactions between them, to migrate from the can coating into

foods. Thus existing and especially new coatings need to be evaluated for their safety for contact with food and beverages.

We will illustrate this evaluation using the example of epoxyphenolic can coatings based on bisphenol A epoxy resins. These are cured by stoving with phenolic resins to produce a three-dimensional crosslinked network to provide the chemical and pack resistance required for food and beverage cans. The epoxy monomer bisphenol A diglycidyl ether (BADGE, see Figure 1) participates in these polymerization reactions via its reactive epoxide groups. However, it can also undergo addition from attacking nucleophiles such as water or solvents to give lower molecular weight products that might migrate into the packed food [1–3]. These potential migrants need to be identified.

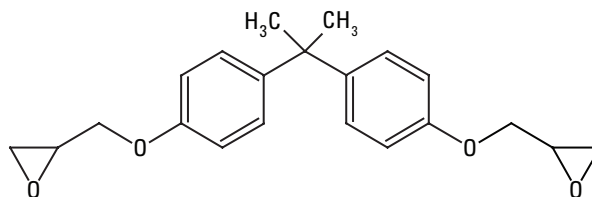


Figure 1. Chemical structure of BADGE, C₂₁H₂₄O₄.

The accurate mass measurements provided by time-of-flight (TOF) mass spectrometry (MS) for unknown compounds makes this identification process possible without the need for authentic standards of every possible minor impurity and reaction by-product.



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Experimental

Sample Extraction

A metal panel (250 cm²) coated with an epoxyphenolic lacquer and stoved under industrial conditions was cut into pieces (approximately 1 cm²) and extracted by immersion in acetonitrile (100 mL). After 18 hours the extract was evaporated to a small volume (1 mL).

LC Conditions

Instrument: Agilent LC 1200 SL
Mobile phases: A: water
B: acetonitrile
Gradient: 20% B to 50% B over 25 min, hold 20 min, 100% B at 60 min, hold 10 min, return to 20% B over 10 min
Flow rate: 0.2 mL/min
Column: Agilent ZORBAX Eclipse XDB, 100 mm × 2.1 mm, 3.5- μ m particles
Part number 961753.902
Injection: 5 μ L

MS Conditions

Instrument: Agilent 6210 LC/MS TOF in positive ion ESI mode
Nebulizer press.: 30 psi
Capillary: 4000 V
Gas temp.: 300 °C
Drying gas: 7 L/min

Results and Discussion

TOF-MS parameters were optimized using solvent standards of BADGE, as mainly BADGE derivatives were expected to be extracted from the coating [1]. A fragmentor value of 150 V was used first, to cause no fragmentation, and so molecular ion adducts were seen. Figure 2 shows the TIC for the acetonitrile extract of the epoxyphenolic coating. There are many unknown peaks, and the one at 27.2 min was chosen for this example.

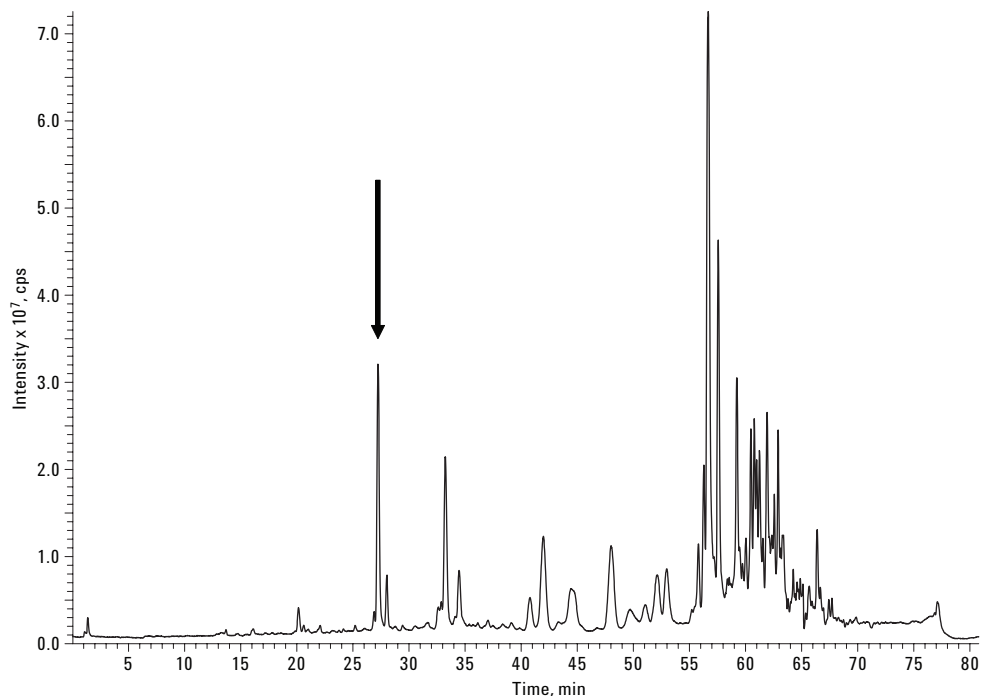


Figure 2. Total ion chromatogram of the acetonitrile extract of the epoxyphenolic coating.

Figure 3 shows the mass spectrum of the peak at 27.2 min. The differences in masses between the ions suggest that these are due to the protonated, ammoniated, sodiated, and potassiated molecule. No ammonia, sodium, or potassium was added to the mobile phase, and it is likely that these adducts arose due to contamination from other work carried out on the instrument, or were present in the solvents used in the mobile phase.

The formula calculator was used to propose identities for the peak, using the accurate mass determined for $[M+NH_4]^+$, as it was the most intense.

Only one possible empirical formula was provided limiting the elements to C, H, O, and only one N within the 5 ppm mass error limit.

For the experimentally derived mass 494.3118, the formula $C_{27}H_{44}O_7N$ was proposed (theoretical mass 494.3112, 1.15 ppm error). As it is proposed that this is the ammoniated adduct (subtract NH_4), this gives a formula of $C_{27}H_{40}O_7$ for the unknown peak. Furthermore, it is suspected that this peak is a BADGE derivative (subtract $C_{21}H_{24}O_4$ from the formula) and this suggests that the unknown peak is $BADGE + C_6H_{16}O_3$.

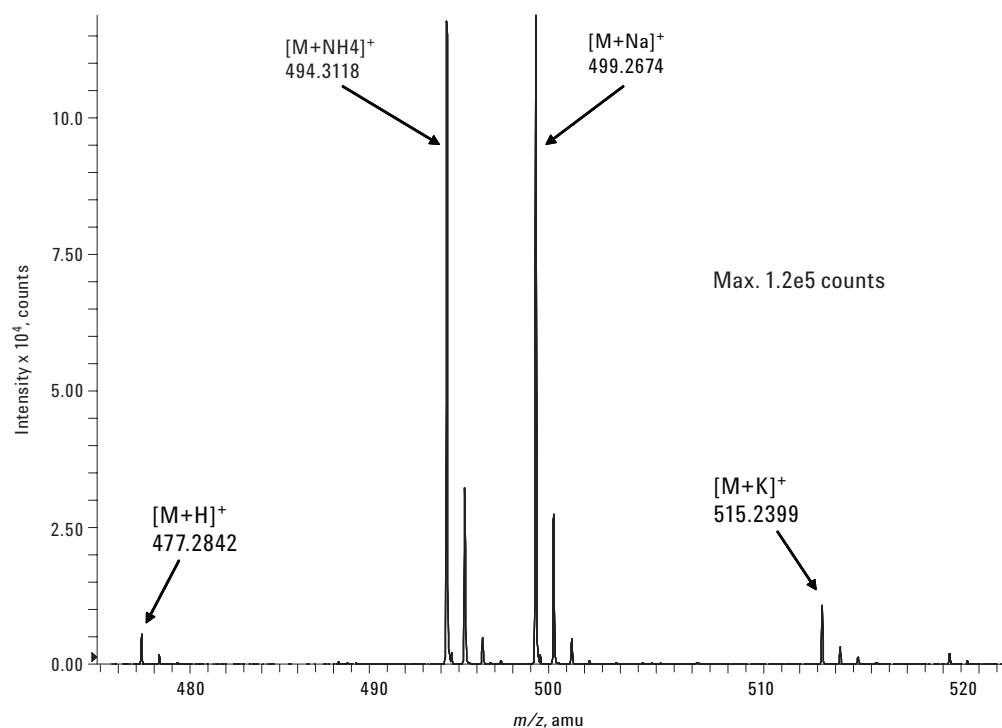


Figure 3. Mass spectrum of the unknown peak at 27.2 min (fragmentor = 150 V).

Fragmentation experiments were carried out to aid the identification process. A fragmentor value of 275 V dissociated the ammoniated molecular adduct into fragment ions, see Figure 4.

The accurate masses of the fragment ions were put into the formula calculator and the structures of the ions were theorized from the proposed empirical formulae. The fragment ions confirmed the presence of the BADGE unit (m/z 341.1727), that one of the epoxide rings had reacted with water (fragment ion at m/z 209.1149), and the other had reacted with butoxyethanol (BuOEtOH, $C_6H_{16}O_3$) (fragment ion at m/z 309.2036), a solvent used in the manufacturing process of the coating formulation. Figure 5 shows the structure of BADGE.H₂O.BuOEtOH.

Using the same approach, the identity of virtually all of the peaks in Figure 2 was established and different can coating chemistries have been studied.

Conclusions

Solvent extracts of epoxyphenolic can coatings have been analyzed by LC/TOF-MS to identify potential migrants into food and beverages. Accurate mass data of the parent compound and the fragment ions allows confident assignment of previously unknown peaks. Using the LC/TOF-MS has helped the testing of existing can coatings and guided the development of new coating chemistries.

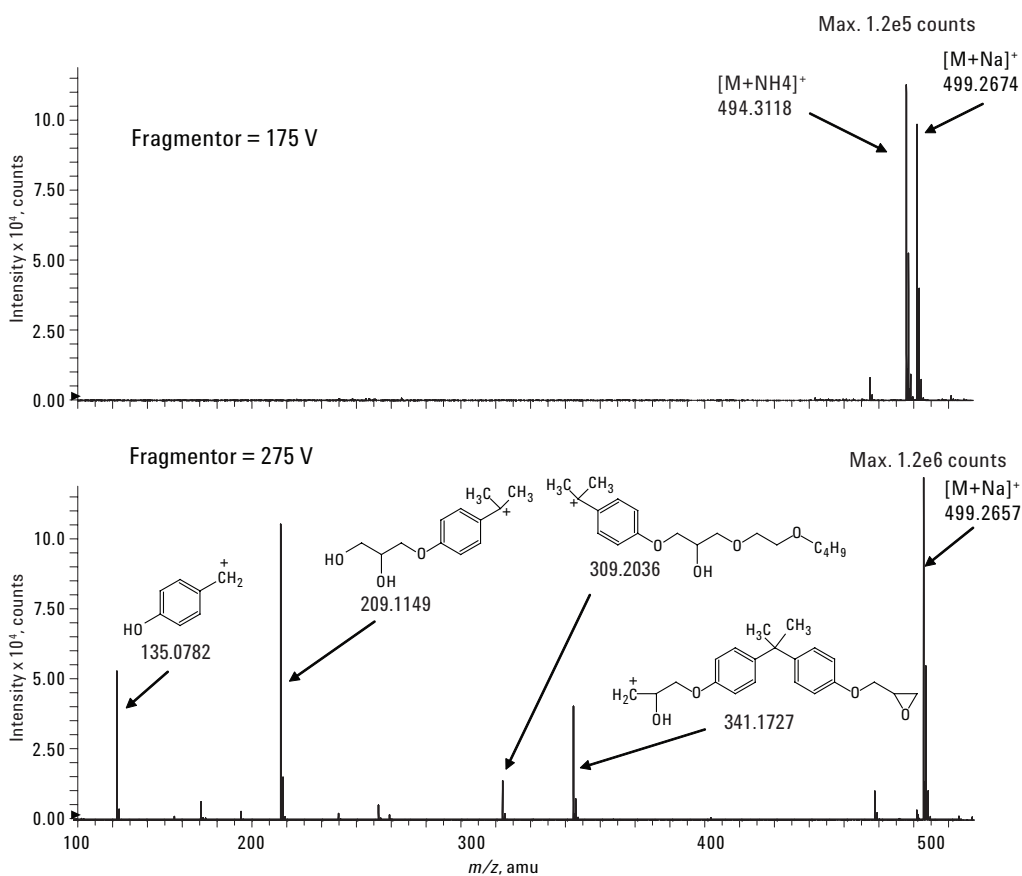
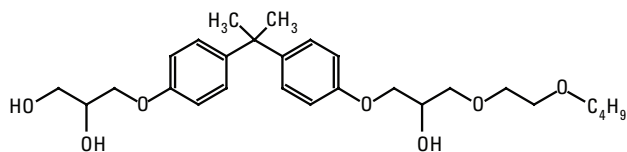


Figure 4. TOF-MS of the unknown peak at 27.2 min.



**Figure 5. Structure of the identified compound:
BADGE.H₂O.BuOEtOH.**

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