Development of a sensor system for on-line prediction of PCDD/PCDF content in waste incineration residues (fly and boiler ash)

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Introduction

The reduction of stack emission of polychlorinated dibenzodioxins and –furans (PCDD/PCDF) from waste incineration plants is mainly due to secondary measures like the installation of exhaust gas cleaning devices. However, an eminent part of the dioxin load remains in the solid residues, e.g. fly and boiler ash. Since a sustainable operation of the plants is eligible, there is a demand for improving the quality of the residues.

This goal may be reached by applying a recirculation of high contaminated fractions of the fly and boiler ash into the combustion chamber. This would lead to an almost complete destruction of the PCDD/PCDF and other toxic organics' content in the solid material. To avoid possible corrosion effects due to heavy metal and halogen load, which would also be recirculated with the residues, it is preferable to accurately select the fly ash fractions containing high PCDD/PCDF loads. For this purpose, it is necessary to detect these high contaminated fractions on an on-line, real-time basis. This objective should be achieved by setting up a sensor array consisting of several single sensors, whose combined signal outputs would give reliable information on PCDD/PCDF content of the residues. Although there are numerous publications on surrogate compounds for PCDD/PCDF concentration in the flue gas [e.g. 1-5], little is known about indicator substances for the dioxin content of solids. Therefore, profound knowledge about such surrogate compounds, which are also suitable for on-line detection, is required to select the essential parts for such a sensor array.

Materials and Methods

Data taken from three measurement campaigns at different waste incineration plants comprising various concentrations of chemical compounds such as polychlorobenzenes, polychlorophenols, and polycyclic aromatic hydrocarbons were collected. The sampling setup, cleanup and analysis procedures for gas phase analysis are described elsewhere[5]. Furthermore, various additional data, e.g. concentrations of inorganic compounds as well as physical properties such as temperatures and air supply were recorded. For this, data from the plants' process monitoring systems were used as well as measurements were carried out with a gas analyzer (Testo 360).

Subsequently, these data were compared with the corresponding PCDD/PCDF concentration in the residues (fly and boiler ash). A multivariate statistical analysis of the data was performed to evaluate correlations of properties measured in the gas phase to the PCDD/PCDF content of the fly and boiler ash. This statistical analysis was performed with the STATISTICA program

package. To carry out this analysis, normal distribution of the data is necessary. Therefore, the data was transformed to a logarithmic scale with the exception of the data derived directly from the plants (e.g. temperatures, concentrations of inorganic compounds), which showed almost a normal distribution in their original state.

Since previous work has shown, that the summed up gas phase concentration of PAHs with a molecular weight larger than 200 amu could play an important role as an indicator compound for the PCDD/PCDF content[6], experiments were carried out to investigate the principle practicability of an on-line sensor for the detection of PAHs. The sensor is based on resonance enhanced multiphoton ionization (REMPI)[7,8] of the aromatic molecules and subsequent detection of the integral ion current in an ionization cell. Thus, no sophisticated and expensive mass spectrometry methods are required.

Figure 1A shows a drawing of the mobile measurement device. An excimer laser system (Tui Laser AG) is used to produce alternate beams with wavelengths of 248 nm (KrF) and 308 nm (XeCl), respectively. The beams are guided into a cylindrical ionization cell (4 cm long, 8 cm radius). They are coupled in by means of quartz glass windows and pass the gaseous sample between two parallel metal plates (Figure 1B). A positive voltage of 600 V is applied to one electrode, while the other one remains on ground potential. Thus, the formed electrons occurring from the ionization process are collected by the positive charged electrode (Figure 1C). The resulting current signal is amplified and, alternatively, the signal could be integrated.
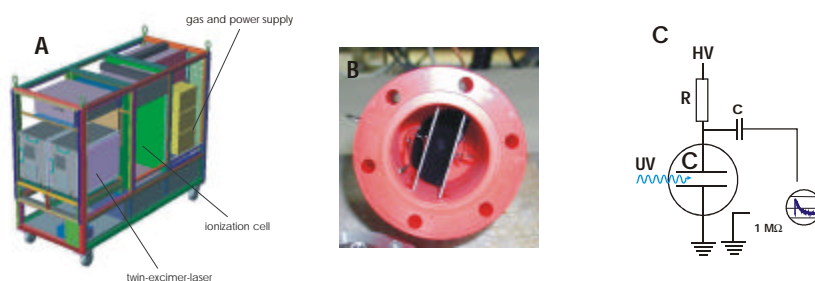

Figure 1A: Drawing of the mobile device.B:Photograph of the ionization cell.C:Circuit diagram

Results and Discussion

With the collected data from the waste incineration plant measurements, uni- and multivariate data analysis was performed. The univariate analysis revealed relatively bad correlations of the dioxin content of residues to the dioxin concentration in the gas phase. Furthermore, polychlorobenzenes and -phenols also showed no convenient correlation. In terms of the determination of the parameters best suited for the description of PCDD/PCDF concentration in the residues, the multivariate data is most important. Table 1 shows exemplarily some results of the multivariate data analysis from one incineration plant.

The data reveals that there could be the possibility to constrain the number of parameters. Especially plant parameters such as temperatures and air supply and the concentration of PAHs with masses larger than 200 amu are needed for a thorough description of the dioxin load of residues. Additionally, inorganic molecules such as HCl may be important. Other measurements not shown here in detail exhibited the crucial role of SO_2 and CO under certain conditions.

Table 1: Multivariate Data Analysis of correlation to PCDD/PCDF content in residues

Number of Parameters	Chosen Parameters	Correlation-coefficient R	Partial axis-intercept B	Partial slope beta
3	Air supply	0,82	0,407	1,3E-05
	HCl in flue gas		-0,013	-2,4E-06
	Sum of PAHs > 200 amu		-0,663	-0,195
3	Boiler temperature	0,86	0,544	0,009
	Combustion chamber exit temperature		-0,481	-0,002
	Sum of PAHs > 200 amu		-0,777	-0,229
3	Air supply	0,90	0,571	1,9E-05
	Combustion chamber exit temperature		-0,499	-0,002
	Sum of PAHs > 200 amu		-0,946	-0,278

Figure 2 shows the single shot sensor signal received at 248 nm from a gas standard containing 10 ppm of benzene, toluene and p-xylene (BTX), respectively, and of another standard mixture containing 10 mg/l of phenanthrene, pyrene, perylene, chrysene and coronene, respectively, dissolved in acetone. A gaseous stream of synthetic air was used with the latter to transport those PAH molecules into the ionization cell, which are in the gas phase above the liquid. Regarding the vapor pressures of the PAHs, their sum gas phase concentration could be roughly estimated to 150 ppb including phenanthrene and approximately 10 ppb save phenanthrene.
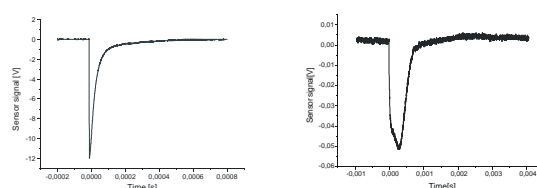

Figure2: Single shot sensor response signal using an excitation wavelength of 248 nm for 30 ppm BTX (left side) and the PAH mixture(right side)
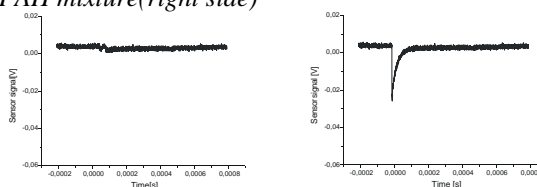

Figure3: Single shot sensor response signal using an excitation wavelength of 308 nm for 30 ppm BTX(left side) and the PAH mixture(right side)

From the signal of BTX the detection limit could be calculated to 15ppb. Figure 3 shows the sensor response signal at 308 nm for both mixtures. For BTX, no signal could be observed, and the signal for the PAH mixture is much lower compared to the previous case, where 248 nm is used as excitation wavelength. With pure acetone, no signal could be observed by either wavelength.

This behavior can be explained with the different ionization potentials and electronic transitions of the various compounds (see Figure 4). At 248 nm, BTX and all investigated PAHs have suitable electronic transitions in such a way, that they are easily ionized in a two step 1+1 REMPI process. However, at 308 nm, the photon energy is not sufficient to reach the ionization potentials of the BTX molecules. Since the IP of the PAHs decreases with increasing molecular weight, the heavier PAHs can still be ionized. The lower signal of the PAH mixture at 308 nm is due to the different behavior of phenanthrene, which exhibits no utilizable electron transition. Therefore, the remaining signal at 308 nm is due to the other four PAHs with atomic masses larger than 200 amu. This shows, that it is possible to detect selectively this group of PAHs that could be valuable for the sensor array, while the signal received at 248 nm gives information about the whole aromatic content of a gaseous mixture[9].
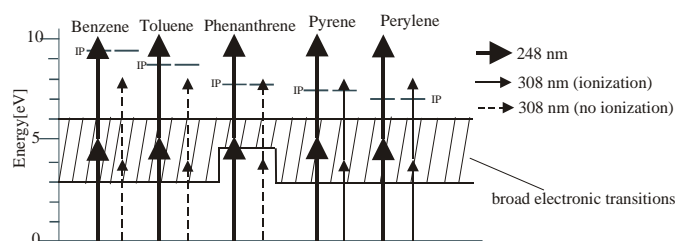

Figure 4: Energy diagram for various aromatics by REMPI ionization at 248 and 308 nm

Future research on this topic will comprise a refinement of the statistical database and further investigation of the experimental methods. In particular, a more thorough investigation of the behavior of the REMPI sensor will be needed and a solution for combining the various sensor signals received from the array to get reliable information whether fly ash fractions should be recirculated.

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