COMPARISON OF DB-5MS AND CP-SIL 8 CB LOW BLEED/MS GAS CHROMATOGRAPHY COLUMNS FOR ASSIGNMENT OF 2,3,7,8-SUBSTITUTED PCDDS/PCDFS IN EMISSION SAMPLES FROM COLOMBIAN INCINERATORS

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) currently known as dioxins are a family of 210 highly stable lipophilic aromatic chemicals highly persistent in the environment comprising 75 PCDDs and 135 PCDFs. However, only 17 congeners (7 PCDDs and 10 PCDFs) with chlorine atoms in the 2,3,7 and 8 positions are considered to be of toxicological significance and their relative potencies are estimated by the toxic equivalent factor (TEF). The toxic equivalence of each compound (TEQ_i) is calculated by multiplying the concentration of the congener (C_i) by its I-TEF_i. The sum of the 17 individual TEQs gives a total TEQ value which is equivalent to the toxicity of all toxic dioxins and furans in the sample if they were present as the most toxic compound 2,3,7,8-TCDD. In order to establish the "true" TEQ value, accurate determination of isomer-specific concentrations of 17 toxic 2,3,7,8-substituted dioxins and furans is required[1]. GC–MS in the electron impact selected ion monitoring (EISIM) mode is generally used for analysis of dioxins. The separation of dioxins from other interfering compounds can be achieved using high-resolution (HR) GC–HR-MS and HR-GC–MS–MS techniques[2]. Most official organizations suggest the use of DB-5 GC column[3]. However, all toxic 2,3,7,8-substituted dioxins and furans cannot be separated from their other closely co-eluting isomers in this column and a complementary column such as DB-225, SP-2330, DB-Dioxin or Cp-Sil 88 is recommended to separate unresolved isomers, particularly 2,3,7,8-TCDF[3]. Nevertheless, little guidance is given for separation of the higher chlorinated 2,3,7,8-substituted dioxins and furans, especially the penta- and hexa-isomers where interferences are also present. Consequently for any series 5 GC columns it was reported that the total TEQ value will always be biased high[1]. Recently, "non-conventional" Series 5 GC columns such as DB-5MS, ZB-5UMS, CP-Sil 8 CB LowBleed/MS have been commercialized and appear to be a better choice for analysing polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in spite of some co-elutions[1]. Calculated TEQ values were lower when using the DB-5MS and CP-Sil 8 CB LowBleed/MS columns compared to "conventional" GC columns (DB-5, HP-5MS, Rtx-5MS. Equity-5)[1]. In this contribution we compare congener concentration and I-TEQ results of samples from hazardous waste incinerators in Colombia obtained using DB-5MS and CP-Sil 8 CB LowBleed/MS columns by high resolution gas chromatography coupled to ion-trap low resolution mass spectrometry (HRGC-QITMS/MS). Results were also compared with those obtained by HRGC/HRMS equipped with a DB-5 MS column in the Mass Spectrometry Laboratory, Dioxin Laboratory from Barcelona (Spain).

Materials and Methods

Sampling collection, Extraction and Clean-up

Samples were collected in incineration plants from different colombian cities following the method described in European Standard EN-1948:1996-1. XAD-2 resin (Supelco) was extracted with toluene. Then, extracts were rotary concentrated and clean-up was performed by liquid-solid adsorption chromatography at atmospheric pressure using glass columns filled with silica, florisil and alumina as adsorbents. Standard solution mixtures of labelled PCDFs EN-1948-SS, EN-1948-ES and EN-1948-IS from Wellington were used during sampling, extraction and injection, respectively. EN-1948:1996 standard solutions in nonane (CS1 to CS6, Wellington Labs., Guelph, Ontario, Canada) were used for calibration.

HRGC-QITMS/MS measurements

Purified extracts were analyzed by high resolution gas chromatography coupled to ion-trap low resolution mass spectrometry (HRGC-QITMS/MS) in a CP-3800 GC equipped with an 8400 autosampler and coupled to a Saturn 2000 ion-trap spectrometer. The operating conditions were: trap temperature 220ºC, manifold temperature 80ºC, transfer line temperature 280ºC and turbo current 205 mA. The optimum MS/MS parameters were found for each dioxin and furan congener group depending on the type of column used:
DB-5MS (60 m x 0.25 mm I.D., 0.25 µm film thickness). The final column oven program was: 130ºC (held for 1.5 min) to 200ºC at 20ºC/min (held for 1.3 min), to 230ºC at 1ºC/min (held for 7 min) and 290ºC at 10ºC/min (held for 20.7 min). Splitless injection was 2 µL and the injector temperature was 300ºC. Helium was used as carrier gas at a head pressure of 45 psi with pulse duration of 1.1 min, then the flow was constant at 1.0 mL/min. Chromatography windows are: Fil/Mult Delay (0-30 min), TCDF (30-37.08 min), TCDD (37.08-41.76 min), PCDF/PCDD (41.76-49.24 min), HxCDD/HxCDF (49.24-53.94), HpCDD/HpCDF (53.94-60.23), OCDD/OCDF (60.23-70.00).
CP-Sil 8 CB LowBleed/MS (30 m x 0.25 mm I.D., 0.25 µm film thickness). The final column oven program was: 60ºC (held for 3 min) to 235ºC at 25ºC/min (held for 10 min), to 275ºC at 10ºC/min (held for 3 min) and 300ºC at 10ºC/min (held for 3 min). Splitless injection was 2 µL and the injector temperature was 300ºC. Helium was used as carrier gas at a head pressure of 18 psi with pulse duration of 1.6 min, then the flow was constant at 1.0 mL/min. Chromatography windows are: Fil/Mult Delay (0-15 min), TCDF (15-16.35 min), TCDD (16.35-18.38 min), PCDF (18.38-20.67 min), PCDD (20.67-22.78 min), HxCDD/HxCDF (22.78-25.56), HpCDD/HpCDF (25.56-29.20), OCDD/OCDF(29.20-32.50).

Quantification and limit of detection

Quantification of PCDDs/PCDFs was performed using the isotope dilution method. Relative Response Factors (RRFs) were determined using CS1 to CS6 injections and area comparison with ^{13}C labeled internal standards. Congener identification was carried out by retention time comparison between labeled and native compounds based on co-elution concept. Toxic equivalent quantity (I-TEQ) was determined using I-TEF factors. The limit of detection (LOD) has been calculated as 3.0 times noise value for all 17 toxic 2,3,7,8-substituted native congeners. Noise was determined by Varian Saturn Workstation software using baseline peak-to-valley height ratio

HRGC-HRMS measurements

Samples were also analyzed by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) on a GC 8000 series gas chromatograph (Carlo Erba Instruments, Milan, Italy) equipped with a CTC A 200S autosampler and coupled to an Autospec Ultima mass spectrometer (Micromass, Manchester, UK). A positive electron ionization (El+) source at 250ºC was used. The filament current was 500 µA and electron energy was 37 eV and the acceleration voltage was 8000 V. The resolution was 10000 at 10% valley on the analyzer mode SIR. DB-5MS (60 m x 0.25 mm I.D., 0.25 µm film thickness) column was used. The temperature programme was: 140ºC (1 min) at 20ºC/min to 200ºC (1 min) then at 3ºC/min to 300ºC and held isothermally for 20 min at 300ºC. Splitless injection was 1-2 µL, at 280ºC. Identification and quantification of toxic congeners was the same as previously reported [3].

Results and discussion

Table 1 shows I-TEQ pg/Nm^3 and Limit of Detection (LOD pg/Nm^3) using CP-Sil 8 CB Low Bleed/MS and DB-5MS chromatography columns. Note that LODs of some congeners are higher than I-TEQ values of the corresponding congeners because the latter value is the product of congener concentration times I-TEF. As shown in table 1, there are large LOD differences for CP-Sil 8 CB LowBleed/MS column with respect to DB-5MS, specifically for TCDD, TCDF, PCDF and HpCDF congeners, indicating problems with determination and isolation of these isomers. Interestingly LOD determined by HRGC-QITMS/MS and by HRGC-HRMS (not shown) in DB-5MS column are similar. Besides, DB-5MS gives better peak definition and isolation in the most crowded hexa-congener window, of both dioxins and furans. Figure 1 shows a typical profile in the HxCDD window indicating that DB-5MS column can separate target congeners successfully. On the contrary, CP-Sil 8 CB LowBleed/MS column presents co-elution of toxic and no-toxic congeners and peaks of toxic isomers are not well defined.

Table 2. I-TEQ pg/Nm^3 (L.O.D pg/Nm^3) using CP-Sil 8 CB Low Bleed/MS, DB-5MS chromatography columns with HRGC-QITMS/MS

Congeners	I-TEQ pg/Nm^3 (LOD pg/Nm^3)							
	Sample 1		Sample 2		Sample 3		Sample 4	
DIOXINS	CP-Sil 8 CB Low Bleed/MS	DB-5MS	CP-Sil 8 CB Low Bleed/MS	DB-5MS	CP-Sil 8 CB Low Bleed/MS	DB-5MS	CP-Sil 8 CB Low Bleed/MS	DB-5MS
2378-TCDD	1662.09 (190.70)	1522.22 (3.81)	927.33 (160.40)	1141.03 (7.02)	561.52 (64.43)	432.91 (0.63)	1345.95 (157.43)	1048.68 (1.91)
12378-PCDD	821.44 (29.38)	2515.03 (3.18)	875.37 (31.31)	2030.94 (21.62)	388.11 (13.88)	674.51 (12.69)	1174.74 (42.02)	2100.03 (5.25)
123478-HxCDD	113.86 (15.73)	40.69 (1.63)	103.85 (14.35)	47.16 (5.57)	42.56 (5.88)	7.67 (0.99)	142.69 (19.71)	38.77 (10.70)
123678-HxCDD	102.64 (11.06)	100.27 (4.25)	177.34 (19.11)	90.13 (7.02)	91.67 (9.88)	11.24 (1.37)	164.42 (6.66)	78.12 (5.99)
123789-HxCDD	178.54 (20.95)	188.78 (4.23)	258.85 (30.37)	142.10 (8.46)	110.69 (12.99)	9.57 (1.93)	250.08 (29.34)	152.48 (5.06)
1234678-HpCDD	16.73 (21.71)	27.28 (1.51)	21.81 (28.30)	44.66 (1.51)	28.91 (37.52)	53.67 (3.45)	28.64 (37.17)	61.41 (2.00)
OCDD	0.69 (9.12)	1.55 (1.83)	0.28 (3.66)	2.55 (18.90)	2.49 (32.71)	7.03 (20.50)	1.13 (14.88)	2.58 (18.26)
TOTAL DIOXINS	2896.00	4395.82	2364.83	3498.57	1225.94	1196.60	3107.66	3482.06
FURANS								
2378-TCDF	1409.12 (210.00)	1008.93 (79.33)	1438.02 (210.00)	599.40 (55.79)	548.15 (210.00)	302.03 (37.78)	392.01 (210.00)	418.36 (45.33)
12378-PCDF	358.23 (368.76)	697.01 (2.52)	914.37 (1188.69)	625.93 (17.88)	186.79 (192.28)	222.65 (18.53)	440.44 (453.38)	506.06 (19.95)
23478-PCDF	4494.15 (304.22)	8874.20 (20.57)	8995.70 (608.94)	3452.37 (31.80)	2811.16 (190.29)	2475.23 (29.39)	3856.56 (261.06)	5302.70 (34.00)
123478-HxCDF	107.84 (6.11)	863.10 (28.87)	808.46 (45.80)	832.98 (64.04)	249.66 (14.15)	463.33 (18.13)	759.17 (43.01)	1079.96 (13.71)
123678-HxCDF	480.72 (34.38)	937.51 (34.44)	815.72 (58.35)	1197.36 (63.21)	411.63 (29.44)	703.74 (23.39)	893.76 (63.93)	1244.93 (13.08)
234678-HxCDF	547.09 (37.31)	719.56 (9.27)	462.30 (31.53)	520.30 (22.86)	603.31 (41.14)	482.74 (6.38)	778.74 (53.11)	1016.82 (7.95)
123789-HxCDF	45.22 (15.94)	98.61 (11.34)	154.61 (55.82)	217.08 (47.43)	119.07 (41.98)	109.27 (10.07)	252.62 (89.07)	324.79 (8.83)
1234678-HpCDF	102.56 (75.84)	98.82 (6.47)	227.18 (168.00)	160.37 (42.67)	317.06 (234.46)	187.44 (8.52)	183.91 (136.00)	216.93 (19.37)
1234789-HpCDF	24.50 (160.66)	24.05 (10.67)	79.27 (519.72)	30.21 (40.58)	34.22 (224.46)	8.68 (4.17)	66.22 (434.18)	76.03 (20.26)
OCDF	0.70 (20.28)	0.97 (6.38)	1.84 (53.14)	4.45 (39.36)	6.10 (175.89)	6.71 (3.34)	6.15 (177.40)	5.86 (4.64)
TOTAL FURANS	7570.14	13322.74	13897.46	7640.45	5287.16	12883.54	7629.58	10192.43

However, some problems with DB-5MS were observed identifying 13C-HxCDD due to difficult to optimize MS/MS parameters. For this reason some HxCDD determined by HRGC-QITMS/MS show high deviation compared to HRGC-HRMS (not shown).

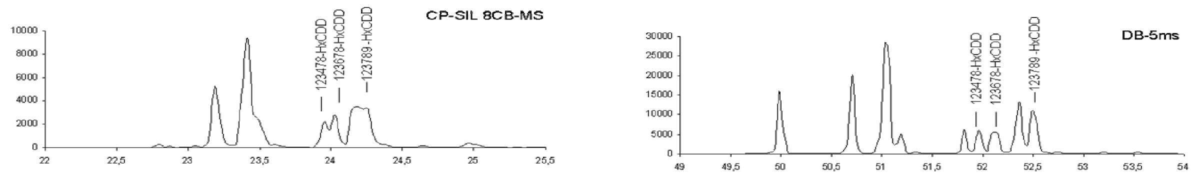

Figure 1 HRGC-QITMS/MS chromatogram of HxCDD congeners in sample 1 using CP-SIL 8CB-MS and DB-5MS columns.

Table 2 shows total I-TEQ (ng/Nm^3) determined using DB-5 MS and CP-Sil 8 CB LowBleed/MS by HRGC-QITMS/MS and DB-5 MS by HRGC-HRMS. Results with DB-5 MS and CP-Sil 8 CB LowBleed/MS obtained by QITMS/MS are comparable to those obtained by HRGC/HRMS even though in three out of four samples lower I-TEQ values were obtained with CP-Sil 8 CB LowBleed/MS. These results are in agreement with those obtained by Fishman et al.[1] who observed differences in isomer resolution between DB-5MS and CP-Sil 8 CB LowBleed/MS. In this work better congener separation in DB-5MS might be ascribed to its larger length.

Table 2 Total I-TEQ (ng/Nm^3) of samples using CP-SIL 8CB-MS and DB-5MS by HRGC-QITMS/MS compared to the value obtained using DB-5MS by HRGC-HRMS

Total I-TEQ (ng/Nm^3)	**Sample1**	**Sample 2**	**Sample 3**	**Sample 4**
CP-SIL 8CB-MS (HRGC-QITMS/MS)	10.5	16.5	6.5	10.6
DB-5MS (HRGC-QITMS/MS)	17.7	11.1	6.1	13.7
DB-5MS (HRGC-HRMS)	14.4	14.2	7.0	15.6

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