




Advantages of LCMS-IT-TOF Mass Spectrometry in Identifying Polymer Additives

A White Paper by Shimadzu Scientific Instruments

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Plastics are as ubiquitous in the 21st century as naturally occurring molecules such as wood and water. They are simply part of how we define our world and our place in it. Hundreds of polymers are used in thousands of applications, from shelter to transportation to food and beverage packaging. As innovation expands polymer types and uses, formulations become increasingly complex. That's because new applications almost always require additives to produce performance properties – toughness, flexibility, conductivity, antistatic qualities and such – to match polymers to applications.

Further, adding performance modifiers can cause changes in look, feel, color, adhesion, flammability, durability or countless other characteristics. So, formulators must add even more modifiers to compensate for these unwanted transformations.

Processing characteristics – melt point, flow, density, mold release, etc. – often necessitate even more additives. One polymer line from one manufacturer may contain dozens of different additives or additive blends among the line's individual products, depending on each polymer's grade and intended use.

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Thus, identifying additives in polymer formulations is critical to product formulation for performance, health, safety and cost of manufacture. It also allows for analysis of competitive products and investigating alternative technologies.

This white paper will examine the use and advantages of using LCMS-IT-TOF mass spectrometry to identify unknown additives in polymer formulations. It will explain applications for this technology, look at polymer additives and their functions, and show sample methodologies and results.

The Need for Analysis

Bottled water has become one of the most visible applications for polymers in our plastic-filled world. But even products as well researched and mature as plastic water bottles can demonstrate the need for analytical examination of polymers. In late 2008, Environmental Working Group (EWG), a non-profit environmental and health awareness organization, released the results of its independent study of bottled water purchased at locations around San Francisco. It revealed a surprising array of chemical contaminants in every brand.

The EWG analysis, conducted by the University of Iowa Hygienic Laboratory, examined 10 brands of bottled water. It revealed a wide range of pollutants, most that seem to have been present in the water prior to bottling. But others may have been introduced during or after processing, including a broad range of industrial chemicals used as plasticizers, viscosity modifiers and propellants. One of the most prevalent pollutants was trihalomethane, which is commonly used as an industrial solvent. It has been linked to cancer and reproductive problems.¹

The study is just one of many that points to a need for ongoing analysis of plastics with LCMS.


Advantage of LCMS-IT-TOF Mass Spectrometry

Liquid chromatography (LC) is the right tool for separating soluble polymers because it separates molecules independent of their molecular weight, according to differences in end groups.² It can be executed in three different modes: size-exclusion chromatography (SEC), liquid chromatography at critical conditions (LCCC), and gradient LC (adsorptions or precipitation-redissolution).³ The first methodology is governed by entropy (separation by hydrodynamic volume); adsorption LC is driven by enthalpic effects. LCCC is driven by a balance of enthalpic and entropic effects. Gradient LC of polymers enables separation according to differences in chemical composition distribution (CCD). For copolymer analysis this a powerful tool to measure polymer composition and assess the distribution of the composition.⁴

The 3-D ion trap time-of-flight mass spectrometer (LCMS-IT-TOF) is used to analyze mass of components eluting from the HPLC column, and for structural elucidation. Time-of-flight (TOF) has quickly established itself as the preferred type of mass analyzer for the characterization of synthetic macromolecules. TOF combines a high sensitivity with a broad mass range and a high spectral resolution and accuracy.

The ability to conduct MSⁿ measurements, along with accurate mass, makes identification with LCMS-IT-TOF fast and easy.

The instrument's design allows for high-speed MSⁿ analysis because the ion acceleration method used to remove ions from the trap ballistically ejects all of the ions simultaneously from the ion trap towards the TOF. The precursor ion automatic selection measurement mode conducts MS, MS² and MS³ analyses in order of intensity during peak elution. High-speed polarity switching allows analysis of different types of ions in a single run.



The technique of determining the compositional formula by MS^n , along with searching a compound database using that composition formula as a keyword, is a realistic method for identifying polymer additive candidates. Utilization of the predicted structure obtained from the compound database compared with the MS^n spectrum obtained from the accurate mass can be considered a unique method enabled by the use of the LCMS-IT-TOF system. It is the ability to conduct MS^n measurements, along with accurate mass, that makes identification fast and easy. In addition to polymer additives, this technique can be applied to identification of many compounds, including natural products, metabolites, impurities and degradation byproducts.

LCMS-IT-TOF mass spectrometry provides fast, accurate identification of polymer modifiers for:

- Quality control
- Quality assurance of raw materials
- Ingredient transfer or transformation caused by degradation or oxidation

Pharmaceutical and food and beverage packaging are areas of particular concern for polymer formulators because of the potential for incidental human consumption and corporate liability. In these applications, LCMS-IT-TOF analysis is particularly well suited to:

- Preclinical study of drug/packaging interactions
- Evaluations of lipids, acids and other food and beverage ingredients with packaging, particularly new, reformulated or repackaged products

Finding Suitable Substitute Additives

Using LCMS-IT-TOF analysis to identify additives is effective for choosing additives for new polymeric solutions, but is particularly well suited to altering existing products. Producers may need to change a polymer formulation to:

- improve performance;
- reduce risk of hazardous chemical exposure;
- gain compliance with new/revised regulations;
- shorten manufacturing cycles; or
- reduce production costs by using less expensive raw materials.

Chemists must consider a significant number of factors during substitution formulation. The replacement additive or additive blend:

- cannot significantly impact the physical properties of the final goods;
- cannot slow manufacturing by negatively impacting solubility, cure times, thermal stability or other process characteristics; and
- cannot cause alternative polymerizations and/or reactions.

Adjusting Solutions Without Bisphenol A

One high-profile example of why a polymer producer would need to alter a polymeric system is the recent discoveries about human exposure to bisphenol A (BPA). This product is used in plastic linings in food cans, plastic baby bottles and numerous other polycarbonate-based consumer products used in the kitchen.

BPA has been shown to leach from food can linings, plastics cleaned with harsh detergents, and plastics used to contain acidic or high-temperature liquids. Microwaving polycarbonate food containers was shown to further release toxins.

Studies by the Centers for Disease Control found bisphenol A in the urine of 93% of children and adults tested in 2003-04.⁵ Infants fed with liquid formula are among the most exposed, and those fed formula from polycarbonate bottles can consume up to 13 micrograms of BPA per kg of body weight per day ($\mu\text{g}/\text{kg}/\text{day}$).⁶ The EPA considers exposures up to 50 $\mu\text{g}/\text{kg}/\text{day}$ to be safe.

Thus, polymer producers were forced to reduce or eliminate BPA from formulations as quickly as possible.

Adjusting Solutions Without Phthalates

Several studies of phthalic acid esters (phthalates) used as plasticizers in numerous consumer products and building materials reveal phthalate exposure among residents in industrialized countries. The groups identified include dimethyl, diethyl, benzylbutyl, diisononyl, and diisodecyl phthalates. Consumer food containers commonly contain diisobutyl, dibutyl, and di-2-ethylhexyl phthalates.

Recent toxicological studies have demonstrated the potential of these most commonly used phthalates to disturb the human hormonal system, sexual development and reproduction. Phthalates are also suspected to trigger asthma and dermal diseases in children.⁷

Case Sample

Starting with the assumption that the most likely additives are fairly common commercial materials, LCMS-IT-TOF mass spectrometry can provide accurate mass measurement using MS^n to quickly narrow the composition formula candidates to just the most likely compounds.

A typical preparation consists of adding sample material in 1 mL THF/methanol (50/50) solution, and then extracting the additives by placing the vial in an ultrasonic bath for 30 minutes. Analysis can be conducted by injecting 10 μ L of the supernatant directly into the HPLC column.



Fig. 1: Polymer Beads Used for Measurement

This study was undertaken to identify the polymer additives used in a particular type of polymer. The 3-D ion trap time-of-flight mass spectrometer (LCMS-IT-TOF) is used to analyze the masses of the components eluting from the HPLC column, and for structural elucidation. Taking advantage of the high-speed performance of this instrument, the precursor ion automatic selection measurement mode is utilized to conduct MS , MS^2 and MS^3 analyses in order of intensity during peak elution. High-speed polarity switching was used to allow analysis of different types of ions in a single run.

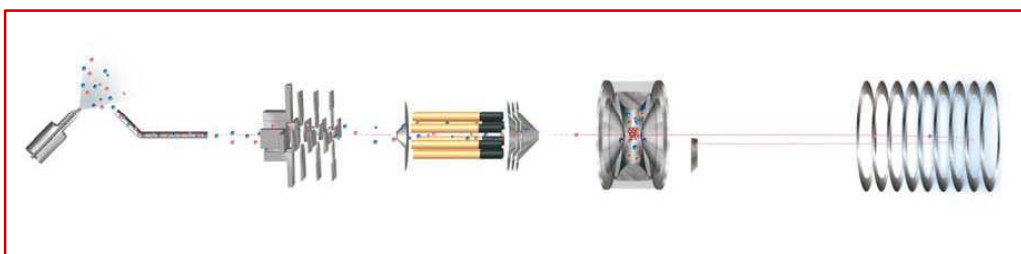


Fig. 2: LCMS-IT-TOF Ion Path

Analytical Conditions

Column:	Imtakt Cadenza CD-C18 3.0 mm I.D.x 75 mm L
Mobile phase A:	5 mM ammonium acetate-water
Mobile phase B:	Acetonitrile
Gradient program:	50% B (0 min) \rightarrow 100% B (20-40 min) \rightarrow 50% B (40.01-50 min)
Flow rate:	0.4 mL/min
Injection volume:	10 μ L
Column temp:	40 $^{\circ}$ C
Ionization mode:	ESI (+) ESI (-)
Nebulizing gas:	1.5 L/min
Drying gas press:	100 kPa
Probe voltage:	+4.5 kV -3.5 kV
CDL temp:	200 $^{\circ}$ C
BH temp:	200 $^{\circ}$ C

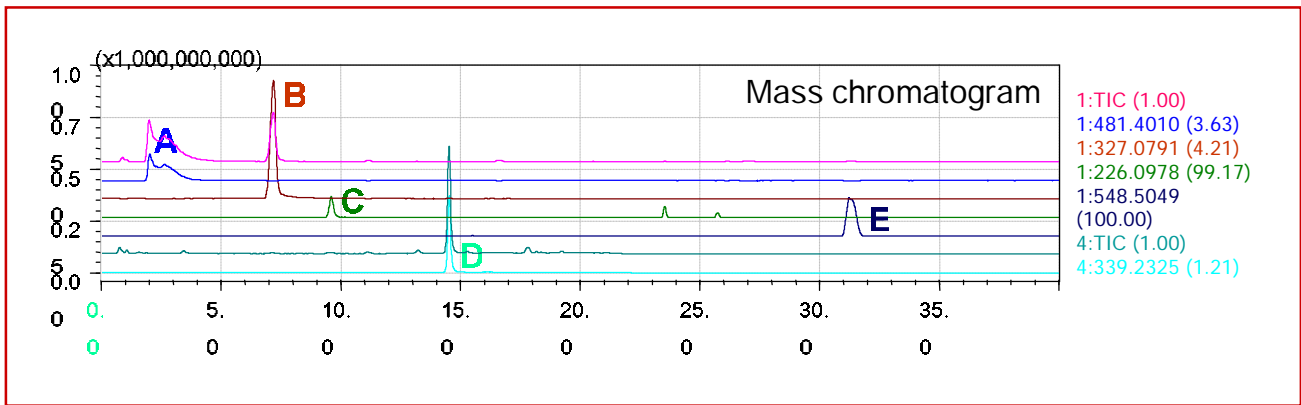


Fig. 3: Mass Chromatogram; Peaks A, B, C and E were detected by ESI+, peak D was detected by ESI-.

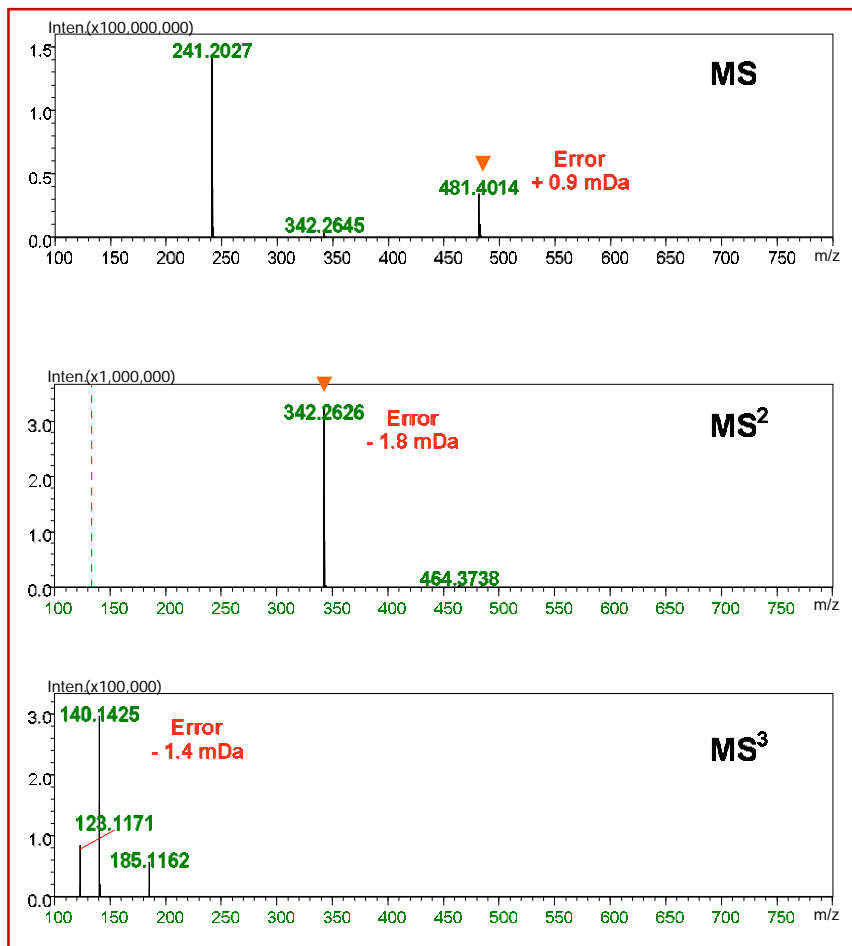


Fig. 4: MS, MS² and MS³ Spectra of Peak A

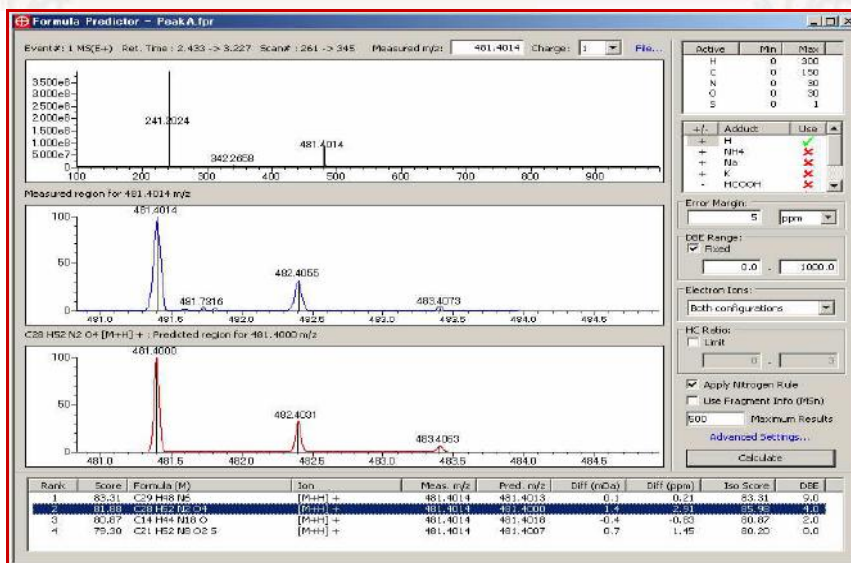


Fig. 5: Predicted Composition Results by Formula Predictor (Electron mass is not considered.)

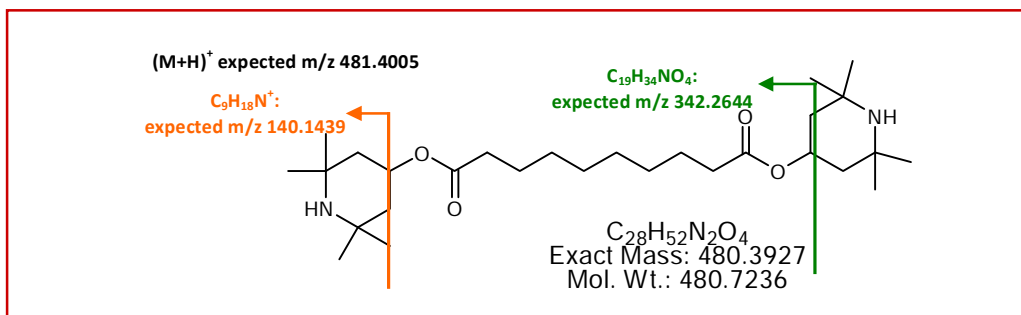


Fig. 6: Predicted Structure and MS², MS³ Spectra Assignments

Compound name	MW	Formula	Calc. (M+H) ⁺	Meas. (M+H) ⁺	ERR (ppm)	Calc. (M-H) ⁻	Meas. (M-H) ⁻	ERR (ppm)
A Decanedioic acid bis (2,2,6,6-tetramethyl-4-piperidyl) ester	480.3927	C ₂₈ H ₅₂ N ₂ O ₄	481.4005	481.4014	1.87			
B Triphenyl Phosphate	326.0708	C ₁₈ H ₁₅ O ₄ P	327.0786	327.0788	0.61			
C Tinuvin P	225.0902	C ₁₃ H ₁₁ N ₃ O	226.0980	226.0981	0.44			
D 2,2-Bis (3-sec-butyl-4-hydroxyphenyl) propane	340.2402	C ₂₃ H ₃₂ O ₂				339.2324	339.2322	-0.59
Compound name	MW	Formula	Calc. (M+NH ₄) ⁺	Meas. (M+NH ₄) ⁺	ERR (ppm)	Calc. (M-H) ⁻	Meas. (M-H) ⁻	ERR (ppm)
E Irganox 1076	530.4699	C ₃₅ H ₆₂ O ₃	548.5043	548.5067	4.38			

Fig. 7: Identification Table. Other peaks were identified by this technique. For some of these compounds, the predicted composition formula and mass accuracy are summarized.

Summary

Identifying additives in polymer formulations is a critical step for product formulation. Additives must be examined for performance, health, safety and cost of manufacture. Liquid chromatography with 3-D ion trap time-of-flight mass spectrometry (LCMS-IT-TOF) is an ideal way to analyze a mass of components eluting from the HPLC column, and for structural elucidation.

It is also important to note that other methods are available for polymer analysis, including pyrolysis gas chromatography mass spectrometry (PYR-GCMS) and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOFMS). In combination, these three methods provide researchers with a comprehensive solution to detect any polymer additive.

¹ "Bottled Water Quality Investigation: 10 Major Brands, 38 Pollutants"

Published October 15, 2008. Olga Naidenko, PhD, Senior Scientist; Nneka Leiba, MPH, Researcher; Renee Sharp, MS, Senior Scientist; Jane Houlihan, MSCE, Vice President for Research.

² A. A. Gorshkov *et al.*, *Journal of Chromatography*, 523, 91-102 (1990) as cited in "Fast, Ultra-Fast and High-resolution LC for Separation of Small Molecules, Oligomers and Polymers" M. Pursch *et al.*, Chromatography Online, March 1, 2008; retrieved March 20, 2009.

³ HPLC of Polymers, Springer, Berlin, Germany 1998. H. Pasch, author; B. Trathnigg, editor, as cited in "Fast, Ultra-Fast and High-resolution LC for Separation of Small Molecules, Oligomers and Polymers" M. Pursch *et al.*, Chromatography Online, March 1, 2008; retrieved March 20, 2009.

⁴ "Fast, Ultra-Fast and High-resolution LC for Separation of Small Molecules, Oligomers and Polymers" M. Pursch *et al.*, Chromatography Online, March 1, 2008; retrieved March 20, 2009.

⁵ "Exposure of the U.S. population to bisphenol A and 4-tertiary-octylphenol: 2003-2004." Calafat, A. M., Ye, X., Wong, L. Y., Reidy, J. A., Needham, L. L. (2008). *Environ. Health Perspect.* 116 (1): 39-44. doi:10.1289/ehp.10753. PMID 18197297.

⁶ "European Food Safety Authority Opinion" (Abstract). www.efsa.europa.eu/en/science/afc/afc_opinions/bisphenol_a.html. Retrieved on 3/15/2009.

⁷ "What Are the Sources of Exposure to Eight Frequently Used Phthalic Acid Esters in Europeans?" M. Wormuth, M. Scheringer, M. Vollenweider, and K. Hungerbühler, *Risk Analysis*. 2006 Jun;26(3):803-24.