MATERIALS ANALYSIS

HIGH THROUGHPUT ANALYSIS OF POLYMER STABILIZERS WITH THE AGILENT 6420 TRIPLE QUADRUPOLE LC/MS

Solutions for Your Analytical Business

Markets and Applications Programs

Authors

Susanne Beißmann, Michael Reisinger, Christian W. Klampfl, Wolfgang Buchberger

Johannes Kepler University Linz, Austria.

Andreas Reimann, Agilent Technologies.

Abstract

The capability of highly sensitive and rapid flow injection coupled to multiple reaction monitoring mass spectrometry for comprehensive analysis of several polymer stabilizers, belonging to quite different chemical classes, is demonstrated. A critical factor is the choice of the ionization mode, as no separation of the different stabilizers was performed prior to MS-detection. Differences between several ionization techniques regarding matrix effects are pointed out. Atmospheric pressure chemical ionization was found to be the most suitable ionization technique, with hardly any matrix effects observed. The developed method has a linear dynamic range over two to three orders of magnitude, with correlation coefficients better than 0.99 for all analytes.

The method allowed quantitation down to 0.0001 - 0.04 wt% in plastic materials depending on the stabilizer. The suitability of the optimized method for analysis of real samples was proven by the comparison of results with an established chromatographic approach.

INTRODUCTION

The importance of plastic materials has increased over the years and nowadays they are deployed in nearly every aspect of our lives. Without proper stabilization, polymers are susceptible to degradation caused by reactions with oxygen and/or UV-light, which lead to undesirable changes in the properties of these materials. To minimize decomposition, different kinds of stabilizers are added to the polymer, whereby its protection depends on the presence of these additives in sufficient concentrations.

Therefore, the identification and quantitation of stabilizers are of major importance in order to evaluate suitability of materials of unknown origin for certain application areas, to clarify reasons for failure of materials or for comparison of materials from different suppliers. Since the complexity of additives and additive formulations has increased over the last decade and the amount added is often small (and can even be further decreased due to degradation), both identification and quantitation in the polymer can be very challenging. As stabilizers belong to quite different chemical classes, methods allowing comprehensive analysis of the large variety of commercially used stabilizers are desirable.

Nowadays there are various different analytical tools for analyzing polymer additives. Thereby two approaches can be distinguished, analysis of the plastic product as it is and analysis after dissolution of the polymer and subsequent extraction of the stabilizers. If reliable quantitative results are required, the latter approach is the more favorable one. Focusing on the chromatographic separation of such extracts, pyrolysis GC [1], supercritical fluid chromatography (SFC) [2] and high performance liquid chromatography (HPLC) [3-6] are most widely employed.

Whereas pyrolysis GC only provides information on additive fragments, HPLC is restrictive when it comes to the analysis of large, lipophilic hindered amine light stabilizers (HALS), which may show irreversible adsorption to silica-based stationary phases. Besides, another disadvantage of chromatographic methods is the fact that they may be quite time-consuming.

Flow injection in combination with mass spectrometry (FI-MS) offers the advantage of being a much faster, simpler technique than conventional quantitative methods, but it is known that lack of chromatographic separation between analytes and matrix may lead to suppression or enhancement of the ionization process, especially when electrospray ionization (ESI) is employed. Atmospheric pressure chemical ionization (APCI) and atmospheric pressure photo ionization (APPI) are reported to be less prone to matrix effects, so their application is becoming more and more popular [7, 8].

The present work is a detailed study on the potential of high-throughput quantitation of polymer additives using FI multiple reaction monitoring-MS (MRM-MS) without prior chromatographic separation. Different ionization methods were compared to determine their suitability for the analysis of additives in real polymer samples. The main purpose was to develop a highly sensitive, accurate and rapid method for simultaneous identification and quantitation of the most commonly used stabilizers.

EXPERIMENTAL

Instrumentation

FI/MRM-MS measurements were performed on an Agilent 6420 Triple Quadrupole MS System (Agilent Technologies, Waldbronn, Germany) equipped with ESI, APPI and APCI sources. A thermostated autosampler maintained at 30°C was used for sample injection. Injection volume was 5 µL throughout this work, but larger volumes can be used for samples with lower analyte concentrations. A binary pump (Agilent 1260) with a vacuum degasser was used for the delivery of a continuous carrier stream. The carrier stream consisted of a mixture of methanol / 0.025 M aqueous ammonium formate (95/5) for ESI and APCI and methanol / acetone for APPI. The flow rate was set to 0.6 mL min-1 with an acquisition time of 1 min. Other conditions for the QqQ MS instrument are shown in Table 1.

	ESI	APCI	APPI
Nebulizer gas pressure / psi	35	50	50
Drying gas flow rate / L min-1	10	7	7
Drying gas temperature / °C	325	325	325
Capillary voltage / V	4000	4500	4500
Vaporizer temperature / °C	-	350	350
Corona needle current / nA	-	-	10000

Table 1: QqQ MS instrument parameters

Materials

The following polymer additives (technical grade) were obtained from various commercial sources: Antioxidants: Cyanox 1790, Irganox 1330, Irganox 1076, Irganox 1010, Irganox 3114, Sumilizer GA 80, Naugard 445; hydroperoxide decomposers: Irganox PS 800, Irgafos 168; UV-absorbers: Uvinul 3040, Tinuvin 326, Tinuvin 234, Tinuvin 328, Chimassorb 81; metal deactivators: Irganox MD 1024, Naugard XL-1; hindered amine light stabilizers: Chimassorb 944, Cyasorb UV-3529, Tinuvin 770, Uvinul 4050 H.

Sample preparation:

Internal standard and standard solutions:

1000 mg L-1 stock solutions were prepared by dissolving the pure stabilizers in toluene (except for Irganox MD 1024 which was dissolved in methanol). For calibration and determination of linearity and detection limits, standards were diluted from 10 mg L-1 down to the 0.01 mg L-1 level. Oligomeric HALS showed somewhat higher detection limits, so the calibration curves for these substances were obtained between 50 mg L-1 and 0.5 mg L-1. An internal standard (Cyanox 1790, 0.5 mg L-1) was added to each solution.

Polymer material samples:

Prior to analysis the various additives were extracted from the polyolefin material using a dissolution/precipitation procedure. About 20 mg of stabilized polymer sample was mixed with 50 µL of the internal standard solution (100 mg L-1 in toluene), as well as 10 µL of tributylphosphite (5000 mg L-1 in toluene) and 0.44 mL toluene. Afterwards, the solution was heated to 130°C for 1 h in a closed vial. After cooling, 0.5 mL methanol was added to the mixture and the sample was centrifuged. A defined volume of the supernatant fluid (100 µL) was diluted 10-fold with methanol. The resulting solution was used without any further treatment for FI/MRM-MS analysis.

Results and discussion

Qualitative analysis

Several analytes were selected that include the most frequently used stabilizers from the different chemical classes. As a first step, their suitability for FI/MRM-MS was investigated using standard solutions of individual analytes at concentrations of about 10 mg L-1. Identification of the precursor ions was performed in the full scan mode (100 to 2200 m/z). Both positive and negative ionization were investigated.

The positive mode proved to be better suited as it allowed the detection of all compounds and in most cases provided better sensitivity. For this reason, positive ionization was chosen for further investigation. In the next step, different ionization sources, namely ESI, APCI and APPI, were compared. ESI showed a somewhat better sensitivity for almost all analytes. Furthermore, ESI ionization offers the advantage of multiple charging, thus allowing detection of analytes with molecular masses exceeding the QqQ mass range (e.g. some high molecular oligomers of HALS).

These findings make ESI the preferred ionization source for identification. The major focus of the present work was to develop a reliable and efficient method suitable for both identification and quantitation of the most frequently used stabilizers. Therefore, the evaluation of possible interferences like ionization suppression or enhancement was considered very important, in order to prevent biasing of quantitation measurements.

Investigation of matrix effects

For studying matrix effects, two sets of calibration curves were constructed. One based on the measurements of the respective analyte in methanol, the other by standard addition to a polypropylene extract. Subsequently, the slopes of the obtained calibration curves were compared in order to evaluate the matrix influence. The results for three stabilizers are shown in Figure 1. ESI and APPI showed a high susceptibility towards matrix effects, visible by the significantly different slopes obtained for the calibration curves. In APCI-Detection, the slope of the two lines (with and without matrix) was identical for all analytes. This indicates that matrix effects are negligible for this ionization source, making it the most suitable for quantitative measurements.

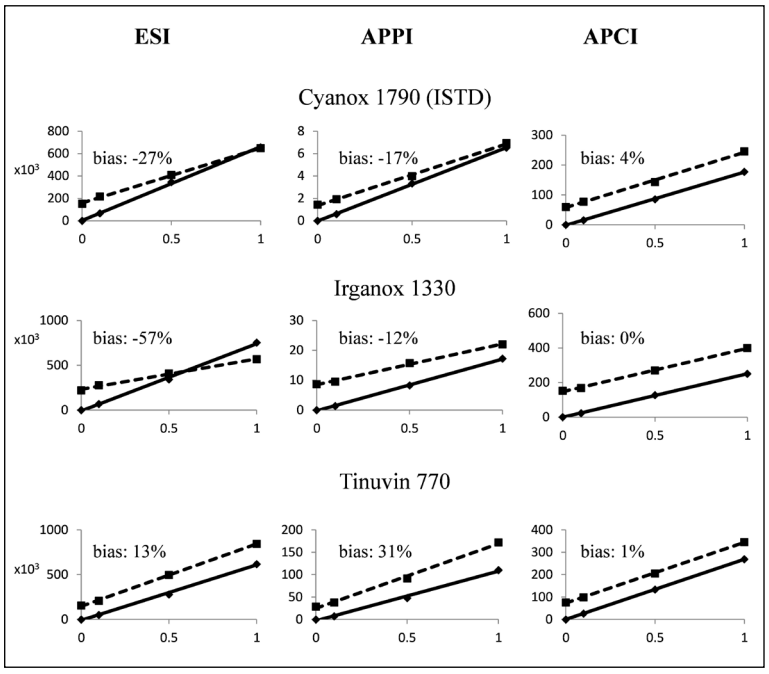

Figure 1: Identification of matrix effects by means of standard addition; dashed line: standard addition to a polypropylene extract; continuous line: standards in methanol; Bias%: (kmatrix – kstandard) / kstandard, is the relative error between the slopes of the two standard addition curves.

FI/MRM-MS for quantitative analysis

Fragmentor voltage and collision energy were optimized to produce the highest response among products ions for MRM-monitoring. The Agilent optimizer software was used, which provides a means of automatically optimizing these crucial parameters, by ramping the fragmentor voltage and collision energy for each product ion. Subsequently, a list of the top four product ions with the highest intensities was generated. The fragmentor voltage was varied in the range of 50 to 400 Volts and the collision energy in the range of 5 to 80 Volts. The cell accelerating voltage was 7 Volts for all measurements. For each stabilizer, the higher response MRM was used for quantitation and the next highest level was monitored for confirmation purposes. The peak area ratio of the quantifier versus qualifier must be consistent and within a tolerance of +/- 20%. **Chimassorb 944** showed only one transition with sufficient intensity, so no qualifier ion was used for this compound. The optimized MRM transitions are shown in Table 2.

	MRM	Fragmentor Voltage / V	Collision energy / V	Detection limit (LOD) / wt%
Irganox 1010	1194.8 → 219.3 (163.2)	240	80 (80)	0.0006
Irganox 1076	548.5 → 107.1 (149.1)	130	34 (22)	0.0002
Irganox 1330	792.6 → 291.3 (203.2)	190	30 (70)	0.0002
Irganox 3114	801.6 → 219.2 (203.2)	165	26 (78)	0.0001
Sumilizer GA 80	758.5 → 163.1 (177.1)	165	54 (66)	0.0001
Naugard 445	406.3 → 196.1 (91.1)	210	42 (50)	0.0004
Uvinul 3040	229.1 → 151.0 (77.1)	120	18 (42)	0.0003
Tinuvin 326	316.1 → 57.1 (260.1)	130	26 (18)	0.0001
Tinuvin 234	448.2 → 370.2 (91.1)	175	18 (62)	0.0003
Tinuvin 328	532.2 → 43.2 (282.2)	185	38 (22)	0.0001
Chimassorb 81	327.2 → 137.0 (81.0)	140	30 (62)	0.0004
Irganox PS 800	515.4 → 143 (329.2)	140	14 (10)	0.0001
Irgafos 168	647.5 → 147.2 (235.1)	180	58 (58)	0.0001
Irgafos 168 oxidized	663.5 → 495.3 (327.1)	195	34 (62)	0.0002
Irganox MD 1024	553.4 → 181.2 (441.3)	180	30 (10)	0.0001
Naugard XL-1	714.5 → 159.1 (307.2)	135	54 (34)	0.0003
Cyasorb UV-3529 Oligomer 1	687.6 → 72.1 (560.4)	205	54 (34)	0.0247
Cyasorb UV-3529 Oligomer 2	921.7 → 154.1 (768.6)	205	46 (42)	0.0154
Tinuvin 770	481.4 → 58.2 (140.2)	175	38 (26)	0.0002
Uvinul 4050	451.4 → 58.2 (140.2)	180	46 (30)	0.0002
Chimassorb 944	994.0 → 140.0	325	66	0.0443
Cyanox 1790 (ISTD)	717.5 → 191.2	125	34	-

Table 2: MRM Acquisition parameters and quantitation limits for each stabilizer (Qualifier ion settings in brackets); wt% related to the polymer

Method validation

Eight different levels of standard solutions, with concentrations ranging from 0.5 to 50 mg L-1 for the oligomeric HALS (**Chimassorb 944** and **Cyasorb UV-3529**) and 0.01 to 10 mg L-1 for all the other analytes, were used to produce calibration curves. The results were obtained from the average of triplicate injections for all samples. Almost all analytes were found to be linear over the entire working range. For two analytes, namely **Irganox 1010** and **Cyasorb UV-3529**, a quadratic regression showed a slightly better fit than a linear one. Correlation coefficients better than 0.99 were obtained for all analytes. In Figure 2 the calibration curves obtained for 6 analytes from different chemical classes are shown. Quantitation limits (LOQ) were calculated, with S/N better than 10/1 for the quantifier transitions and better than 3/1 for the qualifier transitions. The results are shown in Table 2. Recovery tests were performed to monitor the effect of the procedure, whereby recoveries were found to be in the range of +/- 10% for all analytes, except **Irganox PS 800** which was in the range of 15%. Low variabilites were observed with standard deviations not exceeding 2.5 %.

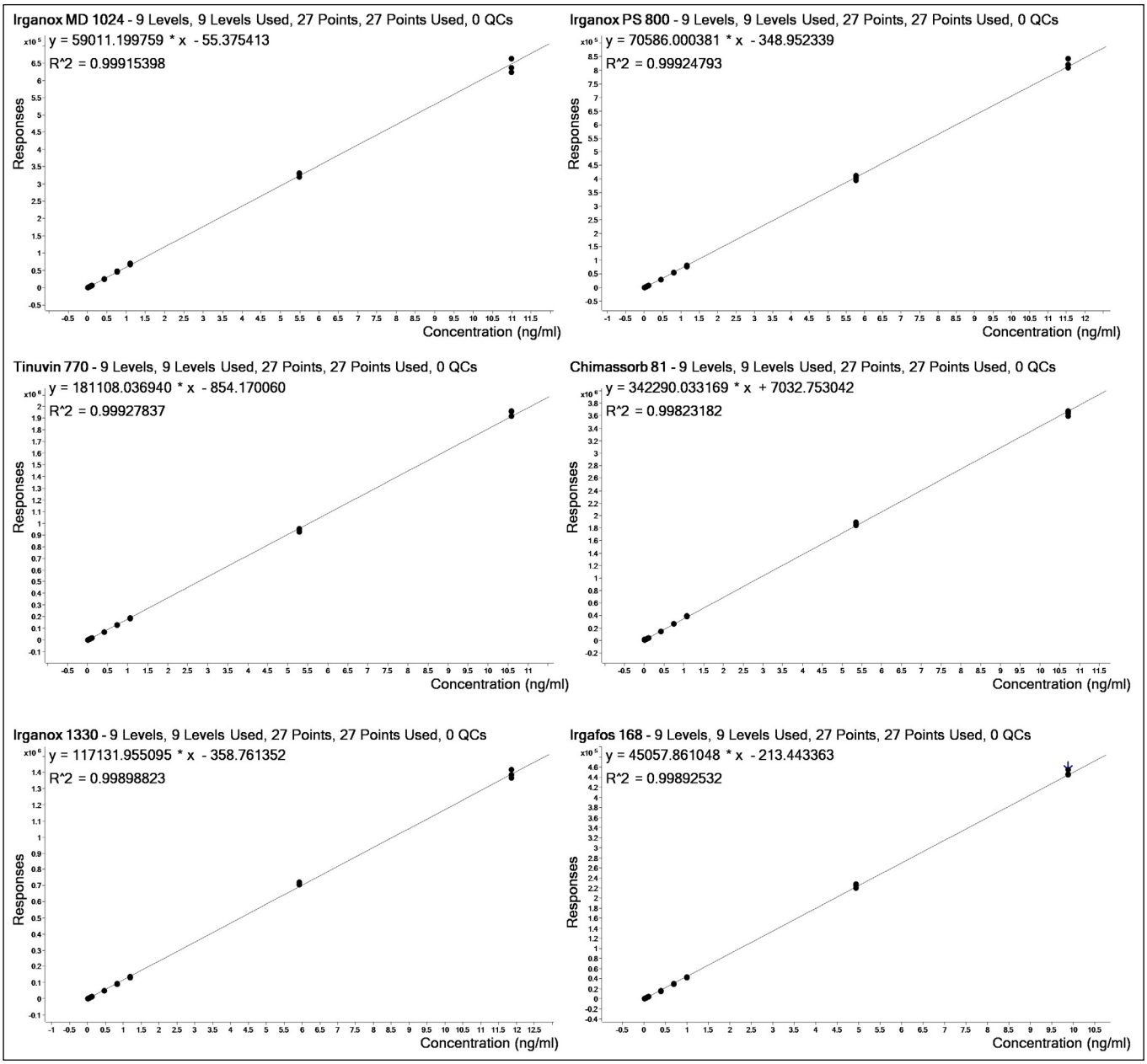

Figure 2: Calibration curves obtained for six different stabilizers

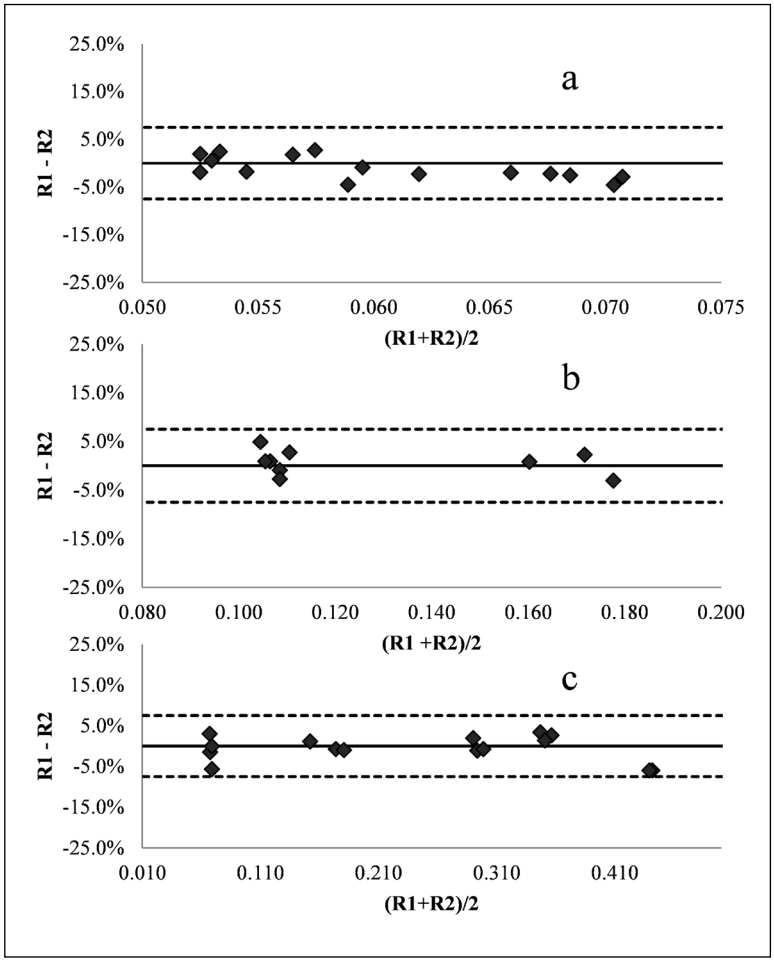

Figure 3: Comparison of FI/MRM-MS analysis (R1) and the reference HPLC-UV analysis (R2); (a) **Irgafos 168,** (b) **Irganox 1010**, (c) **Irganox 1330**

FI/MRM-MS for quantitative analysis

In order to study the applicability of the developed method for analysis of additives in real samples, five different polymer specimens, containing **Irganox 1330** and **Irgafos 168** (three of them also containing **Irganox 1010**) were selected. Stabilizers were extracted three times from each matrix as described in the experimental section and analysis of the extracts was performed by FI/MRM-MS and also by a validated HPLC-UV method for comparison purposes. The results were plotted to view possible discrepancies between the methods. As can be seen in Figure 3, the two methods showed very good correlation and differences were less than 7.5% (dashed line) for all measurements. These results prove that the newly developed method has the same relative accuracy as the well-established HPLC-UV method.

CONCLUSION

In the work presented in this paper, applicability of FI, without prior chromatography, hyphenated to highly sensitive MRM-MS could be clearly demonstrated for both the quantitative and qualitative characterization of several commonly used polymer stabilizers [9, 10]. Compared with the APCI source, the ESI signal intensities are higher for almost all analytes with comparable baseline noise. Additionally, detection of some high molecular oligomers of HALS-additives is not possible with APCI or APPI as no multiply charged ions were observed and singly charged ions were not within the detectable mass range (up to 2200 m/z). However, ESI as well as APPI showed a much higher susceptibility towards ion suppression compared to APCI, which makes the latter one the preferred tool for quantitation measurements. With APCI-MS, low limits of detection were obtained and the detector response was shown to be linear over a wide concentration range. In comparison with a validated HPLC-method, the same relative accuracy could be achieved for the analysis of real samples, with the advantage that the proposed methodology allows analyses in a much shorter time than using chromatographic methods.

REFERENCES

[1] Wang FC. Polymer additive analysis by pyrolysis-gas chromatography IV. Antioxidants. J Chromatogr A. 2000;891:325-36.

[2] Carrott MJ, Jones DC, Davidson G. Identification and analysis of polymer additives using packed-column supercritical fluid chromatography with APCI mass spectrometric detection. Analyst. 1998;123:1827-33.

[3] Beißmann S, Stiftinger M, Grabmayer K, Wallner G, Nitsche D, Buchberger W. Monitoring the degradation of stabilization systems in polypropylene during accelerated aging tests by liquid chromatography combined with atmospheric pressure chemical ionization mass spectrometry. Polym Degrad Stabil. 2013;98:1655-61.

[4] Block C, Wynants L, Kelchtermans M, De Boer R, Compernolle F. Identification of polymer additives by liquid chromatography-mass spectrometry. Polym Degrad Stabil. 2006;91:3163-73.

[5] Himmelsbach M, Buchberger W, Reingruber E. Determination of polymer additives by liquid chromatography coupled with mass spectrometry. A comparison of atmospheric pressure photoionization (APPI), atmospheric pressure chemical ionization (APCI), and electrospray ionization (ESI). Polym Degrad Stabil. 2009;94:1213-9.

[6] Munteanu D, Isfan A, Isfan C, Tincul I. High-Performance Liquid Chromatographic Separation of Polyolefin Antioxidants and Light-Stabilizers. Chromatographia. 1987;23:7-14.

[7] Cappiello A, Famiglini G, Palma P, Pierini E, Termopoli V, Trufelli H. Overcoming Matrix Effects in Liquid Chromatography-Mass Spectrometry. Anal Chem. 2008;80:9343-8.

[8] Trufelli H, Palma P, Famiglini G, Cappiello A. An Overview of Matrix Effects in Liquid Chromatography-Mass Spectrometry. Mass Spectrom Rev. 2011;30:491-509.

[9] Beißmann S, Reisinger M, Reimann A, Klampfl CW, Buchberger W. High-throughput quantification of stabilizers in polymeric materials by flow injection tandem mass spectrometry. Rapid Commun Mass Sp. 2014;28:939-47.

[10] Beißmann S, Reisinger M, Toelgyesi L, Klampfl C, Buchberger W. Fast screening of stabilizers in polymeric materials by flow injection-tandem mass spectrometry. Anal Bioanal Chem. 2013;405:6879-84.

Published in USA, November, 2014
5991-5316EN