

DEVELOPMENT OF A JET-REMPI BASED CONTINUOUS EMISSIONS MONITOR FOR DIOXINS

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ABSTRACT

The need for a continuous emissions monitor (CEM) for the determination of dioxins and furans at realistic (parts per trillion or lower) concentrations in real time (minutes) is widely recognized in the waste management community. Such an instrument would enable rapid, and real-time experimentation on incinerators, so as to test and develop control strategies. It would also be extremely useful in laboratory kinetics experiments seeking to understand formation, interconversion, and destruction processes for dioxins and their precursors. Finally, it could be used for continuous compliance monitoring, or rapid, low-cost, facilities certification. The key issues for a dioxin CEM are; overall sensitivity, and selectivity among the many congeners found in real applications, and the ability to detect and distinguish these compounds in the presence of a very complex background. The U.S. EPA Office of Solid Waste (OSW), which regulates hazardous waste treatment processes, has identified continuous dioxin monitoring as a research priority. The OSW recognizes that CEMs offer continuous compliance assurance, compared with infrequent extractive sampling. Their policy provides the economic incentive for waste facilities to use CEMs by eliminating waste feed characterization, compliance testing, and operating parameter monitoring for pollutants when a facility uses CEMs.

Although 210 chemically different dioxins can be produced during combustion, it is currently believed that fewer than 20 are toxic enough to warrant monitoring. SRI has initiated a research program to develop a CEM that can be used to study the emission levels of these key dioxins, leading eventually to an improved understanding of the formation of these molecules and to improved means of monitoring and control. A database can be built using emissions from actual waste treatment processes to correlate operating conditions with dioxin formation. Such a database can be used to devise operating strategies to prevent formation of dioxins, and to identify surrogates or indicators that can be monitored more easily than the dioxins themselves, leading to less expensive, more widely implemented, compliance and control strategies.

Our approach for the real-time dioxin CEM combines a pulsed gas jet with resonance enhanced multi-photon ionization (REMPI) and time-of-flight mass spectrometry (TOFMS). We estimate that a minimum detectability of approximately 1 ng/m^3 can be realized for dichlorinated dioxins using commercial off the shelf technology with minimal development. Using the current one-color REMPI scheme, the sensitivity decreases with increasing chlorination, making detection of the more highly chlorinated dioxins problematic. REMPI will need significant enhancements to reach the sub- ng/m^3 detection limits required for a compliance CEM. Potential enhancements include, among others, the use of sample preconcentration, improved pulsed nozzle and ion optics designs, a two-color REMPI scheme, and higher repetition rate laser systems.

Based on previous research with REMPI, and our understanding of dioxin regulatory structure, our primary research thrusts are: (1) determination if tri-, tetra-, and higher chlorinated dioxins will require a 2-color REMPI scheme; and (2) measurement of detection limits for congeners as a function of chlorination, and improvement in the detection limits via system improvements and sampling methods. We are also working closely with other dioxin research groups to ensure that the dioxin mechanistic studies are integrated into our work to determine which congeners should be measured, and at what concentration in order to provide measurements for regulatory compliance and process control.

INTRODUCTION

This article describes our initial efforts to develop a laboratory instrument that can provide continuous monitoring of the emission levels of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) generated by incineration equipment. Once developed, this instrument will be used to systematically study the emission levels of key dioxins and furans that contribute to the toxic equivalency (TEQ). This information, combined with mechanistic modeling studies being undertaken elsewhere [3], will lead to the design specifications for a real-time, autonomous dioxin CEM that can be used for system control and, eventually compliance monitoring, at waste incinerators.

Experts in this area suggest that a dioxin CEM should be used first as a research tool in laboratories studying dioxin formation and control [1]. As such, the instrument must make rapid, accurate measurements of dioxins but at concentrations much higher than needed for a compliance CEM. This type of instrument will greatly accelerate our understanding of dioxin formation and the availability of prevention and control techniques. Researchers have a limited understanding of how combustion processes affect dioxin formation, largely due to their need to relate time-integrated sampling data with dynamic formation mechanisms and combustor conditions after an often multi-week analysis lag period. A real-time CEM will provide immediate feedback on how variations in combustion operating parameters affect dioxin formation and/or destruction, thus allowing more accurate correlations and much more comprehensive data analysis. An instrument capable of making these types of measurements would also be valuable as new waste treatment processes are evaluated and readied for permitting/public acceptance.

CEMs also provide data for stakeholder's assurance that the combustion processes are operating safely. Stakeholders such as public interest groups, permit writers, and local citizens groups, can play a major role in permitting waste treatment facilities. Real-time emissions data may accelerate their acceptance, saving time and money during the permitting process.

Why Measure Dioxins?

Current techniques to monitor emissions of PCDDs and PCDFs use sampling times in excess of hours, during which the analytes are collected on adsorbing materials followed by sample extraction and preparation for subsequent gas chromatography/mass spectrometry (GC/MS) analysis. These costly and time consuming methods have drawbacks in that compliance measurements are made only infrequently (perhaps once or twice per year). The consequences are regulatory strategies that rely on indirect process monitoring rather than direct monitoring and dioxin prevention strategies, often leading to over-designed air pollution control systems.

In light of these limitations, a continuous emission monitor (CEM) for PCDD and PCDF offers four benefits to users:

- Direct, rapid detection of PCDD and PCDF congeners, their indicators (compounds measured in lieu of PCDDs and PCDFs that indicate the parallel presence of PCDDs and PCDFs), or their precursors (compounds that have been shown to be chemical progenitors of PCDDs and PCDFs).
- Combustion system optimization through continuous, on-line monitoring and process control.
- A method to advance prevention of PCDD and PCDF formation rather than rely on flue gas cleaning controls.
- Assurance to stakeholders (permit writers, public, etc.) that the process is operating safely.

The U.S. EPA Office of Solid Waste (OSW, which regulates hazardous waste treatment processes) has identified continuous PCDD and PCDF monitoring as a research priority, because PCDDs and PCDFs can drive risk assessments [2]. The OSW recognizes that the continuous compliance assurance of CEMs is much preferred to infrequent, extractive sampling. Their policy provides the economic incentive for waste facilities to use CEMs by eliminating waste feed characterization, compliance testing, and operating parameter monitoring for pollutants when a facility uses CEMs. However, with no other PCDD/PCDF CEM technologies under development, this alternative mode of compliance will not be possible. A CEM for compliance purposes will likely require higher performance capabilities (especially for sensitivity) than if the CEM were used for research purposes or as a method of combustion optimization. Sensitivity for a dioxin CEM is a primary issue, requiring measurements at concentrations two to four orders of magnitude lower than ever achieved before.

As our understanding of PCDD and PCDF formation improves, it would be valuable to build a database using emissions from actual waste treatment processes to correlate operating conditions with PCDD and PCDF formation. Such a database could be used to devise operating strategies to prevent formation of PCDD and PCDF. This database could also be used to identify surrogates or indicators that can be monitored more easily and cheaper than the PCDD and PCDF themselves, leading to less expensive, more widely implemented compliance and control strategies.

Which Dioxins to Measure?

Two critical issues must be addressed before a dioxin CEM can be successfully developed:

- What would you measure? There are 210 PCDD and PCDF congeners, with widely varying levels of toxicity, and most are not considered toxicologically significant.
- To what minimum concentration (sensitivity) would you need to measure it? The draft MACT rule proposes an emission limit of 0.2 ng/m^3 2,3,7,8 TCDD toxic equivalence (TEQ).

Toxic equivalence factors (TEF) are defined as a set of weighting factors expressing toxicity of each compound relative to the toxicity of 2,3,7,8 TCDD. TEFs vary from 1.0 to 0.001 for 17 different polychlorinated compounds. Each of these 17 congeners contain chlorine atoms

in the 2,3,7, and 8 positions, with additional chlorine substitutions at one or more other positions. The total TEQ is calculated by multiplying the concentration of each PCDD and PCDF by its corresponding factor TEF. Several weighting schemes are available. NATO has proposed a scheme assigning factors to the 17 most toxic polychlorinated dioxins and furans, and assigning no factor to the remaining 193 congeners. Estimates of performance needs for a dioxin CEM for regulatory compliance can be made based on the existing knowledge of TEF and TEQ. Considering only the 17 compounds in the total TEQ, the sensitivity required for a dioxin CEM would need to be a factor of ten less than the emission limit for each of the 17 congeners (i.e., divide the TEQ by 17 x 10). Hence, the required minimum detection limit is equivalent to the emission limit divided by 170, or 0.001 ng/m³ or better, for each congener in the TEQ.

In the best case, if you could argue that the probability of formation of each congener was about equal, then the minimum detection limits could be higher for compounds with a lower TEQ factor. In other words, given a minimum detection limit of 0.001 ng/m³ for 2,3,7,8 TCDD, the other 16 PCDD/F congeners having TEFs between 0.5 to 0.001 would have corresponding minimum detection limits of 0.002 ng/m³ to 1.0 ng/m³.

As shown in the estimates above, the detection limits must be very low to directly measure all 17 congeners in the TEQ. A proposed alternative is to monitor precursors or surrogates, identified using a dioxin CEM in research laboratories to collect real-time data. This real-time data would be invaluable to develop mechanistic understandings, leading to surrogates or precursors that can be measured at much higher concentrations. It has been suggested [3] that the study of lightly chlorinated (mono-, di-, or tri-) dioxins would be acceptable, because these congeners are easier to measure than the more highly chlorinated dioxins. The molecules are very similar to those in the TEQ and would likely lead to correlations describing the formation of TEQ congeners.

Laboratory experiments for studying dioxin formation and control usually operate at total dioxin concentrations around 100 to 1000 ng/m³. Depending on how many of the 210 total congeners are present, detection limits around 5 ng/m³ for each congener of interest would be more than enough. The first step in developing a dioxin CEM suitable for compliance monitoring is, therefore, to develop a laboratory instrument capable of speciating dioxin congeners, precursors, or surrogates, and measuring their concentrations in real-time with a sensitivity in the low ng/m³ range. By combining this information with sophisticated combustion models, it will be possible to determine the specific target chemicals that must be measured by a dioxin CEM, and the levels to which they must be measured. Only after this information is available can a dioxin CEM suitable for compliance use be developed.

Why REMPI?

In recent years, many significant improvements have been made in the detection of dioxins resulting from various combustion processes. Several research groups, including DLR (Deutsche Forschungsanstalt für Luft und Raumfahrt) in Stuttgart, Germany [4,5], The Technical University of Munich, Germany [6,7], and Sandia National Laboratories [8] in Livermore, CA, have demonstrated stack monitoring instruments or components of instruments based on REMPI. To date, however, none of these research programs has achieved the sensitivity required for either compliance monitoring or a research CEM to study formation and control of dioxins. The possibility of a commercial dioxin CEM becoming available within the next five to ten years is

questionable without a development program focused on achieving specific performance goals for a dioxin CEM.

Of particular interest and promise for the real-time characterization of dioxins is the combination of a pulsed gas jet with REMPI and time-of-flight mass spectrometry (TOFMS). Using this approach, the group at DLR Stuttgart has measured non-, mono-, di-, tri-, and tetra-chlorinated dioxins at the EPA National Risk Management Laboratory (NRML) facility during tests from July to October, 1996 [9]. The measured minimum detectability for dichlorinated dioxins was approximately 20 ng/m^3 . We estimate that this detection limit can be improved quickly by at least one order of magnitude to about 1 ng/m^3 for dichlorinated dioxins. Using the current one-color REMPI scheme, the sensitivity decreases with increasing chlorination, making detection of the more highly chlorinated dioxins problematic.

REMPI will need significant enhancements to reach the sub- ng/m^3 detection limits required for a compliance or system control CEM. Potential enhancements include, among others, the use of sample preconcentration, improved pulsed nozzle and ion optics designs, a two-color REMPI scheme, and higher repetition rate laser systems. As a research dioxin CEM, however, the current REMPI-TOFMS scheme may need to be improved by only one or two orders of magnitude.

Based on previous research with REMPI, and our understanding of dioxin regulatory structure, four major areas must be studied to develop a REMPI-based dioxin CEM:

- Determination if tri-, tetra-, penta- and higher chlorinated dioxins will require a two-color REMPI scheme.
- Measurement of detection limits for congeners as a function of chlorination, and improvement in the detection limits via system improvements and sample preconcentration.
- Development of a particle desorber/separator to liberate dioxins adsorbed on particles for detection by the REMPI analyzer.
- Development of a mechanistic understanding of dioxin formation and control to determine which congeners should be measured, and at what concentration, to provide measurements for regulatory compliance and process control.

Our ongoing research program covers the first three areas and provides the tools necessary to address the fourth. We are also working closely with dioxin research groups to ensure that the dioxin mechanistic studies are integrated into the instrument development work.

Description of the Technology

Resonance enhanced multiphoton ionization is a highly sensitive, highly species-selective, gas-phase analysis technique that has been applied to numerous problems in molecular spectroscopy and combustion research. SRI has been using multiphoton-mass spectrometric techniques to study spectroscopy and trace-level detection for more than a decade. We pioneered the application of these methods to the detection of aromatic and chlorinated organic compounds [10,11]. 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. The enhanced population of the ground state gives an increase in sensitivity, while the narrower line

widths give rise to very sharp REMPI transitions. One or two lasers are used to ionize the cooled gas molecules by absorption of two or more photons, one which is resonant with an electronic transition in the target molecule.

Ions produced by REMPI are often detected using a TOF-MS that takes advantage of the pulsed nature and well-defined temporal character of laser ionization. Many REMPI experiments performed at SRI and elsewhere have successfully used the TOF-MS approach. The simultaneous detection by mass and wavelength yields high chemical selectivity. Typical sensitivities of conventional REMPI TOF-MS systems that do not use sample molecule cooling are in the mg/m^3 range and higher, which is greatly insufficient either for a laboratory system or for regulatory monitoring of chlorinated aromatics in a waste treatment process such as an incinerator.

A major improvement in sensitivity without loss in selectivity is achieved using a pulsed gas valve that produces a supersonic expansion. In a supersonic jet, the temperature drop occurs only in a relatively narrow zone downstream of the nozzle but upstream of the Mach disk, or shock front. Laser ionization in the region of the Mach disk provides the highest sensitivity due to the local maximum in gas density. This phenomenon was exploited by SRI in a 1987 study of the four-photon dissociation and ionization of H_2 in a pulsed jet [12].

Figure 1 is a diagram of the laboratory prototype REMPI TOF-MS instrument that we have assembled for this effort. The TOF-MS was originally developed for NASA to provide real-time chemical characterization of tropospheric aerosol particles. The pulsed gas inlet and all optical components shown in Figure 1 were added to the existing TOF-MS instrument for this project.

Data obtained using such a combination of REMPI and the pulsed gas injection method by the research group from DLR, Stuttgart, Germany, indicate that the detection limit for the dichlorodibenzodioxin [4] is approximately 20 ng/m^3 . For the trichlorodibenzodioxin and tetrachlorodibenzodioxin, the detection limits have not been measured, but they have been estimated as 150 ng/m^3 and $1 \text{ } \mu\text{g/m}^3$, respectively. Each chlorine atom added to the molecule, seems to make detection harder using the current, one-color, two-photon, ionization method. For this reason, we plan to investigate two-color, two-photon, ionization methods that will improve the detectability of the tri- and tetra- chlorodibenzodioxins.

Sampling and Preconcentration

An approach to increasing the sensitivity of the REMPI method is through the use of a sample preconcentrator. By preconcentrating the emissions from a stack for a relatively short period of time, e.g. 5 minutes, followed by the rapid introduction of the sampled material into the instrument, a significant improvement in the detection limit can be achieved. Many preconcentration schemes are available, typically involving the use of a sorbent material. Stack emissions are passed through the sorbent where the organic vapors are preferentially collected. High sample flow rates can be used to sample large volumes of stack emissions in a short time period. Following the sampling period, the preconcentrator is pneumatically isolated from the stack flow and carefully heated to thermally desorb the sampled material without significantly

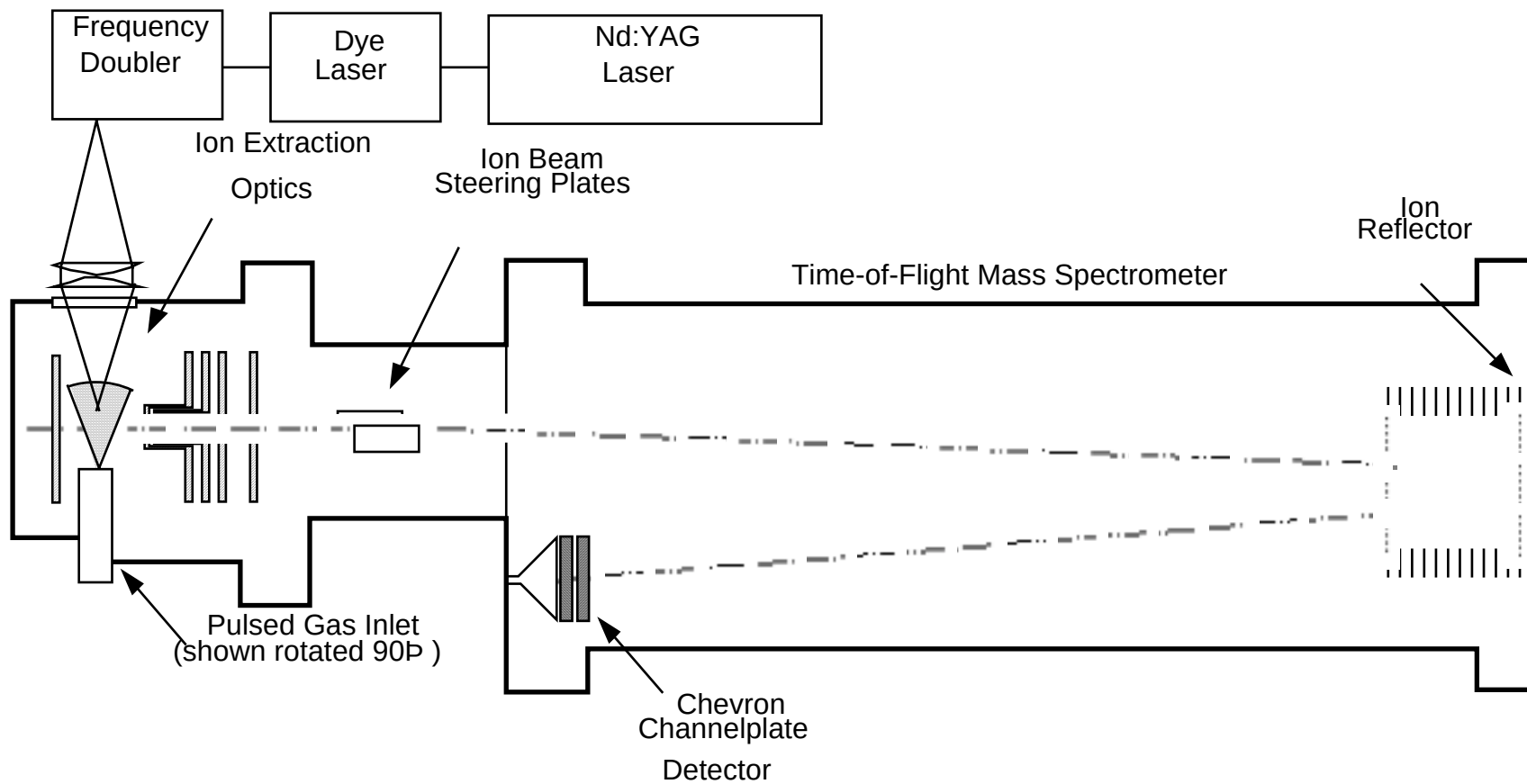


Figure 1. SRI REMPI-based dioxin continuous emission monitor.

altering sample composition. A stream of clean carrier gas is used to sweep the desorbed vapors into the instrument for analysis.

Sorbent-based preconcentrators can yield sensitivity improvements of two to three orders of magnitude, depending on the sorbent material, the target compounds, the preconcentration time, and the sample flow rate.

A related strategy for increasing the detection sensitivity is the desorption of PCDDs and PCDFs that are adsorbed onto fly ash particles. By combining a particle desorption stage with a preconcentrator, dioxins can be efficiently transferred from the fly ash to a temperature-controlled sorbent bed where they will be collected over a period of time, thus increasing the amount of material available for subsequent detection. Dioxin desorption from fly ash has not been addressed in laboratory demonstrations of dioxin detection, despite its critical importance.

Pulsed Gas Inlet

Pulsed valve-type gas inlets have been used in a wide variety of mass spectrometric and laser spectroscopy schemes for more than 30 years. SRI first combined the use of a pulsed gas inlet with REMPI as early as 1987 in studies of the ionization of H₂ [12] and F₂ [13]. Since those early studies, we have continued to use and develop pulsed gas valve sources for a range of spectroscopic and detection applications. 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 (translational and rotational) temperatures leading to enhanced spectroscopic resolution. The major shortcomings of pulsed valves are their reduced throughput and duty cycle as compared with a continuous gas inlet, and their increased mechanical complexity. When combined with a pulsed ionization laser, however, the reduced duty cycle of a pulsed valve as compared with a continuous gas inlet is no longer a factor.

Many pulsed valve designs have been developed based on simple electromechanical solenoid mechanisms, piezoelectric actuators, magnetic repulsion devices, and modified fuel injectors. Pulsed durations range from a few microseconds to hundreds of microseconds, while repetition rates reach up to 80 Hz, or higher, depending on the pulse duration and valve design. A critical parameter for the pulsed valve in a dioxin CEM is the temperature at which it can operate. Because of the low volatility of the heavier dioxin congeners, the inlet sampling lines and pulsed valve must be continuously heated above 250° C. Although many of the earlier valve designs could not be heated much above 100° C due to the temperature limits of the sealing materials, designs [14,15] now exist for pulsed valves that can operate routinely at temperatures above 400° C.

The details of the pulsed valve design that we will use in our laboratory prototype dioxin instrument have not been established, and will depend on many design factors, including the type of valve actuator mechanism chosen and the desired operating temperature, pressure, flow rate, pulse duration, and duty cycle. Some of these factors are influenced by the choice of laser system, and by the particular chemical species to be studied. The design of the pulsed valve, on the other hand, influences the design of the ion optics used to extract and inject ions into the TOF spectrometer. Because of the tradeoff between maximum gas density (and hence ion signal) and maximum internal cooling of the dioxin molecules (and hence optimum spectroscopic selectivity), the most desirable laser ionization region has a very limited spatial extent. This

limited ionization region requires that the ion optics be carefully designed to efficiently extract the nascent ions while accounting for any distortions in the electric fields associated with the nearby pulsed valve.

REMPI

Resonance Enhanced Multi-Photon Ionization is an efficient and highly selective ionization method and as such, REMPI is well suited to combination with mass spectroscopy. Figure 2 is a diagram of REMPI. A molecule is raised from the ground state S_0 to the first excited state S_1 by one photon, and subsequently ionized by a second photon. Although the two-

Figure 2. Diagram of the REMPI process.

photon REMPI, as shown in Figure 2, is the most common, both the excitation and ionization steps each can be performed with two or more photons. Selectivity is provided primarily by the resonance of the first photon with the excited state S_1 . High power lasers allow good ionization efficiency, particularly when only two photons are required.

Many vibronic levels in the excited state can be used for REMPI. Choice of the vibronic level is influenced by the transition strength, Franck-Condon factor, ground state population, excited state lifetime, the distance to the ionization potential, and fragmentation that may occur in association with the ionization. For large molecules, cooling of the sample (for example through a supersonic expansion) is very important for improving selectivity and sensitivity. The cooling reduces the transition linewidths 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. Cooling increases the population in the lower rotational levels of the ground state while reducing the population in higher levels. The reduced number of initial levels reduces the complexity of the REMPI spectrum, thus improving selectivity through reduced interferences, while the increased population in the remaining levels improves sensitivity.

Further considerations for REMPI include the use of one or two wavelengths (colors) for ionization. One color is simpler to implement. However, in certain cases, using a second color is preferable or essential. For example, if the excited state lies higher than half the ionization

energy, the second photon will not have enough energy to ionize the molecule. For TCDD, the energy of the S_1 level is approximately half the ionization potential [16]. Thus, single-color REMPI may or may not be effective for TCDD. Two-color REMPI using a second, higher energy laser beam may be a more efficient technique for TCDD detection. The second beam need not require an additional laser. For example, when using a Nd:YAG pumped tunable laser, the second color could be the fourth harmonic light produced using nonlinear crystals.

Reaching the first excited state of chlorinated dioxins requires a laser wavelength in the range of 250 to 350 nm. We can produce this wavelength currently with frequency-doubled dye lasers pumped by either a Nd:YAG laser or an excimer laser. However, rapid changes of wavelength are not readily obtained using dye lasers. A more practical system for field measurements would be based on a tunable solid state laser such as Ti:Sapphire or an optical parametric oscillator (OPO). The harmonics of the Ti:Sapphire laser have gaps and cannot continuously cover the wavelength range from 250 to 350 nm. Thus, for the research proposed here, the OPO is the more appropriate and practical system for field measurements. A more practical prototype or even commercial system would likely use compact and efficient sources such as direct diode-laser-pumped Cr:LiSAF.

Mass Spectrometry

A primary consideration in the choice of a mass spectrometric analysis technique is the method of ion formation. For a dioxin CEM, the ionization scheme of choice is based on a pulsed laser, multiphoton approach. Although several mass spectrometric methods can be used with REMPI, TOF has been the method of choice. TOF is an inherently pulsed technique that matches well with the pulsed laser ionization, and it offers the advantage of generating a complete mass spectrum from each laser pulse.

The mass spectrometric requirements of a dioxin CEM instrument are modest: an upper mass range of 400, with unit mass resolution. Typical TOF mass analyzers can meet these requirements using a simple, linear flight path when combined with a short duration, pulsed laser, ionization source. Low signal levels that may result from the use of a very narrow ion formation pulse can be compensated for by signal averaging using multiple scans. To optimize this mode of operation, a high repetition rate ionization laser would be desirable. Achieving high mass resolution with a TOF instrument is straightforward using a pulsed laser for ionization because of the narrow spatial, temporal, and energy spread of the nascent ions.

An increasingly common TOF approach is the use of an ion mirror, or reflectron-type TOF. The properties of this device are well known, and a number of computer codes have been developed to assist with their design. Resolving powers ($m/\Delta m$) of more than 1000 can be readily obtained using a reflectron with a pulsed laser ionization source. Although mass resolving powers in excess of 1000 are not necessary to separate adjacent mass peaks even at the highest mass-to-charge ratios expected in a dioxin CEM, high resolution gives rise to signals with much narrower, and hence much higher, peaks. The increased peak amplitude leads directly to an increased signal-to-noise ratio.

A significant improvement in resolution and signal level can also be obtained through the careful design of the ion extraction optics. As a result of the pulsed laser ionization scheme, ion formation is constrained to occur over a very limited spatial region. Normally, a well-constrained ion formation region can be readily coupled with high efficiency to a TOF mass analyzer using simple ion extraction optics. In the proposed instrument, however, an additional

spatial constraint is imposed by the use of a pulsed gas inlet. Pulsed valves can produce a supersonic molecular beam as the gas expands and cools adiabatically. An optimum location downstream from the orifice exists where the internal molecular temperature will have reached a minimum while the local gas density remains high. Ionization at this location will yield the optimum optical spectroscopic selectivity with maximum ion signal level. Because this optimum ionization region will typically be only a few centimeters from the exit orifice, the ion optics must be carefully designed to include the influence of the pulsed valve on the extraction fields. Fortunately, sophisticated ion optical design codes, such as SIMION 6.0 are available to simplify this task.

RESULTS AND CURRENT STATUS

The development effort described above has only recently been initiated. To date, we have begun the assembly of the instrument starting with a conventional reflectron time of flight mass spectrometer. As an initial configuration, we are using a commercially available ion source [17] suitable for laser ionization MS, as well as an off-the-shelf, pulsed gas valve [18]. These components, along with a Nd:YAG-pumped dye laser will be used to establish a baseline instrumental capability from which many of the improvements described above will be implemented.

Because this program is in an early stage of development, no results are yet available to report. At the conference, we will present a progress report on the first seven months of development of the SRI instrument. We anticipate at that time having a working instrument with laboratory test data on several dioxins, albeit at higher-than-ambient concentration levels, together with initial projections of achievable sensitivity.

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