Quick Pretreatment Prep Study for Dioxin Analysis

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[Purpose]

- The need for performing dioxin analysis is increasing in Japan due to the concerns over dioxin contamination. The findings from these analyses greatly impact society. Therefore, it is very important to obtain accurate, reliable test results. Laboratories are investing a significant amount of time and money to build accuracy into dioxin testing.

- To shorten analysis time while maintaining high accuracy, we evaluated Supelco's multi-layer silica gel column and dual-layer carbon column connected in series for sample preparation. We found this method to be very useful for dioxin analysis.

[Experiment]

- We used a Supelco multi-layer silica gel column(Cat.No.21267-U). A similar column was cited in the JQA study reported at the 10th symposium of Environmental Chemistry last year.[1]

- The multi-layer silica gel column was conditioned by running 200mL n-Hexane through the column.

- We evaluated a Supelco, dual-layer carbon reversible column(Cat.No.21239-U). It is composed of two different carbon layers, with distinct binding characteristics (Fig.1)
- The dual layer carbon reversible column was conditioned with 15mL n-hexane using a glass syringe.
- The conditioned multi-layer silica gel column and conditioned carbon column were then connected in series as shown at Fig.1

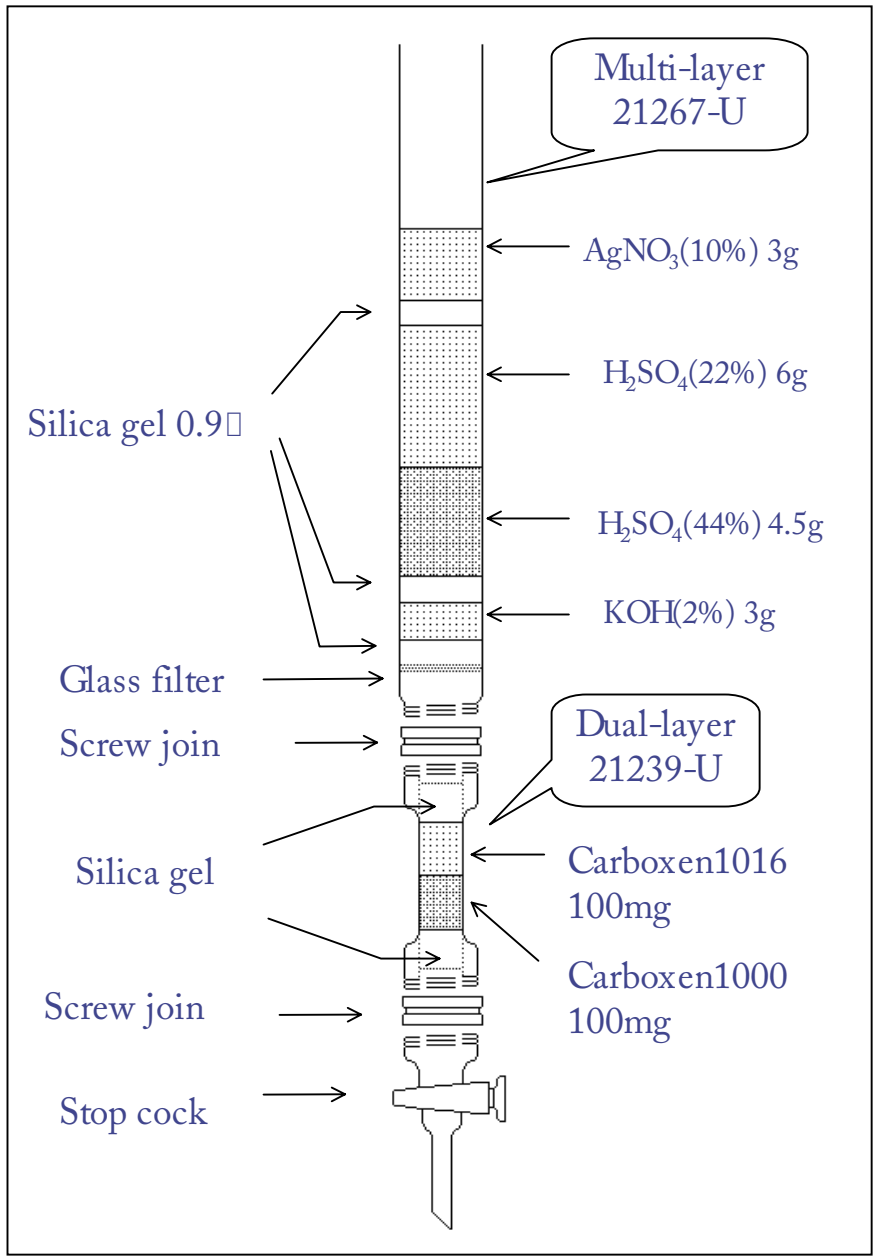


Fig. 1 Multi-layer silica gel column and dual-layer carbon column connection

- To confirm the elution of dioxins, we spiked a fly ash sample with a 14 component ^{13}C Co-planar PCB mix.
- With the multi-layer silica gel column and the dual-layer carbon reversible column connected as shown in Fig. 1, the sample was loaded on the top layer of multi-layer column. 200mL n-hexane was passed through the columns.
- The carbon column was then disconnected and 300mL toluene was passed through the carbon column in the reverse direction. The eluate was concentrated and injected on GC/HRMS.
- We repeated this analysis four times(n=4) with a toluene volume of 200mL.

- We then applied this method to stack gas, fly ash, waste water, and environmental air and compared it to our current method, carbon dispersed silica gel. In the joint method, 100 ml of toluene was used to elute the dioxins from the Supelco carbon column. In the other system, the eluate from the multi-layer silica gel column was loaded on to the carbon dispersed silica gel column. The column was washed with 20 ml toluene.
- The analysis was done according to JIS K 0311-1999 by GC/MS(Nippon Denshi JMS700). Sample preparation and chromatographic conditions are shown on the next two pages.

Fig. 2-1 Analysis flow for stack gas Current Method

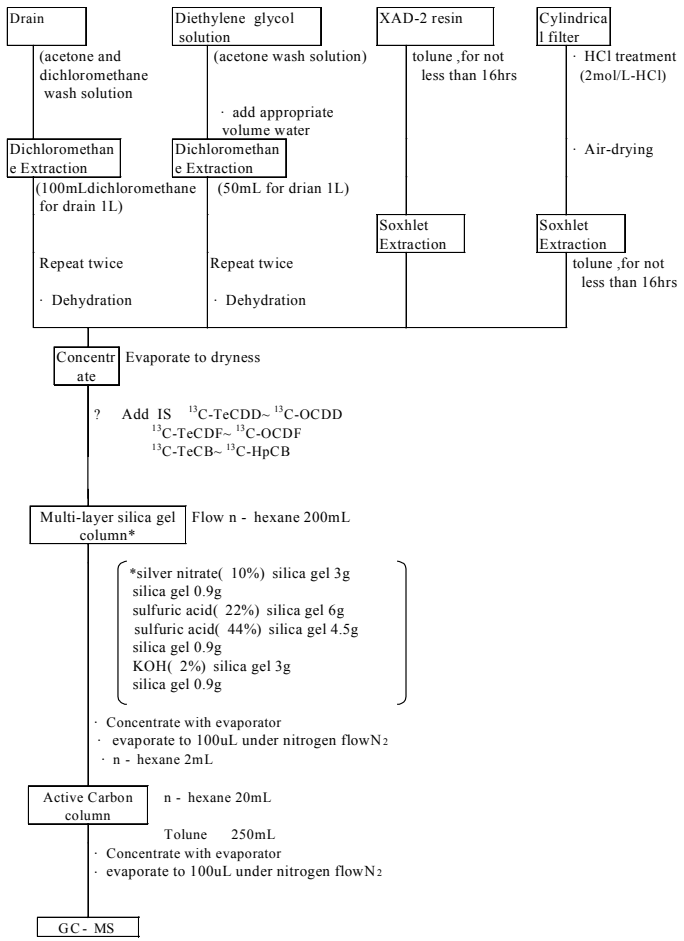
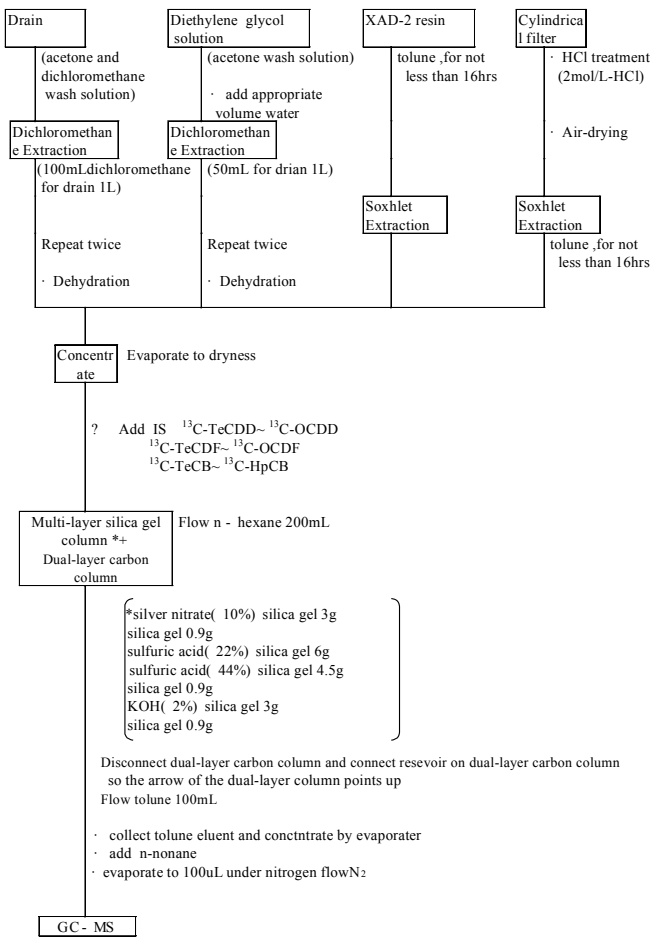


Fig.2-2 Analysis flow for stack gas Joint method



GC(HP-6890)

Te-HxCDDs, Te-Hx CDFs

Column: SP-2331 60m x 0.32mmi.d x 0.20df (Supelco)
Temp. 100□ (1.5 min)→(20□/min)→200□
→(2□/min)→260□(14 min)
Inj.port. Temp 260□
Splitless (60 sec)

Hp-Octa CDDs, Hp-Octa CDFs

Column: DB-17 0.32mm i.d× 30m
Temp 100□ (1.5 min)→(20□/min)→200□
→(10□/min)→280□ (13 min)
Inj.Port temp. 280□
Splitless (60sec)

Coplanar PCBs

Column: DB-5MS 0.32mm i.d× 60m
Column temp. 150□ (1.5 min)→(20□/min)→185□
→(2□/min)→245□ (3 min)
→(6□/min)→290□ (2 min)
Inj.port temp 280□
Splitless (60 sec)

HR-MS JMS700
Resolution 10,000 or over
ionization current 500 A
Ion acceleration voltage 38 eV
Monitoring MS

Dibenzo dioxin

TeCDD:319.8965□321.8936□^{13}C-TeCDD:331.9368□333.9339
PeCDD:353.8576□355.8546□^{13}C-PeCDD:365.8978□367.8949
HxCDD:389.8157□391.8127□^{13}C-HxCDD:401.8559□403.8530
HpCDD:423.7766□425.7737□^{13}C-HpCDD:435.8169□437.8140
OCDD :457.7377□459.7348□^{13}C-OCDD :469.7780□471.7750

Dibenzo furan

TeCDF:303.9016□305.8987□^{13}C-TeCDF:315.9419□317.9389
PeCDF:339.8597□341.8567□^{13}C-PeCDF:351.9000□353.8970
HxCDF:373.8208□375.8178□^{13}C-HxCDF:385.8610□387.8580
HpCDF:407.7818□409.7789□^{13}C-HpCDF:419.8220□421.8191
OCDF :441.7428□443.7399□^{13}C-OCDF :453.7830□455.7801

Coplanar PCB

TeCB:289.9224□291.9194□ ^{13}C-TeCB:301.9624□303.9594
PeCB:325.8804□327.8775 □^{13}C-PeCB:337.9204□339.9175
HxCB:359.8415□361.8385 □^{13}C-HxCB:371.8815□373.8785
HpCB:393.8025□395.7995 □^{13}C-HpCB:405.8428□407.8398

[Result]

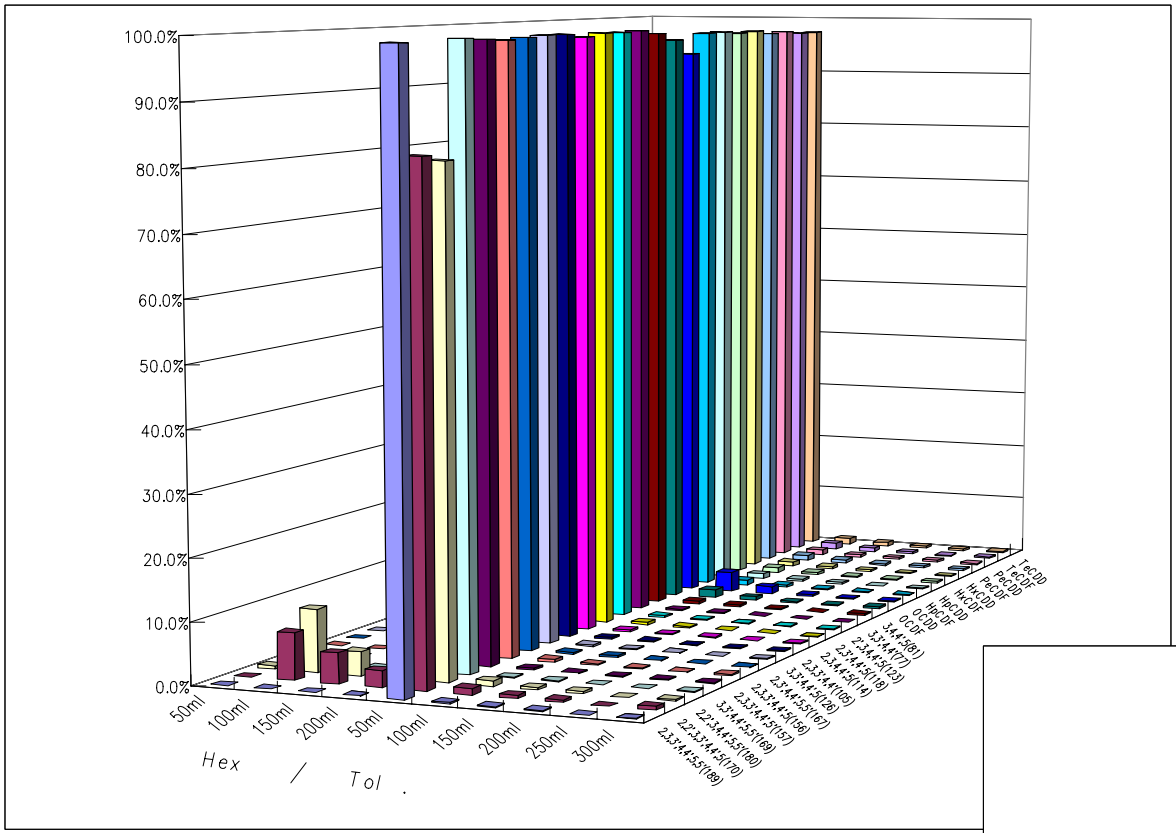
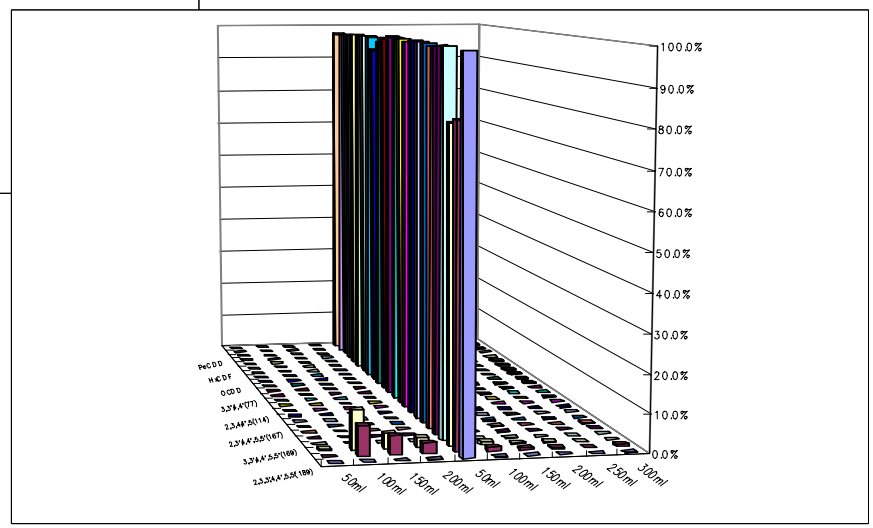


Fig. 3 Toluene elution

- All co-planar PCBs and PCDDs/PCDFs were adsorbed on the dual-layer carbon column. They were recovered with 200mL toluene.



- A small amount of di-ortho PCB was eluted during flushing out with n-hexane.

- Reproducibility was tested using a fly ash sample.
- As described in Table 1, good reproducibility and high recovery were observed.

Table 1. Reproducibility (unit ng-TEQ/g(dry))

Compound			No.1	No.2	No.3	No.4	Average	CV(%)
Dioxin	PCDF	2,3,7,8-TeCDF	0.58	0.56	0.58	0.60	0.58	2.8
		1,2,3,7,8-PeCDF	1.05	1.05	1.0	1.25	1.09	10.2
		2,3,4,7,8-PeCDF	11	11.5	11.5	12	12	3.5
		1,2,3,4,7,8-HxCDF	4.6	4.7	4.9	4.8	4.8	2.7
		1,2,3,6,7,8-HxCDF	4.5	4.5	4.4	4.7	4.5	2.8
		1,2,3,7,8,9-HxCDF	0.41	0.39	0.36	0.40	0.39	5.5
		2,3,4,6,7,8-HxCDF	3.5	3.5	3.5	3.7	3.6	2.8
		1,2,3,4,6,7,8-HpCDF	1.8	1.8	1.8	1.8	1.8	0.0
		1,2,3,4,7,8,9-HpCDF	0.22	0.22	0.20	0.18	0.21	9.3
		OCDF	0.0063	0.0063	0.0062	0.0066	0.0064	2.7
	Total PCDFs		27.6663	28.2263	28.2462	29.4366	28.3939	2.6
	PCDD	2,3,7,8-TeCDD	2.8	2.8	2.9	3.7	3.1	14.3
		1,2,3,7,8-PeCDD	24	25	24	25	25	2.4
		1,2,3,4,7,8-HxCDD	3.7	3.7	3.5	3.7	3.7	2.7
		1,2,3,6,7,8-HxCDD	3.8	3.9	3.7	3.6	3.8	3.4
		1,2,3,7,8,9-HxCDD	5.0	5.1	5.1	4.8	5.0	2.8
		1,2,3,4,6,7,8-HpCDD	2.4	2.3	2.4	2.6	2.4	5.2
		OCDD	0.029	0.027	0.029	0.029	0.029	3.5
	Total PCDDs		41.729	42.827	41.629	43.429	42.404	2.1
	Total (PCDDs + PCDFs)		69.3953	71.0533	69.8752	72.8656	70.7974	2.2
coplanar PCB	non-ortho	3,4,4',5 -TeCBï ü 81ï	0.000036	0.000048	0.000049	0.000041	0.000044	14.1
		3,3',4,4'-TeCBï ü 77ï	0.00035	0.00035	0.00032	0.00032	0.00034	5.2
		3,3',4,4',5-PeCBï ü 126ï	0.47	0.46	0.47	0.49	0.47	2.7
		3,3',4,4',5,5'-HxCBï ü 169ï	0.017	0.014	0.013	0.022	0.017	24.5
	mono-ortho	2',3,4,4',5-PeCBï ü 123ï	0.000062	0.000053	0.000063	0.000051	0.000057	10.7
		2,3',4,4',5-PeCBï ü 118ï	0.00020	0.00021	0.00023	0.00022	0.00022	6.0
		2,3,3',4,4'-PeCBï ü 105ï	0.00025	0.00026	0.00025	0.00023	0.00025	5.1
		2,3,4,4',5 -PeCBï ü 114ï	0.000090	0.000075	0.000080	0.000090	0.000084	9.0
		2,3',4,4',5,5'-HxCBï ü 167ï	0.0000044	0.0000048	0.0000051	0.000011	0.0000063	49.5
		2,3,3',4,4',5 -HxCBï ü 156ï	0.00038	0.00037	0.00039	0.00090	0.00051	51.0
		2,3,3',4,4',5'-HxCBï ü 157ï	0.00039	0.00031	0.00035	0.00075	0.00045	45.3
		2,3,3',4,4',5,5'-HpCBï ü 189ï	0.00017	0.00016	0.00016	0.00021	0.00018	13.6
	Total coplanar PCB		0.4889324	0.4758408	0.4848921	0.514823	0.4911221	3.4
Total@ TEQ			70	72	70	73	71	2.1
Recoveryï ü ï			96.7	99.5	96.2	99.5		

- Stack gas, fly ash, waste water and air were analyzed using the current method and joint method. The results for both methods are presented in Table 2. Both methods were similar for stack gas, fly ash and air sample. However the new method showed a slightly lower value for waste water, but it's result was satisfactory.
- A chromatogram of Co-planar PCBs from the stack gas sample is shown in Fig.4.

Table 2-1 Comparison data (Toluene 200mL□

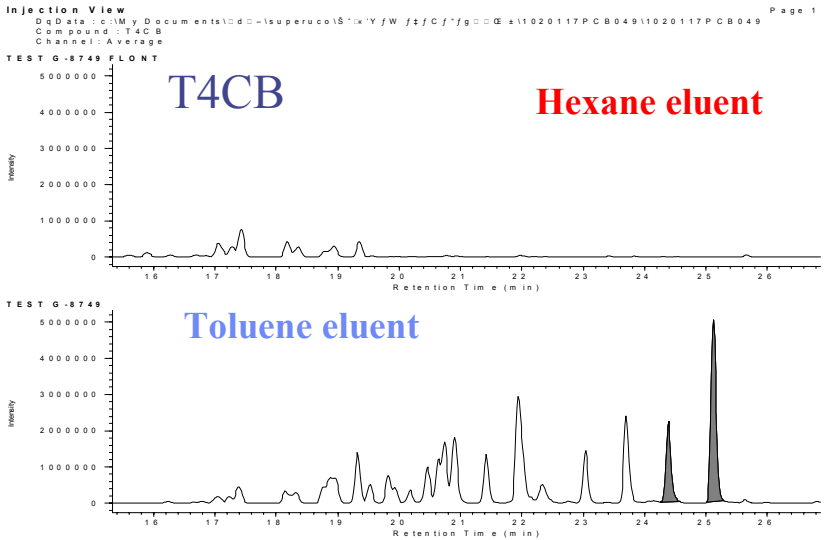
	Stack gas (ng-TEQ/m□□)		Fly ash (ng-TEQ/g(dry))		Waste water(pg-TEQ/L)	
	Current Method	Joint method	Current Method	Joint method	Current Method	Joint method
PCDD	0.40	0.38	44	43	0.29	0.13
PCDF	0.90	0.82	28	29	0.37	0.31
Co-PCB	0.085	0.082	0.40	0.51	0.031	0.022
Average Recovery(%)	92.5	98.2	86.4	99.5	86.4	90.7

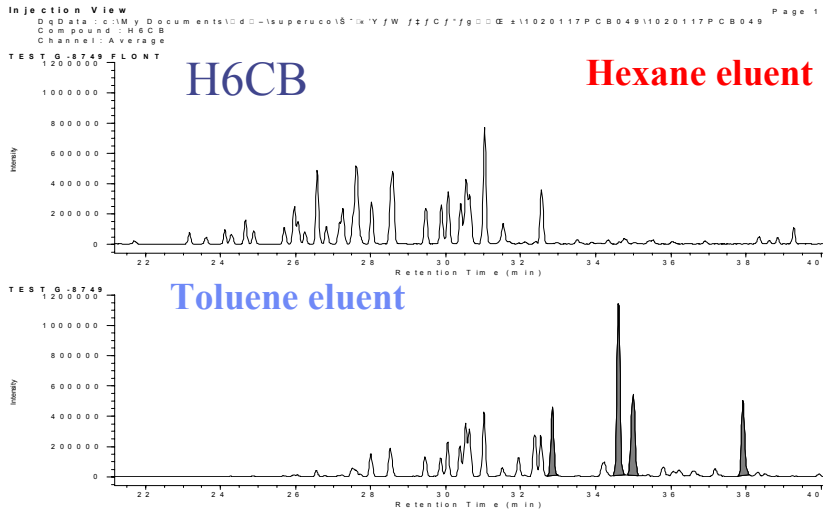
Table 2-2 Comparison data (Toluene 100mL)

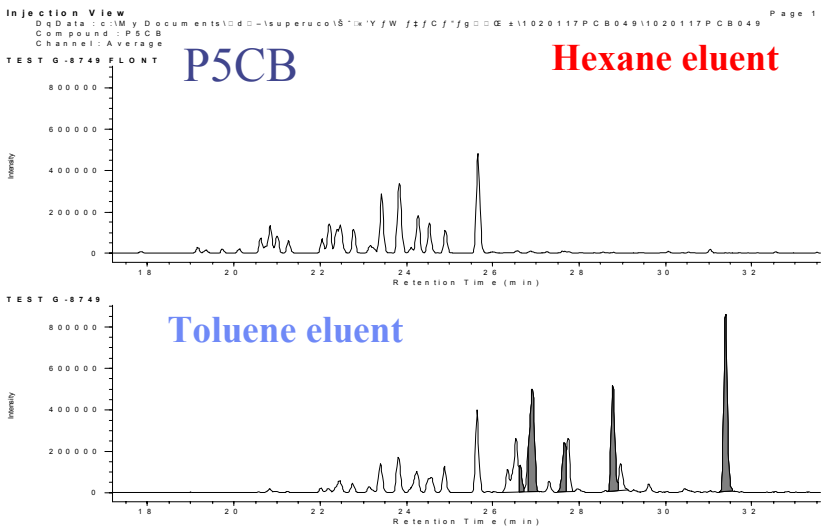
	Stack gas(ng-TEQ/m□□)		F.A.(ng-TEQ/g(dry))		Air(pg-TEQ/m□)		Air(pg-TEQ/m□)	
	Current Method	Joint method	Current Method	Joint method	Current Method	Joint method	Current Method	Joint method
PCDD	10	10	1.0	1.0	0.0090	0.000092	0.00014	0.00012
PCDF	8.8	9.1	1.2	1.1	0.0085	0.0090	0.018	0.0083
Co-PCB	0.67	0.70	0.034	0.038	0.0011	0.0021	0.0016	0.0013
Average Recovery(%)	91.7	99.6	94.4	98.2	83.6	98.7	92.7	106.8

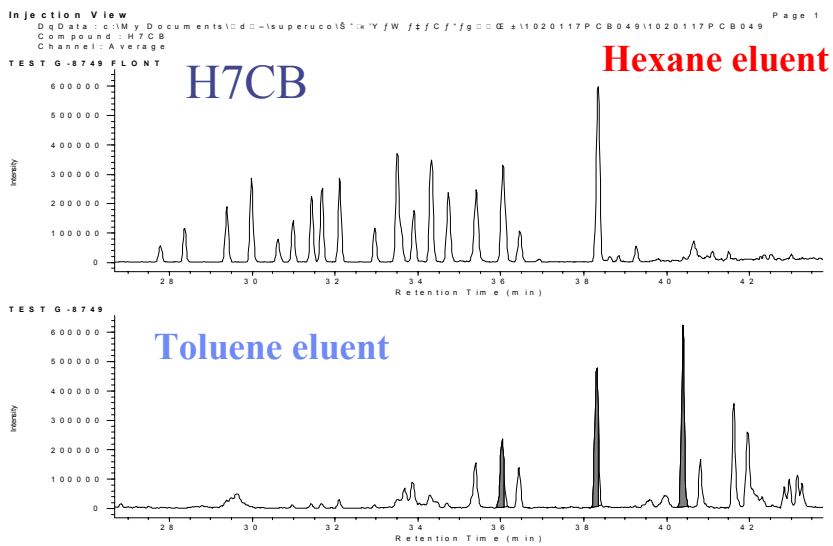
Note□TEQ of air sample less than limit of detection (LOD) is regarded as 0 for calculation

Fig.4 Co-planar PCB chromatogram









- Table shows the results of a blank analysis.
- The concentrations of certain PCBs observed in the blank are below the detection limit an do not present a problem for most analyses.
- The concentrations of PCBs in the blank had an effect on the quantitation of the water samples.

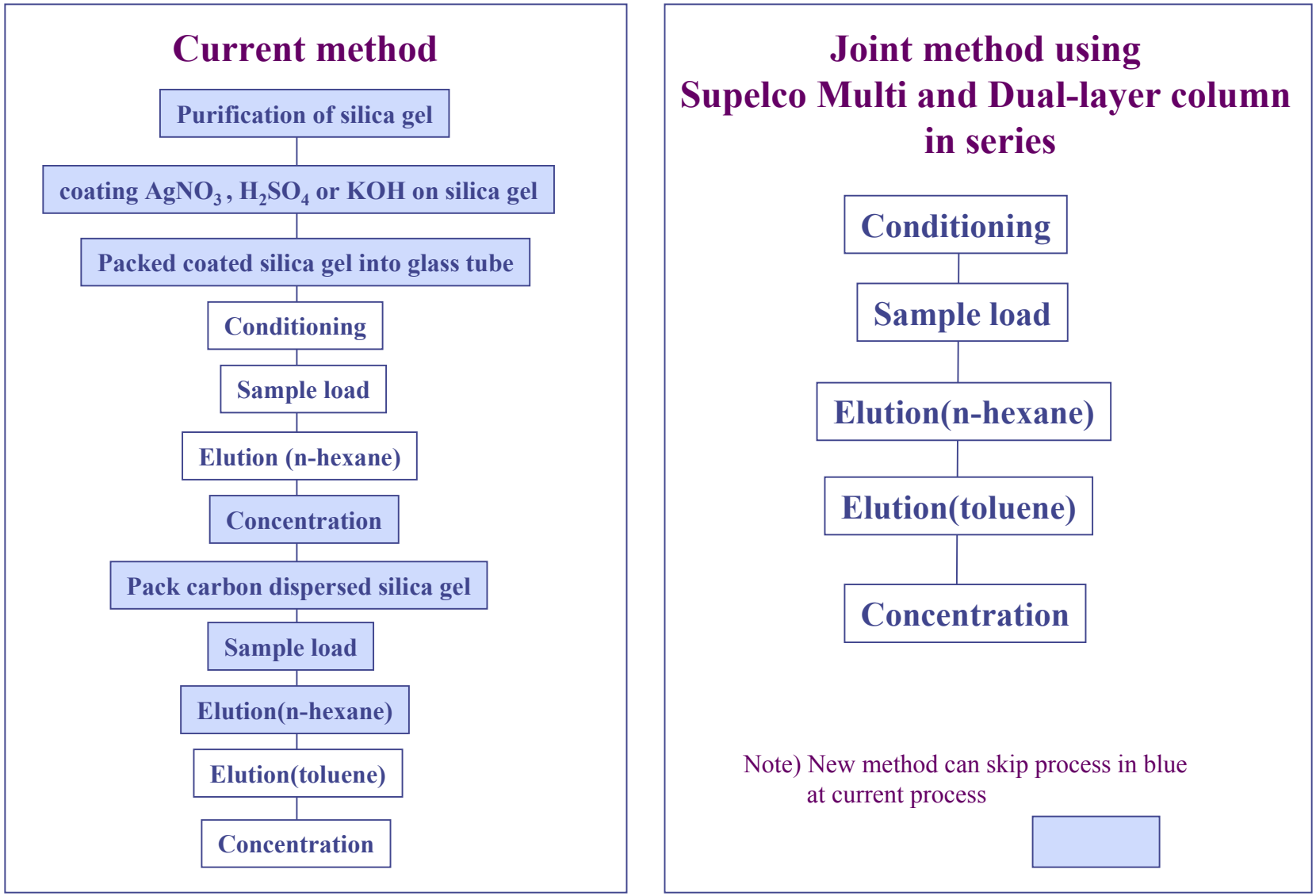
Table: Blank test result

PCDFs	2, 3, 7, 8- TeCDF	N D
	1, 2, 3, 7, 8- PeCDF	N D
	2, 3, 4, 7, 8- PeCDF	N D
	1, 2, 3, 4, 7, 8- HxCDF	N D
	1, 2, 3, 6, 7, 8- HxCDF	N D
	1, 2, 3, 7, 8, 9- HxCDF	N D
	2, 3, 4, 6, 7, 8- HxCDF	N D
	1, 2, 3, 4, 6, 7, 8- HpCDF	5. 9
	1, 2, 3, 4, 7, 8, 9- HpCDF	0. 36
	OCDF	4. 0
PCDDs	2, 3, 7, 8- TeCDD	N D
	1, 2, 3, 7, 8- PeCDD	N D
	1, 2, 3, 4, 7, 8- HxCDD	N D
	1, 2, 3, 6, 7, 8- HxCDD	N D
	1, 2, 3, 7, 8, 9- HxCDD	N D
	1, 2, 3, 4, 6, 7, 8- HpCDD	5. 3
	OCDD	6. 3
PCBs	3, 4, 4' , 5 - TeCBi□ ▽ 81j□	N D
	3, 3' , 4, 4' - TeCBi□ ▽ 77j□	6. 0
	3, 3' , 4, 4' , 5- PeCBi□ ▽ 126j□	0. 83
	3, 3' , 4, 4' , 5, 5' - HxCBi□ ▽ 169j□	N D
	2' , 3, 4, 4' , 5- PeCBi□ ▽ 123j□	N D
	2, 3' , 4, 4' , 5- PeCBi□ ▽ 118j□	5. 7
	2, 3, 3' , 4, 4' - PeCBi□ ▽ 105j□	1. 3
	2, 3, 4, 4' , 5 - PeCBi□ ▽ 114j□	N D
	2, 3' , 4, 4' , 5, 5' - HxCBi□ ▽ 167j□	N D
	2, 3, 3' , 4, 4' , 5 - HxCBi□ ▽ 156j□	N D
	2, 3, 3' , 4, 4' , 5' - HxCBi□ ▽ 157j□	N D
	2, 3, 3' , 4, 4' , 5, 5' - HpCBi□ ▽ 189j□	N D

[Summary]

- The suitability of using a multi-layered silica gel column for the clean up of samples before dioxin analysis was shown previously. Our current objective was to evaluate the suitability of using a multi-layered silica gel column in series with a dual-layered carbon column to achieve shorter sample preparation times while maintaining analytical accuracy.
- Figure 5 shows a comparison of the old process flow method versus the new joint method.

Fig 5 Comparison of Process Flow



- As shown in Fig.3, co-planar PCBs/PCDDS/PCDFs are recovered in the toluene eluent. Dioxins are not eluted during flow of 200mL n-hexane through the multi-layer silica gel column and dual-layer carbon column in series.
- The dual-layer carbon column works well for trapping dioxins from a large volume of hexane. Highly chlorinated substituted dioxins are recovered very well due to the 2 different carbon adsorbents in the dual-layered column.

- As shown in Table I, the reproducibility is very good. The joint method shows the same results as the current method. We used 200mL or 100mL for elution.
- It was shown that 100 ml toluene is enough for dioxin elution.

- We found the joint method (multi-layer silica gel column + dual-layer carbon column) to be very useful. We were able to combine two processes into one and omit a concentration step. This saves time and reduces solvent usage.

[References]

- 1) Masaaki Maeoka et al. Study on saving time for dioxin analysis based on JIS Method, 10th Symposium on Environmental Chemistry, 2001, p.314-315
- 2)Megumi Matsumoto et al. Study on sample preparation for dioxins, 9th Symposium on Environmental Chemistry, 2000, p.238-239
- 3)Chisato Matsumura et al. Simplifying sample preparation for dioxins sample preparation, 8th Symposium on Environmental Chemistry, 2000, p.202-203