

Time-resolved PIC Measurement in Incinerator Flue Gas Coupling of DLR-Jet REMPI to the Pilot Scale Incinerator TAMARA

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Abstract

Process optimization requires sensitive and selective on-line monitors for species concentrations. This applies in particular if feeds of varying compositions are involved. Current REMPI (= resonance enhanced multiphoton ionization) mass spectrometers would be suitable instruments in terms of selectivity and on-line capability, their sensitivities, however, are generally too low. By contrast, the DLR-Jet REMPI geometry provides a major sensitivity improvement. An extended test series shows that this is achieved without paying a price in terms of selectivity. In order to find out whether these favorable features apply also under practical conditions, the Jet REMPI machine was coupled to the pilot scale incinerator TAMARA. The paper provides first results of this test series. Steps needed to make Jet REMPI suitable for industrial use are given.

Introduction: Monitors for process optimization and control

Current pollutant abatement technologies mostly involve air pollutants cleaning devices (APCs) that are simply added to the primary process in order to trap or destroy pollutants formed there. Hence they are called end-of-the-pipe techniques. The complementary approach is given by head-end techniques aiming at the reduction of pollutant formation. This can be accomplished by optimizing the process through carefully tailoring its design and operation parameters.

The other problem quite often involved in incineration is that the composition of the feed is subject to rapid changes. This requires that such an optimization has to be based on time-resolved concentration measurements of relevant species in the process gas. This type of process control could not be carried out in the past due to lack of sufficiently sensitive monitors. Such a monitor has to meet basically three requirements.

On-line capability in order to cope with transient conditions. A typical time resolution should be in the order of 1 measurement per half minute. (Obviously, for compliance measurements much lower frequencies are acceptable.)

Selectivity, which means that a signal corresponding to a particular component should remain essentially unaffected by contributions from other components of this mixture. As the raw gas of thermal processes is generally highly complex selectivity is a very important feature. In addition, when monitoring incineration gases it should be possible to discriminate between isomers because toxicities of chlorinated dioxins and furans are extremely dependent on their respective constitutions. Selectivity is usually achieved by using two-dimensional analytical methods such as GC/MS, which is unfortunately not suitable for time-resolved measurements as it uses time as analytical parameter.

Sensitivity is probably the most crucial feature of monitors for process optimization as the relevant species are only found in traces. Target compounds relevant to dioxin abatement may be either

chlorobenzenes which are used as indicator substances /1/ or chlorophenols because of their roles as precursors to dioxin formation /2/. As discussed recently /3/ the concentrations of suitable dichloro or trichlorobenzenes lie in the 10 to 30 ppt (mol fraction) range. Comparable concentrations may be expected for relevant chlorophenols (see /3/). As a consequence, the detection limit of an on-line monitor should be in the low ppt range. Obviously, such detection limits would not allow to determine TEQs in the raw gas, let alone in the stack gas.

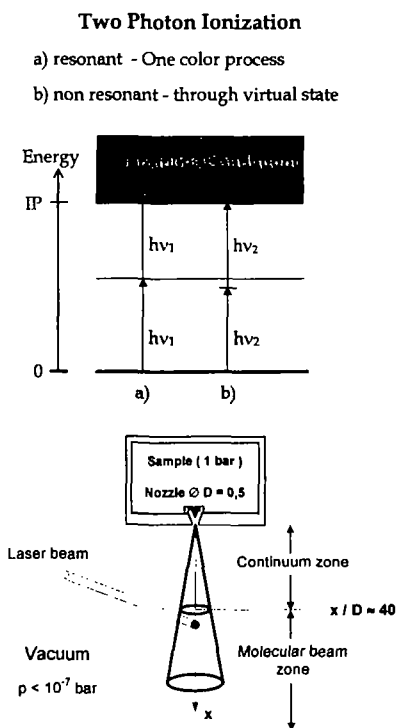
2. Experimental

2.1 REMPI mass spectrometry and the idea of Jet-REMPI

Mass spectrometry using REMPI is a fast two-dimensional analytical technique. In addition to the usual mass discrimination, the second dimension is provided by the ionization process itself. It consists in its simplest case of excitation of a sample molecule into a real electronic state (mostly S_1 state) through resonance absorption of a photon emitted by a suitably tuned laser, followed by subsequent ionization of the excited molecule through absorption of a photon of the same color, so-called 1+1 REMPI, see scheme (a) of Fig. 1. This process is distinguished by the lifetime of the excited state. By comparison, the lifetime of a virtual state as in scheme (b) is much shorter rendering this process insignificant compared to the resonant transition. The first REMPI mass spectrometers have been described nearly 20 years ago by two independent groups /4, 5/. A recent series of excellent reviews has been provided by Lubman /6/.

In order to get spectra with distinct and intense lines one has to cool the sample and this is usually done through adiabatic cooling in a free jet delivered by a nozzle (mostly a gated nozzle to reduce pump requirements). The novel feature of Jet REMPI is that it makes use of the fact that the desired temperature drop occurs only within the continuous regime of the expanding beam, the so-called jet (see /7, 8/ for details). Under typical nozzle conditions its extension is only about 15 to 25 mm downstream of the nozzle (see Fig. 1). The jet regime is followed by a transition zone (not shown in Fig. 1) and then the molecular regime, where due to lack of molecular collisions no further cooling occurs. Therefore, the region of maximum cooling and highest beam density is just behind the jet. Consequently, for maximum sensitivity, ionization should be carried out there, hence the name Jet REMPI.

Details of our earlier mobile Jet REMPI system have been described /9/. This machine was equipped with an all-solid state OPO. These systems have become available only recently. They are relatively compact and not very sensitive to vibrations. To switch from one preselected wavelength to another is now a matter of only seconds and can be carried out automatically by computer control. Another important feature is that now pulse energies between 1 and 2 mJ are available throughout the entire tuning range between 220 and 350 nm. An excellent beam profile is obtained and the spectral resolution is 0.15 cm^{-1} . In addition, we



equipped pump laser and OPO which temperature controlled envelopes.

2.2 TAMARA, pilot scale incinerator at Research Center Karlsruhe

As relevant incineration research cannot be performed in laboratory scale only, TAMARA was built up and started in 1987. "TAMARA" stands for "test facility for waste combustion, flue gas cleaning, residue treatment and water purification". It models a grate incinerator equipped with a fabric filter and a two-stage wet scrubbing system (see Fig. 2). As geometry of the combustion chamber a contra, center, and parallel flow configuration may be chosen by installing variable roof elements (Fig. 2). The walls are made of SiC.

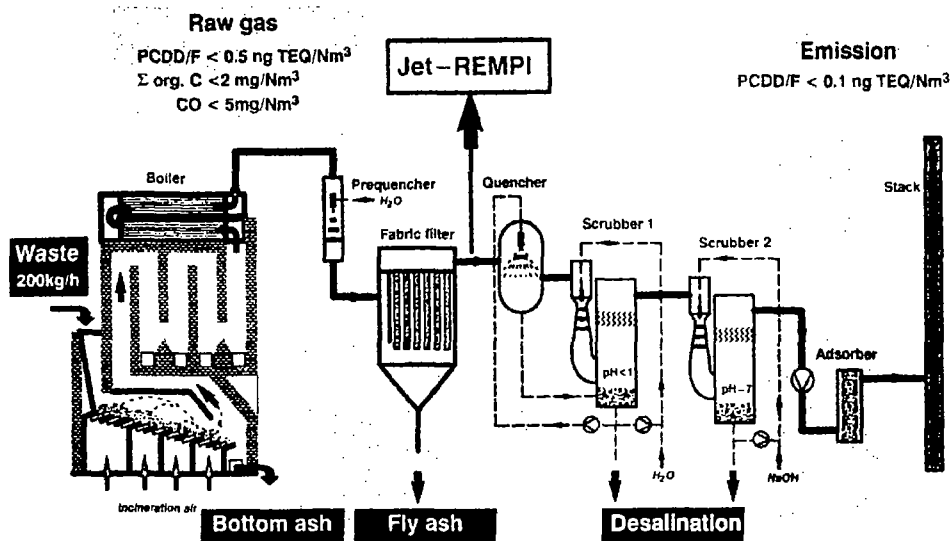


Fig. 2: TAMARA plant

The grate has a uniform inclination and comprises 4 zones that are controlled independently with respect to primary air supply, stroke and feed rate. Raw and cleaned flue gas can be recycled to all air ports. For the cooling of the flue gas a boiler is installed on top of the furnace consisting of 5 radiation sections followed by a water wall tube boiler. Downstream of the boiler is a prequencher enabling adjustment of the gas temperature to approx. 180 °C in order to prevent PCDD/F formation in the fabric filter. The latter consists of 36 PTFE tubes coated with GORTEX membranes. The operation temperature is 160-180 °C.

The basic fuel burnt in TAMARA comprises a homogenized and sieved (< 80 mm) residential waste, the heating value of which can be adjusted by addition of a pelletized refuse derived fuel (RDF). The typical feed composition is 75% of the pretreated waste fraction and 25% of the RDF. The composition of the fuel mix is well representing today's Central European municipal solid waste.

3. Results

Our first example, chlorobenzene, is a typical member of the PIC's found in incineration. The required wavelengths are approximately in the middle of our wavelength range. Fig. 3a shows a

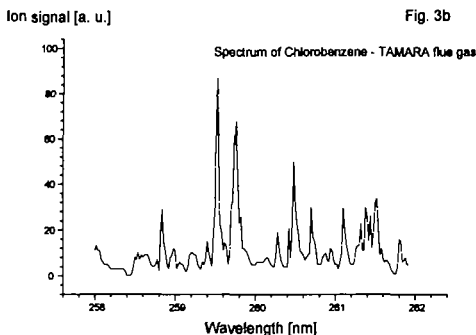
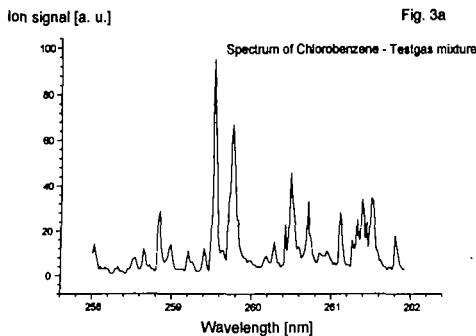


Fig. 3: Chlorobenzene spectra
 a) Laboratory conditions
 b) TAMARA flue gas

during a change of TAMARA operation conditions. Fig. 4 displays the REMPI benzene profile with some temporary superimposed spikes. The trace of the laser power plotted simultaneously (not in Fig. 4), shows that these spikes are not caused by a laser instability. Unfortunately, the benzene spikes cannot be compared to signals of the FID measurements or to the CO trace, both being shown in Fig. 4. The reason is that both measurement systems are at their limit, which is another

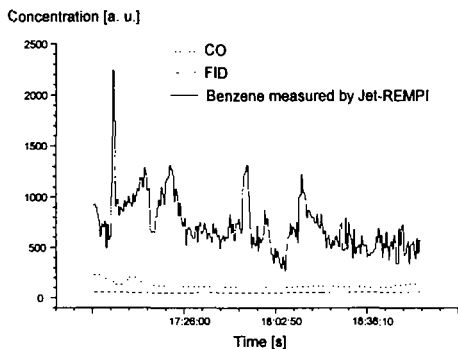


Fig. 4: Time-resolved monitoring

spectrum with highly resolved lines obtained in the laboratory using a test gas mixture. In our earlier papers (see e.g. /3, 9/) it has been pointed out that the Jet REMPI sensitivities obtained with test mixtures should be well sufficient for monitoring precursors to dioxin formation or indicator species, also in the real case. With Jet REMPI, however, this real case could never be tested in the past as we were only able in spring 1998 to couple our machine to an incinerator, in this case the pilot scale incinerator TAMARA of Research Center Karlsruhe in Germany. The first one of a series of very promising results is shown in Fig. 3b. Here, chlorobenzene in the flue gas of TAMARA is displayed, the sample being taken right after the fabric filter. The spectra of Fig. 3a and Fig. 3b are undistinguishable with regard to line resolution or background level. This demonstrates that our laboratory results can be extrapolated to the real case, so that Jet REMPI can indeed be used for monitoring relevant species under practical conditions.

The other example shows traces recorded during a change of TAMARA operation conditions. Fig. 4 displays the REMPI benzene profile with some temporary superimposed spikes. The trace of the laser power plotted simultaneously (not in Fig. 4), shows that these spikes are not caused by a laser instability. Unfortunately, the benzene spikes cannot be compared to signals of the FID measurements or to the CO trace, both being shown in Fig. 4. The reason is that both measurement systems are at their limit, which is another indication for the extraordinary sensitivity of Jet REMPI. Although the details of the Jet REMPI trace are not yet completely understood, they demonstrate that

- (i) time-resolved measurements are needed for a fuller understanding and
- (ii) measurement of only CO is insufficient for process control.

4. Discussion: Research needs for time-resolved monitoring under practical conditions

Although the results of Jet REMPI are quite promising a lot of R&D remains to be done towards application under industrial

conditions. Our present apparatus is still too bulky. A particularly weak device is the inlet valve which under practical conditions survives only a couple days of operation without maintenance.

Given the improved capability of time-resolved measurement, a systematic search should be carried out to assign certain compounds and their flue gas concentrations to operation conditions such as residence times or temperatures in the furnace.

Up to now, due to lack of sufficiently resistant probes, measurements have mostly been carried out downstream of the boiler. Hence, the next step would be to develop probes allowing measurements in the afterburner section. These data when supported by modelling could help to develop head-end strategies for pollutant minimization.

Concerning the Jet REMPI, potential improvements include a re-designed geometry of the ionization section and a short pulse (10 ms) valve instead of the conventional one. Advantages of such a valve are that at a given pump speed, a higher repetition rate is possible or alternatively a larger nozzle diameter in order to improve cooling. These means should account for a sensitivity enhancement by approximately a factor of 100.

However, even if this improvement comes true, toxic dioxin/furan congeners are not accessible as they require detection limits in the sub ppq range. Therefore, for the TEQ determination one has to develop pre-concentration techniques.

Finally, the issue of the laser light source needs to be addressed. In our simplified scheme (see fig. 1) it was assumed that the S_1 state is just above halfway between groundstate and ionization and that this state has a sufficient lifetime. Both assumptions do not apply in all cases. Upon chlorination the S_1 state may drop below halfway (see e.g. /11/) and in this case two-photon REMPI is only possible if a second color of fixed and shorter wavelength is used to enable the transition into ionization.

The problem of reduced lifetime (also pertinent to higher chlorinated species /11/) can be circumvented, at least in the laboratory, by using short pulse (ps) lasers /12/. At present, these devices seem to be too expensive and too complicated for use under industrial conditions.

Acknowledgements

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