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Use of REMPI–TOFMS for real-time measurement of trace aromatics during operation of aircraft ground equipment

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Abstract

Emissions of aromatic air toxics from aircraft ground equipment (AGE) were measured with a resonance enhanced multiphoton ionization–time of flight mass spectrometry (REMPI–TOFMS) system consisting of a pulsed solid state laser for photoionization and a TOFMS for mass discrimination. This instrument was capable of characterizing turbine emissions and the effect of varying load operations on pollutant production. REMPI–TOFMS is capable of high selectivity and low detection limits (part per trillion to part per billion) in real time (1 s resolution). Hazardous air pollutants and criteria pollutants were measured during startups and idle and full load operations. Measurements of compounds such as benzene, toluene, ethylbenzene, xylenes, styrene, and polycyclic aromatic hydrocarbons compared well with standard methods. Startup emissions from the AGE data showed persistent concentrations of pollutants, unlike those from a diesel generator, where a sharp spike in emissions rapidly declined to steady state levels. The time-resolved responses of air toxics concentrations varied significantly by source, complicating efforts to minimize these emissions with common operating prescriptions. The time-resolved measurements showed that pollutant concentrations decline (up to $5\times$) in a species-specific manner over the course of multiple hours of operation, complicating determination of accurate and precise emission factors via standard extractive sampling. Correlations of air toxic concentrations with more commonly measured pollutants such as CO or PM were poor due to the relatively greater changes in the measured toxics' concentrations.

Keywords: Aircraft ground equipment; Emissions; Auxiliary power unit; REMPI; Aromatic air toxics; Hazardous air pollutants; Measurement; REMPI–TOFMS; Real time; Diesel generator

1. Introduction

Hazardous air pollutants (HAPs), comprising 188 organic and metal compounds, are regulated under Section 112(b) of the Clean Air Amendments of 1990 (US EPA, 1990). Regulatory compliance is often determined by estimates of both activity projections and similar-source emission factors. Emission factors are preferentially determined by source sampling/monitoring rather than use of source-generic emission factors. However, both sampling data and emission factors are limited in breadth—relatively few sources have been characterized for the 188

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HAPs due to the difficulty and cost of assessing each source.

Protocols for source emissions characterization are a function of sampling and analytical limitations. Analytical detection limits also determine sampling protocols, primarily related to sample volume (collection time) necessary to avoid non-detects. For HAPs, these limitations can be particularly influential, since HAP concentrations are typically significantly lower than other pollutants such as criteria pollutants NO_x, CO, and SO_2. Hence, sampling protocols for HAPs typically require long-term, steady state monitoring. This requirement prevents observation of HAP transients. An inability to characterize HAP transients can be particularly limiting for sources whose emissions vary greatly with load changes, process control changes, and frequent startups/shutdowns. The inability to rapidly follow HAP concentrations during process transients limits prospects for understanding how process controls and other source-specific changes can bring about lower emissions.

Advances in laser and mass spectrometry technology (Boesl et al., 1998; Oudejans et al., 2004) have enabled the development of extremely sensitive compound detectors that have real-time capability, such as resonance enhanced multiphoton ionization–time of flight mass spectrometry (REMPI–TOFMS), covered in this paper. The sensitivity and rapidity of REMPI–TOFMS exceeds the restrictions of current extractive methods, enabling characterizations of transients and immediate feedback to the operator of the emissions source. Previous work on gasoline engines (Frey et al., 1995; Nagel et al., 1996) and diesel engines (Nagel et al., 1996) using REMPI–TOFMS determined HAP emission factors, both for steady state and transient operations, such as start-ups. This paper extends that work to a gas turbine, contrasting the HAP concentration trends during startups, shutdowns, and load changes and demonstrating the ability to monitor these trace pollutants. Concentrations were compared to published emission factors available in EPA databases and the referenced literature to determine the efficacy of the REMPI–TOFMS method.

Two gas turbine units using JP8 fuel, included in the general category of aircraft ground equipment (AGE), were previously characterized (Gerstle et al., 1999). The AGE classification system includes aircraft support equipment such as air compressors, floodlights, bomb lifts, turbines, generators, and heaters. Auxiliary power units (APUs) (GTCP85-180 and GTCP165-1) from C-130H and C-5A/B aircraft, respectively, were tested at constant power settings, or about $120\,\mathrm{kg\,fuel\,h^{-1}}$. Ambient air samples were taken to allow for background correction. The authors found from testing with these and aircraft engine sources that of the 120 or so compounds identified, only a few compounds were universally detected, suggesting that emission characterization is fairly engine- or source-specific. Benzene, toluene, and xylene were prevalent and formaldehyde was over 90% of the aldehydes/ketones present. The authors mentioned the possibility of reducing the characterization effort by monitoring a few surrogate compounds, but were unable to test this theory due to an insufficient database (lack of replicates on a single source).

This work examines the ability of REMPI–TOFMS to detect and characterize emissions of aromatic air toxics from an AGE unit and to determine whether operational transients significantly affect emission factors.

2. Experimental

2.1. AGE

The exhaust of a turbine engine compressor, USAF type A/M32A-95 (Large Aircraft Starting unit), was sampled with the REMPI–TOFMS system. This AGE is used to furnish pneumatic power for ground support of aircraft systems. Its primary mission is to start engines for a variety of aircraft. The turbine engine, fuel and electrical systems, as well as the air delivery system are enclosed inside a four-wheeled, towable cart. The cart contains a 300 L metal fuel tank which holds JP-8, a kerosene-based fuel (MIL-T-83133) used as the standard military fuel (US Army, 2001). It is comprised of paraffins, olefins ($\leqslant 5\%$ by vol), and aromatics ($\leqslant 25\%$ by vol) with less than 0.3% sulfur (S) by mass and a minimum net heat content of $42{,}700\,\mathrm{kJ\,kg^{-1}}$ (Kimm et al., 1997). Annual fuel consumption per AGE unit is typically low (on the order of $750\,\mathrm{L\,year^{-1}}$) but the number of units make AGE a high category of total usage. The JP-8 fuel headspace above the liquid layer of a nearly empty fuel barrel (at $25\,^{\circ}\mathrm{C}$) was sampled into the REMPI–TOFMS sampling line. Concentrations of target analytes were determined by calibrating the measured ion signals with those from an Aromatics Subset (Supelco) gas standard cylinder mixture