



Aldehydes

Radiello components to be used:

blue diffusive body code 120-1

supporting plate code 121

vertical adapter code 122 (optional)

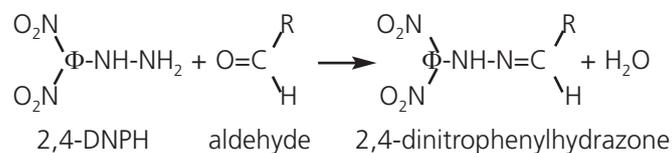
chemiadsorbing cartridge code 165

filtration kit code 174 (only for analysis)

Or: *radiello-ready-to-use sampler* code 123-4 (also see page A8)

Principle

Code 165 is a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil®. Aldehydes react with 2,4-DNPH to give the corresponding 2,4-dinitrophenylhydrazones



The 2,4-dinitrophenylhydrazones are then extracted with acetonitrile and analyzed by reverse phase HPLC and UV detection.

Sampling rates

Sampling rates values Q at 298 K (25 °C) and 1013 hPa are listed below:

	Q ₂₉₈ rate ml·min ⁻¹	linearity range µg·m ⁻³ ·min	limit of quantitation ¹ µg·m ⁻³	uncertainty at 2σ %
acetaldehyde	84	1,000÷12,000,000	0.1	15.9
acrolein	33	3,000÷3,000,000	0.3	16.5
benzaldehyde	92	1,000÷8,000,000	0.1	17.2
butanal	11	9,000÷10,000,000	0.9	23.5
hexanal	18	5,000÷15,000,000	0.6	20.2
formaldehyde	99	1,000÷4,000,000	0.1	13.8
glutaric aldehyde	90	1,000÷3,000,000	0.1	14.5
isopentanal	61	1,500÷12,000,000	0.2	17.0
pentanal	27	4,000÷12,000,000	0.4	22.9
propanal	39	3,000÷8,000,000	0.3	17.1

¹after 7 days exposure

Effect of temperature, humidity and wind speed

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

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^{0.35}$$

where Q_K is the sampling rate at the temperature K and Q₂₉₈ is the reference value at 298 K. This produces a variation of ± 1% 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.



Calculations

The average concentration **C** over the whole sampling time (in $\mu\text{g}\cdot\text{m}^{-3}$) is calculated according to the expression:

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

where:

m = mass of aldehyde in μg

t = exposure time in minutes

Exposure

The optimum exposure duration varies with the expected concentration. Taking formaldehyde as an example, concentration values of 5-30 $\mu\text{g}\cdot\text{m}^{-3}$ are usually found in outdoor urban measurements while 20-200 $\mu\text{g}\cdot\text{m}^{-3}$ are expected in workplace environments. In workplace environments concentrations may be as high as 2,000-3,000 $\mu\text{g}\cdot\text{m}^{-3}$ for short time intervals: it can therefore be interesting to evaluate the peak value (usually referred to by **STEL**). The corresponding advised exposure time is shown in the table below:

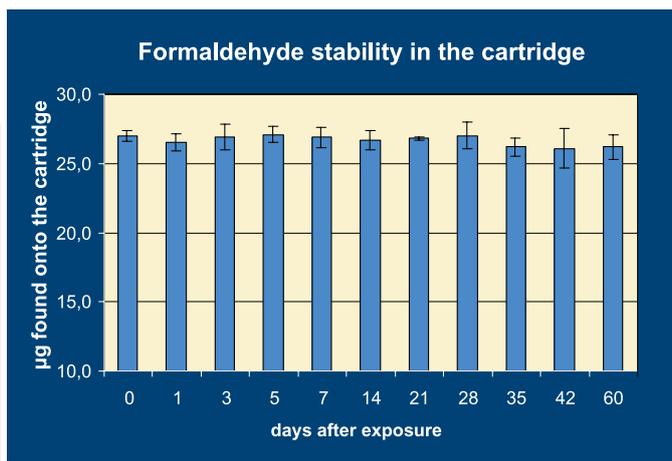
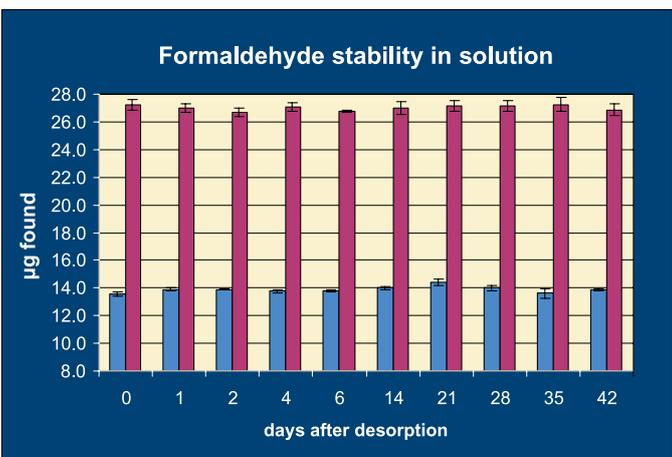
Advised exposure times

	outdoor environment	indoor environment	workplace environment average conc.	workplace environment peak conc.
minimum	8 h	8 h	2 h	15 minutes
maximum	7 days	7 days	8 h	1 h

Do not expose all of the cartridges belonging to the same lot: keep at least two cartridges as blanks.

Storage

The cartridges need to be kept in a dark place at 4 °C. Closed in their bags, they are stable at least six months from the production date. Each cartridge has a blank value of formaldehyde less than 0.1 μg , corresponding to a concentration in air less than 0.1 $\mu\text{g}\cdot\text{m}^{-3}$ over one week of exposure or 2 $\mu\text{g}\cdot\text{m}^{-3}$ over 8 hours. The blank value may increase with time. The expiry date (printed onto the plastic bag) indicates when the expected content of formaldehyde (for a correctly stored cartridge) will probably exceed 0.2 μg .



Formaldehyde stability in the cartridge after the sampling (on top) and in solution (left). The stability tests were performed upon cartridges exposed for one week in a standard atmosphere chamber at 25 °C and with 50% relative humidity and at two different concentration levels. Each bar in the plot represents the average and error from the analysis of six samples.



After exposure keep the cartridges well capped at 4 °C, they are stable for 60 days. After solvent desorption (see Analysis) and extraction of the cartridge from the tube, the resulting solution, well capped and stored at 4 °C, is stable for at least 42 days (see on page C2).

Analysis

Desorption

Materials

- HPLC or spectroscopy grade acetonitrile
- class A volumetric pipette, capacity 2 ml
- micropore filter membranes, porosity 0.45 µm, solvent resistant

Procedure

Introduce 2 ml acetonitrile directly in the cartridge tube, recap and stir from time to time for 30 minutes. Discard the cartridge. Filter the resulting solution and keep it well capped until analysis time. If analysis has to be delayed, store the solution at 4 °C.

Instrumental analysis

The method suggested below is only indicative; the analyst can choose an alternative method, on the basis of its personal experience.

Materials

- reverse phase C₁₈ HPLC column, length 150 mm, 4.6 mm diameter, 5 µm packing particle size (e.g. Ascentis C18, Supelco cat.no. 581324-U)
- HPLC apparatus capable of elution gradient and UV detection

Procedure

Set the detector at the wavelength of 365 nm. Inject between 10 and 50 µl of solution and elute as follow:

- flow: 1.9 ml·min⁻¹
- Isocratic elution with acetonitrile/water 38:62 v/v for 10 minutes, up to acetonitrile/water 75:25 v/v in 10 minutes, reverse gradient to acetonitrile/water 38:62 v/v in 5 minutes.

On the right: the chromatogram of a real sample analyzed under the described conditions.

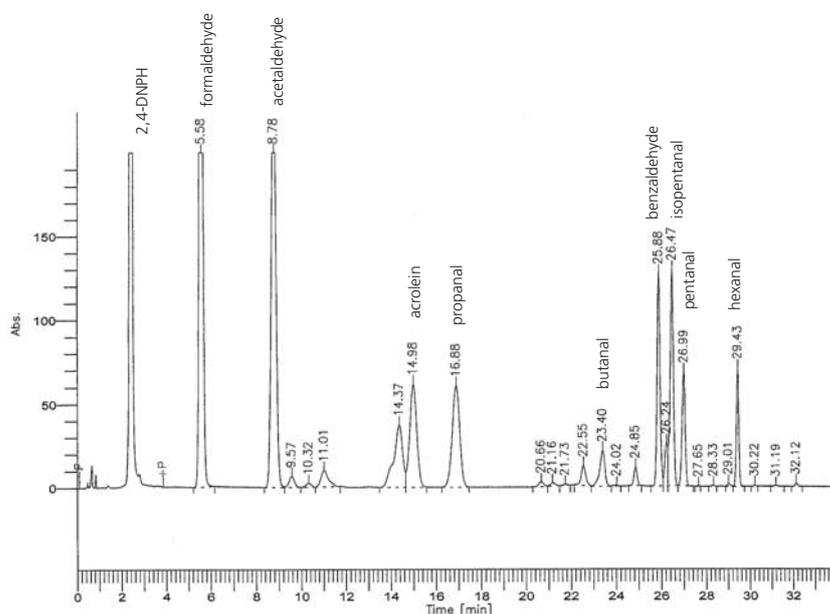
USER TIP

For extracting the cartridges use SPECTRANAL Acetonitril Fluka Cat. No. **34921** with low aldehyde content.

For a reliable and rapid filtration employ the filtration kit **code 174**.

To obtain an accurate calibration curve we offer you the calibration solution **code 302**.

IMPORTANT: verify the presence and the abundance of the 2,4-DNPH chromatographic peak: otherwise, the cartridge could be saturated.



HPLC chromatogram of aldehydes sampled by radiello

IMPORTANT

Acrolein gives place to three chromatographic peaks, two of them are unresolved. Calculate the concentration basing onto this most abundant peak and ignore the others.

Isopentanal appears as two unresolved peaks: its concentration should be obtained by integration of both peaks as a sum.



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.

Interferences

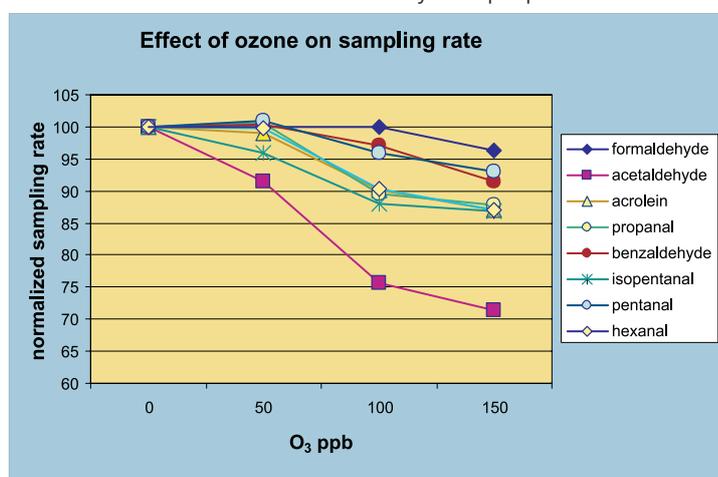
Other carbonyl compounds

All carbonyl compounds, ketones included, react with 2,4-DNPH but do not interfere in the analysis if proper chromatographic parameters are selected. In the described chromatographic conditions acetone-2,4-DNPH peak is well resolved from acrolein-2,4-DNPH. Nevertheless, if acetone concentration is higher than $50,000 \mu\text{g}\cdot\text{m}^{-3}$, acrolein-2,4-DNPH peak intensity is depressed by 25%.

Ozone

Examples of ozonolysis of dinitrophenylhydrazones on active supporting materials as silica gel are found in the literature.

On code 165 cartridge, packed with coated Florisil®, ozonolysis is much less important than on any other commercial aldehyde sampling device, either diffusive or pumped, and becomes appreciable only if ozone concentration, averaged over the whole exposure time interval, is higher than 100 ppb. Since this is not usually the case, generally no correction is needed to take into account ozone concentration. If there is firm evidence that ozone concentration is equal or higher than 100 ppb over the whole exposure time, make use of the corrected sampling rate values shown in the table below, where $[\text{O}_3]$ is ozone concentration in ppb.



Sampling rate as a function of ozone concentration normalized to 100 for $[\text{O}_3]$ equal to zero. Apart from acetaldehyde, ozone effect becomes relevant only at concentration levels higher than 100 ppb as an average over the whole exposure time interval.

analyte	corrected sampling rate $Q_{298} \text{ ml}\cdot\text{min}^{-1}$
acetaldehyde	$84 - 0.018[\text{O}_3]^*$
acrolein	$33 - 0.027[\text{O}_3]$
benzaldehyde	$92 - 0.05[\text{O}_3]$
formaldehyde	$99 - 0.02[\text{O}_3]$
hexanal	$18 - 0.02[\text{O}_3]$
isopentanal	$61 - 0.06[\text{O}_3]$
pentanal	$27 - 0.01[\text{O}_3]$
propanal	$39 - 0.03[\text{O}_3]$

*apply for ozone concentration higher than 50 ppb

The listed values are referred to the temperature of 298 K (25 °C), for deviations larger than ± 10 °C substitute the base value (e.g. $99 \text{ ml}\cdot\text{min}^{-1}$ for formaldehyde) with the corrected value calculated according to equation on page C1.

No experimental data is available for butanal and glutaric aldehyde.

Sampling rate for ozone concentration $[\text{O}_3]$ in ppb (apply only if $[\text{O}_3] > 100$; for acetaldehyde $[\text{O}_3] > 50$ ppb)