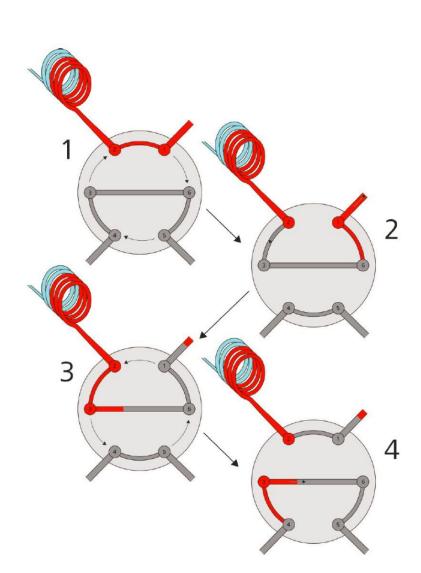
- 1 Electronic Supplementary Material
- 2



4 **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

7 separation columns. (https://www.metrohm.com/de-de/produkte/ionenchromatographie/ionen

8 chromatographie-inline-probenvorbereitung/, 10th August 2018)

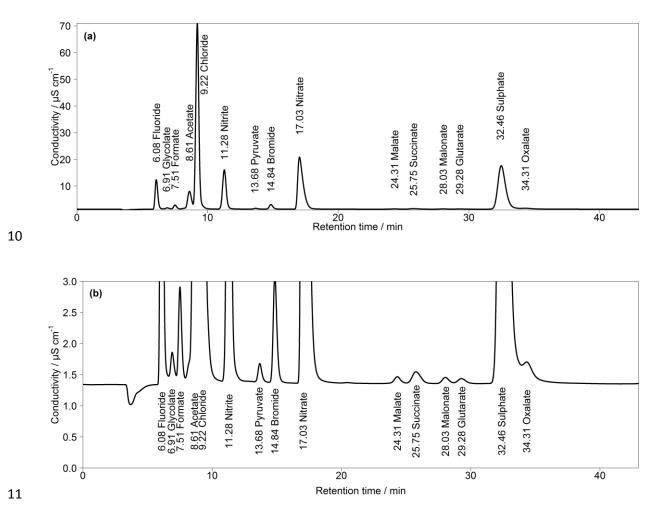


Figure S2. (a) Chromatogram of a standard solution with aqueous concentrations of 150 μ g l⁻¹ for Cl⁻, NO₃⁻, SO₄²⁻, 75 μ g l⁻¹ for NO₂⁻, 15 μ g l⁻¹ for F⁻, Br⁻ and 3 μ g l⁻¹ for all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min⁻¹. (b) Zoom in of (a).

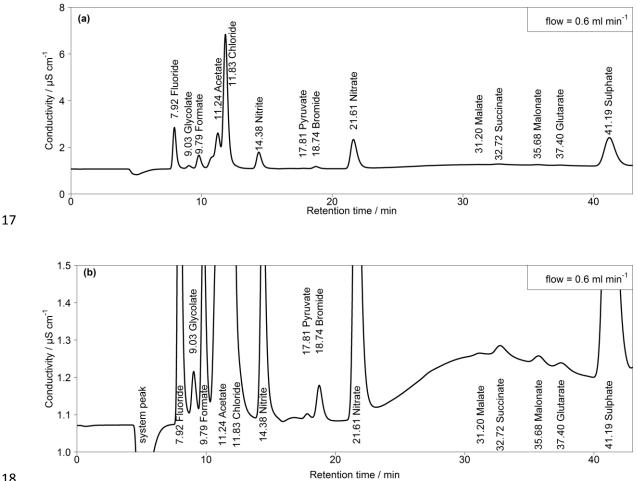


Figure S3. (a) Chromatogram of a standard solution with aqueous concentrations of $10 \ \mu g \ l^{-1}$ for Cl⁻, NO₃⁻, SO₄²⁻, 5 μ g l⁻¹ for NO₂⁻ and 1 μ g l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 0.6 ml min⁻¹. (b) Zoom in of chromatogram in (a).

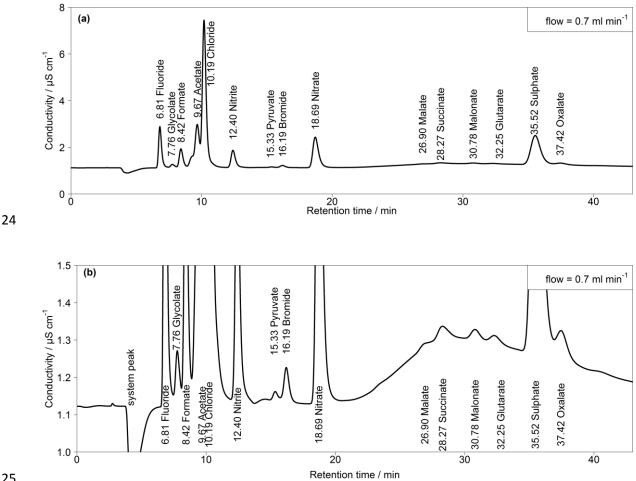


Figure S4. (a) Chromatogram of a standard solution with aqueous concentrations of $10 \ \mu g \ l^{-1}$ for Cl⁻, NO₃⁻, SO₄²⁻, 5 μ g l⁻¹ for NO₂⁻ and 1 μ g l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 0.7 ml min⁻¹. (b) Zoom in of chromatogram in (a).

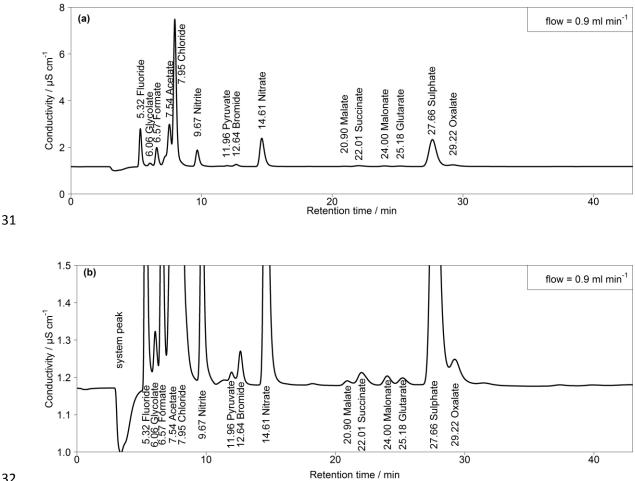


Figure S5. (a) Chromatogram of a standard solution with aqueous concentrations of $10 \ \mu g \ l^{-1}$ for Cl⁻, NO₃⁻, SO₄²⁻, 5 μ g l⁻¹ for NO₂⁻ and 1 μ g l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 0.9 ml min⁻¹. (b) Zoom in of chromatogram in (a).

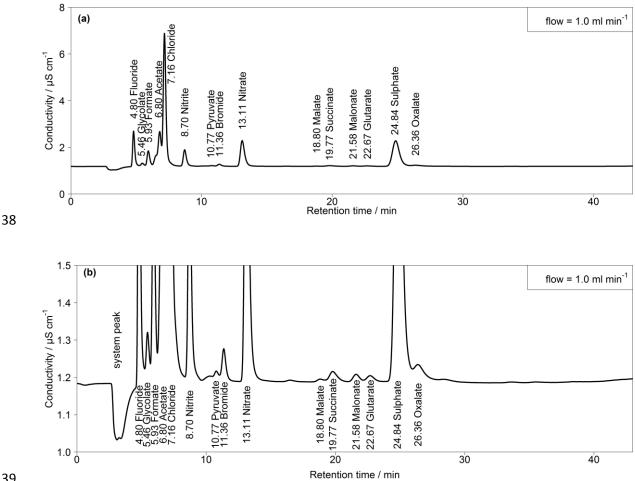
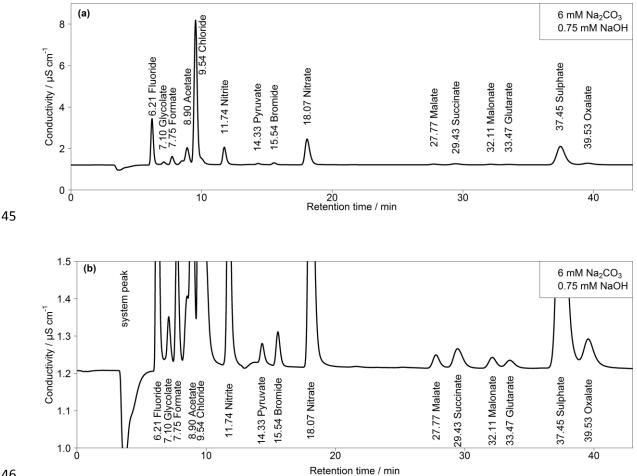


Figure S6. (a) Chromatogram of a standard solution with aqueous concentrations of $10 \ \mu g \ l^{-1}$ for Cl⁻, NO₃⁻, SO₄²⁻, 5 μ g l⁻¹ for NO₂⁻ and 1 μ g l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 1.0 ml min⁻¹. (b) Zoom in of chromatogram in (a).



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Figure S7. (a) Different eluent concentration of 6 mM Na₂CO₃ and 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 μ g l⁻¹ for Cl⁻, NO₃⁻, SO₄²⁻, 5 μ g l⁻¹ for NO₂⁻ and 1 μ g 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).

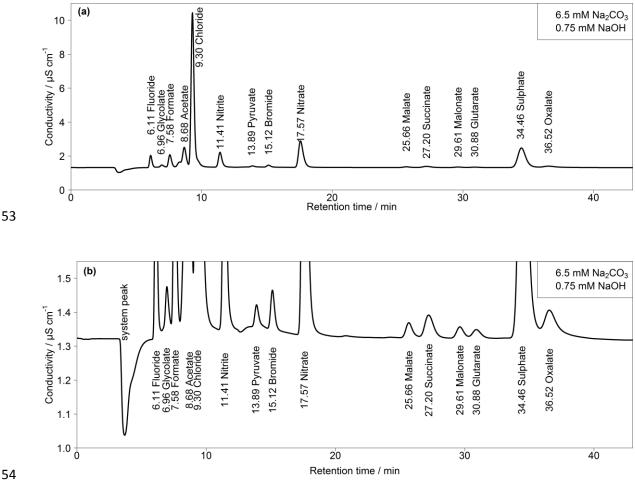


Figure S8. (a) Different eluent concentration of 6.5 mM Na₂CO₃ and 0.75 mM NaOH. 55 Chromatogram of a standard solution with aqueous concentrations of $10 \,\mu g \, l^{-1}$ for Cl⁻, NO₃⁻, 56 SO_4^{2-} , 5 µg l⁻¹ for NO₂⁻ and 1 µg l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of 57 the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 0.8 ml min⁻¹. (b) Zoom in 58 59 of chromatogram in (a).

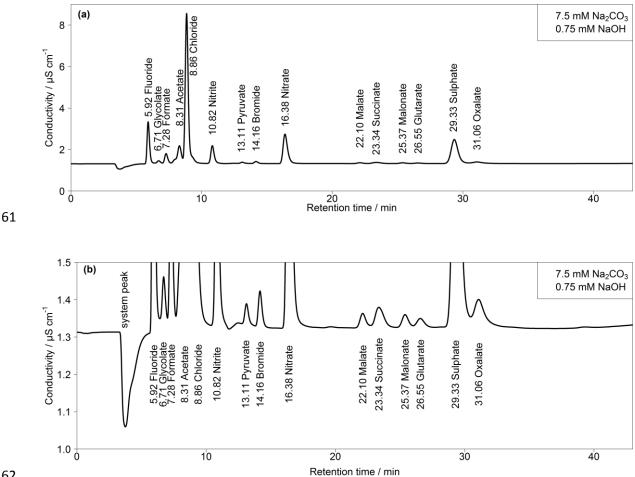


Figure S9. (a) Different eluent concentration of 7.5 mM Na₂CO₃ and 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of $10 \,\mu g \, l^{-1}$ for Cl⁻, NO₃⁻, SO_4^{2-} , 5 µg l⁻¹ for NO₂⁻ and 1 µg l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 0.8 ml min⁻¹. (b) Zoom in of chromatogram in (a).

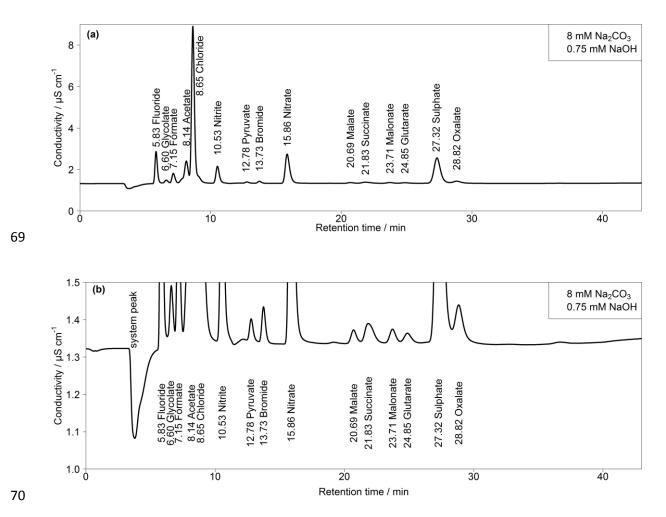


Figure S10. (a) Different eluent concentration of 8 mM Na₂CO₃ and 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 μ g l⁻¹ for Cl⁻, NO₃⁻, SO₄²⁻, 5 μ g l⁻¹ for NO₂⁻ and 1 μ g l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. T = 65 °C and eluent flow of 0.8 ml min⁻¹. (b) Zoom in of chromatogram in (a).

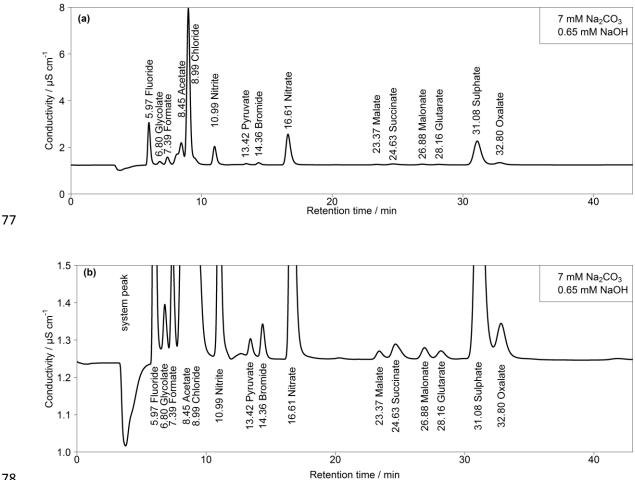


Figure S11. (a) Different eluent concentration of 7 mM Na₂CO₃ and 0.65 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of $10 \,\mu g \, l^{-1}$ for Cl⁻, NO₃⁻, SO_4^{2-} , 5 µg l⁻¹ for NO₂⁻ and 1 µg l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 0.8 ml min⁻¹. (b) Zoom in of chromatogram in (a).

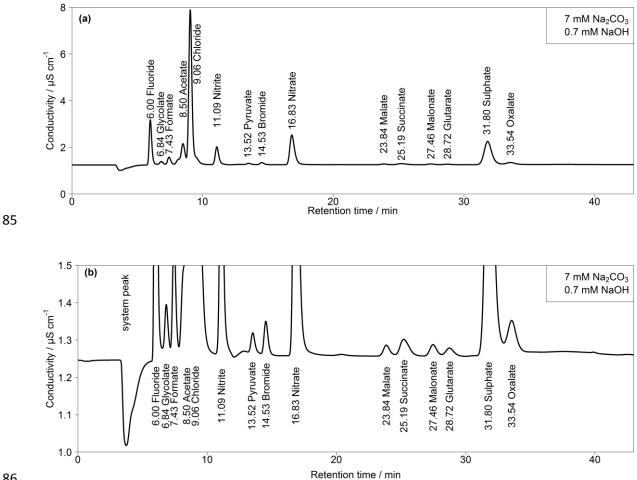
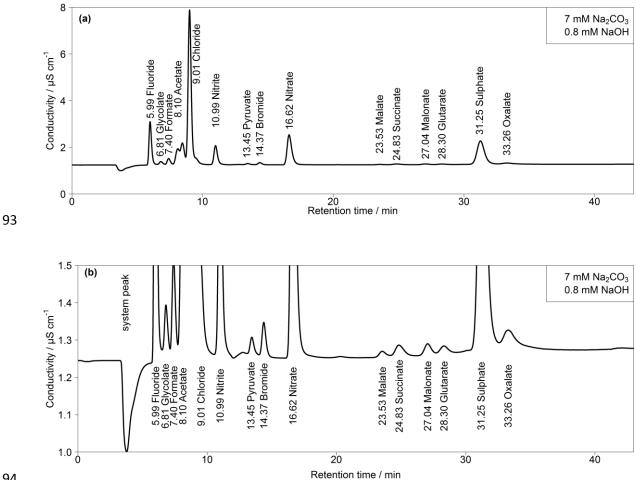


Figure S12. (a) Different eluent concentration of 7 mM Na₂CO₃ and 0.7 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of $10 \,\mu g \, l^{-1}$ for Cl⁻, NO₃⁻, SO_4^{2-} , 5 µg l⁻¹ for NO₂⁻ and 1 µg l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 0.8 ml min⁻¹. (b) Zoom in of chromatogram in (a).



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Figure S13. (a) Different eluent concentration of 7 mM Na₂CO₃ and 0.8 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 10 μ g l⁻¹ for Cl⁻, NO₃⁻, SO₄²⁻, 5 μ g l⁻¹ for NO₂⁻ and 1 μ g 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).

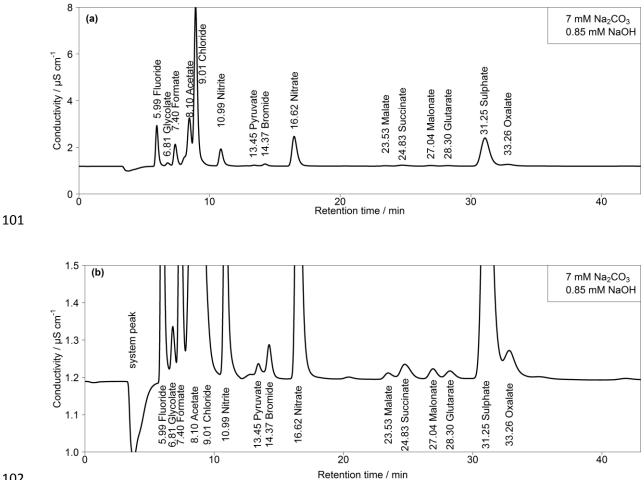
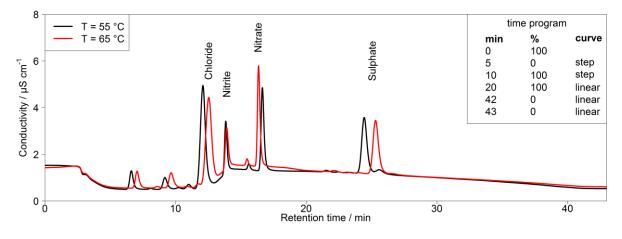


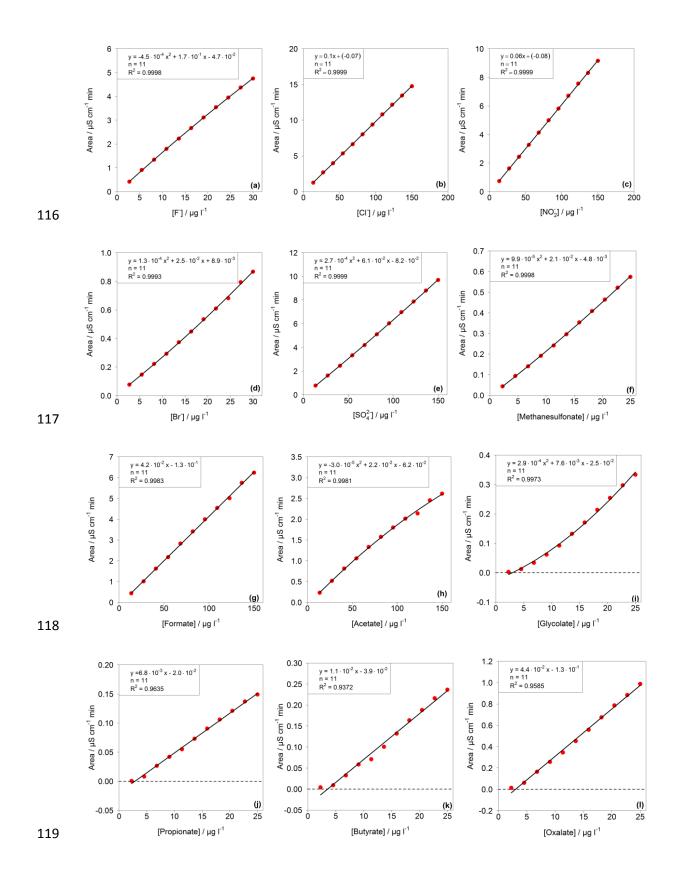
Figure S14. (a) Different eluent concentration of 7 mM Na₂CO₃ and 0.85 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of $10 \ \mu g \ l^{-1}$ for Cl⁻, NO₃⁻, SO_4^{2-} , 5 µg l⁻¹ for NO₂⁻ and 1 µg l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the retention times. $T = 65 \text{ }^{\circ}\text{C}$ and eluent flow of 0.8 ml min⁻¹. (b) Zoom in of chromatogram in (a).



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Figure S15. Temperature variation of the column oven for 55 °C (black) and 65 °C (red). Eluent concentration of 1-14 mM Na₂CO₃ and 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 50 μ g l⁻¹ for Cl⁻, NO₃⁻, SO₄²⁻, 25 μ g l⁻¹ for NO₂⁻ and 3 μ g l⁻¹ for F⁻, Br⁻ as well as all organic acids. Numbers in front of the ion names are the

114 retention times. Eluent flow of 1.0 ml min^{-1} .



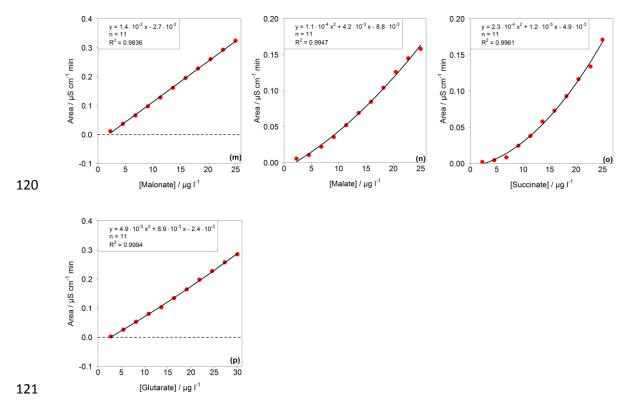


Figure S16. Calibration functions of (a) F⁻, (b) Cl⁻, (c) NO₃⁻, (d) Br⁻, (e) SO₄²⁻, (f)
methanesulfonate, (g) formate, (h) acetate, (i) glycolate, (j) propionate, (k) butyrate, (l) oxalate,
(m) malonate, (n) malate, (o) succinate and (p) glutarate.

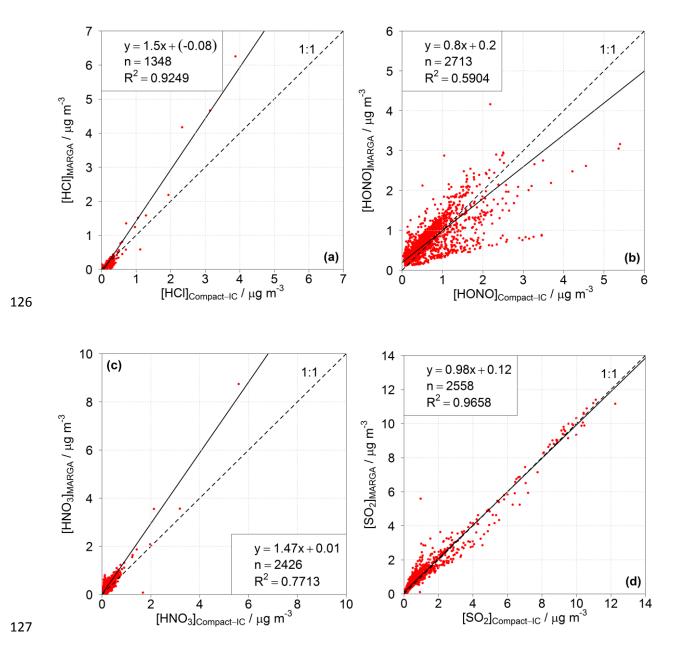


Figure S17. Scatter plots of (a) HCl, (b) HONO, (c) HNO₃ and (d) SO₂ for MARGA and Compact-IC measurements in Melpitz during one-year measurement campaign.

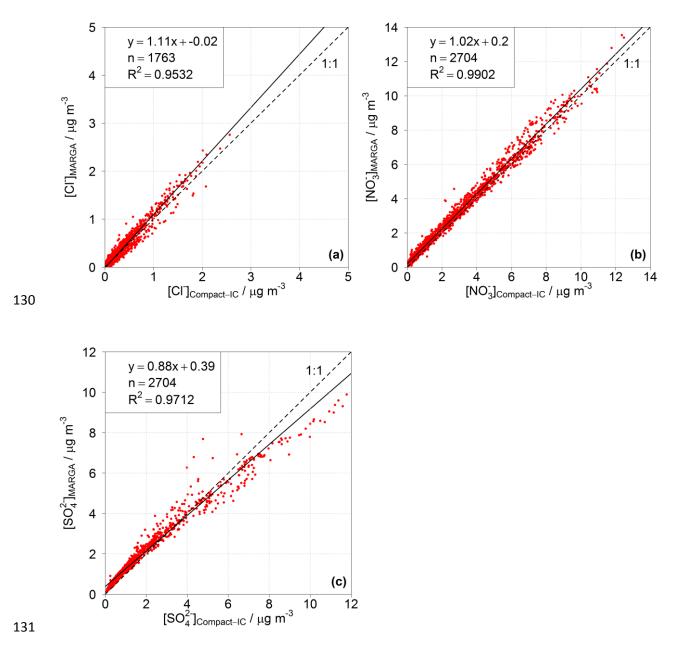


Figure S18. Scatter plots of (a) Cl^{-} , (b) NO_{3}^{-} and (c) SO_{4}^{2-} for MARGA and Compact-IC measurements in Melpitz during the one-year measurement campaign.

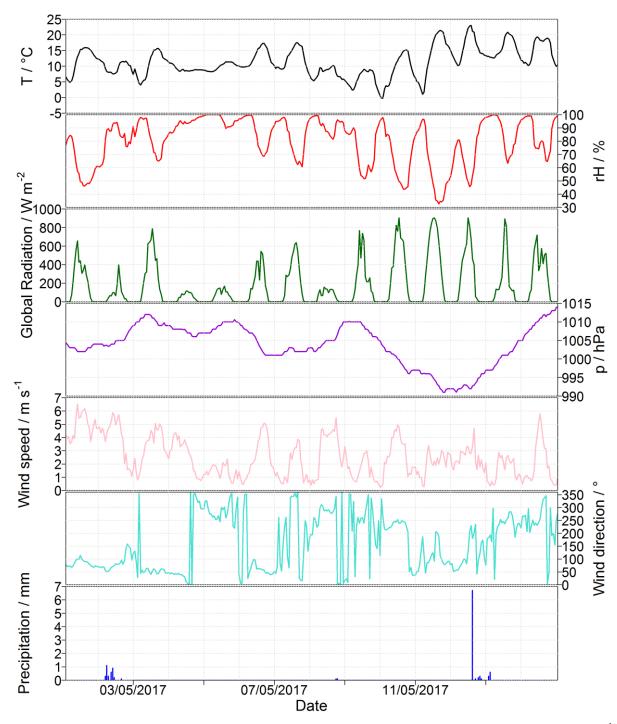


Figure S19. Meteorological parameters during the example application from 1st May until 14th
 May 2017.

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TV	Linearity
56.9	quadratic
0.2	linear
2.4	linear
16.4	quadratic
2.6	linear
26.4	quadratic
36.8	quadratic
1.6	linear
24.6	quadratic
34.9	quadratic
0.3	linear
9.1	linear
267.8	quadratic
2.8	linear
10.7	linear
23.7	quadratic
88.8	quadratic
16.8	quadratic
	56.9 0.2 2.4 16.4 2.6 26.4 36.8 1.6 24.6 34.9 0.3 9.1 267.8 2.8 10.7 23.7 88.8

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