



Significance of measuring non-2,3,7,8-substituted PCDD/PCDF congeners and the identification of a new mechanism of formation for a high-temperature industrial process



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HIGHLIGHTS

- 136 PCDD/Fs data provide valuable insights in understanding emission deviations.
- Correlation observed between non-2,3,7,8-substituted congeners and TEQ emissions.
- Data point to role played by chlorination reactions during purification process.
- Study highlights the importance of the chlorine addition step and the kinetics.

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ABSTRACT

Many studies involving polychlorinated dibenzo-*p*-dioxins and dibenzofurans (Cl₄–Cl₈) are limited to the 17 2,3,7,8-substituted congeners, which are used for the computation of the toxic equivalent concentration (TEQ) and often are the basis for regulatory actions. The values determined for total homolog groups may also be reported in some cases, e.g., Total Tetra-Dioxins, and such results provide some additional information but do not reveal the subtle details that can be derived from the study of individual congeners. There are 136 possible structures for tetra- through octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans, including the 17 2,3,7,8-substituted congeners. In this work, the valuable role that inclusion of the other 119 congeners plays in understanding emission deviations (upsets) compared to normal operating conditions for a secondary aluminum smelter facility is illustrated. An exponential correlation was observed between the concentrations of specific non-2,3,7,8-substituted tetrachlorinated congeners (e.g., 2,3,6,7/3,4,6,7-TCDFs vs. 1,3,6,8-TCDD and 1,3,7,9-TCDD) and the TEQ-based emissions at the outlet of a baghouse pollution control device. The correlation possibly points to the additional and occasionally essential role played by metal-catalyzed stereoselective chlorination reactions taking place during the melting-purification process, as well as (conceivably) inside the air pollution control device. This chlorination in turn highlights not only the importance of the chlorine addition step and the kinetics involved with regard to regulating emission levels but also the role of measuring all 136 PCDD/F congeners.

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1. Introduction

Aluminum can be produced from bauxite ore or recovered by recycling aluminum scrap. During the secondary production process from scrap, aluminum is melted in a furnace and impurities are typically removed using chlorine until the aluminum reaches the desired purity (USEPA 310-R-95-010). The facility at which the data described in this paper were obtained melts scrap

aluminum sourced from processes such as rolling mills, and from other secondary aluminum production facilities. The scrap is relatively clean (i.e., free of organics) although some rolling oils may be present. The process line that was tested consists of a melting furnace, a holding furnace, and an in-line degassing unit. Natural gas is fired in both the melting furnace and holding furnace. Gaseous chlorine or chlorine in the form of salt can be added to the melting furnace and/or the holding furnace to purify the molten metal. Gaseous chlorine is added at the in-line degassing unit. The emissions from both furnaces and the degasser are all ducted to a common fabric filter baghouse that minimizes the emissions of

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particulate matter (PM). Lime is injected into the exhaust gas stream just upstream of the baghouse to reduce hydrogen chloride (HCl) emissions. To purify the molten metal, chlorine is used as the fluxing agent. The type of chlorine addition (gaseous chlorine or salt), where the chlorine is added (in the melting furnace and/or the holding furnace), how and when during the melt cycle the chlorine is added, and the presence of organics on the scrap metal charged to the melting furnace, all may affect the formation of PCDD/Fs. The owner of the facility agreed to allow the authors to use the PCDD/Fs emission test results to publish this study; however the name and location of the facility and actual PCDD/Fs emission levels cannot be divulged. All of the data are expressed herein on a relative scale because this report's emphasis is on the chemistries involved and kinetic aspects.

In spite of the utility of monitoring all 136 tetra- to octa-chlorinated PCDD/Fs (Shields et al., 2006), relatively little data are generated for them. Most analyses to this day still report only the 17 2,3,7,8-chlorinated PCDD/Fs and the totals of each homolog group. Several factors account for this seeming disparity. First, existing regulations on the monitoring of PCDD/Fs only specify limits for the TEQ or total mass balance (TMB). Thus, no regulatory imperative exists for monitoring these non-2,3,7,8-substituted congeners. In addition, existing EPA methods (and other methods based on them) only provide for the analysis of the 17 2,3,7,8-chlorinated congeners and total PCDD/Fs. Such analyses are adequate to determine TEQs and, to some degree, TMB. Therefore, the primary impetus to identify and quantify (however approximately) all 136 tetra- to octa-chlorinated PCDD/Fs is the ability to deduce the chemical behavior occurring during formation of PCDD/Fs or other forensic purposes (Tondeur and Hart, 2008; Tondeur et al. 2009a, 2012).

2. Materials and methods

2.1. Sampling

The PCDD/Fs were measured using US Environmental Protection Agency Reference Method 23 (EPA Method 23, 1995) sampling equipment and procedures. A sample of stack exhaust (baghouse outlet) gas was withdrawn isokinetically over the test period. Test runs were either 6 h or 24 h in duration. Each of the 24 traverse points was sampled for 15 min or more depending on the duration of the sample run. The sampling apparatus consisted of a stainless steel probe sheath/pitot tube, glass nozzle and glass probe liner, heated and pre-cleaned glass fiber filter with a Teflon support, non-contact chilled water coil condenser, XAD-2 adsorbent module and five impingers sample train. A submersible pump was used to circulate chilled water through the coil condenser and the XAD module to maintain a sample gas temperature of <20 °C. The PCDD/Fs were collected on the filter and in the XAD module. All of the glassware that came in contact with the sample gas stream was rinsed with acetone, then methylene chloride, and then toluene. These solvent rinse fractions were analyzed along with the filter and XAD module sample fractions.

The exhaust gas conditions, such as the gas velocity, exhaust gas temperature, oxygen content, and carbon dioxide content were all relatively constant (Stack Gas Velocity = 110 ft s⁻¹, Stack Gas Temperature = 93.3 °C, O₂ Content = 20%, and CO₂ Content = 0.5%). In addition, the volume of sample gas collected during the test runs was relatively constant from test to test (525–550 dscf). Therefore, it was decided to use the analytical data (pg per sample train) rather than the mass emission rates from the stack.

2.2. Analysis

2.2.1. Analytical standards

Quantitative standards for all 136 tetra- to octa-chlorinated PCDD/F congeners are not commercially available; however,

qualitative standards for all 136 are commercially available (Cambridge Isotope Laboratories – CIL, Andover, MA, USA). Thus, while strictly quantitative measurements are not possible, one can accurately perform relative measurements from sample to sample. Unlike the 17 2,3,7,8-chlorinated PCDD/Fs, stable isotope labeled standards are not available for all 136 tetra- to octa-chlorinated congeners. Thus, the measurement of the non-2,3,7,8-chlorinated congeners is carried out by internal standard measurement. Each non-2,3,7,8-chlorinated congener is measured relative to the closest eluting stable isotope labeled extraction standard. The average relative response factor of all the 2,3,7,8-chlorinated congeners in the same homolog group is used for calculating the concentration of each non-2,3,7,8-chlorinated congener. Without a quantitative standard, these response factors are only approximate, as are the concentrations that result from using them. Importantly, the qualitative standards allow for definitive identification of each of the non-2,3,7,8-chlorinated congeners. Using them, false positives can be identified and rejected. These standards also make possible the identification of each congener, which provides information critical in detecting specific reactions taking place in the formation of PCDD/Fs.

USEPA Method 23 does not require labeled standards be used to monitor, for example, the cleanup steps of sample preparation. It only requires the use of 18 labeled standards, whereas our procedures use 32 labeled standards (Tondeur, 2013a). The additional labeled PCDD/F standards provide feedback information on the laboratory's performance for specific tasks or steps in the laboratory's procedure (e.g., controlling selective losses that can alter or distort the congener profiles, documentation of extraction efficiencies for target analytes in the filter containing the PM, or the transfer and extraction efficiencies of target analytes present in the solvent rinses and associated PM; Tondeur et al., 2013b). These extra standards are above and beyond method requirements. They avoid the conundrum of "quantitation without representation", in which assumptions must be made about the performance of individual sample preparation steps. The use of these additional standards avoids the need to make such assumptions and pinpoint analytical difficulties on a per-sample basis.

2.2.2. Sample preparation

The sample extractions and fractionations are carried out according to an enhanced and highly refined version of USEPA Method 23 (Tondeur, 2013a).

2.2.3. HRGC/HRMS

The GC (Agilent 6890 Series; Palo Alto, CA, USA) is equipped with a capillary column (60-m ZB-5ms) and is coupled to a magnetic sector instrument (Waters AutoSpec Ultima; Milford, MA). The mass spectrometer is operated as described in US EPA Methods 8290/23.

2.2.4. Quality control

For each extraction batch and set of target analytes, a laboratory method blank and a batch control spike are prepared and analyzed alongside the samples. There are several functions associated with the batch control spikes (Tondeur et al., 2010). They allow an assessment of the spiking solutions' correctness as well as the accuracy of the technique used in dispensing those solutions (Tondeur and Hart, 2009b). Furthermore, they serve as verification of the calibration of the measurement system, and of the GC and MS performances. Thus, the method bias, laboratory bias, and analytical run bias are minimized or compensated for with the batch control spike, allowing the result to be closer to the true value within the repeatability error.

In addition to the usual qualitative analysis requirements in Method 23, the use of all 136 tetra- to octachlorinated PCDDs/

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