

ON-LINE DETECTION OF AROMATIC COMBUSTION BY-PRODUCTS
FROM A LEAN METHANE FLAME USING JET-REMPI-TOFMS

Harald Oser¹, Lukas Oudejans^{2,3}, Michael J. Coggiola¹, Gregory W. Faris¹, David R. Crosley¹, and Brian K. Gullett²

¹SRI International, Molecular Physics Laboratory, Menlo Park, CA 94025, USA

²U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, E305-01, Research Triangle Park, NC 27711, USA.

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Introduction

A number of rapid and sensitive analytical techniques and methods are under development to measure toxic aromatic emissions with time-scale resolution on the order of minutes. These developing analytical techniques include resonance-enhanced multiphoton ionization coupled with time-of-flight mass spectrometry (REMPI-TOFMS) and its more sensitive and selective variant, Jet-REMPI-TOFMS.

In recent years, several research groups have contributed to significant improvements in the development and application of instruments based on REMPI-TOFMS¹⁻¹². These include field applications at incinerators^{7,12} for on-line detection of aromatic by-products. Combustion research has focused in recent years on studies involving the formation of toxic combustion by-products as well as formation studies of dioxins and furans from relatively simple combustion systems¹³. For this purpose, an entrained flow reactor (EFR) was developed and in this paper we will present the first results from the application of the Jet-REMPI-TOFMS technique to this combustion system as a combustion by-product monitor. To the best of our knowledge, this is also the first time that the Jet-REMPI-TOFMS technique (or any of the similar versions of it) has been used to study in detail the presence of monocyclic aromatic combustion by-products in the off-gas stream from a relatively clean and controlled combustion process such as that of a methane flame. Note that most on-line studies that have been performed involved rather complex gas streams in which the presence of polycyclic aromatic hydrocarbons (PAHs) dominated. The combination of a Jet-REMPI-TOFMS instrument and flow reactor in a single research facility opens unique opportunities to study in detail relations between the formation of combustion by-products and combustion control parameters such as reactor temperature profiles and equivalence ratio. This technique can provide more time-resolved information regarding the potential of surrogate detection for dioxin and furan toxicity measurements¹⁴.

Materials and methods

Experiments were conducted in an EFR for which a detailed description is given elsewhere¹³. The EFR consists of two (one horizontal and one vertical) concentric tube quartz reactors connected in series. An electrically heated (1000 °C), horizontal, diffusion flame burner supplies combustion products to the vertical reactor, which was kept at 200 °C in this study. Combustion of methane (CH₄) in oxygen (O₂) provided by-product hydrocarbons. A constant flow of 10 L/min was employed in all experiments, giving rise to a total residence time of about 2 s. For background ("flame off") signal verification of target analytes, preheated nitrogen (N₂) was substituted for the CH₄ and O₂ content. The off-gas stream was filtered using a glass microfiber filter and fed through a 1.8 m long, 1.25 cm diameter heated quartz tubing to the Jet-REMPI-TOFMS instrument. Gas was sampled directly without

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preconcentration at a rate of typically 1 mL/min from the total off-gas stream. The initial detection of aromatics was recorded at an equivalence ratio $F = 0.65$ for the CH_4 flame.

A brief summary of the laboratory Jet-REMPI-TOFMS instrument is given here while a more detailed description can be found elsewhere ⁵. The sample is introduced into the ionization chamber through a pulsed valve (General Valve Series 99) that delivers 150 ms sample pulses at atmospheric backpressure through a 0.5 mm orifice at a repetition rate of 10 Hz. The laser system consists of a Continuum Powerlite Precision 9010 Nd:YAG and Sunlite EX OPO including frequency doubling with a nominal tuning in the ultraviolet (UV) range between 225 and 350 nm, a 6 ns pulse width, and a repetition rate of 10 Hz. The optical linewidth of the system is approximately 0.1 cm^{-1} . The laser beam was unfocused, with a beam area of about 10 mm^2 and pulse energy of approximately 5 mJ for the OPO output. Ions were mass analyzed by a reflectron type TOFMS (R. M. Jordan) with a mass resolution of 1000, amplified by an Ortec 9306 preamplifier (gain = 85, bandwidth = 1 GHz) and recorded by a 500 MHz digitizer (Signatec DA500A).

Results and Discussion

Among the most intriguing observations was the detection of several interesting species that were identified in a nominally “clean” methane flame (equivalence ratio $F = 0.65$). Benzene (C_6H_6), phenol ($\text{C}_6\text{H}_5\text{OH}$), and aniline ($\text{C}_6\text{H}_5\text{NH}_2$) were detected in the off-gas stream of the reactor under the described test conditions. For all species, the measured spectra are essentially identical to those recorded using a “clean” calibration gas mixture, and all were detected in the exhaust stream with concentrations well above the detection limit of this system, which was estimated to be approximately 5 ppt for benzene. Furthermore, their presence could be entirely attributed to the methane combustion chemistry, as the background levels were not detectable in the absence of the flame.

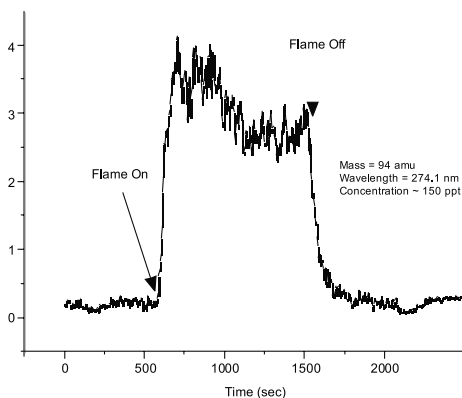


Figure 1. Time dependence of phenol measured in a lean ($F=0.65$) CH_4 flame.

Figure 1 shows the time dependence of the phenol signal at a mass-to-charge ratio (m/z) of 94 with the laser tuned to the primary $S_1 \rightarrow S_0$ transition at 274.1 nm (uncalibrated wavelength). The time resolution of these data was 1 s, corresponding to 10 laser shots per data point. Between $t = 0$ and 250 s, the background signal was measured with no reactant gases flowing. At $t = 250$ s, the O_2 reactant was introduced. Note that, prior to flame ignition at 600 s, the phenol signal was essentially absent. At the point indicated in the figure, the flame was ignited by adding methane to the premixed gas flow, and the phenol signal rose rapidly and remained more or less constant until the flame was extinguished.

With the flame off, the phenol signal initially decreased rapidly, followed by a slower decrease back to the baseline. The slower decay was likely due to residual phenol in the sampling line and pulsed valve. Increasing the temperature of these components and reducing the “dead volume” the similar ionization probability for phenol in comparison with benzene ¹⁵.

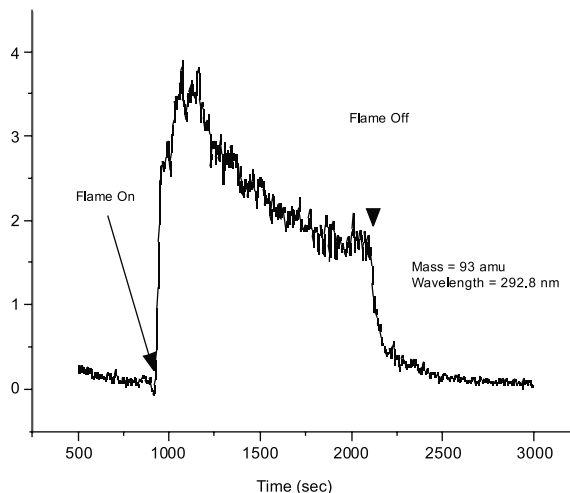


Figure 2. Time dependence of aniline measured in a lean CH₄ flame.

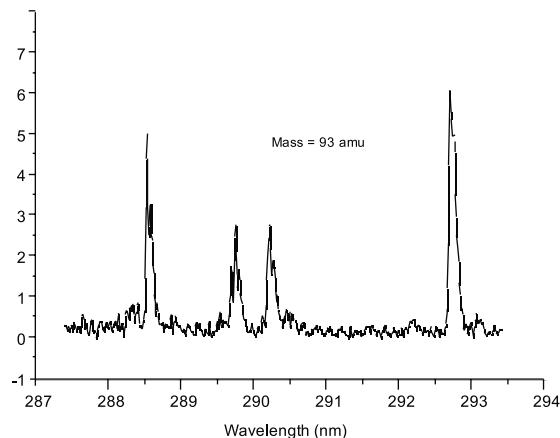


Figure 3. (Uncalibrated) wavelength dependence of the aniline jet-REMPI signal measured in a lean CH₄ flame.

Figure 2 shows a similar time history recorded for the aniline signal at a m/z of 93 and at a wavelength of 292.8 nm, chosen as the primary resonance line (Fig. 3). In this measurement, the methane flame equivalence ratio F was also 0.65. Again, the aniline signal was absent until the flame was ignited, at which point it rose rapidly and remained readily measurable until the flame was extinguished. No estimate has been made yet for the concentration of aniline in the exhaust gas stream. The cause for the decline in aniline ion signal during the combustion process has not been determined.

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Since the phenol profile does not show this strong decline, one could argue that this is a combustion effect, rather than a sampling issue. Further research is needed to determine the cause of such behavior.

The observation of aniline in the exhaust stream from a nominally pure methane flame was rather unexpected. To the best of our knowledge, aniline has been detected only once as a combustion by-product, namely, in the flue gas of a pilot-scale incinerator⁸ with a Jet-REMPI-TOFMS instrument that was similar to the one used here. Other, more elaborate studies of the flue gas of incinerators¹² have used fixed-frequency laser-REMPI-TOFMS techniques, which tend to be less selective. To confirm the aniline identification, a wavelength scan was recorded at a m/z of 93. Figure 3 shows the measured REMPI signal at the wavelength range from 287.5 to 293.5 nm with the methane flame ignited. This spectrum corresponds to the known REMPI absorptions for aniline under jet-cooled conditions¹⁶.

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