

Title: Burning Questions: Measuring PFAS Mineralization in Thermal Technologies

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## Abstract

The growing regulatory pressure surrounding PFAS has intensified demand for validated destruction technologies. Conventional PFAS analytical methods have involved inherent compromises in sensitivity, selectivity, and comprehensiveness. While these limitations have been tolerable for site investigations comparing results for select PFAS to regulatory standards, demonstrating complete mineralization of all PFAS now requires more rigorous analytical approaches as investment in destruction technologies accelerates.

Recent advancements in analytical tools and method modifications have improved our ability to assess complete PFAS mineralization, though challenges remain. The U.S. EPA has published OTM-45 for the collection and analysis of semivolatile PFAS from source air emissions, while the newer OTM-50 targets ultra-short chain and volatile PFAS that are the suspected products of incomplete destruction (PIDs). High resolution mass spectrometry or full scan tentatively identified compounds (TICs) enable non-targeted analysis to identify additional PIDs, but this is not a quantitative tool. There are methods which aim to capture non-discrete PFAS mass such as Total Organic Fluorine (TOF), thought to be necessary to complete a mass balance calculation. Collectively, these analytical methods aim to close the mass balance, but each is susceptible to certain limitations.

Advancements have been made to lessen the gap between the varied approaches but some gaps remain. For example, method development has been conducted to improve the isolation of organic fluorine from inorganic fluorine in gas phase extracts, yielding more accurate total organic fluorine measurements in the gas phase. Enhanced extraction efficiency has improved PFAS quantitation in complex matrices such as pyrolysis oil, a product of pyrolysis, providing a more accurate representation of destruction efficiency.

This presentation will provide attendees with insights into the latest PFAS measurement methodologies as applied to the assessment of PFAS treatment technologies, examining both opportunities and challenges within the evolving regulatory landscape. We will explore the technical nuances of EPA OTM-45/50 and present critical considerations for an effective PFAS air emissions assessment.

Our presentation showcases real-world data from thermal treatment applications, specifically examining PFAS fate during thermal oxidation and biosolids processing via pyrolysis (500-800°C, oxygen-free) and gasification (800-1000°C, limited oxygen). Comprehensive understanding of PFAS fate throughout these processes has proven elusive to date. We will present novel findings on PFAS distribution across multiple process streams: influent biosolids, effluent char, effluent pyrolysis liquid, and effluent gas phases. Our analysis reveals critical insights into removal efficiencies, transformation pathways, and possible destruction, including the previously unexplored effects of biosolids drying. Most importantly, our research establishes distinctions between PFAS removal (mere phase transfer), molecular transformation, and true destruction, distinctions essential for accurately evaluating treatment effectiveness.