

**Monitoring of Ultratrace Products of Incomplete Combustion  
during Incineration, with a Novel Mobile Jet-REMPI Device.**

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*Purpose of this work*

With regard to incineration sensitive and selective analytical methods may serve two purposes: (i) measurements of the profiles and of the temporal evolution of selected species support the understanding of the complex chemistry involved, (ii) on-line signals of relevant species such as dioxin precursors or indicator compounds enable a continuous process optimization so that less pollutants are formed and costly tail-end clean-up technologies can be at least partly saved.

The selectivity requirements for such an analytic tool are very high because of the complexity of the gas mixtures and because isomers should be discriminated. It is known that REMPI-mass spectrometry (= resonance enhanced multiphoton ionization) has the potential to meet these requirements<sup>1,2</sup>. Sensitivities, however, need to be also extremely high because precursors and indicators are formed in concentrations between ppb and ppt, dioxins and related compounds generally even in sub-ppt levels<sup>3</sup>. With current REMPI techniques detection limits in the order of ppb are found<sup>4</sup>, i.e. insufficient for the proposed task.

Therefore, this work pursues the following goals

- (i) to improve the REMPI sensitivity
- (ii) to implement the new technique on a car so that this device can be brought to an incinerator
- (iii) to perform laboratory tests prior to the practical use.

*Jet-REMPI in comparison to conventional REMPI*

The use of molecular beam/REMPI/TOF-MS (= time-of-flight mass spectrometry) for trace gas analysis and its application in particular to chlorocarbons is well known from the literature (for a review see<sup>5</sup>). In Fig. 1a, REMPI is illustrated using the most simple case of resonant two-photon ionization (R2PI) which quite often applies to aromatic molecules. Here the first excited singlet states,  $S_1$ , have conveniently accessible vibronic levels at energies just exceeding half of the molecular ionization energy. Thus, single color R2PI schemes (1+1 REMPI) can be used. An advantage of the R2PI 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. To achieve good wavelength resolution the sample has to be cooled down. To facilitate this the sample is introduced through a nozzle which is gated. The adiabatic expansion in the vicinity of the nozzle results in low sample temperatures leading to very sharp REMPI transitions. Additionally the population in the ground state is increased.

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gements, a skimmer is used downstream of the nozzle and ionization is carried out well within the molecular regime of the beam.

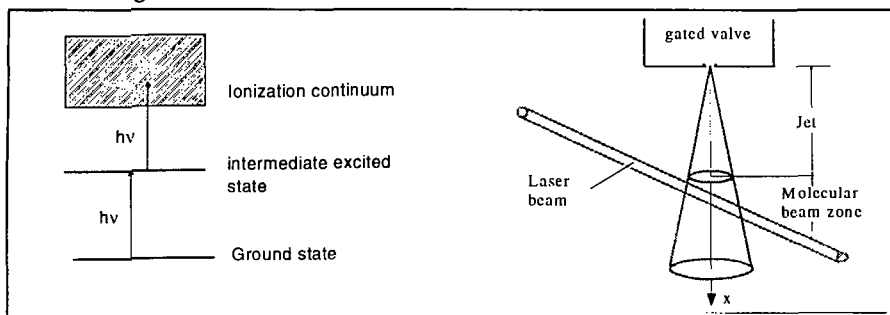


Fig. 1 a) Simplified energy level diagram for a R2PI process  
b) Structure of the sample beam

Our approach of improving the sensitivity involves ionization in the transition regime of the beam where concentrations are higher than in the molecular region (Fig. 1b). The beam itself consists of two regions. In the first zone the beam forms a continuum "jet" where cooling of the gas occurs. There is approximately a quadratic reduction in concentration with distance,  $x$ , from the gated nozzle. In the second zone, virtually no further cooling of the gas occurs due to the lack of molecular collisions, but the concentration continues to drop. Ideally, the optimum location for ionization is in the transition region between zone 1 and 2 which is a position where the highest degree of cooling has been essentially achieved but the species concentration is still relatively high. This region is close to the regime where the beam is described by a supersonic jet. Consequently, we call our method "Jet-REMPI", in contrast to the more commonly used ionization in the molecular region. The distance where the highest degree of cooling is achieved is characterised by the terminal mach number  $M_T$ . Andersen and Fenn (see <sup>6)</sup>) found that, for a monoatomic gas, the terminal mach number can be expressed as

$$M_T = 133 (p_0 \times d)^{0.4}$$

$p_0$  = pressure/bar

$d$  = nozzle diameter/cm

For "typical" conditions such as  $p_0 = 1013$  mb and  $d = 0.05$  cm, the distance  $x_T$  between the nozzle and the location of the terminal mach number may be calculated to be about 2 cm (see <sup>7)</sup> for a fuller discussion).

The development of the new ion source, further improvements beyond the geometric optimization, and details of the mass spectrometer have been reported in <sup>8)</sup> along with results referring to the stationary laboratory version. A complete sketch of the apparatus and details of the new mobile version are given in <sup>9)</sup>.

## *Some results of the laboratory tests*

The test series to verify the mobile system was started using benzene, toluene, and the mono- and dichlorinated derivatives as test substances for which the REMPI spectra are well defined <sup>1,2,10)</sup>. For these aromatic molecules the simple ionization scheme shown in Fig. 1a applies and soft ionization may be achieved. This is demonstrated in Fig. 2 which shows a typical mass spectrum for 2-chlorotoluene measured at the resonance wavelength of 267.7 nm. The peak-heights of the parent peaks reflect the isotopic abundance of the chlorine atoms, namely 3:1. The small fragmentation

peak at 91 amu is caused through Cl loss. It can be easily avoided by a slight decrease of the photon density.

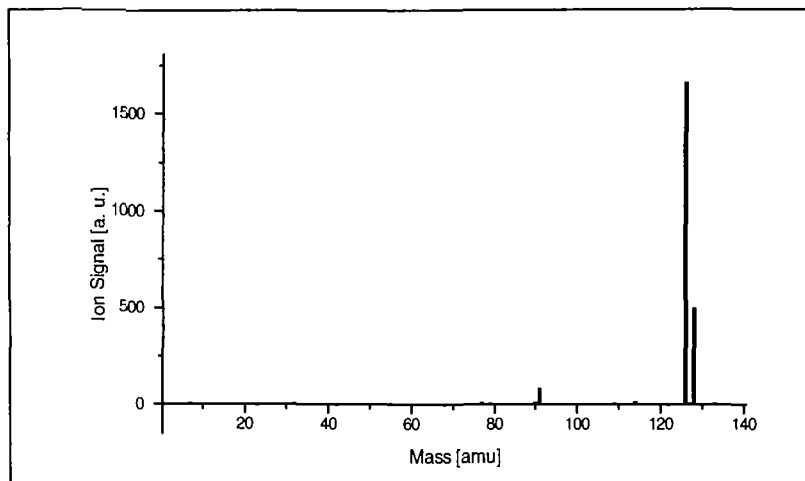


Fig. 2 Mass spectrum of 2-Chlorotoluene at 267.7 nm

Soft ionization is an essential feature if mixtures are to be analyzed as shown in Fig. 3. The two dimensional detection scheme for a mixture of toluene, 2-chlorotoluene and 2,5-dichlorotoluene yields only the parent peaks at their respective masses so that no cross sensitivities occur. From the results of Fig. 3 it is also clear that we have good optical resolution for our measured REMPI spectra. This indicates a sufficient cooling of the sample beam even though the ionization zone is in the transition regime between continuum zone and molecular beam zone.

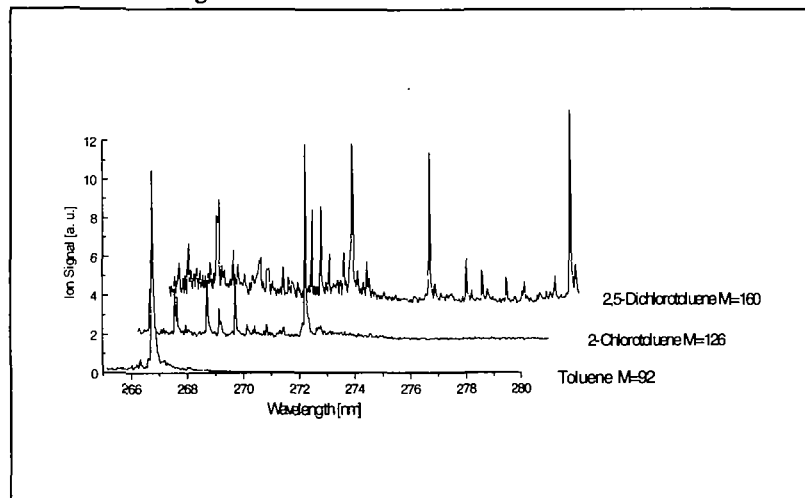


Fig. 3 Wavelength dependent REMPI spectra for Toluene, 2-Chlorotoluene, and 2,5-Dichlorotoluene

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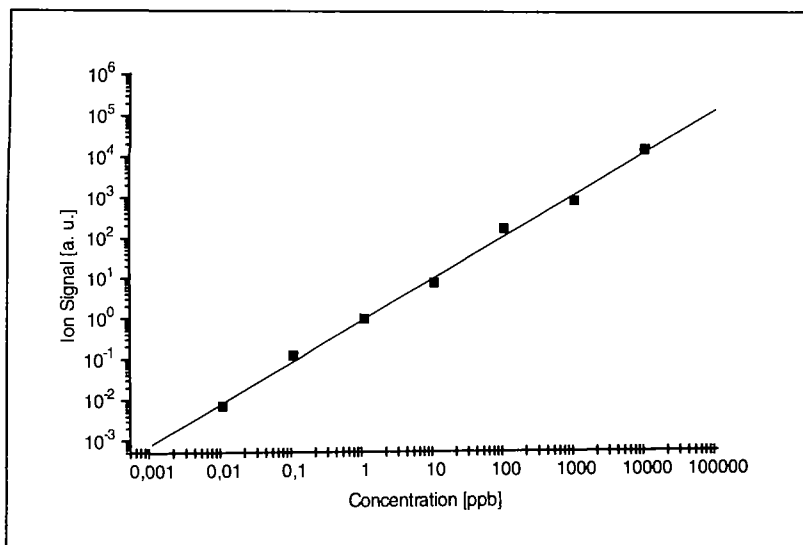


Fig. 4 Calibration curve for Benzene at 252.87 nm

We also tested the sensitivity of the mobile instrument with the probe nozzle as close as possible to the ionization zone, i.e. in the region of relatively high concentrations. The smallest possible distance between nozzle and ionization zone was 25 mm for this particular configuration (an improved version is underway). Using benzene as the test substance, it was possible to measure sample concentrations down to 10 ppt with a signal to noise ratio of 10 (Fig. 4). As a consequence we have determined a detection limit for benzene of 1 ppt. This is an improvement in sensitivity by a factor of 90 compared to earlier results<sup>3)</sup>. The solid line is the best fit on a log-log scale, gradient=1, indicating a linear relationship between signal and concentration over 6 orders of magnitude. We have obtained comparable results also for other compounds such as toluene or naphthalene.

For each concentration value we take 100 laser shots so that with our current repetition rate of 30 s<sup>-1</sup> it takes only seconds to obtain the result of the measurement.

In terms of sensitivity and on-line capability these results are unprecedented. They suggest that our device may be readily used for on-line control of incinerators. An obstacle, however, which also has been mentioned in the literature<sup>2)</sup> is the quenching effect caused by chlorine substitution. According to our own measurements<sup>9)</sup>, the resultant sensitivity loss will impose severe constraints on the choice of indicator substances. Pentachlorobenzene, for example, which has been suggested as a highly significant indicator<sup>11)</sup> is not a good candidate for REMPI measurements.

## Conclusion

A mobile Jet-REMPI device has been constructed for use under practical conditions. Ionization is accomplished nearly without fragmentation so that very low cross sensitivities are achieved. Sensitivities, on the other hand, are very high, e.g. sub ppt level for benzene. Due to the effect of chlorination, the sensitivities for dioxin surrogates (chlorobenzenes) or precursors (chlorophenols) are lower. Selectivity is also high.

On-line measurements of relevant precursors should be possible in a MWI without pre-concentration procedures as may be concluded by comparison with realistic MWI data.

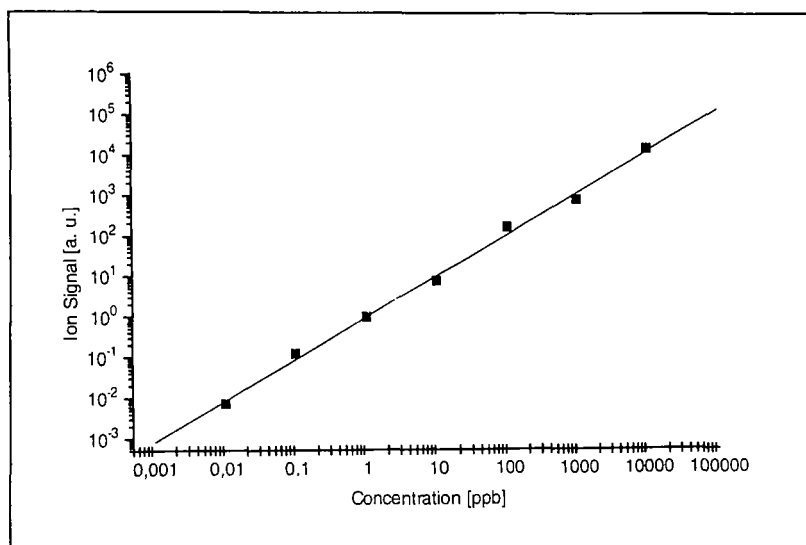


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