An assessment of different extraction and quantification methods of penta- and hexa-chlorobenzene from SRF fly-ash

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ABSTRACT

Highly chlorinated benzenes, produced in the presence of organic matter and chlorine, are considered PCDD/Fs precursors, and are used as cost and time convenient substitute indicators for the indirect measurement of the latter. In this study penta- and hexa-chlorobenzene are quantified for the determination of the organochloride load of fly ash from solid recovered fuel incineration. Some of the chlorobenzenes are formed under 'de novo' conditions, through heterogeneous (ash particles/flue gases) reactions and are therefore deeply incorporated within fly ash. Accelerated solvent extraction (ASE) and ultrasonic solvent extraction (USE), along with the equivalent clean-up methods suggested by literature were compared to traditional Soxhlet. The extraction efficiencies achieved were 83 ± 7.5% for Soxhlet, 111 ± 19% for PFE, and 67 ± 17% for ultrasonication. Soxhlet extraction and clean-up through a multilayer silica gel column gave more precise results compared to the other sample preparation methods. Furthermore, performance comparison of gas chromatography fitted with either a mass spectrometer operated in single ion monitoring mode (GC-MS-SIM), or electron capture detector (GC-ECD) highlighted that ECD can be used for measuring chlorobenzenes traces down to 0.21 ng g^{-1}, when the equivalent LOQ for MS-SIM was 3.26 ng g^{-1}. The results further suggest that ECD can provide better peak integration than MS-SIM in the detection of chlorobenzenes in fly ash extracts, due to the detector's sensitivity to halogenated compounds.

1. Introduction

In response to the EU Landfill Directive diverting targets [1], the number of mechanical–biological treatment (MBT) plants in Europe has nearly doubled in the last 8 years [2]. This growth has resulted in a significant increase of refuse derived fuel (RDF) and solid recovered fuel (SRF) being generated [3]. Notwithstanding the great potential for power generation of these materials, their market uptake is still relatively limited due to their fuel composition reliability and in particular to their concentration of chlorine. The latter, in particular has potential negative impact on both the boiler and its emissions [4] and pivotal to its monitoring, is the extraction and quantification of its derivatives (such as polychlorinated dibenzo-p-dioxins and dibenzofurans) in gas and fly-ash. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are persistent organic pollutants (POPs), which are highly toxic for humans. They are formed during thermal treatment processes mainly by *de novo* synthesis from chlorine and carbonaceous materials and condensation reactions from precursors such as chlorobenzenes (PCBz) and chlorophenols (PCP) [5–7].

Their quantification involves extensive sample preparation and technical skills-intensive analytical measurements [8]. Such quantification, although standardized, can present challenges even for specialised laboratories leading to high variations in the results, as shown from inter-laboratory comparison exercises [9]. Furthermore, high costs for instrumentation such as, high resolution gas chromatograph coupled to high resolution mass spectrometer (HRGC/HRMS), and specialised consumables (^{13}C enriched compounds), along with time constraints due to the complexities of the extraction methods and the high number of isomers (210), make PCDD/Fs analysis quite demanding.

Research for a time and cost effective substitute method for the indirect monitoring of PCDD/Fs in gaseous emissions, especially in waste incineration processes, started in the 1980s. Statistical

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correlation patterns between the PCDD/Fs and their major precursors have been investigated to estimate organochloride load in flue gases without the need to fully characterise the dioxins content. Several studies have demonstrated that hexa-, penta- and tetra-chlorobenzene can be used for the estimation of the international toxicity equivalents (I-TEQ) values of PCDD/Fs [7,10–12]. Furthermore, CBs were found to be good indicators of organochloride load in fly ash residues in dechlorination/detoxification studies [13,14], and in studies for the catalytic effect of metals in the formation of chlorinated organics [15, 16].

A wide range of methods is described in literature for the extraction and quantification of CBs in solid matrices (Table 1), but no standard method is yet available. Usually a pre-treatment such as grinding [17] and/or acid digestion [13,14,18] is used to increase the transfer of the target species to a liquid phase. Fly-ash from municipal incinerator has proved difficult to extract and requested matrix destruction with acid treatment [18]. Then a solvent extraction stage is used to separate the target species. Soxhlet extraction (Dean-Stark modified, or automated) is the most frequently applied technique and often used as a reference for the efficiencies of other extraction methods. Major disadvantages of Soxhlet extraction include: the amount of time needed (18–48 h per sample); the large volume of solvent used (120–400 ml per sample) [14,19]; and the subsequent losses of volatile and semi-volatile species during concentration of extracts (ranging between 5 and 20% for highly chlorinated benzenes, depending on the evaporation method used). A comparison between Rotavapor (RV) and TurboVap II (TV) for the extraction of PXDD, PXDF, PCB, PAH, CBz, and CPh, showed that when the RV samples were further evaporated to final volumes in the same order as the TV (0.5 ml), recoveries of mono CP and diCBz were 40–50% lower. This is linked to the higher vapour pressures of diCBz (90 Pa for 1,4-diCBz) compared to monoCP (0.002 for hexaCBz) [18].

Accelerated solvent extraction (ASE), also called pressurised fluid extraction (PFE), utilises elevated temperature and pressure conditions and thus smaller amounts of solvents (10–50 ml per sample) and time (10–40 min) and has been used for chlorinated benzenes extraction in several studies [17,20,21]. Extraction improvements of this method using lower solvent volumes are possible due to a combination of temperature and pressure cycles above the boiling point of the organic solvent, which increases diffusion rates, analytes' solubility and decreases solvent viscosity. These in turn help the solvent penetration into the matrix and produce higher recoveries. More recently, ultrasonic solvent extraction (USE) has been employed in fly ash samples for the extraction of chlorinated benzenes and recoveries equivalent to Soxhlet have been reported [22]. Furthermore, ultrasonication has

the same advantages as ASE in terms of volume of solvents, and time needed for the analysis, compared to traditional Soxhlet extraction. Other techniques exist, such as microwave assisted extraction [19] but were not available at the time of the study'.

Finally, in the quantification of CBs the selection of the clean-up method and the GC detector depends on the expected interferences from the matrix and the concentrations of the target pollutants. A multilayer silica gel column (anhydrous Na_2SO_4, 10% $AgNO_3$ silica gel, 22% H_2SO_4 silica gel, 44% H_2SO_4 silica gel, KOH silica gel) [19] [23] has been reported to be efficient in the absorption of interferences from fly ash enabling the separation and speciation of CBs with GC/MS. For example, Korenkova et al. [22] extracted CBs using ultrasonication and the quantification was achieved, simply after paper filtration, using large volume injection (LVI) GC/MS. Therefore, the need for extensive sample clean up, is also related to the available instrumentation. Other combination of clean-up methods and detection instruments are summarised in Table 1.

In this paper, penta- and hexa-chlorobenzene were selected for the evaluation of the organochloride load of fly ash, collected from the cyclone of a fluidised bed combustor, from solid recovered fuel (SRF) incineration. In this context, alternative sample preparation methods to the traditional Soxhlet method were compared for their recoveries, precision and ease of use. Further to this, two GC detectors including mass spectrometer using Single Ion Monitoring mode (SIM) and electron capture detector (ECD) chromatographic detectors were assessed and compared in terms of detection and quantification performance.

2. Material and methods

2.1. Origin and preparation of samples

Solid recovered fuel (SRF) is the term used to describe waste derived fuels from non hazardous sources, with standardized information regarding their net calorific value, chlorine and mercury content [24]. The SRF used in this case, was the combustible output of a mechanical-biological treatment (MBT) plant in East London. Details on the waste fuel, and the combustion experimental conditions under which the fly ash was produced, are reported in a previous paper [25].

Briefly, the 50 kW fluidised bed combustor used for the trial consisted of a screw feeding hopper, the main bed chamber (dimensions 173*30*30 cm), a secondary combustion chamber that leads to a vertical ash deposition/combustion system, a water cooling tower, a cyclone and an exhaust fan prior to the stack. The rig was monitored by 19 thermocouples, CO, CO_2, and O_2 online gas monitoring systems, HCl and gaseous chlorobenzenes capturing

Table 1
Pre-treatment, extraction, clean-up methods and instrumentation for the quantification of chlorobenzenes from solid matrices.

Pre-treatment	Extraction	Clean- up	Detection	Reference
Acetic acid	Soxhlet- Dean- Stark	Silica gel column	GC-MS	[18]
HCl digestion	Refluxing	Multilayer silica gel column	HRGC-LRMS[a]	[13]
_	Soxhlet	_	HRGC-MS-SIM	[15]
_	Ultrasonication	_	GC-MS-SIM	[30]
_	Ultrasonication	Filter paper	LVI[b]-GC-MS	[22]
_	Soxhlet	Multilayer silica gel column	GC-MS	[19]
Acetic acid	Soxhlet- Dean- Stark	Multilayer silica gel column	GC- MS-MSD[c]	[14]
Grinding	PFE	Silica/alumina column	GC-MS-MS/GC-HRMS	[17]
_	Ultrasonication	Alumina column	GC-MS-SIM/GC-ECD	[26]
	Photochemical (photolysis tube)		GC-MS (SIM)	[31]

[a] LRMS: Low resolution mass spectrometry.
[b] LVI: Large volume injection.
[c] MSD: Mass selective detection.

bubblers. The bed area was filled with 30.2 kg of silica sand [particle size 1.00–0.5 mm, 16/30 grade, density 1556 g/l, bed static dimensions = 30*30*15.35 cm]. The FBC was vacuum cleaned the day before the experiment for the removal of residual ash and particles from previous trials. Furthermore, it was operated overnight, burning natural gas resulting in a bed temperature of 460 °C for the elimination of organic species. The supply of primary, secondary air and natural gas before the SRF feeding was 500, 400 and 25 l/min, respectively. The SRF incoming flow varied throughout the trial with a mean value of 117 g/min and a lambda [λ] coefficient equal to 1,6. The duration of the test was 300 min and the bed temperature was kept at 800 ± 20 °C. Finally, the CO readings in the flue gasses ranged at low levels 50 ± 30 ppm.

The fly ash was collected using vacuum from the cyclone of the fluidised bed combustor. Sample replicates of 10 ± 0.01 g each, were homogenised using a mortar and screened through a 0.5 mm sieve. The samples were spiked with 1 ml of 800 ng ml^{-1} 1,3,5-tribromobenzene in toluene (extraction standard). 30 ml of dichloromethane was added, to cover the ash in a conical flask, and shaken mechanically at least for 24 h, until dry, to allow the incorporation of the standard within the ash matrix. The schematic representation of the following extraction methods is shown in Fig. 1.

2.2. Extraction methods

The solvents used for the extraction were HPLC grade (Rathburn, UK). The glassware (separation funnels, transfer vials, rotary flasks, micro syringes) was decontaminated using a two-step process with acetone and dichloromethane. The extraction standards were prepared in-house (Sigma-Aldrich, CAS 626-39-1). The recovery standards were purchased already prepared (Sigma-Aldrich, CAS 2199-69-1). The limits of detection (LOD) and quantification (LOQ) were determined to be the mean concentration of the analytical blank controls and 3 and 5 times the standard deviation of the

analytical blank controls, respectively.

2.2.1. Soxhlet and accelerated solvent extraction

Fourteen replicates and two blank matrix samples were each digested with 100 ml of 2 M HCl in conical flasks. The flasks were shaken periodically for about an hour, until no further foaming reaction was observed. The mix was separated using vacuum filtration and the cake was washed with deionised water to reduce acidity. Continuous vacuum was applied for 12 h to allow the air drying of the cakes, which were then transferred with the filter papers in the Soxhlet cellulose thimbles, and the ASE extraction cells.

Half of the cakes were Soxhlet extracted using 200 ml of toluene for 20 h, and the other half were extracted using a Dionex accelerated extractor (ASE 200) with 60 ml of toluene. The ASE settings were as follows: 175 °C, 1500 psi, static time = 8 min, static cycles = 2, flush = 70%, purge = 60–120 s. The aqueous solutions were extracted three times with 100 ml of dichloromethane per litre of solution. The solvent extracts were washed twice with deionised water (50% v/v). The two extracts from each sample were mixed, concentrated using a rotary evaporator (38 °C, 68 mbar), filtered through a multilayer silica gel column (anhydrous Na$_2$SO$_4$, 10% AgNO$_3$ silica gel, 20% H$_2$SO$_4$ silica gel, 40% H$_2$SO$_4$ silica gel, 30% KOH silica gel) and eluted with hexane equivalent to double the volume of the column. The column's elutes were further evaporated using a rotary evaporator (35 °C, 200 mbar) and finally concentrated to 1 ml using a nitrogen flow concentrator. The samples were finally spiked with 100 μl of 1.6 μg ml^{-1} of 1,2 dichlorobenzene-d^4 (recovery standard).

2.2.2. Ultrasonic solvent extraction

Seven replicates of spiked fly ash samples, and a blank matrix sample consisting of decontaminated silica sand were placed in 50 ml PTFE tubes with 40 ml of acetonitrile. The samples were extracted using an ultrasonic bath at 30 °C for 2 h, centrifuged
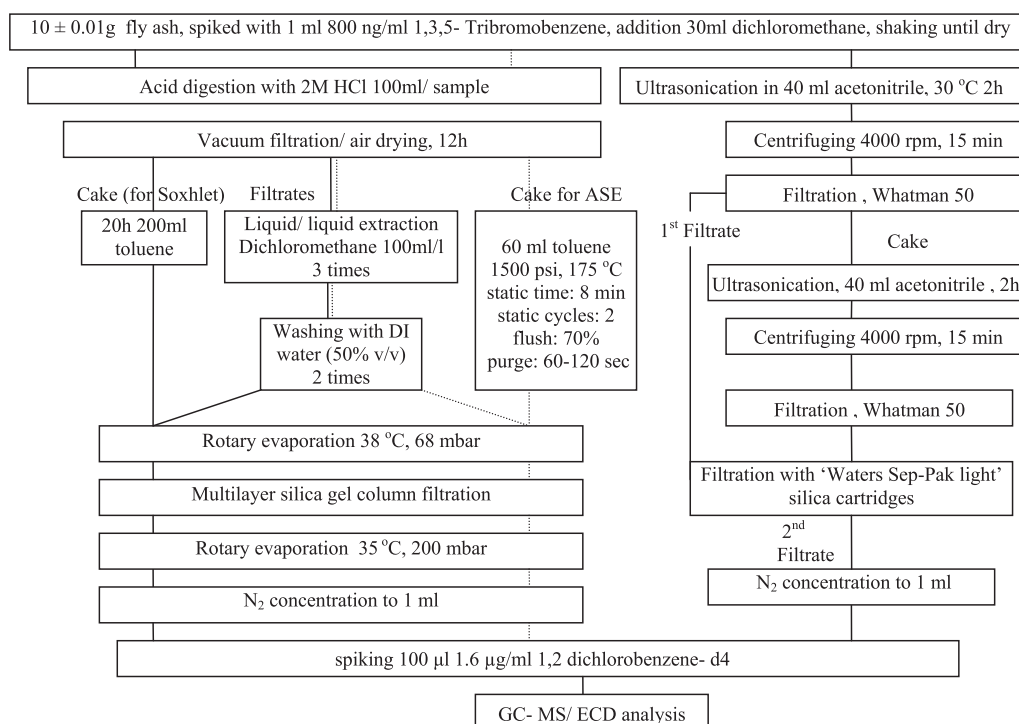

Fig. 1. Overview of solvent extraction methods used for chlorobenzenes extraction.

(15 min, 4000 rpm) and filtered using Whatman-50 filter paper. The extraction was repeated under the same conditions, with fresh solvent, and the two filtrates were mixed and evaporated under a gentle nitrogen flow to 1 ml. Optimum extraction conditions (ultrasonication time, solvent/matrix ratio, ultrasonication cycles, and filtration method) were the same as reported previously [22]. A lipid phase residue observed in the final concentrate, prevented direct chromatography injection, and a further purification step was employed using 'Waters Sep-Pak light silica' cartridges attached to gas tight syringes, and eluted with 5 ml acetonitrile. Finally the samples were concentrated again with a nitrogen flow down to 1 ml, and each was spiked with 100 μl of 1.6 μg ml^{-1} 1,2 dichlorobenzene-d4 (recovery standard).

2.3. Instrumental analysis

All samples were stored at 4 °C until GC-MS/GC-ECD analysis. The chromatographic column used for the two detection systems was a Thames-Restek Rtx$^{®}$- 1MS- 100% dimethyl polysiloxane (15 m × 0.25 mm ID, 0.25 μm film thickness). The GC conditions were as follows: 125 °C at 30 °C min^{-1}; followed by a second increase to 300 °C at 15 °C min^{-1} and then held at this temperature for 6 min. The carrier gas was helium and the injection volume was 1 μl at a split ratio 100:1 at 300 °C. The GC-ECD used was an Agilent Technologies − 6890N Network GC system equipped with a ^{63}Ni ionisation source and the identification was based on the retention times of the target species. The GC/MS was a Perkin Elmer- Autosystem XL/Turbo Mass Gold instrument operated in positive ion mode (+70 eV) and the mass spectrometer was operated using the selective ion monitoring (SIM) mode. The selected masses were: m/z = 150, 148, 152 corresponding to the [M^{+}] ions of 1,2-dichlorobenzene-d4, m/z = 314, 316, 312 corresponding to the [M^{+}]

ions of tribromobenzene, m/z = 252, 250, 248 corresponding to the [M^{+}] ions of pentachlorobenzene, and m/z = 284, 286, 282 corresponding to the [M^{+}] ions of hexachlorobenzene. A typical sequence of injections consisted of one blank, six unknowns, one blank, four standards, one blank, and an analytical blank.

3. Results and discussion

Extraction efficiencies, calibration coefficients, LOQs, and mean concentrations for penta- and hexa-chlorobenzene obtained for each sample preparation method and the two investigated systems of detection are summarised in Table 2.

3.1. GC detection systems: ECD vs MS-SIM

Comparison of the LOQs obtained from the two detectors showed a difference, with ECD being able to detect limits approximately 15 and 10 times lower than MS-SIM, for pentachlorobenzene and hexachlorobenzene respectively. Quantification of the 1,3,5 tribromobenzene extraction standard showed increased recovery (extraction efficiency) in MS-SIM, for all the sample preparation methods: 197 ± 25% for Soxhlet, 159 ± 19% for ASE, and 114 ± 31% for ultrasonication, against 83 ± 7.5%, 111 ± 19%, and 67 ± 17%, respectively when analysed with ECD. In general, the background noise when using ECD was lower for MS-SIM (Fig. 2), with signal: noise being 4 times higher for ECD than for MS-SIM.

These results suggest that sample matrix strongly interfere with the ion quantification in the MS-SIM, and contribute to the enhanced extraction efficiency results obtained for both control and target compounds. Further purification of samples would be required for improving accuracy of final measurement e.g. purification using an aluminium oxide filtration column [26].

Table 2
Extraction efficiencies, calibration coefficients, LOQs, and mean concentrations for penta- and hexa-chlorobenzene for the three sample preparation methods and the two detectors.

Detector	Sample	Sample preparation method								
		Soxhlet			PFE			Ultrasonication		
		Extraction efficiency %	*Cl$_5$Bz ng g^{-1}	*Cl$_6$Bz ng g^{-1}	Extraction efficiency %	*Cl$_5$Bz ng g^{-1}	*Cl$_6$Bz ng g^{-1}	Extraction efficiency %	*Cl$_5$Bz ng g^{-1}	*Cl$_6$Bz ng g^{-1}
MS-SIM	1	146	7.62	-^{a}	145	20	11.47	73	3.6	-^{a}
	2	208	13.6	-^{a}	147	9.37	12.64	125	-^{a}	-^{a}
	3	195	9.12	-^{a}	134	12.5	15.67	156	-^{a}	-^{a}
	4	218	6.77	-^{a}	166	8.50	11.26	151	-^{a}	-^{a}
	5	222	12.5	-^{a}	169	10.8	11.27	93	3.4	-^{a}
	6	193	-^{a}	-^{a}	195	-^{a}	10.29	88	-^{a}	-^{a}
	7	−	−	−	158	8.72	15.73	-^{a}	-^{a}	8.2
	mean	197	9.92	−	159	11.65	12.62	114	3.5	8.2
	± s	25	2.67	−	19	3.9	2	31	0.1	−
	RSD (%)	13	2.7	−	12	3.4	1.6	28	0.3	−
	LOQ ng g^{-1}		4.2	5.57		4.8	5.8		3.26	4.1
	r^2		0.997	0.985		0.997	0.985		0.997	0.985
ECD	1	71	8.6	8.27	89	18.40	8.00	90	6.36	-^{a}
	2	92	14.8	3.00	106	12.82	8.23	73	9.14	-^{a}
	3	81	11.7	2.46	134	12.31	5.53	79	4.98	-^{a}
	4	84	8.45	1.50	105	14.98	7.83	74	10.9	-^{a}
	5	89	11.3	1.44	136	13.78	5.94	57	9.45	-^{a}
	6	79	9.33	1.87	90	19.73	10.9	59	10.4	-^{a}
	7	−	−	−	114	15.00	10.3	38	17.2	-^{a}
	mean	83	10.68	3.34	111	15.28	8.11	67	9.77	−
	± s	7.5	2.4	2.8	19	2.8	2	17	3.90	−
	RSD (%)	9	2.3	8.5	17	1.8	2.5	26	4.0	−
	LOQ ng g^{-1}		0.25	1.44		0.21	2.9		0.28	0.4
	r^2		0.9999	0.9999		0.9999	0.9999		0.9999	0.9999

*Corrected values according to extraction and recovery efficiencies.
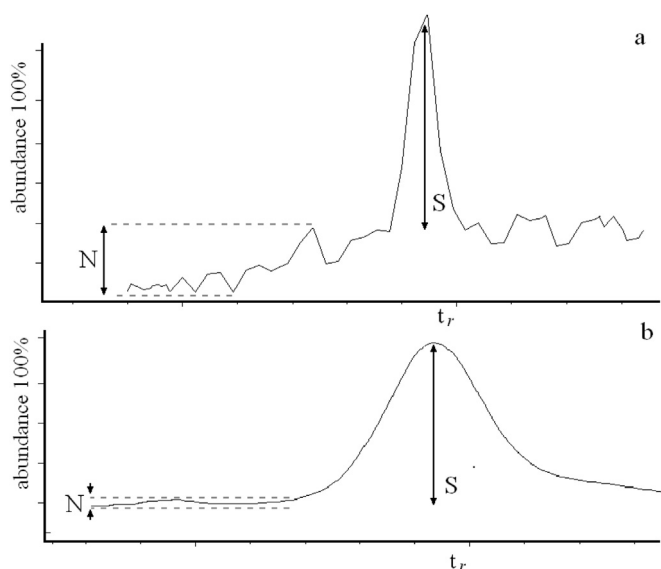- ^{a} Values lower than LOQ.

Fig. 2. Representative chromatograms of penta-chlorobenzene for the same sample extracted by Soxhlet (a) MS- SIM m/z = 252- S/N = 19, (b) ECD- S/N = 84.

Fig. 3. Comparison of ECD signal to noise ratio for penta- and hexa-chlorobenzene obtained for the three extraction methods.

Furthermore, when MS-SIM is used the utilisation of ^{13}C labelled extraction/recovery standards is essential for the minimisation of sample matrix interferences.

The halogenated compounds significantly affect the ECD detector signal, in comparison to other noise e.g. trace hydrocarbons, which build up the peak of interest at a specific retention time. This is evidenced by the lower extraction efficiencies reported for standard recovery. These results are in agreement with those reported in the literature e.g. Refs. [27–29]. In this case the advantages of ECD are based on the complexity of the environmental matrix studied, and the high selectivity of the electron capture detector halogenated compounds, resulting to better chromatograms for CBs, and eliminating the need for extensive sample purification. Given these results, the ECD quantification results have been used in the subsequent analyses for comparing the extraction/ sample preparation methods.

3.2. Comparison of solvent extraction methods

Of the three solvent extraction methods assessed, Soxhlet provided the most consistent extraction efficiency, with the lowest RSD (Table 2). ASE and USE showed enhanced and inferior extraction capabilities, respectively, compared to Soxhlet extraction. Both methods also presented large distributions around the mean values. A one way ANOVA (p = 0.05) confirmed that there is a statistically significant difference in the extracted pentachlorobenzene, with ASE resulting in greater concentrations (15.28 ± 2.8 ng g^{-1}), than Soxhlet (10.68 ± 2.4 ng g^{-1}) or ultrasonic extraction (9.77 ± 3.9 ng g^{-1}). This finding is partially explained by the enhanced extraction efficiency of ASE. The high pressure helps solvent molecules to reach matrix pores and allows the extraction of analytes deeply enclosed in the matrix. Furthermore, the circulation of solvent in a closed system, can minimise analyte losses. Fly ash composition are linked to the nature of the SRF material and to the system used to neutralise organic pollutants. For example, when lime or activated carbon is used to adsorb the pollutants formed during the process in the flue-gas, the residual are left in the fly ash which are then very difficult to extract. Similarly to what reported by Ref. [20] ASE also extracted more hexachlorobenzene (8.11±2 ng g^{-1}) than Soxhlet (3.34 ± 2.8 ng g^{-1}), while the values for hexachlorobenzene using ultrasonic extraction were below the LOQ.

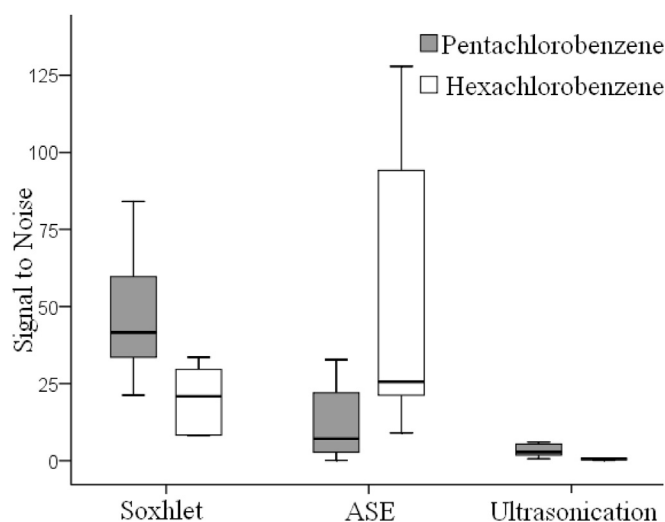The poor performance of ultrasonication as an extraction technique highlights the importance of matrix digestion for the specific analysis. Some of the chlorobenzenes are possibly formed under 'de novo' conditions, through heterogeneous (ash particles/flue gases) reactions and are therefore deeply incorporated within fly ash. In this case the matrix is the pollutant, and further examination of the efficiency of ultrasonic extraction in digested matrices would be interesting for future comparisons.

Even if direct comparison is difficult due to the difference in matrix and method of reporting, similar trends have been identified by other studies [15, 22].

Although, the methods present differences in the sample preparation, extraction and the clean-up techniques, a comparison of their general extraction efficiency can be based on the detector's signal against the background noise, and thus the extraction against the clean up efficiencies, respectively. The results are plotted in Fig. 3, which illustrates that Soxhlet and the subsequent multilayer silica gel column clean up give better results for both compounds between the examined methods.

Based on these results, one can argue that ASE gave relatively good results compared to Soxhlet. The disadvantages of ASE were the enhanced recovery (extraction efficiency) and a wide RSD (17%) among replicates. Finally the method that incorporated ultrasonication showed poor performance in terms of extraction efficiency, S/N, and precision (RSD 26%) compared to Soxhlet and ASE.

4. Conclusions

For the determination of highly chlorinated benzenes in fly ash from SRF fluidised bed combustion, three different extraction methods have been compared. The results suggest that matrix digestion followed by Soxhlet extraction and multilayer silica gel column filtration, produce precise results with better signal to noise chromatograms than ASE and ultrasonication. We conclude that if time efficient and solvent saving extraction methods, such as ASE and ultrasonication are to be used instead of traditional methods, they need to be clearly defined and optimised for the specific matrix and species.

Furthermore, the detection limits and the consistency of the readings of ECD against MS-SIM have been investigated. The results demonstrated that ECD can provide less noise, and thus better peaks integration than MS-SIM for the detection of penta- and

hexa-chlorobenzene in fly ash extracts. The use of ECD minimises the need for extensive sample clean up, and subsequent solvent use, or ^{13}C labelled standards. When mass resolution is needed, further sample purification and/or high efficiency instrumentation (HRGC/HRMS) is essential for the quantification of penta and hexa-chlorobenzenes in relevant matrices.

Acknowledgments

References

[1] Council of the European Union, Directive 1999/31/EC on the Landfill of waste. Off. J. Eur. Communities L 182. (199) 1—19.
[2] C. Cimpan, A. Maul, M. Jansen, T. Pretz, H. Wenzel, Central sorting and recovery of MSW recyclable materials: a review of technological state-of-the-art, cases, practice and implications for materials recycling, J. Environ. Manag. 156 (2015) 181—199.
[3] ERFO European Recovered Fuel Organisation Facts and Figures about SRF, Bruxelles, 2012.
[4] C. Velis, S. Wagland, P. Longhurst, B. Robson, K. Sinfield, S. Wise, S. Pollard, Solid recovered fuel: influence of waste stream composition and processing on chlorine content and fuel quality, Environ. Sci. Technol. 46 (2012) 1923—1931.
[5] G. McKay, Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review, Chem. Eng. J. 86 (2002) 343—368.
[6] G. Liu, W. Liu, Z. Cai, M. Zheng, Concentrations, profiles, and emission factors of unintentionally produced persistent organic pollutants in fly ash from coking processes, J. Hazard. Mater 261 (2013) 421—426.
[7] H. Zhou, A. Meng, Y. Long, Q. Li, Y. Zhang, A review of dioxin-related substances during municipal solid waste incineration, Waste Manag. 36 (2015) 106—118.
[8] BSI, Stationary Source Emissions- Determination of the Mass Concentration of PCDDs/PCDFs and Dioxin like PCBs- Part 2: Extraction and Clean-up of PCDDs/PCDFs. BSI 1948, 2006, p. 2006.
[9] J.L. Stevens, N.J.L. Green, R.J. Bowater, K.C. Jones, Interlaboratory comparison exercise for the analysis of PCDD/Fs in samples of digested sewage sludge, Chemosphere 45 (2001) 1139—1150.
[10] T. Oberg, J.G.T. Bergstrom, Hexachlorobenzene as an indicator of dioxin production from combustion, Chemosphere 14 (1985) 1081—1086.
[11] A. Kaune, D. Lenoir, U. Nikolai, A. Kettrup, Estimating concentrations of polychlorinated dibenzo-P-dioxins and dibenzofurans in the stack gas of a hazardous-waste incinerator from concentrations of chlorinated benzenes and biphenyls, Chemosphere 29 (1994) 2083—2096.
[12] Z. Du, J. Mo, Y. Zhang, Risk assessment of population inhalation exposure to volatile organic compounds and carbonyls in urban China, Environ. Int. 73 (2014) 33—45.
[13] Y. Huang, M. Takaoka, N. Takeda, Chlorobenzenes removal from municipal solid waste incineration fly ash by surfactant-assisted column flotation, Chemosphere 52 (2003) 735—743.
[14] L. Lundin, S. Marklund, Thermal degradation of PCDD/F, PCB and HCB in municipal solid waste ash, Chemosphere 67 (2007) 474—481.
[15] T. Oberg, B. Bergbaeck, M. Filipsson, Catalytic effects by metal oxides on the formation and degradation of chlorinated aromatic, compounds in fly ash, Chemosphere 71 (2008) 1135—1143.
[16] T. Oberg, T. Ohrstrom, J. Bergstrom, Metal catalyzed formation of chlorinated aromatic compounds: a study of the correlation pattern in incinerator fly ash, Chemosphere 67 (2006) S185—S190.
[17] Dionex, Rapid determination of persistent organic pollutants (POPs) using accelerated solvent extraction, Appl. Note 352 (2005) 1—8.
[18] P. Liljelind, G. Soderstrom, B. Hedman, S. Karlsson, L. Lundin, S. Marklund, Method for multiresidue determination of halogenated aromatics and PAHs in combustion-related samples, Environ. Sci. Technol. 37 (2003) 3680—3686.
[19] Y. Sun, M. Takaoka, N. Takeda, T. Matsumoto, K. Oshita, Application of microwave-assisted extraction to the analysis of PCBs and CBzs in fly ash from municipal solid waste incinerators, J. Hazard. Mater 137 (2006) 106—112.
[20] H. Bautz, J. Polzer, L. Stieglitz, Comparison of pressurised liquid extraction with Soxhlet extraction for the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans from fly ash and environmental matrices, J. Chromatogr. A 815 (1998) 231—241.
[21] USEPA, Pressurised Fluid Extraction. Method 3545A, 2000.
[22] E. Korenkova, E. Matisova, J. Slobodnik, Application of large volume injection GC-MS to analysis of organic compounds in the extracts and leachates of municipal solid waste incineration fly ash, Waste Manag. 26 (2006) 1005—1016.
[23] D.C. Harris, Quantitative Chemical Analysis, Macmillan, 2010.
[24] CEN/TS, Solid Recovered Fuels- Specifications and Classes- Draft for Development, British Standards Institution. CEN/TS 15359, 2006, p. 2006.
[25] D. Balampanis, N. Simms, R. Villa, Transfer Coefficients and Organochloride Load of a 'chlorine-class 2'solid Recovered Fuel in Fluidized Bed Combustion, 2008.
[26] P.Y. Liu, M.H. Zheng, B. Zhang, X.B. Xu, Mechanism of PCBs formation from the pyrolysis of chlorobenzenes, Chemosphere 43 (2001) 783—785.
[27] S.D. Abreu, P. Caboni, P. Cabras, A. Alves, V.L. Garau, A comparison of a gas chromatographic with electron-capture detection and a gas chromatographic with mass spectrometric detection screening methods for the analysis of famoxadone in grapes and wines, J. Chromatogr. a 1103 (2006) 362—367.
[28] M. Leong, S. Huang, Dispersive liquid—liquid microextraction method based on solidification of floating organic drop combined with gas chromatography with electron-capture or mass spectrometry detection, J. Chromatogr. A 1211 (2008) 8—12.
[29] H. Fujita, K. Honda, N. Hamada, G. Yasunaga, Y. Fujise, Validation of high-throughput measurement system with microwave-assisted extraction, fully automated sample preparation device, and gas chromatography-electron capture detector for determination of polychlorinated biphenyls in whale blubber, Chemosphere 74 (2009) 1069—1078.
[30] V. Pekarek, R. Weber, R. Grabic, O. Solcova, E. Fiserova, M. Syc, J. Karban, Matrix effects on the de novo synthesis of polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls and benzenes, Chemosphere 68 (2007) 51—61.
[31] S. Barreca, S. Orecchio, A. Pace, Photochemical sample treatment: a greener approach to chlorobenzene determination in sediments, Talanta 129 (2014) 263—269.