Investigations regarding separate sampling of PCDD/F in gas and solid phase of incineration flue gas by filtration techniques

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Introduction

Sampling of PCDD/F is a key step in the interpretation of PCDD/F data in incinerators. The basic elements of a PCDD/F sampling equipment consist of filtration, absorption by impinger and adsorption on a filtration material (e.g. XAD). It is of high interest to separate gas phase and solid phase PCDD/F for the interpretation of the flue gas property especially for bag filter dynamics. The difficulties of separate sampling of gas and solid phase PCDD/F are adsorption, desorption and *de novo* formation on the dust trapped on the filter in the sampling equipment during long time sampling period.

Therefore we evaluate sampling methods regarding separate detection of gas and solid phase PCDD/F in flue gas including a method for high volume sampling.

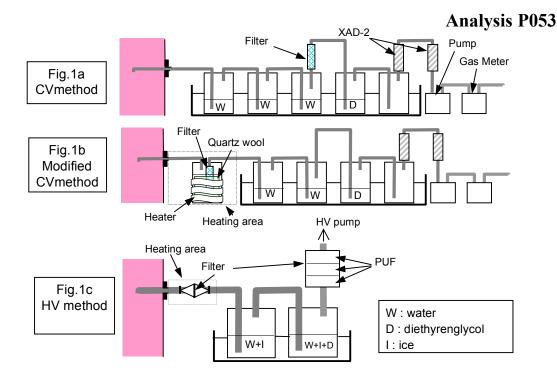
Experiments

The experiments were conducted in a test plant branched from the outlet of the municipal waste incinerator A equipped with a bag filter ¹).

We define that the solid phase is trapped on the filter and the gas phase is passed through the filter. Three sampling methods were compared (Fig.1). The conventional (CV) method for standard sampling is shown in Fig.1a. Due to the low filter temperature and low sampling speed, this method is not appropriate for the separate sampling of gas and solid phase PCDD/F. The modified CV (MCV) method (Fig.1b) aims to separate gas and solid phase PCDD/F by heating the filter. The high volume (HV) method (Fig.1c) consist of short time sampling (5 min) with large impinger and polyurethane foam (PUF) as adsorbent. With the HV method, we sample volumes up to 200L/min while for the CV and MCV method 10-15 L/min are sampled.

For the HV method adsorption and desorption experiments were performed both with dust and without dust on the filter. Weight measurement of the filters and temperature monitoring was also carried out. Because of short sampling period (5min), the HV method was expected to avoid *de novo* formation also for filter temperature above 200°C.

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The filtration speed are as follows; bag filter: 1m/min, low volume sampling (modified CV method): 6m/min, HV method: 70m/min.

As methods for extraction, clean up and HRMS analysis of PCDD/F the Japanese standard methods of the ministry of Health and Welfare have been used.

Results and Discussion

We found that the MCV method is useful for isokinetic sampling also for high dust concentrations. Table 1 shows the results of PCDD/F concentration in gas phase and solid phase by this low volume sampling method. The concentration of gas phase of PCDD/F in high dust concentration is relatively low compared to the bag out measurement which we assume as gas phase PCDD/F. These indicate the adsorption of PCDD/F from gas phase on the dust trapped on the filter during this sampling. For the adsorption of gas phase PCDD/F on the filter dust we reconfirmed by comparison of sampling using a "clean" filter (blank) and a filter spiked with 0.5g fly ash settled the filer inside the duct. We found that up to 230°C part of the gas phase PCDD/F adsorb on the added fly ash(Table 1). Additionally at these temperatures (>200°C) we already found *de novo* formation on the filtered fly ash, limiting the temperature which could be applied for heating the filter. It is considered that here the fixed carbon in the dust has an important role for both the adsorption of gas phase PCDD/F and the *de novo* formation.

For the HV method we found that the PCDD/F measurement was possible under short time sampling period up to sampling volumes of 200 L/min. Most of the PCDD/F was trapped in the first drain and no PCDD/F could be detected after the PUF.

ORGANOHALOGEN COMPOUNDS 276 Vol.40 (1999) Fig.2 shows the results of the desorption experiment using preheated air to test the desorption rate from the dust on the filter.

Table1. PCDD/F concentration and ratio in gas phase and solid phase in low volume sampling method.

1	Place	method	Gas	Dust	unit	Total PCDDs		Total PCDFs		Total TEQ	
	FIACE	method	Temp	conc.	unit	TUIAI	10005	TUIDIT	ODE2	TULA	
			remp	0010.							
				0		Solid	gas	solid	gas	solid	gas
		Japanese	150°C	10g/m³N	ng/m3N	2000	1.6	510	1.2	18	0.023
	BF-IN	method									
					%						
					0.9	<u>→ 200 °C desorption rate</u> 0.800					
					0.8	0 765			0.800		
					0.7						
					0.6		0.567				
					0.5	-					
					0.4	-	0.389			0.377	
					0.3					0.213	
					0.0		146 0.118	205 0.160		0.213	0.147
					0.2		0.0	060 0.046	0.063 0.03	8 0.048 0.053	
					0.0						
					0.0			ç o	T P	н Н	o l
						T4CDDs	H6CDDs P5CDDs		P5CDFs T4CDFs	H7CDFs H6CDFs	08CDF
						Ds	Ds Ds Ds	, ō	FsFs	FsFs	Ť
	Fig. 2 Desorption rate of PCDD/F from filter dust								lust		
		during HV sampling with pre heated air.									
1					%	99.92	0.08	99.77	. 0.23	99.87	0.13
	Test plant	modified	150°C	10g/m ³ N		2500	2	570	1	20	0.023
	BF-IN	CV	100 0	109/1111	% %	99.92	0.08	99.82	0.18	99.89	0.11
	Test plant	modified	230°C	10g/m ³ N		1200	0.00	510	0.18	21	0.007
	BF-IN	CV	200 0	109/III 1	% %	99.98	0.02	99.96	0.04		0.03
	Test plant	Filter in	230°C	<3mg/	ng/m3N	6.7	23	0.94	9.8	0.051	0.32
	reactor -IN	the duct	200 0	m ³ N	% %	22.56	77.44	8.75	91.25	13.75	86.25
	Test plant	Filter in	230°C	Add dust		110	1.2	79	0.87	2.8	0.021
			200 0						0.01		0.021

The maximum desorption ratio of the PCDD/F isomer were <0.23% at 150°C and <0.8% at 200°C. Low chlorinated congeners showed relatively higher desorption ability compared to the low volatile high chlorinated congeners.

98.92

%

0.5g on

the filter

1.08

98.91

99.26

0.74

1.09

Fig.3 shows the homologue profile of PCDD/F for the CV (1hr) and HV (5min) method sampled after bag filter at a flue gas temperature of 200°C. The HV run **g** without dust on the filter showed almost the same homologue profile compared to the CV method without dust. However with HV run **h** including addition of 3g dust on the filter we found relatively low levels of PCDD/F in the gas (drain + PUF) phase compared to HV run **g**. This indicates a considerable adsorption of PCDD/F from flue gas on the spiked dust.

Fig. 4 shows the adsorption ratio of PCDD/F from flue gas on the filter at 150 and 200°C. There were no adsorption at "clean" (blank) filter. However with HV run **h** and **f** including spiked dust we found already a considerable adsorption of higher chlorinated PCDD/F from flue gas on the

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reactor -IN

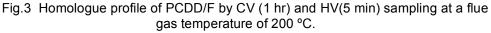
the duct

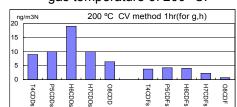
dust. Part of the T4CDF were already desorbed at 200°C from the filter dust and additionally at this temperature we observe *de novo* formation.

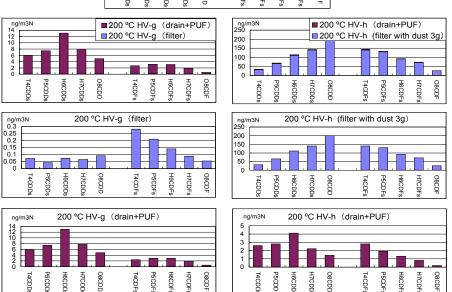
These indicate that separate sampling of gas and solid phase PCDD/F are impossible even under the short time high volume sampling conditions with a filtration speed of 70m/s. Here adsorption and desorption phenomena take place at the same time depending on the property of the dust. The fixed carbon plays a crucial rule in these complex processes².

Therefore it became clear that separate sampling of PCDD/F in gas and solid phase is impossible using filtration technique.

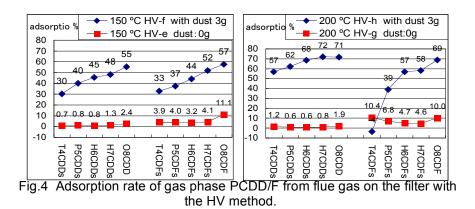
However the investigated HV method seems a good approach for short time sampling.







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