

# Omni Spray<sup>®</sup> Ion Sources

## Desorption Electrospray Ionization

### Direct identification of antioxidant on LDPE surface using DESI and accurate mass spectrometry

#### Introduction

Low Density Polyethylene (LDPE) is used in many applications requiring low temperature flexibility, toughness and durability. It is widely accepted as a material for transporting water, air and chemicals. Based on the targeted use of LDPE, several types of additives can be added in the manufacturing process, typically these include antioxidants (in containers, crates, bottles, plastic bags), flame retardants (wires and pipes) and light stabilizers (materials with exposure to light).

#### Experimental Description

A sample of LDPE surface was analyzed using *Omni Spray* Ion Source coupled to Waters LCT Premier mass spectrometer with accurate mass measurement capability. A 2cm<sup>2</sup> square of LDPE film was carefully fastened on a standard microscope slide with double sided tape and the slide was placed in the *Omni Spraysource*. The source and instrument settings are listed in Table 1. The spectra were acquired in positive and negative ion mode.

Parameter	Setting
ES voltage	2.6 kV
Solvent flow rate	2 µl/min
Gas pressure	150 psi
Distance from tip to surface	3 mm
MS inlet temperature	150° C
Spray Impact angle (α)	65°
Collection angle (β)	~ 10°
Solvent	70% ACN
Surface material	LDPE

\* Refer to *Understanding Omni Spray<sup>™</sup> Ion Source Operating Parameters* for a description of the parameters listed.

#### Discussion of Results

The spectrum of LDPE surface was recorded with 1s scan time and 0.1s interscan time for 1 minute (55 scans total) in negative V mode. Figure 1 shows combined and centroid spectrum where peak at 255.2324Da, present in the instrument background and identified as palmitic acid (C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>), was used as a LockMass for spectrum recalibration. A distinct peak at m/z 437.3406Da can be observed. A module of MassLynx 4.0 software for an elemental composition was used to obtained the formula based on accurate mass and isotopic peaks intensities.

**Figure 1.** Combined and centroid spectrum of LDPE surface obtained with DESI MS on Waters LCT Premier

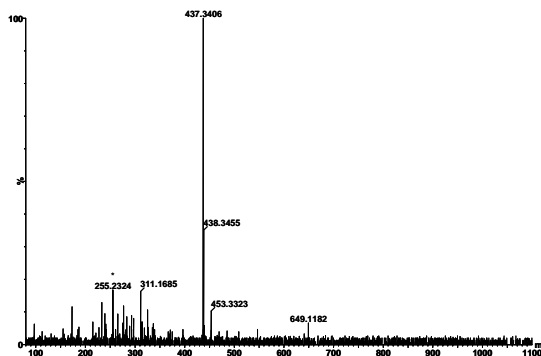
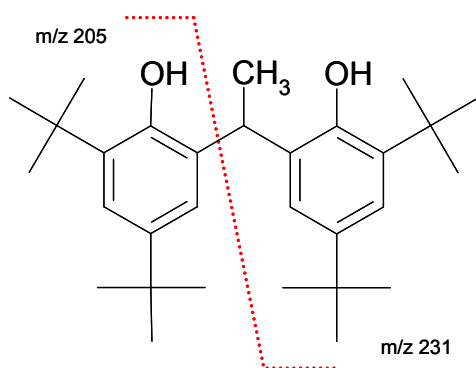


Table 2 presents several possible elemental compositions within set limits (mass tolerance 5mDa). The result with best fitted isotopic distribution (i-FIT score 0.1) is shown as C<sub>30</sub>H<sub>45</sub>O<sub>2</sub> (deprotonated). A database search of known polyethylene modifiers returned a known phenolic antioxidant Anox 29 (2,2'-Ethylidene-bis(4,6-di-*tert*-butylphenol) as a possible structure (Figure 2).

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
<b>437.3406</b>	<b>437.3420</b>	<b>-1.4</b>	<b>-3.2</b>	<b>8.5</b>	<b>0.1</b>	<b>C<sub>30</sub> H<sub>45</sub> O<sub>2</sub></b>
437.3396	1.0	2.3	5.5	0.2		C <sub>28</sub> H <sub>46</sub> O <sub>2</sub> Na
437.3393	1.3	3.0	9.5	0.2		C <sub>26</sub> H <sub>41</sub> N <sub>6</sub>
437.3379	2.7	6.2	4.5	0.6		C <sub>25</sub> H <sub>45</sub> N <sub>2</sub> O <sub>4</sub>
437.3369	3.7	8.5	6.5	0.7		C <sub>24</sub> H <sub>42</sub> N <sub>6</sub> Na
437.3451	-4.5	-10.3	0.5	2.4		C <sub>19</sub> H <sub>45</sub> N <sub>6</sub> O <sub>5</sub>
437.3441	-3.5	-8.0	2.5	2.7		C <sub>18</sub> H <sub>42</sub> N <sub>10</sub> O Na
437.3425	-1.9	-4.3	1.5	4.0		C <sub>15</sub> H <sub>41</sub> N <sub>12</sub> O <sub>3</sub>
437.3401	0.5	1.1	-1.5	5.7		C <sub>13</sub> H <sub>42</sub> N <sub>12</sub> O <sub>3</sub> Na
437.3398	0.8	1.8	2.5	6.2		C <sub>11</sub> H <sub>37</sub> N <sub>18</sub> O
437.3374	3.2	7.3	-0.5	8.2		C <sub>9</sub> H <sub>38</sub> N <sub>18</sub> O Na
437.3358	4.8	11.0	-1.5	10.4		C <sub>6</sub> H <sub>37</sub> N <sub>20</sub> O <sub>3</sub>

**Table 2.** Results of elemental composition fit for peak at m/z 437.3406 Da

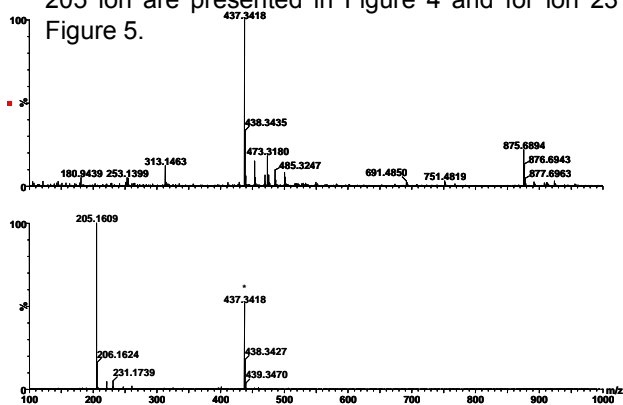
By ramping the Aperture 1 voltage of mass spectrometer to 90V, in source fragmentation of the molecule was obtained showing two main fragment ions at m/z 205 and 231.



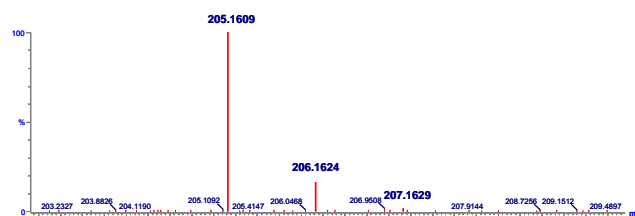
**Anox 29** C<sub>30</sub>H<sub>46</sub>O<sub>2</sub>  
Phenolic Antioxidant

**Figure 2.** Structure of known antioxidant Anox 29 (2,2'-Ethylidene-bis(4,6-di-*tert*-butylphenol))

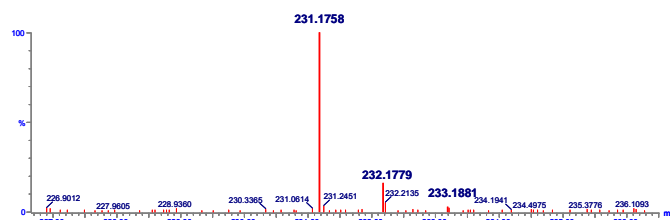
In order to confirm the identity of the compound a standard was acquired (Aldrich #372137). A 10g/L standard solution was prepared in 50% methanol which was subsequently diluted with 50% methanol to 0.1g/L working solution. One microliter of the working solution was deposited on Omni Slide and analyzed using the DESI Omni Spray Source and conditions listed in Table 1. The combined spectrum of 1min acquisition is shown in Figure 3 (top). The spectrum shows intense peak at 437.34Da, some Na<sup>+</sup> and K<sup>+</sup> adduct peaks and also present is [2M-H]<sup>-</sup> ion at 875.69Da. The fragmentation spectrum (Aperture 1 =90V) was also obtained for the standard and is shown in Figure 3 (bottom). Fragment ions at m/z 205 and 231 are distinctly present confirming the identity of LDPE additive as Anox 29. The fragmentation spectrum was centroided using main peak as LockMass (437.3420) and elemental composition was calculated for fragment ions using MassLynx software. The best fit results for 205 ion are presented in Figure 4 and for ion 231 in Figure 5.



**Figure 3.** DESI mass spectrum of Anox 29 standard (top) and fragmentation spectrum (bottom).



**Figure 4.** Best fit elemental composition table for m/z 205 fragment ion



**Figure 5.** Best fit elemental composition table for m/z 231 fragment ion

Figure 2 shows the proposed location of fragmentation resulting in the product ion masses observed. The elemental formula calculated based on the product ions' accurate mass and isotopic distribution also supports this fragmentation.

**Conclusions**

The *Omni Spray* Ion Source combined with the accurate mass measurement capabilities of Waters LCT Premier mass spectrometer allowed for direct analysis of LDPE surface and the identification of the plastic additive: an antioxidant Anox 29.

To obtain accurate mass of the ions seen, the spectrum was recalibrated using background ion as the LockMass. The deprotonated palmitic acid molecule at m/z 255.2324 in negative ion mode.

DESI MS facilitates the quick – 'no sample preparation', direct analysis polymer surfaces.