

Real-Time Combustion Monitoring of PCDD/F Indicators by REMPI-TOFMS

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Introduction

Analyses for polychlorinated dibenzodioxin and dibenzofuran (PCDD/F) emissions typically require a 4 h extractive sample taken on an annual or less frequent basis. From a regulatory or public interest viewpoint, this results in an infrequent and potentially minimally representative monitoring scheme. More recently, methods for continual sampling of emissions make approximately two week, cumulative measurements^{1,2} possible. These methods are useful for delayed assurance of compliance and may provide eventual insight into overall plant performance. However, both the 4 h annual sample and the cumulative sampling methods require laboratory analysis, resulting in emission results weeks (typically) after sampling. Methods for on-line monitoring of PCDD/F would have benefits of continual facility compliance characterization, feedback to the plant operators for pollutant formation minimization, assurance to the public of compliance, and minimization of over-design of gas cleaning systems.

On-line PCDD/F monitoring methods³⁻⁶ are more recent developments and include resonance-enhanced multiphoton ionization (REMPI) coupled to time of flight mass spectrometry (TOFMS)^{7,8}. REMPI is a laser-based, two photon ionization process in which the laser wavelength can be tuned to resonantly enhance the excitation and ionization process. The system is isomer selective and reaches low ppb-level detection limits for many common aromatic-structured combustion pollutants. REMPI-TOFMS, like all of the on-line monitors, requires a correlation with measurable indicator compound(s) to indicate either total PCDD/F or the PCDD/F toxic equivalency measure, TEQ. This correlation is necessary due to lack of sensitivity (relevant concentrations are typically on the order of parts per quadrillion, ppq) as well as an inability to measure all of the 17 TEQ-weighted congeners. Indicator compounds are determined by conventional sampling and analysis (gas chromatography/mass spectrometry, GC/MS) and are chemically similar compounds to the PCDDs/Fs. These indicator compounds may be precursors to PCDDs/Fs or pollutants formed in similar, parallel reactions. Common indicator compounds have included lowly-chlorinated (less than 4 Cl's) PCDD/F congeners⁹; the sum of mono- plus di-chlorobenzenes¹⁰; specific compounds such as 1,4-dichlorobenzene, 2,4,6-trichlorodibenzofuran, and 2,4-dichlorophenol¹¹; and 1,2,4-trichlorobenzene¹². The universality of these indicator compounds across facility types remains to be investigated, but they likely vary somewhat depending on the plant type, the waste and fuel types, and operating and combustion conditions.

The presence of an on-line monitor raises the first possibility to provide operational feedback to minimize the formation of PCDD/F, as well as characterization of PCDD/F emissions during operational transients. This would be an important capability for distinguishing effects of operating modes or air pollution control equipment failures on PCDD/F emissions. Indeed recent work^{13,14} has demonstrated seven-fold increases in PCDD/F emissions during 1 h combustor shutdowns and startups, consistent with others' work^{15,16} in which PCDD/F raw gas levels increased by one to two orders of magnitude during transient combustion conditions. The extent to which these transient emissions may affect short- and long-term stack emission values and, hence, compliance issues, is undetermined. The rapid variation of PCDD/F, as well as other co-pollutants, due to transients, fuel changes, and operating

variations suggest that fast on-line monitoring is necessary in order to effect changes in operating conditions that will reduce or prevent conditions favorable to PCDD/F formation. Work with REMPI-TOFMS at an industrial hazardous waste incinerator was successfully able to monitor aromatics including monochlorobenzene during the introduction of barrels of liquid hazardous waste¹⁷, finding transient evolution of the pollutants.

The ability to measure facility transients for indicator concentrations with REMPI-TOFMS and to correlate their levels with TEQ values has yet to be established. Past work at a municipal waste combustor (MWC) facility sampled for semi-volatile organic compounds to determine a correlative model between REMPI-measurable compounds and PCDD/F TEQ. Ten 60-min samples showed that 1,2,4-trichlorobenzene correlated with the TEQ values with an R^2 value of 0.94¹². Work in this paper reports the first REMPI-TOFMS measurements for a specific PCDD/F indicator compound (1,2,4-trichlorobenzene) along with simultaneous conventional sampling for PCDD/F TEQ values.

Materials and Methods

REMPI-TOFMS was employed at an MWC with multiple refuse-derived-fuel (RDF) fired boilers to sample flue gas concentrations after the boiler chamber and prior to the air cleaning devices. The boiler was operated under steady state conditions, shutdowns, and startups. Boiler shutdowns would normally occur with operating problems such as jams in the fuel feeding system or for routine maintenance but were initiated for these tests to observe the pollutant response during transient operating conditions.

Flue gas sampling for REMPI-TOFMS was accomplished with a glass-lined, stainless steel sampling probe coupled to a heated ($T = 170\text{ }^\circ\text{C}$) line. A heated filter ($T=150\text{ }^\circ\text{C}$) prior to the REMPI inlet prevented particulate matter from clogging the pulsed inlet valve. The filter was changed daily to minimize adsorption or desorption phase bias of target analytes. Sampling was sub-isokinetic to minimize particle collection. REMPI was operated in a 2-color, 2-photon mode. The wavelength of the first laser, 284 nm, was set in resonance with the origin of the $S_1 \leftarrow S_0$ transition for 1,2,4-trichlorobenzene (TrClBz), a suspected PCDD/F indicator compound. A fixed 213 nm wavelength completed the ionization process.

Continuous CO , O_2 , and CO_2 measurements were taken from the plant's post-boiler, pre-stack monitors. The possible presence of concentration gradients within MWC ducts were evaluated for their potential detrimental effects on establishing concentration correlations. Simultaneous measurements were taken at 30% and 50% of the cross-duct width to check for stratification of PCDD/F concentrations.

In parallel to the REMPI-TOFMS measurements, 74 PCDD/F samples (modified EPA Method 23) were taken over a four day period. Typically, three 5-min duration samples were collected over 1-h periods during steady-state, shutdown, and startup conditions. There was approximately 15 min between samples. The samples were analyzed by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) for all three TrClBz (1,2,3-; 1,2,4-; and 1,3,5-TrClBz) compounds and by HRGC/high resolution mass spectrometry (HRMS) for the 17 toxic equivalency factor (TEF) weighted compounds that comprise the PCDD/F TEQ measure. A field blank and an XADTM sorbent blank showed minimal levels of 1,2,4-trichlorobenzene compared to the lowest measured sample level.

The choice of units from which to compare compound concentrations depends on the purpose of the comparison. The various operational modes at the facility result in different RDF feedrates, boiler temperatures, and flue gas flowrates. For example, comparison of steady state emissions versus those during facility shutdowns in units of mass per waste feed could make the latter exceptionally high if pollutant production is more related to mass of waste on the grate or the amount of deposits on the boiler. In this paper, concentrations are compared on a time basis to understand how different process options at the plant affect the rate of PCDD/F production.

Results

Pre-APCS PCDD/F TEQ concentrations are reported in Table 1. Transient operating conditions resulted in higher average PCDD/F TEQ values and relative standard deviations by almost 4-fold. Peak concentrations of PCDD/F TEQ exhibit at least a 10-fold increase during startups over those of the average steady state values.

Operating Condition	Four Day Averages ($\mu\text{g TEQ}/\text{min}$)			
	High	Low	Avg	RSD
Steady State (SSTS#)	208	109	154	23%
Shutdown (SSHD#)	349	98	203	64%
Startup (SSUP#)	1262	181	529	86%

Table 1. PCDD/F TEQ Emission Rates.

Integrating the mass concentration rate curve suggests that the TEQ levels during a combined shutdown and startup period are ~25 percent of the plant's projected daily PCDD/F TEQ concentrations. The effect on plant stack emissions, however, remains to be determined.

Simultaneous samples taken across the duct showed less than 10% relative standard deviation (RSD) between the values, confirming that measurements of PCDD/F indicator compounds are amenable to correlation analyses. GC-measured di- and tri-chlorinated benzene isomers showed excellent correlation with PCDD/F TEQ. Two of the three diCIBz isomers showed an average correlation (R^2) with PCDD/F TEQ of 0.85. All three of the triCIBz isomers, including target 1,2,4-triCIBz, had an average R^2 of 0.90 with PCDD/F TEQ. These results suggest that any one or combination of these target CIBz isomers would make excellent indicators.

The REMPI-TOFMS analysis of 1,2,4-triCIBz concentration at the MWC was hindered by the presence of additional compounds of masses 180/182/184 that also ionized at 284 nm, obscuring the discrete 1,2,4-triCIBz spectrum. Also, discrete changes in the relative abundance of the mass 180/182/184 intensities were observed during shutdown and startup that can not be explained by relative ion abundances of trichlorobenzene(s) only. GC/MS analyses suggest that these compounds are substituted PAHs, such as trans-1,2-diphenylethylene ($\text{C}_{14}\text{H}_{12}$, stilbene) or methylfluorene ($\text{C}_{14}\text{H}_{12}$) for mass 180. The presence of the mass 180 interferents highlights the hazard in locating indicator compounds by a dissimilar technique (GC/MS) to that of the monitoring method (REMPI-TOFMS, in this case). Nonetheless, the mass 180 compounds predict PCDD/F TEQ values well on two of the four days, with R^2 of 0.76 and 0.79. Predictions on the other two days result in an R^2 of 0.79 and 0.80 when the PCDD/F TEQ values are allowed to lag the REMPI-TOFMS mass 180 measurement by one sampling period. PAHs are known to be early indicators of combustion upsets and appear to have compound-specific lag times¹⁸. Since all combustion shutdown/startup operations do not necessarily occur under the same conditions, and our sampling intervals would not necessarily have been at the same exact onset of the process changes, consideration of a single sampling period lag seems reasonable. These results demonstrate the ability of REMPI-TOFMS to provide real time feedback on correlative PCDD/F levels and offer promise for operational feedback to minimize emissions.

Acknowledgements

The sampling and analytical efforts of Drs. Christelle Briois, Barbara Wyrzykowska, Shawn Ryan, and Emily Gibb Snyder are gratefully acknowledged. The host plant personnel offered much-appreciated assistance and cooperation. The sampling efforts of Ms. Johanna Aurell and Messrs. Donnie Gillis, Steve Terll, and Matt Clayton (ARCADIS U.S., Inc.) were critical to this effort.

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