

Initial Development Of Continuous Emissions Monitor Of Dioxin

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1. Introduction

The need for a continuous emissions monitor for the determination of dioxins and furans at realistic (ppt or sub-ppt) concentrations in real time (minutes) is widely recognized in the waste combustion community. The key issues are overall sensitivity, and selectivity among the many congeners found in real applications. At SRI International we are currently developing an instrument to meet these needs. Our instrument is based on supersonic jet expansion and cooling, followed by resonantly enhanced multiphoton ionization (REMPI) into a mass spectrometer. This furnishes the dual selectivity of tuned laser absorption and mass analysis. We have made a systematic study of the internal temperature of jet-cooled molecules subjected to REMPI in our instrument, and based on those results, we have developed an improved system design that optimizes the ionization efficiency.

2. Objective

Emission control strategies must ultimately rely upon a careful assessment of the link between health effects and ambient, human exposure levels to hazardous air pollutants (HAPs). Because polychlorinated organic compounds in general, and dioxins and furans in particular, are among the most toxic of HAPs, SRI International is developing a continuous emission monitor (CEM) for these species using the jet-REMPI technique under support from DOE. The unique capability for real-time detection and identification of these and other toxic HAPs directly in incinerator emissions using a CEM instrument is an essential component of emissions modeling, dispersion modeling, source apportionment, and ultimately, of human exposure modeling. Jet-REMPI is the only instrumental technique that can provide the speed, breadth, and sensitivity of measurement capabilities that are required in support of the development of a comprehensive strategy to monitor and control emissions of dioxins and furans from waste incinerators.

Our technique will provide real-time dioxin and furan concentrations rather than the multi-hour or multi-day averages as in the case for existing, conventional sampling and analysis methods. This capability will allow a detailed investigation of the relationship between dioxin emissions and the incinerator operating parameters and waste feed characteristics. Such a study may reveal that "puffs" (transient pollutant emission events) account for a majority of the dioxin emissions, and hence only short-term control methods would be required to meet time-averaged regulatory emission limits. Such control strategies may be much more cost effective than full-time emission control approaches. Tailoring the emission control strategy in response to minute-by-minute changes in the emission of hazardous pollutants can only be accomplished if a suitable CEM is available, such as our jet-REMPI based instrument.

3. Approach and Technology Description

Our analytical approach for continuous monitoring of dioxin and furan levels, jet-REMPI, has been described in some detail elsewhere¹⁻⁴ and only a basic overview will be given here.

A schematic of our laboratory prototype dioxin CEM is shown in Figure 1. Ions produced by resonance enhanced multiphoton ionization (REMPI) are typically detected using a time-of-flight mass spectrometer (TOF-MS) that takes advantage of the pulsed nature and well-defined temporal character of laser ionization. The simultaneous detection by mass and wavelength yields extremely high chemical selectivity crucial to identifying one trace compound in the midst of many other similar ones. Typical sensitivities of conventional REMPI TOF-MS systems that do not use sample molecule cooling are in the mg/dscm range and higher, which is totally insufficient either for a laboratory system or for regulatory monitoring of chlorinated aromatics in a waste treatment process such as an incinerator.

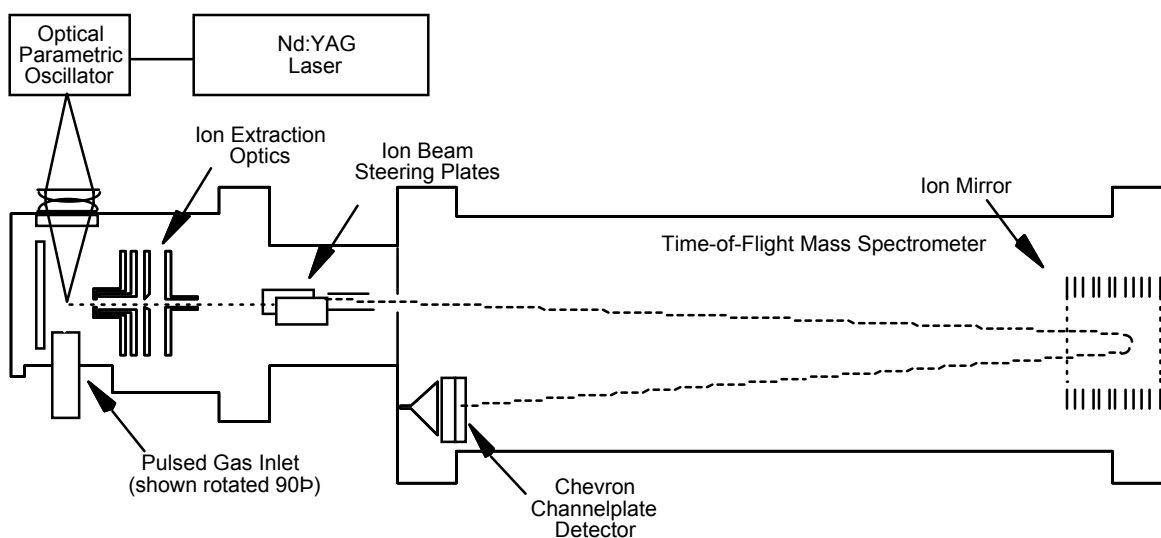


Figure 1. Schematic of the laboratory prototype jet-REMPI apparatus.

A major improvement in sensitivity without loss in selectivity can be achieved using a pulsed gas valve that produces a supersonic expansion. Pulsed gas valves provide a number of advantages over continuous gas inlets, including reduced gas flow and hence smaller vacuum pumps, higher local gas densities, well-defined spatial distribution, significantly reduced translational energy distribution orthogonal to the propagation direction, and reduced internal (vibrational and rotational) temperatures leading to greatly enhanced spectroscopic resolution.

In our instrument, ions are produced by REMPI and detected using a time-of-flight mass spectrometer (TOF-MS) that takes advantage of the pulsed nature and well-defined temporal character of the laser ionization process. The simultaneous detection by mass and wavelength yields extremely high chemical selectivity crucial to identifying one trace compound in the midst of many other similar ones. A major improvement in sensitivity without loss in selectivity is achieved using a pulsed gas valve that produces a supersonic expansion. Pulsed valves provide a number of advantages over continuous gas inlets, including reduced gas flow and hence smaller vacuum pumps, higher local gas densities, well-defined spatial distribution, significantly reduced translational energy distribution orthogonal to the propagation direction, and reduced internal (vibrational and rotational) temperatures leading to greatly enhanced spectroscopic resolution.

REMPI is a highly sensitive, highly species-selective, gas-phase analysis technique that has been applied to numerous problems in molecular spectroscopy and combustion research. For REMPI of complex molecules, such as dioxins, the spectra can be simplified greatly by expansion through a nozzle. Adiabatic expansion results in low sample temperatures, which increases the electronic ground state population and narrows the resonance line widths through reduction in molecule velocities (reduced Doppler or temperature broadening) and through reduction in transition-perturbing collisions (reduced pressure broadening). These reduced linewidths lessen the ionization of other molecular species (interferences) – leading to improved selectivity – and make the peak absorption larger—leading to improved sensitivity. One or more wavelengths are used to ionize the cooled gas molecules by absorption of two or more photons, one of which must be resonant with an electronic transition in the target molecule.

Our laser system consists of a Continuum Powerlite Precision 9010 Nd:YAG and Sunlite EX OPO (optical parametric oscillator) with a nominal tuning range in the visible between 445 and 710 nm, a 5 ns pulse width, and a repetition rate of 10 Hz. Frequency doubling is achieved using a Continuum FX-1 system. The optical linewidth of the system is approximately 0.1 cm^{-1} . The pulsed valve is an unmodified General Valve series 9 unit, with an orifice diameter of 0.5 mm. The nominal opening time was 150 μs , with a 2.5 cm separation between the exit of the valve and the ionization region. Typical ionization conditions included a pulse energy of approximately 1mJ in a 1.5 mm diameter laser beam. Ion signals from the reflectron TOF-MS are amplified by a Ortec 9306 preamplifier with a gain of 85 and a 1 GHz bandwidth, and recorded by a 500 MHz, Signatec DA500A digitizer.

4. Results

The effective internal temperature of sample molecules in the supersonic jet is important for determining both sensitivity and selectivity of the jet-REMPI method. To determine the optimum operating conditions for obtaining the lowest temperature in combination with the maximum signal level, we performed two types of experiments. First, the sensitivity and temperature distribution in the pulsed supersonic beam was measured as a function of the valve opening time. The opening time directly affects the collisional behavior in the supersonic beam, and to a lesser extent, the density distribution. The latter is expected to increase as the opening time is increased, achieving a maximum value for opening times greater than the time required for the pulsed valve to fully open. The second type of measurement determined the effect on sensitivity and rotational temperature of the distance between the gated valve and the laser beam. This distance is important for allowing the collisional cooling to extract as much random thermal energy from the molecular beam as possible. Benzene was used as a thermometric species owing to its well-established REMPI spectroscopy. In particular, the band near 259 nm was studied. Band profiles were calculated as described below and fitted to the measured spectra, allowing a determination of the temperature to an accuracy of approximately 1°K.

Band profiles require calculation of the individual relative line intensities, I_{KJ} which are given by

$$I_{KJ} = C \nu A_{KJ} g_{KJ} e^{-F(K,J)/kT}$$

where C is proportional to the Franck-Condon Factor (constant for a single vibration level), ν is the photon frequency, A_{KJ} is the line strength (given by the Hönl-London formulae for a perpendicular transition in a symmetric top), g_{KJ} are the statistical weights of the lower state (for molecule with D_6 rotational symmetry), $F(K,J)$ is the energy of the lower level, J is the total

angular momentum and K is the projection of J onto the figure axis of the symmetric top, both for the lower state. A complete band consists of P, Q, and R subbands corresponding to $\Delta J=0,\pm 1$, with subband origins distributed along Fortrat parabolas corresponding to $\Delta K=\pm 1$. Accurate band profiles require that Coriolis energies be included for the upper state.

We chose benzene as the test molecule because its optical absorption spectrum is well characterized. We made measurements of a single band contour for benzene, shown in Figure 2. This spectrum was taken at a distance of 2.3 cm from the nozzle following a delay from the valve opening that provided the best ion intensity and cooling for this distance. The band shown is part of the lowest singlet-singlet transition ($S_1 \leftarrow S_0$) of benzene near 259 nm. This specific transition has the spectroscopic identification ${}^1B_{2u} \leftarrow {}^1A_{1g} 6^1_0$ ($l = \pm 1$). The band shown corresponds to many overlapping rotational lines. From the overall contour of these overlapping lines, we can determine an effective rotational temperature of the benzene molecules.

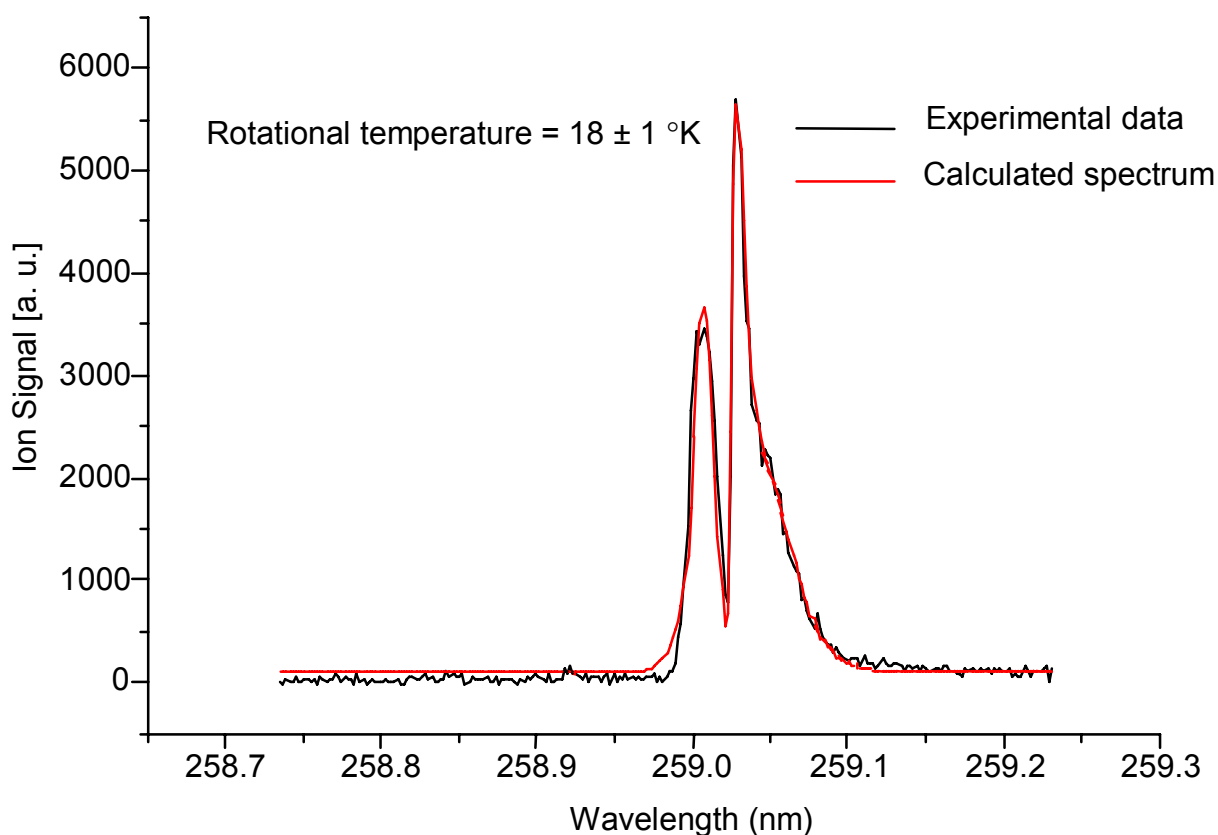


Figure 2. Comparison of the measured and calculated band profiles for a valve-to-laser separation of 2.3 cm for a $S_1 \leftarrow S_0$ transition in benzene.

To determine the temperature, we wrote a computer program to fit the simulated the form of the band contour as a function of temperature. This program used the most recent values for the spectroscopic parameters for the transition⁵ and the appropriate statistical weights⁶. The result of this fitting program gives the best estimate of the rotational temperature of the benzene molecules, which is 18 ± 1 °K for this measurement. The high quality of the calculated fit is

shown in Figure 2. This rotational temperature is very low, and indicates that our gas expansion is near optimum in terms of its cooling characteristics.

To complete this initial series of measurements, we determined the REMPI signal for the same band in benzene as a function of the valve-to-laser distance. These measurements provided two important pieces of information; the local gas density as a function of distance, and the degree of internal cooling as a function of distance. Figure 3 shows a plot of the local gas density, as determined by the integrated REMPI signal, as a function of the inverse square of the valve-to-laser separation. In this representation, the expected quadratic falloff in intensity with distance should result in a straight line. A second order polynomial produces an excellent least squares fit to our data with a correlation coefficient of 0.996. The minimum distance for which we could measure the REMPI signal was approximately 2.3 cm, while the maximum was approximately 7.4 cm.

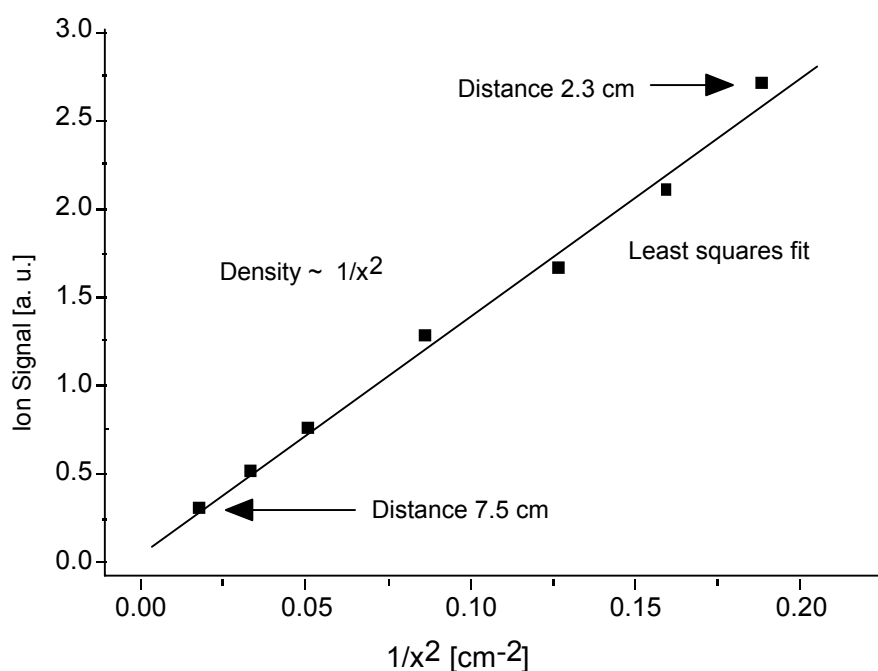


Figure 3. Variation of the jet-REMPI signal for benzene measured at 78 amu and a wavelength of 259.1 nm as a function of the laser-valve separation.

While this quadratic dependence of intensity with distance is to be expected, the dependence of the internal cooling with distance was not anticipated. Using our temperature fitting program, we determined that there was essentially no change in the rotational temperature of the benzene molecules as a function of the valve-to-laser distance. This surprising result implies that molecular cooling is complete within a very short distance from the exit of the jet nozzle. Based on this observation, the maximum REMPI signal intensity is only a function of the local gas density, which is easily estimated from the quadratic behavior exhibited in Figure 3.

At the smallest valve-to-laser separation of 2.3 cm, the measured and calculated band profiles were shown in Figure 2. Figure 4 shows the corresponding results for the largest valve-to-laser separation of 7.5 cm. The best fit rotational temperature for this data set was 18.5 ± 1 °K.

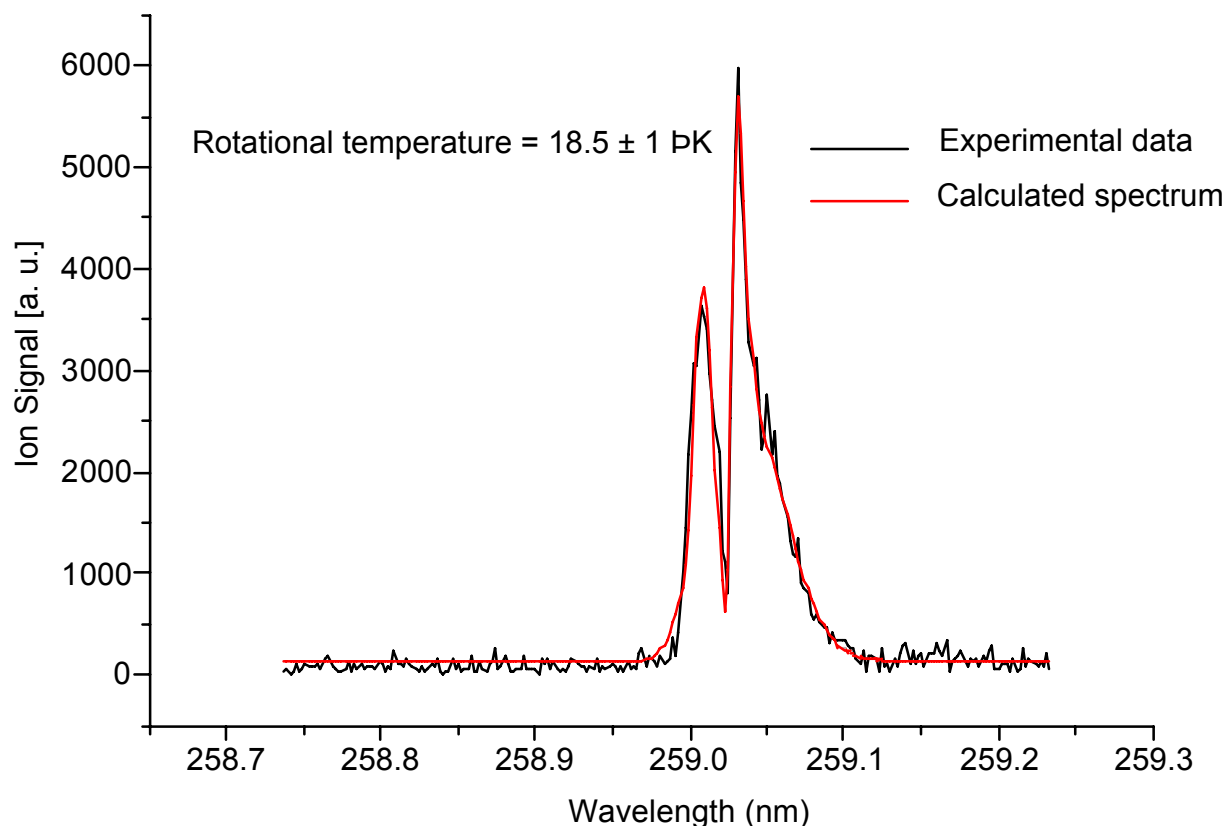


Figure 4. Comparison of the measured and calculated band profiles for a valve-to-laser separation of 7.5 cm for a $S_1 \leftarrow S_0$ transition in benzene.

The relative lack of a strong temperature dependence on the valve-to-laser separation is not unexpected. At a separation of 2.3 cm, the benzene molecules are most likely already in a collision-free regime, hence, no further reduction in temperature will occur. While the valve-to-laser separation does not influence the internal temperature of the beam, the $1/x^2$ drop in local density measured in Figure 3 confirms the importance of fixing the valve-to-laser separation at the smallest value possible consistent with the mechanical constraints of the ion extraction optics and the gas pumping.

The other key variable in optimizing the REMPI signal is the delay between the valve pulse and the ionization laser pulse. To investigate the dependence of the benzene REMPI signal on this parameter, we made a series of band profile measurements while varying the delay time. The results are shown in Figure 5. The solid line in Figure 5 shows the variation in the signal strength of the 78 amu benzene parent ions measured with a time delay of between 300 and 1100 μs . As expected, the ion signal initially rises as the delay time increase, reflecting the increase in gas density as the molecular beam forms and flows past the ionization region. As the delay time become longer than approximately 450 μs , the signal level begins to decrease as the bulk of the gas pulse has passed the laser beam.

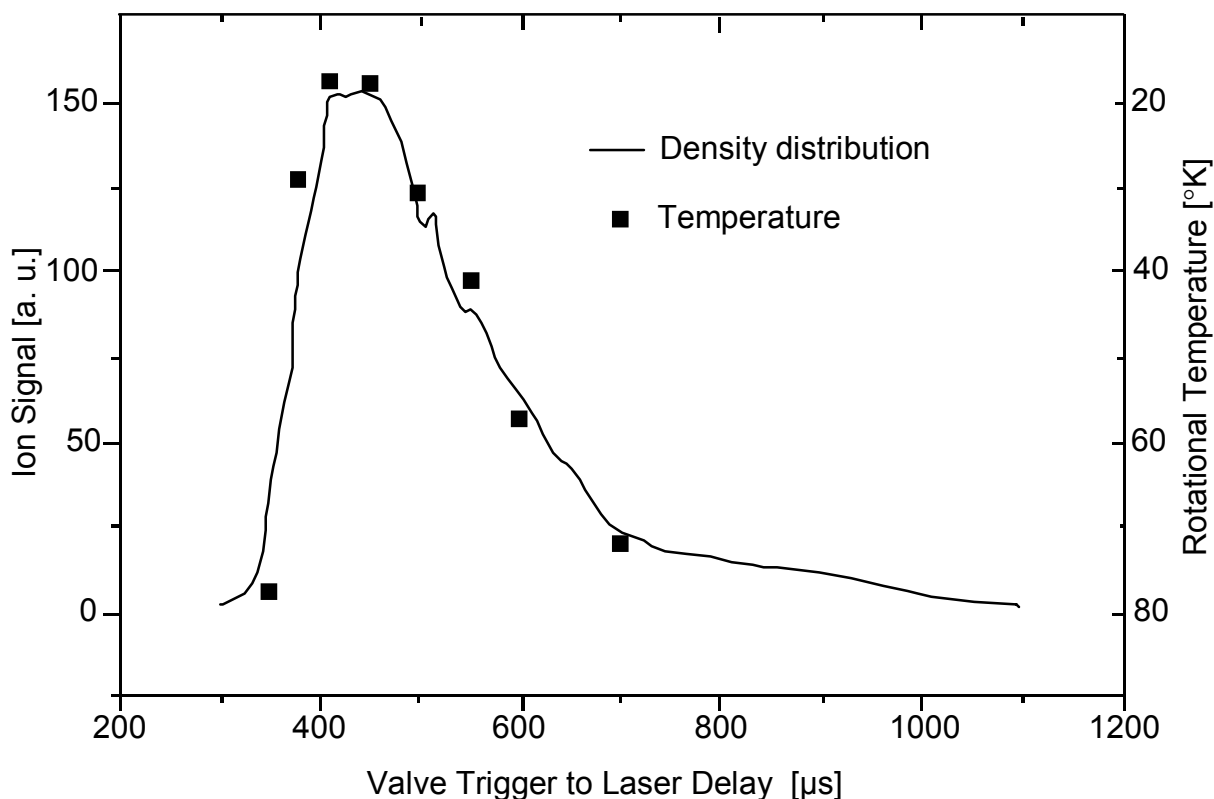


Figure 5. Variation of the jet-REMPI density distribution (signal level) for benzene measured at 78 amu and a wavelength of 259.1 nm as a function of the delay between the valve trigger and the laser pulse. The corresponding rotational temperature as determined by fitting the band profiles is also shown.

Also shown in Figure 5 are the fitted rotational temperatures measured at a number of time delays. Using only a simple vertical scaling of the two sets of data, we find that the rotational temperature exactly follows the gas density variation. This indicates that the peak density corresponds to the coolest neutral molecules. Presumably, this correspondence arises because the cooling mechanism depends on intermolecular collisions, which will be most probable when the local gas density is at a maximum. That these two dependencies occur at a common time delay greatly simplifies the optimization of the signal with respect to this parameter.

5. Applications

There are at least two different applications for a dioxin CEM in connection with waste incineration. The first would be in support of pollution prevention at the source. For this application, on-line monitoring of suitable precursor compounds would be needed to control dioxin and furan formation and release. The requirements for this application include an instrumental sensitivity in the ppt range, and a thorough knowledge of formation chemistry within the incinerator.

A second application of a dioxin CEM is for compliance monitoring. In this application, on-line monitoring of stack emissions is required to determine the toxic equivalence (TEQ) value. This measurement requires instrumental sensitivity in the ppq range, below the detection limits of any current CEM. Possible approaches to achieve this sensitivity include development

of fast preconcentration techniques and/or the use of indicator substances for the TEQ determination. Surrogate compounds might include chlorobenzenes or lowly chlorinated dioxin and furan congeners. The use of surrogates requires determination of the correlation between the TEQ and the levels of the indicator compounds. This correlation may be strongly dependent on the specifics of the incinerator, its operating conditions, and the feedstock.

6. Future Activities

We are continuing to investigate the spectroscopy of lowly chlorinated dioxins and furans which are of toxicological interest. Extension of the method to more highly chlorinated congeners is also being undertaken. A number of improvements are being made in the ion optics, and pulsed valve design that will significantly increase the instrumental sensitivity. Accurate calibration of the limits of detection will be determined using a metered dioxin delivery system.

Because there will likely be numerous other chlorinated and unchlorinated organic species present in the exhaust stream of a waste incinerator, we have also begun a measurement program to examine the REMPI excitation spectra of some of these compounds. Examples include cresols, xylenes, and phenols.

7. Acknowledgements

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