Degradation and by-products identification of benzothiazoles and benzotriazoles during chlorination by LC-HR-MS/MS

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Abstract

Nowadays, chlorination is the most prevalent disinfection method applied for water treatment in Europe. Chlorine can be supplied as sodium hypochlorite (NaOCl) which reacts in water to produce the disinfectants hypochlorous acid (HOCI) and hypochlorite ion (OCl−), otherwise known as free chlorine. Although the primary purpose of chlorination is the elimination of micropollutants via oxidation, several investigations have shown that chlorine reacts with natural organic matter leading to the production of undesired by-products. 1,3-benzothiazoles (BTHs) and 1,2,3-benzotriazoles (BTRs) are classified as high production volume emerging environmental pollutants due to their broad industrial and domestic application, and even though recently several analytical methods have been applied for their determination, there is still a lack of research for their by-products’ identification.

Initially, the degradation of three BTHs (BTH, 2-OH-BTH and 2-amino-BTH) and four BTRs (1-H-BTRi, TTRi, XTRi and 1-OH-BTRi) during chlorination was investigated by UHPLC-MS/MS (QqQ). Although chlorination appeared to be an insufficient degradation process for BTH and 1-H-BTRi, all their examined substituted derivatives seem to be significantly degraded when the molar ratio of sodium hypochlorite and the target analytes was between 5000:1 – 1000:1. Then, LC high resolution MS/MS (q-TOFMS) was used to investigate the formation of by-products in the chlorinated samples. Two suspect by-products of 2-amino-BTH and one of XTRi were tentatively identified based on their probable structure, mass accuracy, retention time and fragmentation and isotopic pattern. An interesting observation was the formation of 1-H-BTRi as a degradation product of 1-OH-BTRi during chlorination. Moreover, post-acquisition non-target treatment of the MS data revealed several unknown by-products of the tested analytes.

Experimental

Investigation of the molar ratio:

BTHs:
- 2-amino-BTH: decrease over 90%, within the first 5 min, regardless of the molar ratio
- 2-OH-BTH: decrease over 50% within the first 10 min
- BTH: not significantly reacting

BTRs:
- As molar ratio decreases, degradation rate of all analytes decreases
- 1-H-BTRi: decrease over 50%, when molar ratio is 30000:1

Kinetic experiment (t1/2, kobs):
Pseudo-first-order plots were revealed
Determination of t1/2 and kobs (the slope of the linear time-course plot) of 1st (analyzed) fraction

According to their degradation rate:
- Very fast degraded: 2-amino-BTH
- Fast degraded: 1-H-BTRi, TTRi, XTRi & 2-OH-BTH
- Slowly degraded: 1-OH-BTRi & BTH

Background subtraction (chlorinated-zero-time sample)
Revelation of “hidden” peaks (unknown by-products can now be identified)

By-products investigation:
- 2-amino-BTH: 2-amino-5-chloro-1,3-benzothiazol & 2-amino-5,6-dichloro-1,3-benzothiazol were tentatively identified (mass accuracy/1 fragmentation & isotopic pattern)
- XTRi: chloro-5,6-dimethyl-benzotriazole was detected (MS/MS spectrum)
- 1-H-BTRi: 1-H-BTRi was produced (confirmation with reference standard)

Results and discussions

Chlorination experiments:
- Author vials
- Buffer CH3CONa: 1 mM (pH = 7.0 ± 0.12)
- Stock solutions of the analytes 1000 μg/mL
- Commercial chlorine (4.8 g NaOCl in 100 g Na2SO4) with the residual chlorine and the oxidation reaction

Kinetic experiment (t1/2, kobs):
Molar ratio which provokes at least 50% decrease
1-H-BTRi & TTRi vs 8000:1, 1-OH-BTH & 2-OH-BTH vs 1000:1, 1-OH-BTRi vs 5000:1, 2-amino-BTH vs 1000:1

By-products investigation:
TTRi, XTRi & 2-OH-BTH vs 2000:1, 1-OH-BTRi vs 1000:1 & 100:1

Fig. 1. Degradation charts of benzothiazoles and benzotriazoles depending on the molar ratio of Cl/analytes.

Table 1. Determination of t1/2 and kobs

<table>
<thead>
<tr>
<th>Analyte</th>
<th>t1/2 (min)</th>
<th>kobs (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-H-BTRi</td>
<td>0.063</td>
<td>11.4</td>
</tr>
<tr>
<td>1-OH-BTRi</td>
<td>0.272</td>
<td>33.1</td>
</tr>
<tr>
<td>TTRi</td>
<td>0.241</td>
<td>3.22</td>
</tr>
<tr>
<td>XTRi</td>
<td>0.265</td>
<td>2.74</td>
</tr>
<tr>
<td>BTH</td>
<td>0.020</td>
<td>35.1</td>
</tr>
<tr>
<td>2-OH-BTH</td>
<td>0.034</td>
<td>5.30</td>
</tr>
<tr>
<td>1-OH-BTRi</td>
<td>0.024</td>
<td>30.4</td>
</tr>
</tbody>
</table>

Fig. 2. Linear time-course plot of (Lx=2amino-BTH)/(Lx=2amino-BTH).

Conclusions
- The degradation rate of the benzothiazoles seems to increase proportionally to the molar ratio of Cl/analyte. Benzothiazoles are either degraded within the first 10 min, or they do not significantly react.
- Chlorination kinetic parameters (kobs and t1/2) were determined for all the analytes, that were classified according to their degradation rate (very fast, fast and slowly degraded).
- One and two by-products were tentatively identified in the chlorinated samples of XTRi and 2-amino-BTH, respectively, while 1-H-BTRi seems to be produced by the chlorination of 1-OH-BTRi. Furthermore, numerous by-products’ peaks were revealed in the chlorinated samples of 2-amino-BTH and XTRi.

Fig. 3. MS and MS/MS spectrums of the identified by-products.

Fig. 4. Background subtraction for the revelation of more unknown by-products.