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Analysis of Polymer Additives in Plastic Food Containers Using the Quadrupole TOF Mass Spectrometer

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1. Overview

In this study, we introduce an example of qualitative and quantitative analysis of several types of polymer additives included in commercial food packing containers and food packing films. LCMS-9030 Quadrupole TOF mass spectrometer was used for LC-MS analysis, and the ACD/MS Structure ID Suite™ software was used for supporting the identification of the compound .

2. Introduction

The polymer additives such as antioxidant, ultraviolet light absorbent and flame retardant are essential for polymer materials. Because the performance and function of polymer depends on these additives, conducting qualitative and/or quantitative analysis of the additives in these polymers makes it possible to obtain information pertaining to mixing technology and new additives.

3. Methods

Fourteen polymer additives were investigated in this study.
The food packing films and food packing containers(A,B,C,D and E) were obtained from the food products purchased at a retail store. 0.1 g of each sample was cut into fine pieces, added 1 mL of THF, sonicated for 1 min, and added 1 mL of methanol. Filtered supernatants were diluted by methanol and measured using LC-MS and LC-MS/MS. Standards of polymer additives were solved with THF and diluted with methanol to an appropriate concentration and then analyzed by LC-MS/MS.
Analysis was performed by an LCMS-9030 (Shimadzu Corporation) system. All compounds were detected on ESI mode. The column used was Kinetix 2.6u XB-C18 and mobile phases were water containing 10 mmol/L ammonium formate/methanol. LabSolutions Insight Explore™ (Shimadzu Corporation) was used for peak picking and chemical formula prediction. ACD/MS Structure ID Suite™ (Advanced Chemistry Development, Inc.) was used for identification of components by combination of Pubchem database screening and ranking based on the mass fragmentation patterns.
Quantitative analysis was performed on MS/MS mode. *m/z* of precursor and product ions and collision energies were optimized in advance. Samples were diluted 1000 to 1, 100 to 1 or 10 to 1 with methanol.

Table 1 LC-MS condition

UHPLC conditions

Column	: Kinetix 2.6u XB-C18 (75 mm × 2.1 mm I.D., 2.6μm)
Mobile phase A	: Water containing10 mmol/L Ammonium formate
Mobile phase B	: Methanol
Flow rate	: 0.5 mL/min
Time program	: 35% (0 min) → 100% (4-7.5 min) → 35% (7.51-10 min)
Column Temp.	: 40 ℃
Injection vol.	: 2μL

MS conditions

Ionization	: ESI positive/negative
Neblizing gas flow	: 2.0 L/min
Drying gas flow	: 10.0 L/min
Heating gas flow	: 10.0 L/min
DL temp.	: 250 ℃
BH temp.	: 400 ℃
Interface temp.	: 300 ℃

4. Results

4-1. Detection of polymer additives in plastic food packing containers and food packing films

We performed the analysis of the food packing container and food packing films.
LC-MS measurement was performed under the condition shown in Table 1.
Figure 1 shows the result of peak picking by using LabSolutions Insight Explore™ . We picked up peaks on the EICs of *m/z* 637.4941, *m/z* 386.3057, *m/z* 1194.8190, *m/z* 548.5039 and *m/z* 647.4591,that were equivalent to the weight of the ion coming from Irganox1098, Cyanox425, Irganox1010, Irganox1076 and Irgafos168, respectively.
As an example, for the peak on the EIC of *m/z* 637.4941(Peak X) , the formula was found to be $C_{40}H_{64}N_2O_4$ after formula prediction(Figure 2). Furthermore, We performed Pubchem database screening in offline using MS Structure ID Suite™ to check the name and chemical structure of the compound. This software can list compounds from the PubChem database based on the chemical formula and rank by correspondence to measured mass fragmentation patterns. As the result of database screening, 71 compounds were listed up and the compounds of Pubchem ID 90004 which was equivalent to Irganox1098 showed the best score (Figure 3). For certain qualitative analysis, we performed the LC-MS/MS analysis of the standard samples of polymer additives. After we compared the MS/MS spectra of Peak X and the peak of standard sample, it was confirmed that Peak X was Irganox1098. The compound's names of other peaks also were confirmed by similar procedure.

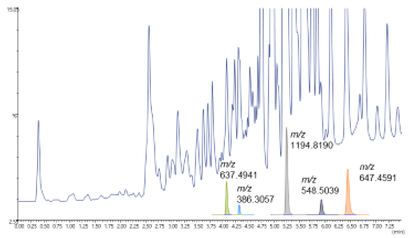

Figure 1 EICs of food packing film A using the Find algorism of Insight Explore

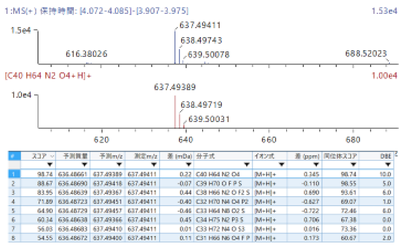

Figure 2 Result of formula prediction of Peak X (upper: measured spectrum, middle: theoretical spectrum, lower: table of candidates)

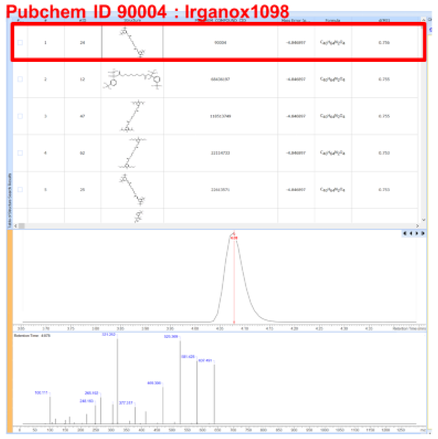

Figure 3 The result of Database screening and ranking of the Peak X using MS Structure ID Suite™

4-2. Quantitative analysis of plastic food packing containers and food packing films

We obtained MS/MS chromatograms for quantitative analysis of the food packing containers and food packing films.
The dilution series of mixed standard samples were analyzed. Table 2 shows the linearity of each compounds. Figure 4 shows the representative calibration curves.
Samples for Qualitative analysis were diluted 10 to 1, 100 to 1 or 1000 to 1 with methanol. The 1000 to 1 dilution of sample contained approximately 1.85 to 40 ppb Irgafos168. Therefore, it was determined that each food packing container and food packing film contains 37 to 800 μg/g Irganox168. On the other hand, some samples contain approximately 0.27 to 0.82 μg/g IrganoxMD1024, 1.70 to 113.92 μg/g Irganox1010and 1.48 to 25.45 μg/g Irganox1076.Table 3 shows the summary of quantitative results and Figure 5 shows the representative result of quantitative analysis of food packing film A.

Table2 Linearity of 14 polymer additives

Compound	Ionzation	Precursor Ion	Product Ion	Range(ppb)	Coefficient(R^2)
TinuvinP	ESI positive	226.0975	120.0556	1-1000	0.999
Irganox245	ESI positive	604.3844	177.1279	0.05-50	0.998
IrganoxMD1024	ESI positive	570.4265	181.0972	0.1-100	0.995
Irganox1098	ESI positive	637.4939	321.2537	0.1-100	0.996
Cyanox2246	ESI negative	339.2330	163.1128	0.1-100	0.999
Cyanox425	ESI negative	367.2643	367.2643	0.1-100	0.999
Irganox1035	ESI positive	660.4292	249.1485	0.05-50	0.998
Tinuvin120	ESI positive	439.3207	233.1531	0.01-10	0.999
Tinuvin328	ESI positive	352.2383	282.1601	0.1-100	0.999
Irganox1010	ESI positive	1194.8179	1194.8179	0.1-100	0.995
Irganox1330	ESI positive	792.6289	219.1743	0.05-50	0.995
Irganox565	ESI positive	589.3968	250.1009	0.5-100	0.993
Irganox1076	ESI positive	548.5037	475.4146	0.5-100	0.997
Irgafos168	ESI positive	647.4588	647.4588	0.5-100	0.999

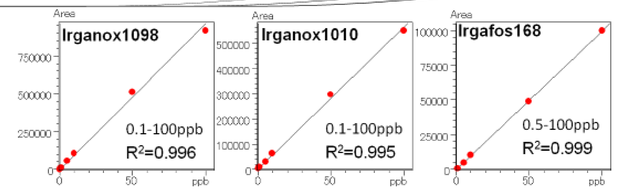

Figure 4 Representative calibration curves (Irganox1098,Irganox1010,and Irgafos168)

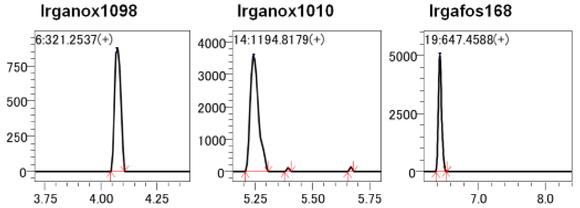

Figure 5 Representative result of quantitative analysis of Food packing film A 1 to 1000 dilution (Irganox1098,Irganox1010,and Irgafos168)

5. Conclusions

We performed the qualitative analysis for polymer additives in plastic food packing containers and food packing films using the quadrupole TOF mass spectrometer.
It was confirmed that the combination of LC-MS analysis using quadrupole TOF mass spectrometer, database screening and ranking based on the mass fragmentation patterns was useful for qualification of polymer additives in food packing containers and food packing films .
As a result of quantitative analysis, we found a tendency of polymer additive's concentration in a plastic food packing container.

6. Acknowledgement

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