Determination of odour threshold concentrations and dose–response relations in water of several minor disinfection by-products: aldehydes and alkyl nitriles

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Abstract The odour threshold concentrations (OTCs) levels of aldehydes and alkyl nitriles, two groups of disinfection by-products of water treatment, have been studied in order to know if some of these compounds can be associated with off-flavour events. For aldehydes, as a result of the values obtained, which are in the low µg/L range, it is possible that they are related to these events. This is not the case for the other group, alkyl nitriles, with very high OTC values.

Keywords Aldehydes; alkyl nitriles; disinfection by-products; drinking water; flavour profile analysis; off-flavours

Introduction
Disinfection by-products (DBPs) form as a consequence of common water disinfection practices, and some taste and odour problems are the indirect result of water treatment. Trihalomethanes and haloacetic acids are the most abundant DBPs usually detected in any treated water; however, only bromoform and iodoform with odour threshold concentrations (OTCs) of 50 µg/L and 0.3 µg/L, respectively (Bruchet et al., 1989), have been associated with off-flavour episodes. The OTC values of iodinated trihalomethanes have been recently published (Cancho et al., 2001) showing that diiodinated species also have sub-µg/L OTCs. Whereas the sensory characteristics of disinfectants such as chlorine and chloramine species have been investigated thoroughly, little is known about many DBPs. Thus, the aim of this study is to investigate the OTCs of several groups of DBPs, such as aldehydes and alkyl nitriles, in order to know if they could be associated with taste and odour events. Aldehydes are generally known as ozonization by-products but they also form from chlorination of aminoacids (Bruchet, 1992; Hrudey et al., 1990) as well as haloacetonitriles, whereas alkyl nitriles form upon further chlorination/chloramination of aldehydes (Hrudey, 1989). Low molecular weight aldehydes were considered the compounds causing odour in drinking water treatment (Hrudey et al., 1988; Daignault et al., 1988; Froese et al., 1999).

Methods
Panellists
Panellists were a group of 18 students ranging from 20 to 24 years old, including both men and women. They had been carefully selected so that their sensibilities were above average in relation to the basic tastes and odours, and had been trained in water and description. They were familiar with analyses of odours in natural and supply waters. Each time five to seven carried out the odour threshold tests. Panellists were changed round during the different sessions and did not always have the same session colleagues.
Glassware

All glassware was washed with soapy water and rinsed with tap water and with ultrapure water from a Milli-Q water purification system (Millipore, Bedford, MA). The glassware used in the tests was not used for other purposes.

Reagents

Commercial aldehydes and alkyl nitriles were from Aldrich. Still, natural mineral water (conductivity: 430 µS/cm) was used to prepare the solutions and the same water was used as blanks.

Standard solutions and samples

Dilutions and samples were prepared the same day the tests were performed and in a different room from the one used for the sensory analysis. 1,000 mg/L stock solutions were prepared in methanol, while, from this standard solution, the other stock solutions were prepared in ultrapure water. Samples were dissolved in commercial mineral water and the same water was used as blanks.

Determination of the guide-concentration

Prior to the panel session and if there was no idea at all of the odour threshold of the compound, the organiser had to determine the Guide-Concentration, i.e. that concentration similar in order to the odour threshold. So, five ascending concentrations of the compound from 50 ng/L to 500 µg/L were prepared in Erlenmeyer flasks (500 mL) with ground-glass stoppers and with 200 mL of mineral water. The sample with the Guide-Concentration had to have a faint smell compared with the samples of immediately superior and inferior concentrations.

Preparation of the samples

Once the Guide-Concentration was obtained, a set of increasing-concentration dilutions of each individual compound was prepared spiking several volumes, from 2.4 µL to 640 µL, of stock solution to 200 mL of mineral water in Erlenmeyer flasks (500 mL) with ground-glass stoppers. The concentration of the sample with 100 µL of stock solution corresponds to the Guide-Concentration. Dilutions were presented to the panellists from the most diluted to the most concentrated, and different blanks were inserted among these samples. All of them were coded at random and only known by the organiser.

Once the samples were prepared, they were put with the blanks into a bath at a controlled temperature of 45 ± 1°C half an hour before the sessions began.

Flavour Profile Analysis (FPA)

Odour was assessed by swirling the sample, taking the stopper off and immediately applying the nose to the mouth of the flask, sniffing the vapours. All the assessors had a blank water sample to compare with the samples and to clean their nasal cavities and they had to note down on the result sheet whether the sample was a blank or not and to estimate the response of odour intensity of the series. If it was not considered a blank, the taster described the odour and indicated its intensity on a 1 (beginning of perception) to 12 (very strong) scale, with all intermediate values: 2 (very faint), 4 (faint), 8 (moderate).

Measurement of the OTC

The threshold concentration for each panellist was that concentration from which that panellist correctly identified beakers with samples and beakers with blanks, although he was incapable of recognizing the odour.
The experimental threshold concentration for a compound (OTC$_{exp}$) was defined as the lowest concentration found by any of the panellists.

The average intensities for each compound were recorded and plotted versus all the concentrations studied as a Weber–Fechner curve, which relates odour intensity to the logarithm of odourant concentration. From the equation obtained, the OTC was defined as the value of the log of the concentration corresponding to an average intensity of the unity ($I = 1$).

**Results and discussion**

**Odour threshold concentrations**

The OTCs obtained in this study are listed in Table 1. This table includes the lowest concentration at which any of the panellists detected an odour (OTC$_{exp}$), with the number of assessors detecting that concentration shown in brackets. In most compounds, only one of the panellists detected the concentration shown. Just in one compound, isovaleronitrile, the six panellists participating in the session detected an odour from the same concentration. Since a few panellists detected the OTC$_{exp}$ and since there is a possible margin of error associated with that concentration because dilution intervals are of factors of about 2.5, OTC values obtained from the extrapolation of the dose–response Weber–Fechner plots at $I = 1$ also appear in the tables.

The table also includes the $R^2$ values for the Weber–Fechner plot, which range from 0.9198 to 0.9991, being better for alkyl nitriles than for aldehydes.

The experimental odour threshold concentrations of aldehydes range from 0.03 µg/L for undecanal to 47 µg/L for benzaldehyde. It is interesting to note that decanal, undecanal and dodecanal have lower OTCs than low molecular weight aldehydes. On the contrary, among straight chain aldehydes, C$_3$, C$_4$ and C$_5$ present the highest OTC, between 2 and 12 µg/L.

Octanonenitrile and dodecanenitrile show the lowest OTC (0.5 and 0.09 µg/L, respectively) from the alkyl nitriles studied, while butyronitrile and isobutyronitrile show the highest.

**Odour descriptors**

Table 1 summarises the odour descriptors which were most frequently used by panellists. The main odour for aldehydes is fruity, mostly citrus fruits. Some of them are sweet and some others rancid or decaying aromas, or even insecticide odours. Propanal above 200 µg/L and butanal have solvent aromas.

![Figure 1](https://iwaponline.com/wst/article-pdf/49/9/267/421101/267.pdf)  
**Figure 1** Shows an example the Weber–Fechner curves for an aldehyde (pentanal) and for an alkyl nitrile (hexanenitrile).
Alkyl nitriles appear to have mostly solvent odours, although fruity ones as well. Some of them have unpleasant or decaying odours, although some others have sweet ones.

For some chemicals, the descriptors changed with increasing concentrations. For example, the odour of hexanal was predominantly described as “green, grass, earthy” at concentrations lower than 80 µg/L, and mainly “green apple, fruity, candy” at higher concentrations. Similar changes in odour descriptors were observed with other compounds.

**Presence in waters**

Unfortunately, information regarding the tastes and odours imparted to drinking water by aldehydes and alkyl nitriles is really limited.

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**Table 1** Odour descriptors and odour threshold concentrations for aldehydes and for alkyl nitriles

<table>
<thead>
<tr>
<th>NP</th>
<th>OTC&lt;sub&gt;exp&lt;/sub&gt; (µg/L)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt; values OTC</th>
<th>Descriptors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanal</td>
<td>6</td>
<td>12 (3)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9983</td>
</tr>
<tr>
<td>2-Methyl propanal</td>
<td>6</td>
<td>0.32 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9653</td>
</tr>
<tr>
<td>Butanal</td>
<td>4</td>
<td>2 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9944</td>
</tr>
<tr>
<td>3-Methyl butanal</td>
<td>6</td>
<td>0.8 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9931</td>
</tr>
<tr>
<td>Pentanal</td>
<td>5</td>
<td>5 (3)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9818</td>
</tr>
<tr>
<td>Hexanal</td>
<td>5</td>
<td>0.32 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.957</td>
</tr>
<tr>
<td>Heptanal</td>
<td>5</td>
<td>0.25 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9198</td>
</tr>
<tr>
<td>Octanal</td>
<td>5</td>
<td>0.32 (4)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9961</td>
</tr>
<tr>
<td>Nonanal</td>
<td>7</td>
<td>0.32 (3)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9965</td>
</tr>
<tr>
<td>Decanal</td>
<td>5</td>
<td>0.08 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9891</td>
</tr>
<tr>
<td>Undecanal</td>
<td>5</td>
<td>0.03 (2)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.985</td>
</tr>
<tr>
<td>Dodecanal</td>
<td>5</td>
<td>0.13 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9881</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>6</td>
<td>47 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9573</td>
</tr>
<tr>
<td>Phenylacetaldehyde</td>
<td>6</td>
<td>0.3 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9991</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>5</td>
<td>12 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.983</td>
</tr>
<tr>
<td>Butyronitrile</td>
<td>6</td>
<td>32 (3)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9842</td>
</tr>
<tr>
<td>Isobutyronitrile</td>
<td>6</td>
<td>64 (2)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.975</td>
</tr>
<tr>
<td>Valeronitrile</td>
<td>6</td>
<td>13 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9939</td>
</tr>
<tr>
<td>Isovaleronitrile</td>
<td>6</td>
<td>3.2 (6)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9847</td>
</tr>
<tr>
<td>Hexanenitrile</td>
<td>5</td>
<td>3.2 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9817</td>
</tr>
<tr>
<td>Octanonitrile</td>
<td>7</td>
<td>0.13 (1)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9934</td>
</tr>
<tr>
<td>Dodecanenitrile</td>
<td>6</td>
<td>0.32 (2)</td>
<td>R&lt;sup&gt;2&lt;/sup&gt; = 0.9959</td>
</tr>
</tbody>
</table>

*NP: number of panellists; OTC<sub>exp</sub>: odour threshold concentration directly smelled by the trained panel, number of panellists detecting an odour in brackets; OTC: odour threshold concentration obtained by Weber–Fechner (WF) plot*
Aldehydes have been quantitatively analyzed in several articles (AWWARF, Lyonnaise des Eaux, 1995). Table 2 shows the results of the analyses carried out in waters treated at several plants before and after ozonation (Glaze et al., 1989 a, b), in waters treated at the outlet of a treatment plant (Cancho et al., 2002) and in an episode determining that aldehydes were responsible for odour/taste (Romero and Ventura, 1996). These data are compared with the thresholds obtained from compounds in the present article. Thus, aldehydes may be considered to be responsible for odour in ozonised waters and in specific complaints.

Conclusions

For alkyl nitriles, only long chain nitriles (>C₈) presented OTC values <1 µg/L, while most aldehydes did. Only low molecular weight aldehydes and benzaldehyde exhibited OTC values higher than alkyl nitriles. While fruity odours were the main ones in aldehydes, solvent odours were mostly present in alkyl nitriles.

From the results obtained and taking into account the low OTCs accomplished for most aldehydes, these compounds can be involved in taste and odour events in waters. On the other hand, the high OTC levels obtained for alkyl nitriles make it reasonable to discard them as a potential group of compounds to be associated with off-flavour events.

References


