Development of a hollow fiber liquid-phase microextraction method coupled with capillary electrophoresis/mass spectrometry for determining nitrophenolic compounds from atmospheric particles

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Motivation

- Nitrophenolic compounds are known for their negative effect on human health as they are genotoxic.
- Nitrophenols have the ability to absorb solar radiation from the near ultraviolet to low visible wavelengths, thus they are also contributing to the so-called brown carbon.
- Most of the available methods for determining nitrophenols in particulate matter are using organic solvents for extraction. However, those methods are not applicable if one wants to focus only on the water-soluble fraction.
- Hollow fiber liquid-phase microextraction (HF-LPME) provides a simple setup for enrichment from water with potential for high enrichment factors
- Analysis from small volume samples are carried out by capillary electrophoresis-ion trap mass spectrometry (CE-ITMS)

HF-LPME

- Preconcentration of water extract by HF-LPME (method reviewed in Pedersen-Bjergaard and Rasmussen 2008)
- Organic solvent is immersed in the pores of the hollow fibre forming the supported liquid membrane (SLM)
- Acceptor phase is introduced into the hollow fibre

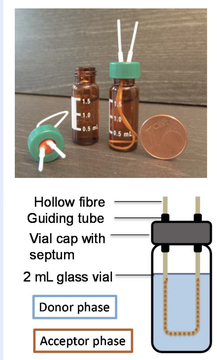

Fig. 1: HF-LPME device.

Starting point for parameter optimization based on van Pinxteren et al. 2012:
- Donor phase: 1.8 mL
- aqueous standard solution (pH 2)
- Supported liquid membrane (SLM): dihexyl ether (DHE)
- Acceptor phase: 15 µL 50 mM NH_4OH
- t = 2 h; 2000 rpm

Separation conditions

CE conditions:
- Electrolyte: 20 mM ammonium acetate
- pH 9.7
- 15% (v/v) methanol as additive to electrolyte

ITMS conditions:
- Sheath liquid: ispropanol/H_2O (80:20); 0.4 mL/h
- Electrospray ionisation: negative mode; 4.5 kV
- Nebulizing gas: 4 psi
- Drying gas: 10 L/min

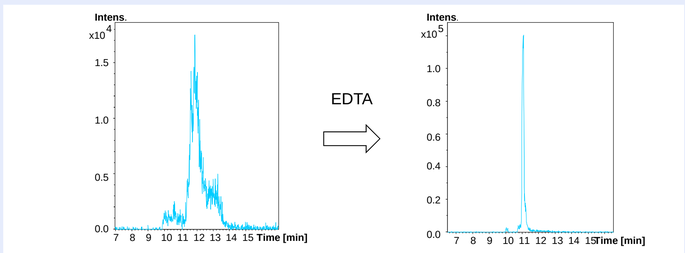

Fig. 2: Extracted ion chromatogram of 4-nitrocatechol. Improvement of peak shape by flushing the capillary with EDTA solution.

- 4-nitrocatechol showed a very broad peak and peak tailing
- Kitanovski et al., 2012, suggested that this observation might be caused by metal ions forming complexes with 4-nitrocatechol. They used ethylenediaminetetraacetic acid (EDTA) as a complexing agent
- Flushing the capillary with 5 mM EDTA solution prior to analysis acceptable results

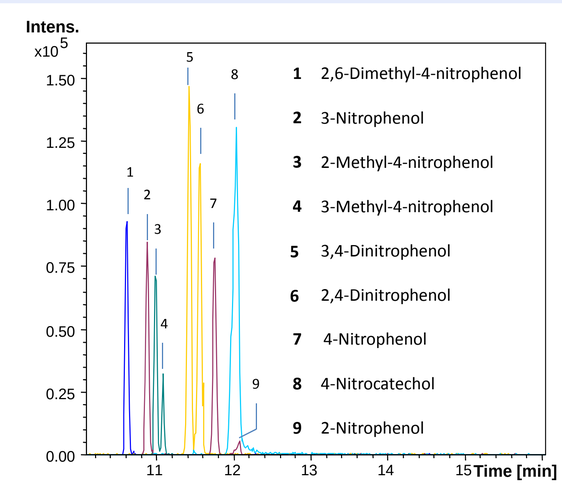

Fig. 3: Example of an electropherogram of a standard solution containing target species.

Optimization of extraction parameters

1. Composition of liquid membrane

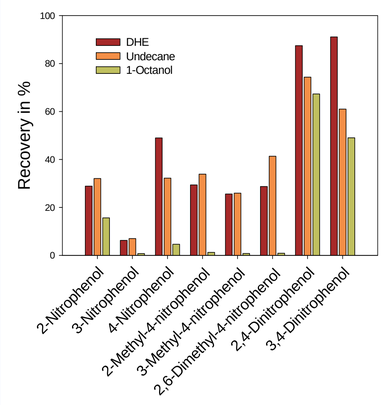

Fig. 4 :Influence of different organic solvents on recovery.

DHE was chosen as the liquid membrane

DHE was kept as liquid membrane phase without addition of trioctylphosphine oxide (TOPO)

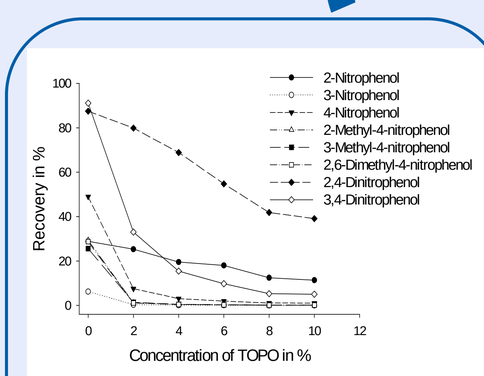

Fig. 5: Influence of the TOPO concentration on recovery.

2. Salting out effect

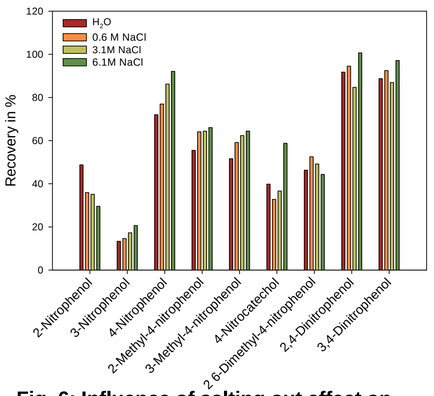

Fig. 6: Influence of salting out effect on recovery.

no salt was added to the donor phase for further experiments

3. Optimization of acceptor phase pH

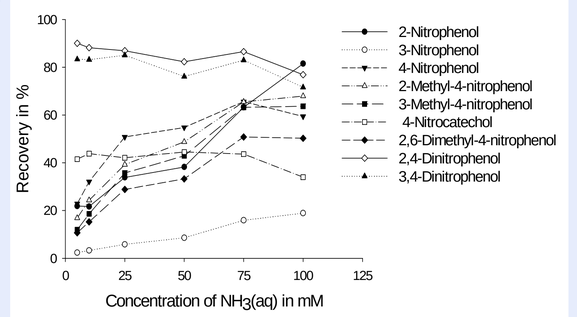

Fig. 7: Influence of acceptor phase pH on recovery.

100 mM NH_3(aq) was chosen as acceptor phase

4. Effect of extraction time

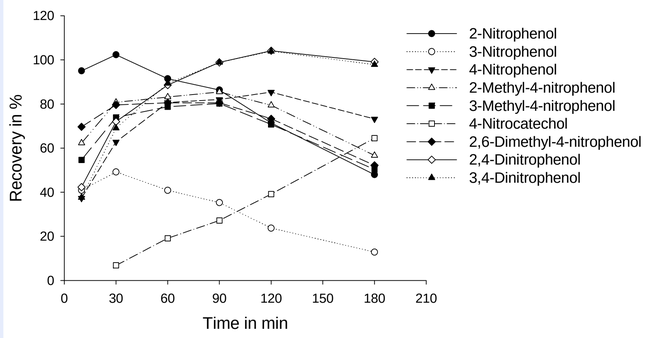

Fig. 8: Influence of extraction time on recovery.

60 min was chosen as a compromise between short extraction times and high recoveries

Final parameters:
15 µL 100 mM NH_3(aq) as acceptor phase, DHE as SLM, 1.8 mL donor phase, pH 2 with H_2SO_4, 1 h extraction time

5. Figures of merit

Table 1: Figures of merit for CE-ITMS and the final HF-LPME method

m/z	Compound	MT min	c(Donor)[a] µmol L^{-1}	Intraday Repeatability (RSD PA, n=5)		Interday Repeatability (RSD PA, n=14)		R	EF	LOD		
				CE-ITMS (%)	HF-LPME (%)	CE-ITMS (%)	HF-LPME (%)	HF-LPME (%)	HF-LPME (%)	CE-ITMS (µmol L^{-1})	HF-LPME (µmol L^{-1})	Atmosphere[b] (ng m^{-3})
166.16	2,6-Dimethyl-4-nitrophenol	13.3	0.4	12	10	9	7	65	78	0.125	0.001	0.01
138.11	3-Nitrophenol	13.7	0.8	6	6	5	10	30	36	0.1	0.004	0.04
152.14	2-Methyl-4-nitrophenol	13.9	0.8	12	14	6	9	75	90	0.05	0.004	0.04
152.14	3-Methyl-4-nitrophenol	14.0	0.4	9	15	6	10	51	62	0.025	0.0004	0.004
154.11	4-Nitrocatechol	14.2	0.8	6	59	7	48	11	13	0.5	0.04	0.5
183.11	3,4-Dinitrophenol	14.6	0.4	6	14	7	6	69	83	0.05	0.0004	0.01
183.11	2,4-Dinitrophenol	14.7	0.4	12	12	6	8	63	75	0.05	0.0004	0.01
138.11	4-Nitrophenol	15.0	0.8	3	15	5	9	64	77	0.1	0.0008	0.01
138.11	2-Nitrophenol	15.4	2.5	22	17	28	35	21	25	7.5	0.25	2

a) Donor phase concentration used to determine HF-LPME repeatability, recovery (R), and enrichment factor (EF).
b) Calculated for a sampled air volume of 25.9 m^3 per 1.8 mL donor phase.
MT: migration time; PA: peak area; LOD: limit of detection; CE-ITMS: capillary electrophoresis-ion-trap mass spectrometry

Application to ambient filter samples

Table 2: Mass concentrations obtained from three filter samples compared with concentrations determined in other studies

Analyte	Mass concentration in ng m^{-3}								
	This study[a] Melpitz, Germany						Kitanovski et al. [a] Ljubljana, Slovenia	Zhang et al. [b] Mainz, Germany	Cecinato et al. [c] Rome, Italy
	24.01.12		30.08.12		23.10.12		Winter 2010/2011	May 2006 – June 2007	Feb 2003 – Apr 2003
	SA[d]	ExCal[d]	SA[d]	ExCal[d]	SA[d]	ExCal[d]	(n=15)	(n=58)	(n=12)
2-Nitrophenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD		1.81 (<LOD-8.51)	3.5
3-Nitrophenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD			
4-Nitrophenol	0.77	0.97	0.06	0.07	0.54	0.58	1.8 (0.5-3.7)	3.78 (<LOD-12.52)	17.8
2-Methyl-4-nitrophenol	0.51	0.58	<LOD	<LOD	0.16	0.17	0.75 (0.31-1.5)		
3-Methyl-4-nitrophenol	0.46	0.51	<LOD	<LOD	0.09	0.09	0.61 (0.25-1.2)		7.8
4-Nitrocatechol	0.62	1.30	<LOD	0.48	0.52	2.61	75 (16.9-152)	4.49 (<LOD-28.72)	
2,6-Dimethyl-4-nitrophenol	0.04	0.06	<LOD	<LOD	<LOD	<LOD			5.9
2,4-Dinitrophenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.02 (0.02-0.05)		
3,4-Dinitrophenol	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD			

a) PM10.
b) Total suspended particles.
c) PM5.
Standard addition (SA) and external calibration (ExCal) were compared for three samples.

- The external calibration curve was obtained from aqueous standard solutions at different donor concentration levels after extraction with HF-LPME.
- Five nitrophenols could be successfully determined in the aerosol particle samples
- The ExCal gave two to five times higher concentrations compared to standard addition for 4-nitrocatechol.
- As 4-Nitrocatechol is a good complexing agent, interferences with metal ions may influence the extraction of this compound. Thus, quantitative data for 4-nitrocatechol carry substantial uncertainty and should be taken with care when external calibration has been applied.

Conclusions

- The developed HF-LPME method combined with capillary electrophoresis-mass spectrometry (CE-MS) analysis, yielded very low limit of detections in the range of nanomole per liter.
- Satisfactory interday and intraday repeatabilities could be obtained for most of the investigated compounds.
- Persistent peak shape problems observed for 4-Nitrocatechol could be improved by flushing the capillary with EDTA solution.
- Five nitrophenols could be quantified in three filter samples with 4-nitrophenol and 4-nitrocatechol showing the highest concentrations.

➢ HF-LPME combined with CE-MS analysis provides an attractive alternative to the more established methods with high enrichment factors and good repeatability. It was found suitable to determine low concentrations of nitrophenols in aerosol particles.

➢ Further details can be found in Teich et al. 2014

References

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