Quantitative Determination of Phthalate Esters from Air Sample using a Solid-Phase Extraction-Type Collection Device

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Abstract

In this study, a solid-phase extraction-type collection device, with styrene–divinylbenzene polymer particles (Sunpak-H) as the adsorbent, was used for the precise determination of phthalate esters in air samples. The collection and elution recoveries of eight volatile phthalate esters, i.e., dimethyl phthalate, diethyl phthalate, dipropyl phthalate, diisobutyl phthalate, dibutyl phthalate, butyl-benzyl phthalate, di(2-ethylhexyl) phthalate, and dioctyl phthalate, were quantitatively evaluated. All analytes were collected using the device up to a sampling volume of 10,000 L at a sampling temperature of 35°C without breakthrough. During air collection, moisture was not trapped on the adsorbent. The collected analytes were completely eluted from the device by passing 3 mL of acetone. The eluted solvent was injected into a gas chromatography–mass spectrometry system after the eluted solvent was concentrated, if necessary. After washing the adsorbent using acetone the device could be reused more than 50 times. The limit of quantification for the analytes was less than 1 ng L⁻¹ in air at a sampling volume of 600 L with solvent concentration. This device was successfully applied for the quantitative determination of phthalate esters in real air samples, including in-door and in-car air.

Key words Phthalate ester, sample preparation, semi-volatile organic compounds, gas chromatography-mass spectrometry
Introduction

Phthalate esters are mainly used as plasticizers for increasing the flexibility of polyvinyl chloride (PVC). Flexible PVC is applied in flooring and wall covering, electrical cables, automotive applications, and synthetic leather goods. However, some phthalate esters are endocrine-disrupting compounds; hence, their use is restricted. The EU, US, Japan, and other countries have restricted the use of six phthalates (namely, dibutyl phthalate (DBP), butyl-benzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP), respectively) in children's toys and child care articles. From July 2019, the EU RoHS directive has also issued a ban on the use of four phthalates (namely, diisobutyl phthalate (DIBP), DBP, BBP, and DEHP, respectively) for all electrical and electronic equipment.

In Japan, the Ministry of Health, Labor and Welfare has adopted reference values and a typical method for measuring 13 volatile organic compounds including DBP and DEHP. The reference values for DBP and DEHP were set at 220 ng L\(^{-1}\) and 120 ng L\(^{-1}\), which will be revised to 17 ng L\(^{-1}\) and 100 ng L\(^{-1}\), respectively, in the near future. Two sample preparation methods, i.e., solid-phase adsorption followed by solvent extraction and solid-phase adsorption followed by thermal desorption, have been reported as methods typically used for analyzing DBP in air. In addition, these methods have been described in ISO 16000-33:2017 for the determination of phthalates in air. However, a relatively expensive, specially designed desorption instrument is utilized for typical thermal desorption, and a low desorption recovery for semi-volatile organic compounds (SVOCs) such as DBP and DEHP can
sometimes pose a problem.\textsuperscript{10,11} Our research group has developed needle-type extraction device for extraction of VOCs in gaseous and aqueous samples.\textsuperscript{12,13} In this extraction method, the extracted analytes can be thermally desorbed in the heated GC injection port without modification of GC injector. However, desorption temperature is limited by heat resistant temperature of the extraction medium.\textsuperscript{14,15} Styrene–divinylbenzene polymer particles, Florisil,\textsuperscript{9,16} and XAD\textsuperscript{17} are typically used as adsorbents in solvent extraction. However, the use of only organic solvents to an unsatisfactory elution recovery for the extracted analytes. To obtain quantitative elution recovery, ultrasonic extraction is probably required. However, multistep sample preparation steps are required, and the extraction device cannot be used again. In addition, US Occupational Safety and Health Administration has adopted air sampling using OVS-Tenax tubes, desorbed with toluene, and flame ionization detection (FID).\textsuperscript{18} However, the method sensitivity is not satisfactory for the determination of phthalate esters in typical in-door air due to lower sensitivity of FID.

Meanwhile, our research group has developed devices for extracting SVOCs from air samples. For the simple collection or elution of SVOCs, solid-phase extraction (SPE)-type collection devices have been reported, and their collection and elution performance has been quantitatively evaluated.\textsuperscript{19-21} Recently, newly designed styrene–divinylbenzene polymer particles (Sunpak-H) have been reportedly used as an adsorbent. A Sunpak-H-packed device has been successful for the collection and elution of polycyclic aromatic hydrocarbons\textsuperscript{22} and sesquiterpenes\textsuperscript{23} from air. In this study, phthalate esters from indoor air were quantitatively determined using a Sunpak-H-packed SPE collection device. To rapidly
and quantitatively determine phthalate esters, the material and shape of the cartridge were extensively
examined. Finally, the as-developed collection device was successfully applied for the quantitative
determination of phthalate esters from in-door air and in-car air.

**Experimental**

**Chemicals**

Dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), DIBP, DBP,
BBP, DEHP, and DNOP were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). Acetone was
obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). DIDP was purchased from Junsei Chemical
Co., Ltd (Tokyo, Japan). Table 1 summarizes the analyte phthalates examined herein.

**Collection devices**

Sunpak-H with a 50/80 mesh size was prepared by Shinwa Chemical Industries, Ltd. (Kyoto,
Japan). The specific surface area and average pore diameter of the adsorbent were 100–150 m² g⁻¹ and
30 nm, respectively. A specially designed glass cartridge, stainless-steel cartridge, PTFE cartridge and
PFA cartridge (i.d. of 14.9 mm) were prepared by HORIBA STEC (Kyoto, Japan). The stain-less steel,
PTFE, and PFA cartridges have an internal groove for embedding a snap ring. The collection cartridge
was prepared as follows. First, a metal wire mesh (HORIBA STEC) was placed inside the cartridge.
Second, a glass fiber filter (GA-200, ADVANTEC Co., Ltd.) with an i.d. of 15 mm (specially
prepared) and Sunpak-H were packed inside the cartridge. The packing amount of Sunpak-H was optimized. After packing another glass fiber filter, a C-shaped stainless steel snap ring was placed in the cartridge to fix the adsorbent. A PTFE O-ring was used to fix the adsorbent in the glass cartridge device. A PTFE adapter (HORIBA STEC) was used to connect the cartridge to a gas-sampling pump. Figure 1 shows the schematic of the prepared collection devices. The collection device was washed with acetone before use, and analytes were not detected on the method blank.

Analytical method

The collection and elution performance of the developed devices was evaluated using a standard stock solution (100 mg L\(^{-1}\) for DMP, DEP, DPP, and DIBP and 300 mg L\(^{-1}\) for DBP, BBP, DEHP, and DNOP). First, 100 μL of the standard solution was dropped on the tip side of the collection device (on the glass filter). PTFE tubes were connected to both ends of the device, followed by the immersion of the device in a water bath maintained at 35°C for 3 min. Then, clean air was collected using a prototype gas-sampling unit (HORIBA STEC) at a sampling speed of 10 L min\(^{-1}\). For evaluating the collection recovery of the analytes, another collection device was connected in tandem, and air was collected using both devices. The collection recovery was calculated from the ratio of the peak areas obtained in the former device to the total of the peak areas obtained in the former and latter devices. The analytes collected in the device were eluted by passing acetone as the elution solvent. The elution solvent volume was optimized in the following experiments. The eluted solution was
concentrated to 1 mL by a flow of N₂ if necessary, with no observed losses during concentration. The
eletion recovery of the analytes was calculated by the peak area obtained in the first desorption to the
total of the peak areas obtained in the first and sequential second elutions from the collection device.
Figure 2 shows the analytical method developed herein. The collection device can be reused after
washing the adsorbent using acetone and drying the packed particles with 5 L min⁻¹ of N₂ flow for 10
min. Degradation of collection and elution performances were not observed after more than 50 times
of reuse.

GC-MS measurements

A JEOL JMS-Q1000 GCMk-II system (JEOL, Tokyo, Japan) was used for GC–MS measurements. Helium (>99.999% purity) was used as the carrier gas at a head pressure of 100 kPa. The injector and interface temperatures were set at 300 and 320°C, respectively. Split mode injection at a ratio of 10:1 was carried out, and 2 μL of the sample solution was injected. A fused-silica HP-5 capillary column (30 m × 0.25 mm, 0.25 μm film thickness, Agilent Technologies, CA, Santa Clara, USA) was used for analyte separation. Initially, the column temperature was maintained at 100°C for 1 min, followed by a programmed increase to 320°C at a rate of 20°C min⁻¹. The mass spectrometer was operated in the selected-ion-monitoring mode. Table 1 also summarizes the primary and secondary ions for detecting phthalate esters. The chromatogram was monitored by these ions. Quantification of each analyte was made by using respective primary ions.
Results and discussion

Optimization of the cartridge material

In our previous work, a wide bore collection cartridge (24 mm i.d.) was employed for collection of environmental air for 24 h.\textsuperscript{22} In this study, considering the typical sampling time of indoor air (30 or 60 min), the inner diameter of the collection cartridge was fixed to 15 mm. Narrower bore collection device expected that higher elution recovery with fewer elution solvent. First, a glass cartridge (Fig. 1A), which contained 1 g of Sunpak-H as the adsorbent, was used to prepare the collection device. The Sunpak-H packed glass cartridge exhibited a high collection power, with collection recoveries of >99.9% for the investigated phthalate esters at a sampling volume of 10,000 L at 35°C. The air sampling speed was fixed at 10 L min\textsuperscript{-1}, with a typical indoor air sampling time of 30 min or 60 min. This collection power is extremely high for analyzing phthalate esters in indoor air.

The collected analytes were eluted using 8 mL of acetone (Table 2). The pressure drop of this collection device was greater than 25 kPa at a sampling speed of 10 L min\textsuperscript{-1}. Therefore, the packing amount of Sunpak-H is decreased to 0.3 g.

For preparation of 0.3 g of Sunpak-H packed collection device, glass (Fig. 1B), stain-less steel, PFA, and PTFE (Fig. 1C) cartridges were investigated. All analytes were completely recovered at a sampling volume of 10,000 L. This collection recovery was confirmed at sampling speed of 5, 10, and 15 L min\textsuperscript{-1}. The upper limit of loading capacity was confirmed by spiking 10% of analyte solution
(100 μL) onto the device. Then, another collection device was connected in tandem and clean air was collected for 600 L. This corresponds to sampling of 16.7 μg L⁻¹ of phthalate ester containing air sample for 600 L. In this experiment, any analytes were detected on the latter collection device. This result indicates that the device has substantial sample loading capacity for phthalate esters. Table 2 summarizes the elution recoveries of these devices. The PFA device showed a complete elution of the analyte using 5 mL of acetone, and the glass device exhibited a high elution recovery with a lower volume of elution solvent compared to the other analytes that were completely eluted using 3 mL of acetone. In addition, this elution recovery was achieved using three glass cartridges, with an elution time of within 3 min. The pressure drop for a 0.3 g-packed glass cartridge was 22 ± 2 kPa at sampling speed of 10 L min⁻¹. Therefore, the glass cartridge packed with 0.3 g of Sunpak-H was employed for further studies.

**Method evaluation**

The limit of detection (LOD) for the proposed method was investigated. The LOD of the method was determined as a signal-to-noise ratio of 3. Table 3 summarizes the LODs for a standard phthalate ester solution (in acetone). As the collection and elution recoveries of the analytes using the Sunpak-H 0.3 g-packed glass device were >99.9%, the LODs of the analytes from the air sample can be calculated using the air sampling volume (Table 3). A lower LOD was achieved by the concentration of the elution solvent (3 mL) to 1 mL. By successfully eluting the collected analytes
with a relatively less volume of solvent, satisfactory sensitivity can be achieved by the direct injection of the eluted solvent (without concentration).

The total recovery for the analytes was investigated. First, standard stock solution was diluted 10-fold with acetone, and this solution was measured by GC–MS. Next, standard stock solution of 100 μL was spiked onto the device, and then, 600 L of clean air was collected. The analytes were eluted by 3 mL of acetone, and the solution was concentrated to 1.0 mL. The total recovery of the analytes was calculated by comparing the analyte peak areas obtained for the standard solution (diluted stock solution) and sample solution (recovered solution). Total recoveries range from 97.6 to 105% for the investigated 8 phthalate esters.

The repeatability of the proposed method was confirmed by spiking 100 μL of the standard solution into the glass device. After collecting 600 L of clean air, the analytes were eluted using 3 mL of acetone, and the eluted solvent was measured by GC–MS. Each sample measurement was carried out in triplicate. The relative standard deviations (RSDs) of the peak areas for the standard analytes (n = 5, repetitive sample spiking, air collection, and elution) were less than 9.0%. These RSDs were the same as those obtained with the repetition of the GC–MS measurements for one sample. This good repeatability is probably related to the complete collection and elution of the phthalate esters using the developed Sunpak-H packed device.

Adsorption of moisture from the air samples was investigated by collecting humid air (relative humidity above 88%, temperature ca. 20°C) in the Sunpak-H packed device. The collection device
developed herein was also not affected by moisture, where the weight of the device did not increase
after the sampling of humid air (1,000 L). In addition, the elution recovery and the collection recovery
after humid air sampling were same as the dry air sampling.

Real sample analysis

The glass collection device packed with 0.3 g of Sunpak-H was applied for the determination
of phthalate esters from indoor and in-car air. Six hundred liters of real air samples was collected (10 L
min⁻¹ for 60 min). For collecting in-car air, the sampling pump was placed outside the car to prevent
the collection of exhaust air from the pump. Sampling temperatures ranged from 17 to 25°C. The
collected analytes were eluted using 3 mL of acetone and concentrated to 1 mL. Table 4 summarizes
the results obtained from the quantification of phthalate esters from real air sample. The DMP and
DBP in all sample were determined at a concentration of less than 1 ng L⁻¹. A relatively higher DEHP
concentration was determined from the in-car air samples, especially car (C). Figure 3 shows the
chromatogram for the determination of phthalate esters from the sample of air from car (A). As shown
in the chromatogram, analyte peaks were eluted without any interference peaks, and trace target
analytes are clearly found.
Conclusion

In this study, a novel SPE-type collection device with a glass cartridge packed with 0.3 g of Sunpak-H was developed for the precise determination of phthalate esters from air samples. The device exhibited satisfactory collection power for all analytes. The collected analytes were completely eluted using 3 mL of acetone into the cartridge. Therefore, the method does not require Soxhlet extraction or ultrasonication, and phthalate esters are rapidly and quantitatively eluted. The eluted solvent was directly injected into a GC–MS system without concentration owing to the minimized volume of the elution solvent. This device is expected to be used for the precise determination of airborne SVOCs.
Acknowledgment

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References


18. Occupational Safety and Health Administration, Sampling and Analytical Methods: Dimethyl Phthalate (DMP), Diethyl Phthalate (DEP), Dibutyl Phthalate (DBP), Di-2-Ethylhexyl Phthalate (DEHP), and Di-n-Octyl Phthalate (DNOP), Method No. 104, 1994.


Figure captions

Figure 1  Schematic of the collection devices packed with Sunpak-H. (A) glass cartridge packed with 1.0 g of Sunpak-H, (B) glass cartridge packed with 0.3 g of Sunpak-H, (C) stain-less steel, PTFE, and PFA cartridges.

Figure 2  Schematic of the analytical method.

Figure 3  Typical chromatogram for the determination of phthalate esters from in-car air. The air sample was sampled from car (A) shown in Table 4.
<table>
<thead>
<tr>
<th>Phthalate ester</th>
<th>Abbreviation</th>
<th>Primary ion</th>
<th>Secondary ion</th>
</tr>
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<tr>
<td>1 Dimethyl</td>
<td>DMP</td>
<td>163</td>
<td>77</td>
</tr>
<tr>
<td>2 Diethyl</td>
<td>DEP</td>
<td>149</td>
<td>177</td>
</tr>
<tr>
<td>3 Dipropyl</td>
<td>DPP</td>
<td>149</td>
<td>191</td>
</tr>
<tr>
<td>4 Diisobutyl</td>
<td>DIBP</td>
<td>149</td>
<td>223</td>
</tr>
<tr>
<td>5 Dibutyl</td>
<td>DBP</td>
<td>149</td>
<td>223</td>
</tr>
<tr>
<td>6 Butyl-benzyl</td>
<td>BBP</td>
<td>149</td>
<td>206</td>
</tr>
<tr>
<td>7 Di(2-ethylhexyl)</td>
<td>DEHP</td>
<td>149</td>
<td>279</td>
</tr>
<tr>
<td>8 Di-n-octyl</td>
<td>DNOP</td>
<td>149</td>
<td>279</td>
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### Table 2  Elution recoveries of phthalate esters

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<th>Cartridge</th>
<th>Acetone volume / mL</th>
<th>DMP</th>
<th>DEP</th>
<th>DPP</th>
<th>DIBP</th>
<th>DBP</th>
<th>BBP</th>
<th>DEHP</th>
<th>DNOP</th>
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<tr>
<td>Glass (Sunpak-H 1.0 g)</td>
<td>7</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>99.9</td>
<td>99.9</td>
<td>99.8</td>
<td>99.7</td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Glass (Sunpak-H 0.3 g)</td>
<td>2.5</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>99.8</td>
<td>99.8</td>
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<tr>
<td></td>
<td>3</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>3</td>
<td>100</td>
<td>100</td>
<td>99.9</td>
<td>99.9</td>
<td>99.5</td>
<td>99.7</td>
<td>99.7</td>
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<td>99.7</td>
<td>100</td>
<td>99.8</td>
<td>100</td>
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<tr>
<td>PTFE</td>
<td>3</td>
<td>99.7</td>
<td>99.7</td>
<td>99.6</td>
<td>99.8</td>
<td>99.3</td>
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<td>99.3</td>
<td>100</td>
<td>99.6</td>
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<tr>
<td>PFA</td>
<td>3</td>
<td>99.6</td>
<td>99.7</td>
<td>99.5</td>
<td>99.5</td>
<td>99.9</td>
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Table 3  LOD of the method

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<tr>
<th></th>
<th>DMP</th>
<th>DEP</th>
<th>DPP</th>
<th>DIBP</th>
<th>DBP</th>
<th>BBP</th>
<th>DEHP</th>
<th>DNOP</th>
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<tr>
<td>Standard solution (ng mL&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>250</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>50</td>
<td>500</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Air (ng L&lt;sup&gt;-1&lt;/sup&gt;) (1 mL solvent)</td>
<td>0.42</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.083</td>
<td>0.83</td>
<td>0.17</td>
<td>0.17</td>
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<tr>
<td>Air (ng L&lt;sup&gt;-1&lt;/sup&gt;) (3 mL solvent)</td>
<td>1.26</td>
<td>0.51</td>
<td>0.51</td>
<td>0.51</td>
<td>0.25</td>
<td>2.49</td>
<td>0.51</td>
<td>0.51</td>
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Air sampling volume: 600 L.
Table 4  Results from the quantitative determination of phthalate esters from real air samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>DMP</th>
<th>DEP</th>
<th>DPP</th>
<th>DIBP</th>
<th>DBP</th>
<th>BBP</th>
<th>DEHP</th>
<th>DNOP</th>
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<tr>
<td>Clean room</td>
<td>0.50</td>
<td>0.27</td>
<td>0.25</td>
<td>N.D.</td>
<td>0.16</td>
<td>N.D.</td>
<td>0.44</td>
<td>N.D.</td>
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<tr>
<td>Laboratory (A)</td>
<td>0.52</td>
<td>0.44</td>
<td>N.D.</td>
<td>0.43</td>
<td>0.72</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
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<tr>
<td>Laboratory (B)</td>
<td>0.50</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>0.49</td>
<td>N.D.</td>
<td>N.D.</td>
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<tr>
<td>Teachers room</td>
<td>0.64</td>
<td>0.44</td>
<td>N.D.</td>
<td>0.62</td>
<td>0.69</td>
<td>N.D.</td>
<td>N.D.</td>
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<tr>
<td>Lecture room</td>
<td>0.51</td>
<td>0.46</td>
<td>N.D.</td>
<td>0.44</td>
<td>0.57</td>
<td>N.D.</td>
<td>N.D.</td>
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<td>Car (A) (10 years)</td>
<td>0.43</td>
<td>N.D.</td>
<td>N.D.</td>
<td>1.01</td>
<td>0.87</td>
<td>N.D.</td>
<td>15.4</td>
<td>N.D.</td>
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<tr>
<td>Car (B) (4 years)</td>
<td>0.55</td>
<td>0.44</td>
<td>N.D.</td>
<td>0.45</td>
<td>0.55</td>
<td>N.D.</td>
<td>7.47</td>
<td>N.D.</td>
</tr>
<tr>
<td>Car (C) (3 months)</td>
<td>0.46</td>
<td>N.D.</td>
<td>N.D.</td>
<td>0.45</td>
<td>0.75</td>
<td>N.D.</td>
<td>115.6</td>
<td>N.D.</td>
</tr>
<tr>
<td>Car (D) (0 months)</td>
<td>0.69</td>
<td>0.64</td>
<td>N.D.</td>
<td>0.54</td>
<td>0.76</td>
<td>N.D.</td>
<td>4.20</td>
<td>N.D.</td>
</tr>
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</table>

N.D.: not detected.
Fig. 1
Fig. 2
Fig. 3