

Development and Validation of PCDD/F Testing Approaches for Mobile Source Engines over Transient and Steady-State Cycles

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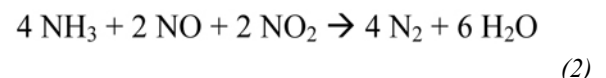
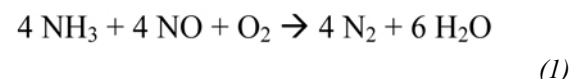
ABSTRACT

Advances in aftertreatment technologies, such as Diesel Particulate Filters (DPF) and Selective Catalytic Reduction (SCR) catalysts, have responded to increasingly stringent PM and NO_x requirements for diesel engines. Potentially viable SCR materials include copper and iron zeolite, which possess high thermal durabilities and conversion efficiencies. However, concern exists over the metal-catalyzed synthesis of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), especially since typical SCR operating temperatures overlap with optimal PCDD/F formation from the de novo and precursor mechanisms. Due to the lack of standardized testing methodology for measuring PCDD/F emissions from mobile sources, this study adapted EPA methods 0023A and TO-9A from their original applications of industrial stack and ambient air sampling. The modifications detailed in this paper accommodated the measurement of PCDD/Fs from a dynamometer-controlled engine, addressing considerations such as temperature excursions, concentrated emissions, transient conditions, and engine vibrations. To validate the modified TO-9A approach, measurements were compared to the previously published results of an EPA-certified CVS tunnel for NO_x, CO₂, and PM emissions and a CRC study for PAHs and aromatics emissions. The modified TO-9A approach was further compared to the modified 0023A approach by performing simultaneous tests over a steady-state cycle using an engine equipped with a copper zeolite SCR system. Although both approaches were capable of detecting ultra-low concentrations of total PCDD/Fs, the modified 0023A approach showed better detectability for the 17 toxic PCDD/F congeners. Furthermore, the modified 0023A approach demonstrated higher precision as determined

from statistical analysis of sample-to-sample variation. However, application of the modified 0023A approach to transient conditions would require further development of proportional sampling, without significantly compromising the detectability and precision associated with raw gas analysis.

INTRODUCTION

Increasingly stringent NO_x and PM regulations, including the U.S. 2010 and Euro VI standards for heavy-duty diesel engines, have prompted the development of advanced diesel aftertreatment technologies such as selective catalytic reduction (SCR). SCR accomplishes NO_x reduction through two primary mechanisms: the “standard” reaction ([Equation 1](#)) and the “fast” reaction ([Equation 2](#)) [2,3,4].



Though desirable, the “fast” reaction requires a significant amount of NO₂ [2, 3], a condition frequently untenable in certain engine operations where NO predominates. Thus, in addition to providing NO_x conversion over the range of exhaust temperatures, SCR catalysts must be capable of adapting to less-than-optimal NO/NO₂ ratios.

The traditional use of vanadium SCRs reflects their low temperature performance as well as their resistance to sulfur and hydrocarbon poisoning [2, 5,6,7]. However, elevated temperatures associated with active DPF regeneration have

frequently surpassed the never-to-exceed temperature of vanadium SCR_s, hindering their widespread application [8] and prompting the search for alternative catalytic formulations with improved thermal durability. While both copper and iron zeolite possess higher thermal durability than vanadium, copper zeolite outperforms iron zeolite in the low-temperature operating regime of diesel engines. Copper zeolite SCR_s also display less sensitivity to the NO/NO₂ ratio which likely enhances performance during cold starts [9, 10].

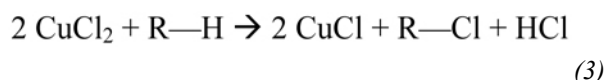
However, concern exists over the metal-catalyzed synthesis of PCDD/Fs, whose optimal formation overlaps with typical SCR operating temperatures. Under certain engine and chlorine doping conditions, Heeb et al. found that copper additives induced formation of PCDD/Fs from diesel exhaust aftertreatment systems, in contrast to the negligible effect of iron additives [11,12,13]. Due to the toxicological hazards of PCDD/Fs, the World Health Organization (WHO) has issued a maximum daily allowance of 1 to 4 pg of tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD) equivalents/kg bodyweight, and the U.S. Environmental Protection Agency (EPA) has placed PCDD/Fs on the Mobile Source Air Toxics (MSAT) list [14]. Currently, no standardized methodology exists for measuring PCDD/Fs from mobile source engines.

This study modified two EPA methods for measuring PCDD/Fs, adapting their application from stationary sources to mobile source diesel engines. The modifications to methods TO-9A and 0023A accommodate typical engine conditions such as wide temperature excursions, concentrated emissions, transient conditions, low exhaust dilution, and engine vibrations. To explore the applicability of the modified TO-9A approach, validation tests compared experimental measurements to the previously published results of an EPA-certified CVS tunnel for NO_x, CO₂, and PM emissions and a CRC study for PAHs and aromatics emissions. Following the promising results of the validation tests, simultaneous steady-state tests on an engine containing either a copper zeolite SCR system or no aftertreatment components determined the PCDD/F detectability of the modified TO-9A and 0023A approaches. Replicate tests of each engine configuration established the relative precision of the two modified approaches, a metric for determining the optimum approach to measuring PCDD/F emissions from mobile source engines.

MECHANISMS OF PCDD/F FORMATION AND THEIR RELEVANCE TO COPPER ZEOLITE SCR_s

Despite the advantages of copper zeolite SCR_s, mechanistic studies have implicated copper as a catalyst for PCDD/F formation. In the de novo mechanism, where oxidation and chlorination reactions of the carbonaceous matrix produce PCDD/Fs, copper functions as a shuttle for oxygen and

chlorine between the gaseous and solid phases [15]. Isotopic studies with ¹⁸O have identified a possible correlation in which bonded oxygen and gaseous oxygen correspond to lower and higher chlorinated compounds, respectively. Although no such correlation has been found for the case of chlorine, CuCl₂ increases the incorporation of Na³⁷Cl, likely by facilitating carbon-chlorine bonds via a change in oxidation state shown in Equation 3 [16]. Changes in copper speciation throughout the temperature regime of de novo formation lend additional support to its participation in the oxychlorination cycle.



Compared to de novo formation, a more detailed understanding has emerged for the role of copper in precursor formation. Copper oxide acts as a site for the adsorption and reaction of chlorophenols, the likely precursor molecules [16]. A Mars-van Krevelen mechanism accounts for the transfer of oxygen from the copper oxide surface to the adsorbed chlorophenol molecule, with the simultaneous removal of the phenolic group from the latter. Electron transfer from the phenolate to the metal site stabilizes the subsequent formation of a chlorophenoxy radical, accompanied by a change in the oxidation state of the copper. Chlorophenoxy radicals lastly undergo Langmuir-Hinshelwood and Eley-Rideal mechanisms to form PCDD/Fs on the copper oxide surface [16]. Alternatively, reactions of the geminal oxide sites with adsorbed chlorophenoxy radicals produce chlorocatechol and chloro-o-quinone intermediates, which may proceed through separate pathways to produce dibenzo-p-dioxin (DD), monochlorinated dibenzo-p-dioxin (MCDD), and 4,6-dichlorinated dibenzofuran (DCDF) [16].

Although both mechanisms require carbon compounds and a chlorine source, the additional specification of oxygen for de novo formation results in a complex rate dependence. A concentration of free chlorine in excess of 1% can directly determine the PCDD/F formation rate under certain circumstances, but oxygen concentrations up to 2% may instead control the formation rate in the absence of free chlorine [15]. Despite the different kinetics of the two mechanisms, both attain an optimum formation rate at around 200 to 400°C [15], and similar competing processes (such as catalyst poisoning with sulfur and deactivation reactions with ammonia) inhibit PCDD/F formation. Likewise, the interaction of these factors partially determines the extent of PCDD/F formation in industrial processes. For example, the fly ash of industrial incinerators typically contains up to 20% carbon and 5-10% chlorides, with close contact between these species and copper for hours [18] in the electrostatic precipitator (ESP), where temperatures generally remain under 240°C. The U.S. EPA recognized the potential for PCDD/F formation in industrial incinerators and issued

regulations in 2006 that limit most incinerators to 200 pg TEQ/dry scm [19]. Possible similarities between these systems and diesel engines, as well as the incomplete understanding of PCDD/F formation in the literature, motivate the present study of PCDD/F emission in the copper SCR system [11,12,13].

REVIEW OF CURRENT REGULATORY METHODS

In the U.S., no standardized method exists for measuring PCDD/F emissions from mobile sources. The closest analogues for dioxin testing, EPA method TO-9A for ambient air testing and EPA method 0023A for industrial stack testing, target stationary sources. In method TO-9A, ambient air enters a high volume sampler, passes through a PCDD/F-retaining quartz particulate filter and a polyurethane foam (PUF) cartridge, and exits through a venturi meter and exhaust duct. A volume of 325 to 400 m³ of exhaust gas is passed through the PUF cartridge by sampling 0.114 to 0.285 m³/min for 24 hours [20].

In contrast, EPA method 0023A features a more complicated apparatus. A sample of the exhaust isokinetically enters the probe and passes through a filter and condenser before encountering a XAD trap, which retains PCDD/Fs. The remainder of the exhaust proceeds through four glass impingers in series: the first impinger remains empty, the second and third impingers contain 100 mL water, and the fourth impinger contains 200 g silica. After exiting the impingers, the exhaust travels along a vacuum line leading to the dry gas meter and is subsequently vented to the atmosphere through a flow orifice. Relevant parameters include the pressure drop across the orifice (ΔH) and the velocity pressure across the pitot tube (ΔP). The sampling time for method 0023A is a function of the sampling rate as well as the analytical detection limit of the analytes being studied and can be calculated using Equation 4 [14].

$$\text{Sample_Time}(t) = \frac{\text{analytical_DL}}{(\text{Sample_Rate}) * (\text{Desired_Gas_Concentration_DL})} \quad (4)$$

Methods TO-9A and 0023A each offer several advantages for mobile source engine testing. Method TO-9A processes larger sample volumes, more easily accommodates transient conditions, and provides an atmospherically relevant indication of emissions exposure through ambient testing conditions. On the other hand, method 0023A utilizes a XAD with a potentially higher efficiency adsorption than the PUF and observes more rigorous sampling procedures. For example, method 0023A includes temperature specifications of below 20°C for the XAD and 120°C $\pm$ 14°C for the heated filter, glassware precleaning of 400°C baking followed by three rinses each with methylene chloride and toluene, and

sample extraction with three rinses each of acetone, methylene chloride, and toluene which are all included in the laboratory analysis.

MODIFICATIONS TO EPA METHODS TO-9A AND 0023A

Some aspects of the proposed modifications to EPA methods TO-9A and 0023A already appear in the literature. As early as 1989, Hildemann et al. described the operation of a partial-full-partial dilution stack sampler [22], a predecessor to the full-partial-full source dilution sampling (SDS) system proposed in this study [23]. EPA method 0023 has also been previously modified to measure PCDD/Fs from mobile source engines by Ryan et al. [24]. Their modifications include the replacement of the glass condenser with cooled Teflon tubing and the adjustment of the XAD temperature to below 40°C.

MODIFICATIONS TO EPA METHOD TO-9A

To representatively simulate atmospheric conditions for mobile source applications, a full-partial-full source dilution sampling (SDS) system was added to the original EPA method TO-9A apparatus in this study. Liu et al. have previously described the design considerations of the SDS system [23]. Briefly, it is intended to simulate atmospheric dilution and aging conditions, maintain proportional sampling during transient conditions, and reduce particle loss by minimizing thermophoresis, wall effects, and electrostatic forces. Figure 1 shows the schematic of the experimental apparatus for the modified TO-9A approach. The main components of the system consist of a primary dilution tunnel called the critical flow venturi-constant volume system (CFV-CVS), a secondary micro-diluter, a residence time chamber (RTC) for aging and atmospheric conditioning of the sample, and isokinetic sampling probes for various sampling trains.

After dilution and conditioning in the full-partial-full SDS system, the sample proceeds into the high volume sampler used for EPA method TO-9A. The sampler consists of a pre-filter, a PUF cartridge, a rotometer, and a flow venturi for flow control.

<figure 1 here>

MODIFICATIONS TO EPA METHOD 0023A

Most of the method 0023A modifications related to the safety considerations of engine operation. To maintain an isolated test cell during engine experiments, remote cameras monitored the XAD coolant level, the urea dosing system, the aftertreatment components, and the oil pressure gauge. The