Jet-REMPI coupled to the Municipal Waste Incinerator Stuttgart One further Step towards Continuous PIC Monitoring

Reinhold Thanner, Matthias Nomayo, Horst-Henning Grotheer, and Roland Stützle*

DLR-Institut für Verbrennungstechnik, Pfaffenwaldring 38, 70569 Stuttgart, Germany
Fax +49 711 6862 578, Phone 378, E-mail HH.Grotheer @dlr.de
* Neckarwerke Stuttgart AG, 70167 Stuttgart

Introduction: On continuous monitoring of PICs in incineration

Development of innovative technologies to monitor hazardous compounds and, more generally, environmental conditions is one of the goals of the EMPACT program (Environmental Monitoring for Public Access & Community Tracking) issued by the US EPA /1/. Not the least purpose of seeking for time-relevant information is to improve acceptance and credibility in the public. Obviously, with regard to incineration it would be mostly desirable to achieve this time-resolved information on toxic emissions such as chlorinated dioxins and furans (PCDD/Fs). For concentration reasons, such measurements are nearly impossible on a real-time basis.

There is, however, another important issue of continuous monitoring of thermal plants and this is to correlate operation conditions of the hot section (furnace and boiler) to the toxic freight of the raw gas. This approach gains further importance as high temperature dioxin formation mechanisms seem to have been underestimated in the past /2,3/. The idea is to identify conditions that are prone to enhanced formation of hazardous compounds. By avoiding these conditions the average raw gas quality should thus improve, ultimately allowing to save costs for the cleaning system. As emission peaks occur under transient conditions such an approach requires time-resolved measurements.

Jet-REMPI has been shown to potentially meet these requirements, at least in the laboratory /4,5/. The key question of this paper is therefore whether these promising features are preserved when the method is applied to real incinerator flue gasses.

Experimental: a) Jet-REMPI and its demonstration with the pilot incinerator TAMARA

REMPI (Resonance enhanced Multiphoton Ionization) mass spectrometry (see e.g. /6/) is a potentially two-dimensional analytic method. In addition to separating ions by their mass, the ionization process itself may be operated selectively with regard to the wavelength of the ionizing laser. This requires that the sample molecules are adequately cooled so that they are distributed closely to the ground state leading to resonance transitions into the first excited singlet state within only a narrow range of wavelengths. This is the reason for the potentially high selectivity of the method which makes clean-up procedures quit often obsolete. Experimentally, selectivity is observed through narrow lines in the ionization spectrum (number of sample ions vs. wavelength). Jet-REMPI in turn is a variant to enhance sensitivity by a proper choice of the location of the ionization regime within the beam. It has been fully described in the literature (see /4,5,7/ and references therein) including this series /8/.

It could be shown /4,8/ that for typical PICs spectra of the same quality of resolution were obtained when comparing laboratory results to those measured at the pilot scale incinerator TAMARA of Research Center Karlsruhe which is tantamount to an unperturbed selectivity. These TAMARA experiments made it also possible to determine the sensitivity of Jet-REMPI as shown in Fig. 1.

Here, Monochlorobenzene and 1,2 Dichlorobenzene were measured simultaneously and to this end the ionization laser was shifted periodically between the two preselected resonance wavelengths. Due to the stable operation conditions of TAMARA the absolute concentration of the Dichlorobenzenes could be determined by conventional methods using sample collection. (See /5/ for details). These data led to a detection limit as low as 0.5 ppt for 1,2 Dichlorobenzene when two compounds are monitored simultaneously in which case the laser is tuned for only 15% of the total time to this single component. This detection limit is unprecedented by any other REMPI method. Using a single component mode, the detection limit would be even lower. Consequently, the next question was whether these promising features are also found in conjunction with a full-scale incinerator such as the one in Stuttgart operated by Neckarwerke.

Fig. 1: Sensitivity of Jet-REMPI

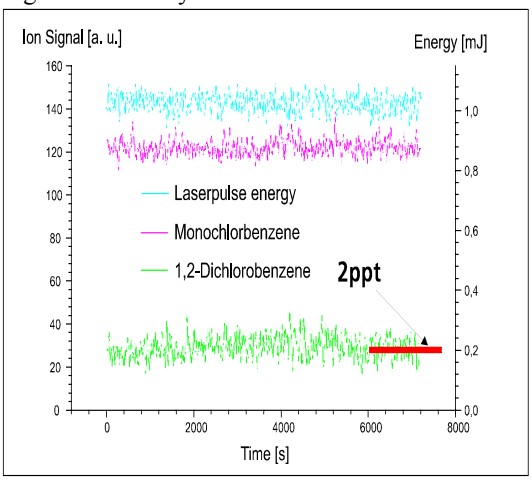
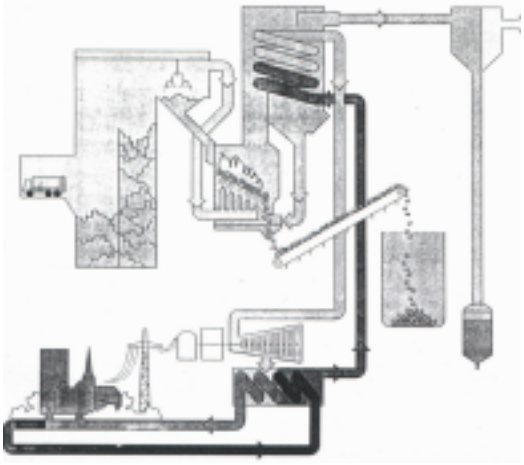


Fig. 2: Municipal waste incinerator of Stuttgart



Experimental: b) The (full-scale) municipal waste incinerator of Stuttgart

The set-up of the Stuttgart MWI has been described in the literature /9/. Its hot portion is displayed in Fig.2 The main components of the plant include three combustion lines followed by a modern air pollution control (APC) system not shown in Fig. 2. The APC removes hazardous compounds very efficiently so that emissions are always significantly below the limits required by the German regulation, the so-called 17. BImSchV. The typical throughput of waste is 20 tons per hour for each combustion line. For the continuous Jet-REMPI test, the line with the most modern furnace built in 1994 was chosen. Its roller grate is fired in co-flow mode. Optimum combustion conditions with regard to high temperatures, long residence times in the grate chamber as well as the afterburning chamber along with good gas phase mixing make it possible that a nearly complete burnout is achieved. Consequently, only minimum amounts of organic material are found in the flue gas.

For the REMPI measurements flue gas samples were drawn via a stainless steel lance positioned right downstream of the baghouse (top-right corner in Fig.2). At this position gas temperatures are approximately 200 °C.

Results and Discussion

The results may be subdivided into 3 sections:

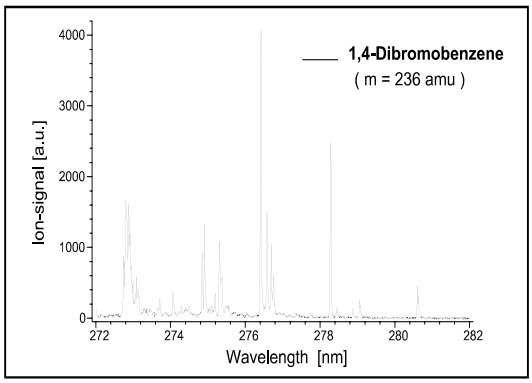
i) Stability of our set-up under technical conditions

All-solid state lasers are currently the best available means to cover a broad wavelength range (just by a mouse-click) and with high spectral resolution /10/. Consequently, they are a good choice when one wishes to monitor a large variety of compounds in a rapid sequence. It is, however, also known /10/ that these devices are sensitive to temperature fluctuations because of the length of the light paths involved and because the refractive indices of the crystals that are temperature dependent. Consequently, we encapsuled our commercial system (Coherent Scan Mate, pumped by an Infinity Nd:YAG laser) by an extra temperature-controlled envelope. Yet even this precaution was insufficient to cope with the large temperature fluctuations prevailing in the vicinity of an incinerator. As a consequence, we were never able to fully optimize the laser adjustment so that only a greatly reduced UV power of some 10 µJ per pulse was available and even then stability was poor.

ii) Spectral resolution for 1,4 Dibromobenzene

Due to the lack of UV power it was impossible to measure spectra of halogenated Benzenes in the dust-free raw gas (right after the bag house) with sufficient sensitivity. Therefore a sample was injected right at the sampling port, i.e. upstream of our sampling line (7 m, 10 mm i.d., Teflon, heated to 200 °C). In this case 1,4 Dibromobenzene was chosen on account of its importance when electronic waste is burnt. The spectrum is shown in Fig. 3. It is seen that the lines are perfectly resolved so that one can expect full selectivity even in this case of incinerator raw gas. For the long wavelength portion of this spectrum an earlier measurement exists /11/ which is in good agreement to our data.

Fig. 3: Spectrum of 1,4-Dibromobenzene



iii) Fluctuation of PICs in the raw gas

Due to their high abundance unchlorinated Benzene and Toluene could be measured in the raw gas even under the improper condition of our instrument. The interesting result is shown in Fig. 4, a and b being measured at subsequent days. Common feature of both curves is a pronounced fluctuation with a time period between 10 and 15 min which is not caused by our sampling line nor by

any other part of our instrument. Conversely, the decline of the measured maxima is presumably a result of our laser instability.

Fig. 4a: Fluctuation of Benzene

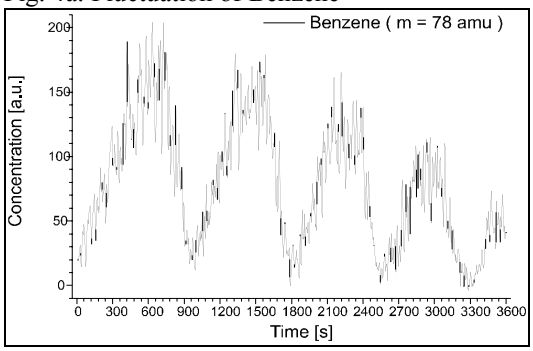
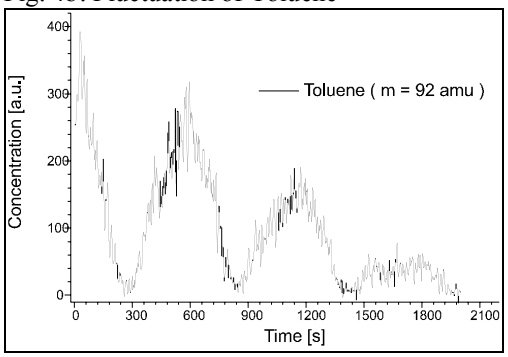


Fig. 4b: Fluctuation of Toluene



Although the cause of these fluctuations is not yet understood two messages may be deduced immediately.

- There is an optimization potential even for a carefully operated plant such as the Stuttgart MWI,
- The detected fluctuations would escape conventional analytical methods. Therefore, there is a need for time-resolved systems.

Summary

Although the reported measurements were greatly hampered by a partial failure of the used laser system, the results are promising and show that for a proper characterization of thermal plants time-resolved methods should be used. Improvements of our apparatus have now been installed and a detailed MWI measurement program will be caried out in due future.

Acknowledgements

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