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Application News

No. C236

LC/MS LCMS™-9030

Analysis of Additives in Food Containers Using LCMS-9030 Quadrupole Time-of-Flight Liquid Chromatograph Mass Spectrometer

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User Benefits

- Simple qualitative analysis of various types of additives contained in polymer materials is possible by using this system.
- Highly accurate quantitative analysis is realized by utilizing the high resolution of the LCMS-9030, even with complex samples.
- The LCMS-9030 demonstrates its effectiveness in evaluations of polymer materials and development/improvement of functional polymers.

■ Introduction

Additives such as antioxidants, ultraviolet absorbers, and flame retardants are added to polymers, namely, plastics and rubber. Because performance and durability can be dramatically enhanced by adding appropriate types and quantities of additives in the development and production of polymer materials, it is extremely important to obtain information on the additives contained in those materials.

Application News No. C79 introduced an example of quantitative analysis of polymer additives using a triple quadrupole (TQ) type high performance liquid chromatograph mass spectrometer (LC-MS). This Application News introduces an example of qualitative analysis and quantitative analysis of the polymer additives in food containers using the LCMS-9030, which is a quadrupole time-of-flight (QTOF) LC-MS.

■ Analysis of Food Containers

In this experiment, the polymer additives contained in five types of food containers were analyzed. Samples for the analysis were prepared by adding 1 mL of THF to 0.1 g of finely-chopped food container materials (pack, film), conducting sonication for 1 min, adding 1 mL of methanol to the sample, filtering the supernatant with a 0.2 µm filter, and then diluting the sample with methanol.

Fig. 1 shows the result of peak picking of the food A film using the "ANALYZE" function of LabSolutions Insight Explore™.

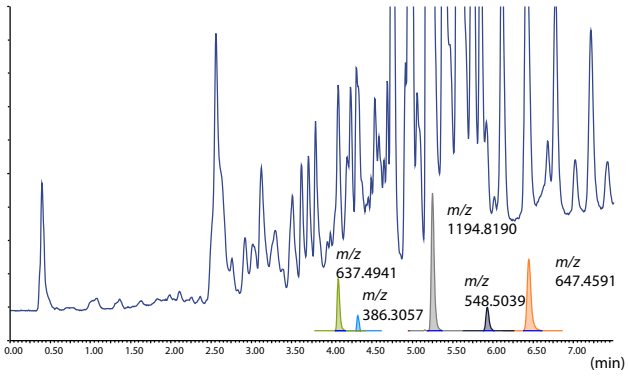
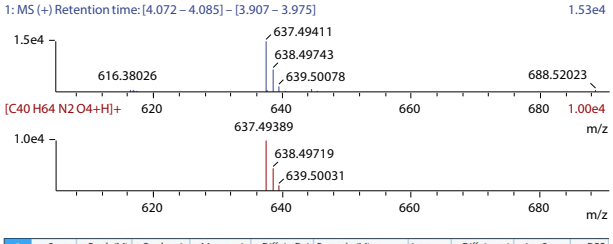


Fig. 1 Result of Peak Picking of Food A Film Using Insight Explore

Peaks were detected on the extracted ion chromatogram (EIC) at *m/z* 637.4941, 386.3057, 1194.8190, 548.5039, and 647.4591. These *m/z* correspond to the *m/z* of ions originating from Irganox® 1098, CYANOX® 425, Irganox® 1010, Irganox® 1076, and Irgafos® 168, respectively.

As an example, Fig. 2 shows the composition estimation results for the peak (peak X) on the EIC at *m/z* 637.4941. It was found that the compositional formula is $C_{40}H_{64}N_2O_4$.



#	Score	Pred. (M)	Pred. m/z	Meas. m/z	Diff. (mDa)	Formula (M)	Ion	Diff. (ppm)	Iso Score	DBE
1	98.74	636.48661	637.49389	637.49411	0.22	C40 H64 N2 O4	[M+H]+	0.345	98.74	10.0
2	88.67	636.48690	637.49418	637.49411	-0.07	C39 H70 O F P S	[M+H]+	-0.110	98.55	5.0
3	83.95	636.48639	637.49367	637.49411	0.44	C38 H66 N2 O F2 S	[M+H]+	0.690	93.61	6.0
4	71.89	636.48723	637.49451	637.49411	-0.40	C32 H70 N4 O4 P2	[M+H]+	-0.627	69.07	1.0
5	64.90	636.48729	637.49457	637.49411	-0.46	C33 H64 N8 O2 S	[M+H]+	-0.722	72.46	6.0
6	60.34	636.48638	637.49366	637.49411	0.45	C34 H75 N2 P3 S	[M+H]+	0.706	67.38	0.0
7	56.03	636.48683	637.49410	637.49411	0.01	C33 H72 N4 O S3	[M+H]+	0.016	73.36	0.0
8	54.55	636.48672	637.49400	637.49411	0.11	C31 H66 N6 O4 F P	[M+H]+	0.173	60.67	2.0

Fig. 2 Result of Composition Estimation of Peak X
(Top: Measured Spectrum, Middle: Theoretical Spectrum, Bottom: Candidates of Compositional Formula)

Table 1 Measurement Conditions

[HPLC conditions]	
Column	:Kinetex® 2.6u XB-C18 (75 mm x 2.1 mm I.D., 2.6 µm)
Mobile phase A	:Water containing 10 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 ˚C
Injection vol.	:2 µL
[MS conditions]	
Ionization	:ESI positive / ESI negative
Mode	:Scan, MS/MS
Nebulizing gas flow	:2.0 L/min
Drying gas flow	:10.0 L/min
Heating gas flow	:10.0 L/min
DL temp.	:250 ˚C
BH temp.	:400 ˚C
Interface temp.	:300 ˚C

■ Compound Search

In addition, an analysis was carried out using ACD/MS Structure ID Suite (Advanced Chemistry Development, Inc., ACD) to confirm the structural formula and compound name of this peak. This software makes it possible to list compounds from the PubChem offline database, which contains approximately 100 million items, based on precise mass and compositional formula information, and assign ranks of compounds from the degree of coincidence (assignment rate) between the product ion obtained by fragment prediction and the product ion observed in the measured MS/MS spectrum.

A database search by the compositional formula $C_{40}H_{64}N_2O_4$ found 71 candidate compounds.

Fig. 3 shows the result of the ranking of the candidate compounds found in the database search. The compound PubChem CID 90004 showed the highest assignment rate. As the result of an online search using PubChem, this compound was identified as Irganox® 1098 (Fig. 4).

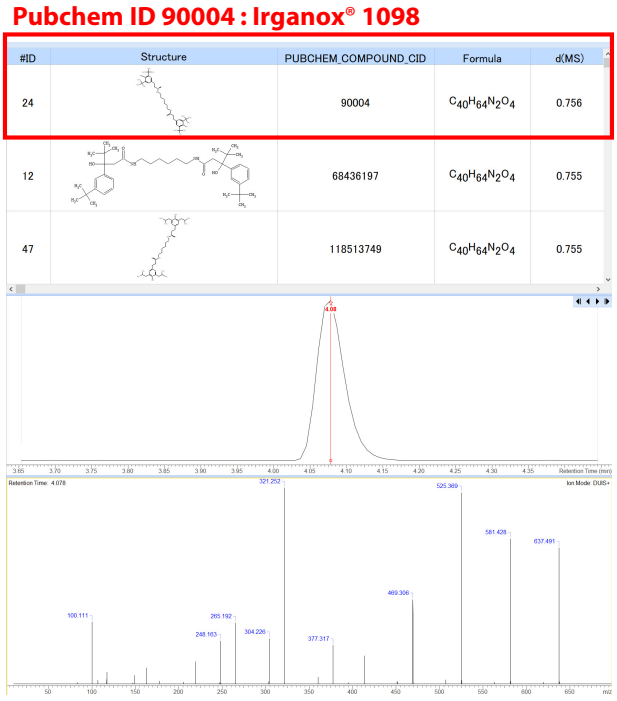


Fig. 3 Results of Database Search and Ranking of Assignment Rates Using ACD/MS Structure ID Suite

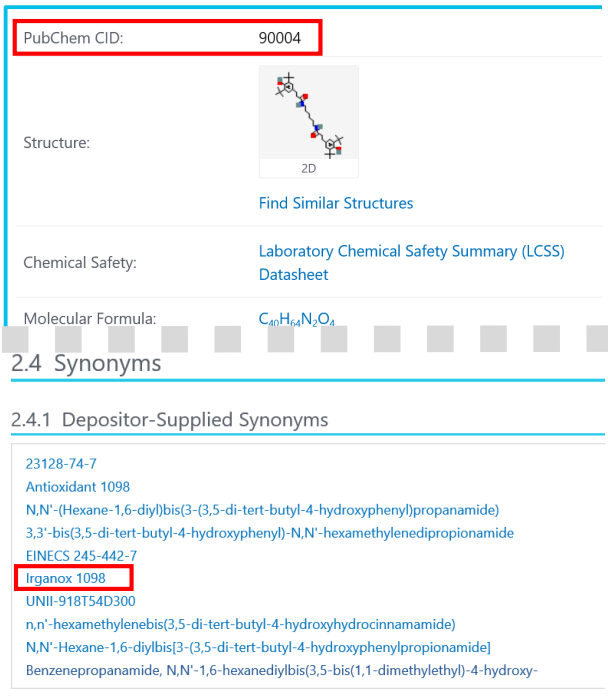


Fig. 4 Result of Compound Search Using Online Database

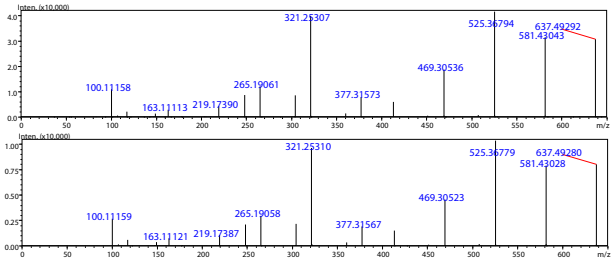


Fig. 5 MS/MS Spectra of (Top) Standard Sample of Irganox® 1098 and (Bottom) Peak X

For a sure qualitative analysis, a standard sample of the additive was measured. The result of confirmation of the retention time of the above-mentioned Irganox® 1098 coincided with the retention time of peak X. The MS/MS spectra of Irganox® 1098 and peak X were also compared (Fig. 5). These results confirmed that peak X is Irganox® 1098.

As described above, it is possible to search the structural formula and compound name of target peaks by a process of ① LC-MS and LC-MS/MS measurement, ② peak picking using Insight Explore, ③ composition estimation of the target peak, ④ search for the structural formula using an offline database, ⑤ narrowing of the candidate compounds based on the assignment rates of fragments, ⑥ search for the structural formula and compound name using the online database, and ⑦ confirmation analysis using a standard sample using Shimadzu LCMS-9030 and LabSolutions Insight Explore and ACD/MS Structure ID Suite.

■ Quantitative Analysis of Polymer Additives in Food Containers

MS/MS chromatograms were acquired for a quantitative analysis of the polymer additives contained in the food containers.

Fig. 6 shows the respective calibration curves, and Table 2 shows the range of the calibration curve and the coefficient of determination (R^2) of each compound.

Samples of the food containers were extracted by the method described above and were diluted from 10 times to 1000 times with methanol. As a result of the quantitative analysis/calculations, it was found that the concentration of Irgafos® 168 in the samples diluted 1000 times was from 1.85 to 40 ppb, and the concentrations in the packs and films were in the range of 37 to 800 mg/g. Table 3 shows the results of the quantitative analysis of each compound including Irgafos® 168, and Fig. 7 shows representative MS/MS chromatograms of the food A film.

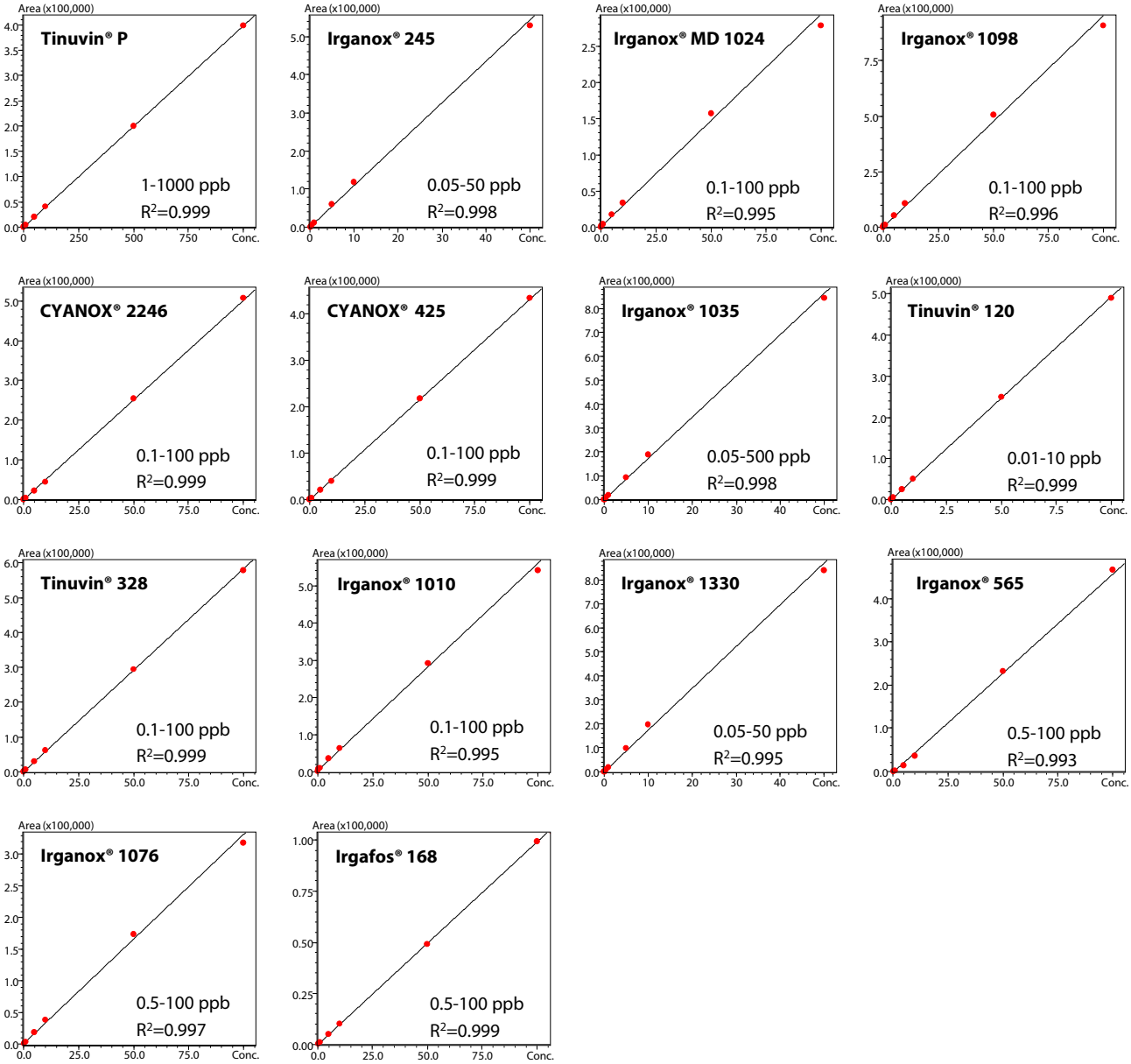


Fig. 6 Calibration Curves of 14 Polymer Additive Components

Table 2 Range of Calibration Curves and Coefficients of Determination of 14 Polymer Additive Components

Compound name	Ionization method	Precursor ion	Monitor ion	Range of calibration curve (ppb)	Coefficient of determination (R^2)
Tinuvin® P	ESI positive	226.0975	120.0556	1-1000	0.999
Irganox® 245	ESI positive	604.3844	177.1279	0.05-50	0.998
Irganox® MD 1024	ESI positive	570.4265	181.0972	0.1-100	0.995
Irganox® 1098	ESI positive	637.4939	321.2537	0.1-100	0.996
CYANOX® 2246	ESI negative	339.2330	163.1128	0.1-100	0.999
CYANOX® 425	ESI negative	367.2643	367.2643	0.1-100	0.999
Irganox® 1035	ESI positive	660.4292	249.1485	0.05-50	0.998
Tinuvin® 120	ESI positive	439.3207	233.1531	0.01-10	0.999
Tinuvin® 328	ESI positive	352.2383	282.1601	0.1-100	0.999
Irganox® 1010	ESI positive	1194.8179	1194.8179	0.1-100	0.995
Irganox® 1330	ESI positive	792.6289	219.1743	0.05-50	0.995
Irganox® 565	ESI positive	589.3968	250.1009	0.5-100	0.993
Irganox® 1076	ESI positive	548.5037	475.4146	0.5-100	0.997
Irgafos® 168	ESI positive	647.4588	647.4588	0.5-100	0.999

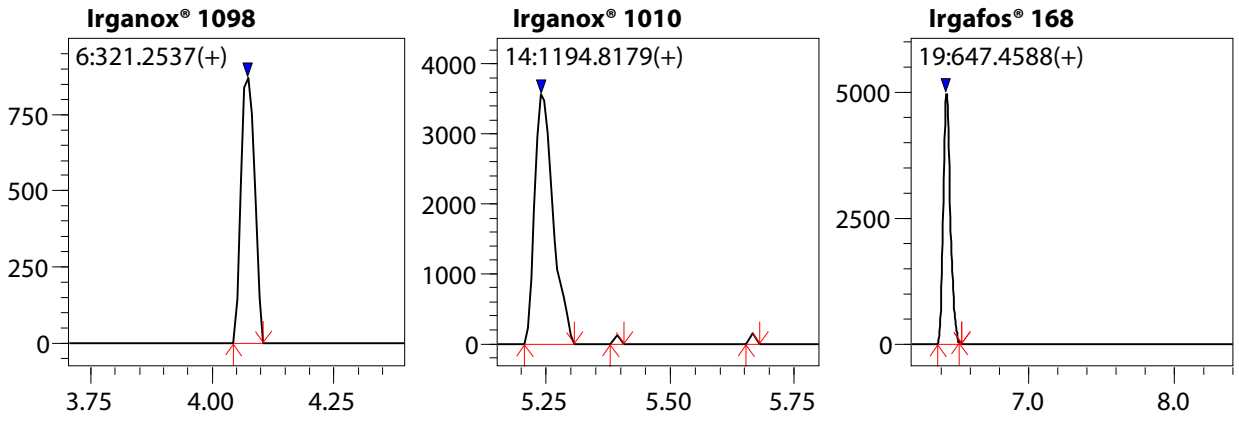


Fig. 7 Representative MS/MS Chromatograms of Food A Film

Table 3 Results of Quantitative Analysis of Polymer Additives in Food Containers

Compound name	Concentration (mg/g)									
	Food A pack	Food A film	Food B pack	Food B film	Food C pack	Food C film	Food D pack	Food D film	Food E pack	Food E film
Tinuvin® P	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Irganox® 245	-----	-----	-----	0.043	-----	-----	-----	-----	-----	-----
Irganox® MD 1024	0.823	0.695	0.627	0.486	0.479	0.430	0.376	0.400	0.318	0.278
Irganox® 1098	-----	7.104	-----	8.64	-----	-----	-----	-----	-----	-----
CYANOX® 2246	-----	0.021	-----	-----	-----	-----	-----	-----	-----	-----
CYANOX® 425	0.130	3.132	-----	0.069	-----	-----	-----	-----	-----	-----
Irganox® 1035	0.011	0.012	-----	-----	-----	-----	-----	-----	-----	-----
Tinuvin® 120	-----	0.005	-----	-----	-----	-----	-----	-----	-----	-----
Tinuvin® 328	0.024	-----	-----	-----	-----	-----	0.268	-----	-----	-----
Irganox® 1010	9.544	51.094	1.698	-----	14.054	76.426	6.260	58.466	15.218	113.920
Irganox® 1330	-----	-----	-----	-----	-----	-----	-----	-----	-----	0.004
Irganox® 565	-----	0.159	-----	-----	-----	-----	-----	-----	-----	0.135
Irganox® 1076	2.140	8.366	-----	25.450	2.636	2.482	7.994	9.644	1.484	8.438
Irgafos® 168	111.04	339.94	119.64	37.1	253.68	799.66	350.10	616.62	205.24	126.96

■ Conclusion

A workflow that includes the processes from detection to qualitative analysis and quantitative analysis of the functional additives contained in polymer materials was realized by using a Shimadzu LCMS-9030 quadrupole time-of-flight liquid chromatograph mass spectrometer and LabSolutions Insight Explore and ACD/MS Structure ID Suite.

This technique is expected to contribute to efficient development and improvement of better synthetic polymer materials.

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