Mass spectrometric approach for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in stack gas emissions by gas chromatography coupled to triple-quadrupole mass spectrometry using the atmospheric pressure chemical ionization source

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19 **Abstract**

20 A gas chromatography coupled to triple-quadrupole mass spectrometry (GC-

21 (QqQ)MS/MS) including a soft-ionization through an atmospheric pressure chemical

22 ionization (APCI) source based method was compared with the high resolution mass

23 spectrometry (HRMS) standard reference method EN1948, for the analysis of

24 polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) in stack gas emissions. The stack

25 emission samples were collected, both, by manual method sampling (from 6 to 8 hours) and

26 by long-term sampling systems (sampling time of several weeks). This work presents the

27 first comparison of GC-(QqQ)MS/MS with APCI source with the European Standard

28 EN1948 technique for stack gas emissions. Sample concentrations ranged from 0.5 to 596

29 pg I-TEQ/Nm^3. Comparative results in all investigated samples showed relative errors that

30 were within ± 15%. These results make GC-(QqQ)MS/MS with APCI suitable for the

31 quantitative analysis of dioxins in the studied samples and create a real alternative tool to

32 the reference sector GC-HRMS instruments.

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1.   Introduction

The standard reference method for determination of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) in emission samples is based on the use of high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS) operated in Electron Impact (EI) mode and fitted with magnetic sector analyzers [1]. This methodology is highly selective and sensitive; however, highly qualified infrastructure and operators are required. In recent years there has been a search for an alternative to HRGC/HRMS and different methods and techniques have been considered such as ion trap based mass spectrometers working in MS/MS mode [2,3], and time of flight based mass spectrometers [4]. Although these techniques have provided promising results, they have not yet culminated in a consistent and robust routine analysis of these pollutants.

In the last years, a new generation of triple quadrupole MS instruments revealed itself as a significant promise, especially with respect to their sensitivity. The recently revived atmospheric pressure chemical ionization (APCI) source designed for GC has allowed the coupling of a GC with last generation QqQ instruments. Additionally, this soft-ionization technique for GC has been designed to overcome the extensive fragmentation that occurs in the EI sources, making possible to select the molecular ion as a precursor ion. This characteristic improves both sensitivity and selectivity of MS/MS methods [5-9] making this technique suitable for the analysis of ultratrace persistent organic pollutants (POPs) such as PCDD/Fs and PCBs [10-11].

Recently, GC-APCI-MS/MS with QqQ has also been used to determine dioxins in different complex samples such as environmental, air and food [5]. Discrepancies in sample concentration observed in a comparison of samples analyzed by GC-APCI-MS/MS with the HRMS methodology led to relative errors lower than 7%. A QA/QC control indicated a

high performance in terms of chromatographic separation, linearity, S/N ratio, and a high

ion abundance ratio of selected transitions. In terms of sensitivity, GC-APCI-MS/MS was

better than the traditional GC-EI-MS/MS systems and comparable to GC-(EI) HRMS for

dioxin determination. After many studies exploring tandem mass spectrometry as a valid

methodology for the analysis of dioxins, GC-MS/MS was recently accepted as a

confirmatory method for the analysis of dioxins in feed and food in the European regulation

[10]. On the contrary, only HRMS approach is accepted in the EN-1948 European Standard

for the determination of PCDD/FS and PCBs in stationary gas emissions. Considering the

good results obtained by GC-(QqQ)MS/MS with APCI in feed and food, it is important to

evaluate this technique in the environmental field. In this work GC-APCI-MS/MS with last

generation QqQ is assessed for the analysis of emissions from stationary sources and

compared with the data obtained by HRGC-HRMS.

2. Materials and methods

2.1   Reagents and standards

All solvents were of organic trace analysis and were readily available as commercial

products. Amberlite XAD-2 was obtained from Supelco (Supelco, Bellefonte PA, USA).

Polyurethane foams (PUFs) and filters were supplied by Monitoring Systems (Monitoring

Systems, Wien, Austria). Multilayer silica, basic alumina and activated carbon were

obtained from FMS Inc. (FMS Inc, Boston, USA). The PCDD/Fs selected for this study

were the toxic compounds, 2,3,7,8 chlorosubstituted congeners, with the toxic equivalence

factor (TEF) assigned by WHO [12]. Standard solutions of PCDD/Fs (EN-1948 CSL, CS1

to CS4, ES and IS) were purchased from Wellington Laboratories Inc. (Guelph, Ontario,

85 Canada) and were used for calibration, quantification and analytical recovery calculations,

86 following the requirements described in EN1948:2006.

87

88 **2.2   Sample collection**

89 Stack gas emission samples were collected by both manual sampling method and long-term

90 sampling method, following the main steps reported in previous papers [13-14]. The study

91 included five samples obtained using long-term sampling system (Cement plant with co-

92 incineration, Municipal Solid Waste Incineration, Hazardous Waste Incineration), and three

93 samples taken by manual method system: Metal Industries and Municipal Solid Waste

94 Incineration (**Table 1**).

95

96 **2.3 Sample preparation**

97 **2.3.1 Extraction and clean-up**

98 Samples from long-term sampling systems, consisting on polyurethane foams and filters

99 were spiked before sampling with a mixture of thirteen ^{13}C-PCDD/F mixture (EN-1948-ES,

100 Wellington Laboratories, Canada) consisting on 4000 pg for tetra to hexa substituted

101 compounds and 8000 pg for hepta to octa-ones. For the manual method, this amount was

102 reduced by a factor of ten. The filter was pretreated according to a previously published

103 protocol [14]. From this point, the analysis was followed with a 50% aliquot for short-term

104 sample extract and with a 5 % aliquot for the long-term ones, as previously suggested by

105 Rivera-Austrui et al. [13]. Finally, the extract aliquots were concentrated and reconstituted

106 with n-hexane prior to clean-up. The cleanup steps were conducted considering short and

107 long term sampling time [13-14]. The following steps were based on the normal routine

108 method according to the European Standard EN-1948:2006.

2.3.2 APCI-MS/MS analysis

The chromatographic analysis were performed using an Agilent 7890A gas chromatograph (Agilent Technologies Inc., Palo Alto, CA, USA), equipped with an Agilent 7693A autosampler, coupled to a triple quadrupole mass spectrometer, Xevo TQ-S (Waters Corporation, Manchester, UK), with an APCI source. The GC separation conditions are those reported by Portolés et al. [7-8]. Mass spectrometer was operated in SRM mode, acquiring one quantification transition and one confirmation transition for both, native and ^{13}C-labelled compounds, SRM transitions used can be found in van Bavel et al. 2015 [5]. In the SRM method, automatic dwell time (values ranging from 20 to 60 ms) was applied in order to obtain at least 15 points per peak. Targetlynx (a module of MassLynx) was used to handle and process the acquired data.

2.3.3   HRGC-HRMS analysis

The HRGC-HRMS analysis met the requirements described in the European Standard EN1948 [1]. These analysis were performed on a gas chromatograph (Agilent 6890N, USA) fitted with a DB-5MS (60 m x 0.25 mm i.d. x 0.25 μm film thickness) fused silica column (J&W Scientific, Folsom, CA, USA) coupled through a heated transfer line kept at 280 ºC to a high resolution mass spectrometer (Waters, AutoSpec Ultima NT) controlled by Masslynx data system and operated in SIM mode at 10,000 resolving power (10% valley definition). Quantitation was performed using the isotopic dilution method. Relative response factors were calculated for each individual analyte from six different calibration solutions for PCDD/Fs. Details of the HRGC-HRMS analysis has been previously reported by our laboratory [13-14].

3   Results and discussion

3.1 Linearity, repeatability and LODs

133 In order to test the reliability/analytical characteristics of the instrumental method,

134 parameters such as linearity, repeatability, and limits of detection (LODs) were evaluated.

135 The linearity of the method was studied by analyzing the standard solutions (in triplicate) at

136 six concentrations (CSL, CS0.5, CS1 to CS4) ranging from 0.1 ng/mL to 40 ng/mL for the

137 Tetra PCDD/Fs, from 0.5 to 200 ng/mL for the Penta through Hepta PCDD/Fs, and from

138 1.0 to 400 ng/mL for the Octa PCDD/Fs. The linearity was satisfactory, with correlation

139 coefficients (r) >0.9990. The relative standard deviation (RSD) of the relative response

140 factors (RRFs), as defined in standard methods EPA 1613 or EU 1948, were also

141 satisfactory and all were <15%, as specified in both methods. Based on area, the

142 repeatability was within 15% (n = 10) for the injection of a 10-fold dilution of the CSL

143 standard (10 fg for tetra PCDD/DFs).

144 Instrumental LODs were estimated by the analysis of a standard solution injection as the

145 concentration level giving a signal-to-noise ratio (S/N) of at least 3. Achieved values were

146 found to be around 2 fg for all studied compounds and around 1 for octa-chlorinated

147 compounds. These estimated LOD for the studied compounds are comparable to those

148 observed by HRMS.

149

150 **3.2 Analysis of samples**

151 Once the method was instrumentally validated, analysis of the eight stack emission samples

152 were performed. All these samples were previously analyzed by using the standard

153 methodology by HRGC-HRMS. The concentrations of 2,3,7,8 chloro-substituted congeners

154 expressed in pg/sample as well as the total I-TEQ per sample analysed by GC-APCI-

155 MS/MS with QqQ and GC-EI-HRMS are presented in the **Table 2.** Good agreement

156 between results obtained with both methodologies can be observed with relative differences

157   below 15% in most cases which validate the developed methodology by GC-APCI-MS/MS

158   for the analysis of PCDD/Fs in stack gas emissions. Further, the total pg I-TEQ/sample

159   comparison for both methods was carried out graphically and statistically (logarithmic

160   scale). As it can be seen in **Figure 1** there is a good correlation between the total pg-I-TEQ

161   obtained by both methods. Similar conclusions have been reported in other comparative

162   studies related to different matrices like food and feed or certified and standard reference

163   materials [5,8]. Alternatively, **Figure 2** shows the results obtained when comparing the

164   concentrations for individual compounds obtained by both methods using a boxplot

165   representation, by sample and by compound, calculated as the relative difference

166    $(100*(X_{APGC} - X_{HRMS})/X_{HRMS})$. In both cases mean differences are very close to zero value

167   (especially when considering by sample all compounds analyzed). In any case, most values

168   included between the first and third quartile are lower than 15%.

169   The highest deviations were a consequence of the unresolved compounds in the DB5-MS

170   column, corresponding to 2,3,4,7,8-PeCDF and 1,2,3,7,8,9-HxCDF as previously reported

171   by Martinez et al [15]. Relative differences in total I-TEQ were in most cases below 5%,

172   being higher deviations related to some of the samples with lowest levels. The highest

173   deviation corresponds to sample "CP-Co", with 0.5 pg I-TEQ/Nm^3 determined from an

174   aliquot of 50%, leading to a total of 5 pg I-TEQ/injection. In a similar way,, Fürst et al. [16]

175   reported the achievement of comparable results by LRMS/MS and HRMS on food and feed

176   samples available in the laboratory, with contamination levels in range of 0,5-3 pg WHO

177   TEQ/g and deviations of 15%. Considering that 5 g of lipid are used for food analysis,

178   these levels are similar to that reported in our case (3-10 pg I-TEQ on-column). On the

179   other hand, García-Bermejo et al. [17], reported in 2015 similar results with deviations of

180   less than 5% in food samples, and advised the lack of data in other matrices, especially for

181   environmental samples. In this sense, and beyond this preliminary study, further analysis

182   with low level environmental samples should be conducted in the near future to confirm the

183   promising results obtained in this work since some discrepancies have arisen at low level

184   concentrations using GC-MS/MS. As an illustrative example, **Figure 3** shows positive

185   finding of 4 Hexa-PCDFs (left) and 3 Hexa-PCDDs (right) in municipal solid waste

186   incineration sample. GC-APCI-MS/MS allowed quantification and identification of these

187   compounds using two SRM transitions (one for quantification and one for confirmation),

188   giving an estimated concentration as low as 5.5 pg/sample for 123789-HxCDF.

189   Finally, method LOQs were estimated as the concentration corresponding to a S/N ratio of

190   10 using the chromatograms of a low I-TEQ sample extract (CP-Co sample). Values

191   estimated ranged from 0.5 to 5 pg/sample for all compounds, except for 2,3,7,8-TCDF,

192   1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF that were around 20 pg/sample. The estimated LOQ

193   (using S/N of 10) was confirmed with some of the compounds that could be found at low

194   levels (close to LOQ) with good accuracy according to GC-HRMS results. Thus,

195   1,2,3,7,8,9-HxCDF with an LOQ estimated of 1 pg/sample, has been accurately quantified

196   at LOQ in sample CP-Co, as well as, 1,2,3,4,7,8,9-HpCDF or 1,2,3,4,7,8 HxCDD in the

197   same sample.

198

199   **4   Conclusions**

200   In this study, comparative results with the reference method (HRMS) have demonstrated

201   that APGC-MS/MS technique is successful in achieving similar results, and then is also

202   suitable for emissions samples analysis. Thus, this technique appears to be adequate in this

203   field, where a broader applicability, less expensive and more flexible instrumentation are

204   key factors to consider, leading to the feasibility of future on-line in-stack determination.

205

5 Acknowledgements

213

6. References

214

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290

291 **FIGURE CAPTIONS**

292

293 **Figure 1.** Graphical and statistical fitting in logarithmic scale of total pg I-TEQ per sample

294 obtained by HRGC-HRMS and GC-(APCI)MS/MS

295 **Figure 2.** Box-whisker plots for the percent of relative change for concentrations of

296 individual compounds obtained by HRGC-HRMS and GC-(APCI)MS/MS for all samples,

297 (a) by sample with all congeners considered and (b) by compound with all samples

298 considered.

299 **Figure 3.** GC-APCI-MS/MS for municipal solid waste incineration.

300

301   **Table 1.** Information of the process and the emission sample collection

Industrial Process		Sampling system	Sampling time (d)	Gas volume (Nm^3)
Municipal Solid Waste Incineration (MSWI)	MSWI1	Long term	28	675
	MSWI2		31	748
Hazardous Waste Incineration (HWI)	HWI1		21	499
	HWI2		23	548
Cement Kiln co-incineration	CP-Co		21	521
Steel Industry	MI1	Manual	0.4	˜6
	MI2		0.4	˜6
Municipal Solid Waste Incineration (MSWI)	MSWI3		0.4	˜6

302

303

Table 2. Concentrations of 2,3,7,8 chloro-substituted congeners expressed in pg/sample and total I-TEQ of each sample analysed by APCI-GC-(QqQ)MS/MS and GC-(EI)HRMS

Compound	MSWI1		MSWI2		HWI1		HWI2		CP-Co		MI1		MI2		MSWI3	
	APGC	**HRMS**	**APGC**	**HRMS**	**APGC**	**HRMS**	**APGC**	**HRMS**	**APGC**	**HRMS**	**APGC**	**HRMS**	**APGC**	**HRMS**	**APGC**	**HRMS**
2378-TCDF	341	348	22821	21279	672	730	4736	5214	1864	1530	2722	2543	149	162	91	90
12378-PeCDF	407	439	34200	30745	1382	1377	10282	10728	142	139	1733	1928	214	177	72	69
23478-PeCDF	814	861	59959	44941	2534	2420	15049	13811	162	142	3966	3797	321	275	158	159
123478-HxCDF	486	547	37276	40127	3966	3732	21414	21459	16	17	1971	1892	232	228	127	135
123678-HxCDF	575	561	37478	39574	5514	5792	25360	26146	12	13	1954	1960	224	262	113	113
234678-HxCDF	718	770	49302	48734	10988	11116	42558	45375	10	8.8	2538	2535	265	279	142	133
123789-HxCDF	46	54	1688	1822	117	130	609	695	1.0	1.2	137	137	18	19	5,5	7,3
1234678-HpCDF	1429	1399	102439	97112	31033	33332	124478	121529	12	13	3253	2971	574	531	467	441
1234789-HpCDF	236	236	6901	6493	3291	2989	16659	14930	2.8	2.5	576	745	149	149	21	19
OCDF	767	807	10294	9727	27395	27076	143646	139663	5.0	5.8	657	683	366	363	58	62
2378-TCDD	64	80	2041	1979	70	66	890	905	18	18	141	137	11	10	7,0	8,4
12378-PeCDD	529	491	11936	11518	380	418	4648	4853	6.6	6.1	498	501	36	35	27	22
123478-HxCDD	623	632	12363	12297	415	418	3043	2949	2.8	3.3	295	281	21	21	24	22
123678-HxCDD	2242	2100	29885	28695	920	931	7006	7127	7.5	6.6	573	558	79	78	41	39
123789-HxCDD	935	774	15424	14904	435	428	3534	3801	4.2	3.9	333	350	56	54	28	27
1234678-	7686	7263	98657	96111	4656	4448	37914	36243	33	34	2217	2390	246	247	148	146

HpCDD																
OCDD	4568	4497	56432	56400	8907	8728	108713	103759	34	41	1610	1776	147	161	221	233
pg/sample	**22466**	**21859**	**589096**	**562458**	**102675**	**104131**	**570539**	**559187**	**2333**	**1985**	**25174**	**25184**	**3108**	**3051**	**1751**	**1726**
pg I-TEQ	**1452**	**1451**	**60543**	**54553**	**4325**	**4325**	**24121**	**24020**	**302**	**258**	**3576**	**3473**	**315**	**294**	**167**	**166**
pg I-TEQ/Nm^3	**2.2**	**2.1**	**80.9**	**72.9**	**8.7**	**8.7**	**44.0**	**43.8**	**0.6**	**0.5**	**596.0**	**578.8**	**52.5**	**49.0**	**27.8**	**27.7**
Sampling Time (d)	28		31		21		23		21		0.4		0.4		0.4	
Gas volumen (Nm^3)	675		748		499		548		521		˜6		˜6		˜6	
Sampling system	**Long term**										**Manual**					

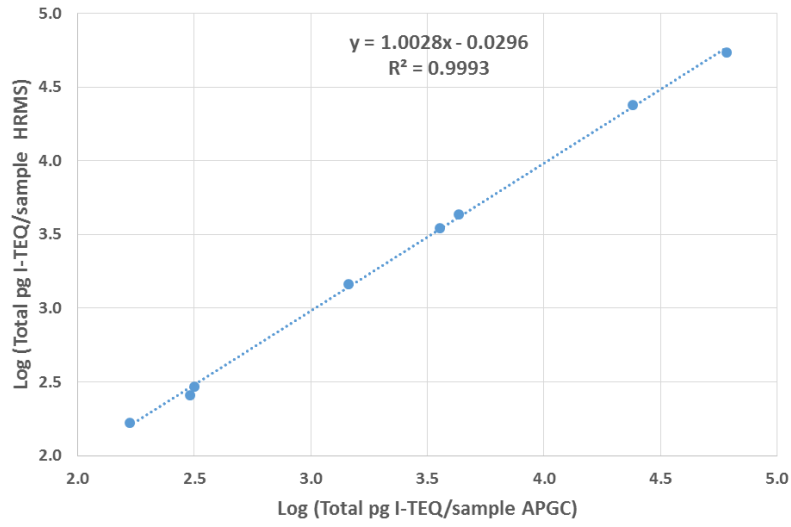**Figure 1.** Graphical and statistical fitting in logarithmic scale of total pg I-TEQ per sample obtained by HRGC-HRMS and GC-(APCI)MS/MS
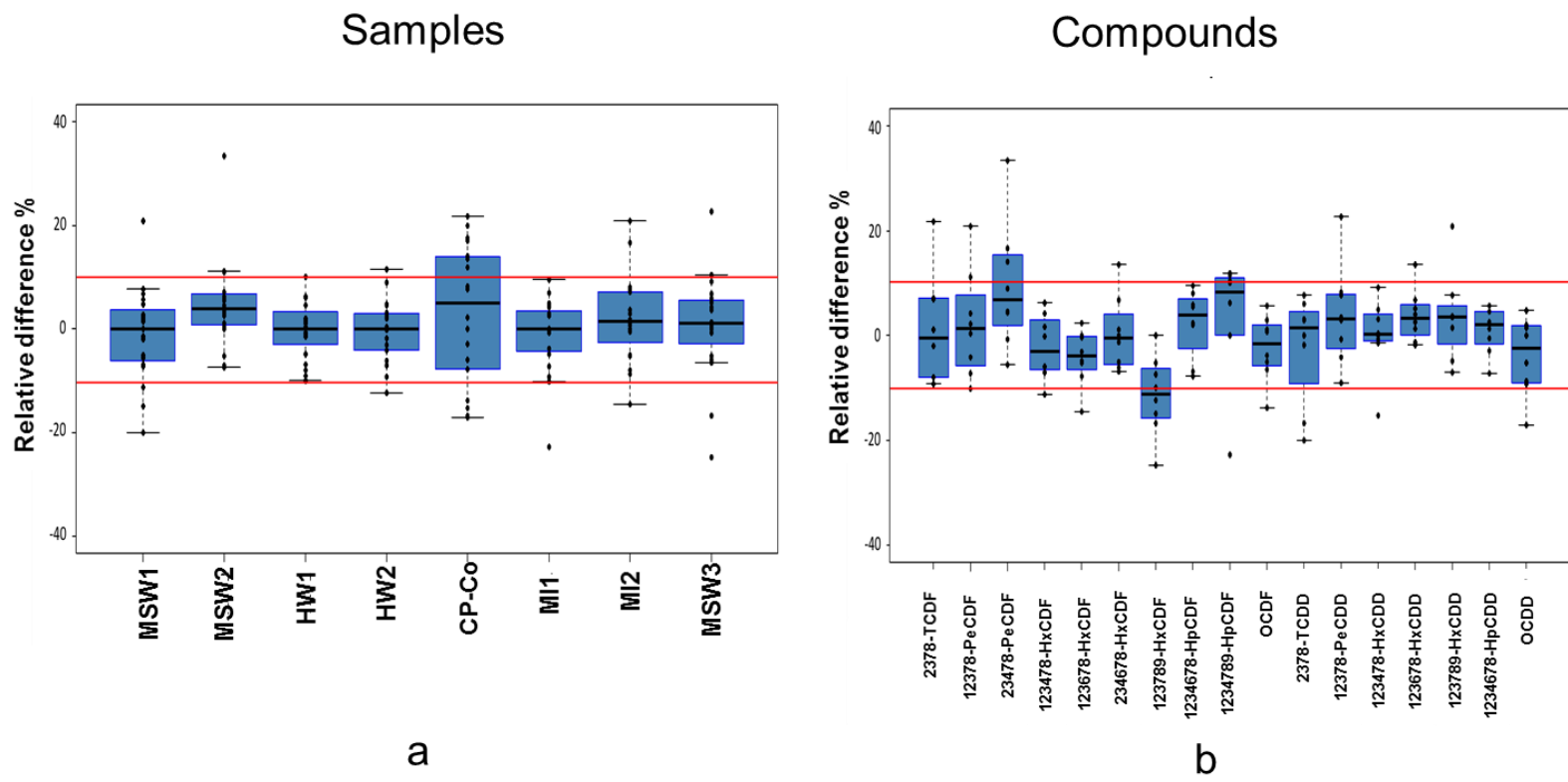
Figure 2. Box-whisker plots for the percent of relative change for concentrations of individual compounds obtained by HRGC-HRMS and GC-(APCI)MS/MS for all samples, (a) by sample with all congeners considered and (b) by compound with all samples considered.
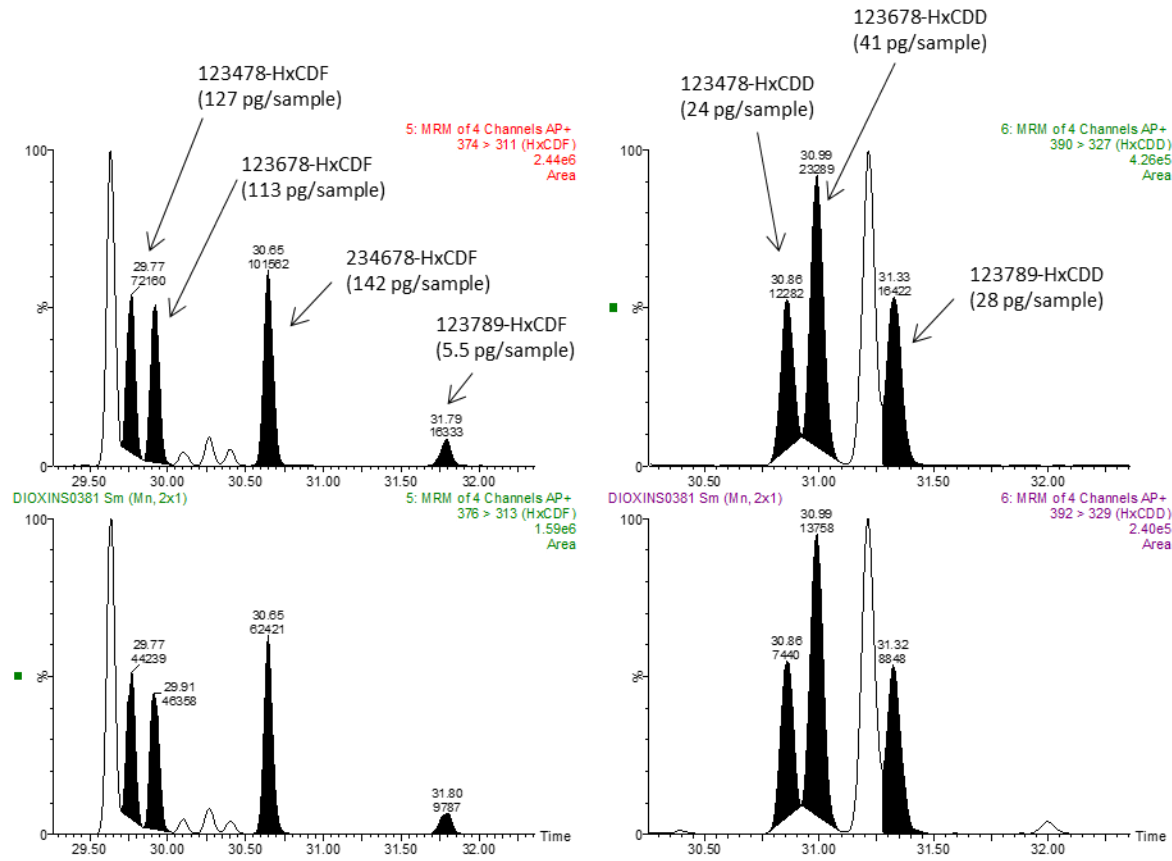
Figure 3. GC-APCI-MS/MS for municipal solid waste incineration