

Motivation

Atmospheric oxidation reactions represent not only a sink process for organic compounds, but also a source for new species. These new compounds may have different toxic properties than their precursor compounds or affect important atmospheric processes (e.g. particle mass production). For this reason, detailed product studies are essential input parameters for the better description of atmospheric processes in models. In particular the characterization and quantification of possible secondary atmospheric formation processes of nitrated phenols is of importance. Lüttke et al. [1] postulated already in 1988 the contribution of aqueous phase oxidation processes to the measured mono- and dinitrophenol levels in atmospheric samples. Therefore, the product distribution of 4-methylphenol oxidation in presence of $\text{NO}_3/\text{NO}_2/\text{OH}$ was studied applying an offline coupling of laser photolysis experiments with liquid chromatography/mass spectrometry (LP-LC/MS, Fig. 1). The obtained results from the reaction between 4-methylphenol and $\text{NO}_3/\text{NO}_2/\text{OH}$ in aqueous solution will be presented and compared with the product distribution from the phenol oxidation.

Results and discussion

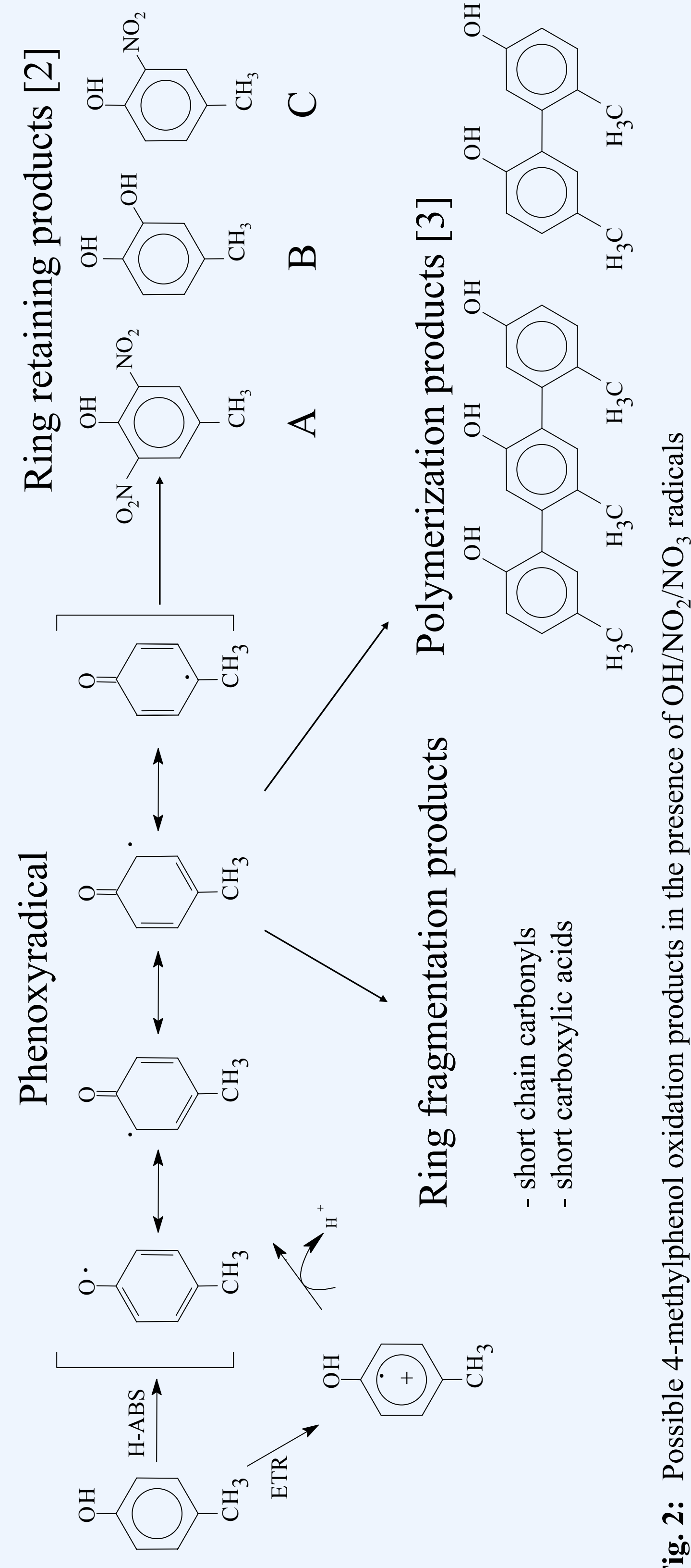
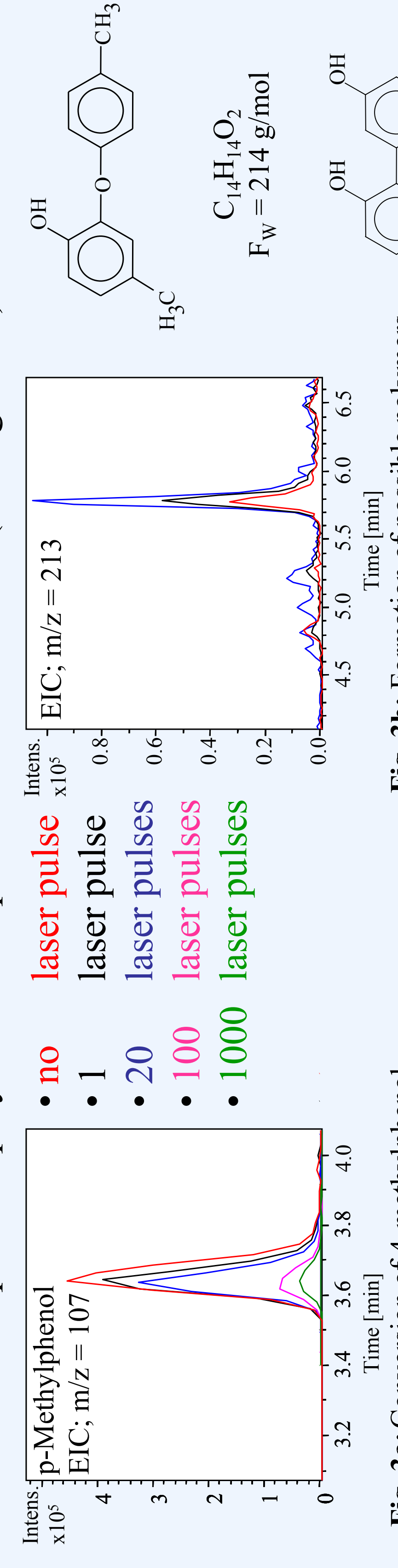


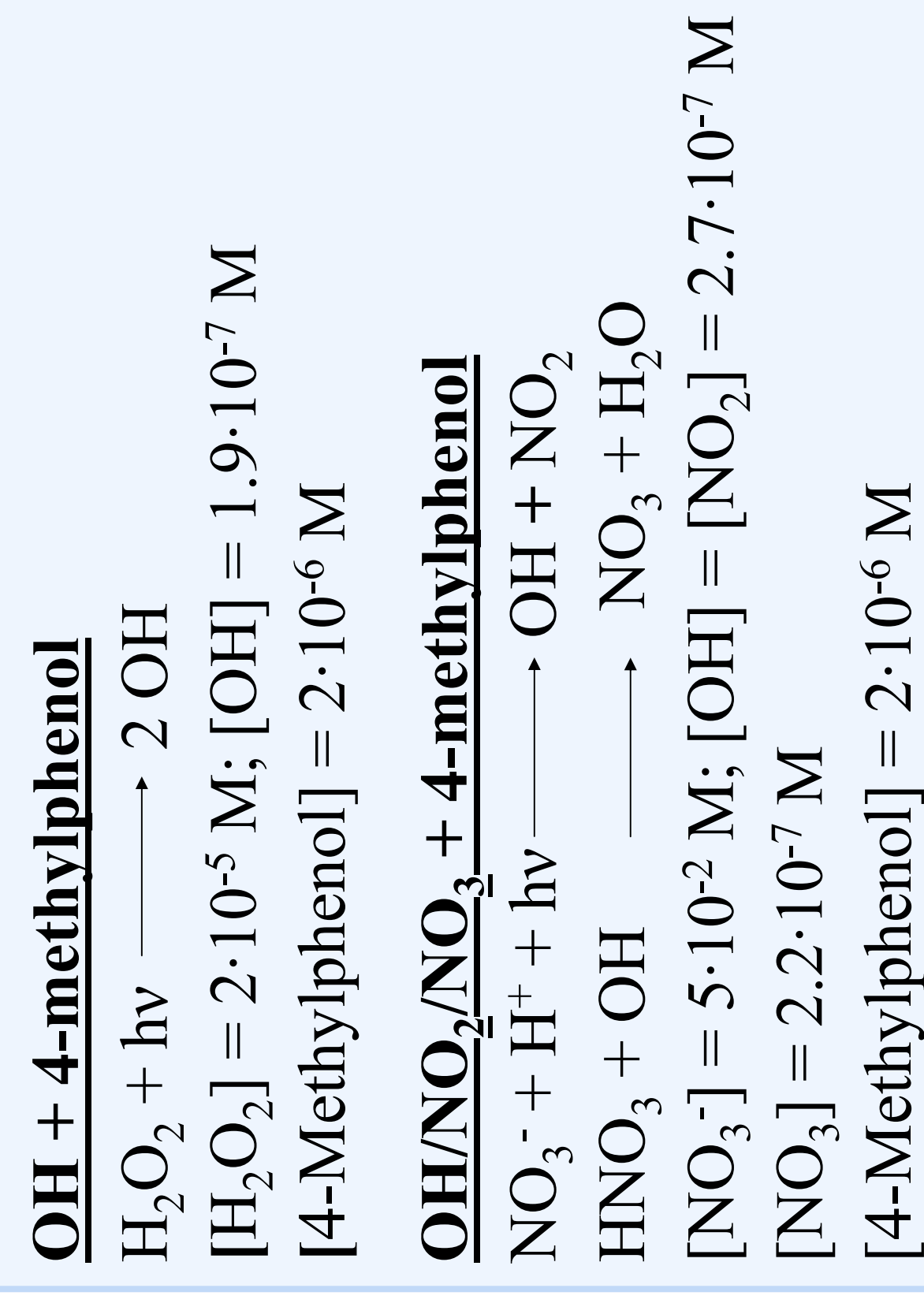
Fig. 2: Possible 4-methylphenol oxidation products in the presence of $\text{OH}/\text{NO}_2/\text{NO}_3$ radicals

1) Photolysis of 4-methylphenol ($\lambda = 248 \text{ nm}$)

- No significant conversion of 4-methylphenol measured
 - Direct photolysis of 4-methylphenol does not influence the obtained experimental results
- #### 2) OH + 4-methylphenol ($\text{pH} = 7, T = 298 \text{ K}$)
- Conversion of 4-methylphenol = 25% (1 laser pulse, see Figure 3a)
 - Conversion of 4-methylphenol > [OH]; maximal up to 40% can be explained by OH reactions
 - Identified oxidation product: 4-methylcatechol (B)
 - Formation of possible polymerization products was observed (see Figure 3b)



Experimental



Excimer Laser

$\lambda = 248 \text{ nm}$ (active medium: KrF)

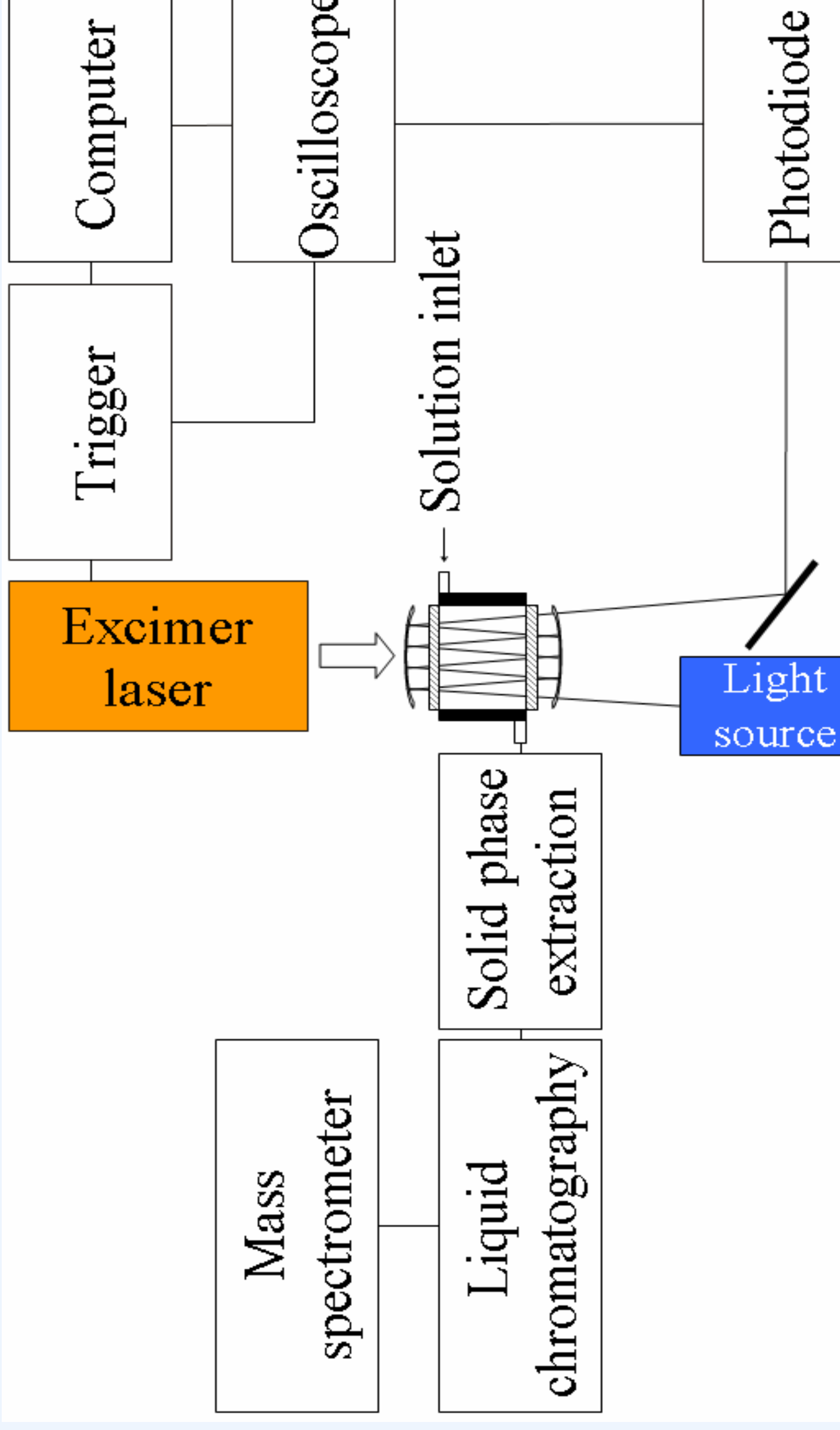


Fig. 1: Off-line coupling of laser flash photolysis – long path absorption setup with solid phase extraction and liquid chromatography/mass spectrometry (LC/MS).

3) OH/NO₂/NO₃ + Phenol ($\text{pH} = 0.5, T = 298 \text{ K}$)

- Conversion of 4-methylphenol = 10% (1 laser pulse)
- Identified oxidation products: 2,6-dinitro-4-methylphenol (A)
 $c = 2.8 \cdot 10^{-7} \text{ M}$
- 2-nitro-4-methylphenol (C)
 $c = 7.3 \cdot 10^{-9} \text{ M}$

Formation of nitrated cresols is not influenced by the number of laser pulses

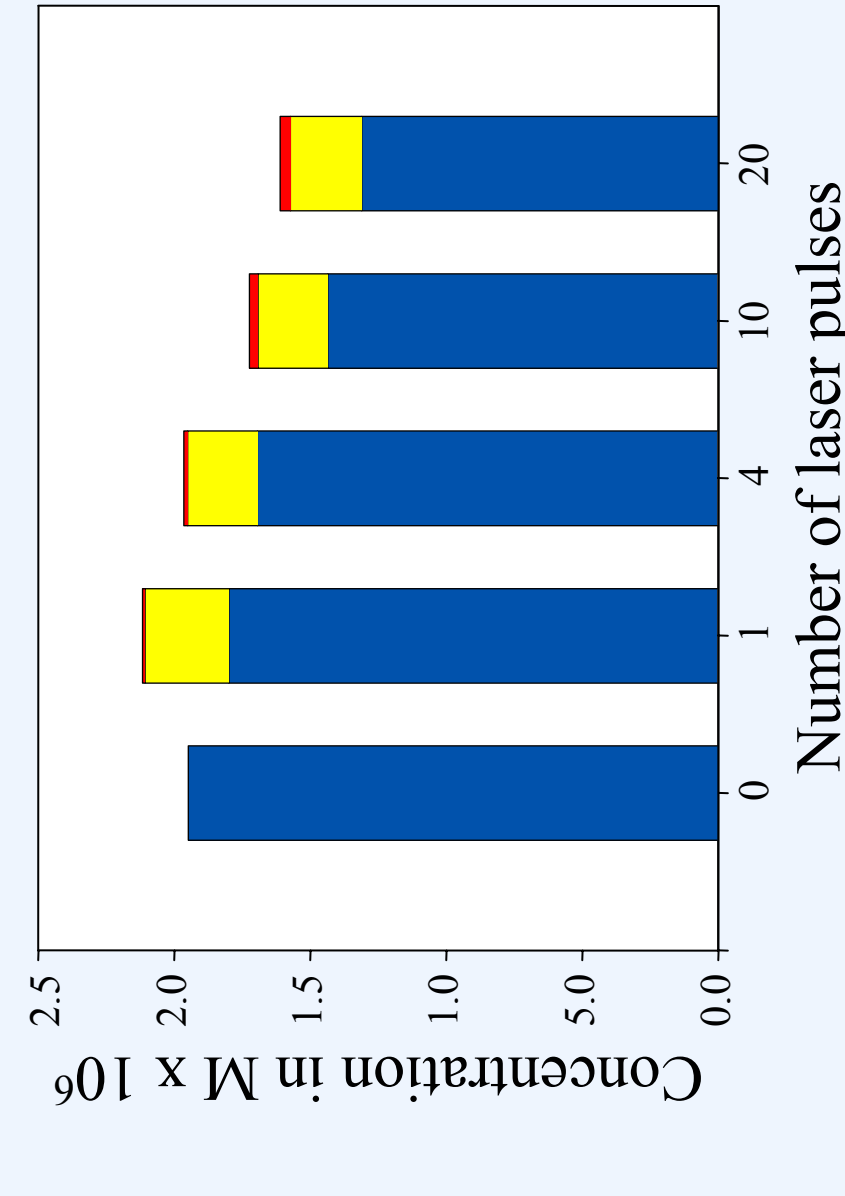
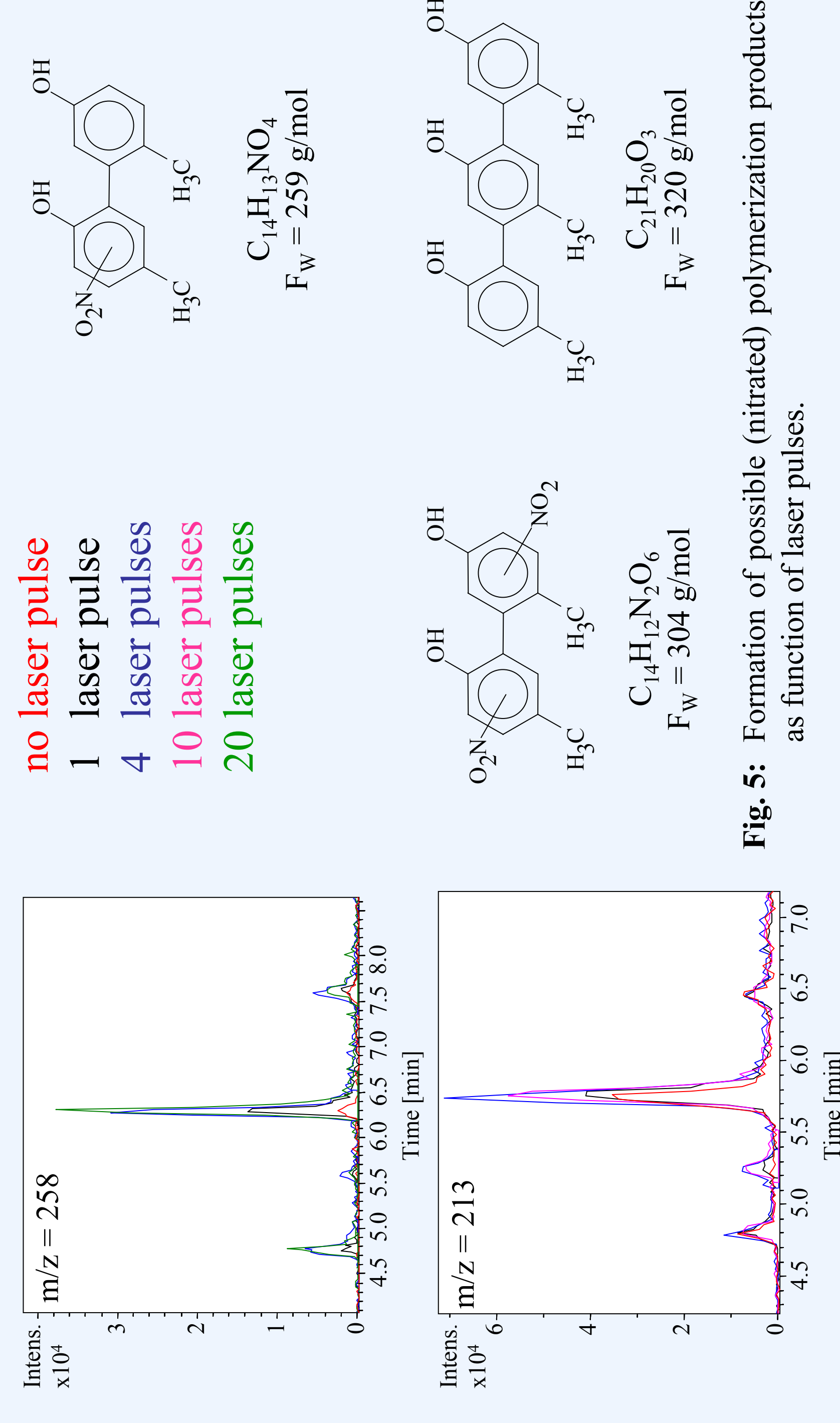


Fig. 4: Observed concentrations of identified products as a function of the number of excimer laser pulses

Formation of possible polymerization products observed



Comparison with results from the phenol oxidation

OH + Phenol ($\text{pH} = 7, T = 298 \text{ K}, [\text{4I}]$)

- $[\text{H}_2\text{O}_2] = 1 \cdot 10^{-4} \text{ M}; [\text{OH}] = 3.4 \cdot 10^{-6} \text{ M}; [\text{phenol}] = 1 \cdot 10^{-5} \text{ M}; 1 \text{ laser pulse (760 ml)}$
- Conversion of phenol = 60%
- Conversion of phenol > [OH]; maximal up to 67% can be explained by OH reactions
- Identified oxidation products: 2-hydroxyphenol, 4-hydroxyphenol, 4-benzoquinone
- Identified oxidation products explain up to 28% of the total phenol reacted
- No experimental evidence for the formation of polymerization products and ring fragmentation products

OH/NO₂/NO₃ + Phenol ($\text{pH} = 0.5, T = 298 \text{ K}, [\text{5I}]$)

- $[\text{NO}_3] = 1.4 \cdot 10^{-2} \text{ M}; [\text{OH}] = [\text{NO}_2] = 1.6 \cdot 10^{-7} \text{ M}; [\text{NO}_3] = 4.7 \cdot 10^{-8} \text{ M}; [\text{phenol}] = 1 \cdot 10^{-5} \text{ M}; 1 \text{ laser pulse (760 ml)}$
- Identified oxidation products: 2-nitrophenol, 4-nitrophenol, 2,4-dihydroxyphenol
- Identified oxidation products explain up to 50% of the total phenol reacted
- No experimental evidence for the formation of dinitrophenols and polymerization products

Conclusions

- Formation of nitrated cresols was observed
- Experimental indication for the formation of polymerization products
- Polymerization might be important in terms of particle mass production in the atmosphere
- Due to missing standard compounds no clear identification and quantification of potential polymerization products possible at this stage
- Method will be further developed in order to identify and quantify polymerization and ring opening products

References

- [1] J. Lüttke, V. Scheer, K. Levsen, G. Wünsch, J.N. Cape, K.J. Hargreaves, R.L. Storeton-West, K. Acker, W. Wieprecht and B. Jones, *Atmos. Environ.*, **1997**, 31, 2637-2648.
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- [3] H.I. Joschek and S.I. Miller, *J. Amer. Chem. Soc.*, **1966**, 88, 3273-3281.
- [4] P. Barzaghi, *Dissertation*, University of Leipzig, **2003**.
- [5] P. Barzaghi and H. Herrmann, *Phys.Chem.Chem.Phys.*, **2002**, 4, 3669-3675.