Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry. This journal is © The Royal Society of Chemistry 2020

## **Supplementary Information**

Novel approach for determination of the dissolved and the particulate fractions in aqueous samples by flow field flow fractionation via online monitoring of both the cross flow and the detector flow using ICP-MS

Ping Tan<sup>1,2</sup>, Jingjing Yang<sup>1,3</sup>, Volker Nischwitz<sup>1\*</sup>

<sup>1</sup> Central Institute for Engineering, Electronics and Analytics, Analytics (ZEA-3),

Forschungszentrum Juelich, 52425 Juelich, Germany

<sup>2</sup> College of Environment and Resources, Chongqing Technology and Business University,

Nan'an District, 400067 Chongqing, China

<sup>3</sup> Center for Separation and Purification Materials & Technologies, Suzhou University of

Science and Technology, Suzhou 215009, China

\*Corresponding author: v.nischwitz@fz-juelich.de

| Table S1 | Overview | of AF4 | flow rates | and ICP-M | S monitoring | for the | combined | <b>CF-DF</b> met | hod |
|----------|----------|--------|------------|-----------|--------------|---------|----------|------------------|-----|
|          |          |        |            |           | C C          | ,       |          |                  |     |

|          | Time     | Focus pump      | Tip pump        | Syringe pumps   | Switching  | ICP-MS        |
|----------|----------|-----------------|-----------------|-----------------|------------|---------------|
|          | [min]    | (focus flow)    | (elution flow)  | (cross flow)    | valve      |               |
|          |          | $[mL min^{-1}]$ | $[mL min^{-1}]$ | $[mL min^{-1}]$ |            |               |
| Focusing | 0 - 30   | 2.2             | 0.3             | 2               | Cross flow | Monitoring    |
| Step     |          |                 |                 |                 | to ICP-MS  | cross flow    |
| Elution  | 30 - 121 | 0               | 2.5 followed    | 2 followed by   | Detector   | Monitoring    |
| Step     |          |                 | by gradient     | gradient down   | flow to    | detector flow |
|          |          |                 | matching the    | to 0            | ICP-MS     |               |
|          |          |                 | cross flow      |                 |            |               |
|          |          |                 | decrease        |                 |            |               |

**Table S2** Quantitative determination of the dissolved fraction in 5 water samples from Taihu via online monitoring of the cross flow (CF; n=2). For comparison the dissolved fraction obtained by ultrafiltration with offline quantification by ICP-MS is included (UF; n=2). The results are given as mean and standard deviation (SD). In addition, the percentage dissolved fraction based on the total concentrations of the respective elements in the 10 µm filtrates is presented.

| Si       | $CF Mean \pm SD \\ [\mu g L^{-1}]$ | $UF Mean \pm SD \\ [\mu g L^{-1}]$ | Recovery<br>CF / UF [%] | Dissolved (CF) in<br>% of 10 µm total | Dissolved (UF) in<br>% of 10 µm total |
|----------|------------------------------------|------------------------------------|-------------------------|---------------------------------------|---------------------------------------|
| Sample 1 | 940 ± 160                          | 840 ± 30                           | 112 ± 19                | $46 \pm 8$                            | 41 ± 2                                |
| Sample 2 | $690 \pm 120$                      | $550\pm80$                         | 125 ± 28                | $56 \pm 11$                           | 44 ± 8                                |
| Sample 3 | 990 ± 120                          | $840\pm60$                         | 118 ± 16                | 54 ± 7                                | 46 ± 4                                |
| Sample 4 | 920 ± 110                          | $770 \pm 20$                       | 118 ± 14                | $53 \pm 6$                            | 45 ± 2                                |
| Sample 5 | 830 ± 170                          | $650 \pm 20$                       | 129 ± 26                | 57 ± 12                               | 44 ± 2                                |

| Ca       | $CF Mean \pm SD \\ [\mu g L^{-1}]$ | $UF Mean \pm SD \\ [\mu g L^{-1}]$ | Recovery<br>CF / UF [%] | Dissolved (CF) in<br>% of 10 µm total | Dissolved (UF) in<br>% of 10 µm total |
|----------|------------------------------------|------------------------------------|-------------------------|---------------------------------------|---------------------------------------|
| Sample 1 | $37180 \pm 1730$                   | $42850\pm1750$                     | 87 ± 5                  | 105 ± 5                               | 121 ± 5                               |
| Sample 2 | 39100 ± 1180                       | $43840 \pm 1700$                   | 89 ± 4                  | 104 ± 4                               | 116 ± 5                               |
| Sample 3 | $39390 \pm 1600$                   | $45100 \pm 1340$                   | 87 ± 4                  | 106 ± 4                               | 121 ± 4                               |
| Sample 4 | $38840 \pm 3550$                   | $44690\pm1080$                     | 87 ± 8                  | 101 ± 9                               | $116 \pm 3$                           |
| Sample 5 | $38020\pm4070$                     | $44050\pm1000$                     | 86 ± 9                  | 98 ± 11                               | 114 ± 6                               |

**Table S3** Quantitative determination of the particulate fractions in 5 water samples from Taihu (10  $\mu$ m filtrates) using the novel combined CF-DF method (n=1) compared to the original method (DF only, n=1). The percentage amount based on the total concentrations of the respective elements in the 10  $\mu$ m filtrates is given in brackets. The mass balance calculated from the percentage dissolved fraction (Table 3) and the two percentage particulate fractions as well as the third particulate fraction was established for the CF-DF method.

| Mg       | CF-DF method<br>Part. fraction 1<br>[µg L <sup>-1</sup> ] | CF-DF method<br>Part. fraction 2<br>[µg L <sup>-1</sup> ] | CF-DF method<br>Mass balance<br>[%] | original method<br>Part. fraction 1<br>[µg L <sup>-1</sup> ] | original method<br>Part. fraction 2<br>[µg L <sup>-1</sup> ] |
|----------|---|---|-------------------------------------|--|--|
| Sample 1 | 10.2 (0.1%)   | 13.8 (0.2%)   | 95.3                                | 145 (1.6%)   | 49.2 (0.5%)  |
| Sample 2 | 8.4 (0.1%)  | 9.4 (0.1%)  | 93.9                                | 146 (1.5%)   | 41.1 (0.4%)  |
| Sample 3 | 11.0 (0.1%)   | 12.3 (0.1%)   | 95.5                                | 148 (1.5%)   | 42.5 (0.4%)  |
| Sample 4 | 10.8 (0.1%)   | 10.9 (0.1%)   | 92.3                                | 150 (1.5%)   | 41.4 (0.4%)  |
| Sample 5 | 11.2 (0.1%)   | 11.6 (0.1%)   | 93.8                                | 148 (1.5%)   | 42.3 (0.4%)  |

| Si       | CF-DF method<br>Part. fraction 1 | CF-DF method<br>Part. fraction 2 | CF-DF method<br>Mass balance | original method<br>Part. fraction 1 | original method<br>Part. fraction 2 |
|----------|----------------------------------|----------------------------------|------------------------------|-------------------------------------|-------------------------------------|
|          | [µg L-1]                         | [µg L-1]                         | [%]                          | [µg L-1]                            | [µg L-1]                            |
| Sample 1 | 8.0 (0.4%)                       | 200 (9.8%)                       | 57.6                         | 35.2 (1.7%)                         | 163 (8.0%)                          |
| Sample 2 | 7.8 (0.6%)                       | 160 (12.9%)                      | 70.7                         | 20.5 (1.6%)                         | 129 (10.4%)                         |
| Sample 3 | 36.3 (2.0%)                      | 194 (10.6%)                      | 67.9                         | 25.9 (1.4%)                         | 145 (7.9%)                          |
| Sample 4 | 35.5 (2.0%)                      | 179 (10.3%)                      | 66.6                         | 24.3 (1.4%)                         | 132 (7.6%)                          |
| Sample 5 | 49.6 (3.4%)                      | 145 (9.8%)                       | 71.3                         | 24.6 (1.7%)                         | 136 (9.2%)                          |

| Ca       | CF-DF method<br>Part_fraction 1 | CF-DF method<br>Part_fraction 2 | CF-DF method<br>Mass balance | original method<br>Part_fraction 1 | original method<br>Part_fraction 2 |
|----------|---------------------------------|---------------------------------|------------------------------|------------------------------------|------------------------------------|
|          | $[\mu g L^{-1}]$                | $[\mu g L^{-1}]$                | [%]                          | $[\mu g L^{-1}]$                   | $[\mu g L^{-1}]$                   |
| Sample 1 | 69.9 (0.2%)                     | 65.3 (0.2%)                     | 105.8                        | 765 (2.2%)                         | 279 (0.8%)                         |
| Sample 2 | 57.4 (0.2%)                     | 54.5 (0.1%)                     | 104.0                        | 786 (2.1%)                         | 222 (0.6%)                         |
| Sample 3 | 65.4 (0.2%)                     | 57.0 (0.2%)                     | 105.9                        | 783 (2.1%)                         | 221 (0.6%)                         |
| Sample 4 | 58.6 (0.2%)                     | 35.8 (0.1%)                     | 101.0                        | 785 (2.0%)                         | 232 (0.6%)                         |
| Sample 5 | 59.8 (0.2%)                     | 57.3 (0.2%)                     | 98.7                         | 774 (2.0%)                         | 212 (0.5%)                         |

| Mn       | CF-DF method<br>Part. fraction 1<br>[µg L <sup>-1</sup> ] | CF-DF method<br>Part. fraction 2<br>$[\mu g L^{-1}]$ | CF-DF method<br>Mass balance<br>[%] | original method<br>Part. fraction 1<br>[µg L <sup>-1</sup> ] | original method<br>Part. fraction 2<br>[µg L <sup>-1</sup> ] |
|----------|---|--|-------------------------------------|--|--|
| Sample 1 | 0.4 (4.0%)  | 0.9 (10.2%)  | 23.4                                | 1.1 (12.1%)  | 1.1 (12.9%)  |
| Sample 2 | 0.3 (3.7%)  | 0.9 (11.0%)  | 21.6                                | 0.5 (6.7%)   | 1.0 (12.7%)  |
| Sample 3 | 0.4 (6.4%)  | 0.7 (11.0%)  | 21.0                                | 0.4 (5.4%)   | 0.6 (9.3%)   |
| Sample 4 | 0.3 (4.0%)  | 0.7 (8.6%)   | 18.6                                | 0.3 (4.0%)   | 0.8 (9.5%)   |
| Sample 5 | 0.4 (6.0%)  | 0.7 (10.1%)  | 18.4                                | 0.3 (4.4%)   | 0.7 (9.6%)   |