Reaction of methionine with chlorine: kinetics, product formation, and potential use as scavenger in chlorine dioxide-based systems
Electronic supporting information

Mischa Jütte[1], Josephine Heyns[1], Mohammad Sajjad Abdighahroudi[1], Christoph Schüth[2,3], and Holger V. Lutze*[1,3,4]

[1] Technical University of Darmstadt, Institute IWAR, Chair of environmental analytics and pollutants, Franziska-Braun-Straße 7, 64287 Darmstadt, Germany

[2] Technical University of Darmstadt, Institute of Applied Geosciences, Schnittspahnstr. 9, 64287 Darmstadt, Germany

[3] IWW Water Centre, Moritzstraße 26, D-45476 Mülheim an der Ruhr, Germany

[4] Centre for Water and Environmental Research (ZWU), Universitätsstraße 5, D-45141 Essen, Germany

*Corresponding author: h.lutze@iwar.tu-darmstadt.de

Table S1: Chemicals used in this study.

Name	Purity [%]	Purpose of use	Manufacturer
1,4-Dimethylpiperazine	98	Compound under study	Alfa Aesar (Haverhill, Massachusetts, USA)
Acetonitrile	≥ 99.95	Eluent (LC)	Carl Roth (Karlsruhe, Germany)
Formic acid	≥ 99	Eluent (LC)	Sigma-Aldrich (St. Louis, Missouri, USA)
Ammonium acetate	≥ 98	Eluent	Merck (Darmstadt, Germany)
Disodium phosphate		pH Buffer	Merck (Darmstadt, Germany)
Glutathione	≥ 98	Compound under study	Sigma-Aldrich (St. Louis, Missouri, USA)
Glycine	> 99	HOCl Scavenger	Alfa Aesar (Haverhill, Massachusetts, USA)
Hydroquinone	≥ 99	Compound under study	Sigma-Aldrich (St. Louis, Missouri, USA)
L-Methionine	≥ 98	Scavenger / Compound under study	Sigma-Aldrich (St. Louis, Missouri, USA)
L-Methioninesulfoxide		Compound under study	Alfa Aesar (Haverhill, Massachusetts, USA)
Sodium carbonate		Eluent (IC)	Sigma-Aldrich (St. Louis, Missouri, USA)
Sodium chlorate	> 99	Calibration standard	Arcos organics (Fair Lawn, New Jersey, USA)
Sodium chlorite	80	Calibration standard / oxidant	Honeywell | Fluka (Charlotte, North Carolina, USA)
Sodium chloride	>99.5	Calibration standard	Honeywell (Charlotte, North Carolina, USA)
Monosodium phosphate	98	pH Buffer	Arcos Organics (Fair Lawn, New Jersey, USA)
Sodium hypochlorite	11 – 15% FAC	Oxidant	Alfa Aesar (Haverhill, Massachusetts, USA)
Sodium persulfate	> 99	ClO_2 production	Carl Roth (Karlsruhe, Germany)
Phenol	> 99	Compound under study	Sigma-Aldrich (St. Louis, Missouri, USA)

Table S2: Instruments used in this study.

Name	Component	Description	Manufacturer
Ion-Chromatography	Autosampler	Dionex AS-AP	Thermo Scientific (Waltham, Massachusetts, USA)
	Column	Asupp7 – 250mm/4.0 µm	Metrohm (Herisau, Swiss)
	Column department	Dionex ICS-6000 DC	Thermo Scientific (Waltham, Massachusetts, USA)
	Conductivity detector		Thermo Scientific (Waltham, Massachusetts, USA)
	Pump1 (Eluent)	Dionex ICS-6000 SP	Thermo Scientific (Waltham, Massachusetts, USA)
	Pump2 (Suppressor)	Dionex AXP	Thermo Scientific (Waltham, Massachusetts, USA)
	Software	Chromeleon Console	Thermo Scientific (Waltham, Massachusetts, USA)
	Suppressor	Dionex ACRS 500	Thermo Scientific (Waltham, Massachusetts, USA)
Liquid Chromatography	Autosampler	1260 Multisampler	Agilent Technologies (Santa Clara, California, USA)
	Column	HILIC "Luna" NH_2 3µM, 150/2 mm	Phenomenex (Torrance, California, USA)
	Column department	1260 MCT	Agilent Technologies (Santa Clara, California, USA)
	Pump1 (Eluent)	1260 flexible pump	Agilent Technologies (Santa Clara, California, USA)
	Software	Agilent MassHunter	Agilent Technologies (Santa Clara, California, USA)
	UV detector	1260 DAD WR	Agilent Technologies (Santa Clara, California, USA)
	Mass detector	6470 Triple Quad LC-MS/MS	Agilent Technologies (Santa Clara, California, USA)
Photometer	Photometer	Specord 200 Plus	AnalytikJena (Jena, Germany)
pH-meter	pH-meter	Terminal 740	WTW Series inoLab (Weilheim, Germany)
Balance	Balance	SM2285Di-ION-C	VWR (Radnor, Pennsylvania, USA)
Reaction tubes	15 mL CellStar® tubes	Polypropylene	Greiner bio-one (Frickenhausen, Germany)
HPLC Vials	1.5 mL Short thread vial	Amber glass	VWR (Radnor, Pennsylvania, USA)
HPLC Vials	1.5 mL Short thread vial	Polypropylene	VWR (Radnor, Pennsylvania, USA)

Table S3: Ion chromatographic method used in this study.

Flow rate	0.75 mL × Min^{-1}
Measuring time	35 Min
Eluent A (4 mM Na_2CO_3)	90 %
Eluent B (H_2O)	10 %
Suppressor solution	20 mM H_2SO_4
Suppressor flow rate	1 mL × Min^{-1}
Injection volume	25 µL
Temperature autosampler	5 °C
Temperature column oven	45 °C
Retention times	
Cl^-	9.0 Min
ClO_2^-	7.7 Min
ClO_3^-	15.1 Min

Table S4: LC-MS/MS method developed for the detection of MSO

Flow rate	0.3 mL × Min^{-1}
Measuring time	20 Min
Eluent A (ACN)	80 %
Eluent B (H_2O + 0.1 % FA)	20 %
Injection volume	1 µL
Temperature column oven	25 °C
Precursor ion	166 Da
Product ion	74.1 Da
Acceleration energy	5 V
Collision energy	5 V
Polarity	Positive
Retention time MSO	10.8 Min

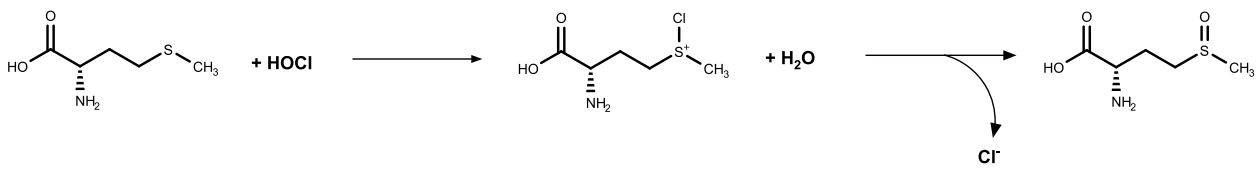
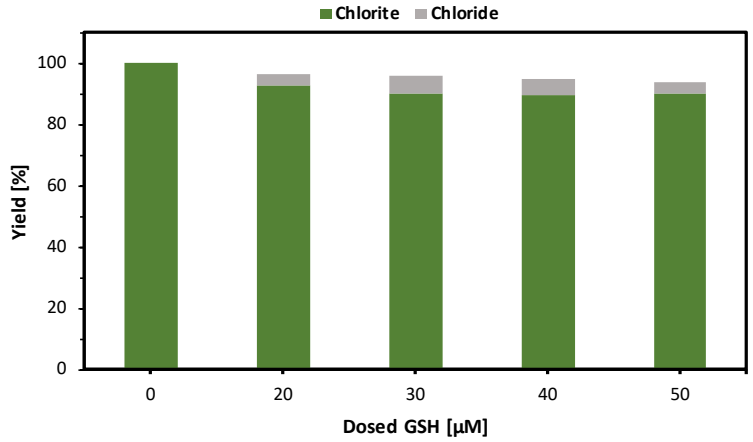
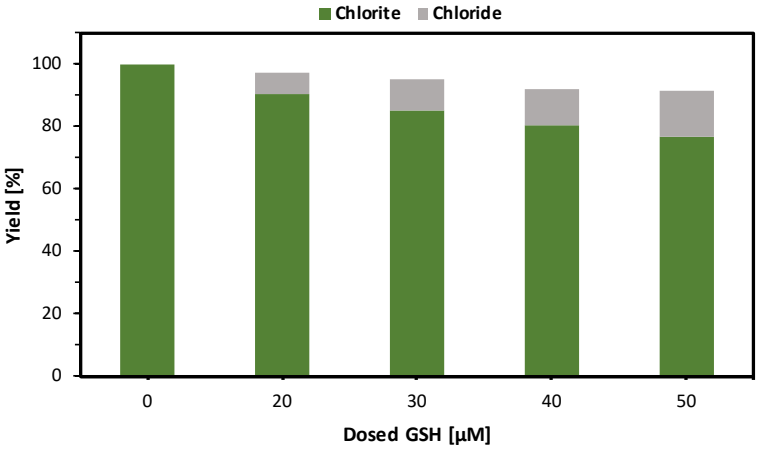


Figure S1: Proposed reaction pathway of methionine with HOCl. Adapted from Deborde et al. 2008.[1]

A



B



C

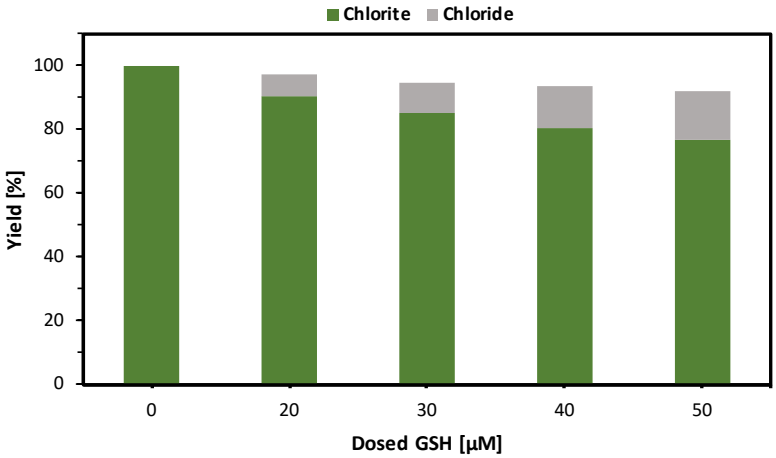


Figure S2: Turnover of ClO_2^- to Cl^- in GSH reaction. Different doses of GSH (0 – 50 µM) were dosed to 100 µM ClO_2^- and chlorine species were measured by IC after different reaction times (A=5min, B = 24 hours, C = 48 hours). The reaction solution contained additionally 10 mM glycine and 5 mM phosphate buffer at pH 7. Note that glycine was added to observe potential FAC formation.

Text S1: Determination of Reaction stoichiometry

For the reaction of GSH with ClO_2 the reaction stoichiometry has been determined as well. In order to determine the consumption of ClO_2 in presence of different concentrations of GSH were measured. Therefore, 200 µM ClO_2 was added to a 3 mL cuvette in presence of 5 mM phosphate buffer and the solution was measured at 359 nm. Different concentrations of GSH were added and the degradation of ClO_2 was determined by direct UV adsorption at 359 nm (Figure S2). The slope of the ClO_2 degradation over the added GSH concentrations equals to the consumed molecules of ClO_2 per molecule of GSH.

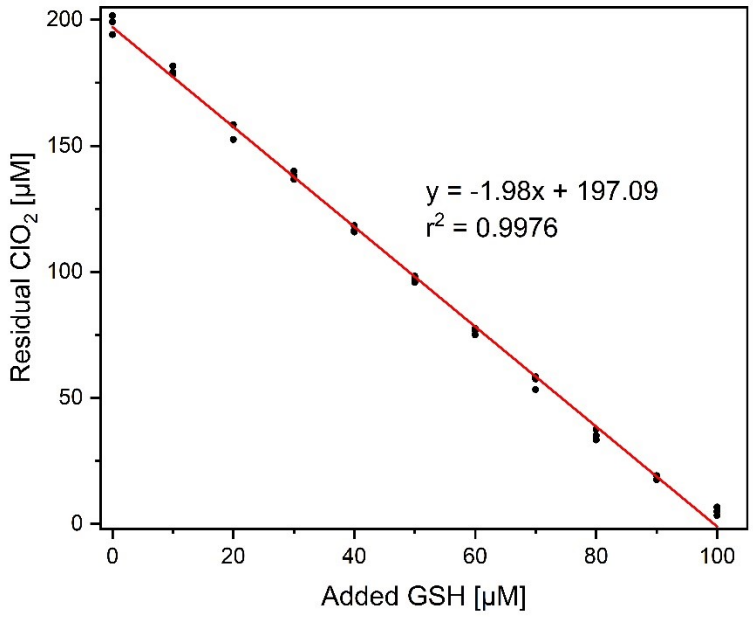
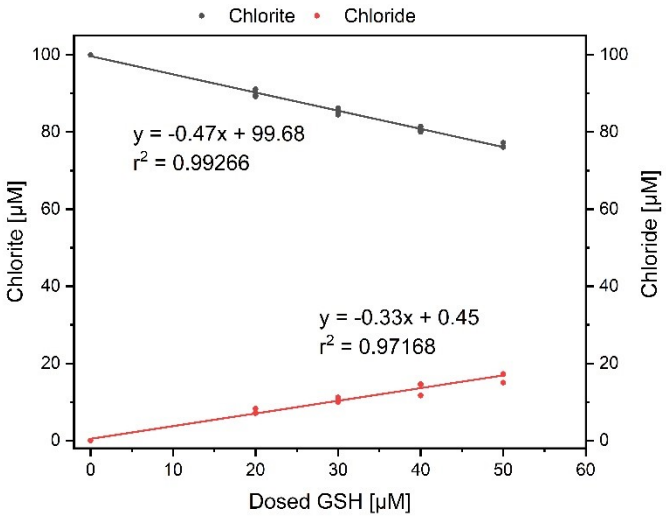


Figure S3: Degradation of ClO_2 by adding different concentration of GSH. Stock solution contained 200 µM ClO_2 and 5 mM phosphate buffer at pH 7. Degradation of ClO_2 was measured by direct absorption at 359 nm. All experiments were carried out in triplicates and the linear regression includes all data points.



47

48 Figure S4: Degradation of ClO_2^- versus added GSH concentration after 24 hours of reaction time. Reaction
49 solution contained 100 µM ClO_2^-, 10 mM glycine, and 5 mM phosphate buffer at pH 7. Experiments were
50 carried out in triplicates and the linear regression includes all data points.

51 **Literature**

52 (1) Deborde, M.; von Gunten, U. *Water Res.* **2008**, *42* (1–2), 13–51.

53