Innovations in Continuous Emission Control of PCDD/PCDF from Municipal Solid Waste Incineration Facilities

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Introduction

With the initial findings of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in fly ash and stack gas of municipal waste incinerators (MWI) in the Netherlands[1], the incineration of wastes was one of the first emission sources to be identified. Therefore, MWI plants have always been in the focus of political and scientific interest. This has led in many central European countries to the introduction of a permissible limit for PCDD/PCDF emissions from MWI plants at 0,1 ng TEQ/m³ in the stack gas. Once these rather low standards were released, the development of flue gas cleaning techniques accelerated enormously. Measuring methods and techniques were also undergoing important changes and standardization measures. However, the determination of PCDD/PCDF concentrations in stack gas according to the relevant standards like the German VDI guideline 3499[2] is time consuming, labour intensive and expensive. Both cost and time considerations make it impractical to perform extensive screening or monitoring programs. In Germany, the emissions of MWI plants are controlled periodically according to the regulations of the 17th BImSchV[3]. The obtained emission values refer only to the plant operation during measurement time. Changes in the intensity of PCDD/PCDF emission due to changes of the operation conditions are not registered.

The aim of the present study was to develop a more time and cost effective measuring method of PCDD/PCDF in stack gas of MWI plants. Out of the four German VDI methods, the VDI 3499, Part 2, was chosen to serve as a basis method. The significant work steps of this method, sampling, analyzing and selective detection, were simplified in order to render possible the automation of the emission control procedure.

The emission limit set forth by the 17th BImSchV is expressed on the basis of the international toxicity equivalents. This concept requires the quantification of all seventeen 2,3,7,8-chlorinated isomers over the whole range of tetra- to octachlorinated dioxins and furans. In stack gas samples of a particular plant the inter special variation in the relative PCDD/PCDF levels is low, which means that the isomer profile is quite constant[4]. Therefore, it is possible to predict the sum of all individual isomers by only anaylzing a few isomers, so-called indicator isomers. By an appropriate choice of indicator isomers and analytical methods, cost and time effective emission control procedures can be developed.

In this paper we will now describe how we selected an indicator isomer for PCDD/PCDF in stack gas of MWI plants. We will also describe a time effective method for sampling and analyzing dioxins and furans in stack gas.

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Selection of indicator isomer

Due to the fact that the PCDD/PCDF emission limit is expressed as toxicity equivalents, the selection of an indicator isomer was principally based on the toxicological relevance. In addition to that, abundance and ease of analysis were the two main criteria. For the selection process a data set of stack gas analysis from different MWI plants all located in Germany was used. From each plant a statistically sufficient number of analyses was available. All the 2,3,7,8-chlorinated isomers were present in detectable concentrations. Of this group of toxic isomers the 2,3,4,7,8-pentachlorodibenzofuran (PeCDF) was chosen as the prime indicator isomer. It is present in high levels, easy to analyze and has a high toxic equivalency factor. In Table 1 the contribution of the 2,3,4,7,8-PeCDF to the total I-TEQ value is given determined in data sets of four different MWI plants. The values in Table 1 show that by quantification of the 2,3,4,7,8-PeCDF more than a third of the total I-TEQ can be determined.

Table 1 Contributions of 2,3,4,7,8-PeCDF to the total I-TEQ value

	Plant 1	Plant 2	Plant 3	Plant 4
2,3,4,7,8-PeCDF [%]	40,847	31,246	32,431	32,355
Relative Standard Deviation (RSD)	9,917	4,327	1,339	4,152

Evaluation of the indicator isomer

To evaluate the indicator isomer the international toxicity equivalent (I-TEQ) levels of PCDD/PCDF were calculated from the indicator isomer levels from the stack gas data of two MWI plants. The results were compared to the actual I-TEQ value determined by analyzing all seventeen toxic isomers. As can be seen in Figure 1 the predicted levels correlate well with the actual values.
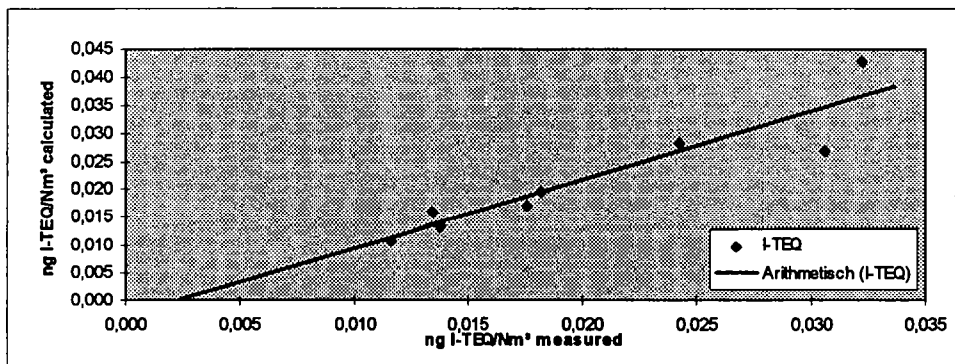

Figure 1 Comparison of measured I-TEQ values with those projected from the concentration of 2,3,4,7,8-PeCDF

Experimental

Sampling method
The sampling method applied in the adopted VDI guideline 3499, Part 2, consists basically of three segments. After collection of the particulate PCDD/PCDF on a filter and condensation of the stack gas for separation of the gaseous dioxins and furans a fixed-bed adsorber is used for retention of the lower

chlorinated isomers. This sampling system results in an extensive sample preparation because all three fractions have to be extracted separately before the extracts are combined for the following multi-step clean-up procedures. Thus, using the complete standardised sampling method is not suitable for a process automation. Among the three fractions the condensate was chosen as the prime fraction due to the possibility of an easy clean-up by means of high-performance liquid chromatography. To investigate the comparability of the PCDD/PCDF results from the VDI sampling method to those of the condensate sampling, comparative measurements were performed in the stack gas of the Müllverwertungsanlage Borsigstraße, Hamburg (Germany). The measurement program comprised three measuring compaigns with sampling periods of 2 to 4 days. All samplings were carried out simultaneously at the same place for six hour runs. Sampling according to VDI 3499, Part 2, was applied by a certified institute, the Meß- und Prüfstelle Technischer Umweltschutz, (Berlin, Germany). Extraction, clean-up and analyses for both sample sets were done by an external laboratory according to VDI 3499. During five of the nine sampling runs a filter was installed upstream of the condenser to investigate the influence of the particulate PCDD/PCDF on the isomer distribution as well as on the operating conditions of the HPLC clean-up system utilized.

Analytical method
Concentration of the organic compounds and separation of the indicator isomer from other persistent organic pollutants present in stack gas as well as from all other PCDD/PCDF isomers was attained by using a high-performance liquid chromatography (HPLC) system. This HPLC method utilizes a coupled column system consisting of a Lichrospher RP-18 column (5 µm, 125×4mm) and a Lichrospher RP-18 ec column (5 µm, 125×4mm). In order to protect the column system from pollution with persistent substances a pre-column (Lichrospher RP 8 4 µm, 4×4mm) was employed. Apart from the columns the RP-HPLC fractionation system consisted of three pumps, a Hitachi L-6200 intelligent pump equipped with a gradient unit, a Waters HPLC pump Type 590 and a Knauer HPLC pump Type 64. Further, the system was composed of a Hitachi 655A-22 UV-VIS detector operating at 235 nm, a Hitachi D-2500 integrator and a Rheodyne 7150 valve injector with a 20 µl loop. The column switching system was built with a Rheodyne 7000 valve.
The condensate was enriched on the RP-18 with the two columns being isolated from one another. Following the enrichment, the two columns were coupled and eluted using methanol as mobile phase in a gradient mode up to 98% methanol, 2% water. The bulk of lower chlorinated PCDD/PCDF and related compounds detectable in UV eluted first and was collected in the waste outlet. When the 2,3,4,7,8-PeCDF started to elute, the flow was directed to a sample vial by switching valves. After two minutes the eluent was redirected to the waste outlet and the column system was purged with methanol as mobile phase. Due to low levels of the 2,3,4,7,8-PeCDF in stack gas, the isomer could not be determined by the UV-detector. The heart-cut technique was therefore performed by using benzo(a)pyrene as a tagging compound. The RP-HPLC heart-cut fraction of 2 mL was further analyzed by GC/MS. Analysis was accomplished using a Fisons MD 800 quadrupole mass spectrometer coupled to a Fisons GC 8000 series using a J&W Scientific DB-5 capillary column in splitless mode.

Results

Sampling method
A comparison of average PCDD/PCDF concentrations of the homologue group totals in ng/Nm³ for the condensate method and the VDI 3499 sampling method is presented in Figure 2. With a few exceptions, the data compares quite favorably. Discrepancies are found to exist mainly for the tetrachlorinated dioxins and furans. These differences may be attributed to the fact that the lower chlorinated isomers are usually retained in the adsorption unit which is not present in the condensate sampling method. Better correspondance is typically observed for the higher chlorinated homologues

with the hexachlorinated isomers showing excellent agreement. Though the condensate sampling method resulted in lower levels for most homologue groups, the VDI 3499 values measured showed a more random scattering with higher or lower values on both sides.
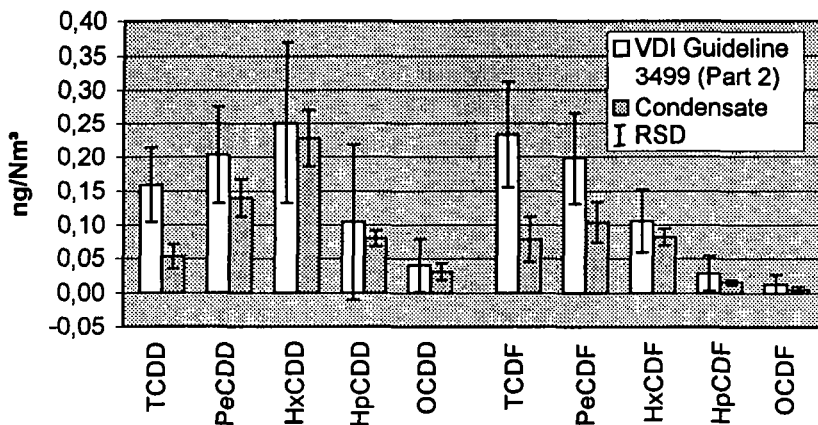

Figure 2 Average values and relative standard deviations (RSD) of PCDD/PCDF concentrations determined with the condensate method and the VDI 3499 method at a MWI plant with PCDD/PCDF emissions lower than 0,1 ng I-TEQ/Nm³

The higher levels of octachlorinated PCDD/PCDF in the condensate samples can not be sufficiently explained because the results of the VDI method should show 100% recoveries for all tetra through octa isomers and for both dioxins and furans. A shifting towards higher recoveries for the lower chlorinated PCDD/PCDF by installing a filter unit upstream of the condenser could not be observed. Average recovery for dioxins and furans for all samples normalized to the VDI method was 66%, with a relative standard deviation (RSD) of 21%. Especially for the selected indicator isomer, the 2,3,4,7,8-PeCDF, a normalized recovery of 64% could be determined, the RSD being 23%. This is within the range of standard deviations accomplished with other methods described in the VDI guideline series 3499. That means that by reducing the sample method to the collection of the condensate fraction at least half of the relevant indicator isomer can be registered.

Analytical method

Figure 3 shows the typical HPLC fractionation chromatogram of a 10 mL stack gas condensate sample. As shown in the HPLC chromatogram in Figure 3, the bulk of UV detectable organic compounds present in the stack gas eluted immediately after the end of the gradient program was reached. Among them were the tetrachlorinated PCDD/PCDF. The higher chlorinated dioxins and furans showed higher retention times and better separation. With the described analytical procedure, RP-HPLC permits, therefore, the collection of the indicator isomer by heart-cut technique. To visualize the 2,3,4,7,8-PeCDF collection window a standard of 10 ng was added to the sample. The benzo(a)pyrene used as the tagging compound eluted directly prior to the indicator isomer peak. After clean-up of 1 L of condensate the peak of the 2,3,4,7,8-PeCDF started to broaden which resulted in an inaccurate collection of the indicator isomer. These problems were caused by uneluted sample material on the column. The aim of our future investigations will be to enhance the stability of the column system by introducing a regeneration step.
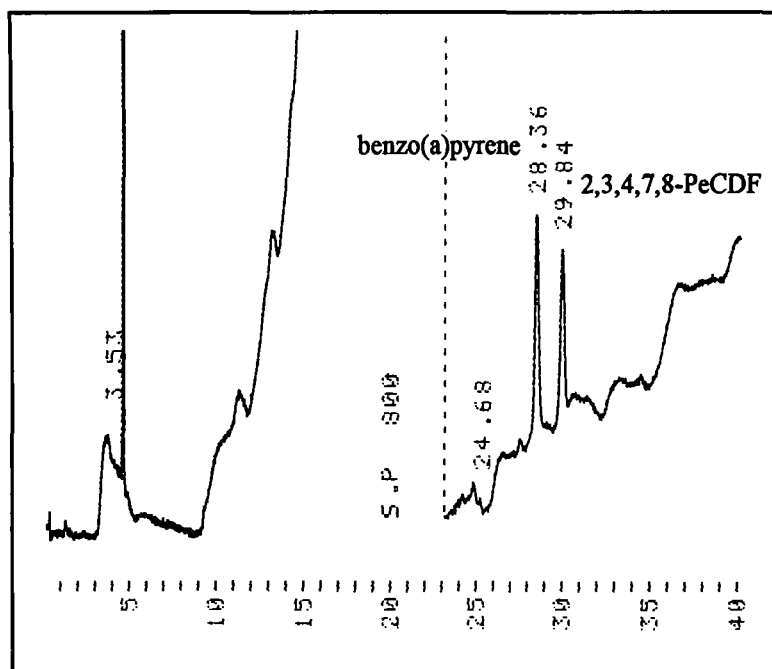
Figure 3 RP HPLC fractionation chromatogram of a 10 mL stack gas condensate sample

For comparison of the HPLC system with the well established liquid column chromatographic method identical samples were analyzed parallel with both clean-up methods. To avoid deviations resulting from inhomogenities the stack gas samples were divided after homogenization. The results of this comparison (Figure 4) show that by using the heart-cut technique a significant reduction of PeCDF isomers was obtained. In the mass chromatogram of the sample subjected to the RP-HPLC clean-up method apart from the relevant 2,3,4,7,8-PeCDF peak only two more pentafurans were detected. They were both determined to be non toxic pentafurans. Because one of these non toxic isomer peaks overlapped the indicator isomer peak, the 2,3,4,7,8-PeCDF had to be analyzed by height integration rather than area integration. However, the quantification of a single peak can more easily be automated than when a mixture of isomers is present in the mass chromatogram.

In order to examine the reproducability of the RP-HPLC clean-up system a series of five 400 mL condensate samples were investigated. The reproducability of the HPLC clean-up system was satisfying with a RSD of 13%. Compared to the results obtained by the liquid column chromatographic method, the RP-HPLC clean-up showed recoveries of 108%. In a further step, a second series of condensate samples was examined in which the sample quantity was successively reduced to half of the previous quantity. The sample quantities correlated well with the obtained isomer concentrations. The method developed is sensitive enough to allow the determination 10 pg of the indicator isomer. The detection limit could be improved by using HRGC/HRMS.

Conclusions

With the selection of an indicator isomer and the reduction of the sampling fractions to the condensate fraction significant time saving simplifications were obtained. The deviation caused by the simplification steps is acceptable when compared to the amount of time saved in the procedure. The results show that the RP-HPLC clean-up is essentially equivalent to established clean-up procedures such as extraction and subsequently liquid column chromatography. This method can be considered as

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a specialized method designed for the isomer profile in the stack gas of a specific plant. However, the method can easily be adopted to any plant providing the isomer profile remains constant. Due to the simplifications of the relevant steps the procedure can now be automated.
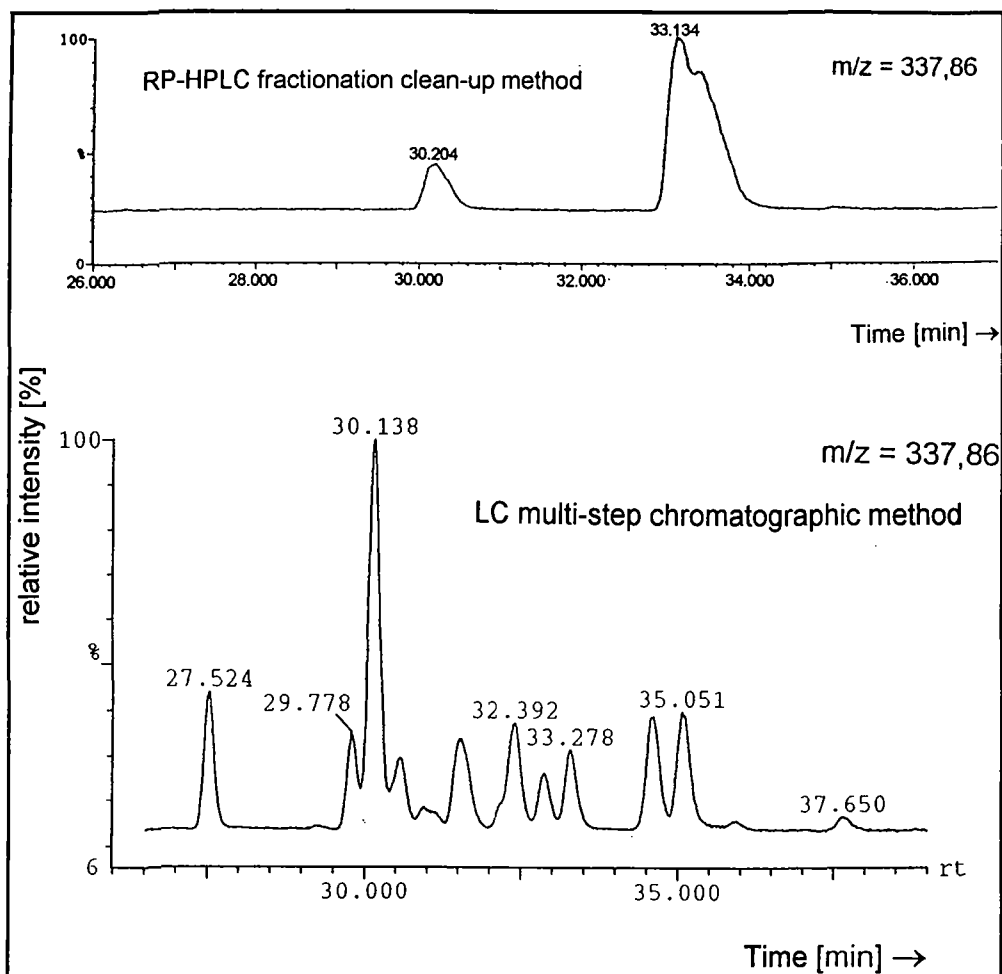

Figure 4 Mass chromatograms of PeCDF in stack gas samples, RP-HPLC clean-up versus liquid column clean-up

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