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Fast Screening of Pesticide Multiresidues in Aqueous Samples by Dual Stir Bar Sorptive Extraction (Dual SBSE) and Thermal Desorption – Fast GC/MS using a Modular Accelerated Column Heater (MACH)

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Dual stir bar sorptive extraction (Dual SBSE), thermal desorption (TD), fast GC/MS, Modular accelerated column heater (MACH), pesticide multiresidues, aqueous samples

Abstract
A method for fast screening of pesticide multiresidues in aqueous samples using dual stir bar sorptive extraction (dual SBSE) - thermal desorption (TD) - fast GC/MS has been developed. Recovery of 82 pesticides – organochlorine, carbamate, organophosphorous, pyrethroid and others – for the SBSE was evaluated as a function of octanol-water distribution coefficients (log $K_{o/w}$: 1.7-8.35), sample volume (2-20 mL), salt addition (0-30 % NaCl), and methanol addition (0-20 %). The optimized method consists of a dual SBSE performed simultaneously on respectively a 20-mL sample containing 30 % NaCl and a 20-mL sample without modifier (100 % sample solution). One extraction with 30 % NaCl is mainly targeting solutes with low $K_{o/w}$ (log $K_{o/w} < 3.5$) and another extraction with unmodified sample solution is targeting solutes with medium and high $K_{o/w}$ (log $K_{o/w} > 3.5$). After extraction, the two stir bars were placed in a single glass desorption liner and were simultaneously

desorbed. The desorbed compounds were analyzed by fast GC/MS using a modular accelerated column heater (MACH). The method showed good linearity ($r^2 > 0.9900$) and high sensitivity (limit of detection: < 10 ng/L) for most of the target pesticides. The method was applied to the determination of pesticides at ng/L levels in river water and brewed green tea.

INTRODUCTION

The determination of pesticide residues in environmental samples, e.g. water and soil, and in agricultural products has been a major subject for many years because of their potential impact on human health, their persistence and their tendency to bio-accumulate. In the past decade, sorptive extraction methods, e.g. solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE), which are simple, solvent-less techniques allowing the extraction and concentration in a single step, have been successfully applied to determination of pesticide residues in various sample matrices, e.g. water, soil and food [1-7]. These methods provide enhanced sensitivity because the extracted fraction (on a fiber or on a stir bar) can be introduced quantitatively into a GC system by thermal desorption. Moreover, the enrichment factor for SBSE, which is determined by the analyte recovery in the extraction phase (polydimethylsiloxane: PDMS), is up to 100 times higher than that of SPME. Several authors indicated that the SBSE method allows high recovery and extremely low limit of detection (LOD) at sub-ng/L level, particularly for solutes having hydrophobic characteristics [5-7].

SBSE recovery can be estimated if the octanol-water distribution coefficient ($K_{o/w}$) of the analyte is known. Hydrophobic solutes with a high $K_{o/w}$ can be extracted with high recovery, while hydrophilic solutes with a low $K_{o/w}$, e.g. polar pesticides, show lower recovery [2, 8]. To increase recovery of more hydrophilic solutes, one could employ salt addition, e.g. 20-30 % NaCl. However, salt addition resulted in decreasing recovery of more hydrophobic solutes [9, 10]. Salt addition in SBSE using a single stir bar will therefore have limited benefit when developing multiresidue methods that include pesticides of widely varying polarities. Recently, we proposed dual SBSE performed simultaneously on two aliquots of a sample under different extraction conditions using two stir bars [11]. Using the dual SBSE approach, one can optimize individually two extractions. In this case, dual SBSE was performed on respectively twofold and fivefold aqueous dilutions of a methanol extract from a non-fatty food sample. After extraction, two stir bars can be simultaneously desorbed with a thermal desorption system. For aqueous samples, one extraction can be optimized for hydrophilic solutes with salt addition [9, 10] and the other extraction can be optimized for more hydrophobic solutes with addition of an organic solvent such as methanol [12].

The SBSE method involves batch sample preparation (parallel extraction of up to 60 samples on one stir-plate, typically for 1 hour) and sequential analysis (separation and detection); sample throughput is mainly determined by the separation step. SBSE methods can therefore provide high sample throughput when combined with fast GC. Several fast GC systems with direct resistive heating have become commercially available in which a capillary column is inserted into a resistively heated metal tube or enclosed in a resistively heated toroid-formed assembly based on Low Thermal Mass (LTM) technology. The latter is commercially available under the name modular accelerated column heater (MACH). MACH systems provide fast temperature programming rates combined with rapid cool-down and short equilibration times for the shortest possible analytical cycle times. Using a MACH-GC system, one can achieve a maximal heating rate of 30°C/s and a cool-down time of less than one minute (e.g. from 280°C to 40°C) [13]. A MACH system can be directly integrated with conventional GC instruments to allow full use of conventional injectors, detectors, sampling systems, and software.

The aim of this study was to optimize and validate dual SBSE for a wide range of solutes with different octanol-water partition coefficients (log $K_{o/w}$: 1.7-8.35) at ultra trace levels (ng/L) in aqueous samples. A fast GC/MS system with MACH and quadrupole MS (qMS) was used in order to provide high sample throughput in combination with dual SBSE.

EXPERIMENTAL

Material. Two standard solutions of 47 and 50 pesticide mixtures at 10 µg/mL each in acetone were purchased from Kanto Kagaku (Tokyo, Japan). Some pesticides in stock solutions are composed of several isomers: bitertanol 1, 2; E, Z-chlorofenvinphos; cyfluthrin 1, 2, 3, 4; cyhalothrin 1, 2; cypermethrin 1, 2, 3, 4; difenoconazole 1, 2; fenvalerate 1, 2; flucythrinate 1, 2; fluvalinate 1, 2; fosthiazate 1, 2; permethrin 1, 2; propiconazole 1, 2; and triadimenol 1, 2. For these compounds, the concentration (10 µg/mL) is the

sum of the concentrations of the individual isomers. Stock standard solutions were then mixed and diluted with acetone to prepare a test mixture containing 97 solutes (82 and 15 isomeric analogues). According to a previous study [11], fifteen pesticides out of these test solutes showed very high standard deviations (RSD > 20 %) or could not be detected in extracts or in direct analysis (TD-GC-MS) at all. These 15 solutes were, therefore, excluded and the remaining 82 solutes were selected for the present study. The list of 82 solutes is given in Table 1. The stock standard solutions were kept at –20°C. Acetone and Methanol, pesticide residues grade, were purchased from Kanto Kagaku. Sodium chloride (NaCl), reagent grade, was also purchased from Kanto Kagaku and baked at 350°C for several hours before use. River water samples were drawn in 1 L glass bottles at Tama River (Tamagahara and Gas-bashi). Green tea samples were obtained from a local store in Tokyo Japan.

Table 1. Pesticides studied and corresponding octanol-water partitioning coefficients (log $K_{o/w}$), selected ions for quantification, linearity, limit of detection (LOD) and recovery obtained for Dual SBSE - TD - fast GC/MS analysis of spiked natural water

No.	Compounds	Log $K_{o/w}$[a]	m/z[b]	r^2 (25-1000 ng/L)[c]	LOD[d] (ng/L)	Recovery (%)[e]	RSD (%) (n = 6)
OCPs							
1	β-BHC	3.68	217	0.9952	6.0	30	7.3
2	δ-BHC	3.68	217	0.9936	4.2	42	6.3
3	Chlorobenzilate	3.99	251	0.9975	1.4	51	4.8
4	α-BHC	4.26	217	0.9992	3.8	63	4.1
5	γ-BHC(Lindane)	4.26	217	0.9980	3.8	53	5.6
6	p,p-DDD	5.87	235	0.9954	1.5	38	5.5
7	p,p-DDE	6.00	246	0.9958	1.5	34	5.6
Carbamate pesticides							
8	Pirimicarb	1.70	238	0.9981	9.7	17	14
9	Bendiocarb	1.72	166	0.9957 [f]	60	12	11
10	Ethiofencarb	2.04	107	0.9520	33	5.3	11
11	Isoprocarb	2.30	121	0.9971	8.3	18	11
12	Fenobucarb	2.79	121	0.9993	3.0	26	10
13	Methiocarb	2.87	168	0.9979	13	32	12
14	Diethofencarb	3.29	267	0.9981	5.4	33	6.7
15	Chlorpropham	3.51	213	0.9968	4.3	48	6.8
16	Thiobencarb	3.90	100	0.9979	2.0	55	7.6
17	Esprocarb	4.58	222	0.9982	1.9	58	6.5
OPPs							
18	Dichlorvos	1.90	185	0.9874	6.4	18	10
19	Fensulfothion	2.35	293	0.9929	6.8	15	8.2
20	Parathion-methyl	2.75	263	0.9872	1.3	51	6.9
21	Malathion	2.75	173	0.9918	3.8	43	12
22	Thiometon	2.88	246	0.9993	4.8	51	8.4
23	Isofenphos oxon	2.89	229	0.9850	3.2	24	14
24	Etrimfos	2.94	292	0.9964	1.1	60	5.7
25	Quinalphos	3.04	298	0.9982	6.0	51	6.2
26	Dimethylvinphos	3.16	297	0.9944	5.0	33	6.7
27	Fenitrothion	3.30	277	0.9893	0.83	57	4.5
28	Pyraclofos	3.37	360	0.9836	9.4	31	11

No.	Compounds	Log $K_{o/w}$[a]	m/z[b]	r^2 (25-1000 ng/L)[c]	LOD[d] (ng/L)	Recovery (%)[e]	RSD (%) (n = 6)
OPPs							
29	Phenthoate	3.47	274	0.9938	2.1	48	7.9
30	Ethoprophos	3.59	158	0.9801	5.6	60	5.7
31	Edifenphos	3.61	310	0.9958	4.3	36	5.3
32	Parathion	3.73	291	0.9907	2.0	62	5.7
33	Diazinon	3.86	304	0.9979	0.83	54	6.2
34	Fenthion	4.08	278	0.9964	1.1	55	5.0
35	E,Z-Chlorofenvinphos	4.15	323	0.9975	3.0	43	7.0
36	Pirimiphos-methyl	4.20	290	0.9970	1.3	58	5.4
37	Terbufos	4.24	231	0.9946	0.58	53	9.4
38	Phosalone	4.29	182	0.9961	8.0	40	6.8
39	EPN	4.47	157	0.9920	2.5	44	7.9
40	Tolclofos-methyl	4.56	265	0.9973	0.86	59	5.3
41	Isofenphos	4.65	255	0.9971	3.8	49	4.7
42	Chlorpyrifos	4.66	314	0.9947	2.5	51	5.7
43	Cadusafos	5.48	159	0.9997	4.7	48	6.8
44	Prothiofos	5.69	309	0.9949	3.3	37	4.5
Pyrethroid pesticides							
45	Cyfluthrin 1,2,3,4	5.74	226	0.9930	45	21	7.9
46	Deltamethrin	6.18	253	0.9698 [f]	100	11	12
47	Cypermethrin 1,2,3,4	6.38	181	0.9966	15	23	6.5
48	Flucythrinate 1,2	6.56	199	0.9961	11	20	7.6
49	Acrinathrin	6.73	181	0.9764	15	15	12
50	Fenvalerate 1,2	6.76	167	0.9962	19	21	6.2
51	Fluvalinate 1,2	6.81	250	0.9967	11	17	11
52	Cyhalothrin 1,2	6.85	181	0.9885	10	25	9.1
53	Tefluthrin	7.19	197	0.9969	4.7	33	6.1
54	Permrthrin 1.2	7.43	183	0.9952	3.1	24	8.5
55	Halfenprox	8.35	263	0.9952	5.6	17	11
Other pesticides							
56	Benfuresate	2.80	163	0.9955	1.1	36	8.9
57	Mefenacet	2.80	192	0.9928	6.7	24	8.1
58	Cyproconazole	2.91	222	0.9927	4.7	20	8.2
59	EPTC	3.02	128	0.9992	2.5	65	6.3
60	Metolachlor	3.24	238	0.9944	2.0	37	5.3
61	Chinomethionate	3.37	234	0.9965	1.9	49	5.4
62	Mycrobutanil	3.50	179	0.9967	8.3	19	7.6
63	Thenylchlor	3.53	288	0.9943	3.3	33	5.4
64	Fenarimol	3.62	251	0.9926	19	22	8.7
65	Butylate	3.85	217	0.9983	0.89	72	4.6
66	Tebconazole	3.89	250	0.9972	8.7	22	7.8
67	Bitertanol 1,2	4.07	170	0.9955	4.2	18	11
68	Propiconazole 1,2	4.13	173	0.9942	5.6	42	8.2
69	E-Pyrifenox	4.20	262	0.9942	1.5	60	7

No.	Compounds	Log $K_{o/w}$[a]	m/z[b]	r^2 (25-1000 ng/L)[c]	LOD[d] (ng/L)	Recovery (%)[e]	RSD (%) (n = 6)
Other pesticides							
70	Z-Pyrifenox	4.20	262	0.9950	1.9	56	6.6
71	Mepronil	4.24	119	0.994	2.5	31	6.0
72	Pretilachlor	4.29	238	0.9948	2.5	50	7.0
73	Pyrimidifen	4.59	184	0.9953	1.9	24	6.3
74	Tebufenpyrad	4.61	318	0.9962	2.1	40	6.8
75	Flutolanil	4.65	323	0.9927	3.8	36	6.1
76	Flusilazole	4.89	233	0.9940	0.90	45	7.1
77	Pendimethalin	5.18	252	0.9861	2.1	53	6.5
78	Difenoconazole 1,2	5.20	323	0.9778	13	28	8.2
79	Pyridaben	5.47	364	0.997	4.7	25	11
80	Pyriproxyfen	5.55	136	0.9967	1.2	35	8.4
81	Imibenconazole	5.64	125	0.9609 [f]	25	37	7.0
82	Silafluofen	8.20	286	0.9976	3.8	15	7.6

[a] Log Ko/w values are calculated with SRC-KOWWIN software according to reference [14]
[b] Selected ion for quantification
[c] Linear range of calibration curve
[d] The LOD was calculated as signal-to-noise ratio = 3.
[e] The absolute recovery was assessed by six replicate analyses of the spiked natural mineral water at 100 ng/L.
[f] Linear range was 100-1000 ng/L.
Red values show less than 0.9900 (r^2).

INSTRUMENTATION

Stir bars coated with 24 µL of PDMS (Twister®) were obtained from GERSTEL® (Mülheim an der Ruhr, Germany). For SBSE, 20 mL headspace vial with screw cap containing PTFE-coated silicone septa (GERSTEL) were used. SBSE was performed with a multiple position magnetic stirrer (20 positions) from Global Change (Tokyo, Japan). The TD - LTM - GC/MS analysis was performed on a system consisting of a TDU thermal-desorption unit (GERSTEL) equipped with an MPS 2 autosampler (GERSTEL), a CIS 4 programmed temperature vaporization (PTV) inlet (GERSTEL) and a MACH system (GERSTEL) installed on an Agilent 6890N gas chromatograph with a 5975 mass-selective detector (Agilent Technologies). The MACH system consists of a wide format column module (5 inch), heated transfer lines, cooling fan, temperature controller, power supply, and a specially constructed GC oven door.

Sample preparation. Brewed green tea samples were prepared by suspending green tea (1.25 g) in 200 mL of boiling water for 5 min. Four fractions of the infusion were placed in closed 50 mL vials and centrifuged for 5 min at 3000 rpm. Water samples and brewed green tea samples (supernatant) were divided into several portions placed in separate flasks. NaCl (0-30 %) or methanol (0-20 %) was added to each flask and dissolved or mixed respectively. Aliquots of twenty milliliters of each sample containing various percentages of NaCl or methanol were transferred to 20 mL headspace vials. The optimal conditions were determined to be a combination of two twenty mL aliquots of a sample, containing 30 % NaCl and 0 % methanol (unmodified sample solution) respectively for extraction of hydrophilic and hydrophobic compounds. To each 20 mL sample, a stir bar was added and the vial was capped with a screw cap. SBSE was simultaneously performed at room temperature (24°C) for 60 min while stirring at 1500 rpm. After extraction, the stir bars were removed with forceps, dipped briefly in Milli-Q water, dried with a lint-free tissue, and placed in a glass liner for thermal desorption. The glass liner was then placed in the thermal desorption unit. No further sample preparation was necessary. Figure 1 shows a dual SBSE procedure for aqueous samples.

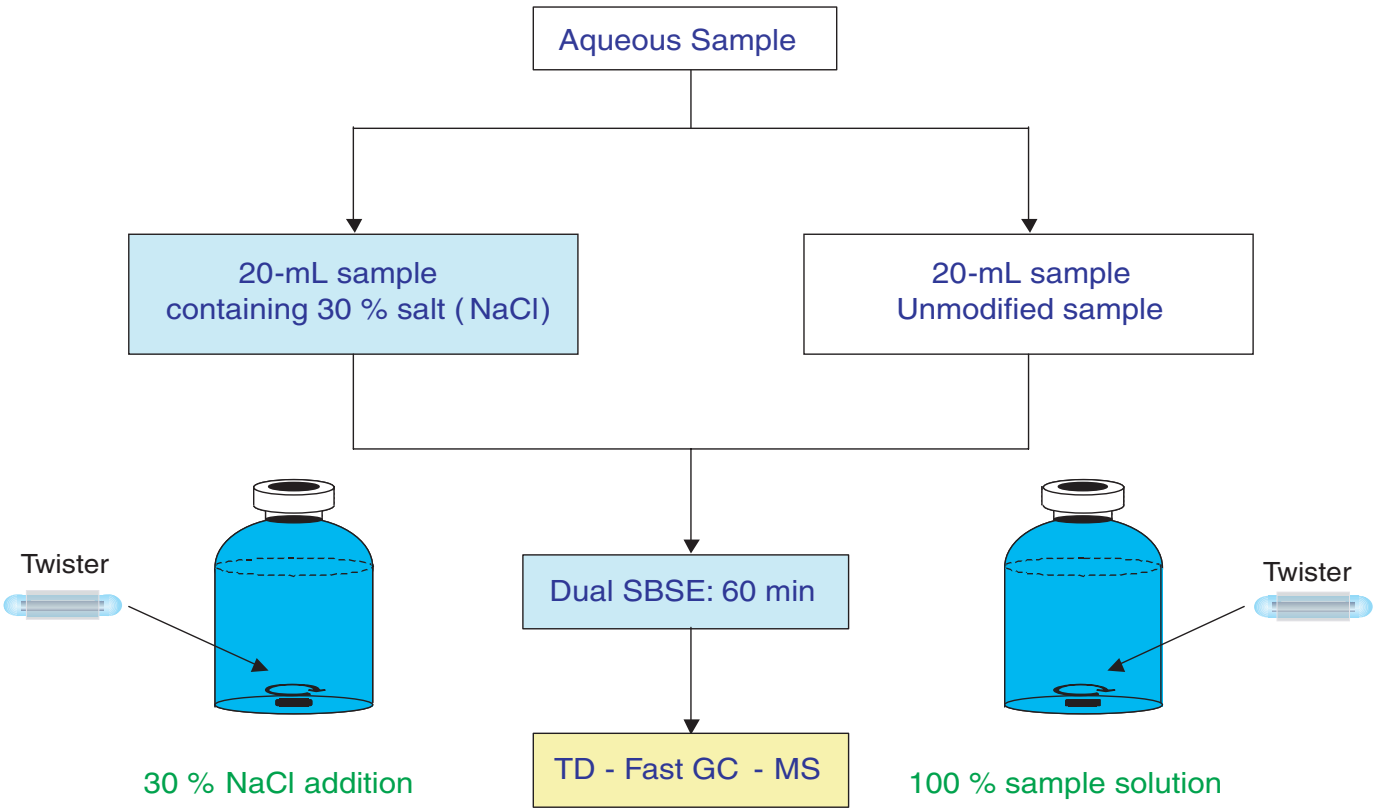

Figure 1. Dual SBSE procedure for aqueous samples.

Reconditioning of the stir bars was performed by soaking them in Milli-Q purified water and a mixture of methylene chloride-methanol (1:1) for 24 h each ; stir bars were then removed from the solvent and dried on a clean surface at room temperature for 1 h. Finally, the stir bars were thermally conditioned for 30 min at 300°C in a flow of helium. Typically, 30 extractions could be performed with the same stir bar.

TD – fast GC/MS. Each stir bar was thermally desorbed by programming the TDU from 40°C (held for 0.5 min) to 280°C (held for 5 min) at 720°C/min with 50 mL/min desorption flow. Desorbed compounds were cryo-focused in the PTV inlet at –100°C on a quartz wool packed liner for subsequent GC-MS analysis. The PTV inlet was subsequently programmed from –100°C to 280°C (held for 5 min) at 720°C/min to inject trapped compounds onto the analytical column. Injection was performed in the splitless mode with a 2 minute splitless time. The separation was performed on a DB-5 fused silica capillary column (10 m x 0.18 mm i.d., 0.18 µm film thickness, Agilent Technologies), which was coiled and packed together with heating wire, sensor, and ceramic fibers in a MACH column module (wide format, 5 inch module). The column was connected to the GC inlet with a 1 m long 0.32 mm I.D. fused silica capillary and to the MS with a 1m long 0.18 mm I.D. fused silica capillary, using press-fit connectors on both sides. The column temperature was programmed from 40°C (held for 2 min) at 75°C/min to 300°C (held for 2 min). Helium was used as carrier gas. The column head pressure was programmed from 82 kPa (held for 2 min) at 36 kPa/min to 207 kPa (held for 2 min) to maintain a carrier gas flow of approximately 1.1 mL/min during the MACH temperature program. The host GC oven and MS interface were kept at a constant temperature of 250°C. The mass spectrometer was operated in scan mode using electron-impact ionization (electron-accelerating voltage: 70V). Scan range was set from m/z 58 to 510 and sampling rate of zero, resulting in scan rate of 10.83 scan/s. The selected ions for determination are shown in Table 1.

Results and Discussion

SBSE method development. To optimize extraction conditions for SBSE, we first examined the effect of sample volume on SBSE using a single stir bar. Four different sample volumes of natural water from 2 to 20 mL were fortified at 5 ng/mL for all solutes. SBSE was performed for 60 min at ambient temperature [11] and each extraction was performed in duplicate during method development. Experimental recovery was calculated by comparing peak areas with those of

a direct analysis of a standard solution for calibration curves, which was spiked on quartz wool placed in an empty thermal desorption liner. Log $K_{O/W}$ values were calculated with a SRC-KOWWIN software package (Syracuse Research, Syracuse, NY, USA) according to a fragment constant estimation methodology [15] for all analytes. Figure 2 shows the influence of sample volume on SBSE recovery for pesticides representing various log $K_{O/W}$ values (1.70-7.43). For all solutes, percent recovery increased as sample volume decreased. The highest recovery obtained for the smallest sample volume of 2 mL were in the range of 3.9 to 107 % (> 80 %: 42 solutes; 60-80 %: 20 solutes; < 60 %: 20 solutes). This is mainly due to the small sample/PDMS phase ratio (ß = 83) of the 2 mL sample [15, 16]. Moreover, the sample is exposed to less glass surface and adsorption of more hydrophobic solutes onto the glass wall of the extraction vessel could be minimized . However, for most of the solutes, the actual extraction quantity increased with increasing sample volume, particularly for solutes having log $K_{O/W}$ in the range of 3 to 6 (Figure 3). In order to obtain LOD as low as possible, we selected a sample volume of 20 mL for further work.

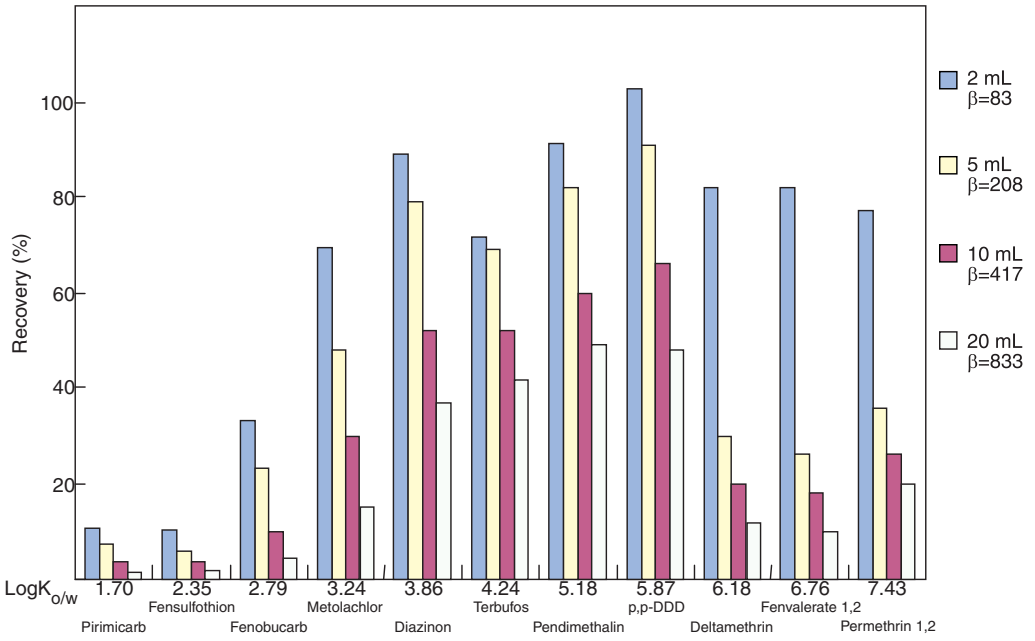

Figure 2. Influence of sample volume (phase ratio: ß = water / PDMS) on SBSE recovery of pesticides from fortified natural water samples at the 5 ng/mL level. The pesticides cover a range of octanol-water partitioning coefficients (log $K_{O/W}$).

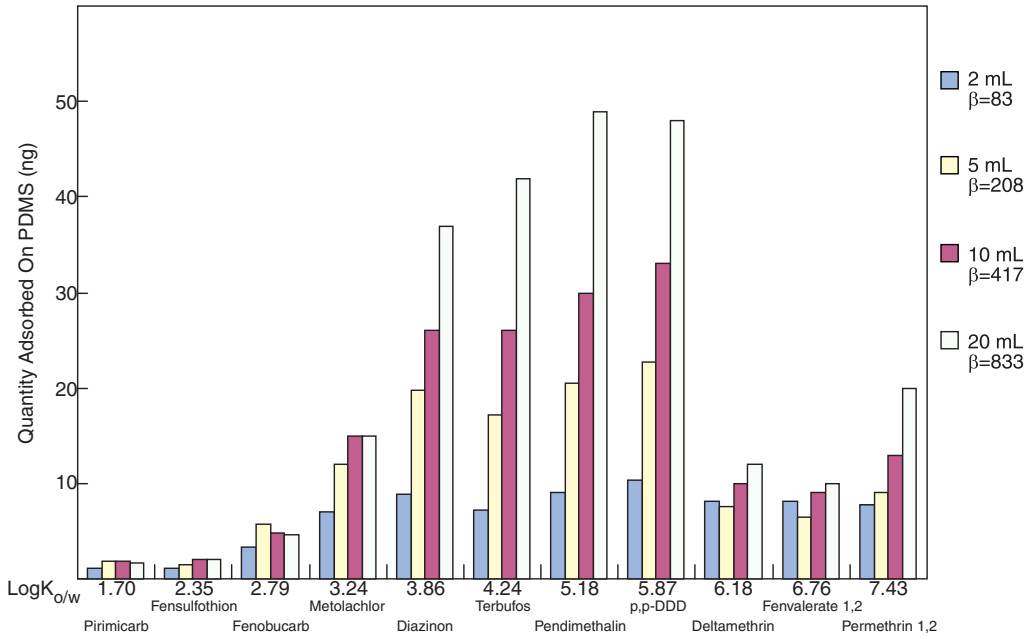

Figure 3. Influence of sample volume (phase ratio: ß = water / PDMS) on quantity extracted from fortified natural water samples at the 5 ng/mL level. The pesticides cover a range of octanol-water partitioning coefficients (log $K_{O/W}$).

Since hydrophilic pesticides are high on the priority list of pesticide monitoring [17], extraction efficiency of SBSE should be optimized for hydrophilic solutes. The effect of salt addition (NaCl: 0-30 %) on SBSE using a single stir bar was examined with fortified natural water at 0.5 ng/mL for all solutes. As several authors have already described [9, 10], recovery for more hydrophilic solutes (log $K_{o/w} < 3.5$) dramatically increased on increasing concentration of NaCl; however, recovery for more hydrophobic solutes (log $K_{o/w} > 5$) drastically decreased, particularly with higher concentrations of NaCl (Figure 4). To compensate for the negative effect of salt addition, we examined the dual SBSE approach with fortified river water at 0.5 ng/mL for all solutes. One extraction was performed with 30 % NaCl for hydrophilic solutes and another extraction was performed with 0-20 % methanol for hydrophobic solutes. Dual SBSE of unmodified sample solution was also performed as a control. Although the absolute recovery of solutes with log $K_{o/w} > 3.5$, was highest with dual SBSE from unmodified sample, the combined approach could compensate the negative effect of the salt for hydrophobic solutes with log $K_{o/w} > 5.0$, while maintaining increased recovery for hydrophilic solutes with 30 % NaCl, as shown in Figure 5.

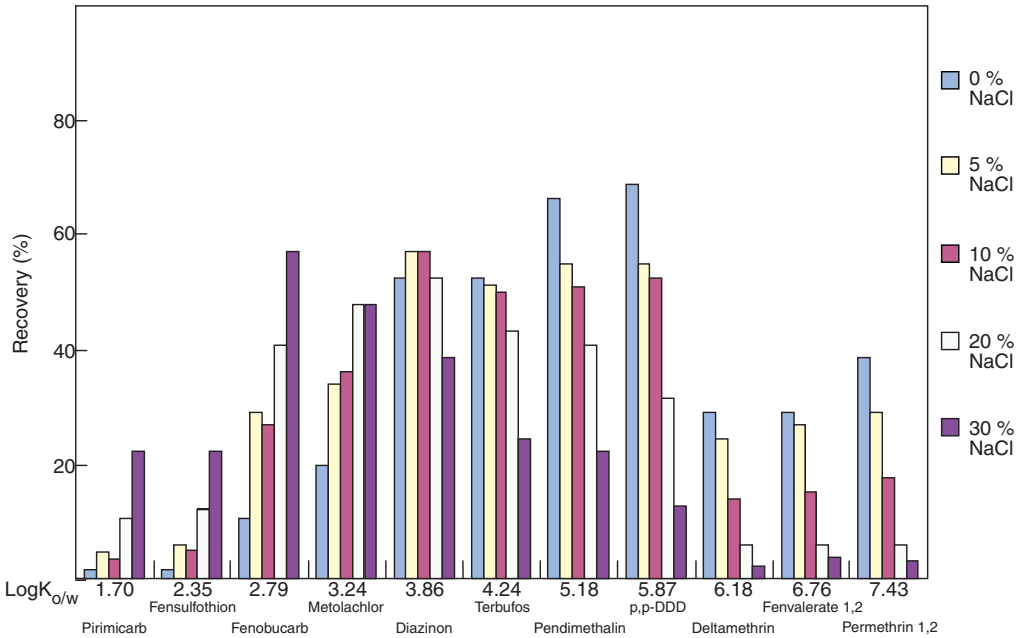

Figure 4. Influence of salt addition (NaCl 0-30 %) on SBSE recovery of pesticides from fortified natural water samples at the 5 ng/mL level. The pesticides cover a range of octanol-water partitioning coefficients (log $K_{o/w}$).

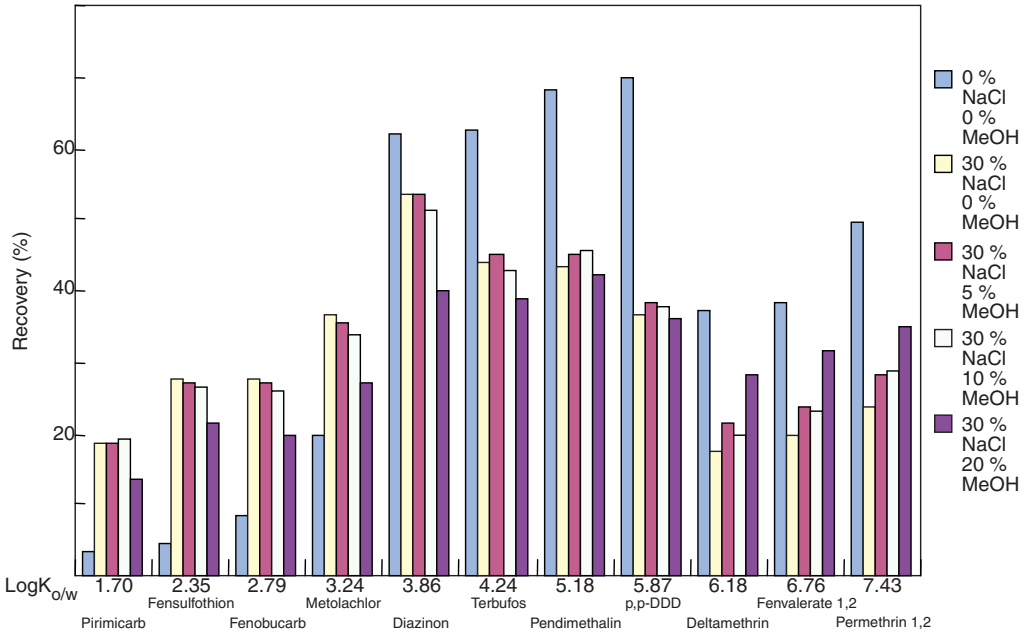

Figure 5. Influence of salt addition (NaCl 0 or 30 %) and methanol addition (MeOH 0-20 %) on Dual SBSE recovery of pesticides from fortified natural water samples at the 5 ng/mL level. The pesticides cover a range of octanol-water partitioning coefficients (log $K_{o/w}$).

The results show that the combined approach gives the most uniform enrichment over the entire polarity/volatility range for pesticide residues. Addition of 5-10 % methanol did not appreciably change recovery for either hydrophilic or hydrophobic solutes; however, a higher concentration of methanol (20 %) reduced recovery of the hydrophilic solutes, while improving recovery of hydrophobic solutes by reducing adsorption onto the glass wall of the extraction vessel. [11]. Dual SBSE with the combination of 30 % NaCl and unmodified sample solution was selected for further work because of the desirable enrichment of hydrophilic solutes and simple operation. Figure 6 shows a typical total ion chromatogram (TIC) and some representative mass chromatograms obtained by the dual SBSE - TD – fast GC/MS of a fortified river water sample at 0.5 ng/mL.

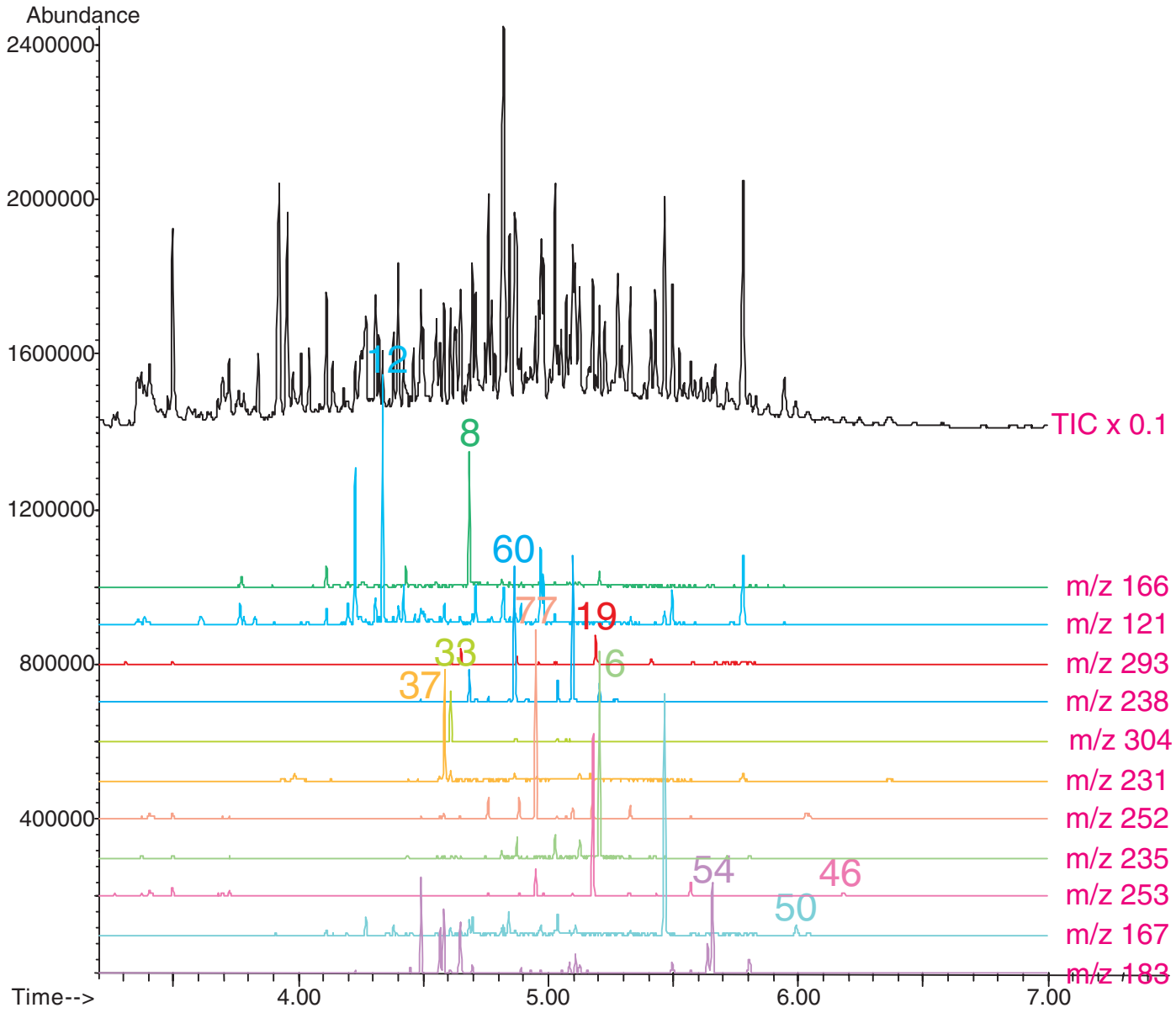

Figure 6. Total ion chromatogram and some representative mass chromatograms obtained by Dual SBSE - TD – fast GC/MS of a river water sample fortified with 82 pesticides at the 0.5 ng/mL level. 8. Pirimicarb (m/z 166; log $K_{o/w}$ = 1.70); 19. Fensulfothion (m/z 293; log $K_{o/w}$ = 2.35); 12. Fenobucarb (m/z 121; log $K_{o/w}$ = 2.79); 60. Metolachlor (m/z 238; log $K_{o/w}$ = 3.24); 33. Diazinon (m/z 304; log $K_{o/w}$ = 3.86); 37. Terbufos (m/z 231; log $K_{o/w}$ = 4.24); 77. Pendimehalin (m/z 252; log $K_{o/w}$ = 5.18); 6. p,p-DDD (m/z 235; log $K_{o/w}$ = 5.87); 46. Deltamethrin (m/z 253; log $K_{o/w}$ = 6.18); 50. Fenvalerate 1,2 (m/z 167; log $K_{o/w}$ = 6.76); 54. Permethrin 1,2 (m/z 183; log $K_{o/w}$ = 7.43)

Method validation and screening of pesticide in river water and brewed tea samples. To validate the dual SBSE method, we evaluated linearity at seven concentration levels between 25 and 1000 ng/L in natural water. For each level, duplicate analyses were performed. For 69 solutes, good linearity was achieved with a correlation coefficient (r^2) above 0.9900. For 13 solutes, the r^2 were in the range of 0.9520-0.9893. The signal-to-noise ratio obtained for the lowest level sample was used to calculate the LOD at a signal-to-noise ratio of three. For 69 compounds, very low LOD in the range of 0.58-10 ng/L was obtained. For 13 solutes, LOD was in the range of 11-100 ng/L. Absolute recovery was also assessed by replicate analyses (n=6) of fortified natural water sample at 100 ng/L. Each recovery was calculated by comparing peak areas with those of a direct analysis of a standard solution for calibration curves, which was spiked on quartz wool placed in an empty thermal desorption liner. The recovery was in the range of 11-72 % with low relative standard deviation (RSD) in the range of 4.1-14 %. Validation of the method is listed in Table 1.

Finally, the method was applied to several river water samples and brewed green tea samples. Determination of pesticides was carried out using standard addition calibration. Figure 7 shows typical chromatograms of river water (Tama River taken at Tamagahara). Although fenobucarb (log $K_{o/w}$ = 2.79) and diazinon (log $K_{o/w}$ = 3.86) were present at ultra trace levels (16 and 4.9 ng/L, respectively), well-defined mass chromatograms for both pesticides were obtained without interference from matrix compounds at acceptable precision (RSD 8.7 % and 12 %, respectively, n = 5).

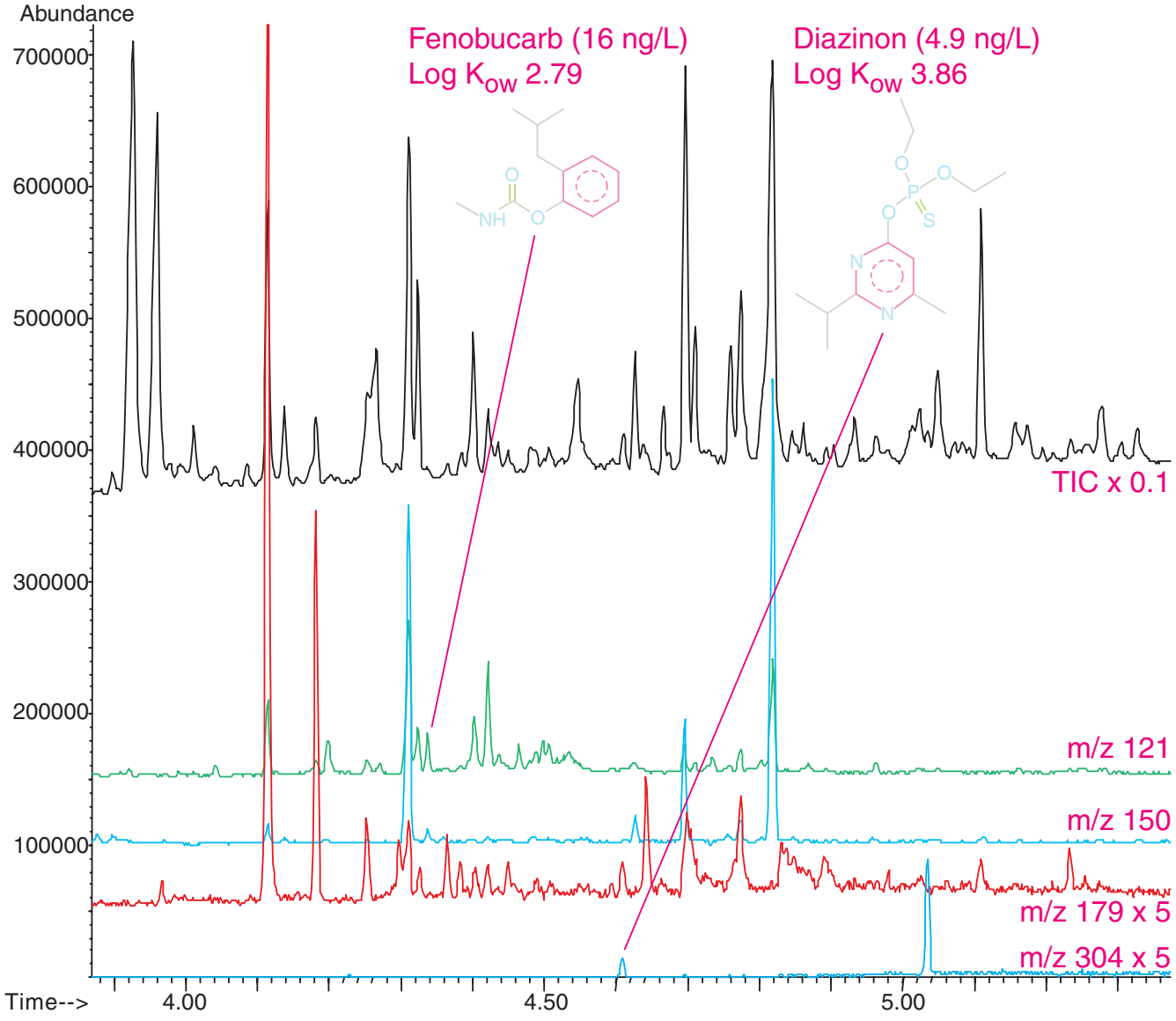

Figure 7. Total ion chromatogram and mass chromatograms obtained by Dual SBSE - TD – fast GC/MS of a river water sample (Tama River taken at Tamagahara). 12. Fenobucarb (m/z 121, 150; log $K_{o/w}$ = 2.79; 16 ng/L, RSD 8.7 %, n = 5), 33. Diazinon (m/z 179, 304; log $K_{o/w}$ = 3.86; 4.9 ng/L, RSD 12 %, n = 5).

A brewed green tea sample was found to contain pirimiphos-methyl (log $K_{o/w}$ = 4.20; 10 ng/L, RSD 7.8 %, n = 5) and tebuconazole (log $K_{o/w}$ = 3.89; 240 ng/L, RSD 8.1 %, n = 5) (Figure 8).

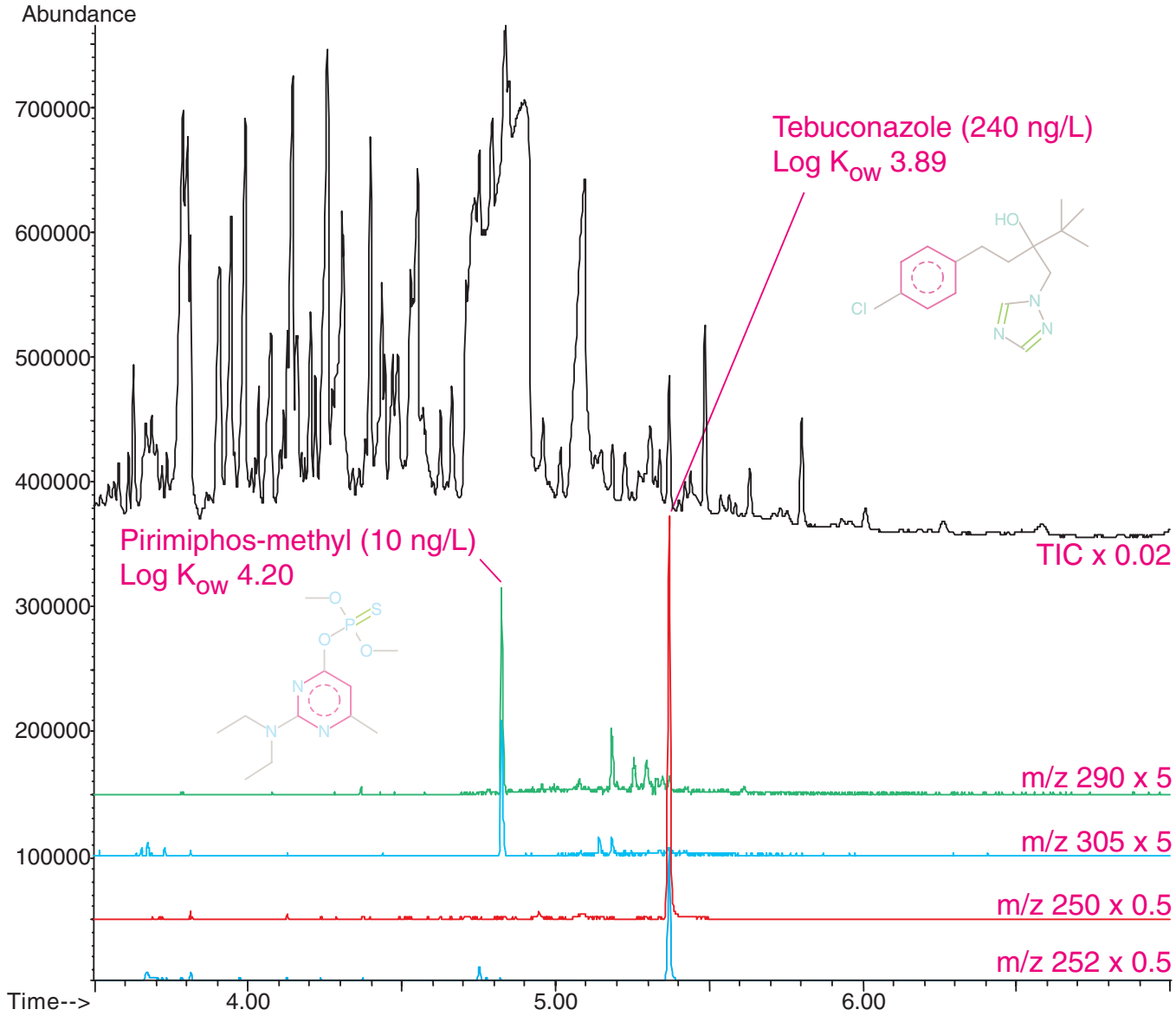

Figure 8. Total ion chromatogram and mass chromatograms obtained by Dual SBSE - TD – fast GC/MS of a brewed green tea sample. 36. Pirimiphos-methyl (m/z 290, 305; log $K_{o/w}$ = 4.20; 10 ng/L, RSD 7.8 %, n = 5), 66. Tebuconazole (m/z 250, 252; log $K_{o/w}$ = 3.89; 240 ng/L, RSD 8.1 %, n = 5).

Conclusion

A Dual SBSE - TD – fast GC/MS method for fast screening of 82 commonly used pesticides in aqueous samples has been described. By using dual SBSE with a combination of 30 % NaCl and unmodified sample solution, a wide range of solutes with different polarities can be extracted and enriched, while the negative effect of salt addition on hydrophobic solute recovery is minimized. Also, the method provides high sensitivity with remarkable precision, and rapid analysis resulting in high sample throughput. Moreover, the method allows determination of ng/L levels of pesticides in river water and brewed green tea samples with low RSD (7.8-12 %, n = 5).

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