Field Study

Measurement of Concentrations of Thioglycolic Acid, Dithiodiglycolic Acid and Ammonia in Indoor Air of a Beauty Salon

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Abstract: Measurement of Concentrations of Thioglycolic Acid, Dithiodiglycolic Acid and Ammonia in Indoor Air of a Beauty Salon: Daisuke Oikawa, et al. Kankyo Research Co., Ltd.—Objectives: Among the many chemicals used in a hair salon, exposure to thioglycolic acid (TGA) used for permanent waving solutions (PWS) potentially causes adverse health effects. However, no report has been previously published on the indoor air concentrations of TGA in a beauty salon that contributes to assessment of exposure to TGA of hairdressers and their customers. This study aimed to demonstrate the present concentration levels of TGA in indoor air of a beauty salon where the PWS containing ammonium thioglycolate was actually used for perm treatments. Methods: A field measurement of TGA, dithiodiglycolic acid (DTDGA, a reaction product of TGA and cysteine residues of hair keratin) and ammonia was carried out in a beauty salon located at Tokyo, Japan, from June 30 to July 2. Both TGA and DTDGA were collected in water using an impinger and determined by high performance liquid chromatography (HPLC). Results: The indoor air concentrations of TGA were below the limit of detection of 0.008 mg m⁻³ at every event and much lower than occupational safety guideline levels set by the NIOSH and ACGIH. Meanwhile, the concentrations of ammonia ranged from 0.15 to 0.87 mg m⁻³, and relatively higher concentrations were found during perm events and in samples collected near stations used for perm treatments. Concentrations of DTDGA varied from <0.026 mg m⁻³ to 0.75 mg m⁻³. Conclusions: There was a different emission process of TGA and ammonia from PWS, and airborne TGA is not important as a possible exposure route for hairdressers and customers in this beauty salon.

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Key words: Beauty salon, Dithiodiglycolic acid, High performance liquid chromatography (HPLC), Permanent waving solution, Thioglycolic acid

Permanent waving treatments for hair have been popularly carried out for many decades. The chemical process occurring in perm treatments consisting of hair reduction and subsequent oxidation involves the reactions mainly concerning thiol (SH) and disulfide (SS). A permanent waving solution (PWS) is commonly used for chemical waving for hair styles, and the major ingredient of PWS is thioglycolic acid (TGA, CAS. No. 68-11-1) added as ammonium salt. In the reduction process, TGA works as a reducing agent to cleave the disulfide bonds of cysteine residues in keratin proteins of hair, i.e., cleavage of cross-links between an intermediate filament and matrix keratin protein (KAP) and between KAP-KAP components. TGA is a colorless and water soluble liquid with 1.3 kPa of vapor pressure at 18°C. Although the odor threshold for TGA is presently not available, TGA vapor usually becomes the source of the specific pungent odor of the permanent waving treatment.

Meanwhile, exposure to TGA has been known to damage organs or systems in animals and potentially cause adverse effects on human health as reported as follows. Rotenberg et al. reported its acute oral toxicity in the rat and mouse, acute inhalation toxicity in the mouse, acute dermal toxicity in the rabbit and chronic inhalation toxicity in rats. Epidemiological studies conducted by Fenton and Blatter and Zielhuis, Kersemaekers et al. and Gan et al. suggested the risk of reproductive disorders in hairdressers tended to increase with exposure to chemicals used for hair treatments. Gan et al. focused on the effect of TGA-containing PWS on the health of human populations of female hairdressers and school teachers in China. The results suggested reproductive function in...
hairdressers can be affected by long-term exposure to PWS, possibly due to the effects of TGA. According to the Occupational Safety and Health Guideline for TGA of the US Department of Labor\(^\text{10}\), whilst the Occupational Safety and Health Administration (OSHA) does not currently regulate TGA, the National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for TGA of 4 mg/m\(^3\) as a time-weighted average (TWA) for up to a 10-hour workday and a 40-hour workweek. The NIOSH also assigned a “Skin” notation, which indicates that the cutaneous route of exposure, including mucous membranes and eyes, contributes to overall exposure\(^\text{11}\). The American Conference of Governmental Industrial Hygienists (ACGIH) has also assigned TGA a threshold limit value (TLV) of 3.8 mg/m\(^3\) as a TWA for a normal 8-hour workday and a 40-hour workweek. The ACGIH has also assigned a “Skin” notation\(^\text{12}\).

However, no report has been previously published on the indoor air concentrations of TGA in a beauty salon that contributes to assessment of exposure to TGA of hairdressers and their customers. In this study, we carried out a pilot field measurement of TGA, dithiodiglycolic acid (DTDGA, a reaction product of TGA and cysteine residues of hair keratin) and ammonia in indoor air of a beauty salon where the PWS containing ammonium thioglycolate was employed for perm treatments.

**Methods**

**Field measurement in a beauty salon**

Field measurements were conducted in one beauty salon located in Tokyo, Japan, where PWS containing ammonium thioglycolate was employed for permanent waving treatments. Figure 1 shows a plane diagram of the beauty salon indicating a regular sampling point. The floor area was 90 m\(^2\) with a height of 3 m. The indoor air was mechanically ventilated with an air change rate of approximately 0.5 h\(^{-1}\). The salon had ten hair treatment stations and a shampoo area. Usually, there were five hairdressers working in the salon. Regular air samplings were mainly conducted close to the center of the salon. Sampling devices were put on a round table, and the sampling nozzle was set at a height of 1.2 m above from the floor. Sampling devices were temporally moved closer to hair treatment stations when customers received a perm treatment. Samplings were conducted within business hours from June 30 to July 2, 2010.

**Measurement of TGA and DTDGA**

TGA and DTDGA in indoor air were collected in a single impinger (G-1 type, Sibata Scientific Technology, Japan) containing 20 ml of pure water (Direct-Q UV, Millipore, Japan) by pulling air at a flow rate of 0.50 l min\(^{-1}\) for 1 hour with MP-Σ30 mini-pump (Sibata Scientific Technology, Japan). After samplings, the trapping solution was made up to 20 ml with pure water, and TGA and DTDGA were subsequently determined by high performance liquid chromatography (HPLC)\(^\text{13,14}\).

The collection efficiency of this system was investigated in advance using two serially connected impingers. A test mixed gas was prepared in a polytetrafluoroethylene bag by evaporating a portion of TGA (reagent grade, purity >90%, Kanto Kagaku, Japan). The concentrations of TGA and DTDGA in the bag were 3.6 mg m\(^{-3}\) and 1.0 mg m\(^{-3}\), respectively. DTDGA came from the reagent as an impurity\(^\text{13}\). The collection efficiency, \(R\) (\%), was calculated from equation (1) and was 100% (n=2) under this sampling condition.

\[
R\ (\%) = \frac{W_1}{W_1 + W_2} \times 100 \tag{1}
\]

In equation (1), \(W_1\) is the collected amount of analyte in the first impinger, and \(W_2\) is that in the backup impinger.

The HPLC analysis was carried out within 24 hours.
after samplings, because the TGA tends to decrease in pure water. A dilution series of calcium thioglycolate (Tokyo Kasei, Japan) and DTGDA (Wako Pure Chemical Industries, Japan) was used for analytical standards. In order to improve the storage problem of TGA solution, 0.1% phosphoric acid was used as the diluting agent, referring to Koyama et al.\textsuperscript{14}. The TGA prepared in 0.1% phosphoric acid became stable for at least 1 week when stored in a cool and dark place. The HPLC system consisted of Agilent technologies model 1,200 series with UV-Vis detector. The following conditions were used for simultaneous determination of the TGA and DTGDA: column, \( \phi = 4.6 \times 75 \text{ mm, } 3.5 \mu \text{m, ZORBAX Eclipse XDB-C18} \) (Agilent Technologies, Japan); eluent, 0.1% phosphoric acid in 95/5 acetonitrile/deionized water (isocratic); detection wavelength, 210 nm; injection volume; 20 \( \mu \text{l} \). Duplicate injections were made for standards, samples and blanks. As shown in the typical HPLC chromatogram (Fig. 2), both peaks were well separated with a separation factor \((\alpha)=3.4\). Good linearity was found between concentrations of analytes, \( C \) ranging from 0 to 50 \( \mu \text{g} \text{ ml}^{-1} \), and their corresponding peak areas, \( p \) (mAUs) with a constant air flow rate of 0.50 \( l \text{ min}^{-1} \) for 1 hour with MP–Σ30 mini-pump (Sibata Scientific Technology, Japan). After samplings, the trapping solution was made up to 20 ml with pure water. A non-suppressor Ion chromatography system (Dionex IC 200) consisting of a pump, injector and conductivity detector was used for determination of ammonium ion under the following conditions: separation column; \( \phi = 4 \times 200 \text{ mm, } 5 \mu \text{m, IonPac CS12A} \) (Dionex, Japan), guard column; \( \phi = 4 \times 50 \text{ mm, IonPac CG12A} \) (Dionex, Japan), eluent; 10 mM \( \text{H}_2\text{SO}_4 \) at 0.4 ml/min\(^{-1}\), injection volume; 100 \( \mu \text{l} \). Since significant contamination by field handling and during storage was not found in both travel and storage blanks, LOD was defined as three-fold the baseline noise (S/N=3) and resulted in 0.01 mg m\(^{-3}\). As well, LOQ was defined as ten-fold the baseline noise (S/N=3) and resulted in 0.033 mg m\(^{-3}\).

**Measurement of particulate matter (PM)**

The PM concentration was supplementary monitored by an IAQ monitor based on a light-scattering photometry (Air Advice, Shin yei Technology, Japan) with 1-minute intervals from June 31 to July 1. The IAQ monitor was fixed at the regular site. Although the IAQ monitor only covers 0.5–22 \( \mu \text{m} \) of particles, the PM concentration may indicate influences of hair cutting in the salon.

**Laboratory test**

In order to support discussions about environmental behaviors of TGA and DTGDA described in section 3, emissions of TGA and DTGDA from calcium thioglycolate solution were separately determined using a small stainless chamber (20 l) with a constant air flow of 0.167 \( l \text{ min}^{-1} \) which corresponds to an air change rate of 0.5 h\(^{-1}\) under controlled temperature of 298 K with 50% of relative humidity, based on JIS A 1901: 2003\textsuperscript{15}. A five milliliters of ammonium thioglycolate solution (45–55% in water, Kanto Kagaku, Japan) was poured into a Petri dish and then transferred into the stainless chamber. Outlet air concentrations of TGA and DTGDA were determined by the impinger-HPLC methodology with a sampling flow rate of 0.167 \( l \text{ min}^{-1} \) for 1 hour, at 5 and 6 hours after commencing the chamber test.

**Results and Discussions**

Table 1 shows analytical results of concentrations of TGA, DTGDA and ammonia in indoor air of the beauty salon at twelve sampling events. The indoor air concentrations of TGA resulted in below LOD at every event and much lower than the occupational safety guideline levels set by the NIOSH and ACGIH.
This means airborne TGA in this beauty salon is not important as a possible exposure route for hairdressers and customers. Meanwhile, the concentrations of DTDGA varied from <LOD to 0.75 mg m\(^{-3}\), and those of ammonia ranged from 0.15 to 0.87 mg m\(^{-3}\) (0.48 ± 0.24 mg m\(^{-3}\)). We should note the efforts of hairdressers for preventing indoor air pollution by chemicals such as the operation of a mechanical ventilation system for 24 hours, use of a room air cleaner and diligent cleaning of hair clippings on the floor. These may contribute to lowering the concentrations of chemicals in this case study. However, differences in the concentrations of TGA, DTDGA and ammonia should be discussed more carefully considering the permanent waving process and physicochemical properties of the chemicals.

The active ingredient ammonium thioglycolate is an ammonium salt of thioglycolic acid, and chemical equilibrium probably occurs in PWS as shown in equation (2), where \(aq\) shows an aqueous form.

\[
\text{HSCH}_2\text{COO}^+\text{NH}_4^+ (aq) \rightleftharpoons \text{HSCH}_2\text{COOH}_{(aq)} + \text{NH}_3 (aq)
\]  

(2)

When PWS is applied to hair fibers, certain fractions of TGA and NH\(_3\) potentially emit in gaseous forms from the PWS and then become a source of indoor air pollution. As can be seen in Table 1, relatively higher NH\(_3\) concentrations were found during perm events and in samples collected near stations with perm treatments (samples #2, 6, 7, 10 and 11). However, TGA was not found even in those samples, probably because it was consumed in the reduction process. According to Ogawa et al. (2008), in the reduction step of the permanent waving treatment, the disulfide bond of cysteine residue forms mixed disulfide (KSSK) and cysteine group (KSH) by the reaction with TGA (HSCH\(_2\)COOH) as shown in the following equation,

\[
\text{KSSK} + \text{HSCH}_2\text{COOH} \rightarrow \text{KSSCH}_2\text{COOH} + \text{KSH}
\]  

(3)

where \(K\) represents the hair keratin chain. In the presence of excess reducing agent, mixed disulfide is further reduced and converted into a thiol group (KSH) and dithio-derivative, DTDGA (HOOC\(_2\)SSCH\(_2\)COOH).

\[
\text{KSSCH}_2\text{COOH} + \text{HSCH}_2\text{COOH} \rightarrow \text{HOOC\(_2\)SSCH}_2\text{COOH} + \text{KSH}
\]  

(4)

Though TGA is miscible with water, it seems to

<table>
<thead>
<tr>
<th>Date</th>
<th>Sample #</th>
<th>Sampling time</th>
<th>Hair treatments conducted</th>
<th>Sampling site</th>
<th>Temp. (°C)</th>
<th>R.H. (%)</th>
<th>Indoor air concentrations (mg m(^{-3}))</th>
<th>TGA</th>
<th>DTDGA</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 30</td>
<td>1</td>
<td>9:00–10:00</td>
<td>Bottling of PWS, coloring at station (St.) 4 and 8, perm at St.5</td>
<td>Regular</td>
<td>25</td>
<td>55</td>
<td>&lt; 0.008</td>
<td>0.75</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10:18–11:18</td>
<td>Coloring at St.2,4 and 8, perm at St.5</td>
<td>Near St.5</td>
<td>25</td>
<td>55</td>
<td>&lt; 0.008</td>
<td>0.23</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>13:00–14:00</td>
<td>Coloring at St.2, cutting at St.4,5 and 8</td>
<td>Regular</td>
<td>25</td>
<td>58</td>
<td>&lt; 0.008 (0.047)</td>
<td>0.27</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>4</td>
<td>16:00–17:00</td>
<td>Cutting at St.2 and 8</td>
<td>Regular</td>
<td>25</td>
<td>59</td>
<td>&lt; 0.008 (0.031)</td>
<td>0.32</td>
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<td></td>
</tr>
<tr>
<td>July 1</td>
<td>5</td>
<td>10:00–11:00</td>
<td>Perm at St.2, coloring at St.8, cutting at St.3</td>
<td>Regular</td>
<td>31</td>
<td>58</td>
<td>&lt; 0.008 &lt; 0.026</td>
<td>0.53</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>6</td>
<td>12:00–13:00</td>
<td>Perm at St.2, 4 and 8, coloring at St.5, cutting at St.3 and 9</td>
<td>Near St.2</td>
<td>25</td>
<td>50</td>
<td>&lt; 0.008 &lt; 0.026</td>
<td>0.72</td>
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<td></td>
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<tr>
<td></td>
<td>7</td>
<td>16:00–17:00</td>
<td>Cutting at St.2 and 8</td>
<td>Regular</td>
<td>25</td>
<td>52</td>
<td>&lt; 0.008 &lt; 0.026</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>July 2</td>
<td>9</td>
<td>9:00–10:00</td>
<td>Bottling of PWS, coloring at St.2,3 and 6, cutting at St.4 and 8</td>
<td>Regular</td>
<td>27</td>
<td>51</td>
<td>&lt; 0.008</td>
<td>0.22</td>
<td>0.19</td>
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<tr>
<td></td>
<td>10</td>
<td>13:00–14:00</td>
<td>Perm at St.4,6 and 8, Cutting at St.2</td>
<td>Regular</td>
<td>26</td>
<td>50</td>
<td>&lt; 0.008 &lt; 0.026</td>
<td>0.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>Near St.4</td>
<td>25</td>
<td>50</td>
<td>&lt; 0.008</td>
<td>0.18</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>16:00–17:00</td>
<td>Cutting at St.2,4 and 8</td>
<td>Regular</td>
<td>26</td>
<td>52</td>
<td>&lt; 0.008 &lt; 0.026</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in parenthesis are below the Limit of quantification (LOQ) but greater than the Limit of detection (LOD). PWS: permanent waving solutions.
be strongly trapped in hair. When a washing process is introduced after hair reduction, the mixed disulfide groups (KSSK and KSSCH,COOH) are also reduced by the reducing agent adsorbed in hair without removing with water:

$$\text{KSSCH,COOH+HSCH,COOH} \xrightarrow{\text{ad}} \text{HOOCCH,SSCH,COOH+KSH}$$

(5)

where, HSCH,COOH is the reducing agent existing in an adsorbed state in hair. Then, the TGA showed behavior that is different from ammonia in the environment, and hence indoor air concentrations were not found in this study.

There is another possible reason why the TGA concentrations were below LOD at every sampling event; TGA is also labile in ambient air and can directly form DTDGA:

$$2\text{HSCH,COOH+[O]} \rightarrow \text{HOOCCH,SSCH,COOH+2H}_2\text{O}$$

(6)

where [O] indicates oxygen atom provided by oxidants in air. Our HPLC analysis showed the ammonium thioglycolate solution obtained from a commercial source contained both TGA and DTDGA at a 9 : 1 of weight ratio. Meanwhile, the emissions of TGA and DTDGA from the ammonium thioglycolate solution measured by the additional small chamber tests showed outlet concentrations at an elapsed time of 5 hours of 0.0018 mg m\(^{-3}\) for TGA and 0.010 mg m\(^{-3}\) for DTDGA (approximately 1 : 5 of weight ratio). Subsequent measurements at 6 hours also showed consistent values: 0.019 mg h\(^{-1}\) for TGA and 0.11 mg h\(^{-1}\) for DTDGA. Since the vapor pressure of DTDGA is much lower (3 × 10\(^{-5}\) Pa at 25°C) than that of TGA, changes in the weight ratio of TGA/DTDGA between the solution and air suggest the direct and immediate formation of DTDGA from TGA in air. Thus, the TGA concentration became lower.

On the other hand, DTDGA potentially forms as shown by equations (4) (5) and (6) during the perm process. However, it tends to exist in a particulate form in air because of its melting point (128−131°C) and lower vapor pressure. Although the presence of DTDGA in the suspended and/or deposited particulate matter was not actually investigated in this study (this was out of focus of this field study, interaction with hair fibers or particles was suggested to determine the DTDGA concentrations in this salon. Figure 3 shows a comparison of indoor air concentrations of DTDGA, ammonia and particulate matter (PM) measured at the regular sampling site from June 31 to July 1. Error bars show the standard deviation of 1-minute interval PM concentrations during the corresponding 1-hour sampling events of TGA/DTDGA. TGA: thioglycolic acid, DTDGA: dithiodiglycolic acid.

Conclusions

As a case study, indoor air concentrations of TGA, DTDGA and ammonia were measured in a beauty salon where PWS containing ammonium thioglycolate was employed for perm treatments. Indoor air concentrations of TGA were below the LOD at every event and much lower than the occupational safety guideline levels, whilst relatively higher concentrations of ammonia were found during perm events or in samples collected near stations with perm treatments. This means that the process of emission of TGA and ammonia from PWS differ and that inhalation of airborne TGA is not important as a possible exposure route to hairdressers and customers in this beauty salon. The concentrations of DTDGA varied from <0.026 mg m\(^{-3}\) to 0.75 mg m\(^{-3}\) and showed a different variation compared with those of ammonia and TGA. This field study demonstrated that complex chemistry determines exposure to chemicals from PWS in a beauty salon.
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