

Analysis of ionic micropollutants using capillary electrophoresis-mass spectrometry and prefractionation with free flow electrophoresis

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Introduction

Monitoring concentrations of environmentally relevant substances in surface waters is challenging due to the high diversity of their physicochemical properties. We here show that CE-MS is a promising alternative to HILIC- and IC-MS especially for ionizable and ionic micropollutants. To meet the detection limits required for environmental analysis, we here combine CE-MS with free flow electrophoresis for analyte enrichment and prefractionation. Fractionation was based on an FFE protocol using a step-wise pH gradient between 5.0 and 10.3.

Conclusion

- 5 model analytes spiked into a wastewater treatment plant effluent were prefractionated with a commercial FFE system.
- Subsequent CE-MS analysis was established resulting in estimated LODs between 20 and 100 µg/L.
- FFE proved to be advantageous for prefractionation and matrix removal with analytes detected in 2-10 out of 40 fractions taken.
- Optimization of width of the fractions and detection limit using higher sample volumes is envisaged.

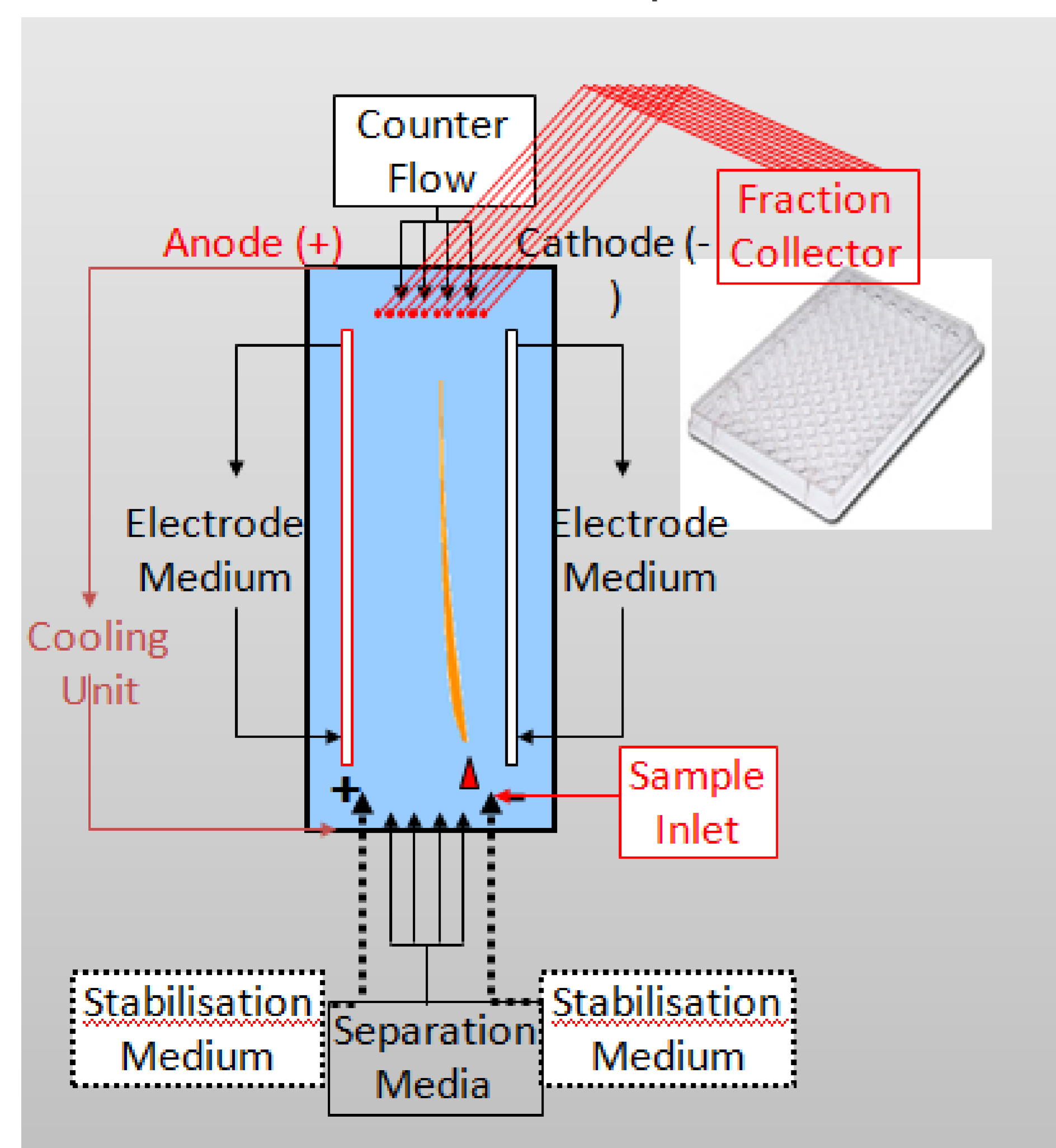
Figures of merit

General compatibility of CE-MS with the FFE-separation was demonstrated by spiking and analyzing the different media used. For three analytes (2-NSA, UMBE and HCT) average recoveries between 105 and 111 % were achieved. Migration time (MT) and peak area precision ranged from 1-1.4 % and 2.3-3.2 % RSD, respectively.

analyte	pKa [1]	RSD in %			est. LOD in µg/L	
		MT	peak area	recovery in %	A2 (pH 5.2)	D8 (pH 9)
2-naphthalene sulfonic acid (2-NSA)	-1.8	1.0	2.6	109	108	23
umbelliferone (UMBE)	7.8	1.4	2.3	105	93	56
sulfamethoxazole (SULFA)	6.2				59	62
ibuprofen (IBU)	4.9				57	59
hydrochlorothiazide (HCT)	9.1	1.3	3.2	111	-	432
phenol (PHE)	10.0					

FFE fractionation

6 separation media were made from a volatile acid and base with different concentration resulting in steps of pH 5.0-10.3. They were injected simultaneously into the separation cell of a commercial FFE-instrument. The step pH gradient was flanked by stabilization media of elevated conductivity (factor 15), on either side of electrodes. Care was taken to avoid analyte loss from the separation cell into the electrode compartment.

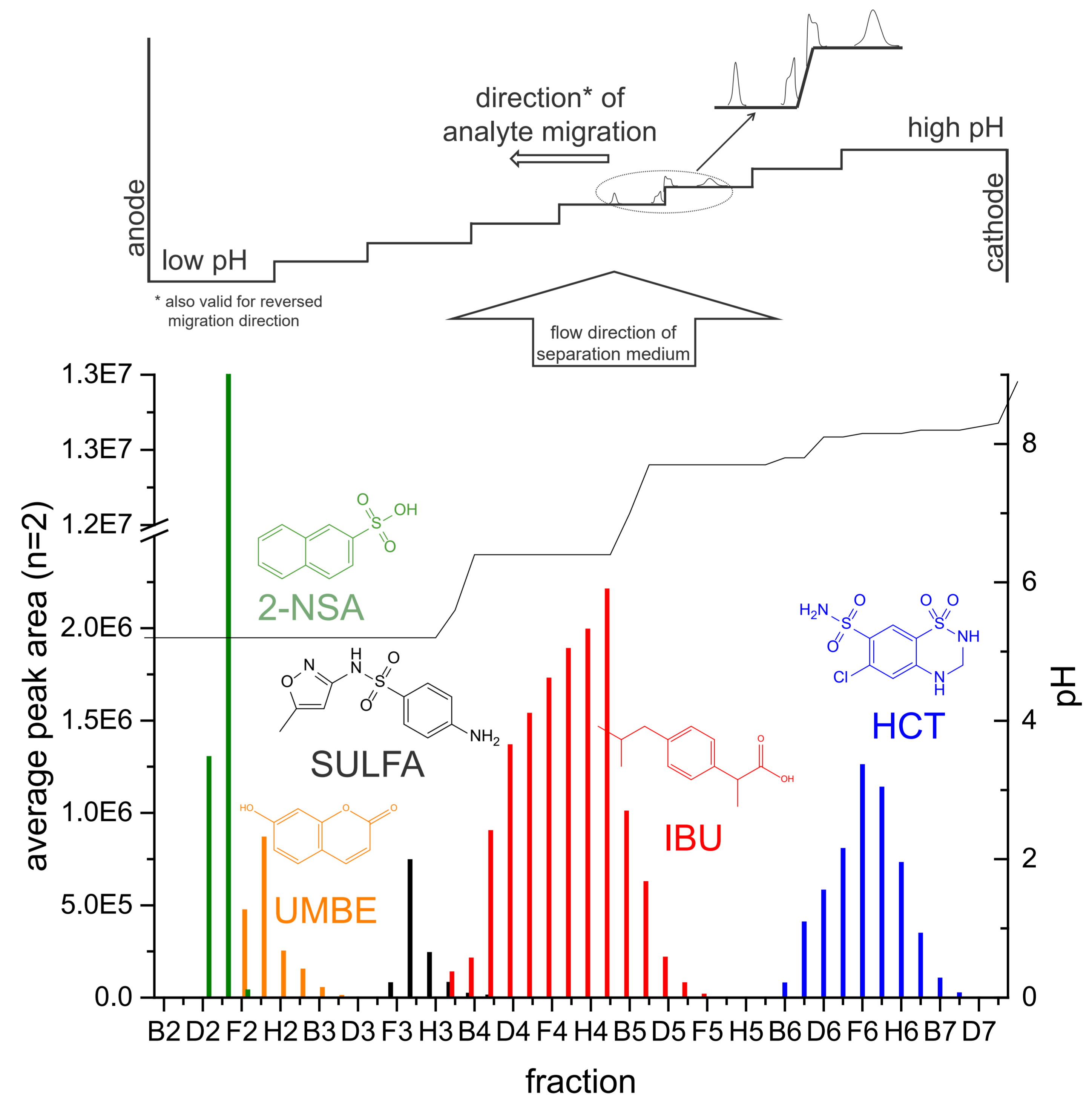


FFE separation parameters were:
1000 V

transit time 5 min

sample injection rate:
100 µL/5 min for interval zone electrophoresis (iZE)-mode of operation)
or
5 mL/h (continuous mode of ZE).

[1]: pK_a values were simulated with ChemAxon



FFE fractions of spiked wastewater effluent were diluted with water (1:10) for CE-MS analysis. Model analytes were present in 2-10 consecutive fractions. Matrix effects and thus LODs were higher in fractions of low pH.

CE-MS analysis

To achieve sufficient ionization of the model analytes, a BGE containing 20 mM NH₄Ac at pH 9 was chosen. A neutral polyvinyl alcohol coating was used to suppress the EOF. To enable direct injection of the undiluted FFE fractions, the ionic strength of the BGE was high with 30 mM NH₄Ac at pH 9. Phenol could not be detected by CE-MS, however, identification with UV-detection was possible in the later fractions at pH 9.

