

**DLR Jet-REMPI as a Continuous Emissions Monitor:
Measurements of Chlorinated Dibenzodioxins**

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ABSTRACT

REMPI (Resonance Enhanced Multi-Photon Ionization) mass spectrometer systems are known for high selectivity, good on-line capabilities, and sensitivities to about 1 ppbv. Use of REMPI as a continuous emissions monitor (CEM) for chlorinated aromatic compounds in flue gases, such as polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF), will require much greater sensitivities. As an improvement to traditional REMPI, the DLR Jet-REMPI™ system has measured compounds such as chlorophenols and chlorobenzenes at pptv levels. These compounds have been shown to be precursors for PCDD and PCDF formation. Direct measurements of PCDD and PCDF will probably require even greater (ppqv) sensitivities. In addition, due to spectroscopic effects, REMPI sensitivities decrease with increasing chlorination of PCDDs and PCDFs, making use of REMPI as a CEM extremely challenging.

In this paper we present new data showing DLR Jet-REMPI measurements of tri- and tetra-chlorinated dibenzodioxins. We believe these are the first data of their kind, and note their significance in demonstrating that single-color (1 wavelength) Jet-REMPI can measure PCDD congeners at this level of chlorination. The current instrument sensitivity is in the low (60) pptv region, and further work will focus on improving sensitivity by at least 1 or 2 orders of magnitude. In particular, sample cooling in the expansion nozzle appears to be insufficient to resolve the more highly chlorinated molecules, likely due to

the heating required in the transfer line to avoid sample condensation. Redesign of the inlet valve assembly will be aimed at correcting this problem.

INTRODUCTION

Current techniques to monitor emissions of polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) 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 /1/. These costly and time demanding methods have drawbacks in that compliance measurements are made only infrequently (perhaps once or twice per year). The consequences are over-designed air pollution control systems and regulatory strategies that rely on indirect process monitoring rather than direct monitoring and dioxin prevention strategies.

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

1. 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);
2. combustion system optimization through continuous, on-line monitoring and process control;
3. a method to advance prevention of PCDD and PCDF formation rather than rely on flue gas cleaning controls; and
4. assurance to stakeholders (permit writers, the public, etc.) that the process is operating safely.

For compliance monitoring, CEMs will limit the uncertainty and cost of compliance based on infrequent, extractive sampling efforts. Development and use of 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. These CEM sensitivity needs will be lessened with the development of a short duration sampling, concentration, and analysis method.

A more likely application for such a monitor is first as a research tool in laboratories studying PCDD and PCDF formation and control. As such, the instrument would need to make rapid, accurate measurements of PCDDs and PCDFs but could do this at concentrations much higher than needed for a compliance CEM. Instrument sensitivities around pptv levels are probably adequate so long as congeners (up to octa-substituted) can be identified. This type of instrument would greatly accelerate our understanding of PCDD and PCDF formation and the availability of prevention and control techniques. Researchers have limited understanding of how combustion processes affect PCDD and PCDF 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 would provide immediate feedback on how variations in combustion operating parameters affect PCDD and PCDF formation and/or destruction, thus allowing more accurate correlations and much more comprehensive data analysis.

Finally, 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 PCDDs and PCDFs. This database could also be used to identify surrogates or indicators that can be monitored more easily and cheaply than the PCDDs and PCDFs themselves, leading to less expensive, more widely implemented compliance and control strategies.

CEMs also provide data important for stakeholders' 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.

The REMPI Technique

REMPI (Resonance Enhanced Multi-Photon Ionization) mass spectrometer systems are a highly sensitive, highly species-selective, gas-phase analysis technology /2/. REMPI appears promising to measure PCDDs and PCDFs at extremely low concentrations, distinguishing between very similar species and congeners, as required for a PCDD and PCDF CEM. One or two lasers are used to ionize the cooled gas molecules in a small volume by absorption of two or more photons, one of which is resonant with an electronic transition in the target molecule. Aromatic molecules have conveniently accessible vibrational levels of the first excited singlet states (S_1 level), at energies just exceeding half of the molecular ionization energy. Thus, single color, resonant two-photon ionization schemes (1+1 REMPI) can be used for these species. An advantage of this approach is that "soft ionization" at relatively low laser intensities is feasible. Typically an unfocused laser beam is used, and there is minimal fragmentation of the parent ion. In contrast, the three-photon (2+1 REMPI) approach used for molecules such as alkyl chlorides requires the use of higher laser intensities which may result in significant ion fragmentation and, thus, may compromise selectivity for some molecules. When coupled with a Time-of-Flight Mass Spectrometer (TOF-MS), this two-dimensional detection scheme by mass and wavelength provides high species selectivity.

REMPI Test Requirements

Measurement of PCDDs and PCDFs with REMPI methods requires consideration of several issues:

- ▶ Only PCDD and PCDF homologues which have at least all of the 2,3,7, and 8 positions occupied by chlorine atoms are important in determining toxicity. There are 17 of these congeners from the tetrachlorinated dibenzodioxin (TCDD) to the octachlorodibenzodioxin (OCDD). The TCDD congener 2,3,7,8-TCDD and the pentachlorodibenzodioxin (PeCDD) congener 1,2,3,7,8-PeCDD are especially important because of their large contribution to toxic equivalency, or TEQ (equivalence factors of 1 and 0.5, respectively). In a CEM that measures congener-specific PCDDs and PCDFs, yet is limited to measurement of a subset of these 17 congeners comprising the TEQ value, it is not yet clear which specific congeners should be measured, and to what level of sensitivity, to be of value as a process-specific CEM.
- ▶ The non-rigidity of PCDD and PCDF molecules, in particular the "butterfly" vibration around the axis through the oxygen atom(s), may demand very intense cooling to increase the electronic ground state population.
- ▶ The work of Zimmermann et al. /3/ indicates that chlorination of aromatic compounds increases the ionization energy and shifts the S_1 state towards lower levels. As a consequence, for the lower chlorinated dioxins, the S_1 state is more than half the ionization gap. However, for higher chlorinated dioxins, the S_1 state will be less than half the ionization gap, which could require a two-color (2 wavelength) REMPI system to excite. Previous research /4/ indicates that the transition of the S_1 state from greater to less than half the ionization energy may occur near the tetrachlorinated congeners. This is important because the TCDD isomers contain the most toxic congener, 2,3,7,8-TCDD, and are therefore significant toward TEQ determination. Therefore, the potential ability of the relatively inexpensive one-color (1+1) REMPI method, described in this work, to excite the TCDD to over half of the ionization gap would drastically simplify detection of this important congener.

- ▶ Increased chlorination of the parent dioxin (or furan) molecule results in a decrease in the lifetime of the first excited state (increased intersystem crossing), leading to reduced REMPI sensitivities or precluding the single wavelength method altogether.
- ▶ Highly chlorinated PCDDs and PCDFs have extremely low vapor pressure. Since REMPI is a gas-phase measurement technique, all sample lines, valves, and pumps must be heated to species-specific temperatures to prevent condensation of the target molecules.

This leads to three key questions:

- ▶ Can TCDD isomers be measured with one-color (1+1) REMPI?
- ▶ Does REMPI show promise for measuring PCDDs and PCDFs, indicators, or precursors with sufficient sensitivity and species selectivity to be useful as a CEM?
- ▶ What are the performance requirements for a PCDD and PCDF, indicator, or precursor CEM?

This paper addresses the first two questions by presenting data from the DLR Jet-REMPI system measuring PCDD isomers with two to four chlorines. The third question is much broader and requires a combination of research in mechanistic studies and a prototype PCDD and PCDF CEM to collect data for identifying surrogates or indicators that can be more easily measured.

EXPERIMENTAL SYSTEM

Jet-REMPI Principle and Apparatus

REMPI is a highly sensitive, highly species-selective gas-phase analysis technique (see e.g., /2/). To achieve good wavelength resolution, the gas sample has to be cooled by expansion through a nozzle. Adiabatic expansion results in low sample temperatures which increase the electronic ground state population. The enhanced population of the ground state gives an increase in sensitivity and very sharp REMPI transitions.

A major improvement in REMPI sensitivity without loss in selectivity was achieved with DLR's Jet-REMPI. In a supersonic jet, the temperature drop occurs only in a relatively narrow zone downstream of the nozzle (i. e., the zone where the beam still forms a jet). If ionization is carried out farther downstream (i. e., in the molecular regime), as in conventional REMPI setups, then the sensitivity drops due to a decrease in beam density. Conversely, when ionizing directly in the transition zone between the jet regime and the molecular regime, the highest sensitivities in conjunction with the lowest temperatures are obtained.

One or two lasers (one in our case) are used to ionize the cooled gas molecules in a small volume by absorption of two or more (two in our case) photons, one of which is resonant with an electronic transition (mostly S1 state) in the target molecule. The laser beam is brought in orthogonal to both the vertical molecular beam axis and the horizontal axis of the mass spectrometer. Tunable REMPI pulses between 275 and 320 nm are generated by a frequency-doubled Nd:YAG (neodymium: yttrium, aluminum, garnet) pumped laser (model Infinity 40-100TM made by Coherent Inc., Santa Clara, CA), system [model Scanmate OPPO™ (optical parametric power oscillator) made by Lambda Physik, Goettingen, Germany].

A linear Reflectron-Time-of-Flight Mass Spectrometer (TOF-MS) (made by Stefan Kaesdorf, Munich, Germany) analyzes the ions by mass. This two-dimensional detection scheme by mass and wavelength provides high species selectivity. Figure 1 shows the arrangement of the DLR Jet REMPI.

The potential for REMPI as a CEM for combustion emissions has been discussed in the literature /5,6/ although the determined detection limits around 1 ppb were not sufficient for practical, target molecule applications. A major improvement in sensitivity without loss in selectivity was achieved with Jet-REMPI. In a supersonic jet the temperature drop occurs only in a relatively narrow zone downstream of the nozzle (i. e., the zone where the beam still forms a jet). If ionization is carried out farther downstream (i. e., in the molecular regime), as in conventional REMPI setups, then the sensitivity drops due to a decrease in beam density. Conversely, when ionizing in the transition zone, between the jet regime and the molecular regime, the highest sensitivities are obtained in conjunction with the lowest temperatures. This simple and effective configuration cannot be implemented with conventional laser ionization sources, so special ion extraction optics were designed.

Sensitivity has been further improved by increasing the ionization volume (without loss in resolution due to focusing techniques) and by minimizing collisions of charged particles with the walls. To implement these improvements a skimmer nozzle (to reduce the pressure in the ion source) is no longer necessary; a pulsed sample valve (General Valve Corporation, Fairfield, NJ) is used instead to jet the samples into the ionization chamber. This valve delivers a 250 ms sample pulse at a repetition rate of 30 Hz.

These improvements have been shown to increase REMPI sensitivity substantially; e.g., by a factor of 200 for dichlorotoluene and by a factor of 1000 for naphthalene. Further sensitivity improvements are possible if desired (for instance by simply increasing the laser repetition rate). For more details see /7-10/.

The prototype Jet-REMPI analyzer was built at DLR Stuttgart. DLR holds a European patent on several features of the system /11/, and a Japanese patent and U.S. patent are pending. The first field test of this prototype was conducted on a small pilot scale incinerator in Karlsruhe, Germany. No PCDDs and PCDFs were measured and, unfortunately, no reference methods were available to compare with Jet-REMPI measurements. However, data showing well-resolved time profiles of particular products of incomplete combustion (PICs) showed an unreliable correlation between PIC formation and carbon monoxide (CO) levels. One disadvantage of this test was the abundance of particulate matter in the ionization zone, which led to a strong background signal. It is essential to prevent particles from entering the ion source by using a sampling system equipped with suitable filters.

Feeder System

To test the ability of Jet-REMPI to measure dioxin species, a temperature-sensitive permeation vial system /12, 13/ (described more fully in /14/) was developed to deliver gaseous species to the Jet-REMPI system. The permeation vial was housed in a glass spiral mounted in the oven of a Hewlett Packard model 5890 gas chromatograph (GC) which acted as a constant temperature ($\pm 1\text{ C}^\circ$) bath. Nitrogen was used to carry the volatilized test compound from the permeation vial to the inlet of the Jet-REMPI analytical system. The mass volatilized was determined by mass loss of the permeation vial and, coupled with a mass flow controller, allowed calculation of concentrations.

EXPERIMENTAL RESULTS

Unchlorinated Dibenzodioxin (UCDD)

Generally, REMPI sensitivities decrease with chlorination by a factor of approximately 6 per substituted chlorine atom /10/. This is due to enhanced intersystem crossing; i.e., a reduction of the lifetime of the excited state (S1). Although the measurement of UCDD is not difficult with regard to sensitivity, it plays an important role in testing Jet-REMPI for the detection of PCDDs and PCDFs in general. All of these compounds possess a so-called butterfly vibration around the symmetry line through

the oxygen (O) atoms. The force constant for this bending vibration is very low, which results in very narrow spacing between the energy levels. If the molecules are insufficiently cooled, the closely adjacent, vibrationally excited states will be populated in addition to the ground state. This leads to more complicated or even clogged spectra. Such an effect may be expected in particular in the case of Jet-REMPI with its characteristic short distance between the nozzle and skimmer.

Figure 2 shows a well-resolved spectrum for UCDD with line widths (full width, half maximum, FWHM) of typically less than 0.1 nm and clearly separated lines. Spectra are shown for the ^{12}C - and ^{13}C -containing parent ions. The cooling achieved with DLR Jet REMPI is obviously sufficient to avoid spectral clogging caused by the high population of excited states. The different peaks in the wavelength-dependent spectra represent the excitation into different vibrational energy levels of the excited electronic state.

The wavelength shift in Figure 2 of the ion signals containing ^{13}C towards higher energies is expected for the vibrations of the heavier isotope. This discrimination between ^{12}C and ^{13}C isotopes is an indication of our high selectivity. In GC/MS, ^{13}C congeners can be separated by mass, whereas the retention times are virtually identical for the ^{12}C and the ^{13}C compounds. By contrast, with Jet REMPI one can use both the mass and the ionization wavelength to discriminate between isomers.

Figure 3 shows the UCDD mass spectrum at a resonance wavelength of 295.82 nm with contributions due to the forementioned parent ions. No fragmentation is observed and this is typical for the soft ionization achieved with our low photon densities.

2,7-dichlorodibenzodioxin (2,7-DCDD)

The wavelength spectrum of 2,7-DCDD is shown in Figure 4. There are many more transitions than for UCDD, but each of them is well-resolved. According to the literature /15, 16/ the greater complexity in the 2,7-DCDD spectrum is due to the fewer degrees of symmetry in this molecule in comparison with UCDD. Again the Jet-REMPI mass spectrum exhibits no fragmentation. Therefore, only the parent signals are shown as an inset in Figure 4.

Figure 5 shows a series of measurements at different concentrations used to estimate the minimum detectability for 2,7-DCDD. Dioxin concentrations were varied by altering the temperature of the dioxin feeder. The concentration at each temperature was determined by pumping the dioxin flow over a trap for several hours and then using gravimetric analysis. These data, when extrapolated to $S/N = 3$, yield a detection limit of 30 ng/dscm at a pulse energy of 0.3 mJ. Actually, we could show that increasing the pulse energy to 1 mJ is possible without fragmentation. In this case we would get a detection limit of 9 ng/dscm which translates into 75 ppt by weight or 60 ppt by volume for DCDD. This is the first on-line detection limit reported for a DCDD isomer. It is very favorable and surprisingly close to what we recently found for o-chlorobenzene /10/.

These experiments showed that efforts must also be taken to ensure that the inlet valve can be sufficiently heated to prevent condensation of dioxins. Such heating influences the beam cooling mechanism and requires careful optimization of the inlet system design.

1,7,8-trichlorodibenzodioxin (1,7,8-TrCDD)

The wavelength spectrum for 1,7,8-TrCDD is much more complicated than that for 2,7-DCDD, as shown in Figure 6. In addition the prototype instrument may not be providing sufficient cooling (to be discussed later). The mass spectrum is again fragment free. However, there are more parent peaks due to the larger number of possibilities in the $^{35}\text{Cl}/^{37}\text{Cl}$ and $^{12}\text{C}/^{13}\text{C}$ distribution as shown in the inset of Figure 6.

Tetrachlorodibenzodioxins (TCDD)

Two problems must be addressed, which may turn out to be limiting factors for reliable measurement of tetra- and higher chlorinated dioxins. From the vapor-pressure data for these species /17, 18/ it is obvious that the sampling line and the inlet valve must be heated very carefully to avoid condensation. As the degree of chlorination increases, it becomes more important to ensure that all parts are well heated. This heat requirement will not only increase the initial sample temperature, but it will also decrease the cooling effect of the jet.

The other important aspect concerns the change in the relative positions of the energy levels upon chlorination, as reported in the literature /3/. In the case of PCDDs and PCDFs, the ionization potential rises while the energy level of the S1 state (which is resonantly excited by the first photon absorbed) decreases. This may jeopardize the applicability of the simple (1+1) single color REMPI scheme.

Figures 7 and 8 show the REMPI spectra of 1,3,7,9-TCDD and 2,3,7,8-TCDD, respectively. These spectra are the first REMPI spectra of TCDDs. Although they show sharp lines, the two spectra are very complicated and there is considerable overlap of the spectra for the two isomers. We regard these spectra as preliminary and it is yet not clear whether we ionized the molecules by excitation of populated rotational and vibrational levels of the electronic groundstate via the vibrationless S1 state or the band origin, the S0 electronic groundstate. From Figures 7 and 8 it would appear possible that a simple single-color REMPI scheme can be used for the detection of TCDD.

The REMPI mass spectrum for 1,3,7,9-TCDD (see Figure 9) is again fragment free. This advantage is fully appreciated by comparison with an electron impact mass spectrum of the congener.

DISCUSSION

We suspect that the complexity of the TrCDD and TCDD wavelength spectra shown in Figures 6 through 8 is at least partly a result of insufficient cooling. The 0.5 mm diameter gated inlet valve has been routinely heated to 100°C, and has appeared to produce adequate jet cooling for a series of rigid organic molecules. /7-10/. However, for these dibenzodioxin tests, to avoid condensation of TrCDD and TCDD, we heated the sample lines, including the inlet valve, to 225°C. This higher initial temperature results in the final temperature rising approximately quadratically. Not only does the cooling process start from a higher initial temperature, but the cooling effect itself is reduced because of the increased mean free path resulting in fewer collisions in the expansion zone. Whereas a higher final temperature might be acceptable for rigid molecules, in the case of dioxins, one has to assume that due to the outer ring flexing about the central oxygens (so-called "butterfly vibrations"), the molecules may, to a significant extent, remain within these vibrational excited states. Insufficient molecular cooling results in a finite population remaining within the excited vibrational energy levels in the electronic ground state. This results in a crowded wavelength-dependent REMPI spectrum and a reduction of sensitivity, because the excitation takes place from many different groundstate energy levels. The question of cooling and final temperature will be checked in subsequent experiments by redesigning the inlet system.

These effects, however, do not necessarily influence whether TCDD can be ionized with a single-color (1+1) REMPI. If the ground state S1 is less than half the ionization gap (as discussed in /4/), one could still try to achieve ionization with a (1+1) single-color system via a vibrationally excited S1 state. This ionization would be unaffected by the sample temperature. Since we were able to measure ion signals from TCDDs with the present arrangement, one can expect that sensitivity will improve only when the sample is more sufficiently cooled. We conclude that monitoring of TCDD is possible with a (1+1) single-color REMPI.

A remaining question is how promising is REMPI as a CEM to measure PCDD and PCDF

congeners, their indicators, or their precursors in combustion flue gas. Sensitivity and species selectivity are both important parts to this question. REMPI certainly has adequate species selectivity, and data presented in this paper show that levels of chlorination up to TCDD can be measured using the simple one-color (1+1) Jet-REMPI approach. Sensitivity is affected by the conflicting requirements to heat the molecules in the sample line to avoid condensation and cooling them in the expansion nozzle to facilitate spectral resolution. These requirements begin to conflict at around TCDD and larger homologues. However, there are several ways around this conflict.

First, the availability of real-time PCDD data may allow the establishment of correlations between measured concentrations of lower-chlorinated dioxins and TEQ. This would allow establishment of TEQ values using measurements of the more REMPI-accessible PCDD homologues. Second, other molecules, such as PCDFs, when coupled with dioxin measurements, may provide strengthened correlations with TEQ. PCDFs have a significantly higher vapor pressure than dioxins (0.43 Pa for 2,3,7,8-TCDD at 150°C and about 6 Pa for 2,3,7,8-TCDF at the same temperature) /17, 18/. Consequently, less heating of the sample lines is required for PCDFs. In addition, due to the relatively rigid carbon-carbon (C-C) bond, PCDFs are less susceptible to the effect of insufficient cooling. Moreover, it is known (see e.g., /19/) that PCDFs are present in incinerator emissions generally more abundantly than PCDDs. This may lead to situations when 50% of the total TEQ consists of a single congener, 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PeCDF). The main disadvantage of PCDFs seems to be that polychlorinated congeners require a two color (1+1) REMPI /4/, making a CEM somewhat more complicated. However, we will continue to investigate the use of PCDFs as a surrogate for TEQ-related CEM measurements.

CONCLUSIONS

Application of Jet-REMPI in this work has determined the first detection limit for a DCDD species and obtained the first known spectra for TrCDD and TCDD species. The detection limit (30 ng/dscm) is too high to make use of Jet-REMPI as a compliance CEM but efforts underway reasonably anticipate 2 orders of magnitude improvement in sensitivity. With less stringent sensitivity limits, Jet-REMPI will be applicable to combustion process control and research studies on PCDD and PCDF formation. As research efforts improve our understanding of PCDD and PCDF formation, it is likely that correlations between indicators or precursors, including the lower chlorinated species measured in this work, will enable us to predict TEQ values from these more REMPI-measurable species. In this manner, a PCDD/PCDF compliance CEM can be developed that will derive continuous measurements from correlative, rather than direct, measurements.

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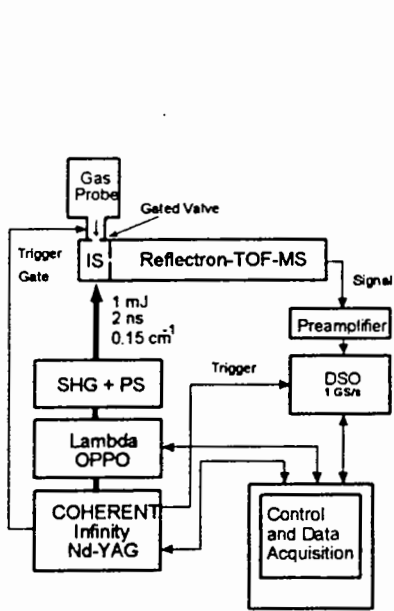


Fig. 1 Setup of the DLR mobile Jet REMPI apparatus. IS = ion source, SHG = second harmonic generation, PS=prism separator, OPPO = optical parametric power oscillator, DSO = digital signal oscilloscope, and GS/s = DSO sampling rate in gigasamples per second.

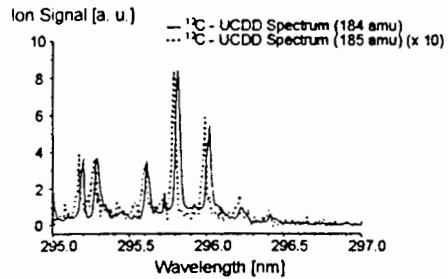


Fig. 2 Wavelength dependent Jet-REMPI spectra for UCDD. Masses 184 and 185 are monitored.

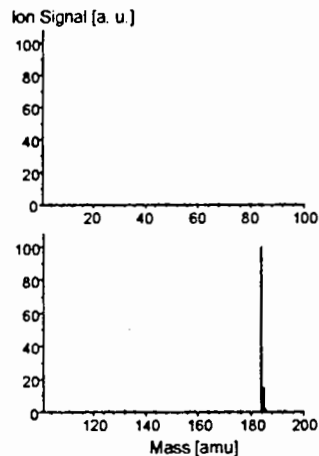


Fig. 3 Mass spectrum for UCDD at a wavelength of 295.82 nm (split for better resolution).

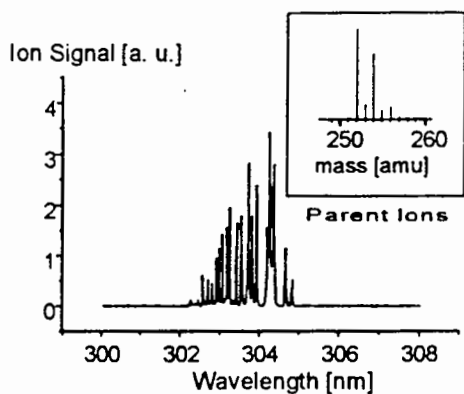


Fig 4 Wavelength dependent REMPI spectrum for 2,7-DCDD. Mass 252 is monitored (Inset: Parent ions at a wavelength of 305.6 nm).

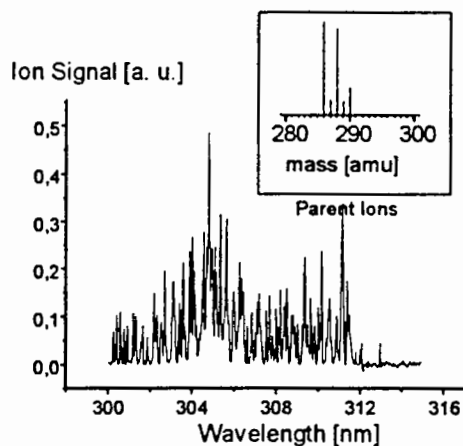


Fig. 6 Wavelength dependent REMPI spectrum for 1,7,8-TrCDD. Mass 286 is monitored (Inset: Parent ions at a wavelength of 304.9 nm).

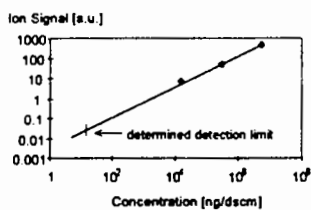


Fig. 5 Jet-REMPI measurements of 2,7-DCDD, showing minimum detectability of approximately 30 ng/dscm.

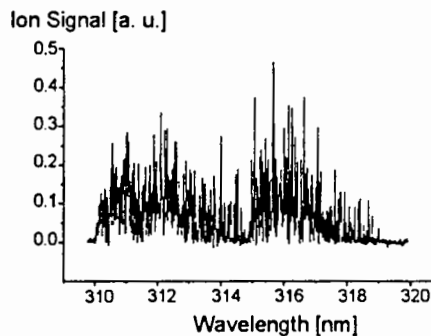


Fig. 7 Wavelength dependent REMPI spectrum for 1,3,7,9-TCDD. Mass 320 is monitored.

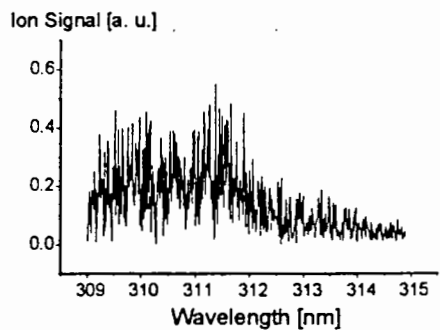


Fig. 8 Wavelength dependent REMPI spectrum for 2,3,7,8-TCDD. Mass 320 is monitored.

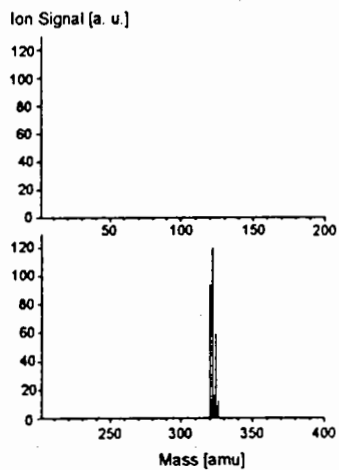


Fig. 9 1,3,7,9-TCDD mass spectrum at a wavelength of 315.65 nm (split for better resolution).

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16. ABSTRACT The paper presents new data showing Deutsche Forschungsanstalt fur Luft und Raumfahrt (DLR) Jet-Resonance Enhanced Multi-Photon Ionization (REMPI) mea- surements of tri- and tetra-chlorinated dibenzodioxins. It is believed that these are the first data of their kind. Their significance in demonstrating that single-color (1- wavelength) Jet-REMPI can measure polychlorinated dibenzodioxin (PCDD) congen- ers at this level of chlorination is noted. The current instrument sensitivity is in the low (60) parts per trillion by volume (pptv) region, and further work will focus on improving sensitivity by at least 1 or 2 orders of magnitude. In particular, sample cooling in the expansion nozzle appears to be insufficient to resolve the more highly chlorinated molecules, likely due to the heating required in the transfer line to avoid sample condensation. Redesign of the inlet valve assembly will be aimed at correc- ting this problem. REMPI mass spectrometer systems are known for high selec- tivity, good on-line capabilities, and sensitivities to about 1 part per billion by vol- ume (ppbv). Use of REMPI as a continuous emissions monitor (CEM) for chlorinated aromatic compounds in flue gases, such as PCDDs and polychlorinated dibenzofurans (PCDFs), will require much greater sensitivities. DLR's Jet-REMPI system has measured compounds at parts per trillion by volume (pptv).			
17. KEY WORDS AND DOCUMENT ANALYSIS			
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