No risk posed by dichromate and mercury fumes

It has now been proved – during analysis of COD with HACH LANGE cuvette tests, no risk is posed by liberated mercury and dichromate.

For the purpose of protecting their employees, employers must take account of the duty of investigation under the German hazardous substances ordinance when assessing a possible risk. Under section 7, they must determine the nature, scope and duration of the presence of the substance in the ambient air and repeat the assessment at regular intervals. Technical and organizational measures must be taken to avoid any exposure. Under section 9, employers must check whether products with a lower health risk are available and, if so, must then use them.

Study of potential risks associated with the use of the COD cuvette tests

Study design

In order to determine the risks associated with the use of COD cuvette tests, a comprehensive series of measurements was carried out. The cuvette test LCK514 was selected for this purpose, because it contains the highest concentration of potassium dichromate (0.7 %). The amount of mercury sulphate is approximately the same in all COD tests.

The dichromate concentration was first measured in the ambient air under normal working conditions (measurement table in the middle of the room, closed windows and doors, no air change). 48 COD analyses were carried out exactly as described in the working procedure.

In a second series of measurements, another 48 COD analyses were carried out with LCK514, but in this case the cuvettes were subjected to the boiling phase (148 °C) without their caps in place (worst case scenario).
The dichromate and mercury concentrations were measured immediately above the thermostats. The background level of dichromate in the ambient air was measured in parallel in a neighbouring room.

**Study results**
The level of dichromate was below the detection limit of the method, irrespective of whether the cuvettes were open or closed during the boiling phase.

When the boiling phase was carried out with open cuvettes, mercury was present immediately above the thermostats in a concentration of only 0.0003 mg/m$^3$.

Determination of COD in the high-temperature thermostat revealed the following:
- The cuvette/lid system forms a hermetic seal at pressures up to 10 bar. When the temperature is increased to 170 °C the pressure in the closed cuvettes is 2 bar.
- If the lid were to leak, only steam would escape, but not sulphuric acid.
- The vapour pressure of the dichromate and mercury salts is so low that a temperature increase from 148 to 170 °C is of only subordinate importance for a transition into the gas phase.

**Summary**
The measurement body, which is accredited under section 18 subsection 2 of the German hazardous substances ordinance, concluded that there is long-term safe compliance with the threshold values for dichromate and mercury during the use of COD cuvette tests, and control measurements are not necessary. Its justification for this conclusion is that the measured value is less than 1/10 of the permissible limiting value.

The Federal German Ministry of Labour and Social Affairs has therefore also reached the conclusion that the advantages of the cuvette test (closed system, small amount of chemicals) contribute towards satisfying the requirements of section 36 of the German hazardous substances ordinance.

The results obtained clearly demonstrate that there is no risk from escaped dichromate and mercury during heating. There is therefore no need for fume extraction equipment when COD is measured with cuvette tests.

Irrespective of the above, it should always be remembered that coming into contact with or swallowing the corrosive and toxic COD solution can impair health. This is why it is necessary to wear protective clothing when carrying out COD analyses.

### Dichromate and mercury liberated during COD determination with LCK514

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
<th>Measured value in the ambient air</th>
<th>Reference measurement background level</th>
<th>48 COD analyses LCK514 with cap closed</th>
<th>48 COD analyses LCK514 without cap</th>
<th>48 COD analyses LCK514 without cap</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichromate</td>
<td>mg/l$^3$</td>
<td>&lt;0.002</td>
<td>mg/l$^3$</td>
<td>mg/l$^3$</td>
<td>mg/l$^3$</td>
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<tr>
<td>Mercury</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Mercury</td>
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<td></td>
<td>0.0003</td>
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</table>