

Analysis of Additives in Polymer Samples by Online Extraction-Chromatography System

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Introduction

Polymers are currently used as thermoplastic resins (general-purpose resins, engineering plastics, and super engineering plastics) and thermosetting resins for livingware, food containers, industrial products, and medical supplies. These are synthesized as a resin having properties and performance according to the purpose of use, and various additives contained in the resin are also crucial for improving the performance and adding new properties. Many of the additives are used for the purpose of antioxidants, ultraviolet absorbers, light stabilizers, thermal-degradation inhibitors, plasticizers, and so on. Several types of additives are often used in a product, and it is necessary to analyze the effect of amount and combination of additives, and figure out the time-dependent change, decomposition, and mechanism of action in polymers.

In order to figure out them, plenty of time, effort, and ingenuity are required over the sample pretreatment, separation analysis, and molecular structural analysis by spectroscopy. The measurement method that connects pretreatment and separation analysis online can be expected to improve the efficiency and precision of analysis including sample pretreatment.

We have developed online extraction-chromatography system (EX-Chromato System) which can be combined SFE or solvent extraction (under controlled pressure and temperature) with SFC or HPLC in one system and reported applications about the measurements of ingredients in natural and medical products using this system^{1, 2)}. In this presentation, we applied the EX-Chromato System to analysis of several additives in polymer samples and investigated the online measurement method combining sample pretreatment by SFE with HPLC analysis.

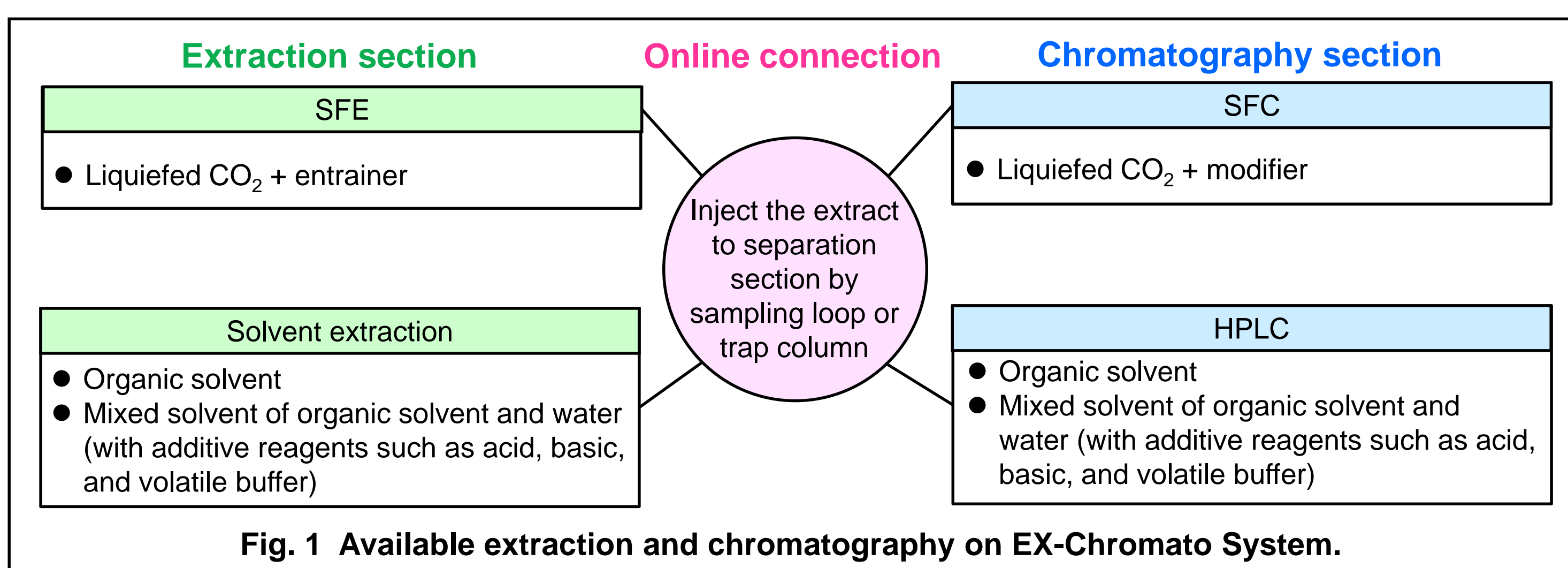


Fig. 1 Available extraction and chromatography on EX-Chromato System.

Experimental Apparatus

The EX-Chromato System was configured using JASCO EXTREMA series. Figure 2 shows the appearance of EX-Chromato System. Figure 3 shows schematic diagram of the system.



Fig. 2 EX-Chromato System.

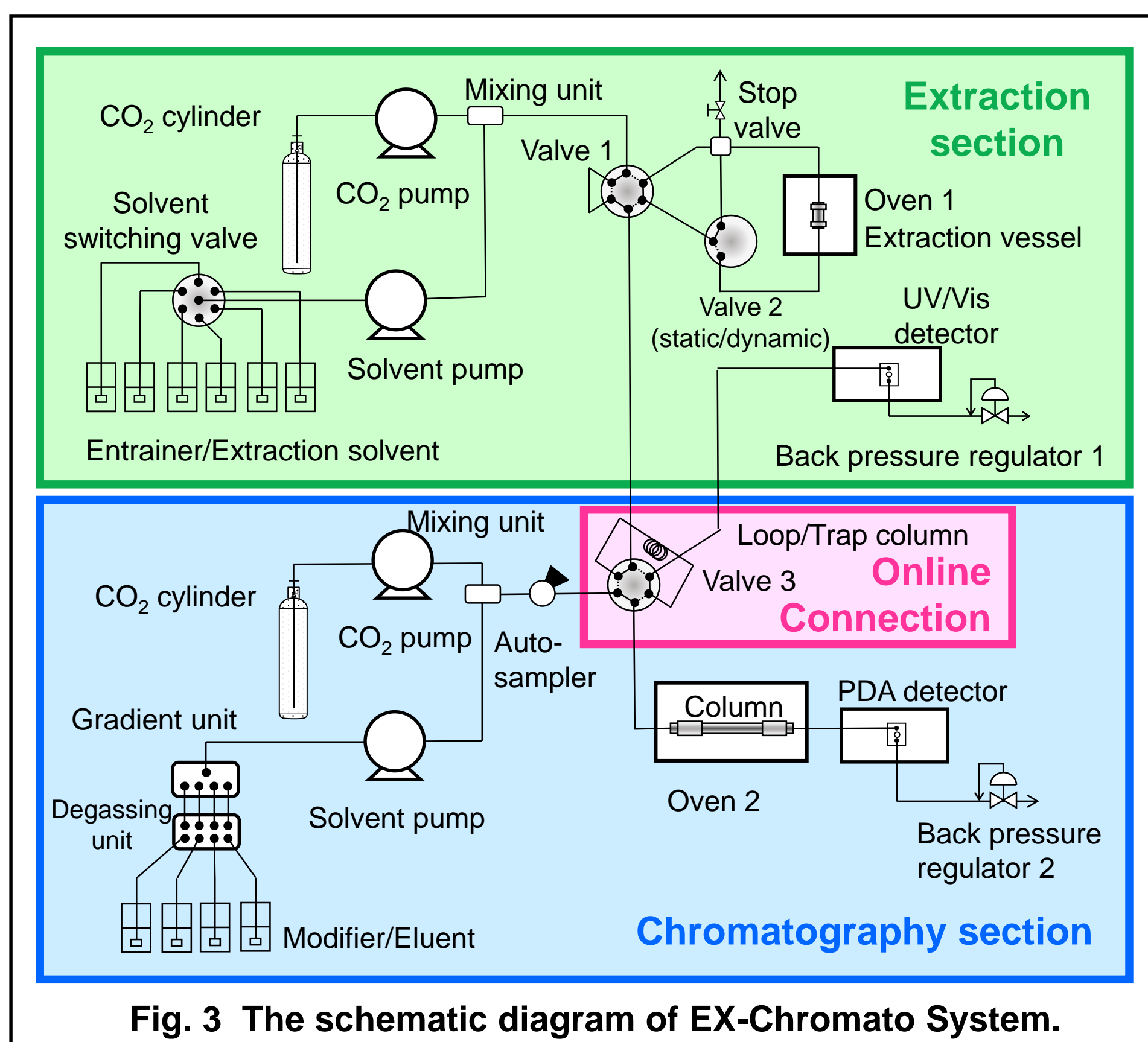


Fig. 3 The schematic diagram of EX-Chromato System.

Sample

Seven additives shown in Fig. 4 were used as standard samples. We used a weather-resistant gardening sheet and plastic shopping bag made of polyethylene as polymer samples (Fig. 5). Quantification was performed using Irganox 1330 as an internal standard (IS), since it was confirmed that Irganox 1010 and Irgafos 168 were contained in these polymer samples.

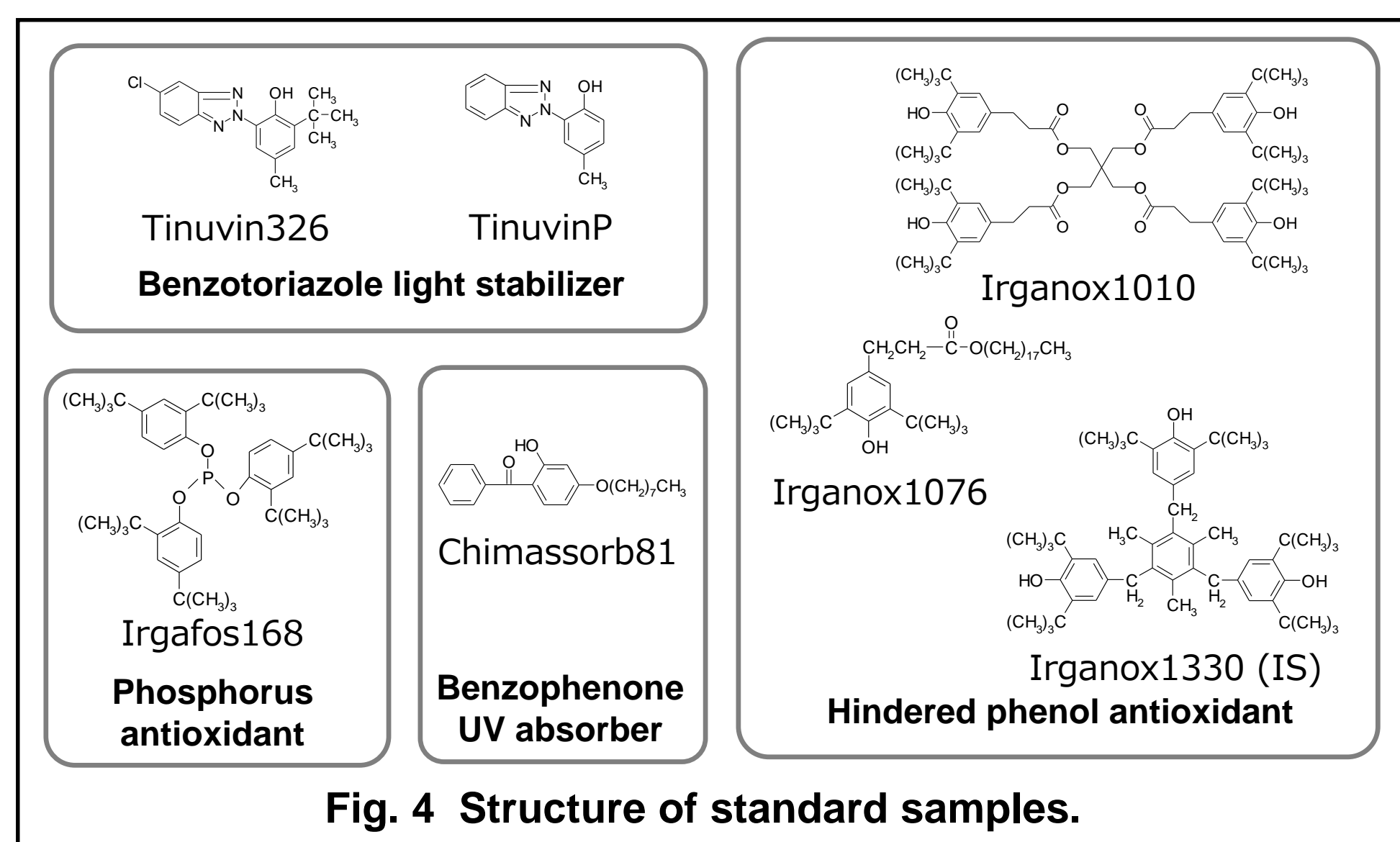


Fig. 4 Structure of standard samples.



Fig. 5 Polymer samples.

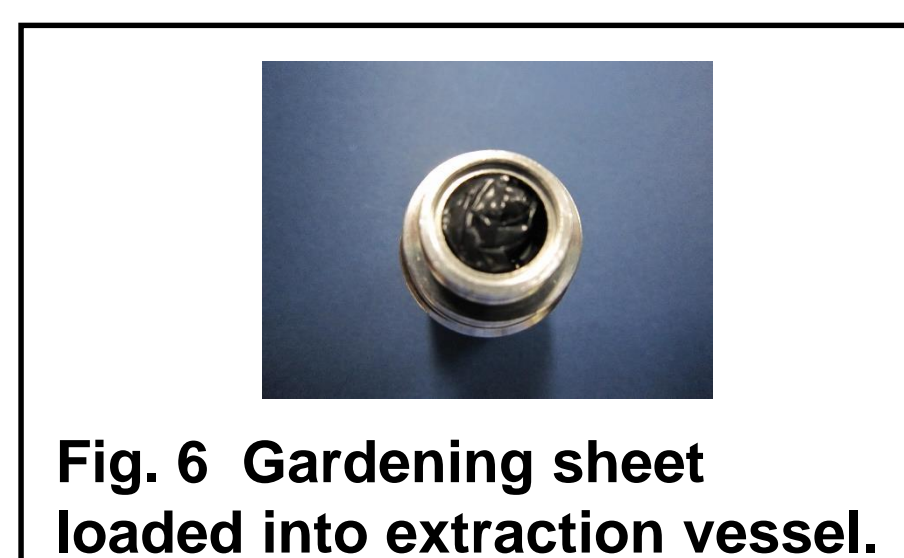
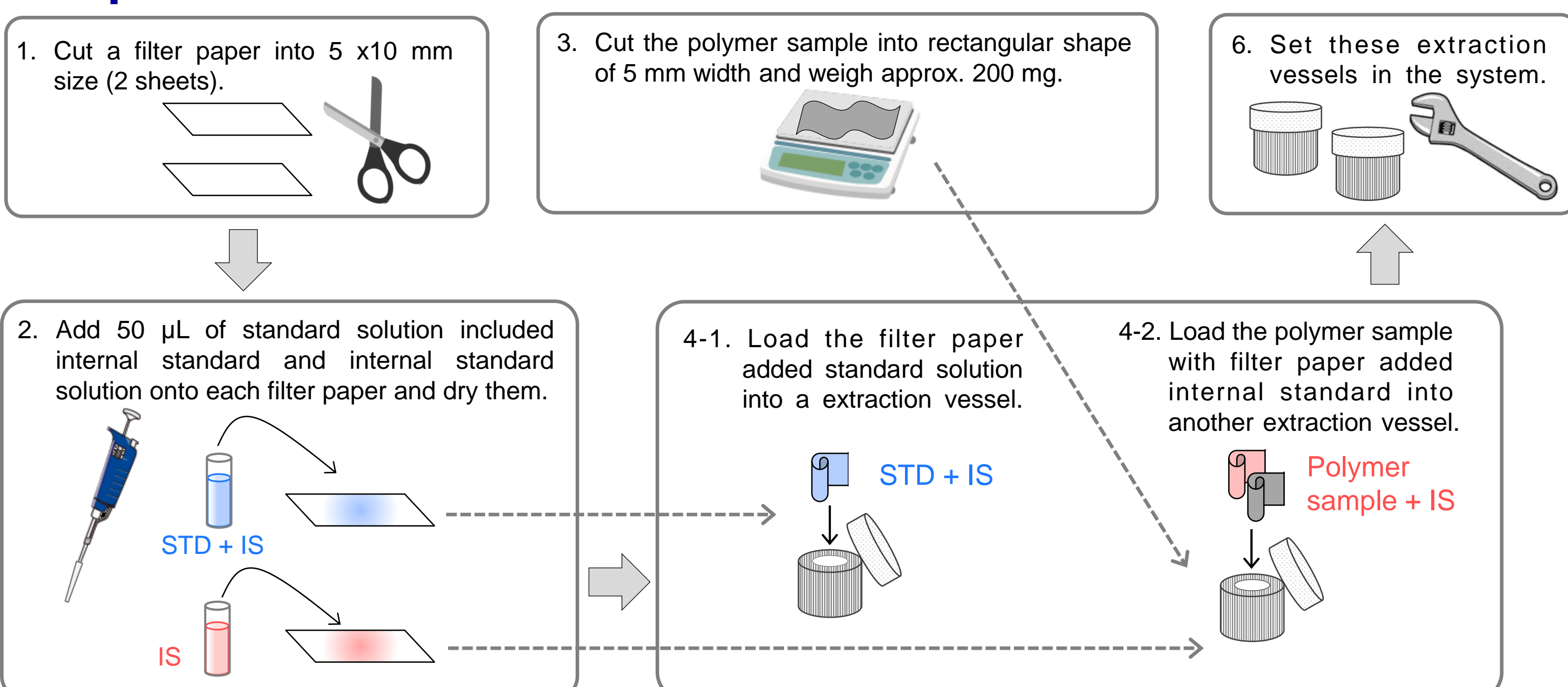


Fig. 6 Gardening sheet loaded into extraction vessel.

Sample Pretreatment



Analysis Conditions

Extraction: SFE

Solvents : A ; Liquefied CO₂
 B ; THF (with stabilizer)
 A/B (50/50)

Flow rate : 2.0 mL/min
 Pressure : 30 MPa
 Temperature : 60 °C
 Time :

Time [min]	operation
0.00 – 1.00	Equilibrating
1.00 – 6.00	Static extraction
6.00 –	Dynamic extraction (Flow rate: 1.0 mL/min)
6.80	Injection to HPLC

Wavelength : 275 nm
 Vessel : EV-01 (1.0 mL volume)

Chromatography: HPLC

Column : Unifinepak C18 (4.6 mm I.D. x 150 mm L, 3 µm)

Eluent : A ; Water/THF* (90/10)
 B ; Acetonitrile/THF* (90/10)
 A/B

Gradient : 0 min (30/70) → 7.0 min (30/70) → 8.0 min (0/100) → 25.0 min (0/100) → 25.1 min (30/70), 1 cycle 45 min

Flow rate : 1.0 mL/min
 Pressure : 11.2 – 14.0 MPa (back pressure ; 5.0 MPa)

Temperature : 40 °C
 Inj. Volume : 5, 10, 20 µL (full fill loop injection)
 Wavelength : 225 nm

* without stabilizer

Results and Discussion

Influence of Injection Volume on HPLC after SFE

Figure 7 shows the chromatogram of standard sample measured by online SFE-HPLC. Figure 8 shows the influence of injection volume on peak shape and symmetry factor by injection volume. As shown in the figure and table, peak shape and peak parameters were deteriorated by increase in injection volume. Therefore, we selected 5 µL as an injection volume.

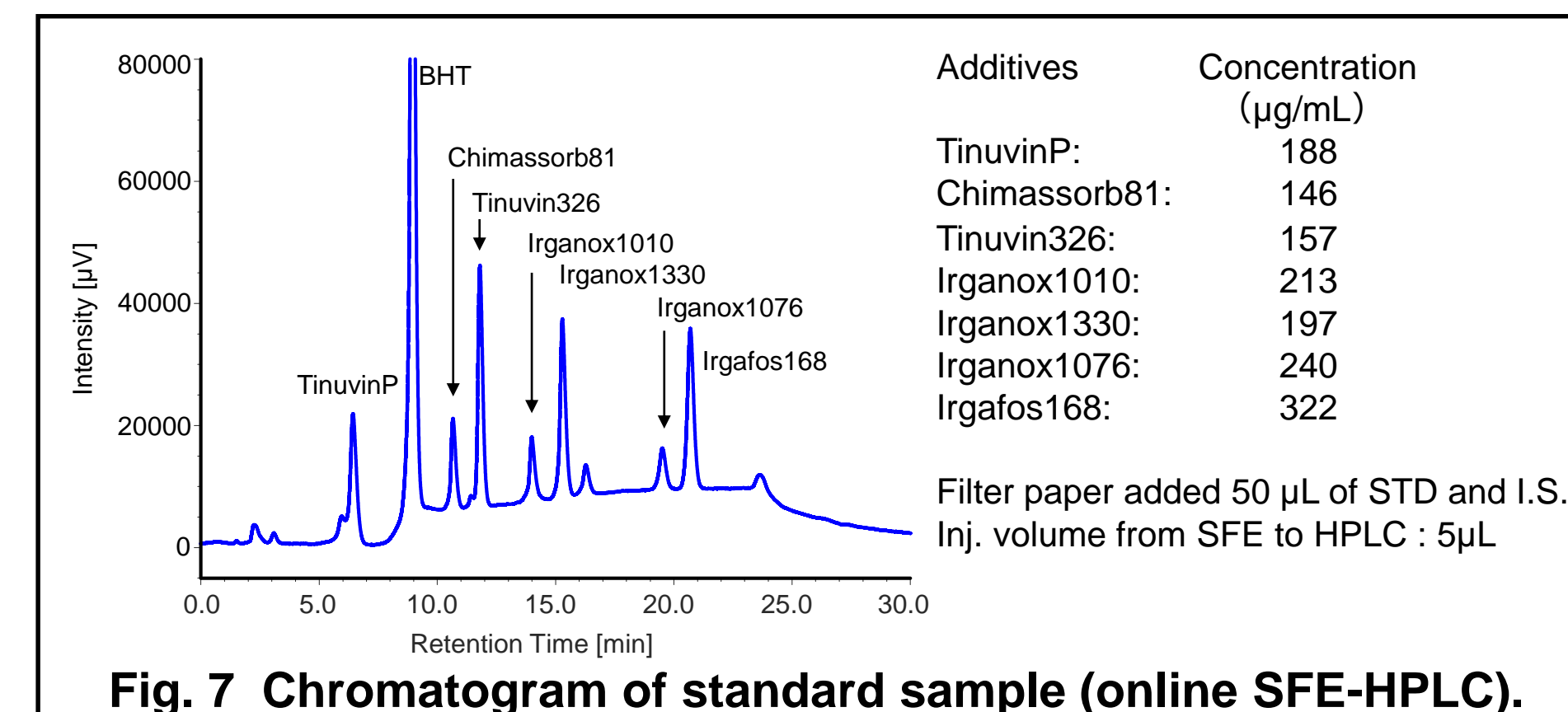


Fig. 7 Chromatogram of standard sample (online SFE-HPLC).

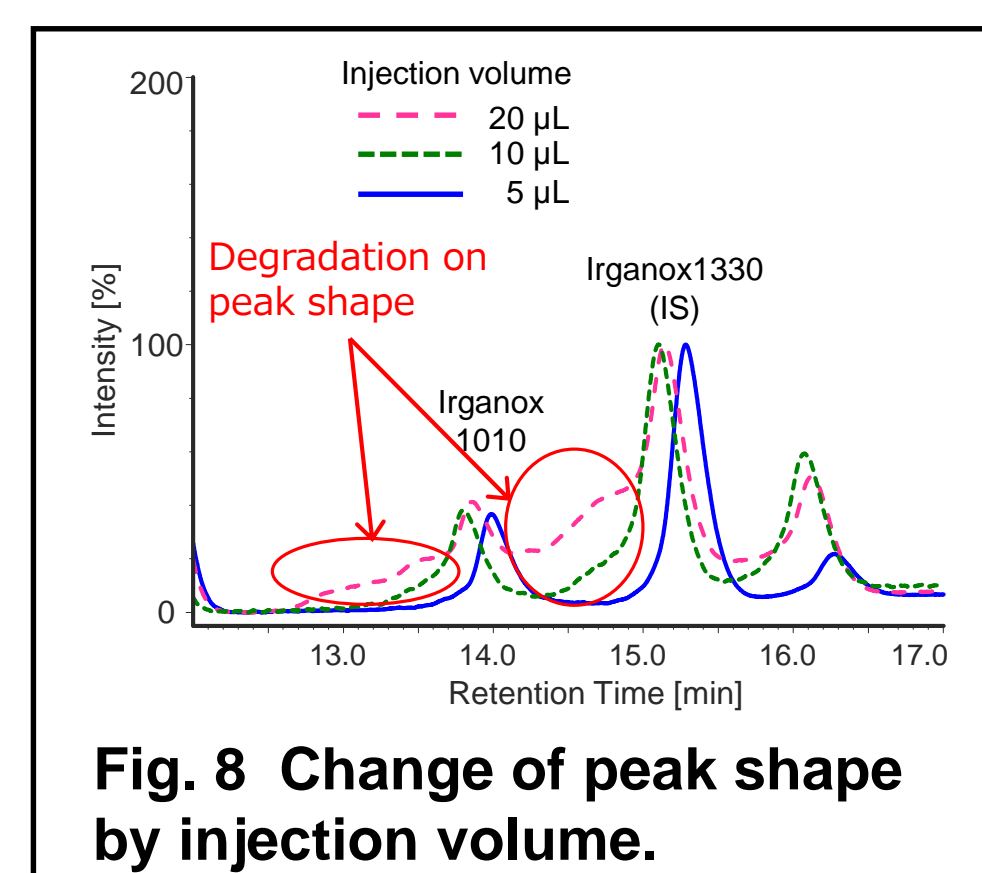


Fig. 8 Change of peak shape by injection volume.

Table 1 Change of NTP and symmetry factor by injection volume.

Additives	Injection volume					
	5 µL		10 µL		20 µL	
	NTP	S	NTP	S	NTP	S
TinuvinP	3180	1.154	2024	0.764	2134	0.646
Chimassorb81	13139	1.018	11563	0.934	7569	0.670
Tinuvin326	16454	1.213	14840	0.824	10954	0.757
Irganox1010	21801	1.100	18118	0.945	19781	0.635
Irganox1330	21950	1.155	20118	1.080	17900	0.716
Irganox1076	28601	0.985	28532	0.974	25846	0.860
Irgafos168	28398	1.130	20593	0.856	27253	1.092

NTP : Number of theoretical plates, S : Symmetry factor

Determination of additives in polymers by online SFE-HPLC

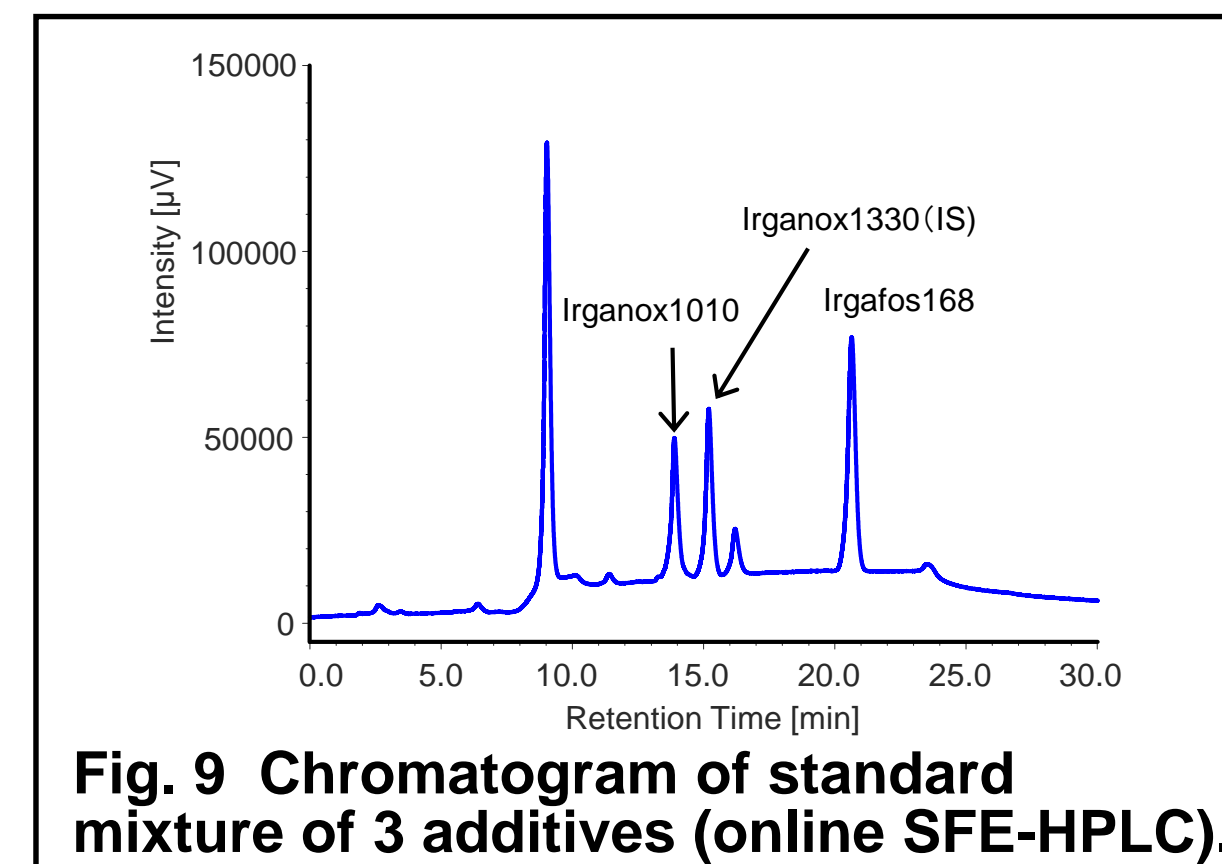


Fig. 9 Chromatogram of standard mixture of 3 additives (online SFE-HPLC).

Table 2 Reproducibility of retention time and peak height ratio of standard mixture (n=6).

Number of injection	Retention time		Peak height ratio*	
	Irganox1010	Irgafos168	Irganox1010	Irgafos168
1st	13.872	20.580	0.835	1.585
2nd	13.832	20.487	0.840	1.505
3rd	13.857	20.512	0.833	1.579
4th	13.993	20.767	0.852	1.512
5th	13.883	20.635	0.842	1.580
6th	13.887	20.640	0.844	1.401
Average	13.887	20.604	0.841	1.520
SD	0.0507	0.0927	0.006	0.073
%RSD	0.36	0.45	0.67	4.79

* peak height of each standard/peak height of Irganox1330 (IS)

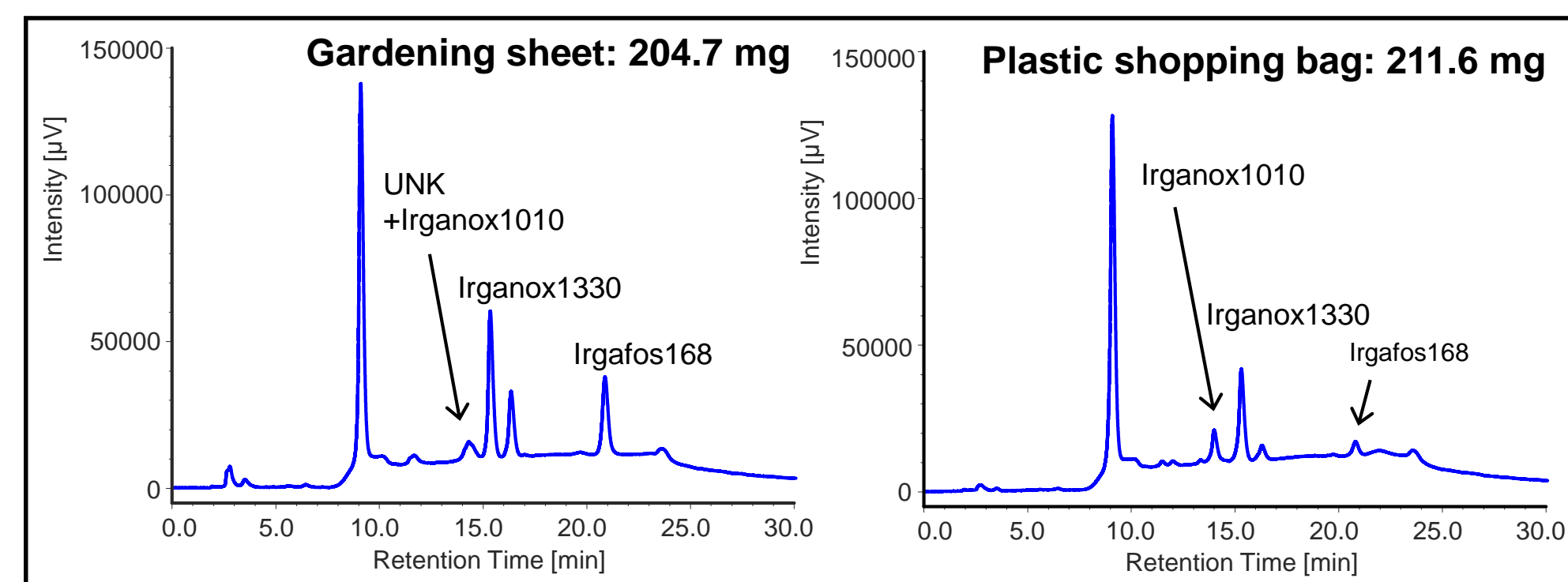


Fig. 11 Chromatograms of polymer samples (online SFE-HPLC).

Table 3 Quantity of additives in polymer samples.

Sample	Quantity [µg/g]*	
	Irganox1010	Irgafos168
Gardening sheet	—	258
Plastic shopping bag	164	71.9

* Maximum values among three measurements were indicated, and reproducibility were approx. 15-20 %RSD.

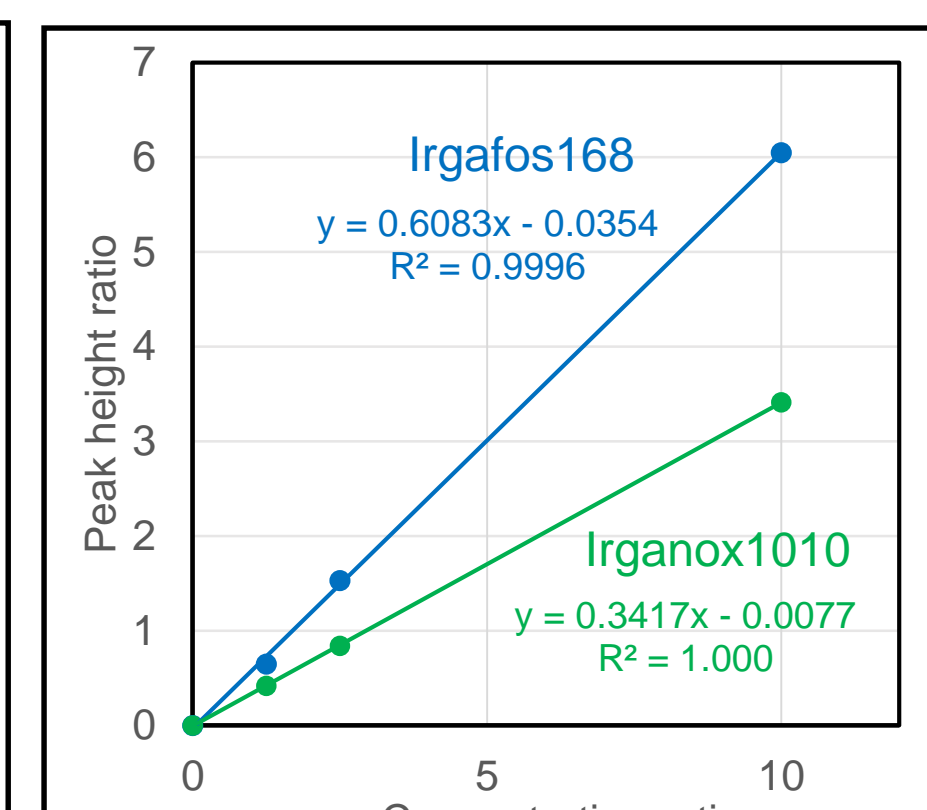


Fig. 10 Linearity by internal standard method (n=3).

UV spectra of co-eluting peak with Irganox1010

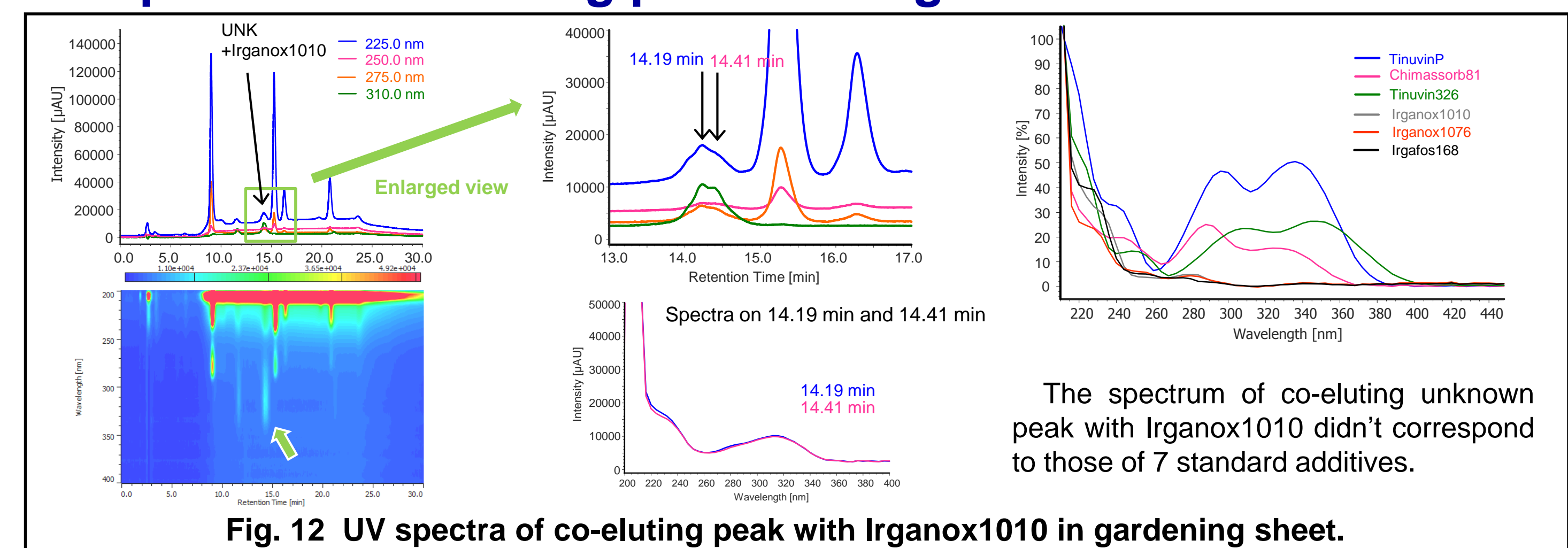


Fig. 12 UV spectra of co-eluting peak with Irganox1010 in gardening sheet.

Conclusion

- Seven types of additives were extracted and separated in a short time by online SFE-HPLC.
- Injection volume of extracts to HPLC after online SFE influenced peak shape in this measurement.
- A lot of unknown peaks were eluted, and identification by UV spectra was insufficient.

Future Tasks

- Identification of unknown peaks by simultaneous measurement using MS and IR spectra
- Examination of recovery rate and improvement on sample shape and loading method into vessels at extraction
- Investigation of extraction conditions and reduction of influence on peak shape in chromatography
- Condensation by a trap column for high sensitive measurement

References

- M. Bounoshita et al, *Chromatography* (in Japanese), 2017, 38, Supp. 1, 36.
- M. Bounoshita et al, *Chromatography* (in Japanese), 2017, 38, Supp. 2, 74.