VdL-Guideline 03

"VdL Guideline on Formaldehyde Determination"

Guideline for the determination of the formaldehyde concentration in water-dilutable paints and varnishes, and polymer dispersions

Edition of October 2018 (1^{st} revision)

Verband der deutschen Lack-
und Druckfarbenindustrie e.V.

Foreword

This Guideline was prepared by the Technical Committee on Decorative Coatings (TKB) within the Paint and Printing Ink Association (VdL). This Guideline defines the procedure for determining the free and total formaldehyde concentration in water-dilutable paints and varnishes, and polymer dispersions.

The use of this VdL Guideline is also recommended for non-members of the German Paint and Printing Ink Association. This is conditional on the submission of a written declaration to the VdL whereby the non-member agrees to comply with this Guideline. The VdL reserves the right to audit the statements given and compliance with this Guideline. In the event of proven violations, the VdL is entitled to revoke the right to refer to the Guideline and to take legal action against misleading declarations.

This version replaces the version dated May 1997, which has received technical and editorial revisions. Key changes are as follows:

- Adjustment of terminology to definitions from ISO 4618
- Updating of references to technical codes of practice
- Updating of technical implementation

All VdL Guidelines are published on the VdL website.

URL as of October 2018: http://www.wirsindfarbe.de/service-publikationen/vdl-richtlinien/

1. Scope

The stated methods describe the quantitative determination of the concentration of free formaldehyde and total formaldehyde in water-dilutable paints and varnishes, and polymer dispersions. Preservatives are important sources of formaldehyde.

The determination method for free formaldehyde is of limited suitability for pigmented systems, since the inherent colouration of the material may, in some circumstances, have an effect on the photometric quantification methods.

2. References to technical rules and regulations

DIN EN 717-1:2005-01 ‘Wood-based panels – Determination of formaldehyde release – Part 1: Formaldehyde emission by the chamber method’

VDI Guideline 3484, Part 2, issued November 2001 ‘Gaseous ambient air measurements – Indoor-air pollution measurements - Measurement of the formaldehyde concentration with the acetyl acetone method’

DIN EN ISO 12460-3:2016-03 ‘Wood-based panels – Determination of formaldehyde release – Part 3: Gas analysis method’

DIN EN ISO 15234:2011-02 ‘Paints and varnishes – Testing of formaldehyde-emitting coatings and melamine foams – Determination of the steady-state concentration of formaldehyde in a small test chamber’

DIN EN ISO 4618 ‘Paints and varnishes - Terms and definitions’

3. Terms, definitions and abbreviations

3.1. Free formaldehyde concentration

The formaldehyde concentration that is determined by using the acetyl acetone method is the free formaldehyde concentration. It determines the amount of formaldehyde in mg related to 1 kg of paint, varnish or polymer dispersion, which is available unbound in the sample at the time of derivatisation.

Note:
The unit [mg/kg] is equivalent to the unit [ppm]. Within this document the unit [mg/kg] is used uniformly.

3.2. Formaldehyde depot substance

Compound that releases formaldehyde over a longer period of time.

3.3. Bound formaldehyde concentration

The concentration of formaldehyde in [mg/kg] remaining bound to the depot substance after equilibrium is established between free formaldehyde and the depot substances, and which could potentially be released by a formaldehyde depot substance (difference between total formaldehyde concentration and free formaldehyde concentration).

3.4. Total formaldehyde concentration

Concentration in [mg/kg] of free and bound formaldehyde in the paint or varnish is called total formaldehyde concentration.

3.5. Water-dilutable dispersion paint or varnish

Paint or varnish in which the organic binder is dispersed in water (Source: DIN EN ISO 4618).

3.6. In-can formaldehyde concentration

Total formaldehyde concentration, i.e. sum of the free and bound formaldehyde concentration, in the liquid paint or varnish in the can.

3.7. In-film formaldehyde concentration

Total formaldehyde concentration, i.e. sum of the free and bound formaldehyde concentration, in the dry paint or varnish.

4. Principle of measurement

When a formaldehyde depot substance is added to a paint or varnish, the equilibrium is established between the formaldehyde that is bound to the formaldehyde depot substance and the free formaldehyde. This equilibrium depends on the pH value, the coating matrix, the formaldehyde depot substance and the temperature.

Within a paint or varnish, a distinction must be made between the total formaldehyde concentration (free and bound formaldehyde) and the free formaldehyde concentration. In the context of this Guideline, the free formaldehyde concentration is understood to mean the formaldehyde concentration that is determined by the acetyl acetone method.
A distinction must also be made between the formaldehyde concentration in the paint or varnish (in-can formaldehyde concentration) and in the coating itself (in-film formaldehyde concentration) once the paint or varnish has been applied and has dried. For the in-film formaldehyde concentration, the formaldehyde essentially bound.

4.1. Fundamentals of the acetylacetone method for determining the free in-can formaldehyde concentration

The free formaldehyde is extracted from the coating material with water and derivatised with acetyl acetone and ammonium ions to 3,5-diacetyl-1,4-dihydrolutidine (Hantzsch reaction). This compound has an absorption maximum at 412 nm. The formaldehyde content is determined using photometry.

4.2 Fundamentals of determining the total in-can formaldehyde concentration by acid steam distillation

The total formaldehyde concentration is determined using acid steam distillation, since this method ensures the release of all formaldehyde available.

The formaldehyde bound to the formaldehyde depot substance is stripped off in an acidic environment and captured after a steam distillation together with the free formaldehyde as total formaldehyde. The total formaldehyde content is determined using photometry by reacting with acetyl acetone (6.2.2) or alternatively by reacting with chromotropic acid (6.2.3).

5. Equipment and test facilities

5.1. Acetyl acetone method (Determination of free in-can formaldehyde)

- Precision balance, resolution of at least 0.001 g
- Spectrophotometer, suitable for a wavelength of 412 nm
- Centrifuge, e.g. Suprafuge 22 model from Heraeus
- Polycarbonate centrifuge tubes with screw cap
- Centrisart® tubes, Sartorius brand, or similar product (as required)
- Graduated cylinder, 25 ml, with ground joint
- Suitable pipettes
- Suitable cuvettes
- Suitable volumetric flasks for calibration
- Single-use filters, e.g. 0.2 µm (as required)
- Single-use syringes
- Acetyl acetone reagent for a volume of 500 ml aqueous solution:
  - 75 g ammonium acetate p.a.
  - 1 ml acetylacetone (2,4-pentandione) p.a.
  - 1.5 ml acetic acid 100% p.a.
  - Fill up to 500 ml with deionised water
- Deionised water
- 30 - 40% formalin solution
- Iodine solution, c(I_2) = 0.05 mol/l (equivalent to 12.69 g I_2/l)
- Sodium hydroxide solution, c(NaOH) = 1 mol/l (equivalent to 40.00 g NaOH/l)
- Hydrochloric acid, c(HCl) = 1 mol/l (equivalent to 36.46 g HCl/l)
- Starch solution, 1% soluble, acc. to Zulkowsky
- Sodium thiosulphate solution, c($Na_2S_2O_3$) = 0.1 mol/l (equivalent to 15.81 g $Na_2S_2O_3$/l)

Note 1:
The acetyl acetone reagent is not stable. If kept at room temperature, it may be used for testing for no longer than 14 days.

Note 2:
Deionised water is susceptible to microbial contamination. Either use deionised water with a low level of microbial contamination (<100 CFU) or perform a test to confirm that potential microbial contamination of the deionised water shall not influence the measurement results. As a preservative, formaldehyde is potentially able to react with microbes.

5.2. Acid steam distillation (Determination of total in-can formaldehyde)

– Steam distillation apparatus, e.g. Vapodest 20s (Gerhard brand)
– Volumetric flasks 250 ml
– Precision balance, resolution of at least 0.001 g
– Spectrophotometer, suitable for a wavelength of 412 nm
– Graduated cylinder, 25 ml, with ground joint
– Suitable pipettes
– Suitable cuvettes
- Sulphuric acid 25% (v/v),
    e.g. made up from 839 ml deionised water and 160 ml conc. sulphuric acid

– Acetyl acetone reagent for a volume of 500 ml aqueous solution:
    – 75 g ammonium acetate p.a.
    – 1 ml acetylacetone (2,4-pentandione) p.a.
    – 1.5 ml acetic acid 100% p.a.
    – Fill up to 500 ml with deionised water
– Deionised water

Note:
The acetyl acetone reagent is not stable. If kept at room temperature, it may be used for testing for no longer than 14 days.

6. Procedure

6.1. Acetyl acetone method (Determination of free formaldehyde concentration)

A sample of (2.5 ± 0.3) g of water-dilutable paint or varnish (note initial sample weight to nearest 0.001 g) is weighed into a graduated 25 ml cylinder, to which 10 ml of acetyl acetone reagent is added before being filled up to 25 ml with deionised water and shaken. After 2 h at room temperature, the supernatant is transferred with a pipette to a centrifuge tube, the tube screwed shut and then centrifuged for approx. 20 min at 22000 rpm. If no clear serum is produced at this speed, a centrifuge capable of 30000 rpm or alternatively Centrisart I tubes (Sartorius brand, max. 4300 rpm for 20 min) (or a comparable product) must be used instead. After centrifuging is complete, the clear supernatant is transferred to the measurement cuvette. If turbidity occurs, the supernatant can be filtered with a syringe through a 0.2 µm single-use filter (for example) before being transferred to the cuvette.

In parallel, a blank solution is also prepared by pipetting 10 ml of acetone reagent into a graduated cylinder, which is filled up to 25 ml with deionised water and then shaken. The hold time for the solution until measurement is 2 h at room temperature.

Both solutions are measured against one another at 412 nm in the spectrophotometer.

Working range:

At formaldehyde concentrations over 100 mg/kg, the diacetyl dihydrolutidine begins to crystallise and turbidity occurs. In this case, select a smaller initial sample weight for the paint or varnish.

Depending on the photometer used, determination limits of up to 0.1 mg/kg are achieved. The limit of determination must be determined individually. It must be ensured that the value expected is within the working range of the method.

Note:
In accordance with the standard procedure from VdL Guideline 03, samples are prepared using water. If no clear supernatant is obtained after the centrifugation step, the photometric determination may contain a systematic error as a result of turbidity. In this case, some other suitable solvent (e.g. methanol) can be used. Since the free formaldehyde is in equilibrium with the bound formaldehyde and the equilibrium can further be influenced by the solvent, this means that the free formaldehyde content determined in water may differ to that determined in some other solvent.
This change in solvent must be documented in the test report and the result for free formaldehyde with the different solvent must be reported.

The samples and the blank solution must always be prepared using the same solvent!

If a solvent other than water is selected, a calibration curve must be created for formaldehyde in this solvent.

6.2. Determination of total formaldehyde concentration

6.2.1. Acid steam distillation

Approx. (10 ± 5) g of a sample (note initial sample weight to nearest 0.001 g) is weighed in the distillation flask on the analytical balance and approx. 50 ml of deionised water is added. After the careful addition of 20 - 30 ml of the 25% sulphuric acid solution (caution: causes foaming), the sample is subjected to steam distillation, whereby around 245 ml of solution is distilled over. The distillate is filled up to the 250 ml mark with deionised water.

6.2.2. Photometric determination with acetyl acetone reagent

A sample of (2.5 ± 0.5) g of the distillate is weighed into a graduated 25 ml cylinder, to which 10 ml acetyl acetone reagent is added. In parallel, a blind solution is prepared with deionised water and 10 ml acetyl acetone reagent in another 25 ml cylinder. Allow the solution to stand for 2 h at room temperature. Both solutions are measured against one another at 412 nm in the spectrophotometer.

6.2.3. Determination with the chromotropic acid method

There are commercially available test kits for the determination of the formaldehyde content using the chromotopic acid method (e.g. Merck KGaA). This method can be utilised as an alternative to the acetyl acetone method for determining the total formaldehyde content in samples following acid steam distillation. The method is not suitable for determining the free formaldehyde concentration.

6.3. Determining the in-film formaldehyde concentration

Determination of the in-film formaldehyde concentration is performed as follows. The paint or varnish is applied to a suitable substrate (glass, aluminium) using a squeegee/film applicator with a 250 µm gap height, and stored at 23 °C and 50% relative humidity. After the desired number of days – but no sooner than after completion of drying time – the paint or varnish film is removed from the substrate and shredded. Steam distillation is performed according to 6.2.1 to release the formaldehyde from the sample.

The formaldehyde concentration is determined using photometry by reacting with acetyl acetone (6.2.2) or alternatively by reacting with chromotropic acid (6.2.3).

7. Calibration

7.1. Creation of a calibration curve – acetyl acetone method for determination of the free in-can formaldehyde concentration

From a 30 - 40% formalin solution, dilution with deionised water is used to produce an approx. 1 g/l formalin solution as a stock solution (note initial sample weight to nearest 0.001 g)

The exact formaldehyde content of this solution is determined using titration, as follows.

Add the following to 20 ml of this solution:
25 ml iodine solution, c(I_2) = 0.05 mol/l (equivalent to 12.69 g I_2/l)
10 ml sodium hydroxide solution, c(NaOH) = 1 mol/l (equivalent to 40.00 g NaOH/l)

After 5 min, add to the solution:
11 ml hydrochloric acid, c(HCl) = 1 mol/l (equivalent to 36.46 g HCl/l)
A few drops of starch solution, 1% soluble, acc. to Zulkowsky. The excess iodine solution is back-titrated with a sodium thiosulphate solution,
c($Na_2S_2O_3$) = 0.1 mol/l (equivalent to 15.81 g $Na_2S_2O_3$/l).

The formaldehyde content is calculated using the following equation:

Equation 1:
$$c(f_{CH2O})\left[\frac{g}{l}\right] = \frac{(V_{iod}[\mathrm{ml}] - V_{thio}[\mathrm{ml}]) \times c_{thio}\left[\frac{mol}{l}\right] \times M_{CH2O}\left[\frac{g}{mol}\right]}{V_{CH2O}[\mathrm{ml}] \times 2}$$

where

$c(f_{CH_2O})$	Formaldehyde concentration in standard stock solution, in g/l
V_{thio}	Volume of sodium thiosulphate solution in ml, to the nearest 0.1 ml
V_{iod}	Volume of iodine solution, in ml
V_{CH_2O}	Volume of formaldehyde solution, in ml
c_{thio}	concentration of the sodium thiosulphate solution (0.1 mol/l)
M_{CH_2O}	molar mass of formaldehyde (30.031 g/mol)

When using 20 ml formaldehyde stock solution and the solutions with the volumes and concentrations as defined above, the equation can be simplified to:

Equation 2:
$$c(f_{CH2O})\left[\frac{g}{l}\right] = (25\ \mathrm{ml} - V_{thio}[\mathrm{ml}]) \times 0.075\ \left[\frac{g}{l \times ml}\right]$$

The formalin stock solution is used for preparing calibration solutions that cover the measurement range, e.g. from 0.1 mg/kg to 100 mg/kg.
A total of 10 ml acetyl acetone reagent is added to each 2.5 g of these solutions and filled up to 25 ml with deionised water. After 2 h hold time at room temperature, the absorbance of this solution at 412 nm versus a blank is determined using a spectrophotometer. By subtracting the absorbance of the blank from the absorbance of the sample, the inherent colouration of the calibration solutions due to the adding of the reagents is compensated.

The concentrations of the calibration solutions are plotted against the corresponding absorbance values. Linear regression is performed allowing for the zero point. The slope *b* of the lines is determined using the following equation:

Equation 3:

$$b\left[\frac{a.u.}{mg/kg}\right] = \frac{\sum R_i[a.u.]}{\sum x_i[mg/kg]}$$

where

b	Slope of calibration curves in a.u./(mg/kg)
i	Calibration solution index
x_i	Formaldehyde concentration of calibration solutions, in mg/kg
R_i	Absorbance of calibration solution in question

The concentration of a sample x_s can then be determined from the sample’s absorbance R_s by using the following equation:

Equation 4:

$$x_S\left[\frac{mg}{kg}\right] = \frac{R_S[a.u.]}{b\left[a.u./(\frac{mg}{kg})\right]}$$

where

x_S	Formaldehyde concentration of sample in mg/kg
R_S	Absorbance of sample in a.u. (arbitrary units)

7.2. Creation of a calibration curve – Determination of total formaldehyde concentration

The creation of the calibration curves is analogous to the steps given at 7.1. Starting from the stock solution a certain number of dilution steps are performed to cover the working range of the instrument, e.g. 0.1mg/l to 10 mg/l.
In place of the instructions given in 7.1, a dilution series is to be made from the standard stock solution. The individual values in this series must range from 0.001 mg to 0.1 mg formaldehyde per 10 ml of solution (concentration range 0.1 mg/l to 10 mg/l).

8. Calculation of results

8.1. Determination of free formaldehyde concentration (acetylacetone method)

The free formaldehyde concentration w in the sample is determined using the following equation:

Equation 5:

$$w(f_{CH2O})\left[\frac{mg}{kg}\right] = \frac{R(f_{CH2O})[a.u.]}{b\left[\frac{a.u.}{mg/kg}\right]} \times \frac{2.500\ g}{m_s[g]}$$

where

$w(f_{CH2O})$	Free formaldehyde concentration of sample, in mg/kg (ppm)
$R(f_{CH2O})$	Absorbance of solution, measured according to 6.1
b	Slope of curve according to 7.1
m_s	Initial sample weight, to nearest 0.001 g

8.2. Determination of total formaldehyde concentration (acid steam distillation)

8.2.1. Evaluation of total formaldehyde concentration using the acetyl acetone method given in 6.2.2

The total formaldehyde concentration *w* determined using the method from 6.2 is calculated for the acetyl acetone method given in 6.2.2, and taking into account the 250 ml sample volume and the initial sample weight of the paint/varnish, as follows:

Equation 6:

$$w^A\left(\sum CH_2O\right)\left[\frac{mg}{kg}\right] = \frac{R_S[a.u.]}{b^A\left[\frac{a.u.}{mg/l}\right]} \times \frac{V_{tot}}{m_s[g]}$$

where

$w^A(\Sigma CH_2O)$	Total formaldehyde content of sample, in mg/kg (in-can), according to the acetyl acetone method
R_S	Absorbance of sample in a.u.
b^A	Slope of calibration of acetyl acetone method from 6.2.2 in a.u./(mg/l)
m_S	Initial sample weight in g
V_{tot}	Volume of volumetric flask (total volume of solution) in l

8.2.2 Evaluation of total formaldehyde concentration using the chromotropic acid method given in 6.2.3

The total formaldehyde content of the solution is determined using the chromotropic acid method, e.g. HCHO test kit from Merck (or a comparable test).

The total formaldehyde content is calculated as follows:

Equation 7: $$w^{chr}\left(\sum CH_2\,O\right)\left[\frac{mg}{kg}\right] = \frac{R_s[a.u.]}{b^{chr}\left[\frac{a.u.}{mg/l}\right]} \times \frac{V_{tot}[l]}{m_s[g]} \times 1000\left[\frac{g}{kg}\right]$$

where

$w^{chr}(\Sigma CH_2O)$	Total formaldehyde content of sample, in mg/kg (in-can)
R_S	Absorbance of sample in a.u.
b^{chr}	Slope of calibration of chromotropic acid method in a.u./(mg/l)
m_S	Initial sample weight in g
V_{tot}	Volume of volumetric flask (total volume of solution) in l

With a predefined calibration function and direct display of the formaldehyde concentration of the sample in [mg/l] instead of the absorbance in a.u., the equation can be simplified to:

Equation 8: $$w^{chr}\left(\sum CH_2\,O\right)\left[\frac{mg}{kg}\right] = D\left[\frac{mg}{l}\right] \times \frac{V_{tot}[l]}{m_s[g]} \times 1000\left[\frac{g}{kg}\right]$$

where

D	Display of determined concentration of formaldehyde in mg/l
$w^{chr}(\Sigma CH_2O)$	Total formaldehyde content of sample, in mg/kg (in-can)
m_S	Initial sample weight in g
V_{tot}	Volume of volumetric flask (total volume of solution) in l

9. Test report

Test reports presenting results according to VdL Guideline 03 must contain the following minimum details:

a) All information necessary to identify the tested sample
b) A reference to this document (VdL Guideline 03, issued October 2018)
c) Measured quantity/quantities determined:
    a. Free in-can formaldehyde concentration
    b. Total in-can formaldehyde concentration
    c. In-film formaldehyde concentration
d) The method used:
    a. Photometric method (free formaldehyde)
    b. Acid steam distillation (total formaldehyde)
    c. Chromotropic acid method (total formaldehyde concentration)
e) The results for the measured quantities determined
f) All deviations from the method as described
g) All irregularities observed
h) Test date

10. Literature

E. Bagda, T. Brenner, M. Wensing, FARBE&LACK 103(1997), no. 8.