

Introduction

Chlorine dioxide is a common chemical for water disinfection. Due to the high impact potential toxic and carcinogenic reaction products can have in this use there is a big interest in these. In previous work only in-situ produced chlorine dioxide was used and the samples were separated with LC. To investigated with ESI in short time scales reaction products that does not seem suitable. To be able

to generate reliable data with ESI out of reaction mixtures there is the need to understand the processes in ESI under the influence of chlorine oxide compounds as the typical reaction product of chlorine dioxide chlorite. As that has a high reactivity itself and is quite sensitive to electro chemistry this leads to complex problems in ESI. This is investigated in this work.

Method

The chlorine dioxide solutions are purified with a stripping apparatus. This technique is based on the work of Bray [1] and Kepinski [2][3]. 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. The samples are infused with a 6-way valve and the eluent flow of 100 μL per minute of a mixture of Acetonitrile/water (50/50, v/v) with an addition of 0.5 v% formic acid is generated by an isocratic Agilent 1200 G1310A pump. The used sample loop has a volume of 20 μL and the injection volume is also 20 μL . The used mass spectrometer is an Sciex6500 Triple Quadrupole mass spectrometer used without a Selexion interface. For tryptophane the m/z ratios 188.0, 205.0 221.0 and 236.0 are measured in the SIM mode.

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

Unique aspects of the experiments

Mixing chlorine dioxide solutions with organic compounds is not complicated nor special. Using pure chlorine dioxide and a dilute and shoot method after a reaction time period is. On the one hand having no ion species of the reaction is simplifies the whole system and let one compare the influence of chlorite as reaction product in longer time scales. Furthermore the dilute and shoot aspect without a chromatographic separation enables a variety of kinetic experiments that are not done until now.

Outlook

Further experiments should focus on different Indol systems and extend the time scale. This also enable kinetic experiments with this setup. These should be supported by conductivity measurements as the chlorite created by the primary reaction can easily be quantified this way. Furthermore the redox chemistry of the chlorine oxide species like chlorate and chlorite in interaction with an electro spray ionization has to be further investigated.

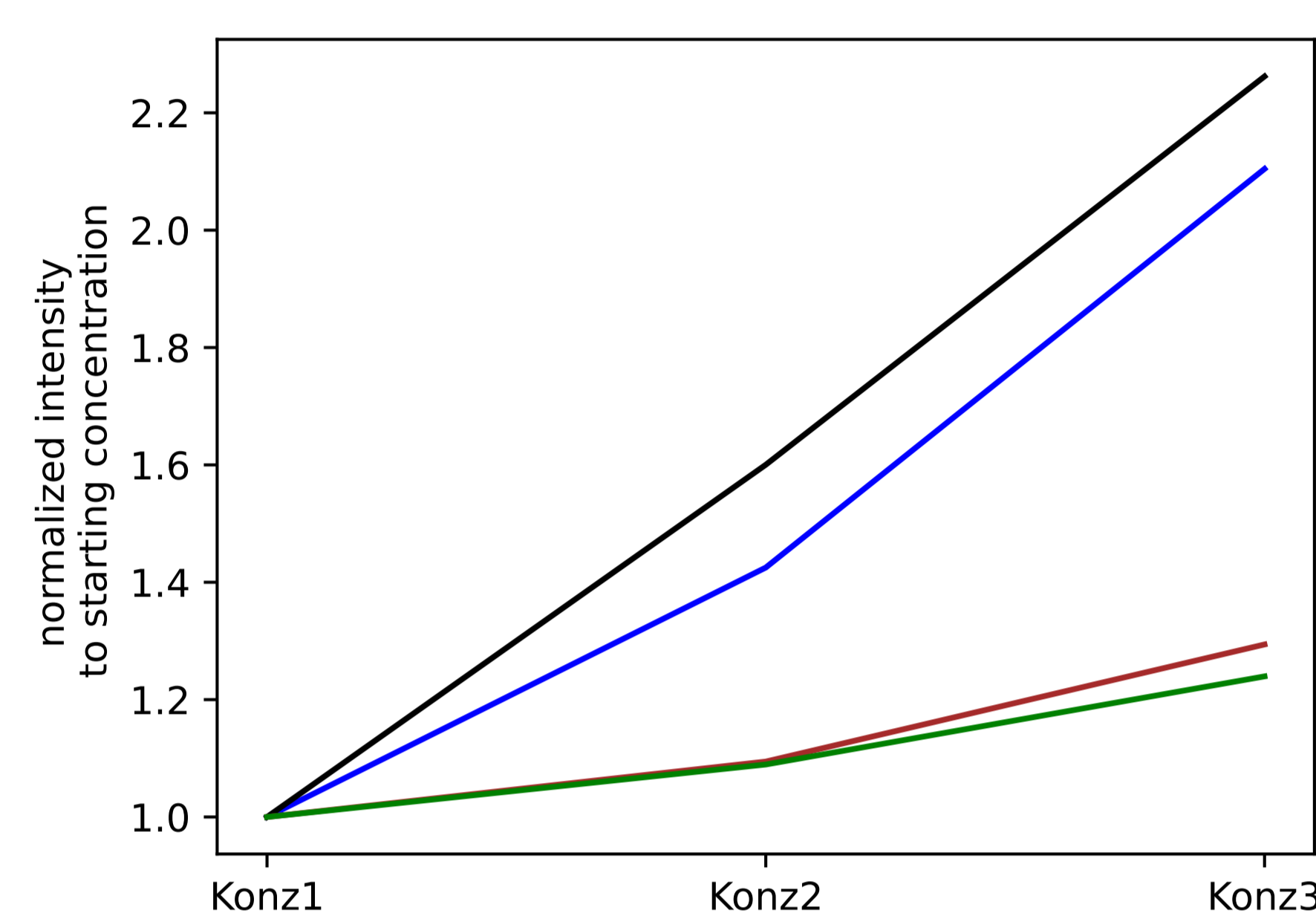
Bibliography

- (1) Bray, W. *Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre* **1906**, *54*, 569–608.
- (2) Kępiński, J.; Kalucki, K. *Ann. Soc. Chim. Polonorum* **1964**, *38*, 201–201.
- (3) Kępiński, J.; Kalucki, K. *Chemia Stosowana* **1964**, *4B*, 467–488.
- (4) Stewart, D. J.; Napolitano, M. J.; Bakhmutova-Albert, E. V.; Margerum, D. W. *Inorganic Chemistry* **2008**, *47*, 1639–1647.

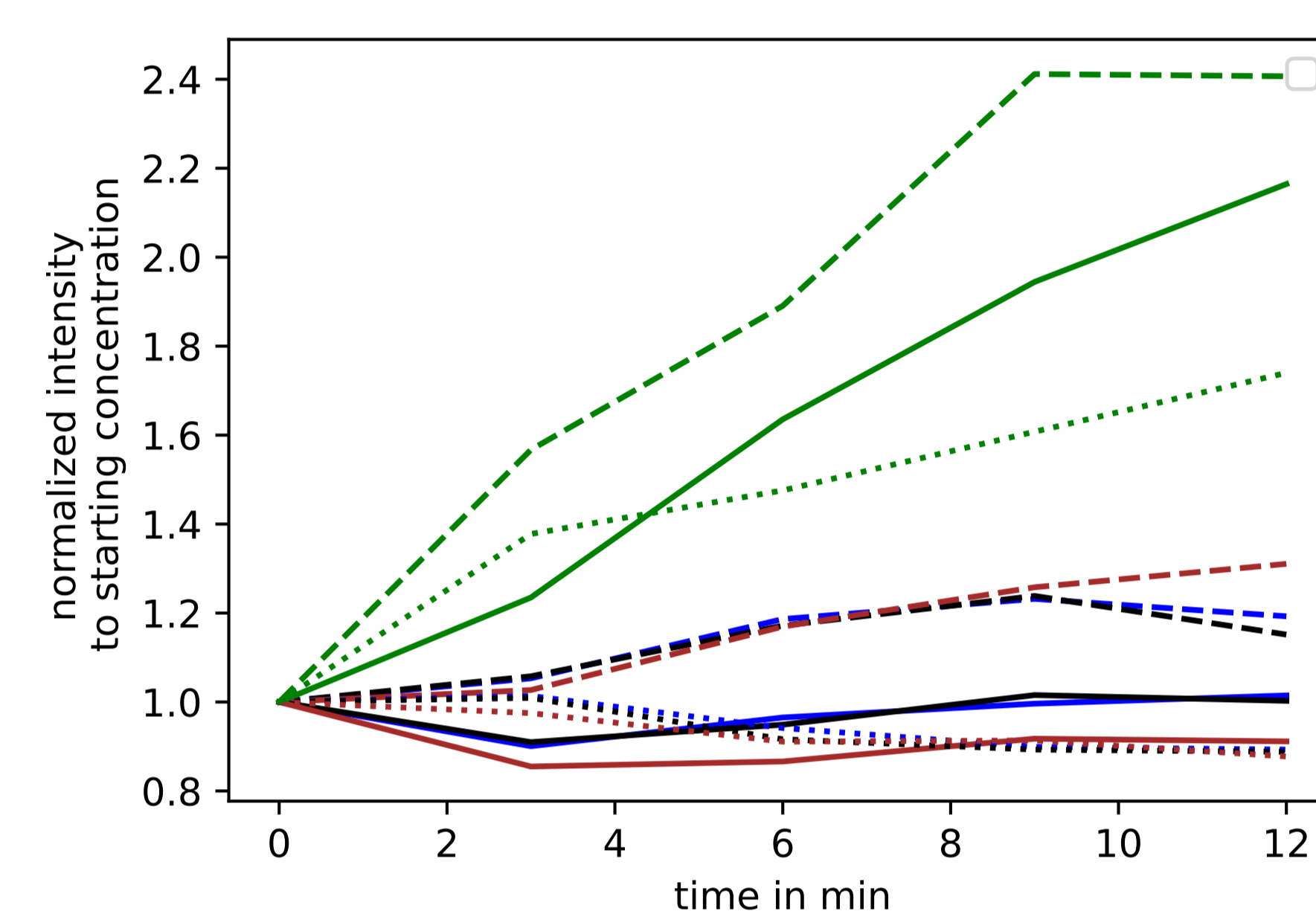
Results

In the following figures the concentration gets varied. This is indicated by the linestyle. Dashed lines are the lowest concentration of 3 μmol followed by double the concentration indicated by solid lines and three times the starting concentration is a dotted line. The observed m/z ratios are marked with following scheme: blue: 188 m/z; black: 205 m/z; brown: 221 m/z; green: 236 m/z. The reaction time is 12 minutes and 5 samples are measured.

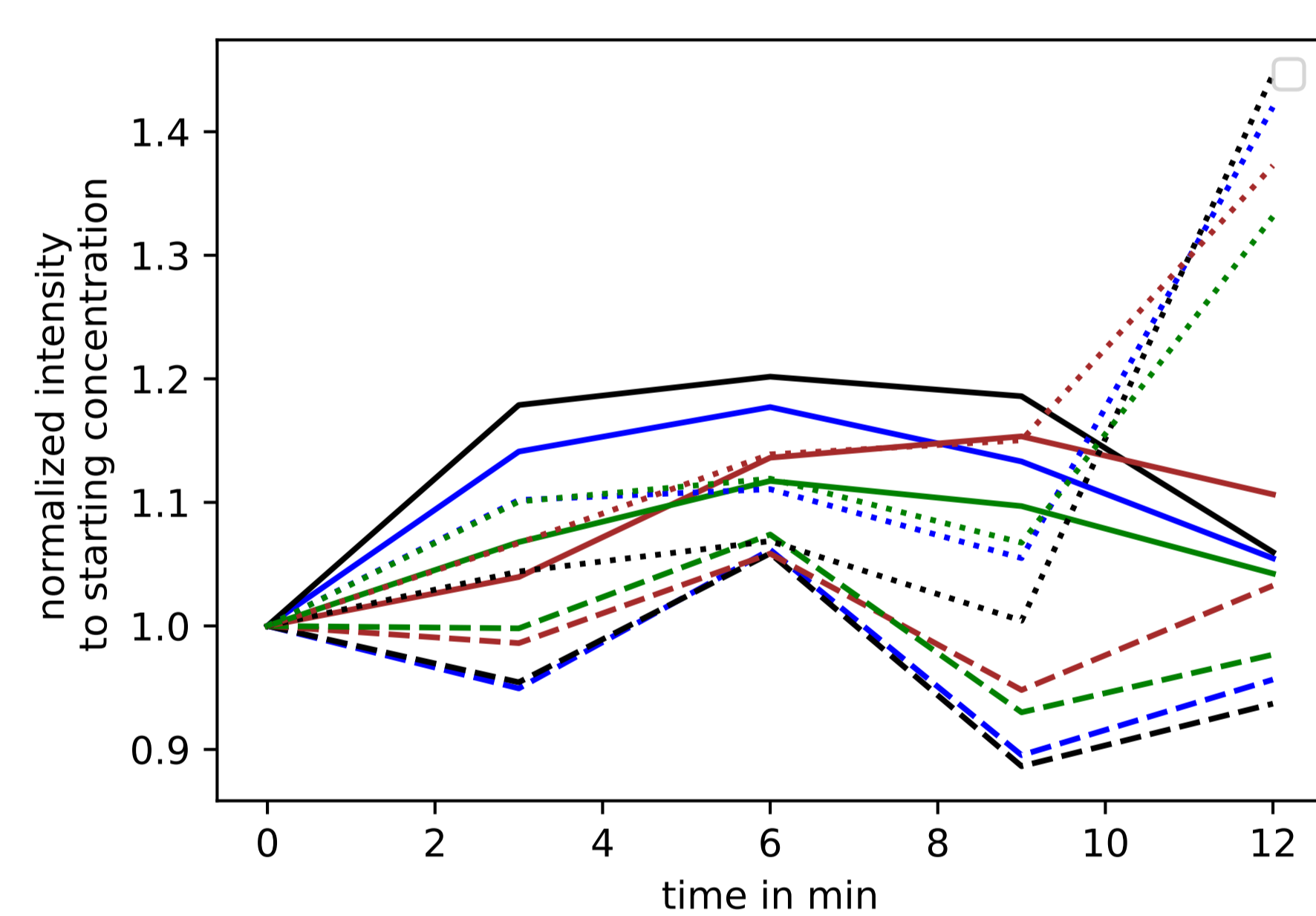
Kalibration tryptophan



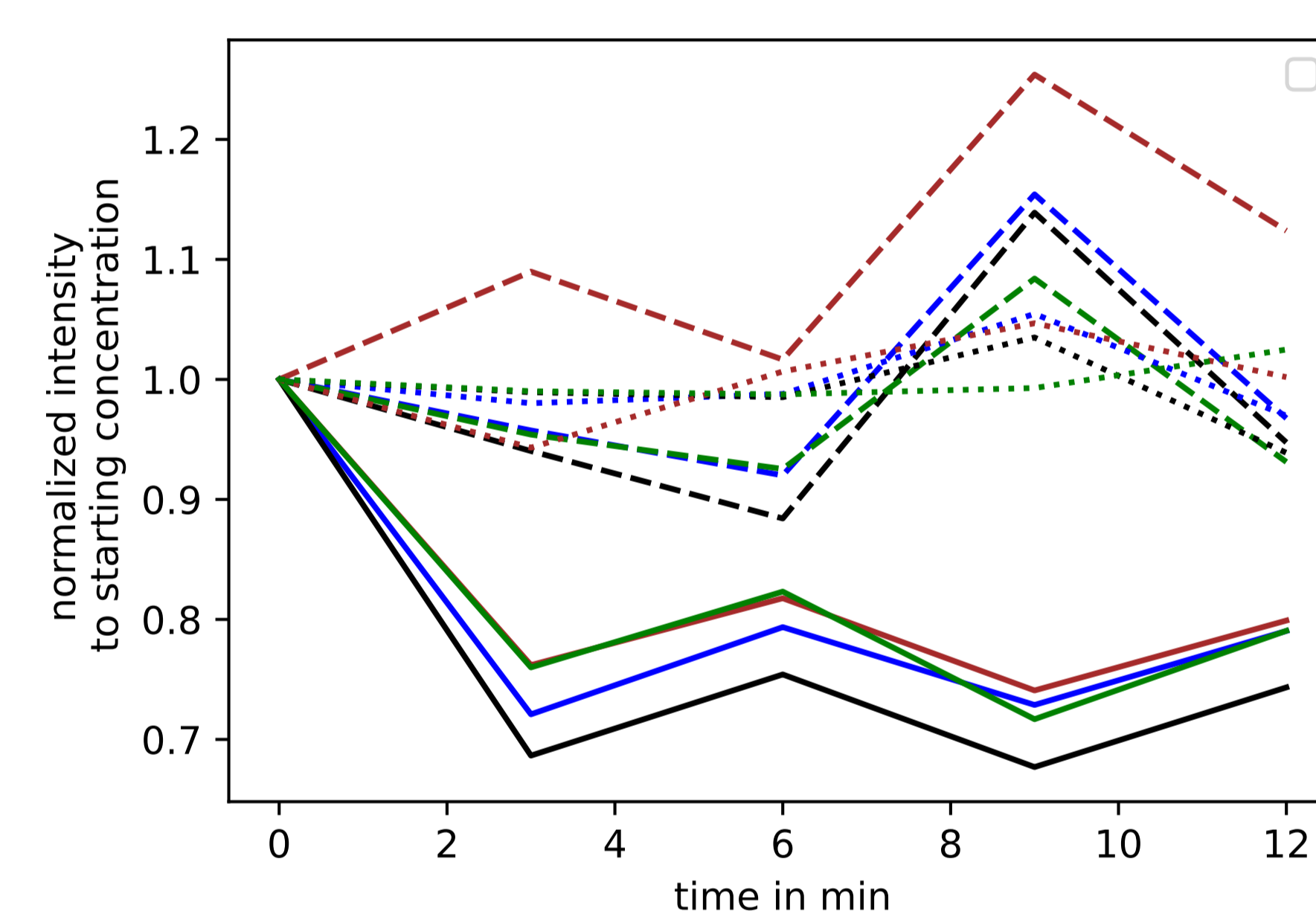
Chlorine dioxide and tryptophan



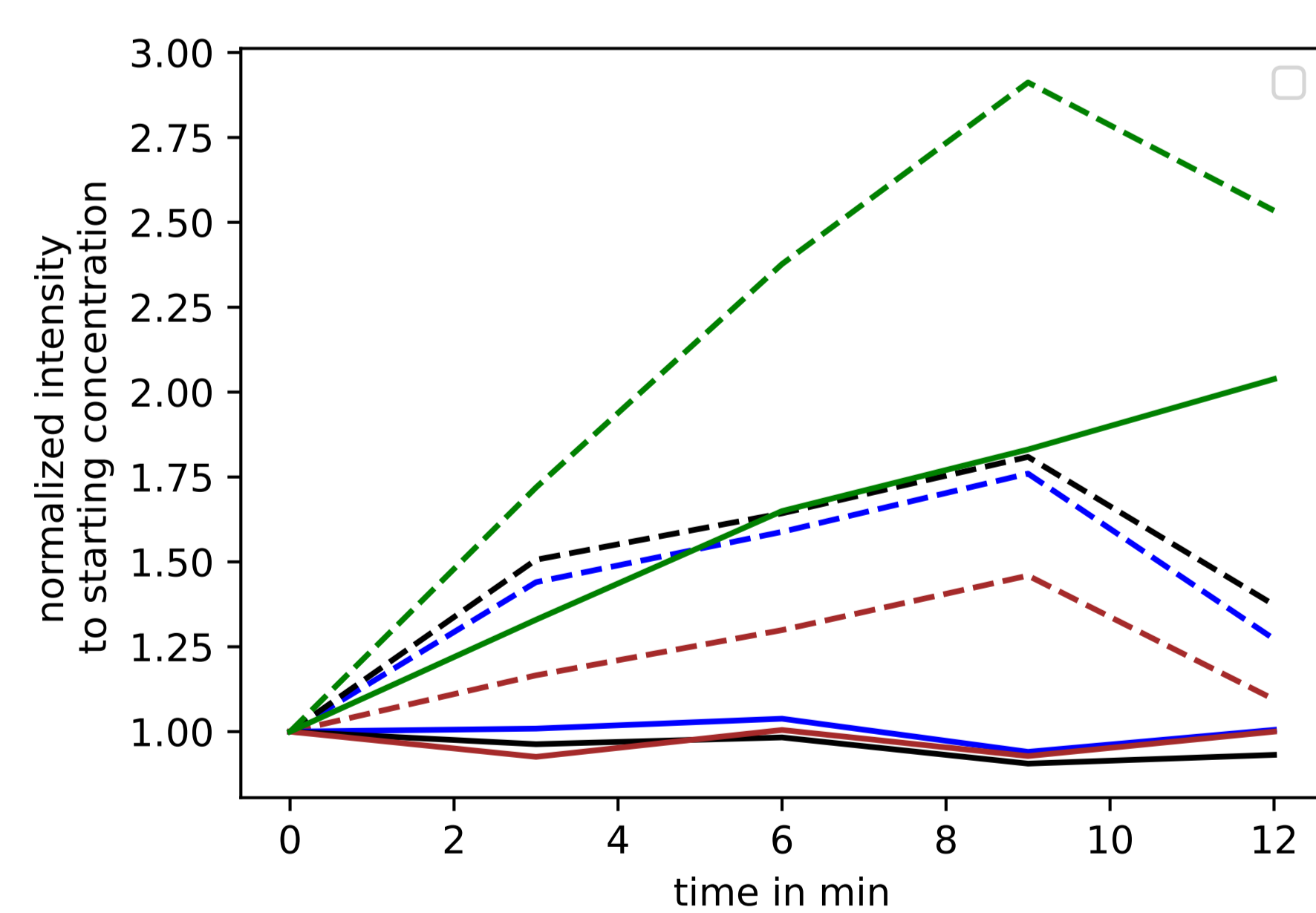
Chlorite and tryptophan



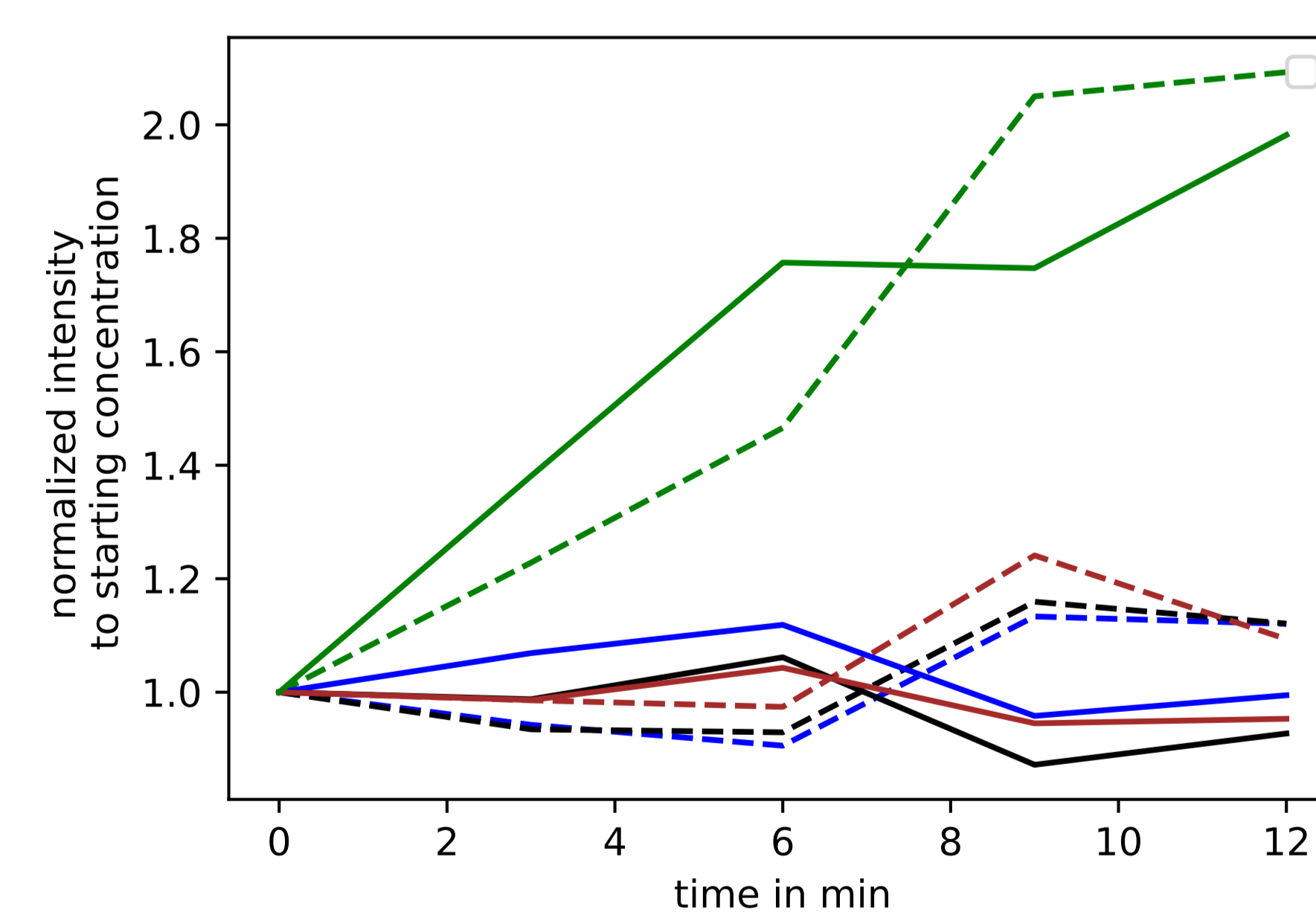
Chlorite and tryptophan



OCIO, NaClO₂ and Try



OCIO, NaClO₃ and Try



Conclusion

It could be seen that the previous results of Margerum et al.[4] could not be reproduced. That leads to big questions. Furthermore the experimental conditions also have a big influence on the found species and intensities. This is mainly rooted in the ion sources. As changing that usually requires a different mass spectrometer the comparability is naturally limited. Previous experiments showed an overall outstandingly bad performance with the method with the Bruker systems overall and a Thermo Finnigan LIT. Furthermore quite interesting results could be seen with tryptophane alone. If its only soluted in water and then injected into the mass spectrometer as oxidation species only the m/z 236 can be found. The influence of oxygen in the atmosphere could not be determined so far. This is also true for tryptophane solutions without chlorine dioxide. That leads to interesting questions what the source of m/z 236 is in Margerums work[4]. Furthermore the oxidative strength of chlorite seems to be neglectible in time frames of these experiments. For further experiments the time scale has to be extended. The same is observed for chlorate. The mixtures showed that the overall reactivity is higher with chlorate. That is quite confusing and needs further investigation as it opposes secondary reactions of chlorite produced by the chlorine dioxide indol reaction.