Determination of Anilines in River Water, Sediment, and Fish Samples by Gas Chromatography–Mass Spectrometry

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Abstract

Traces of aniline and its methyl, methoxyl, and chloro derivatives in river water, sediment, and fish samples were determined by capillary gas chromatography–mass spectrometry after liquid–liquid extraction and steam distillation. Anilines in the concentration range of 0.03–0.10 ng/mL in water could be determined with relative standard deviations of 1.1–22.1%. The detection limits of the anilines in water, sediment, and fish samples were 0.0042–0.031 ng/mL, 1.2–4.0 ng/g, and 0.5–1.7 ng/g, respectively. Their recoveries from river water, sediment, and fish samples (except for 3,4-xylidine, *m*-anisidine, and *p*-anisidine) were 101–121%, 71–136%, and 83–117% with percent relative standard deviations of 2.0–11.9%, 6.4–32.5%, and 3.2–9.7%, respectively.

Introduction

Anilines have been widely used as intermediates in the synthesis of dyes, perfumes, synthetic resins, pesticides, and drugs. They may be present in the environment as a result of industrial discharge from factories that use anilines as intermediates or as a result of the degradation of some herbicides. Several aromatic amines are known to be toxic and are suspected to have induced bladder cancer in factory workers who manufacture dyestuff. Chromatographic methods such as gas chromatography (GC) (1–4), supercritical fluid chromatography (5), and liquid chromatography (6–8) are extensively used for the identification and determination of anilines. Several analytical schemes for the extraction, concentration, and detection of these compounds in water have been appeared in the literature (2,7,8). However, it is difficult to determine traces amounts of anilines due to various kinds of interfering substances in sediment and biota samples.

Recently developed techniques that pair selected ion monitoring (SIM) with gas chromatography–mass spectrometry (GC–MS) have provided excellent sensitivity and selectivity. Because anilines are basic, relatively volatile, and hydrophilic, steam distillation and acid extraction may be suitable techniques to pretreat environmental samples. This paper reports a simple, reproducible method for the determination of anilines in water, sediment, and fish samples at picogram-per-milliliter or nanogram-per-gram levels by capillary GC–MS–SIM.

Experimental

Reagents and apparatus

The following reagents were obtained from Wako (Osaka, Japan) and Tokyo Kasei (Tokyo, Japan): authentic standards of anilines; dichloromethane, ethanol, anhydrous sodium sulfate, and sodium chloride of pesticide grade; and other high-grade reagents. [$^2H_5$]Aniline (aniline-d_5) and [$^2H_8$]naphthalene (naphthalene-d_8) were used as surrogates or internal standards and were obtained from Aldrich (Milwaukee, WI).

A Waters 600E liquid chromatograph (Bedford, MA) and a Nihonbunko 870-UV absorbance detector (Tokyo, Japan) adjusted to 240 nm were employed to estimate the degradation of the anilines. A 25-cm × 4.6-mm i.d. stainless steel column packed with Develosil ODS-5 (Nomura Kagaku; Aichi, Japan) was used. The mobile phase was acetonitrile–water (40:60), and the flow rate was 1.0 mL/min. Steam distillation equipment was used for distillation of analytes from sediment and fish samples. A Poly Toron PT10-30 homogenizer and a Tomy Seiko LCO6-SP centrifuge (Tokyo, Japan) were employed for fish samples.

Gas chromatography–mass spectrometry

A Hewlett-Packard 5790 GC (Avondale, PA) and a Nihondenshi JEOL-DX303 MS (Tokyo, Japan) with a DA-5000 data processing system were employed. The analytical column used was a Carbowax 20M (25 m × 0.32-mm i.d., 0.3-µm film thickness). The GC temperature program was as follows. The initial temperature was 50°C. It was held for 3 min then increased at 5°C/min to 185°C. The temperatures of the injector, transfer line, and ion source were 250°C, 250°C, and 270°C, respectively. The carrier gas was helium at 2.0 mL/min (7.5 psi). The mass

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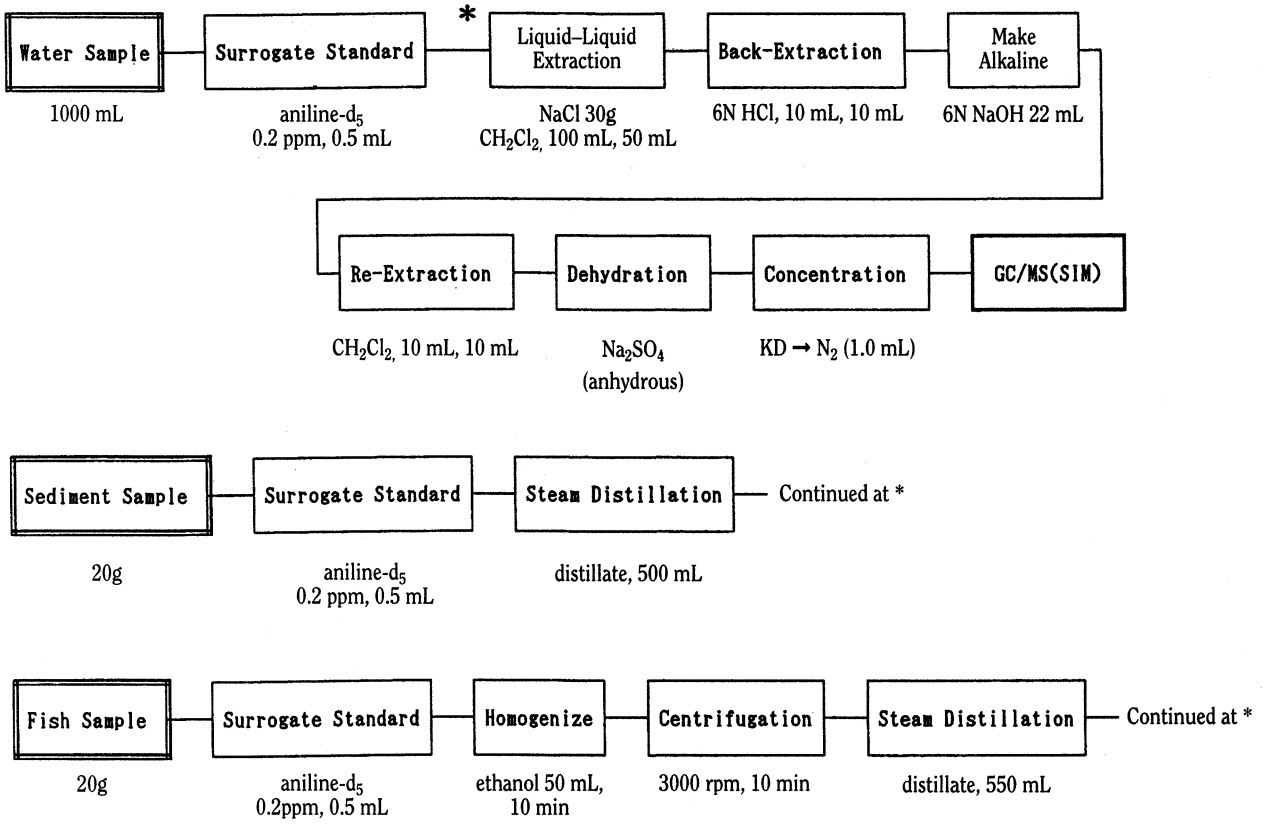

Figure 1. Flow chart for the analytical procedure of the anilines in environmental samples.

Table I. Degradation Test for the Anilines at pH 5, 7, and 9

	pH*	Conc. (mg/L)	Residual (%) After 1 h	Residual (%) After 5 days Dark	Residual (%) After 5 days Light
Aniline	5	53	98	100	–
	7	53	100	104	96
	9	53	98	98	–
2,3-Xylidine	5	61	99	97	–
	7	61	99	95	95
	9	61	99	97	–
2,4-Xylidine	5	50	98	96	–
	7	50	103	100	94
	9	50	102	98	–
3,4-Xylidine	5	56	96	96	–
	7	56	101	102	96
	9	56	102	100	–
o-Anisidine	5	78	95	92	–
	7	78	100	96	94
	9	78	104	100	–
m-Anisidine	5	73	96	100	–
	7	73	98	99	95
	9	73	102	101	–
p-Anisidine	5	57	95	68	–
	7	57	117	100	86
	9	57	119	107	–
o-Chloroaniline	5	59	99	97	–
	7	59	99	95	95
	9	59	99	97	–
m-Chloroaniline	5	69	97	96	–
	7	69	99	97	96
	9	69	99	99	–
p-Chloroaniline	5	78	99	99	–
	7	78	100	101	96
	9	78	99	97	–

* The following concentrations were used: pH 5, 65mM KH_2PO_4; pH 7, 65mM KH_2PO_4–65mM Na_2HPO_4 (4:6); pH 9, 65mM Na_2HPO_4.

spectrometer was operated at 70 eV and 300 µA in the electron-impact mode of SIM. The following ions were monitored: aniline (*m/z* 93), xylidines (*m/z* 106, 121), anisidines (*m/z* 108, 123), chloroanilines (*m/z* 127, 129), aniline-d_5 (*m/z* 98), and naphthalene-d_8 (*m/z* 136).

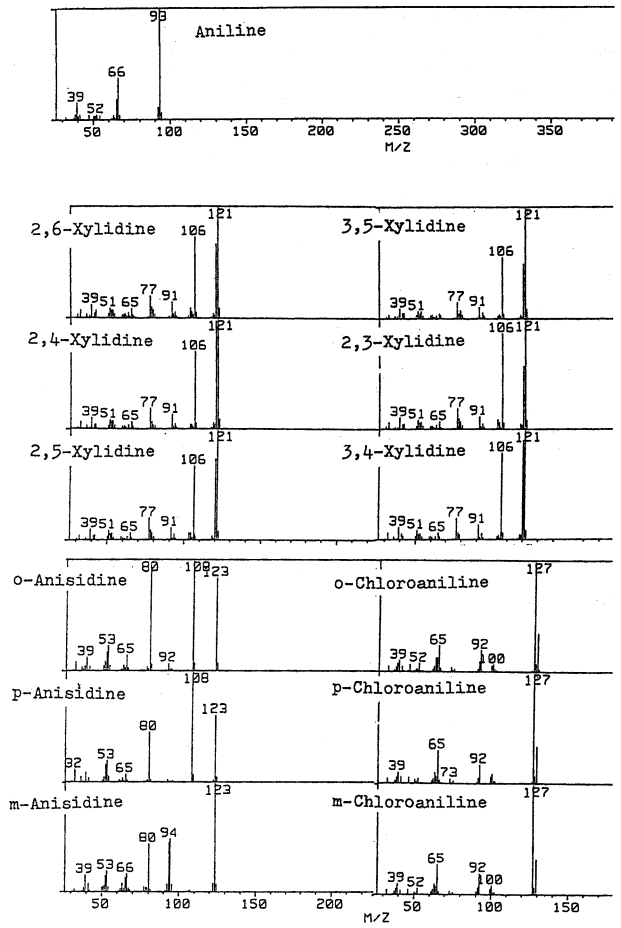

Figure 2. GC–MS spectra of aniline.

Analytical procedure

The pretreatment procedure for the determination of anilines in environmental samples is outlined in Figure 1. A water sample (1000 mL) was placed into a separatory funnel with 30 g NaCl, 100 mL CH_2Cl_2, and the surrogate standard (0.2 ppm aniline-d_5 in CH_2Cl_2, 0.5 mL). The sample was extracted twice with CH_2Cl_2 (100 mL and 50 mL). The organic phases were combined and extracted with two separate 10-mL portions of 6N HCl. The 6N HCl solutions were combined, and 22 mL 6N NaOH was added slowly while the mixture was cooled in an ice bath. The aqueous solution was extracted with two separate 10-mL portions of CH_2Cl_2. The organic phases were combined and dehydrated using anhydrous Na_2SO_4. The dichloromethane phase was concentrated to 3–5 mL by a Kuderna–Danish (KD) evaporative concentrator at atmospheric pressure. The solution was further evaporated to a volume of 1.0 mL under a nitrogen stream. An aliquot was analyzed by GC–MS–SIM.

For sediment samples, a 20-g sample was fortified with the surrogate standard, and 30 mL of pure water was added to the

Table II. Stability of Anilines in River Water

Compound	Conc. (ng/mL)	After 4 days Normal* (ng/mL)	After 4 days Acidic† (ng/mL)
Aniline	0.10	0.05	0.14
2,3-Xylidine	0.10	0.11	0.01
2,4-Xylidine	0.10	0.10	0.00
3,4-Xylidine	0.10	0.04	0.00
o-Anisidine	0.10	0.12	0.00
m-Anisidine	0.10	0.08	0.01
p-Anisidine	0.10	0.03	0.01
o-Chloroaniline	0.10	0.15	0.00
m-Chloroaniline	0.10	0.09	0.01
p-Chloroaniline	0.10	0.08	0.02

* One liter of river water.
† Two milliliters of 6N HCl added to 1 L of river water.

Table III. Percent Dichloromethane Extracted from Anilines at Different pHs

Compound	Conc. of sample† (ng/mL)	Percent dichloromethane pH 3.2	pH 6.5	pH 9.9	pH 10.8	pH 11.1
Aniline	0.5	20	82	83	86	81
2,3-Xylidine	0.5	55	96	95	100	93
2,4-Xylidine	0.5	46	97	96	107	95
3,4-Xylidine	0.5	27	98	102	106	103
o-Anisidine	0.5	51	108	106	108	101
m-Anisidine	0.5	37	88	90	89	87
p-Anisidine	0.5	36	72	78	82	76
o-Chloroaniline	0.5	89	85	88	90	85
m-Chloroaniline	0.5	84	92	92	93	90
p-Chloroaniline	0.5	68	90	91	91	90

* pH was adjusted with NaOH and HCl solution.
† 1000 mL of pure water was spiked with 500 ng of the anilines, and 30 g NaCl was added. The solution was extracted twice (100 mL and 50 mL) with dichloromethane.

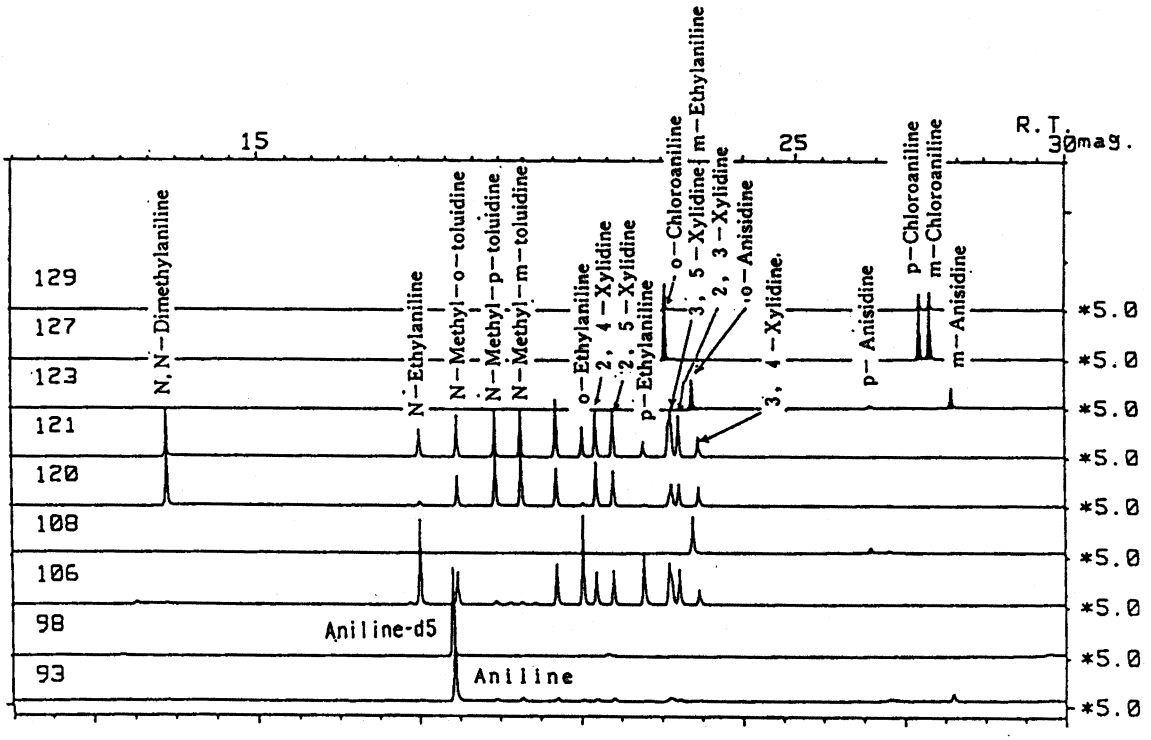

Figure 3. Typical GC–MS–SIM chromatograms of the anilines and the internal standards.

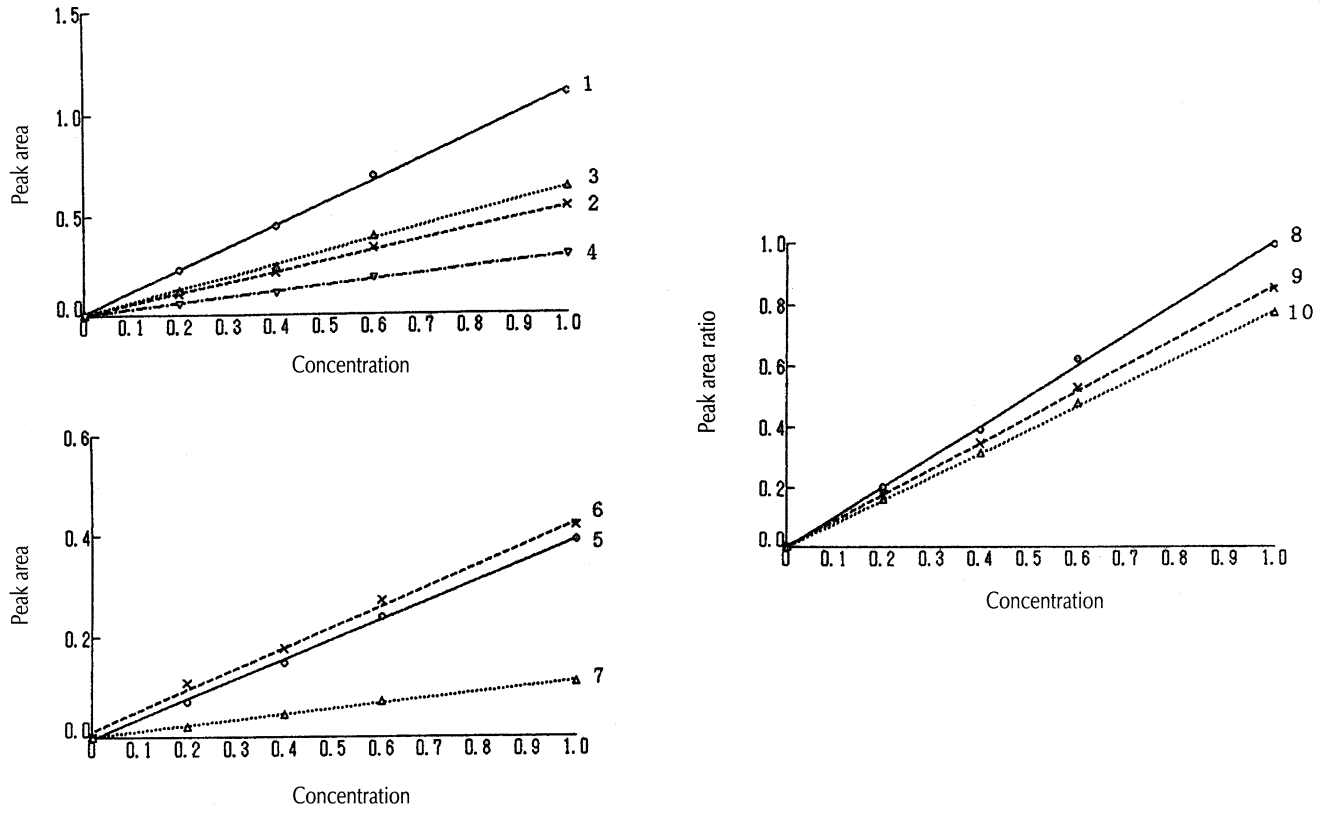

Figure 4. Typical calibration graphs of the anilines: 1, aniline; 2, 2,3-xylidine; 3, 2,4-xylidine; 4, 3,4-xylidine; 5, *o*-anisidine; 6, *m*-anisidine; 7, *p*-anisidine; 8, *o*-chloroaniline; 9, *m*-chloroaniline; 10, *p*-chloroaniline.

Table IV. Acid Extraction of the Anilines at Different HCl Concentrations

Compound	Amount (ng)	Normality of HCl solution (%) 0.1 N	0.5 N	1.0 N	1.5 N	2.0 N	3.0 N	6.0 N
Aniline	500	94	99	100	99	100	100	100
2,3-Xylidine	500	75	94	98	97	99	99	99
2,4-Xylidine	500	81	95	98	98	99	99	99
3,4-Xylidine	500	88	96	98	94	98	97	98
o-Anisidine	500	79	93	96	95	97	97	95
m-Anisidine	500	74	90	98	95	97	100	100
p-Anisidine	500	80	83	94	84	85	96	91
o-Chloroaniline	500	13	15	31	44	58	79	99
m-Chloroaniline	500	29	64	82	89	93	98	100
p-Chloroaniline	500	55	84	94	95	97	99	99

* Dichloromethane (150 mL) spiked with the anilines (500 ng) was extracted once with 20 mL of each normality of HCl.

Table V. Detection Limits (DL) and Precision for the Anilines in Water, Sediment, and Fish Samples

	Pure water				Sediment			Fish		
		Analytical precision				Analytical precision			Analytical precision	
	DL (ng/mL)	Conc. (ng/mL)	Response (n = 4)	RSD (%)	DL (ng/g)	Conc. (ng/g)	Found ± SD (ng/g, n = 7)	DL (ng/g)	Conc. (ng/g)	Found ± SD (ng/g, n = 7)
Aniline	0.0042	0.03	311	2.3	1.3	5.0	5.6 ± 0.42	0.8	5.0	4.2 ± 0.25
		0.05	496	1.1						
		0.10	985	1.4						
2,3-Xylidine	0.0072	0.03	154	3.3	2.4	5.0	5.3 ± 0.75	0.7	5.0	4.8 ± 0.22
		0.05	263	3.7						
		0.10	547	1.7						
2,4-Xylidine	0.0077	0.03	169	3.0	2.0	5.0	5.1 ± 0.64	0.5	5.0	4.8 ± 0.15
		0.05	294	3.5						
		0.10	608	2.2						
3,4-Xylidine	0.025	0.03	76	15.0	3.4	5.0	4.6 ± 1.07	1.6	5.0	2.6 ± 0.50
		0.05	146	10.4						
		0.10	327	6.0						
o-Anisidine	0.015	0.03	121	4.0	2.7	5.0	4.8 ± 0.87	1.3	5.0	4.3 ± 0.42
		0.05	193	7.0						
		0.10	380	4.5						
m-Anisidine	0.016	0.03	118	9.0	3.0	5.0	4.4 ± 0.96	1.7	5.0	2.4 ± 0.56
		0.05	177	6.6						
		0.10	333	4.4						
p-Anisidine	0.031	0.03	29	10.7	3.6	5.0	3.5 ± 1.15	–	5.0	–
		0.05	43	22.1						
		0.10	91	4.8						
o-Chloroaniline	0.0067	0.03	320	3.9	2.6	5.0	6.8 ± 0.83	1.0	5.0	5.8 ± 0.32
		0.05	492	2.2						
		0.10	937	1.9						
m-Chloroaniline	0.010	0.03	337	5.5	1. 2	5.0	5.8 ± 0.37	0.9	5.0	5.5 ± 0.29
		0.05	475	4.2						
		0.10	820	2.8						
p-Chloroaniline	0.014	0.03	278	3.2	4.0	5.0	6.4 ± 1.27	1.2	5.0	5.6 ± 0.38
		0.05	399	7.2						
		0.10	751	4.1						

Table VI. Recovery of the Anilines from Environmental Samples

Compound	Sample	Volume	*n*	Added (ng)	Recovery (%)	RSD (%)
Aniline	River water	1000 mL	3	100	101 (68)*	2.9 (4.2)*
	Sea water	1000 mL	3	100	104 (75)	3.0 (6.2)
	Sediment	20 g	7	100	111 (79)	7.5 (8.4)
	Fish	20 g	7	100	83 (39)	5.9 (11.3)
2,3-Xylidine	River water	1000 mL	3	100	115 (79)	2.0 (1.2)
	Sea water	1000 mL	3	100	101 (68)	3.7 (4.2)
	Sediment	20 g	7	100	107 (74)	14.1 (6.3)
	Fish	20 g	7	100	96 (36)	4.5 (13.9)
2,4-Xylidine	River water	1000 mL	3	100	110 (76)	2.3 (2.2)
	Sea water	1000 mL	3	100	107 (64)	1.8 (3.2)
	Sediment	20 g	7	100	101 (70)	12.6 (5.9)
	Fish	20 g	7	100	96 (36)	3.2 (12.9)
3,4-Xylidine	River water	1000 mL	3	100	120 (81)	7.5 (5.2)
	Sea water	1000 mL	3	100	98 (65)	5.3 (3.8)
	Sediment	20 g	7	100	91 (59)	23.6 (25.9)
	Fish	20 g	7	100	53 (21)	19.0 (23.1)
o-Anisidine	River water	1000 mL	3	100	102 (70)	5.3 (4.1)
	Sea water	1000 mL	3	100	84 (57)	5.0 (3.6)
	Sediment	20 g	7	100	96 (66)	18.1 (10.6)
	Fish	20 g	7	100	86 (36)	9.7 (17.2)
m-Anisidine	River water	1000 mL	3	100	113 (77)	8.6 (6.1)
	Sea water	1000 mL	3	100	101 (66)	3.5 (1.2)
	Sediment	20 g	7	100	89 (62)	21.7 (18.2)
	Fish	20 g	7	100	48 (19)	23.1 (22.9)
p-Anisidine	River water	1000 mL	3	100	104 (77)	11.9 (9.1)
	Sea water	1000 mL	3	100	90 (60)	11.9 (9.0)
	Sediment	20 g	7	100	71 (49)	32.5 (31.8)
	Fish	20 g	7	100	– (29)	– (20.9)
o-Chloroaniline	River water	1000 mL	3	100	116 (78)	2.6 (2.8)
	Sea water	1000 mL	3	100	108 (78)	3.6 (4.9)
	Sediment	20 g	7	100	136 (86)	12.2 (2.1)
	Fish	20 g	7	100	117 (44)	5.5 (10.2)
m-Chloroaniline	River water	1000 mL	3	100	119 (80)	2.0 (2.1)
	Sea water	1000 mL	3	100	109 (73)	2.2 (1.1)
	Sediment	20 g	7	100	117 (79)	6.4 (5.1)
	Fish	20 g	7	100	109 (40)	5.3 (12.7)
p-Chloroaniline	River water	1000 mL	3	100	121 (82)	4.5 (3.0)
	Sea water	1000 mL	3	100	118 (79)	4.3 (1.6)
	Sediment	20 g	7	100	128 (92)	19.9 (11.8)
	Fish	20 g	7	100	96 (37)	7.8 (14.7)

* The values in parentheses indicate the determined values calibrated with the naphthalene-d_8 internal standard. Samples were spiked just prior to GC–MS measurement.

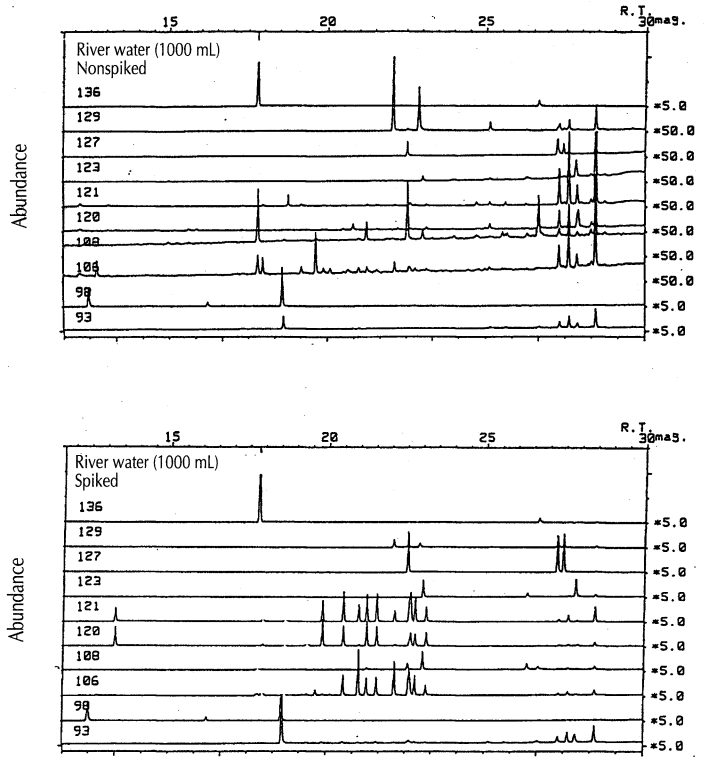

Figure 5. Analysis of the anilines in normal and spiked (100 ng/1000 mL) river water samples. Abbreviations: RT, retention time in min; mag, magnitude.

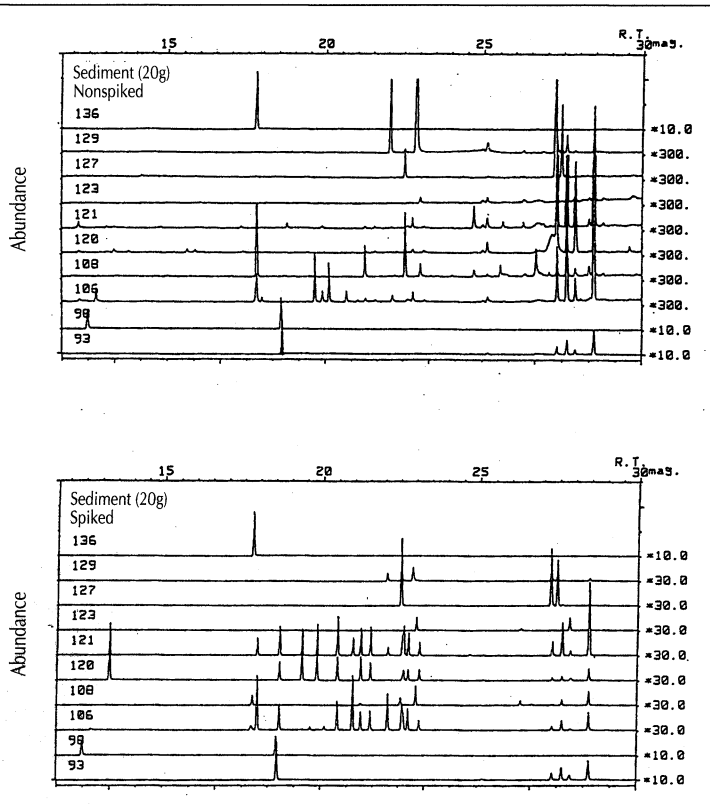

Figure 6. Analysis of the anilines in normal and spiked (100 ng/20 g) sediment samples. Abbreviations: RT, retention time in min; mag, magnitude.

sample with stirring. The muddy mixture was poured into a 1-L round-bottom flask and steam distilled until 500 mL of aqueous distillate was collected. The distillate and 15 g NaCl were poured into a 1-L separatory funnel. Then the sample was extracted twice with CH_2Cl_2 (100 mL and 50 mL). The rest of the procedure is shown in Figure 1 after the asterisk.

For fish samples, 50 mL ethanol was added to 20 g of sample spiked with the surrogate. The sample was homogenized and then centrifuged. The supernatant solution was poured into the 1-L round-bottom flask. Steam distillation was performed, and then a procedure similar to that employed for sediment samples was used.

Results and Discussion

Degradation test

When an analytical method is developed, it is desirable to determine the applicability of the method by examining such properties as chemical stability. To this end, a simple in vitro degradation screening test of the anilines was performed under different pH conditions. Table I shows the percent of residual anilines after 1 h and after 5 days at pH 5, 7, and 9. The percent of residual anilines after 5 days was 86–107%, except for *p*-anisidine at pH 5 (68%). The results suggest that the anilines were relatively stable at any pH conditions and in sunlight.

The stability of low levels of anilines was analyzed. A normal and an acidified river water sample were analyzed. The acidified sample of river water was prepared by adding 2 mL of 6N HCL to 1 L of the river water. Both samples were spiked with the aniline standards (0.1 ng/mL) and stored in a refrigerator. After 4 days, they were analyzed. Table II shows that the anilines decomposed rapidly under the acidified conditions, and even in the normal river water, they decomposed to some extent. Therefore, it is preferable to analyze samples as soon as possible.

Mass Spectra, GC–MS–SIM chromatograms, and calibration

The mass spectra of the anilines are shown in Figure 2. Most of them show the molecular ions as the base peak. The monitored ions were indicated in the experimental section because of their selectivity and sensitivity. Typical GC–MS–SIM chromatograms for the anilines and internal standards are shown in Figure 3. Under these conditions, 3,5-xylidine and *m*-ethylaniline were not completely separated. The calibration graph for the anilines was obtained by plotting the concentration ratio against the peak area ratio of the analyte to the internal standard. An example of a calibration graph is shown in Figure 4. Excellent linearity was obtained in the calibration graphs. Quantitation was performed by the internal standard method.

Extraction with dichloromethane and steam distillation

The efficiency of the dichloromethane extraction technique at different pH levels of water was examined. The percentage of anilines extracted at pH 3.2–11.1 is shown in Table III. The percentage of anilines extracted was more than 72% at pH 6.5–11.2 but decreased to 20–68% at pH 3.2 except for *o*- and *m*-chloroaniline. The percentage of *o*- and *m*-chloroaniline extracted was independent of the pH of water (84–93% at pH 3.2–11.1). The extraction was carried out under neutral conditions because the formation of emulsion most likely occurred when the contaminated water sample was made alkaline. The percentage of anilines extracted at different normalities of HCl are shown in Table IV. Aniline, xylidines, and anisidines could be extracted efficiently even at low normality HCl (0.1N), but chloroanilines needed the higher normality HCl to be extracted. In particular, the extraction of *o*-chloroaniline increased from 13% to 99% with an increase in the normality of HCl from 0.1N to 6N. These results indicate that all of the anilines examined are quantitatively extracted with 6N HCl. The steam distillation process was applied to extract the target compounds from sediment and fish samples. Recoveries of the anilines from various samples including purified water (30 mL), sediment (20 g), and fish samples (20 g) were examined. Before steam distillation, 500 ng of each of the anilines was spiked into those samples. Most of the anilines were recovered in the first 100 mL of distillate, but *m*-anisidine and *p*-anisidine were gradually recovered in the second and even third 100 mL of distillate. Up to 500 mL of distillate was collected.

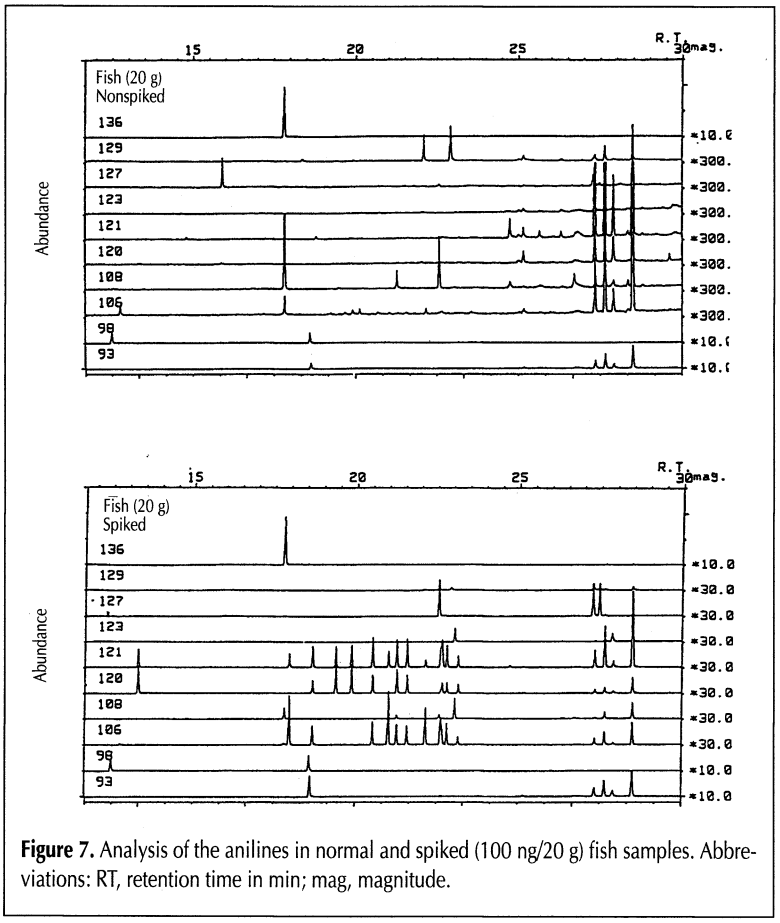

Figure 7. Analysis of the anilines in normal and spiked (100 ng/20 g) fish samples. Abbreviations: RT, retention time in min; mag, magnitude.

Detection limits and analytical precision

The detection limits and analytical precision for the anilines in water, sediment, and fish samples throughout the analytical procedure are shown in Table V. The detection limits of the water sample (DL_W) were calculated from the sensitivity of response, estimating standard deviation as follows (9):

$$D = t(n-1, 0.05)\,\sigma / \sqrt{n}\,(dC/dR),\ DL_W = 3\bar{D} \qquad \text{Eq 1}$$

where D is the detection limit at trace concentrations of the anilines (three different concentrations in this experiment), $\bar{D}$ is the average value of D calculated from different concentrations (DL_W was defined as three times the detection power), $t(n-1, 0.05)$ is the t-distribution at 95% reliability and 2% significance level with $n-1$ degrees of freedom, D is the standard deviation of the response, n is the number of replicates, C is the concentration of the anilines, and R is the peak area ratio of analyte to internal standard. For sediment and fish samples, detection limits (DL_S and DL_F, respectively) were calculated from the following equation:

$$DL_{S,F} = t(n-1, 0.02)\,SD \qquad \text{Eq 2}$$

where $t(n-1, 0.02) = 3.143$ ($n = 7$) is the t-distribution at 98% reliability with $n-1$ degrees of freedom and SD is the standard deviation of the seven replicate analyses.

The anilines were determined in the range 0.03–0.10 ng/mL in water samples with relative standard deviations (RSDs) of 1.2–22.1%. The estimated detection limits of anilines in water were 4.2–31 pg/mL for a 1000-mL water sample. In the case of sediment and fish samples, the estimated detection limits were 1.2–4.0 and 0.5–1.7 ng/g for 20 g of sample, respectively.

Recovery test

Analyte recovery was investigated by using 1000 mL of river or sea water and 20 g of sediment or fish samples spiked with 100 ng of the anilines. Recovery of the target chemicals from the environmental samples is shown in Table VI. The values in parentheses are the experimental values using naphthalene-d_8 as an internal standard. The samples were spiked just prior to the GC–MS measurement and thus indicate net recoveries throughout the analytical procedure. The net recovery was more than half of that calibrated with the surrogate standard. The recovery rates for anilines were 101–121% from river water samples and 84–118% from the sea water samples, with RSDs of 2.0–11.9% and 1.8–11.9%, respectively. For sediment and fish samples, the recoveries were 71–136% and 48–117% with RSDs of 6.4–32.5% and 3.2–23.1%, respectively. The recoveries of 3,4-xylidine, *m*-anisidine, and *p*-anisidine were low, especially in fish samples. This may be because it is difficult to perform steam distillation on these samples and because the compounds may interact with the biota matrix. Their normal and standard spiked chromatograms in river water, sediment, and fish samples are shown in Figures 5, 6, and 7, respectively.

Conclusion

The proposed analytical method involving liquid–liquid extraction and steam distillation procedures and GC–MS–SIM determination may be useful in routinely analyzing aniline, 2,3-, 2,4-, and 3,4-xylidines, *o*-, *m*-, and *p*-anisidines, and *o*-, *m*-, and *p*-chloroanilines in environmental samples (water, sediment, and fish) at picogram-per-milliliter or nanogram-per-gram levels. Furthermore, other xylidine isomers including *N,N*-dimethylaniline, *N*-methyltoluidines, *N*-ethylaniline, and ethylanilines could be determined simultaneously using this method.

Acknowledgment

This work was supported by the Office of Health Studies, Environmental Health Department, Japan Environmental Agency (Project for Development of Analytical Method).

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Manuscript accepted September 8, 1995.