Investigation of the chlorine dioxide redox chemistry in ESI

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Preparation of chlorine dioxide

The chlorine dioxide solutions are purified with a stripping apparatus. This technique is based on the work of Bray [1] and Kepinski [3][2]. The main iteration here is the higher efficiency due to the cyclic design of the apparatus. The chlorine dioxide concentration in the solution is then determined by photometry. As the impact of other ions has to be determined this is one of the main aspects of this work.

Description of the used systems

Two different setups were part of this study to be able to compare the setups:
Thermo system: Components:

- Thermo LTQ XL Finnigan
- Merck-Hitachi L-7200 LC-Pump

The sample is injected in a $20\mu L$ loop in the internal 6-way valve of the mass spectrometer. The liquid flow is $100\,\frac{\mu L}{\text{min}}$ of acetonitril/water/formic acid (50/50/0.1).
Sciex system: Components:

- Sciex 6500
- G1310A Isopump
- G1312A Binary pump

The sample gets deliverd by the integrated syringe pump with a flow of $12\,\frac{\mu L}{\text{min}}$ soluted only in purified water. For injection the integrated 6-way valve with a 20 µL is used and switched every minute for 0.1 minutes. The flow of $100\,\frac{\mu L}{\text{min}}$ water is delivered by the binary pump trough the sampler and mixed with a flow of $100\,\frac{\mu L}{\text{min}}$ acetonitril/formic acid (100/0.2) in the grounded mixing chamber on the ion source. The source settings are the following:

- Curtain Gas: 20.0
- IonSpray Voltage: 5500.0
- Temperature: 300.0
- Ion Source Gas 1: 40.0
- Source Gas 2: 20.0

Sources

(1) Bray, W. *Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre* **1906**, *54*, 569–608.

(2) Kc epiński, J.; Kalucki, K. *Chemia Stosowana* **1964**, *4B*, 467–488.

(3) Kpiński, J.; Kalucki, K. *Ann. Soc. Chim. Polonorum* **1964**, *38*, 201–201.

(4) Stewart, D. J.; Napolitano, M. J.; Bakhmutova-Albert, E. V.; Margerum, D. W. *Inorganic Chemistry* **2008**, *47*, 1639–1647.

Acknowledgement

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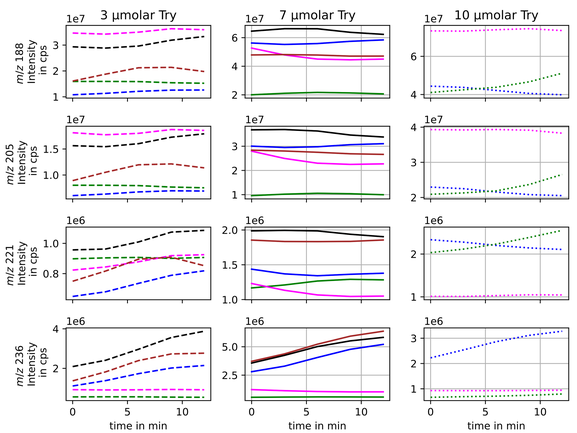
Influence of chlorite and chlorate

Determination of the impact of chlorite and chlorate on the ionization of tryptophan and the influence on the reaction between tryptophan and chlorine dioxide. Each mixture is in isomolar ratio of tryptophan and every added species. The m/z ratios of 221 m/z and 236 m/z are expected as these compounds are well described by Margerum et al[4].



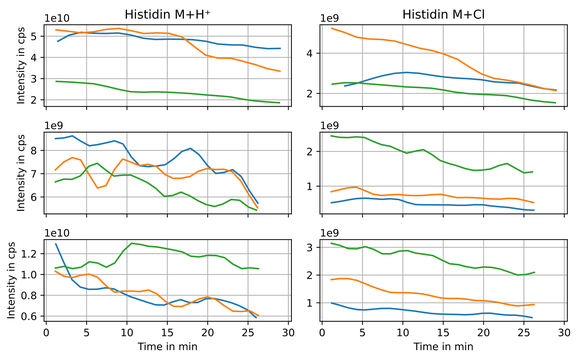
- blue: *mixture with chlorine dioxide*
- green: *mixture with sodium chlorite*
- magenta: *mixture with sodium chlorate*
- brown: *mixture with chlorine dioxide and sodium chlorite*
- black: *mixture with chlorine dioxide and sodium chlorate*

Conclusion

- Chlorine dioxide has a manageable impact on the yield of ions in electro spray ionization. That enables continuous flow measurements, flow injection analysis without the removal of chlorine dioxide and the experiments shown in this work.
- The ionic chlorine oxide species tend to have little to no impact on the reactions in the solution in these concentrations. This further enables flow injection analysis as the limits on these species are lower than here in drinking water.
- The reaction of chlorine dioxide with amino acids can be measured with this method. The concentration has to be kept under $10 molar$ for this. For shorter reaction times this method seems not applicable.
- The use of Sciex instruments is recommended as they tend to have more stable conditions in the ion source due to the higher flow rates of gas and the higher stability of the temperature. Furthermore this indicates further questions regarding the whole electro chemistry in electro spray ionization.

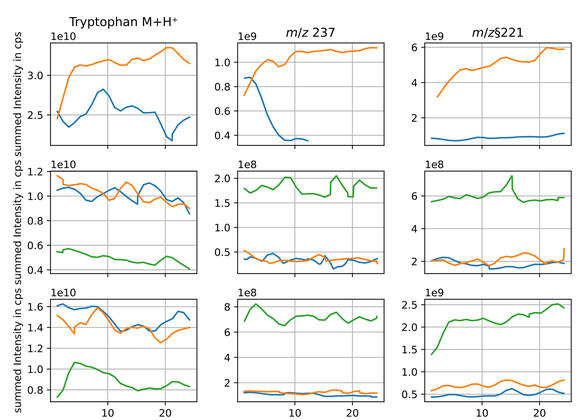
Reaction products of chlorine dioxide and histidin

These experiments show the $M+H^+$ of histidin and a reaction species containing with the *m/z* ratio of M-H+Cl. The ratios between histidin and chlorine dioxide were changed between 2:1 **(blue)**, 1:1 **(orange)** and 1:2 **(green)** for the concentrations of 13 μmolar (bottom), 6 μmolar (middle) and 3 μmolar (top).



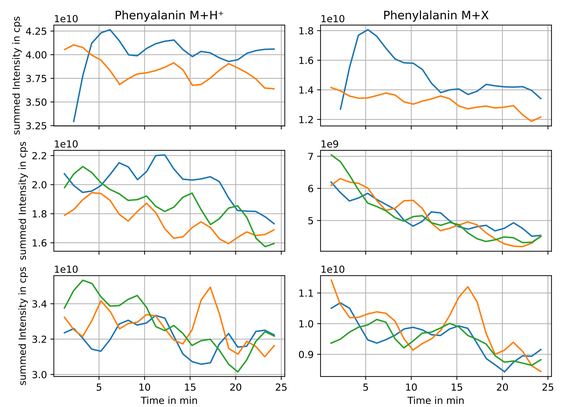
Reaction products of chlorine dioxide and tryptophan

These experiments show the $M+H^+$ of tryptophan and a reaction species containing with the *m/z* ratio of 237 and 221 [4] The ratios between tryptophan and chlorine dioxide were changed between 1:1 **(blue)**, 1:2 **(orange)** and 1:3 **(green)** for the concentrations of 1.3 μmolar (bottom), 3 μmolar (middle) and 6 μmolar (top).



Reaction products of chlorine dioxide and phenylalanin

These experiments show the $M+H^+$ of phenylalanin and a reaction species containing with the *m/z* ratio of 207. The ratios between phenylalanin and chlorine dioxide were changed between 2:1 **(blue)**, 1:1 **(orange)** and 1:2 **(green)** for the concentrations of 13 μmolar (bottom), 6 μmolar (middle) and 3 μmolar (top).



Analysis of the impact of the liquid flow composition

blue: mixed flow each $100\,\frac{\mu L}{\text{min}}$ of water and acetontrile, **orange:** only water $200\,\frac{\mu L}{\text{min}}$, **green:** only acetonitrile $200\,\frac{\mu L}{\text{min}}$; **top row:** TIC, **second row:** $M+H^+$, **third row:** Fragment m/z 188, **bottom row:** Fragment m/z 144