

Wavelength-resolved REMPI mass spectrometry in a hostile industrial environment, limitations and promises of the method

M. Nomayo, R. Thanner, H.-H. Grotheer*

Institute of Combustion Technology, DLR Stuttgart, Pfaffenwaldring 38, 70569 Stuttgart, Germany

Received: 23 February 2000/Revised version: 9 June 2000/Published online: 5 October 2000 – © Springer-Verlag 2000

Abstract. The complementary REMPI (resonance-enhanced multi-photon ionisation) techniques using either a tuneable laser or a fixed-frequency laser are compared. Our Jet-REMPI apparatus, consisting of a tuneable laser unit (Nd:YAG pump laser and OPO) and a reflectron mass spectrometer, is briefly introduced. This machine has been upgraded to cope with the difficult conditions (such as vibrations, temperature fluctuations and dust) prevailing in an incinerator. On-line measurements of the raw gas have been carried out at the municipal waste incinerator (MWI) in Stuttgart. Although this test series could not be completed the results are encouraging. They show that wavelength resolution can provide valuable information beyond that which can be obtained by fixed-frequency REMPI. Examples discussed include identification of phenanthrene as major constituent of the isomeric pair phenanthrene/anthracene and the structural identification of xylene isomers in the incinerator raw gas. Both examples are also of more general interest, the former with regard to investigation of soot precursors and the latter for quality assessment of refinery products. Spectra of some deuterated aromatics are reported for use of these compounds as standards. In addition, a mass spectrum containing DDT is shown and a chlorobenzene profile measured earlier in a pilot scale incinerator as demonstration of the sensitivity of the instrument. As is to be discussed, significant further sensitivity gains through increase of the beam density are limited because of ion collisions within the sample beam.

PACS: 82.80.MS

At present, basically two complementary approaches are being used for REMPI (see [1] for an overview).

- (i) One can resonantly excite target molecules through one or more photons into low-lying electronic states, followed by ionisation out of these states upon further absorption of one or more photons. By using these isolated states, and by additionally cooling the target molecules through

the well-known adiabatic expansion in a supersonic jet, one gets sharp transitions which are molecule specific. Consequently, in addition to separation by ionic mass, the ionisation wavelength is obtained as a second selection criterion, i.e. two-dimensional analysis with high selectivity. The disadvantage is that tuneable laser light has to be provided in the inconvenient wavelength range between about 200 and 320 nm.

- (ii) The second approach starts from conveniently available fixed-frequency laser sources such as ArF (193 nm), KrF (248 nm) or XeCl (308 nm) excimer lasers or a frequency-quadrupled Nd:YAG laser (266 nm). By a proper choice of one of these light sources one can excite the target molecules into higher states where spectral clogging occurs so that resonant states are nearly always found without need of laser tuning. The probability for resonance can be increased by using an effusive inlet system, i.e. by deliberately avoiding cooling. By so doing, selectivity is greatly reduced. On the other hand, only fairly simple laser systems are needed.

These complementary approaches are also reflected by the history of REMPI. Only a few approaches are picked out for illustration. In the first experiments combining laser ionisation with a mass spectrometer [2, 3], fixed-frequency lasers were used. Application of tuneable lasers for the ionisation of polyatomic molecules was pioneered by two groups [4, 5]. Nevertheless the fixed-frequency work was continued as shown by an arbitrarily chosen example. The group of Opsal, Reilly and co-workers [6–9] combined an effusive GC outlet to a mass spectrometer using fixed-frequency ionisation. For instance, they determined relative sensitivities for a series of aromatic compounds.

With regard to incineration, which was a major public concern in the late 1980s, a lot of pioneering work was carried out by two groups [10–15], both using tuneable lasers as a promising approach to tackle the complicated composition of incineration flue gas. In fact, it was Rohlfing [10] who advocated tuneable REMPI mass spectrometry as a method for a continuous emission monitor because of its selectivity and sensitivity. Nonetheless,

*Corresponding author. (E-mail: HH.Grotheer@dlr.de)

neither of these groups took their equipment to an incinerator, probably because of the experimental complexity. This difficult job was done by Zimmermann and co-workers [15–20] who successfully used a method similar to the one of Opsal and Reilly, i.e. under fixed-frequency conditions.

After the introduction of Jet-REMPI [21] our approach to incinerator measurements was to test our apparatus under field conditions using a highly resolving tuneable laser. When combined with a pilot-scale incinerator the Jet-REMPI system showed excellent features [22, 23]. In conjunction with a full-scale incinerator, however, it was only moderately successful [24]. The reason for our difficulties was that the chosen set-up of the complicated tuneable laser system could not sufficiently cope with temperature fluctuations and vibrations that prevail in an incinerator.

The aim of the present paper and of a companion one [25] is to find out which advantages and disadvantages one can expect using a tuneable laser system with a high wavelength resolution. To this end our laser set-up was re-designed so that it could cope with incinerator conditions. The apparatus was coupled to the municipal waste incinerator of Stuttgart immediately downstream of the bag house. Unfortunately, the work presented here could not be completed as the plant had to be shut down for revision and maintenance. Measurements will be resumed in the near future as the results are quite promising and do indeed show that wavelength-resolved REMPI has distinct advantages.

1 Experimental: the idea and design of Jet-REMPI. Coupling to the incinerator

In a supersonic jet as used for the cooling of sample molecules, 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 ionisation is carried out further downstream (i.e. in the molecular regime) as in conventional REMPI set-ups, then the sensitivity drops due to a decrease in the beam density without any gain in terms of cooling. Conversely, when ionising right in the transition zone between the jet regime and the molecular regime, the highest sensitivities in conjunction with the lowest temperatures are obtained.

This simple and effective configuration cannot be achieved with conventional laser ionisation sources. Instead, specially designed ion-extraction optics are needed. Further sensitivity improvements have been accomplished by increasing the ionisation volume (without loss in resolution due to proper focusing techniques) and by minimising collisions of charged particles with the walls. To implement these features an open beam without skimmer is used and the beam is pulsed to meet the vacuum requirements. These improvements have been shown to increase REMPI sensitivity substantially. Details of the ion source and results have been reported in the literature [21, 23, 26].

The measurement system consists of laser light source, mass spectrometer, power units, and electronic equipment for instrument control and data acquisition (see [23] for more details). These components are mounted in a car, 0.9 m wide and 2.5 m long. A linear reflectron time-of-flight mass spectrometer (Käsdorf, Munich) was used. The light source

consists of an optical parametric oscillator (OPO, coherent, type Symphony, no longer available on the market) and second-harmonic generator (SHG), pumped by a Nd:YAG laser (coherent, Infinity 40-100). The complete unit is housed in a massive aluminium box which is insulated and thermostatted (see [25] for details). To improve temperature uniformity a controlled flow of filtered air was circulated in the box. To insulate vibrations the box is coupled to the car by means of wire rope springs. This set-up made it possible to operate the laser over periods of one or two hours with only slight readjustments. These adjustments could be carried out without opening the laser lids (important to prevent dust).

More specifically, this expensive laser set-up was chosen on account of its high repetition rate of 30 s^{-1} and narrow optical bandwidth of 0.3 cm^{-1} (data according to the manufacturer). Wavelength selection is achieved by birefringent angle tuning of the OPO crystal and a subsequent grating. The emitted narrow-band light is used as seed for a subsequent optical parametric amplifier (OPA). Both OPO and OPA are pumped by the third harmonic (355 nm, about 100 mJ, 2.5 ns) of the pump laser. The material of all crystals used (OPO, OPA and SHG) is BBO. In the present work the typical UV pulse energy available for ionisation was 0.5 mJ per pulse. This value was found throughout our range of 250 to 300 nm and somewhat less at its upper end. This is, however, less than the pulse energy that we had in earlier experiments (about 1 mJ). One reason is that the OPA was not pumped with maximum power in order to avoid optical damage, another reason is deterioration of the optical components (see below).

1.1 Measurement procedure

Upon each shot of the ionising laser a complete mass spectrum is recorded in a range between typically 64 and 309 amu. This is an approximate and shiftable mass range given by focusing constraints and by the desire to reduce the amount of data. A further reduction is achieved by recording averages over 100 laser shots for all ions at a given flight time (i.e. same mass). Finally, mass peaks are automatically integrated and replaced by bars (i.e., centroiding). This leads to bar graphs as shown in the subsequent section (see Results, Fig. 1).

Normally, after acquisition of 100 mass spectra the OPO is shifted by a computer-controlled pre-selectable step to the adjacent wavelength, a further measurement is carried out and so on. In the present work a wavelength range between 250 and 300 nm is covered, the limits of this range being given by the properties of the SHG crystal used. Mostly depending on the chosen wavelength stepsize, this procedure is completed within 1 to 2 h and it yields mass profiles as a function of wavelength, examples of which are to be presented below.

Alternatively, one can tune the OPO to a suitable resonance wavelength of a chosen target species, so-called selected-ion monitoring. In this case one gets concentration vs. time profiles for this particular compound, the maximum time resolution being determined by the laser repetition rate (30 s^{-1}). To monitor more than one species

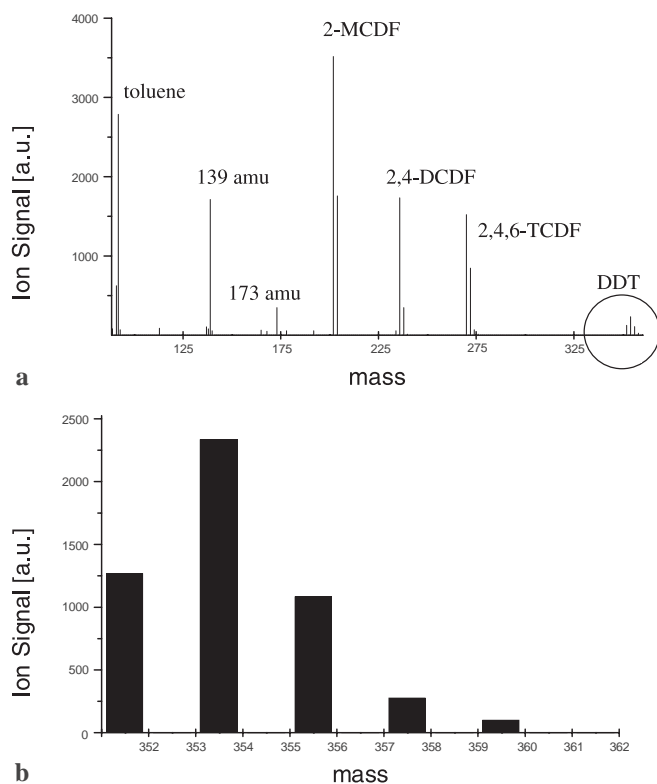


Fig. 1. a Mass spectra at 250 nm of a test mixture (see text) introduced in solid form into the ionisation chamber (warm molecules). Toluene is an impurity of this mixture. Mass peaks at 139 and 173 amu are attributed to memory effects (see text). The weak DDT spectrum is expanded in b. Note that no ^{13}C contributions are seen for the furans and DDT

simultaneously is at the expense of time resolution as the wavelength needs to be shifted after each measurement interval. (An example using this mode is shown in Fig. 5).

The incinerator at Stuttgart served as a test field in order to find out whether our instrument can cope with the severe MWI conditions and what can be measured at all in incineration flue gas. A particular difficulty in linking an optical device to an incinerator is the occasional undesired release of fly-ash. To prevent its detrimental effect on our optical apparatus the latter was covered by a tent which was slightly pressurised. Although this effectively blocked dust, it did not sufficiently shield the moist and corrosive ambient air. As a result, after our eight-week campaign all optical crystals were fogged at their surfaces and needed to be re-polished.

The set-up of the MWI has been described in the literature [27]. The main components of the plant include three combustion lines followed by a modern air pollution control (APC) system. 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 t/h for each combustion line. For the 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 minimal amounts of organic material are found in the flue gas.

For the REMPI measurements flue-gas samples were drawn immediately downstream of the bag house. At this position gas temperatures are approximately 200 °C. As probe we used a 12-mm inside diameter stainless steel lance, closed at one end and immersing about 1 m into the flow. Gas samples were drawn through lateral holes drilled along a cylinder line of the tube. Directly at the sampling port, the tube was connected to a short PTFE hose heated to 180 °C and leading to a heated (180 °C) pair of twin filters arranged in parallel. Each twin filter consisted of a coarse PTFE membrane with 10- μm pores followed by a 1- μm fine filter. One filter pair was always kept clean so that it could be used as a reference filter. From this section a 6.5-m PTFE hose, 10 mm inside diameter and heated to 180 °C led to the Jet-REMPI inlet head which was also heated to 180 °C. The flow into the Jet-REMPI machine via its pulsed valve was about 150 ml/h, i.e. small in comparison to the main flow of about 3 m³/h. The residence time in the sampling line was calculated to be about 1 s. Downstream of the Jet-REMPI machine the main flow was led through a stainless steel trap to remove condensate and then via a Tylan flow meter and a membrane pump back to the incinerator.

For calibration purposes standard samples were prepared consisting of up to six components dissolved in acetone, typical concentrations being 300 $\mu\text{mol/l}$. These samples were continuously injected to the hot gas flow either directly at the Jet-REMPI inlet or upstream at the sampling port. To this end a motorised syringe was used with speeds between 0.1 ml/h and 100 ml/h. At minimum speed and using the stock solution, a mole fraction of about 250 ppt was obtained. Typical reference spectra are shown in the next section.

Upon stepwise injection of the standard at the sampling port, potential adsorption/desorption effects in the filters or the sampling line could be checked. For benzene a fast response within a few seconds was found.

2 Results

Mass spectra obtained through resonance ionisation of cold molecules and in a narrow wavelength range may look very unfamiliar as they may contain only few peaks, mostly depending on the chosen (mean) wavelength. In order to show a more common spectrum, a result is given in Fig. 1a, b obtained under somewhat atypical conditions. In this case sample substances were introduced as solids into the ionisation chamber rather than being injected in solution into the stagnation chamber. The sample mixture of Fig. 1 consisted of 2,4-dichlorophenol, 2,4,5-trichlorophenol, 1,1,1-trichloro-2,2-bis-(4-chlorophenyl)-ethane (DDT), 2-chlorodibenzofuran (2-MCDF), 2-chlorodibenzo-p-dioxin (2-MCDD), 2,4-dichloro-dibenzofuran (2,4-DCDF), 2,7-dichlorodibenzo-p-dioxin (2,7-DCDD) and 2,4,6-trichloro-dibenzofuran (2,4,6-TCDF). In view of the minimal fragmentation occurring under our conditions, mass spectrometric interference should be negligible for this mixture.

Vapour subliming from the solid sample is mostly pumped away, a small fraction being ionised. No REMPI signal could

be detected from 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2-chloro-dibenzo-p-dioxin (2-MCDD) and 2,7-dichloro-dibenzo-p-dioxin (2,7-DCDD). Further signals were seen from toluene (impurity of the introduced solid material) and from masses 139 amu and 173 amu. For each of these latter mass signals about 100 structures can be found in mass spectrometric databases so that without further information no identification is possible. At present we can only say that these signals are a sort of memory effect arising from contaminations of the ion source. Under normal operation conditions, i.e. sample introduction via a supersonic beam, it is not observed because background gas molecules cannot enter the beam efficiently.

As the target molecules are warm no pronounced wavelength dependence can be expected and this was indeed observed in the covered wavelength range between 250 and 265 nm. One question of this experiment was whether the relatively large and floppy DDT molecule exhibits a sufficiently large sensitivity for REMPI. This seems to be the case as indicated in Fig. 1b showing qualitatively the expected isotopic distribution of a five-fold chlorination (mass bar from $m/z = 362$ amu missing because of low intensity). A next step would be to investigate the wavelength spectra of jet-cooled DDT samples to provide a two-dimensional analytical detection scheme for this ubiquitous compound.

Note that we see the ^{13}C -isotopomer of toluene but not those of MCDF or DDT. The absence of dioxin signals in comparison to those of MCDF may be due to vapour pressure or to spectroscopic reasons: for instance, the warm molecules may be distributed over many levels of the butterfly vibration around the O—O-axis. For the phenols it is known [28] that their REMPI sensitivities become very small upon ortho-substitution. More generally, Fig. 1 is an example for the wide range of REMPI sensitivities.

Our second example is taken from a MWI raw-gas measurement and is meant to demonstrate the advantage of our two-dimensional detection, i.e. making use of the wavelength dependence. Figure 2 displays signals at 106 amu as a function of wavelength. Expected contributions to these ion signals are of the three isomeric xylenes, but also of ethylbenzene. These can be distinguished through their wavelength

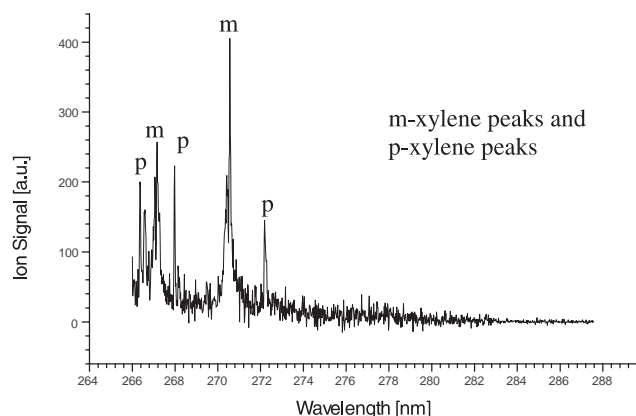


Fig. 2. Municipal waste incinerator (MWI) raw-gas measurement. A short portion of the 106-amu trace is shown as a function of the wavelength. Meta- and para-xylene are identified using earlier reference spectra. Ortho-xylene and ethylbenzene are not detected

dependence as known from earlier work [26]. Comparison with these reference spectra allows the assignment of the corresponding peaks in Fig. 2, leading to the result that a potential contribution of ethylbenzene could be excluded. Of the three xylene isomers, ortho-xylene could be excluded on the basis of our own reference spectra; meta-xylene was found to play a major role.

A further example making use of wavelength separation and discussed in our companion paper [25] is the identification of aniline at 93 amu, superimposed by a ^{13}C -isotopomer of toluene, yet unperturbed by potential phenol fragments.

Our third example shown in Fig. 3 lies between the well-resolved one (Fig. 2) and the unresolved one (Fig. 1). It refers to anthracene/phenanthrene at 178 amu. This pair of structural isomers is of general importance in combustion research due to the role of these compounds as soot precursors. On account of their nearly identical fragmentation patterns they cannot be distinguished by conventional mass spectrometry. The same applies for REMPI mass spectrometry when a fixed frequency is used [15]. As recently shown [29] separation by wavelength-resolved REMPI mass spectrometry is most readily possible when the low-lying states (S_1) are excited. This requires use of two-colour REMPI (see [29]) and is clearly beyond the possibilities of our present apparatus.

In our wavelength range congested spectra are to be expected [17]. As shown in Fig. 3 we find indeed a more or less unresolved spectrum at 178 amu. There is however a fairly sharp peak at 250.66 nm compatible with a tabulated UV transition of 250.63 nm for phenanthrene [30]. For anthracene which is reported to have a REMPI cross section similar to phenanthrene [18], the corresponding peak would be at 251.89 nm. From the absence of this peak we conclude that in our case phenanthrene is the major constituent of the 178 amu signals. This same conclusion was arrived at by Zimmermann and co-workers [18] by comparison to conventional GC/MS measurements.

Reference spectra as given in Fig. 4 must be known for peak assignment. In addition, for quantitative measurements calibrations have to be carried out under measurement conditions and ideally for all relevant species as ionisation efficiencies are very much species dependent and dependent on experimental parameters such as laser power. A common

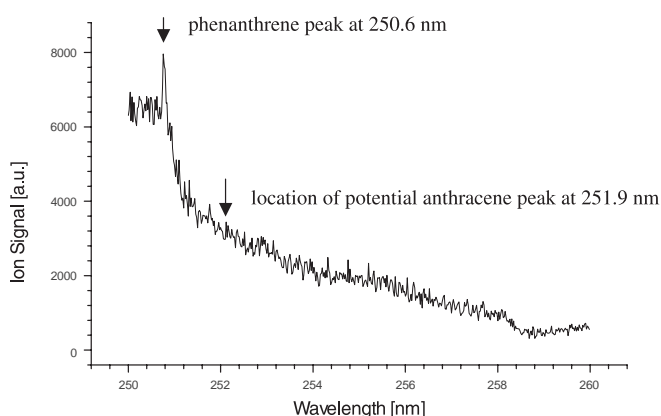


Fig. 3. Municipal waste incinerator (MWI) raw-gas measurement. A short portion of the 178-amu trace is shown as a function of the wavelength. The arrows indicate UV transitions of phenanthrene and anthracene, respectively, taken from the literature [30]

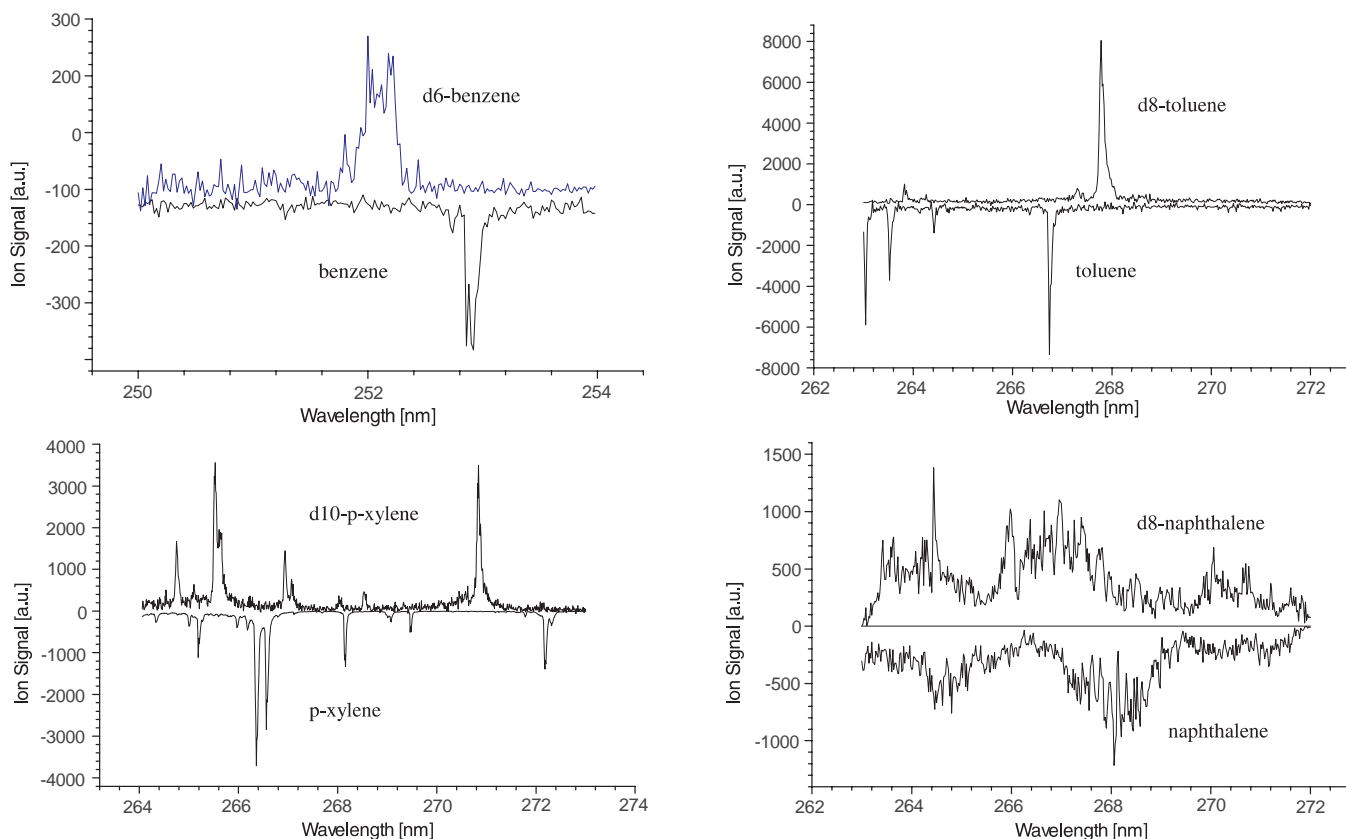


Fig. 4. REMPI action spectra of deuterated aromatics and of their unsubstituted counterparts

method to this end is the addition of samples in known quantities to the test gas. Instead of this we preferred the addition of deuterated standards as in this case test peaks and standard peaks are clearly distinguished and can be measured simultaneously. This helps us to escape instabilities of the apparatus. In Fig. 4 spectra are shown for deuterated benzene, toluene, p-xylene and naphthalene and for their unsubstituted counterparts.

It has been mentioned above that during our MWI campaign our laser system did not work under optimum energy output conditions. Consequently, in order to demonstrate the high sensitivity of our apparatus, we reiterate here a result obtained earlier at the pilot-scale incinerator TAMARA at Research Center Karlsruhe [23, 24]. Gas samples were drawn right downstream of the bag-house, i.e. under conditions similar to those at the MWI. Chlorobenzenes were chosen as reference species due to their potential role as indicators for toxic dioxins (see [24] and further references therein). Figure 5 displays the output energy of the laser (in the UV) along with profiles of chlorobenzene and 1,2-dichlorobenzene. The TAMARA concentrations of both compounds are very low, particularly so the one of the dichlorobenzene. Nevertheless, the signals of the latter are significantly above the noise level and no change of our signals is observed within the noise range.

At the same time, the stable incinerator conditions made it possible to carry out conventional analyses by trapping the sample and subsequent GC/MS analysis. With the column used dichlorobenzenes and higher chlorinated benzenes could be measured. From these results a mole fraction of 2.0 ppt

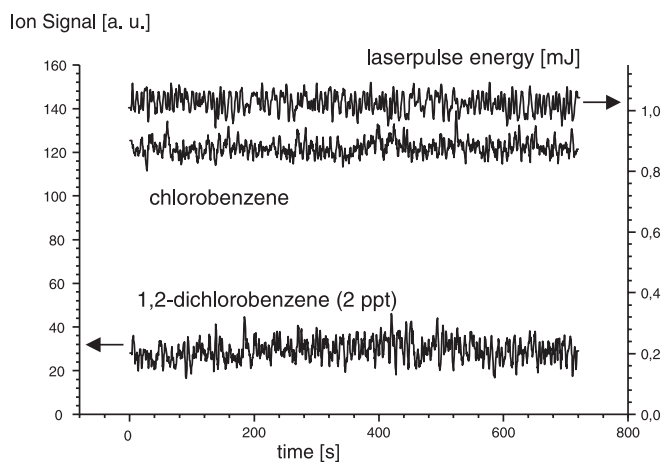


Fig. 5. Raw-gas measurement in the pilot-scale research incinerator TAMARA. The laser wavelength is periodically shifted between 269.88 nm for chlorobenzene and 272.68 nm for 1,2-dichlorobenzene. For the latter compound the 2-ppt concentration level is derived from conventional measurements

could be derived for 1,2-dichlorobenzene. For $S/N = 1$ one extrapolates a detection limit of 0.5 ppt.

3 Discussion

The idea of diminishing the distance between nozzle and ionisation zone in order to gain sensitivity has been advocated

by other authors, too [31]. There is, however, a limitation given by the mean free path of the generated ions. For illustration, figures are given in Table 1 referring to actual conditions that we encountered during our MWI measurement campaign (pressure of the stagnation chamber 0.9 bar, temperature 430 K). For N_2 as carrier gas the density, n , on the beam axis may be estimated [32] according to

$$n = n_0 \times 0.0875(D/x)^2,$$

where D is the diameter of the nozzle, x its distance to the ionisation region, 25 mm in our case; n_0 is the density in the stagnation chamber.

When regarding the beam as gas of species 1 at rest through which species 2 travels, one obtains [33] for the mean free path

$$\lambda = (\sigma_{12}n_1)^{-1}.$$

The cross section σ for loss of benzene ions in N_2 has recently been measured in a “high pressure” mass spectrometer [34] to be 0.179 nm^2 for 750-eV ions.

With these figures a mean free path of 1.62 cm is estimated for benzene in nitrogen, nozzle diameter 0.4 mm. As the distance from the centre of ionisation to the extraction electrode is about 0.9 cm, a reasonable fraction of the benzene ions may be expected to enter the drift tube. If the nozzle diameter is increased the density is indeed increased (see Table 1). This effect, however, is more than counterbalanced by loss of ions through scattering as the mean free path becomes small in comparison to the distance of the extraction electrode. This means that in net, a loss of sensitivity results and this was indeed observed. Consequently, at the given stagnation pressure it cannot be recommended to decrease the x/D ratio significantly below 60.

This limitation should obviously be more pronounced for larger molecules. Ring et al. [34] found that upon alkylation the cross section increases significantly, for example 0.179 nm^2 for benzene in comparison to 0.305 nm^2 for xylenes. The same trend is found for collision diameters of neutral molecules. It was hence no surprise that we scarcely got signals when introducing the large molecules of Fig. 2 into the stagnation chamber equipped with an 1.2-mm nozzle. In the high vacuum of the ionisation chamber collisions do not play a role and the vapour pressure of these substances was sufficient to produce reasonable signals.

The other issue to be addressed here is whether our complicated approach justifies the efforts. Obviously, it suffers three drawbacks.

Table 1. Mean free path (λ) of benzene ions in a hypothetical N_2 sample beam as a function of nozzle diameter D . The beam density n is in cm^{-3} and is calculated for the ionisation regime, i.e. 25 mm downstream of the nozzle

D /mm	$n_{25}(N_2)$	λ /cm
0.4	3.44×10^{14}	1.62
0.8	1.38×10^{15}	0.405
1.2	3.09×10^{15}	0.181

- (i) The machine is relatively bulky, expensive and susceptible to disturbances under difficult technical conditions such as vibrations or temperature fluctuations.
- (ii) Sub-second time resolution for concentration measurements can only be achieved for monitoring of single components. Subsequent measurement of up to 20 components is presently possible, yet at the expense of time resolution.
- (iii) When isolated resonance transitions are utilised, in the ideal case only those components are detected that one wishes to detect. Species to which the laser is not tuned escape detection. Consequently, for a complete analysis a REMPI database for all components in question should be available and this definitely requires more work.

The advantage of our method is obviously the unambiguity of peak identification as reported above and to be further discussed below. To further assess this issue we asked the question which kind of information we would obtain when only a narrow wavelength range of 1 nm is covered, i.e. a fixed-frequency REMPI method was simulated. To this end, for each mass bar averages were calculated from the raw-gas values that we measured between 250.0 and 251.0 nm. A wavelength range of 1 nm is preferred over a single wavelength in order to mimic the energy spread of thermal molecules as obtained from an effusive source. The result is given in Fig. 6a in linear display and in Fig. 6b in logarithmic display, the latter being calculated after noise subtraction. Figure 6a shows that we have some prominent peaks, yet the message of Fig. 6b is that nearly every mass bar is occupied. Whereas such a finding would be trivial in conventional EI mass spectroscopy due to contaminants, pump oil etc., it was not expected to that extent for the much more selective resonance ionisation in the 250.0 to 251.0-nm range. In view of unavoidable mass spectrometric interferences, Fig. 6 demonstrates the necessity to have a second parameter for peak identification and that is the wavelength in our case.

As has been shown in our companion paper [25], it was possible to distinguish the ^{13}C -toluene signal from the aniline signal by wavelength variation, and to exclude a potential contribution of the (M-1) fragmentation peak of phenol.

An example reported in this paper consists of contributions to the 106 signal obtained in the raw gas. A potential contribution of ethylbenzene could be excluded. Of the three xylene isomers, ortho-xylene could be excluded on the basis of our own reference spectra, meta-xylene was found to play a major role.

It has been shown above that a discrimination of anthracene and phenanthrene is possible, even when transitions via higher excited electronic states are used.

To discern isomeric structures is particularly important when the compounds in question are widely different with regard to toxicity. In incineration, chlorinated dioxins and furans are well-known examples of this type of behaviour.

Another interesting example has been recently addressed by Zimmermann et al. [18]. They suggest selectively measuring benzo(a)pyrene as an indicator for PAH toxicity. The separation from its less toxic isomers is possible when a tunable two-colour REMPI system is used as was demonstrated by laboratory measurements [35]. To perform the same meas-

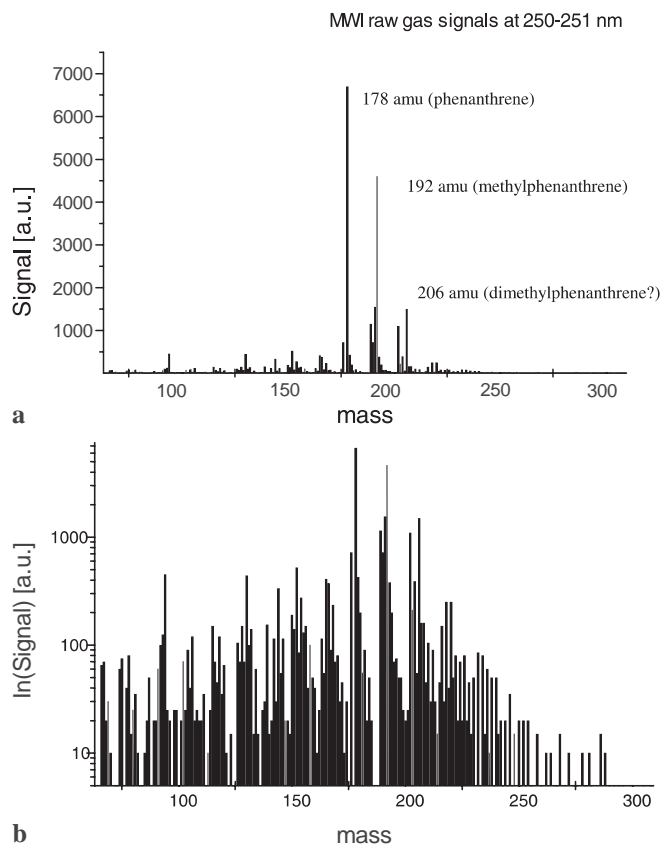


Fig. 6a,b. Municipal waste incinerator (MWI) raw-gas mass spectrum measured over a wavelength range between 250 and 251 nm (a). These conditions are chosen to mimic fixed-frequency ionisation of an effusive beam, i.e. warm molecules (see text). After background subtraction many resonant signals remain (b) indicating a lack of selectivity. Note that a is on a linear scale, whereas b is on a logarithmic scale

urements in an incinerator, however, requires again a tuneable system that tolerates these severe conditions.

It may, however, be questioned whether for the given purpose a narrow-bandwidth laser such as our system is really needed. For typical aromatic compounds in incineration flue gas, linewidths in the order of 10 cm^{-1} have been reported (for example [14]) so that our narrow laser bandwidth cannot be fully exploited. Tuneable laser sources with bandwidths in the order of 2 to 4 cm^{-1} would do the same job and are available on the market. In terms of price, size and ruggedness such an instrument could provide a considerable improvement without significant loss in selectivity.

Acknowledgements. The early development of Jet-REMPI has been supported under the auspices of TECFLAM III. During this period we benefited from helpful discussions with Prof. Wolfrum which we gratefully acknowledge. Improvement of our machine was supported by the German Secretary for Research and Technology under research grant 0327074A. The measurement campaign was supported by the EU MINIDIP project.

Both of these supports are gratefully acknowledged. We thank Neckarwerke AG, Stuttgart for the possibility to carry out these measurements and Dr. R. Stütze and H.J. Bäurle, both of Neckarwerke, for their practical help. Finally, our reviewers are acknowledged for their helpful suggestions.

References

1. D.M. Lubman (Ed.): *Lasers and Mass Spectrometry* (Oxford University Press, New York 1990)
2. N.K. Berezhetskaya, G.V. Varonov, G.A. Delone, N.B. Delone, G.K. Pisskova: *JETP* **31**, 403 (1970)
3. S.L. Chin: *Phys. Rev. A* **4**, 92 (1971)
4. U. Boesl, H.J. Neusser, E.W. Schlag: *Z. Naturforsch.* **33A**, 1546 (1978)
5. V.S. Antonov, I.N. Knyazev, V.S. Letokhov, V.M. Matiuk, V.G. Movshev, V.K. Potapov: *Opt. Lett.* **3**, 37 (1978)
6. G. Rhodes, R.B. Opsal, J.T. Meek, J.P. Reilly: *Anal. Chem.* **55**, 280 (1983)
7. R.B. Opsal, J.P. Reilly: *Anal. Chem.* **60**, 1060 (1983)
8. R.B. Opsal, J.P. Reilly: *Anal. Chem.* **58**, 2919 (1986)
9. C.W. Wilkerson, S.M. Colby, J.P. Reilly: *Anal. Chem.* **61**, 2669 (1989)
10. E.A. Rohlffing: 22nd Symp. (Int.) on Combustion, The Combustion Institute, 1843 (1988)
11. B.A. Williams, T.N. Tanada, T.A. Cool: 24th Symp. (Int.) on Combustion, The Combustion Institute, 1587 (1992)
12. T.A. Cool, B.A. Williams: *Combust. Sci. Technol.* **82**, 67 (1992)
13. T.N. Tanada, J. Velazquez, N. Hemmi, T.A. Cool: *Ber. Bunsen-Ges. Phys. Chem.* **97**, 1516 (1993)
14. T.N. Tanada, J. Velazquez, N. Hemmi, T.A. Cool: *Combust. Sci. Technol.* **101**, 333 (1994)
15. R. Zimmermann, H.J. Heger, A. Ketrup, U. Boesl: *Rapid Commun. Mass Spectrom.* **11**, 1095 (1997)
16. R. Zimmermann, H.J. Heger, M. Blumenstock, R. Dorfner, K.-W. Schramm, U. Boesl, A. Ketrup: *Rapid Commun. Mass Spectrom.* **13**, 307 (1999)
17. H.J. Heger, U. Boesl, R. Zimmermann, R. Dorfner, A. Ketrup: *Eur. Mass Spectrom.* **5**, 51 (1999)
18. H.J. Heger, R. Zimmermann, R. Dorfner, M. Beckmann, H. Griebel, A. Ketrup, U. Boesl: *Anal. Chem.* **71**, 46 (1999)
19. R. Zimmermann, H.J. Heger, A. Ketrup: *Fresenius' J. Anal. Chem.* **363**, 720 (1999)
20. H.J. Heger, R. Zimmermann, H. Ketrup: *VDI-Bericht Nr. 1492*, p. 275 (1999)
21. H. Oser, R. Thanner, H.H. Grotheer: *Combust. Sci. Technol.* **116-117**, 567 (1996)
22. H. Oser, R. Thanner, H.H. Grotheer, A. Merz, H. Seifert: *Organohalogen Compd.* **35**, 57 (1998)
23. R. Thanner, H. Oser, H.H. Grotheer: *Eur. Mass Spectrom.* **4**, 215 (1998)
24. R. Thanner, M. Nomayo, H.H. Grotheer, R. Stütze: *Organohalogen Compounds* **40**, 547 (1999)
25. M. Nomayo, R. Thanner, H.H. Grotheer: *Chemosphere*, in press
26. H. Oser, R. Thanner, H.H. Grotheer: *Chemosphere* **37**, 2361 (1998)
27. R. Stütze, A. Nonnenmacher: *ALS-Jahresbericht 135-143* (1993)
28. R. Tembreull, C.H. Sin, P. Li, H.M. Pang, D. Lubman: *Anal. Chem.* **57**, 1187 (1985)
29. J. Velazquez, L.A. Volobueva, T.A. Cool: *Combust. Sci. Technol.* **134**, 139 (1998)
30. *DMS UV Atlas of Organic Compounds*, Verlag Chemie, Weinheim; (Butterworth, London 1967)
31. M.J. Castaldi, S.S. Senkan: *J. Air Waste Management Assoc.* **48**, 77 (1998)
32. S.R. Goates, C.H. Sin: *Appl. Spectrosc. Rev.* **25**, 81 (1989)
33. W.J. Moore: *Physical Chemistry* (Longman, London 1976)
34. S. Ring, R. Naaman, Y. Rudich: *Anal. Chem.* **71**, 648 (1999)
35. R. Zimmermann, C. Lermer, K.-W. Schramm, A. Ketrup, U. Boesl: *Eur. Mass Spectrom.* **1**, 341 (1995)