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Supplement of

Development of an online-coupled MARGA upgrade for the 2 h interval quantification of low-molecular-weight organic acids in the gas and particle phases

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Electronic Supplementary Material

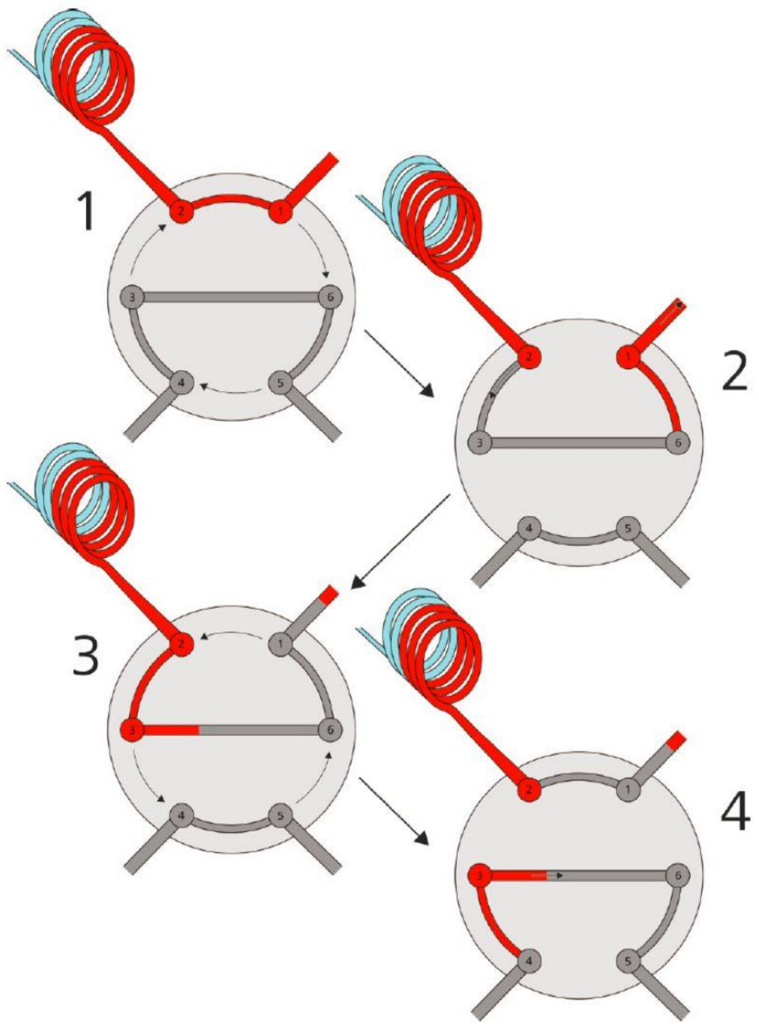


Figure S1. Switch modes of the external 6-way-valve. (1) Sample loop is filled with the sample solutions. In (2) and (3) valve is switched to "fill mode" to pre-concentrate the sample. During the "injection mode" in (4), the eluent dissolved the trapped ions and flows to the separation columns. (https://www.metrohm.com/de-de/produkte/ionenchromatographie/ionen chromatographie-inline-probenvorbereitung/, 10th August 2018)

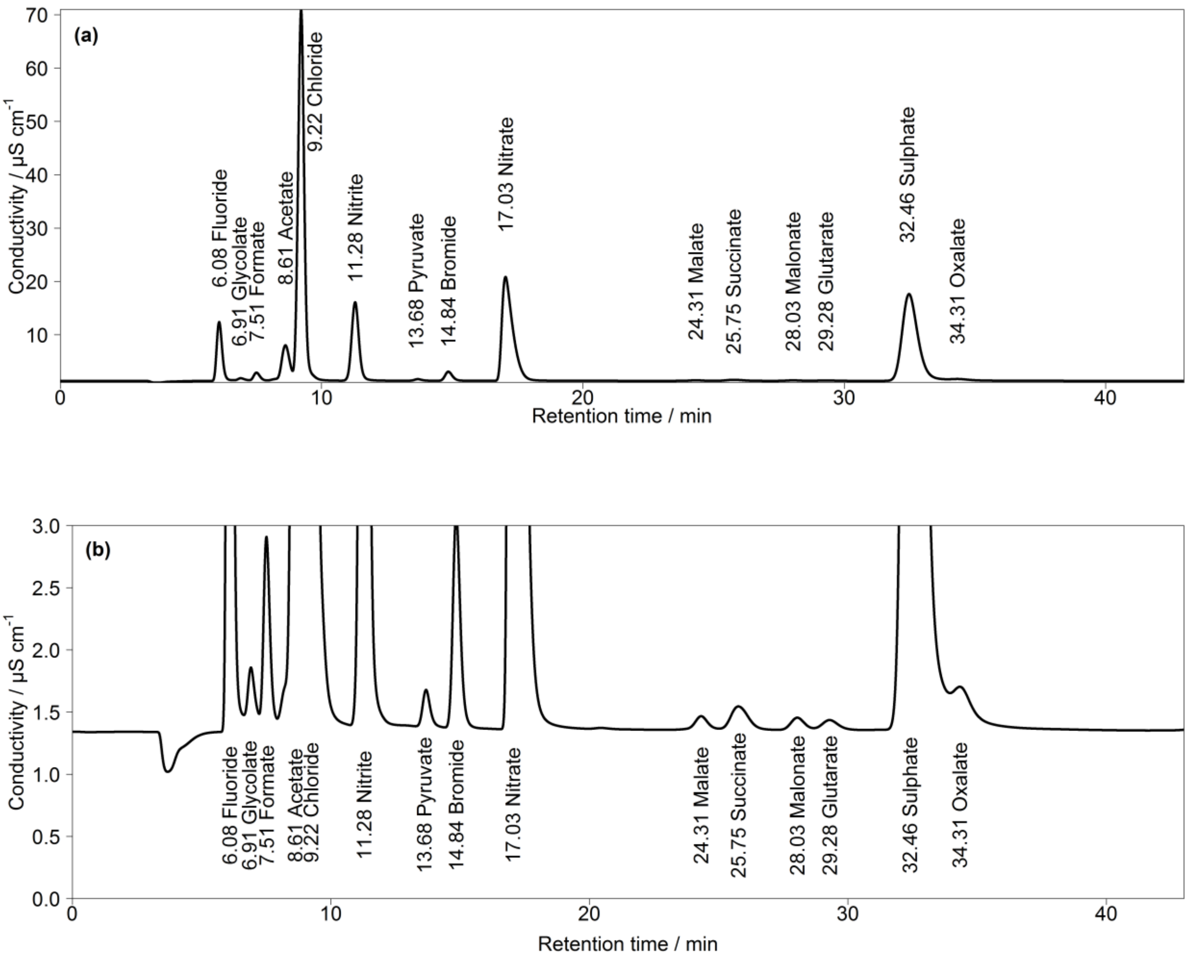


Figure S2. (a) Chromatogram of a standard solution with aqueous concentrations of 150 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 75 µg l^{-1} for NO_2^-, 15 µg l^{-1} for F^-, Br^- and 3 µg l^{-1} for all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of (a).

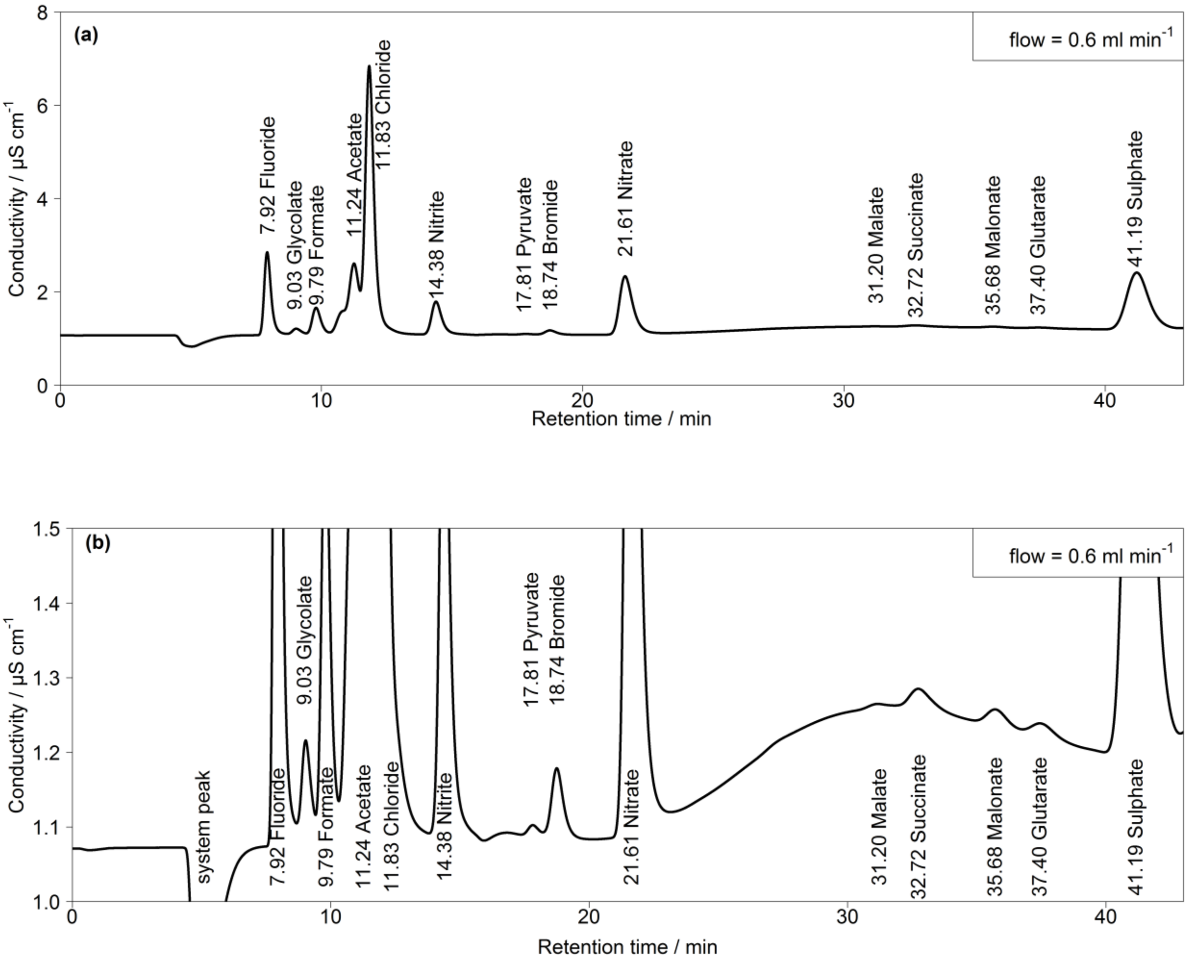


Figure S3. (a) Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.6 ml min^{-1}. (b) Zoom in of chromatogram in (a).

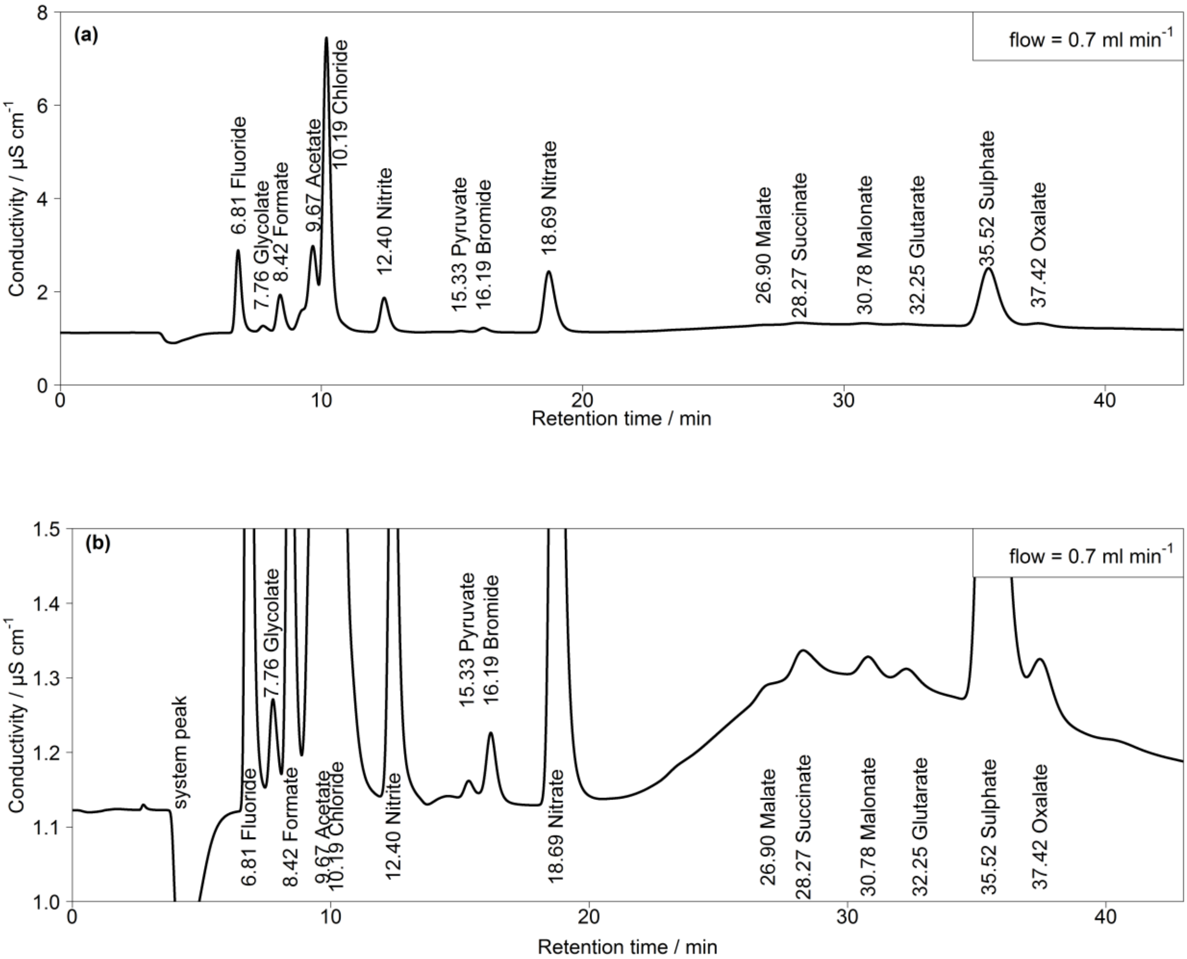


Figure S4. (a) Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.7 ml min^{-1}. (b) Zoom in of chromatogram in (a).

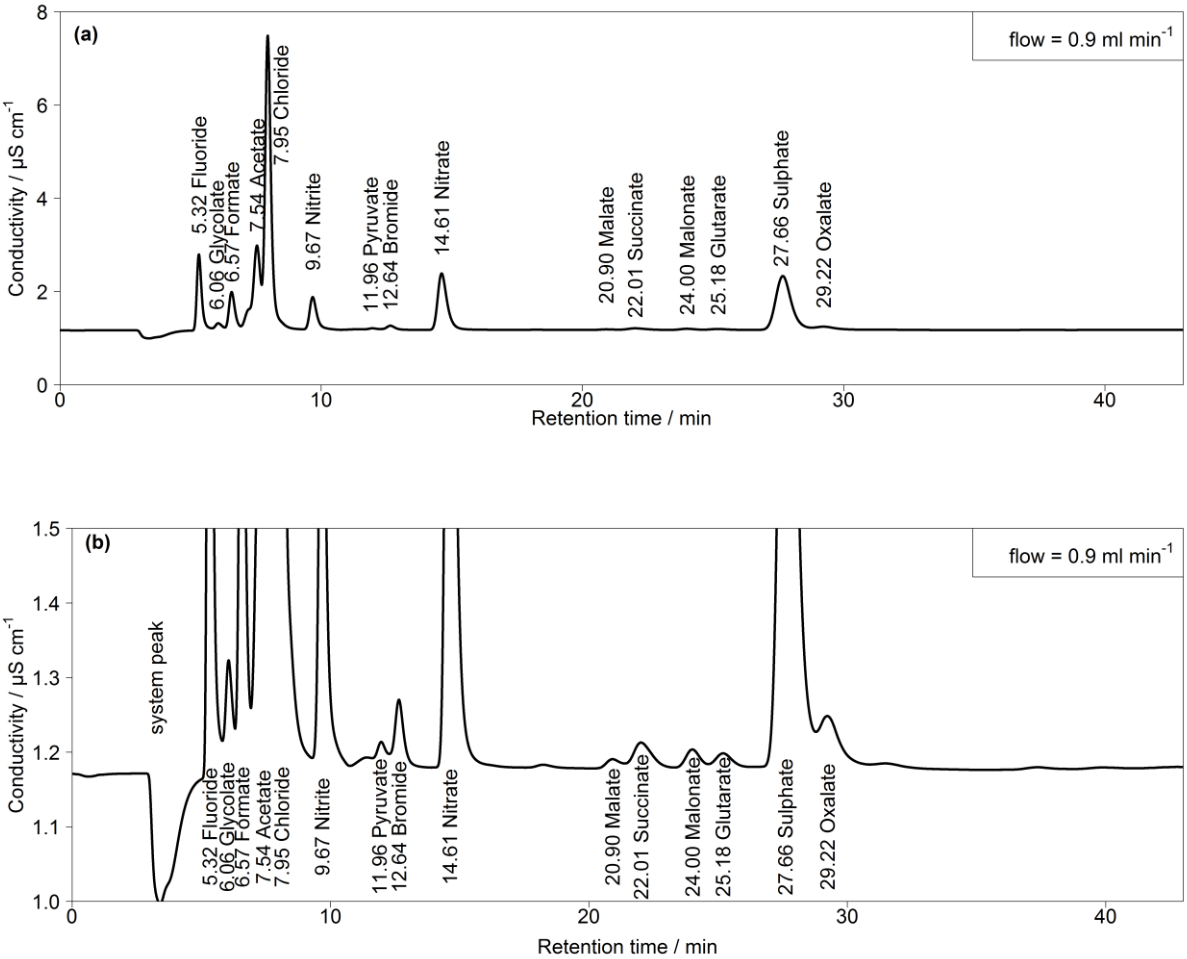


Figure S5. (a) Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.9 ml min^{-1}. (b) Zoom in of chromatogram in (a).

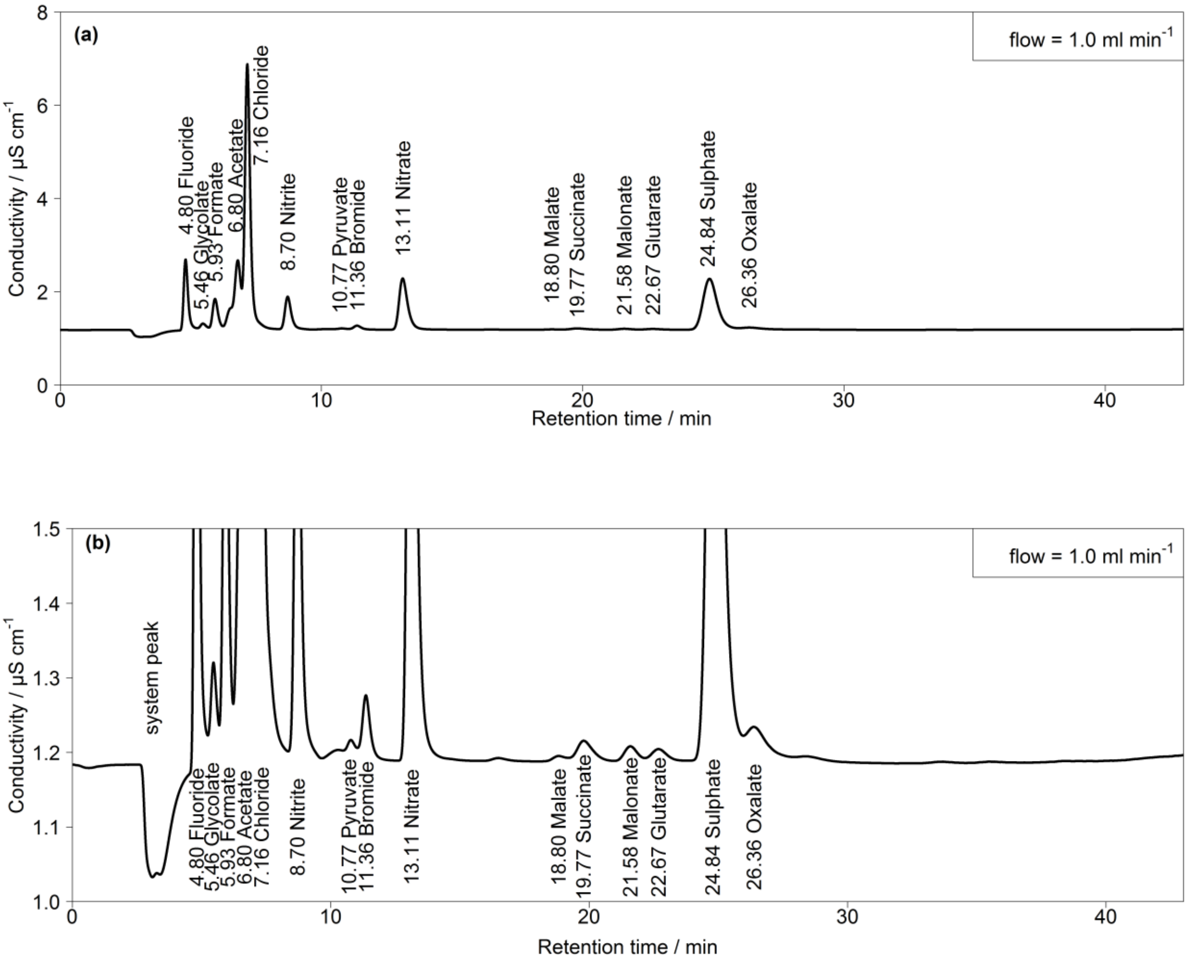


Figure S6. (a) Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 1.0 ml min^{-1}. (b) Zoom in of chromatogram in (a).

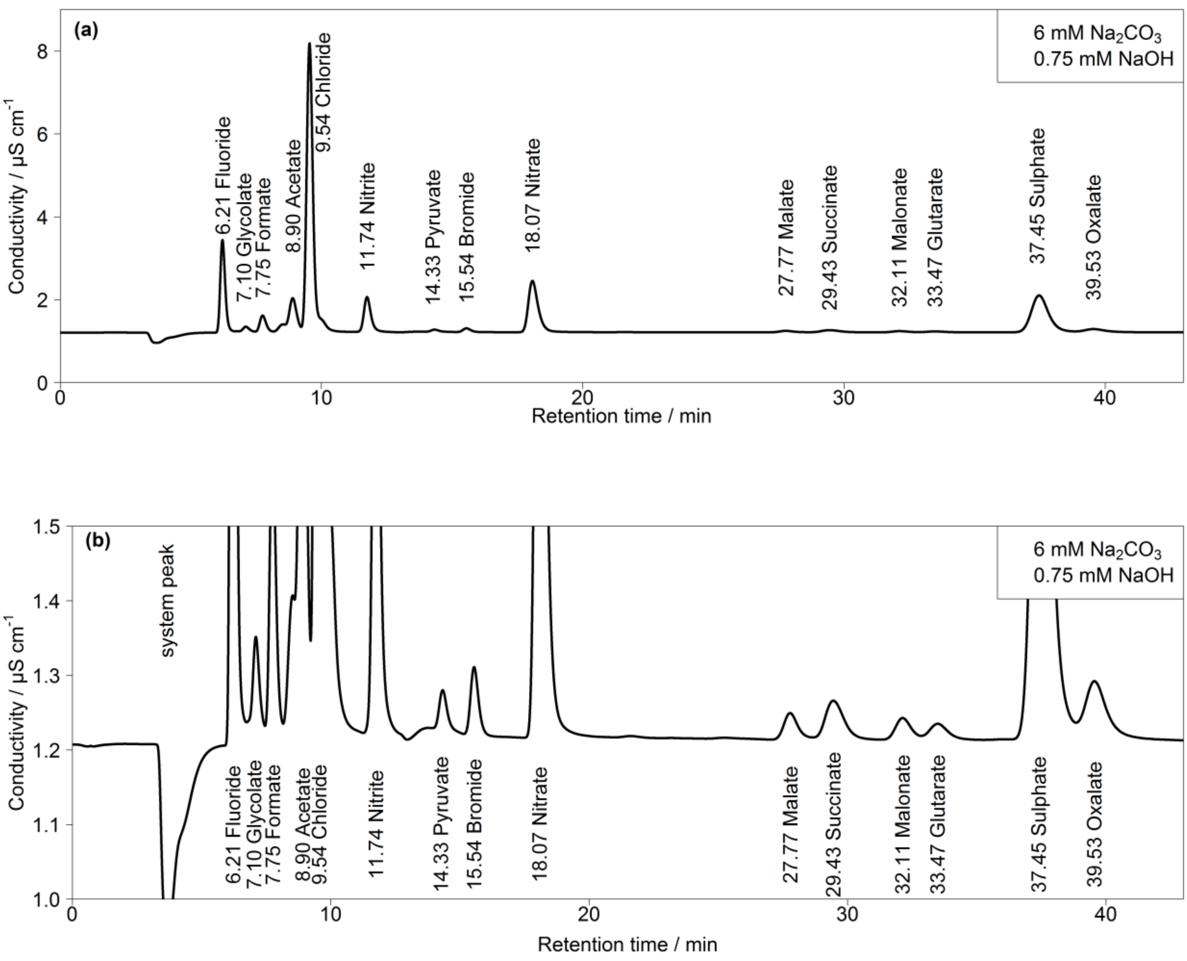


Figure S7. (a) Different eluent concentration of 6 mM Na_2CO_3 and 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of chromatogram in (a).

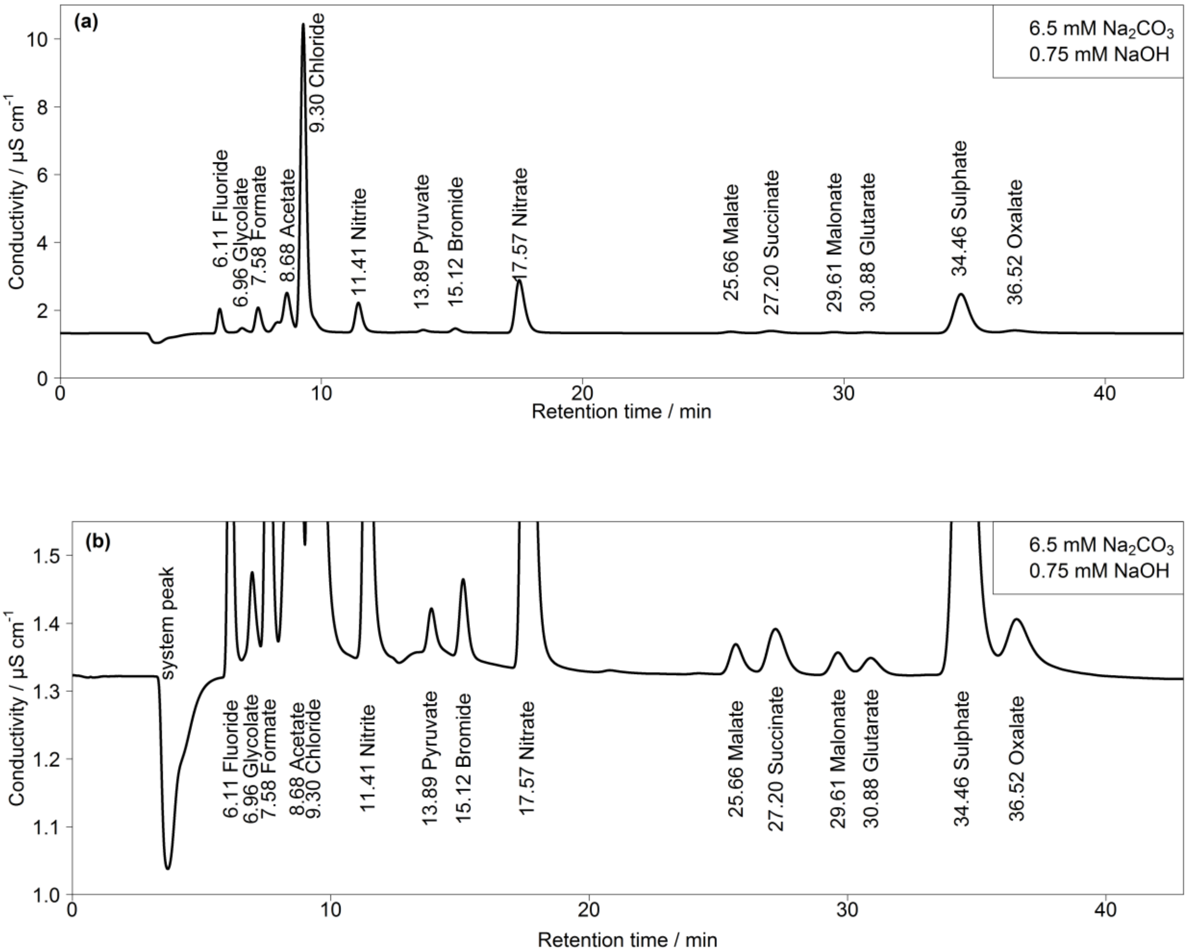


Figure S8. (a) Different eluent concentration of 6.5 mM Na_2CO_3 and 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of chromatogram in (a).

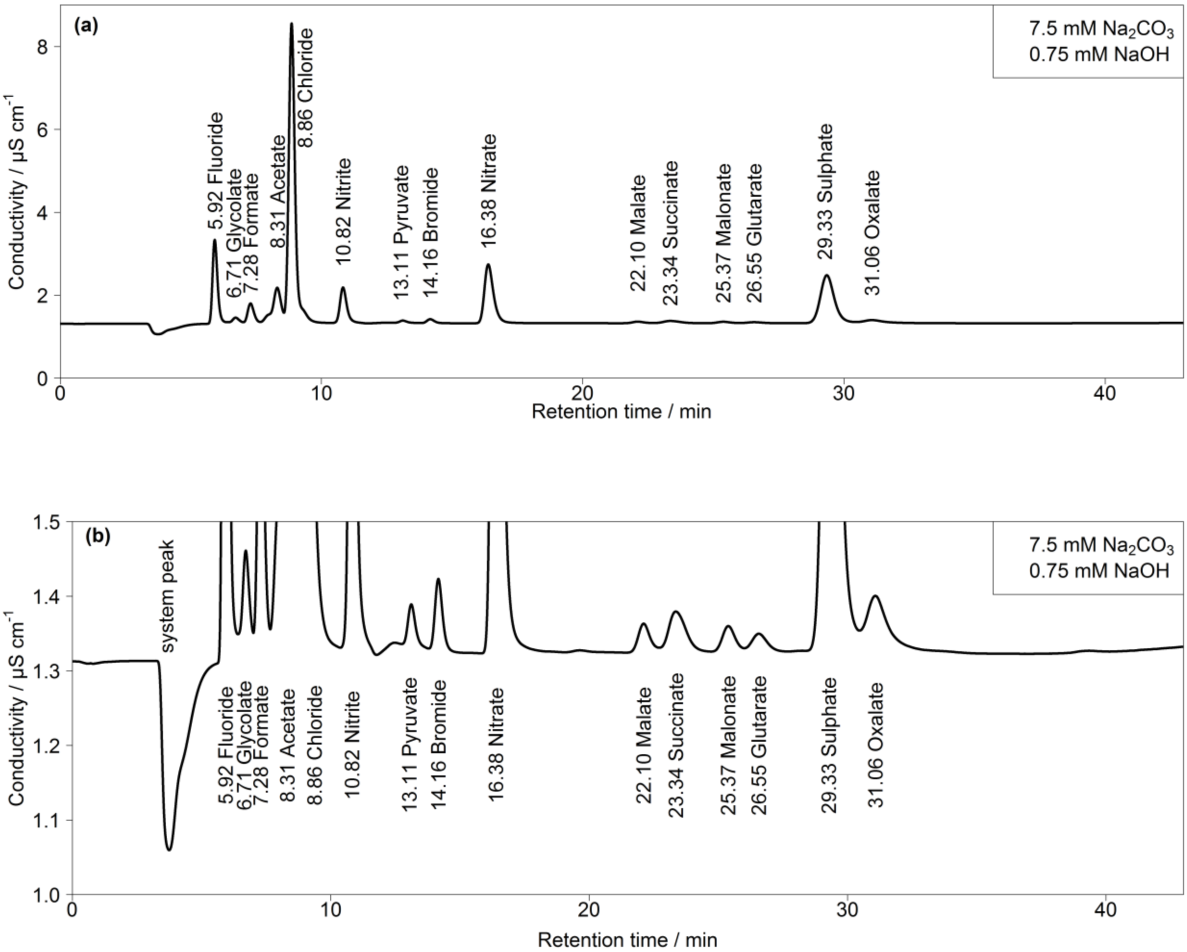


Figure S9. (a) Different eluent concentration of 7.5 mM Na_2CO_3 and 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of chromatogram in (a).

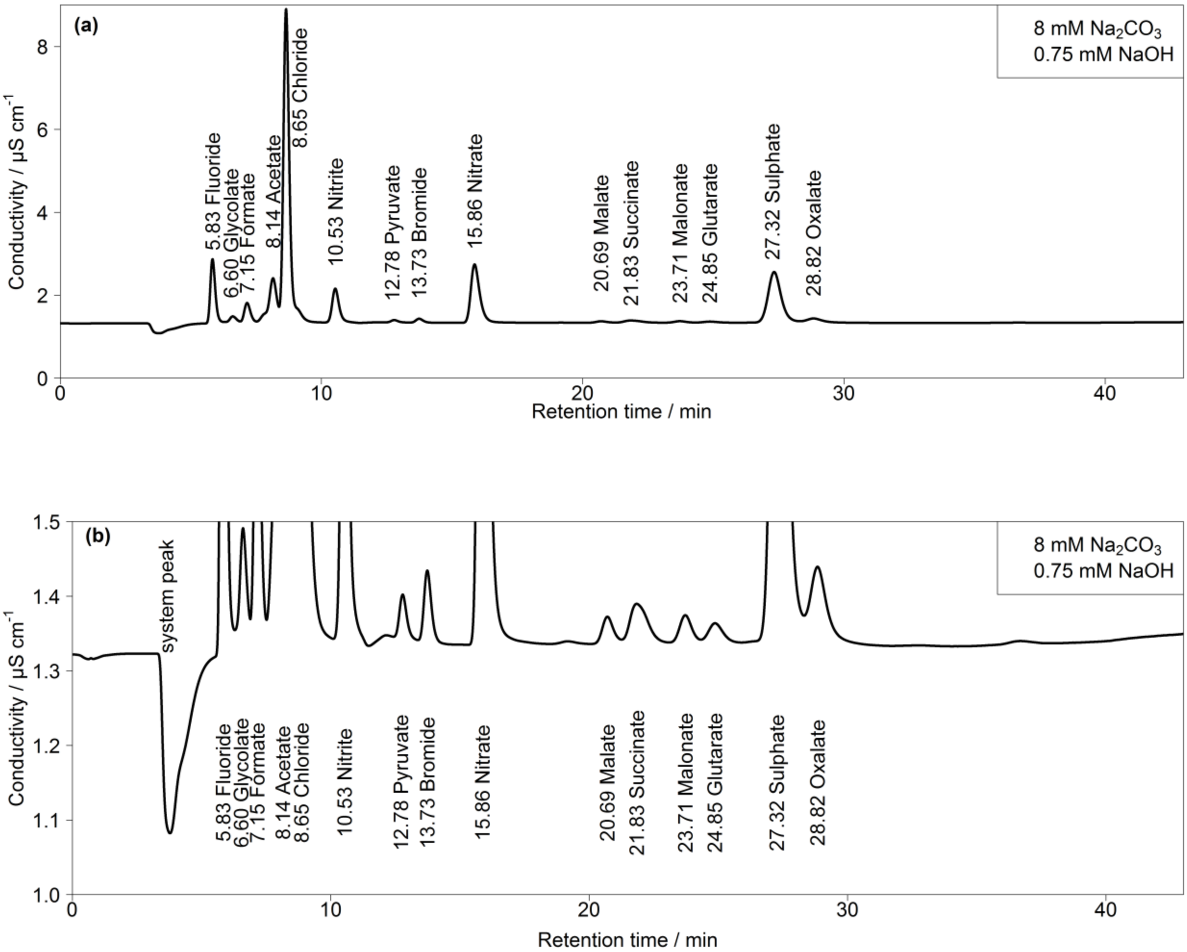


Figure S10. (a) Different eluent concentration of 8 mM Na_2CO_3 and 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of chromatogram in (a).

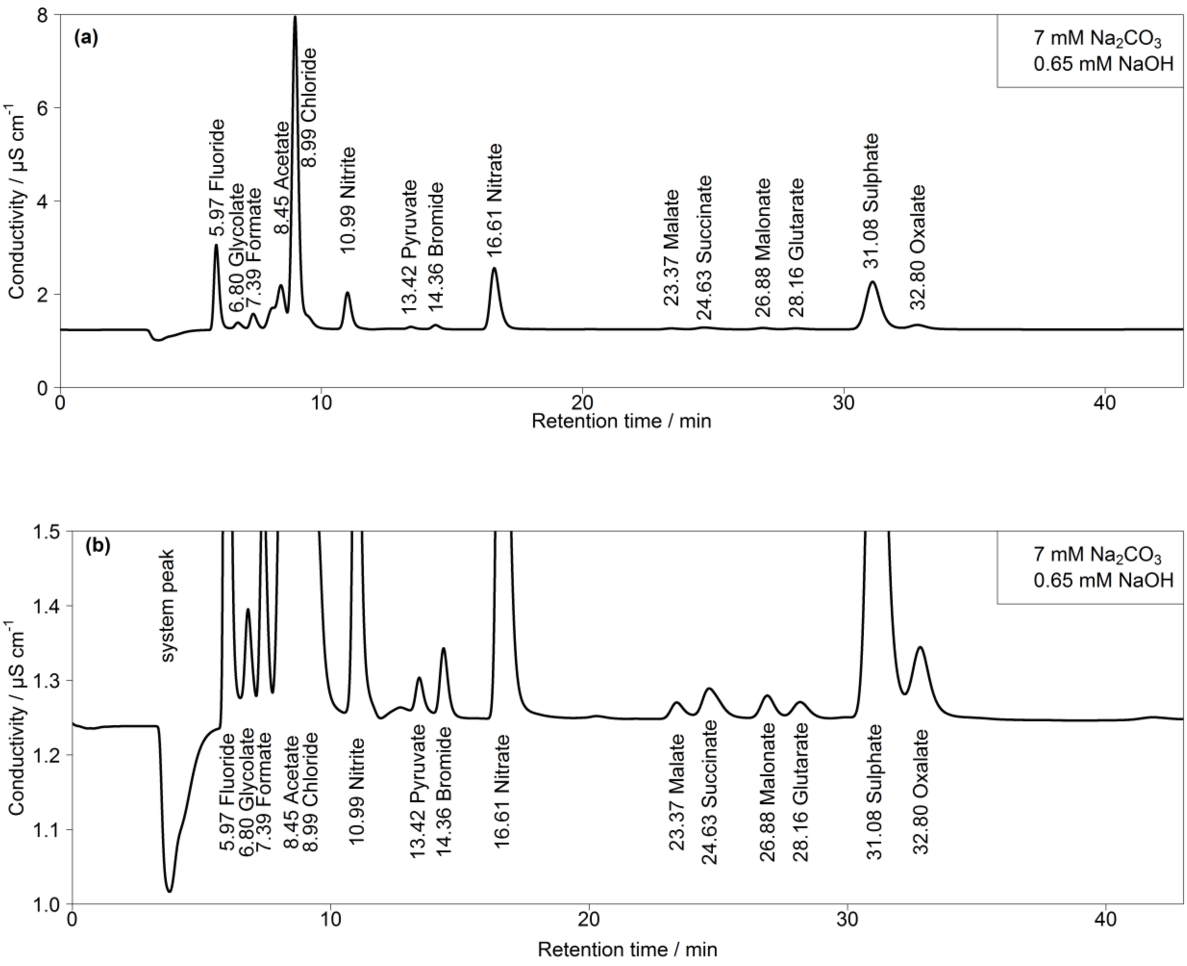


Figure S11. (a) Different eluent concentration of 7 mM Na_2CO_3 and 0.65 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of chromatogram in (a).

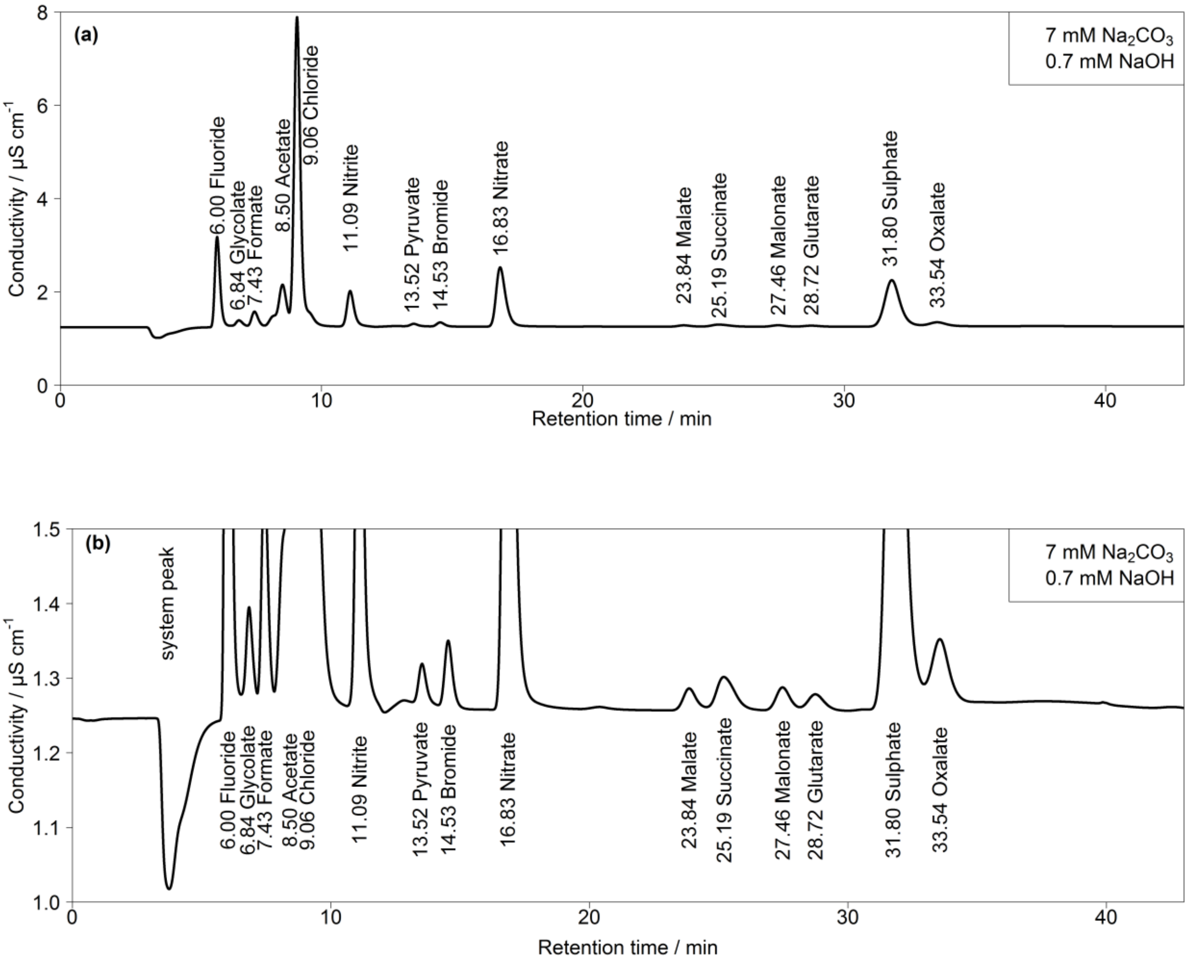


Figure S12. (a) Different eluent concentration of 7 mM Na_2CO_3 and 0.7 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of chromatogram in (a).

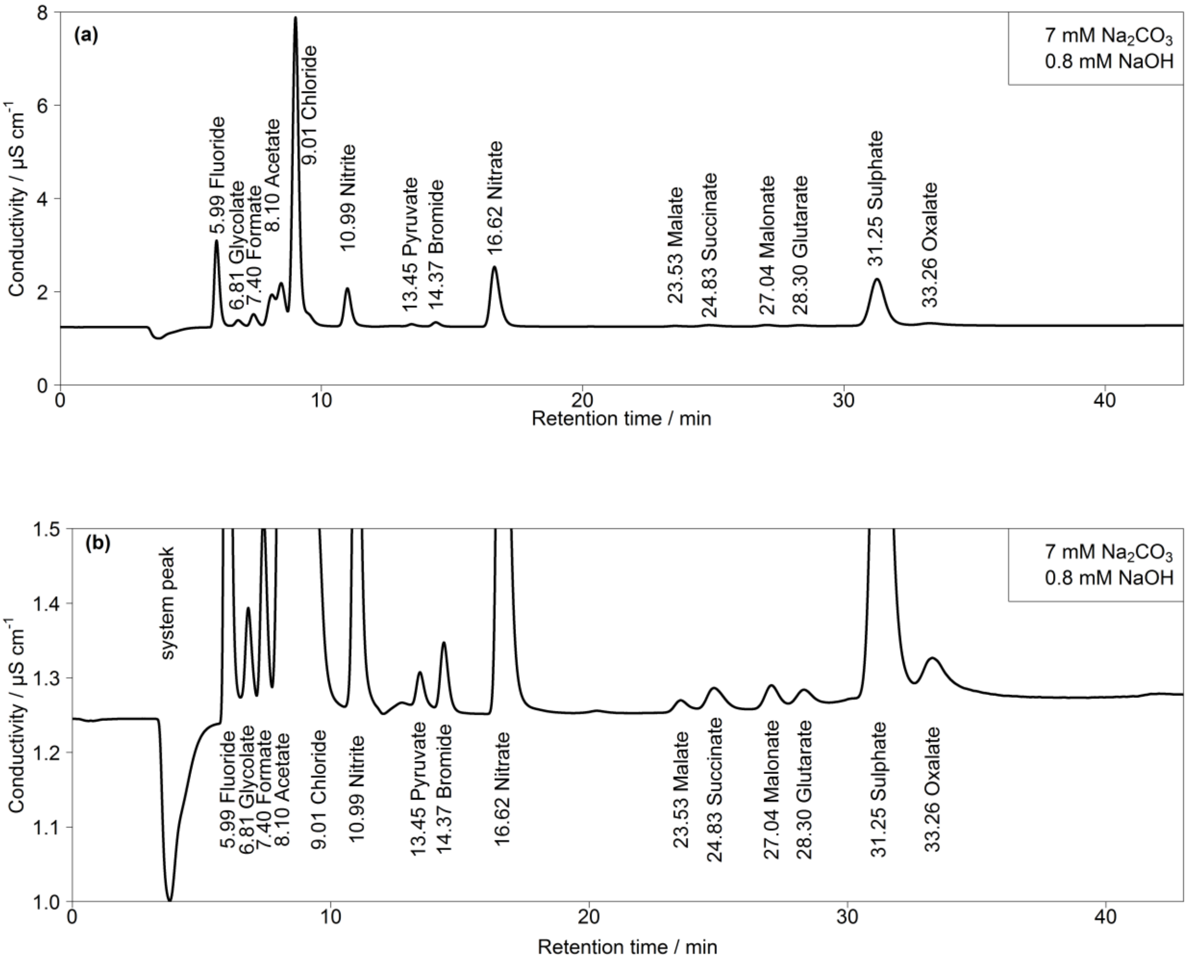


Figure S13. (a) Different eluent concentration of 7 mM Na_2CO_3 and 0.8 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of chromatogram in (a).

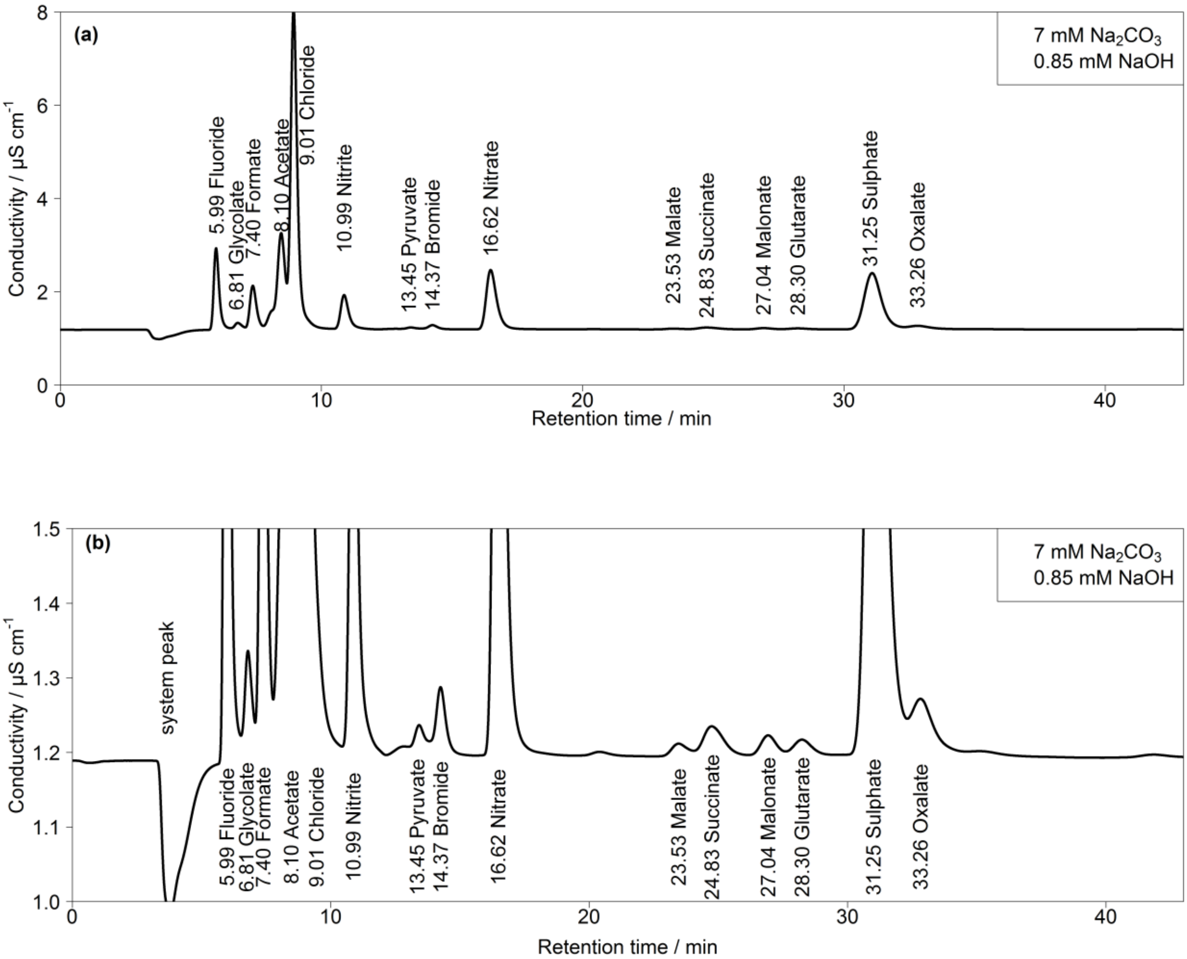


Figure S14. (a) Different eluent concentration of 7 mM Na_2CO_3 and 0.85 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 5 µg l^{-1} for NO_2^- and 1 µg l^{-1} for F^-, Br^- as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min^{-1}. (b) Zoom in of chromatogram in (a).

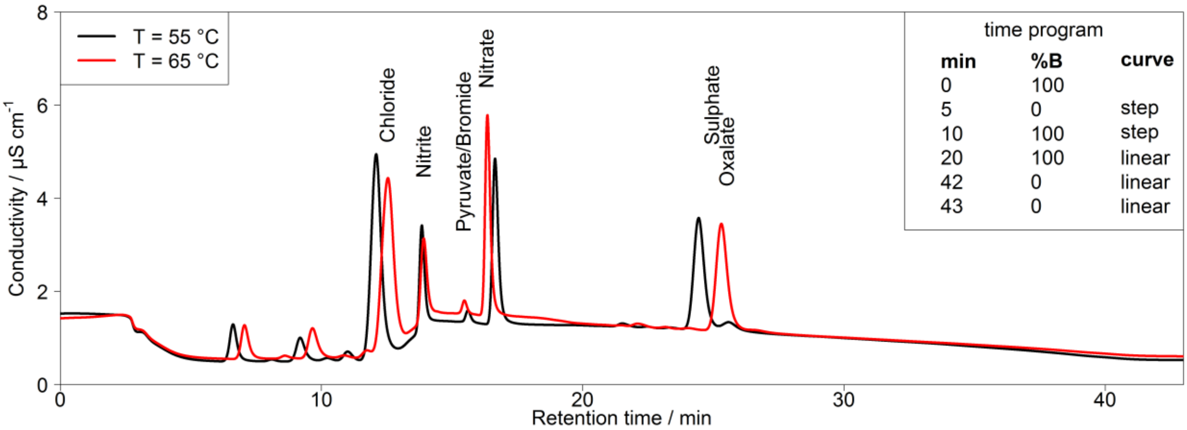
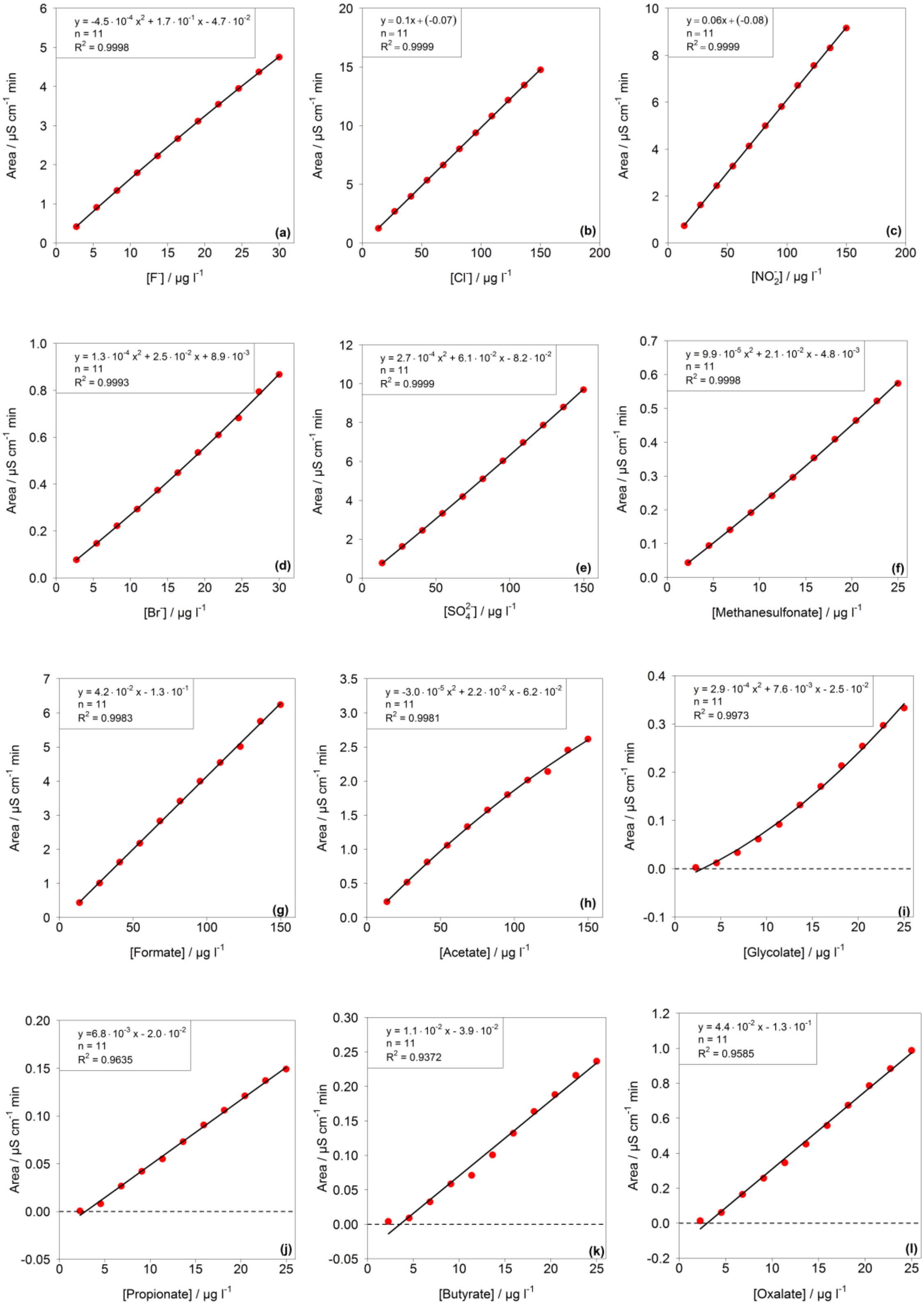


Figure S15. Temperature variation of the column oven for 55 °C (black) and 65 °C (red). Eluent A concentration is 1 mM Na_2CO_3 / 0.75 mM NaOH and eluent B is 14 mM Na_2CO_3 / 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 50 µg l^{-1} for Cl^-, NO_3^-, SO_4^{2-}, 25 µg l^{-1} for NO_2^- and 3 µg l^{-1} for F^-, Br^- as well as all organic acids. Eluent flow of 1.0 ml min^{-1}.



y = -4.5 · 10-4 x2 + 1.7 · 10-1 x - 4.7 · 10-2
n = 11
R2 = 0.9998
(a)
[F-] / µg l-1
Area / µS cm-1 min
y = 0.1x + (-0.07)
n = 11
R2 = 0.9999
(b)
[Cl-] / µg l-1
y = 0.06x + (-0.08)
n = 11
R2 = 0.9999
(c)
[NO2-] / µg l-1
y = 1.3 · 10-4 x2 + 2.5 · 10-2 x + 8.9 · 10-3
n = 11
R2 = 0.9993
(d)
[Br-] / µg l-1
y = 2.7 · 10-4 x2 + 6.1 · 10-2 x - 8.2 · 10-2
n = 11
R2 = 0.9999
(e)
[SO42-] / µg l-1
y = 9.9 · 10-5 x2 + 2.1 · 10-2 x - 4.8 · 10-3
n = 11
R2 = 0.9998
(f)
[Methanesulfonate] / µg l-1
y = 4.2 · 10-2 x - 1.3 · 10-1
n = 11
R2 = 0.9983
(g)
[Formate] / µg l-1
y = -3.0 · 10-5 x2 + 2.2 · 10-2 x - 6.2 · 10-2
n = 11
R2 = 0.9981
(h)
[Acetate] / µg l-1
y = 2.9 · 10-4 x2 + 7.6 · 10-3 x - 2.5 · 10-2
n = 11
R2 = 0.9973
(i)
[Glycolate] / µg l-1
y = 6.8 · 10-3 x - 2.0 · 10-2
n = 11
R2 = 0.9635
(j)
[Propionate] / µg l-1
y = 1.1 · 10-2 x - 3.9 · 10-2
n = 11
R2 = 0.9372
(k)
[Butyrate] / µg l-1
y = 4.4 · 10-2 x - 1.3 · 10-1
n = 11
R2 = 0.9585
(l)
[Oxalate] / µg l-1

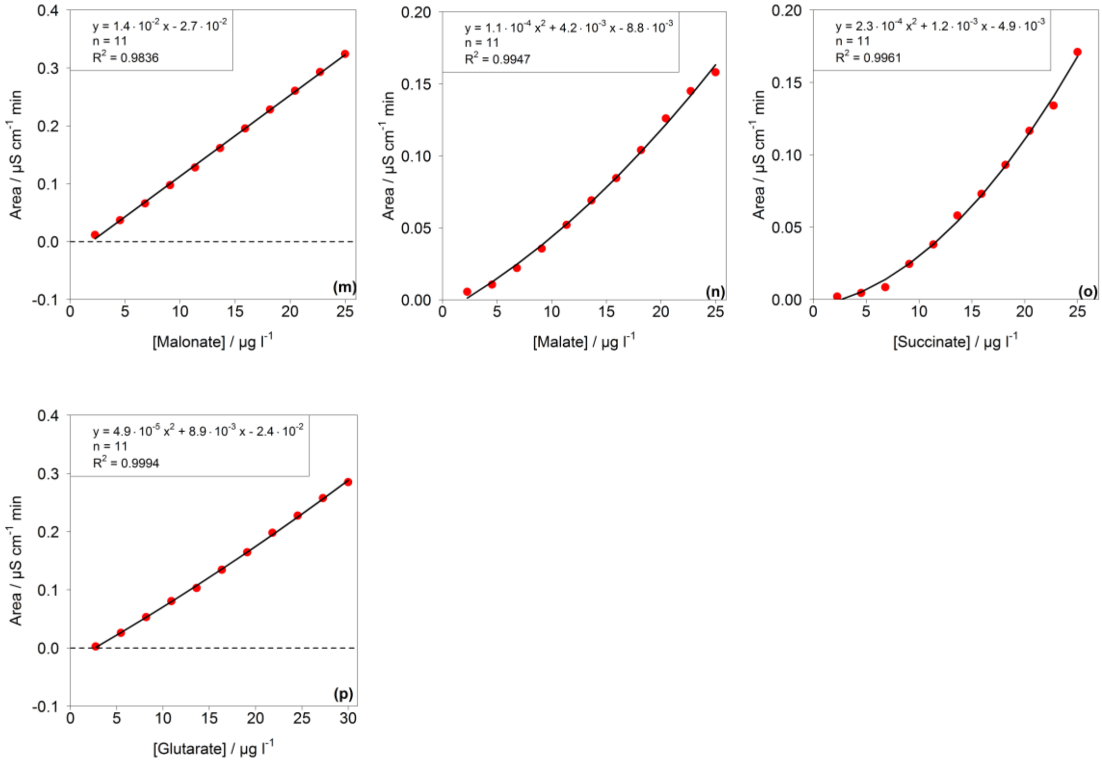


Figure S16. Calibration functions of (a) F^-, (b) Cl^-, (c) NO_3^-, (d) Br^-, (e) SO_4^{2-}, (f) methanesulfonate, (g) formate, (h) acetate, (i) glycolate, (j) propionate, (k) butyrate, (l) oxalate, (m) malonate, (n) malate, (o) succinate and (p) glutarate.

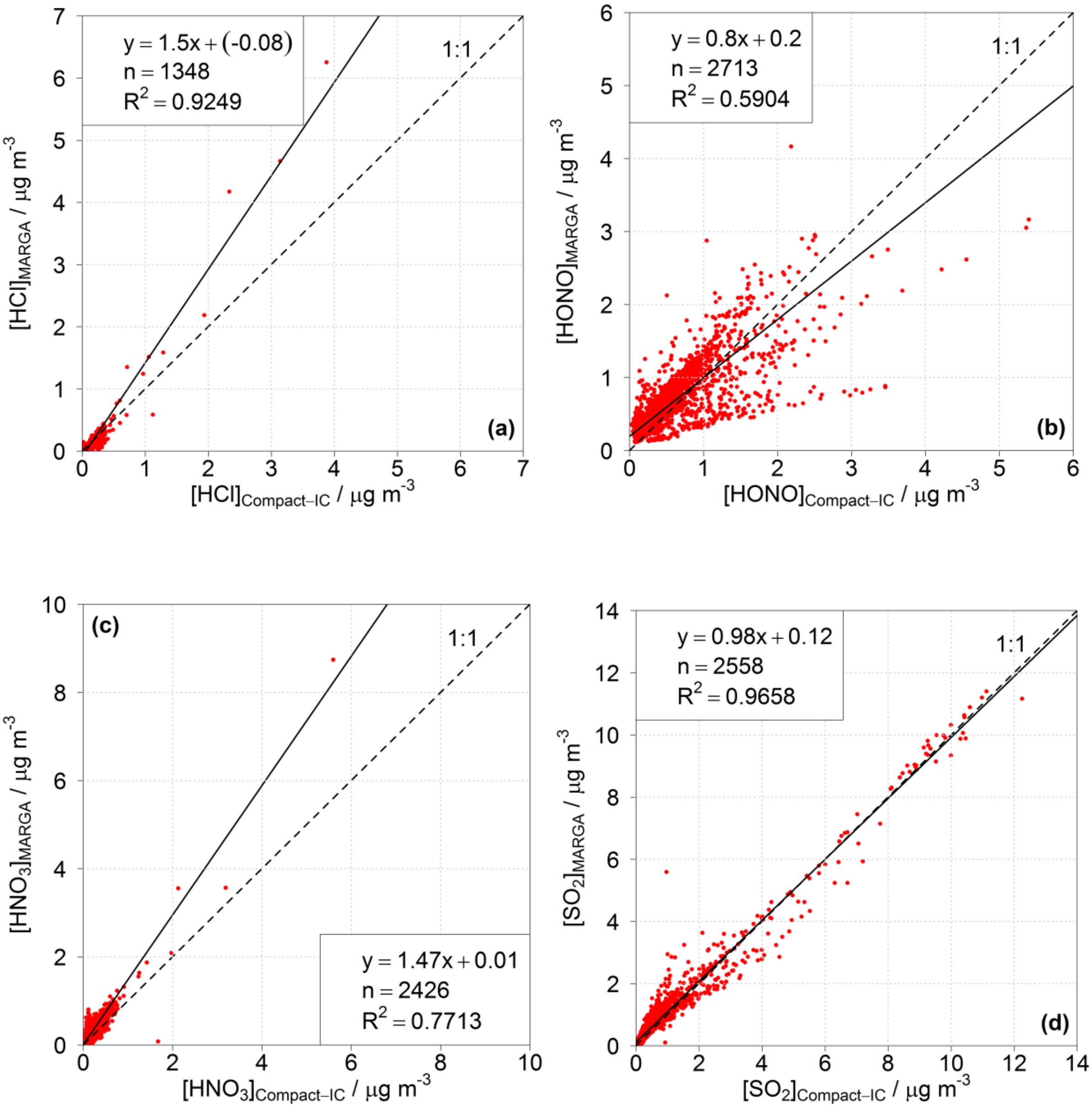


Figure S17. Scatter plots of (a) HCl, (b) HONO, (c) HNO_3 and (d) SO_2 for the MARGA and Compact-IC measurements in Melpitz during the one year long measurement campaign.

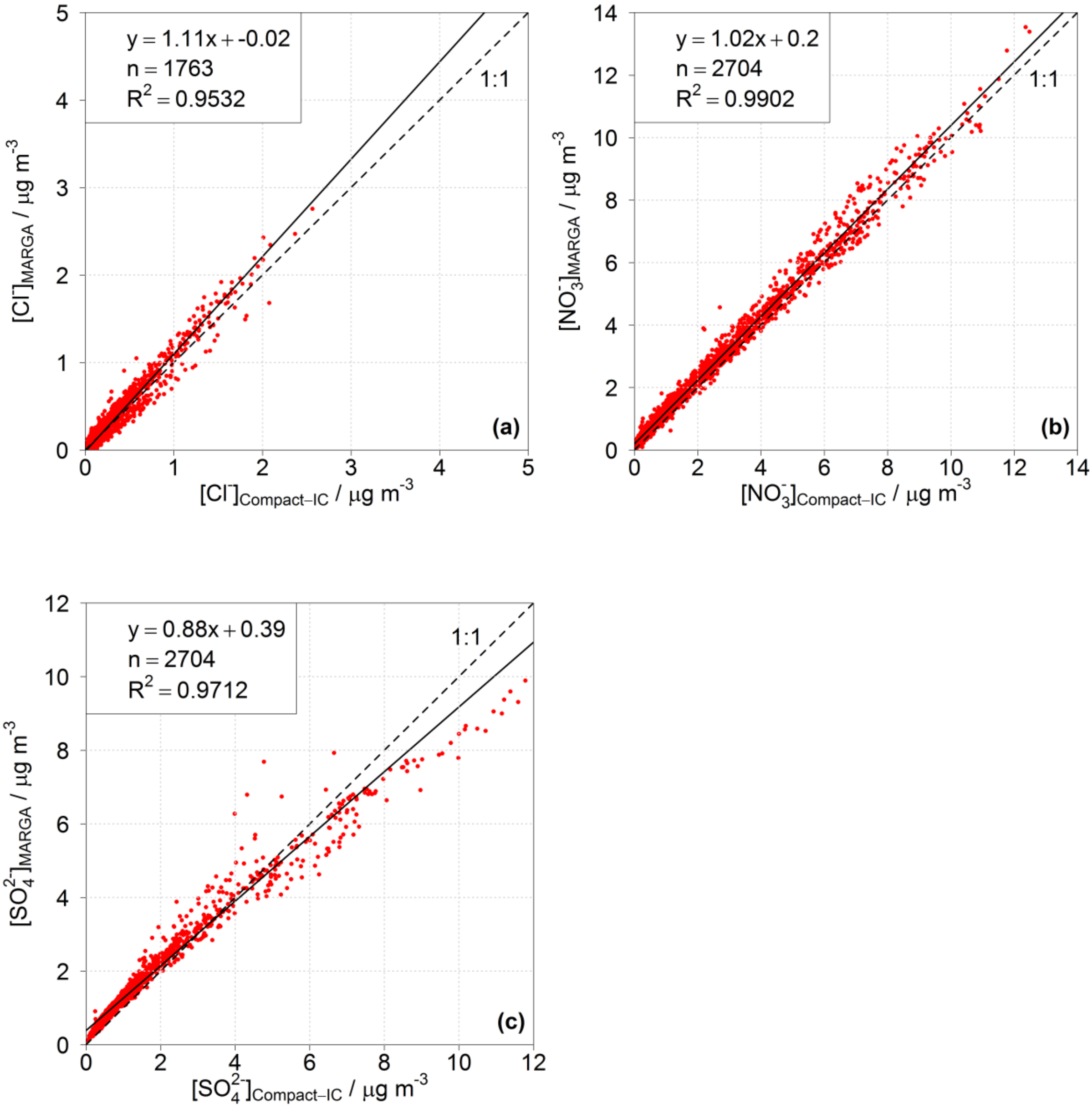


Figure S18. Scatter plots of (a) Cl^-, (b) NO_3^- and (c) SO_4^{2-} for the MARGA and Compact-IC measurements in Melpitz during the one year long measurement campaign.

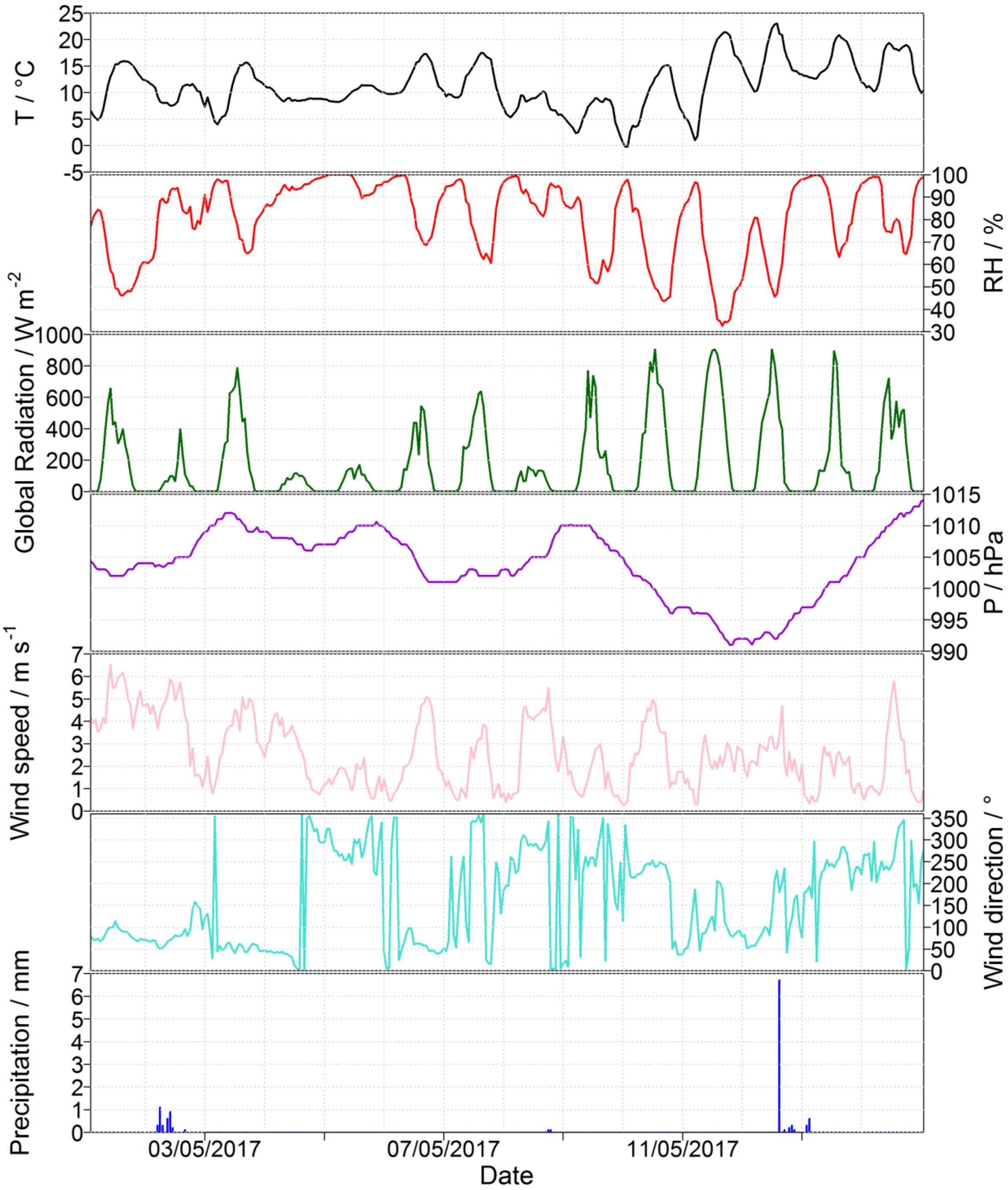


Figure S19. Meteorological parameters during the example application from 1st May until 14th May 2017.

Table S1. Linearity test for the calibration and resulting test values (TV) for each ion.

Ion	TV	Linearity
F^-	56.9	quadratic
Cl^-	0.2	linear
NO_2^-	2.4	linear
Br^-	16.4	quadratic
NO_3^-	2.6	linear
SO_4^{2-}	26.4	quadratic
Methanesulfonate	36.8	quadratic
Formate	1.6	linear
Acetate	24.6	quadratic
Glycolate	34.9	quadratic
Propionate	0.3	linear
Butyrate	9.1	linear
Pyruvate	267.8	quadratic
Oxalate	2.8	linear
Malonate	10.7	linear
Malate	23.7	quadratic
Succinate	88.8	quadratic
Glutarate	16.8	quadratic

WRD efficiency

d_i	-	inner diameter (4.2 cm)
d_o	-	outer diameter (4.5 cm)
d	-	hydrodynamic equivalent diameter ($d_o - d_i = 0.3$ cm)
L	-	length of the denuder (30 cm)
D	-	diffusion coefficient (calculated according to Fuller et al. (1966))
u	-	flow velocity (16.7 l min^{-1})
E	-	denuder efficiency

Table S2. Equations for the calculations of the efficiencies (E) for annular denuders.

	Winiwarter (1989)	Possanzini et al. (1983)	De Santis (1994)	Berg et al. (2010)
X	$\frac{2LD}{d^2u}$	$\frac{\pi LD(d_i + d_o)}{4ud}$	$\frac{\pi LD(d_i + d_o)}{ud}$	Efficiencies were calculated with their described spreadsheet calculator
E	$1 - 9.11 \cdot e^{-3.884^2 X}$	$1 - 0.82 \cdot e^{-22.53X}$	$1 - 0.91 \cdot e^{-7.54X}$	

Berg, J. M., James, D. L., Berg, C. F., Toda, K., and Dasgupta, P. K.: Gas collection efficiency of annular denuders: A spreadsheet-based calculator, Anal Chim Acta, 664, 56-61, 10.1016/j.aca.2010.02.006, 2010.

De Santis, F.: Comment on Wet Effluent Denuder Coupled Liquid/Ion Chromatography Systems: Annular and Parallel Plate Denuders, Anal Chem, 66, 3503-3504, DOI 10.1021/ac00092a032, 1994.

Fuller, E. N., Schettle, P. D., and Giddings, J. C.: A New Method for Prediction of Binary Gas-Phase Diffusion Coeffecients, Ind Eng Chem, 58, 19-+, 1966.

Possanzini, M., Febo, A., and Liberti, A.: New Design of a High-Performance Denuder for the Sampling of Atmospheric Pollutants, Atmos Environ, 17, 2605-2610, Doi 10.1016/0004-6981(83)90089-6, 1983.

Winiwarter, W.: A Calculation Procedure for the Determination of the Collection Efficiency in Annular Denuders, Atmos Environ, 23, 1997-2002, Doi 10.1016/0004-6981(89)90526-X, 1989.