

Motivation

The tropospheric oxidation of aromatic hydrocarbons (benzene, toluene, and isomers of xylene) results in the formation of phenols or cresols as well as ring fragmentation products. Phenols are known to be formed directly in the atmosphere by the OH-initiated atmospheric oxidation of aromatic hydrocarbons[1].

Nitrate radicals in aqueous solution may undergo reactions with aromatic compounds which have been shown to proceed faster than the corresponding gas-phase reactions by orders of magnitude [2]. From phenol, a mixture of *ortho*- and *para*-nitrophenol is formed. The corresponding reaction in the gas phase has been shown to give essentially the *ortho* isomer. The *ortho/para* ratio in the nitration of phenol could be a useful tool for distinguishing among these mechanisms.

The flash photolysis of nitrate anions at $\lambda = 248$ nm and of peroxydisulphate anions at $\lambda = 351$ nm was used to study the oxidation process of phenol by OH / NO₂ and NO₃ / NO₂ in aqueous solution under different experimental conditions. Two different mononitrophenol (isomer *ortho*- and *para*-) and a dihydroxy derivative (catechol) were identified as the main reaction products by means of HPLC-DAD-ED technique and their yields of formation were directly compared with the initial radical concentrations of OH, NO₂ and NO₃, respectively [3]. A complete scheme of the experimental setup is represented in Figure 1.

Results

An isocratic HPLC procedure was developed and used to analyze mixtures of phenols and nitrophenols in laboratory studies since the relative abundance of the isomeric nitrophenols may be significant for the identification of the mechanism of oxidation process involved. A solid phase extraction step (SPE) was applied in order to enrich the sample. Samples were extracted (Figure 2) with LiChrolut ENV cartridges (Merck). No breakthrough was observed under the present experimental conditions and the recovery rates are quantitative (Table 1, 3).

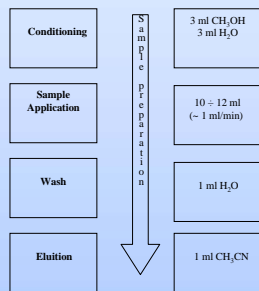


Fig. 2: A schematic representation of the SPE procedure.

Different columns were tested (Table 3) in order to obtain the best resolution for the compounds taken in consideration in this study. A stainless steel column (250 mm x 4 mm I.D.) packed with a regular spherical silica Kromasil (Hyperchrome) with particle size of 5 μ m and porosity of 100 Å derivatized with octadecyl chain was used as stationary phase. The analysis was performed by an isocratic elution with a mobile phase composed by 70% KH₂PO₄ 25 mM (pH = 4 adjusted with H₃PO₄) and 30% CH₂Cl₂ at flow-rate of 0,7 ml/min. All the compounds were good resolved (Figure 3). Quantification was performed using calibration curves at different wavelength where the compounds show relative absorption maxima. Percentage of recovery and calibration curve correlation coefficients are given in Table 3. The electrochemical detector was operated by applying a fixed DC potential to the working electrode of a flow-through electrolysis cell and recording the current resulting from the oxidation of analyte as a function of elution time.

Tab. 2: Columns tested in the present study

Column	Dimension	Description	Particle size(μ m)	Pore diameter(Å)	pH stability	% C
Kromasil C-18	250mm x 4,6	Silica spheric, metal free (Na, Al, Fe < 10ppm)	5	100	2.0 - 7.5	19
Kromasil C-18	250mm x 4,6	Silica spheric, metal free (Na, Al, Fe < 10ppm)	5	100	2.0 - 7.5	16
Zorbax SB C-18	250mm x 4,6	Silica spheric, totally porous	5	80	1.8 - 8.0	-
Nucleosil C-18	250mm x 4	Silica spheric, totally porous	5	100	1.0 - 9.0	24
Lichrospher	250mm x 4	Silica irregular, totally porous	5	100	-	-
Supelkosil abzplus	250mm x 4,6	Silica spheric, bonded phase alkylamide	5	100	2.0 - 7.5	12
Polystyrene-divinylbenzene	250mm x 4,6	polymeric divinylbenzene-polystyrene	5	100	1.0 - 13.0	-

Tab. 3: SPE recoveries and correlation coefficients for the compounds of interest.

Compound	SPE Recovery (%)	UV/DAD Calibration curve corr. coeff.
Phenol	99 ± 4	0.993
2-nitrophenol	89.9 ± 7	0.998
3-nitrophenol	91 ± 6	0.989
4-nitrophenol	98.2 ± 6	0.999
2,4-dinitrophenol	99.1 ± 4	0.997
2,6-dinitrophenol	89.3 ± 5	0.997
1,2-dihydroxybenzene	96.1 ± 7	0.995
1,3-dihydroxybenzene	99.2 ± 4	0.991
1,4-dihydroxybenzene	97.5 ± 5	0.997
1,2,3-trihydroxybenzene	91.1 ± 3	0.988
1,3,5-trihydroxybenzene	93 ± 6	0.988
4-nitrocatechol	92.2 ± 8	0.997

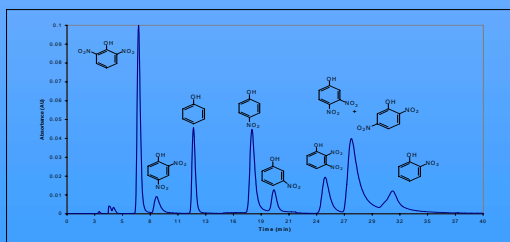


Fig. 3: Chromatogram of the compounds of interest.

Conclusions

- A SPE procedure was developed in order to obtain recovery close to 100% for all of the compounds taken in consideration in the present study
- A HPLC-DAD-EC procedure was developed and coupled with a LFP- LPLA experiment in order to determine the possible oxidation pathways of phenol in aqueous solution. Absolute product yields were determined [3].

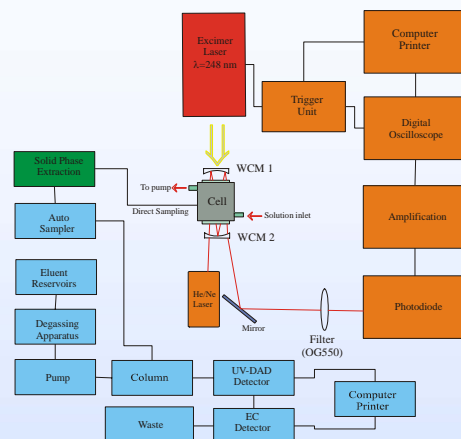


Fig. 1: Experimental set-up LP-LPA - product study (HPLC-UV-EC) experiment

Further studies were performed to get a better detection limit for some of the compounds here presented. Other three stationary phase were taken in consideration and the results are presented in Figure 4 and in Table 4 is reported a comparison of the detection limits achieved in this work with some literature values

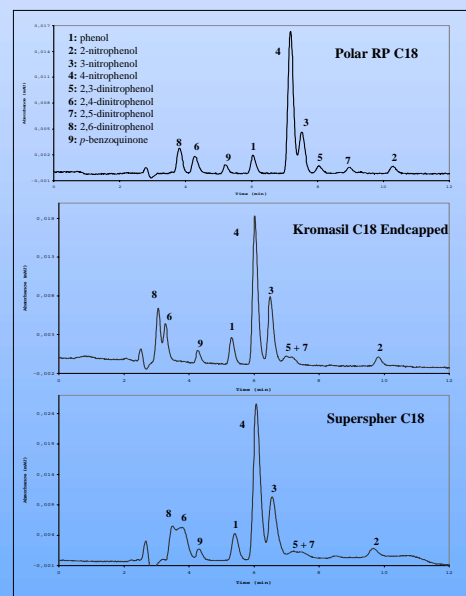


Fig. 4: Comparison of three different column under the same experimental conditions.

Tab. 4: Comparison of the detection limits present in literature

Compound	UV- This work ng/ml	1) UV- ng/ml	EC- This work ng/ml	2) EC- ng/ml	3) CL- a ng/ml	4) FL- a ng/ml	5) FL- b ng/ml
Phenol	40	130	n.d.	0.03	0.4	40	Lower ppt
2-nitrophenol	52	140	2.3	0.08	0.5	n.d.	Lower Ppt
4-nitrophenol	59	112	1.4	0.18	0.4	n.d.	Lower ppt

a. precolumn derivatization with dansyl chloride postcolumn photolysis and peroxyoxalate chemiluminescence detection.
b. postcolumn oxidation of Ce(IV).

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- 3) Kwakman et al. *J.Chromatogr.*, (1991), 553, 345.
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References

- [1] B. Klotz, I. Barnes, K. H. Becker and B. T. Golding, *J. Chem. Soc. Faraday Trans.*, 1997, 93, 1507.
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