Volatile organic compounds (VOCs)
thermally desorbed

Radiello components to be used:
Yellow diffusive body code 120-2
Supporting plate code 121
Vertical adapter code 122 (optional)
Adsorbing cartridge code 145

Or: radiello-ready-to-use code 123-2 (also see page A8)

Principle

Code 145 is a stainless steel net cylinder, with 3x8 μm mesh grid opening and 4.8 mm diameter, packed with 350 ± 10 mg of graphitised charcoal (Carbograph 4), particle size is 35-50 mesh.

Volatile organic compounds are trapped by adsorption and recovered by thermal desorption, analysis is performed by capillary gas chromatography and FID or MS detection.

General considerations

Thermal desorption is an easy-to-use technique, but it implies some precautions and is of less general use than chemical desorption.

The recovery of adsorbed compounds is based onto the different shape of adsorption isotherms at different temperatures. Since quantitative desorption of trapped molecules should ideally be accomplished at moderate temperatures, only weak adsorbing media are employed, with active adsorbing surface between 10 and 50 times smaller than that of activated charcoal.

Use of thermal desorption requires therefore an accurate preliminary investigation about the adsorbed compound - adsorbing medium pair. Stronger adsorbents are suitable for very volatile compounds, but will yield only partial desorption of heavier compounds.

Anyway, backdiffusion (see page A3) is always lying in wait: due to the adsorbing medium weakness heavier compounds will eventually displace the more volatile ones. Once you have made an accurate choice of the adsorbing material, therefore, you should bear in mind that a real atmosphere is composed by a variety of compounds apart from those you are analyzing at unpredictable concentrations. As a consequence, sampling times can not be as long as those allowed by activated charcoal, otherwise lighter compounds will be lost. With the purpose of allowing reasonable sampling times (up to two weeks) the sampling rate has been dramatically reduced by changing the diffusive body from the white type (code 120) to the yellow one (code 120-2).

When in contact with a solid adsorbing medium, a gaseous compound will be adsorbed following the Freundlich isotherm, that is to say the adsorbed mass will be \[ \frac{x}{m} = kC^{1/n} \], where \( x \) is the mass of gaseous compound adsorbed by the mass \( m \) of the solid adsorbent and \( C \) is the concentration of the gaseous compound at the equilibrium in the gas phase. \( K \) and \( n \) depend on temperature and on the adsorbate - adsorbing medium pair. \( K \) increases with decreasing temperature and \( n \) is the closer to 1 the stronger the adsorbent.

At low temperatures, \( \frac{x}{m} \) depends almost linearly on the concentration in air (see the curve at 25 °C): this allows diffusive sampling. At high temperatures, the adsorbent mass is very low whatever the concentration in the gas phase: this allows the recovery of adsorbed compounds by heating (see the curve at 300 °C).

To ensure the best possible recovery yields, \( k \) and \( n \) have to be small. This, however, will compromise sampling efficiency. In other words, compounds strongly adsorbed at room temperature will be only partially recovered by thermal desorption. On the other hand, compounds that are easily desorbed by heating will be sampled at room temperature with low efficiency.
Smaller average pore size and thicker diffusive membrane make the diffusive path longer and, as a consequence, sampling rates are reduced to less than one third compared to those obtained with white diffusive bodies.

Some compounds, moreover, are thermally unstable. Thermal degradation of such compounds will cause an underestimation of their concentration or the appearance of ghost peaks. Thermal desorption is nevertheless an outstanding analytical technique because it is easy to perform, it does not require the use of toxic solvents as carbon disulfide, it ensures very low limits of detection, is suited to mass spectrometric detection and allows the recovery of the adsorbing cartridges. Basing on our experience, we have chosen Carbograph 4 as the best compromise between sampling efficiency and recovery yields for a wide range of organic compounds.

Sampling rates

Sampling rate values at 298 K (25 °C) and 1013 hPa are listed in table on page E3. All of the values shown have been experimentally measured. Exposure tests have been performed up to the levels shown (in μg·m⁻³·min) and sampling rates are guaranteed to be linear up to the limit values and for overall concentration of volatile organic compounds in air not exceeding 2,000 μg·m⁻³.

Effect of temperature, humidity and wind speed

Sampling rates varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation

\[ Q_K = Q_{298} \left( \frac{K}{298} \right)^{1.5} \]

where \( Q_K \) is the sampling rate at the temperature \( K \) and \( Q_{298} \) is the reference value at 298 K. This produces a variation of ± 5% for 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15-90% and with wind speed between 0.1 and 10 m·s⁻¹.

Do not expose directly radiello to rain: even if only small amounts of water are adsorbed by Carbograph 4, they can nevertheless interfere with the analysis.

Calculations

The listed sampling rate values take already into account the recovery yields of adsorbed compounds. The average concentration over the sampling period is therefore calculated from sampled mass of analyte and exposure time without introducing any other corrective factor, apart from temperature variations of \( Q \).

Average concentration \( C \) in μg·m⁻³ over the whole exposure time is calculated according to the following expression:

\[ C [\mu g \cdot m^{-3}] = \frac{m [\mu g]}{Q_k [ml \cdot min^{-1}] \cdot t [min]} \times 1,000,000 \]

where:

- \( m \) = mass of analyte in μg
- \( t \) = exposure time in minutes

Exposure

Workplace environment

The weaker adsorbent Carbograph is not recommended for workplace measurements, as high concentrations, that can be expected, would overload the sorbent. A stronger adsorbent, like activated charcoal, is needed (see page D1).
Other indoor sampling experiments and outdoor campaigns

Thermal desorption is exceptionally suited for long exposure times at low concentrations, as in outdoor campaigns and some indoor environments (e.g. homes, schools, etc...), particularly if the subsequent analysis is performed by HRGC-MS. The recommended exposure times range from 8 hours to the upper limits shown in the table below. It is advisable to reduce sampling time if the estimated overall VOCs concentration is higher than 2,000 μg·m⁻³.

### Sampling rate values Q at 25°C (298 K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( Q_{298} ) ml·min⁻¹</th>
<th>exposure time upper limit (days)</th>
<th>linear up to ( \mu g·m^{-3}·min )</th>
<th>uncertainty (2( \sigma )) %</th>
<th>limit of detection ( \mu g·m^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>27.8</td>
<td>7</td>
<td>410,000</td>
<td>8.3</td>
<td>0.05</td>
</tr>
<tr>
<td>benzene</td>
<td>26.8</td>
<td>14</td>
<td>410,000(^2)</td>
<td>7.5</td>
<td>0.05</td>
</tr>
<tr>
<td>butyl acetate</td>
<td>24.5</td>
<td>14</td>
<td>580,000</td>
<td>12.4</td>
<td>0.05</td>
</tr>
<tr>
<td>2-butoxyethanol</td>
<td>19.4</td>
<td>14</td>
<td>550,000</td>
<td>9.7</td>
<td>0.1</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>27.6</td>
<td>7</td>
<td>470,000</td>
<td>14.7</td>
<td>0.1</td>
</tr>
<tr>
<td>n-decane</td>
<td>22.3</td>
<td>14</td>
<td>450,000</td>
<td>22.4</td>
<td>0.1</td>
</tr>
<tr>
<td>1,4-dichlorobenzene</td>
<td>22.0</td>
<td>14</td>
<td>650,000</td>
<td>9.5</td>
<td>0.1</td>
</tr>
<tr>
<td>dimethyl disulfide</td>
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<td>7</td>
<td>500,000</td>
<td>9.1</td>
<td>0.04</td>
</tr>
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<td>n-heptane</td>
<td>25.3</td>
<td>14</td>
<td>420,000</td>
<td>7.6</td>
<td>0.05</td>
</tr>
<tr>
<td>n-hexane</td>
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<td>7</td>
<td>420,000</td>
<td>10.9</td>
<td>0.05</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>25.7</td>
<td>14</td>
<td>550,000</td>
<td>9.1</td>
<td>0.01</td>
</tr>
<tr>
<td>2-ethyl-1-hexanol</td>
<td>14.3</td>
<td>14</td>
<td>550,000</td>
<td>17.4</td>
<td>0.07</td>
</tr>
<tr>
<td>2-ethoxyethanol</td>
<td>26.0</td>
<td>14</td>
<td>570,000</td>
<td>7.7</td>
<td>0.05</td>
</tr>
<tr>
<td>2-ethoxyethyl acetate</td>
<td>20.9</td>
<td>14</td>
<td>600,000</td>
<td>8.0</td>
<td>0.05</td>
</tr>
<tr>
<td>isopropyl acetate</td>
<td>25.8</td>
<td>7</td>
<td>540,000</td>
<td>9.6</td>
<td>0.1</td>
</tr>
<tr>
<td>limonene</td>
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<td>14</td>
<td>500,000</td>
<td>24.8</td>
<td>0.2</td>
</tr>
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<td>2-methoxyethanol</td>
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<td>7</td>
<td>1,000,000</td>
<td>--</td>
<td>1.0</td>
</tr>
<tr>
<td>2-methoxyethyl acetate</td>
<td>21.0</td>
<td>7</td>
<td>1,000,000</td>
<td>--</td>
<td>0.1</td>
</tr>
<tr>
<td>1-methoxy-2-propanol</td>
<td>26.6</td>
<td>7</td>
<td>600,000</td>
<td>11.6</td>
<td>0.2</td>
</tr>
<tr>
<td>n-nonane</td>
<td>21.0</td>
<td>14</td>
<td>440,000</td>
<td>11.8</td>
<td>0.07</td>
</tr>
<tr>
<td>n-octane</td>
<td>24.1</td>
<td>14</td>
<td>440,000</td>
<td>13.4</td>
<td>0.07</td>
</tr>
<tr>
<td>α-pinene</td>
<td>6.4</td>
<td>14</td>
<td>550,000</td>
<td>29.5</td>
<td>0.2</td>
</tr>
<tr>
<td>styrene</td>
<td>27.1</td>
<td>14</td>
<td>550,000</td>
<td>24.0</td>
<td>0.01</td>
</tr>
<tr>
<td>tetrahydroxyethylene</td>
<td>25.4</td>
<td>7</td>
<td>1,000,000</td>
<td>8.9</td>
<td>0.02</td>
</tr>
<tr>
<td>toluene</td>
<td>30.0</td>
<td>14</td>
<td>550,000</td>
<td>8.3</td>
<td>0.01</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>20.0</td>
<td>7</td>
<td>300,000</td>
<td>13.0</td>
<td>0.1</td>
</tr>
<tr>
<td>trichloroethylene</td>
<td>27.1</td>
<td>7</td>
<td>800,000</td>
<td>9.5</td>
<td>0.02</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>21.9</td>
<td>14</td>
<td>550,000</td>
<td>9.6</td>
<td>0.05</td>
</tr>
<tr>
<td>n-undecane</td>
<td>12.0</td>
<td>14</td>
<td>520,000</td>
<td>32.7</td>
<td>0.05</td>
</tr>
<tr>
<td>m-xylene</td>
<td>26.6</td>
<td>14</td>
<td>550,000</td>
<td>11.3</td>
<td>0.01</td>
</tr>
<tr>
<td>o-xylene</td>
<td>24.6</td>
<td>14</td>
<td>550,000</td>
<td>9.1</td>
<td>0.01</td>
</tr>
<tr>
<td>p-xylene</td>
<td>26.6</td>
<td>14</td>
<td>550,000</td>
<td>11.3</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(^1\) after 7 days exposure and with MS detection; analytical conditions as described in the Analysis paragraph

\(^2\) for overall VOCs concentrations not exceeding 500 μg·m⁻³

### Storage

The cartridges have undergone a complex conditioning procedure that ensures an outstanding chromatographic blank level. If kept in a cool place without VOCs contamination, blank level and adsorbing capacity stay unaltered for at least eighteen months.

After exposure the cartridges, well capped and kept in a cool and solvent-free place, are stable for at least three months.
Analysis

The analytical methods hereafter described have been set up with the Perkin-Elmer Turbomatrix thermal desorber and Agilent 5973 MSD mass spectrometer detector. They may be implemented on other instruments by introducing minor adjustments as suggested by the analyst’s experience and characteristics of employed instrumentation.

In the following we propose two methods, one for BTEX analysis and another for VOCs. The former is suited to outdoor sampling in urban monitoring, where investigation is usually focussed onto benzene, toluene, ethylbenzene and xylene isomers. The latter is conceived for indoor monitoring, allowing quantification of all the compounds listed on page E3 and also extended qualitative analysis. The two methods differ by a few details, such as the higher desorption temperature for VOCs and the higher cryofocusing temperature for BTEX. The latter caution is introduced to avoid freezing of excess humidity gathered during the sampling in the cryofocusing trap.

Desorption

The thermal desorber is equipped with 1/4” OD SS sample tubes, they have to be hollow and free: discard the stainless steel gauze disk which is fitted to the groove and discard also the springs if present.

Code 145 cartridge has been dimensioned to fit the diameter of Turbomatrix thermal desorption tubes. Its length is such that, when the cartridge is introduced into the tube and is stopped by the groove, it is positioned exactly centrally with respect to the tube length.

Inner diameter of Perkin-Elmer tubes is not always exactly the same; it may be the case therefore that a cartridge code 145 does not slide easily into the tube. Some pushing tool may be helpful then, such as a 500 μl syringe piston, a glass bar or an iron wire 2-3 mm thick.

In some cases the tube inner diameter is slightly larger than the cartridge outer diameter: the cartridge can therefore be pushed out from the tube during desorption due to the desorption gas pressure. If this is the case, make use of the springs provided along with the tubes.

Once capped, the Turbomatrix steel tube has to be positioned in the carousel with the grooves on the bottom.

The described conditions have been optimized for seven days exposures to typical concentrations of urban atmospheres and indoor environments. Shorter exposure times or considerably higher concentrations would require different settings of split flows, with the purpose of ensuring good analytical sensitivity or linearity of response.

BTEX

Temperatures and timing

- Desorption: 320 °C for 10 minutes
- Cryofocusing trap (Tenax TA): during primary desorption maintain 2 °C, secondary desorption at 99 °C/sec up to 290 °C, 1 minute at 290 °C
- Six port valve: 150 °C
- Transfer line: 200 °C

Flows

- Carrier gas: helium, 24 psi
- Desorption flow: 100 ml·min⁻¹
- Inlet split: 90 ml·min⁻¹
- Outlet split: 30 ml·min⁻¹

VOCs

Temperatures and timing

- Desorption: at 370 °C for 15 minutes
- Cryofocusing trap (Tenax TA): during primary desorption maintain at -20 °C, secondary desorption at 99 °C/sec up to 290 °C, 1 minute at 290 °C
- Six port valve: 150 °C
- Transfer line: 200 °C

Flows

- Carrier gas: helium, 24 psi
- Desorption flow: 100 ml·min⁻¹
- Inlet split: 90 ml·min⁻¹
- Outlet split: 30 ml·min⁻¹
**Instrumental analysis**

Analytical parameters for BTEX and VOCs are the same, apart from the duration of chromatographic run and final temperature.

We recommended the following conditions:

**Column**

100% dimethylpolysiloxane, length 50m x 0.2.mm, film thickness 0.5 μm (e.g., Petrocol DH 50.2, Supelco Cat.No. 24133-U) the column is directly fitted to the six-port valve of Turbomatrix apparatus.

**Temperatures**

- GC oven: 40 °C for 3 minutes, 8 °C/min up to 80 °C, maintain for 1 minute, 20 °C/min up to 250 °C for BTEX and up to 280 °C for VOCs, final isotherm 1.5 minutes for BTEX and 3 minutes for VOC
- GC-MS interface: 270 °C

**Flows**

- Carrier gas: helium, 0.8 ml·min⁻¹

On page E6 we display two total ion current chromatograms from an outdoor urban site and an indoor sampling respectively.

In the first case, the benzene peak corresponds to an average concentration of 2.2 μg·m⁻³; in the second the concentration of 1,4-dichlorobenzene was 14 μg·m⁻³. Despite the low concentration values, the signal-to-noise ratio is very high in both cases. As a consequence, very reliable mass spectral identification is possible.

**Calibration**

Calibration curves are obtained by gas-phase injection of methanol solutions of the target compounds onto blank cartridges. Injections are performed through a GC injector, where a short piece (10 cm) of wide-bore (0.53 i.d.) deactivated uncoated column is installed. The other end bears a Swagelock reducing connection (1/16”-1/4”). The 1/4” Swagelock nut has to be equipped with a PTFE ferrule instead of the original steel one (use PTFE ferrules that come along with the Turbomatrix caps).

Introduce a blank cartridge in a Turbomatrix tube and fit the tube to the Swagelock nut. Maintain the injector at 200 °C but do not heat the oven. Inject slowly 1 μl of each calibration solution under nitrogen flow (50 ml/min) and let the system purge for 2 minutes. Analyze the cartridge as you would do with a sample.

We suggest you to prepare a complete set of calibration solutions by subsequent dilutions such as they contain, for example, 8, 4, 2, 1, 0.04, 0.02 and 0.01 μg·μl⁻¹ of each compound.

**USER TIP**

If you perform several analyses, a barcode reader will greatly improve productivity in your laboratory and will also minimize the possibility of errors in the copying of sample labels.

Please contact us to help you in the implementation of the reader.

We have also developed software solutions for the analytical data processing and automated production of analysis reports.

**USER TIP**

For a very accurate BTEX calibration we offer the preloaded cartridges code 407.
Cartridge recovery

In principle, the thermal desorption analysis leaves a conditioned cartridge that can be used as it is for another sampling. Actually this is not the case since the desorption yield, even if very high, is never quantitative, particularly for compounds with more than six carbon atoms. We recommend therefore to re-condition the cartridges after analysis, keeping them at 350 °C for eight hours under nitrogen flow.

Graphitized charcoal is a fragile material that exhibits a tendency to turn to dust under mechanical stress during the use on field and in the laboratory. Even if the stainless steel net mesh grid opening is a few micrometers, dust is lost anyway and the cartridge will eventually become empty. As soon as the mass of graphitized charcoal is reduced by 20% the cartridge has to be discarded. Basing onto our experience, this will occur after at least twenty sampling-and-analysis cycles.

TIC chromatograms of an outdoor urban sampling (left) and of indoor air (bottom). Mass spectra of benzene and of 1,4-dichlorobenzene are shown on the bottom of each picture, at concentrations of 2.2 and 14 μg·m⁻³ respectively. Despite the low concentration values, the signal-to-noise ratio is very high in both cases. As a consequence, very reliable mass spectral identification is possible by comparison with mass spectral data libraries with no need of further processing.