

# Ultra-trace metal speciation analysis by coupling of sector-field ICP-MS to high-resolution size exclusion and reversed-phase liquid chromatography

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## Supporting information

### Table of contents

**Tables S1.** Examples ICP-MS methods optimised for the measurements shown in this work.

**Figure S1.** Analysis of copper abundance in an LH1 preparation from *Rhodospirillum rubrum* grown on 2  $\mu$ M Cu<sup>2+</sup>.

**Figure S2.** Measurement of a [Cd]-Chl standard.

**Tables S1.** Description of contents: This supplement describes the technical parameters for adjusting the ICP-MS in order to yield optimal performance for the different tasks described here.

**Cu method for aqueous buffer and organic matrix**

Total time: 60 min

Runs: 505

Passes: 1

Tune in aqueous buffer and with desolvating unit

Tune with methanol and acetone with spray chamber and no desolvating unit

Resolution: Medium

Analyte	Mass window %	Samples/peak	Segment duration (Seconds)
Mg <sup>24</sup>	140	20	1.96
Cu <sup>63</sup>	125	20	2.00
Zn <sup>66</sup>	125	20	2.00

**La method for aqueous buffer**

Total time: 270 min

Runs: 1795

Passes: 1

Tune in aqueous buffer

Resolution: Medium

Analyte	Mass window %	Samples/peak	Segment duration (Seconds)
Mg <sup>24</sup>	125	20	0.625
P <sup>31</sup>	125	20	0.625
S <sup>32</sup>	125	20	0.625
Ca <sup>44</sup>	125	20	0.625
Mn <sup>55</sup>	125	20	0.600
Fe <sup>56</sup>	125	20	0.600
Co <sup>59</sup>	125	20	0.625
Cu <sup>63</sup>	125	20	1.000
Zn <sup>66</sup>	125	20	0.625
La <sup>139</sup>	125	20	1.750

**Cd method for organic matrix**

Total time: 60 min

Runs: 505

Passes: 1

Tune with methanol and acetone with spray chamber and no desolvating unit

Resolution: Medium

Analyte	Mass window %	Samples/peak	Segment duration (Seconds)
Mg <sup>24</sup>	140	20	1.96
Cd <sup>111</sup>	125	20	2.00
Zn <sup>66</sup>	125	20	2.00

**Cd method for aqueous buffer**

Total time: 270 min

Runs: 1260

Passes: 1

Tune in aqueous buffer and desolvating unit

Resolution: Medium

Analyte	Mass window %	Samples/peak	Segment duration (Seconds)
Mg <sup>24</sup>	140	20	1.4000
P <sup>31</sup>	125	20	0.500
S <sup>32</sup>	125	20	2.500
Fe <sup>56</sup>	125	20	0.250
Co <sup>59</sup>	125	20	1.250
Cu <sup>63</sup>	125	20	0.250
Zn <sup>66</sup>	125	20	0.250
Mo <sup>95</sup>	125	20	1.000
Cd <sup>111</sup>	125	20	5.000

**Cr method for aqueous buffer**

Total time: 270 min

Runs: 1160

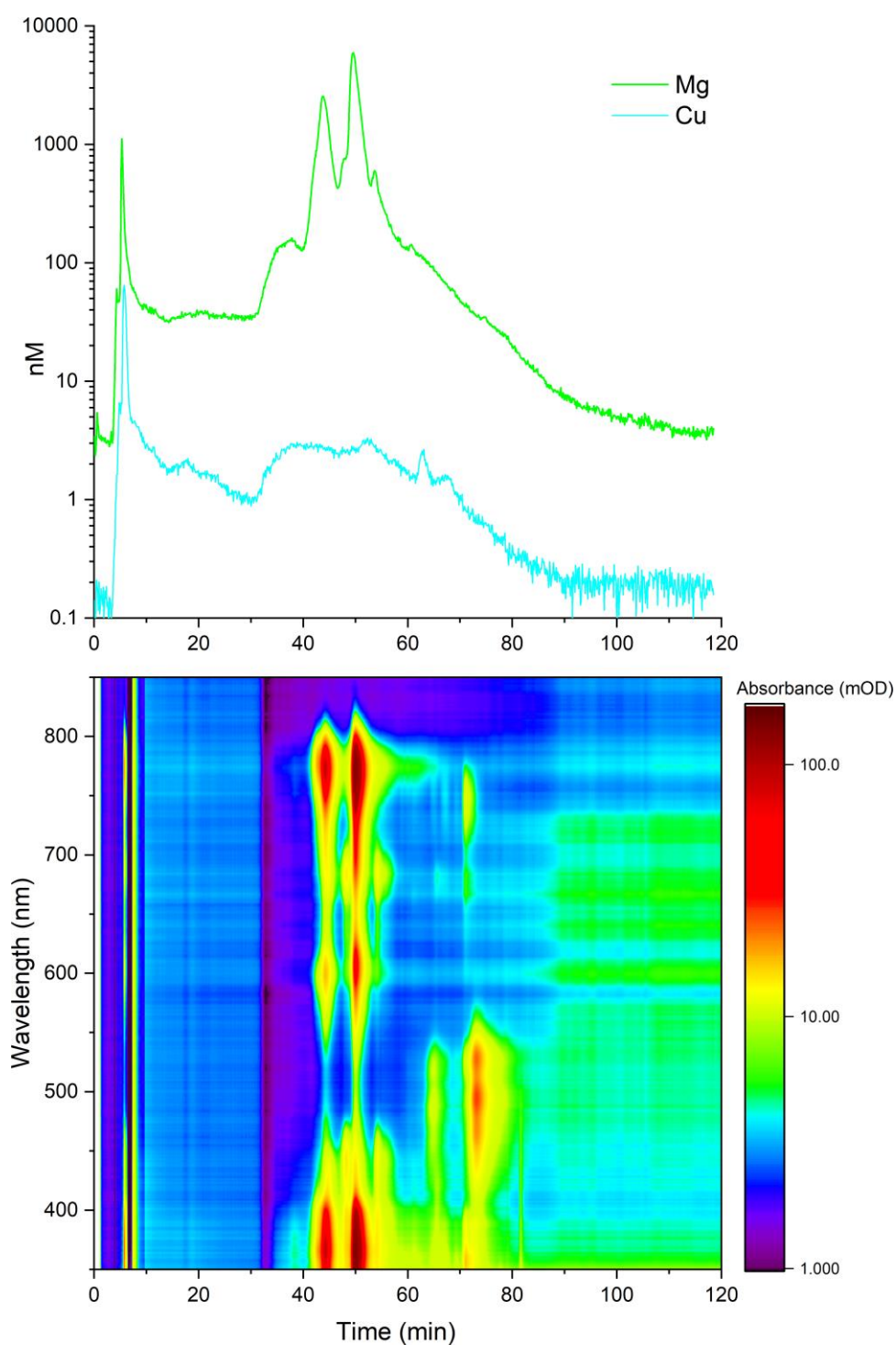
Passes: 1

Tune in aqueous buffer and desolvating unit

Resolution: Medium

Analyte	Mass window %	Samples/peak	Segment duration (Seconds)
Mg <sup>24</sup>	140	20	1.4000
P <sup>31</sup>	125	20	0.500
S <sup>32</sup>	125	20	2.500
Fe <sup>56</sup>	125	20	0.250
Co <sup>59</sup>	125	20	1.250
Cu <sup>63</sup>	125	20	0.250
Zn <sup>66</sup>	125	20	0.250
Mo <sup>95</sup>	125	20	1.000
Cr <sup>52</sup>	125	20	5.000

**Figure S1.** Analysis of copper abundance in an LH1 preparation from *Rhodospirillum rubrum* grown on 2  $\mu\text{M}$   $\text{Cu}^{2+}$ . Acetone extract from the protein preparation of a replicate experiment. The separation was performed on a metal-free PRP-C18 2.1x250 mm column, leading to a much lower background of Cu than the originally used C18 column with steel housing (Fig. 8b), but otherwise confirming the Cu binding to the pigments (Fig. 8b).



**Figure S2.** Description of contents: This supplement shows the HPLC-ICPMS measurement of a [Cd]-Chl standard that was prepared by Küpper et al. (2007). The separation was performed on a C18 4.6x250 mm column as described in more detail in the methods section for pigment HPLC-ICPMS

