

FORMALDEHYDE MEASUREMENT IN EMISSIONS FROM PRESS BOARD AND BONDED FIBRE PRODUCTION

R. De Fré, I. Vanderreydt, W. Swaans

Vito, Flemish Institute for Technological Research, Boeretang 200, B-2400 Mol, Belgium

e-mail: raf.defre@vito.be

Introduction

Formaldehyde is a known carcinogen and its concentrations have to be minimized in industrial emissions. Sectors where formaldehyde containing formulations are applied include mineral wool forming by resin impregnation and the manufacturing of pressed boards. For stack emissions typically limit values of 20 mg/Nm³ are imposed and the test methods have to be validated in this range. In cases where a limit total emission factor expressed as quantity of formaldehyde released per unit of product, e.g. in kg/m³, is specified, additionally the determination of diffuse emissions of formaldehyde is required. This paper describes validation work on formaldehyde measurement in gases and illustrates problems of incomplete recovery of formaldehyde when the DNPH method is used in stack gas sampling. The tests confirmed that the EPA 316 method with spectrophotometrical analysis is suited to deliver accurate results in this range.

Methods for measuring stack gas emissions of formaldehyde

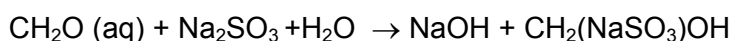
For continuous monitoring of formaldehyde emission an available technique is Fourier transform infrared absorption spectrometry (FTIR) as described in EPA method 318 [1]. Alternative less selective methods are the use of instruments with electrochemical cells or the measurement of total organic carbon content by flame ionization detector (FID).

Manual emission measurement of formaldehyde in stationary sources generally uses the isokinetic sampling of gases and particulates followed by absorption of formaldehyde in an aqueous solution. Analysis is either by spectrophotometry of the pararosaniline derivate, as described in EPA method 316 [2] or by liquid chromatography (HPLC) of hydrazone derivatives of aldehydes and ketones after reaction with 2,4-dinitrophenylhydrazine (DNPH) as in EPA method 0011 [3]. Many other analytical methods for formaldehyde are described in the literature, but these are less common in emission testing, e.g. EPA's Conditional Test Method CTM-037 for measurement of formaldehyde emissions from natural gas-fired stationary sources using the acetyl-acetone derivatization method [4].

Generation of formaldehyde test gases

Formaldehyde is not available as a pure substance or as a certified calibration gas in cylinders. Pure formaldehyde is unstable due to polymerization. It reacts readily or forms reversible adducts with numerous other chemicals including water, alcohols and carbonylic compounds. Therefore the generation of a traceable formaldehyde reference material in the gas phase is a particular problem. Direct chemical generation of formaldehyde from methanol oxidation has been described [5], but as the conversion efficiency may depend on several parameters, this method does not result in a stable and traceable gas standard. For earlier ring tests at Vito in relation with industrial hygiene measurements, a permeation tube filled with paraldehyde heated at 90 °C was used by Goelen et al [6] to generate formaldehyde at concentration levels of 0.3 to 1.3 ppm (0.4 – 1.7 mg/m³). For test gases at the emission level this method has a too limited range and does not allow to produce gaseous formaldehyde in higher concentrations. In this work the test gases were generated by evaporation of an aqueous 37 % formaldehyde solution in a controlled nitrogen flow. Analytical grade 37 % formaldehyde was obtained from Acros, and the concentration of the standard solution is determined according to Walker [5]. This standardisation is based on

titration with a HCl standard of NaOH, which is stoichiometrically released when formaldehyde reacts with Na₂SO₃ to form the bisulfite addition product:



Diluted solutions of formaldehyde can be prepared gravimetrically or volumetrically for use in the test gas generation. Solutions of 1000 ppm are stable over several months, and can be certified by the same titration method.

In the evaporation system the solution is pumped from a continuously weighted container and the dilution gas flows are generated by calibrated mass flow controllers. Traceability of gas formaldehyde concentrations to national standards of time, weight and length was thus assured. A limitation of the test gases generated by this method is the presence of water and methanol that is added as a stabilizer. Small variations of hourly values in the generated formaldehyde concentrations are observed. In table 2, first column, the average "true values" of the generated concentrations are given with their standard deviation. The stability of the test gas generator as relative standard deviation for hourly averages was 1.4 % for the 2 and 20 mg/Nm³ concentration level (Nm³ : normal cubic metre, dry at 0 °C and 1013 mbar).

A flame ionisation detector (FID) type JUM 3-300A was calibrated with propane and tested with formaldehyde vapor at concentration levels of 50 and 200 mg C/Nm³. The C-response factor for formaldehyde was 0.24 at both concentrations. The FID analyser was used further to continuously monitor the stability of the test gases from the generation system.

DNPH method

The DNPH method is most frequently used for determination of aldehydes in industrial atmospheres and in ambient air, and the chromatographic analysis allows for simultaneous determination of several carbonylic compounds. In the reaction the 2,4-dinitrophenylhydrazone derivate is formed which is insoluble in water:



After sampling the hydrazone derivate is recovered in an organic solvent. When an aqueous phase is present this can be extracted repeatedly with methylene chloride and concentrated before solvent change to acetonitrile. Analysis is performed by HPLC on a C₁₈ column with acetonitrile-water eluent and UV detection. Standard solutions of mixed hydrazones can be obtained commercially for calibration. GC-MS is an alternative for higher resolution in the separation of isomers. The DNPH method for stationary source emissions has been published as EPA method 0011. A saturated DNPH solution in 37 % HCl is used. The reagent must be purified and tested for blanks. EPA refers to a sample volume of 1.3 m³ and 400 ml of 0.01 M absorbing solution, resulting in a detection limit of 36 ppb (0.05 mg/Nm³) and a sampling capacity up to 7.5 ppm (10 mg/Nm³), based on a reagent capacity safety factor of 10. For this work we used two impingers with 250 ml of solution and a sampling time of 60 minutes with 0.3 m³ sample volume or 30 minutes and 0.15 m³ respectively. The analytical detection limit is 0.2 µg of formaldehyde per sample, but the blank of the absorption liquid limits the use of the method. The detection limit is estimated at 0.05 mg/m³ and the quantification limit at 0.06 mg/m³, defined as the average blank value plus 3 or 6 times the standard deviation of repeated analysis of blanks.

Table 1 summarizes test results obtained with the DNPH method with test gases on the emission limit level of 20 mg/m³. The first row of results indicates that the recovery is below 60 % or that the trueness of the method has a negative bias of over 40 %, while precision appears to be acceptable as the repeatability standard deviation is 5.8 %. Under field conditions similar observations were made and in the case of wood and fibre compositing plants this has lead to underestimation of the emissions of formaldehyde.

Minor losses during analysis include incomplete recovery of the precipitate, solvent extraction and evaporation to dryness. In order to improve recovery the absorption liquid was extracted repeatedly with methylene chloride. These results are shown at the second row of results in table 1. For 3 of the tests 3 extractions were used, leading to recoveries from 65.2

to 70.5 %, and after 4 - 6 extractions when the yellow color of the reagent has disappeared completely from the aqueous phase a maximum recovery 76.3 % could be obtained. Possible effects explaining the incomplete recoveries obtained by the DNPH method are:

- (1) equilibrium reaction where the hydrazone is not completely formed
- (2) excessive consumption of reagent by side reactions, in combination with (1)
- (3) loss of formaldehyde in aqueous solution due to side reactions
- (4) instability of the reaction product

In the HPLC chromatograms of samples taken with DNPH absorbing solution the reagent peak at 3.0 min was absent (formaldehyde 3.85 min) and a large peak appears at 4.7 min. However with our sampling conditions, the excess of reagent present is more than a factor 10 at the 50 mg/m³ gas concentration level. When the reagent is added after absorption a large reagent peak remains. It is noted that the precipitate has a finer particle size when the reagent is added afterwards.

The bottom line of table 1 shows results where the reagent was added after absorption to avoid the cited effects. However no enhanced recovery is found. The breakthrough to the second absorber in these tests was 10 % since pure water is used as the absorbent. This is caused by the vapor pressure of formaldehyde over aqueous solutions and the same breakthrough ratio is found in tests with EPA 316 method. In DNPH solutions the breakthrough was only 1.2 to 2.2 % indicating that formaldehyde is removed from solution by a chemical reaction.

Table 1. Test results of DNPH method at emission level

Generated mg/Nm ³ dr	Measured mg/Nm ³ dr	Number of tests	Number of extractions	Recovery %	% of total in absorber 1
20.6	12.0	7	2	58.4 ± 5.8	97.8 ± 0.4
18.1 (*)	13.2	6	3-6	73.0 ± 4.5	98.8 ± 1.2
18.1 (**)	10.5	6	3	58.0 ± 5.8	89.6 ± 1.4

(*): tests where number of solvent extractions were increased

(**): tests with absorption in water and reagent added after sampling

The cause of incomplete detection of formaldehyde by the DNPH method therefore appears not to be in the absorption step, but in the chemical reaction. This was also demonstrated by the virtual absence of formaldehyde measured by FTIR and FID after the liquid absorption trains for both systems, when higher calibration gas concentrations were offered.

Pararosaniline method according to EPA 316

In this method gas and particulates are sampled isokinetically from the source and formaldehyde present in the emissions is collected in high purity water in a set of ice cooled impingers. Formaldehyde in the absorption liquid is analysed spectrophotometrically after reaction with acidic pararosaniline and sodium sulfite to a purple chromophore. As formaldehyde is analysed only in the gas phase, during the validation tests described here the probe and filter were omitted from the sampling train.

The range of the pararosaniline method can be adapted widely by changing the sampling parameters. EPA 316 specifies 11.3 ppbv to 23000 ppmv (0.015 – 31000 mg/Nm³) for 30 cu ft (0.85 m³) sample volumes. With our standard equipment for emission testing, a sampling time of 1 hour, a sample rate of 5 l/min and 100 ml of absorption liquid a detection limit of 0.01 mg/m³ and a quantification limit of 0.02 mg/m³ was derived from 6 samplings of pure nitrogen gas. All results were below the analytical detection limit of 0.04 mg/l in solution. A summary of further test results with the generated formaldehyde test gases at emission level is given in table 2. The concentration range tested corresponds to the legal validity requirement for an emission testing method between 0.1 and 3 times the emission limit value (ELV).

The trueness of the method is expressed as % recovery relative to the generation value, since there were small variations in the concentrations of the generated test gases.

Table 2. Characteristics of formaldehyde measurement by pararosaniline method

Generated mg/Nm ³	Number of tests	Measured mg/Nm ³	Recovery (%) (trueness)	Repeatability (% rsd*)
2.12 ± 0.03	7	2.21	104.2	2.4
21.0 ± 0.3	8	21.0	100.0	2.1
59.9 ± 5.2	6	59.7	99.8	4.9
18.1 ± 0.5 (**)	8	17.3	95.5	2.6

*rsd= relative standard deviation

(**) tests without ice bath

The deviation from the true value in all tests is less than 5 %. The repeatability is 2.4 to 2.1 % at the ELV level and 4.9 % at 3*ELV. For the tests at 60 mg/m³ level a few values with different concentrations were included, and the larger standard deviation on the generated value here is not indicative of the performance of the generator.

Breakthrough was tested at 20 mg/m³ and 60 mg/m³ level by separate analysis of impingers. The relative amount of formaldehyde detected in the first impinger was 88.6 ± 1.1 % and 88.9 ± 0.6 %. The average recovery of 11 % in the second impinger is relatively high and by extrapolation would suppose a 1 % loss by incomplete absorption.

The recovery of formaldehyde is still acceptable when no ice cooling of the absorption liquid is applied, however a decreased recovery of 95.5% could indicate a slight negative bias in this case.

Interferences

Interference by other compounds was tested in aqueous solutions at levels corresponding to an approximate equivalent of 5 and 20 mg/Nm³ of the interfering compound in the sampled gas. Fenol and methanol were tested at 10 times higher levels. In table 3 an overview of tested compounds and measured interference is given. Interference from other aldehydes remained below 2 % of the interferent measured as formaldehyde for all tested compounds. The only significant interference was detected from hexamethylene tetramine. However HMT is a solid copolymer of formaldehyde with ammonia that can release formaldehyde and is used for this purpose in industrial formulations. If present in sampling of emissions HMT will be retained on the filter.

Table 3. Interferents in formaldehyde analysis

Compound	% of compound responding as formaldehyde	
	level 5 mg/Nm ³	level 20 mg/Nm ³
Acetaldehyde	1.8	1.4
Acrolein	0.34	1.1
Glutaraldehyde	0.58	1.5
Furfural	0.7	0.05
Hexamethylene tetramine	38	-
Fenol	0.0	0.0
Methanol		0.03

Fourier Transform Infrared spectrometry for emissions of formaldehyde

EPA method 318 for extractive FTIR method defines the optimal spectral range for formaldehyde measurement between 2840.93 en 2679.83 cm⁻¹. Water and methane are spectral interferents. A Diamond-20 instrument from Analect with a Michelson interferometer and a heated gas cell with 10 m path length was used. In figure 1 a sample spectrum with 2.99 % water and 6.3 mg/Nm³ is shown, the same spectrum with subtracted water spectrum and a reference spectrum of 8.6 mg/Nm³ formaldehyde. The detection limit was determined at 3 mg/Nm³. For application with emission limits of 20 mg/Nm³ as in the press board

industry, a useful measuring range of 2 to 60 mg/Nm³ formaldehyde is required. Therefore and considering the problems to use the instrument in the field, the FTIR method is primarily useful to monitor short time variations of formaldehyde at higher concentration levels.

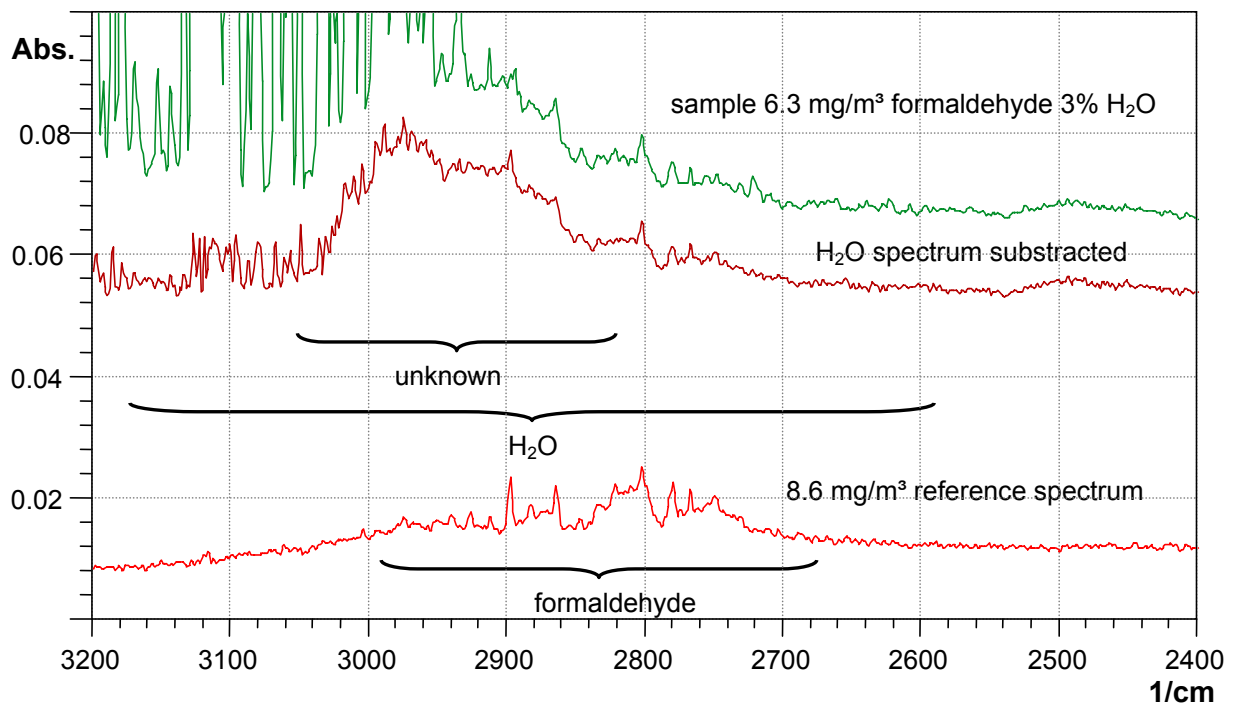


Figure 1. FTIR spectra of formaldehyde

Determination of diffuse emissions of formaldehyde

As formaldehyde is very volatile (normal boiling point -19 °C) diffuse emissions occur in processes where formaldehyde containing products are heated, such as in press board or mineral wool curing machines. These emissions pose a risk for exposure of workers, and generally monitoring is required to assure that the allowable concentrations in work place air, e.g. the 0.3 ppmv TLV-STEL (15 min) limit are not exceeded. The same types of personal monitoring devices that were developed for industrial hygiene measurement can be used in estimating diffuse emissions. The measurement strategy for diffuse emissions is decided primarily as a function of the construction of the ventilation system and the buildings. For a typical situation where emissions occur through slots in the roof or windows, the so called RMST or roof monitor sampling technique can be used. The total diffuse emission equals the sum of fluxes through all finite area elements of the emitting surfaces, as in ducted emissions. Ideally a large number of continuous concentration and flow measurement data would be available and integrated over time. In practice a larger uncertainty must be accepted and the measurement effort will be adapted to the expected relative importance of the diffuse emissions by following methods:

- time averaged formaldehyde concentrations in the air are determined from a set of diffusive samplers. For practical reasons the number of samplers is limited (e.g. 10 – 20) and the most representative sampling points are selected
- the volumetric flow of the diffuse emissions is measured by screening of the wind velocity through individual emitting surfaces with a hot wire anemometer or a large diameter turbine (e.g. 10 cm) anemometer with low starting speed. Alternative methods to estimate the volumetric flow of diffuse emissions are the use of tracer gases (CO₂, SF₆, He), or the estimation of ventilation rates (e.g. design values, energy balance)

The duration of the measurements is chosen to correspond with a known number of production cycles or a given product volume, so that an emission factor can be derived.

Radiello diffusive samplers for aldehydes were used for formaldehyde. The absorbent part of this sampler is a stainless steel mesh wire cylinder containing florisil impregnated with 2,4-DNPH placed at the centre of a cylindrical polyethylene diffusive body. The uptake rate for formaldehyde is approximately 100 ml/min. For an exposure time of 8 hours this results in a detection limit below 0.05 mg/m³, which is sufficient for the actual concentrations in the range from 0.1 to 2 mg/m³.

Conclusions

Method selection is critical for testing formaldehyde emission limit values in the press board and bonded fibre industry. The otherwise sensitive and versatile DNPH method as described in EPA Method 0011 was shown to be inadequate for emission testing due to incomplete recovery of formaldehyde. The average recovery of around 60 % of this method was demonstrated in the laboratory in real conditions has been the cause of false conclusions of compliance with the 20 mg/Nm³ standard in industrial plants. Failure of the method is most likely caused by side reactions in the absorbing solution as the absorption was demonstrated to be sufficient. It remains to be demonstrated whether other aldehydes have the same behavior as formaldehyde. Further research is needed to test if the DNPH can be validated at lower concentrations levels, e.g. by use of gas dilution systems during sampling, or by the use of solid adsorbents in order to eliminate losses by reactions in the liquid phase. Another conclusion of this work appeared to be that a high percentual recovery in the first absorber, like the 98 % of total recovered formaldehyde analysed here in the first DNPH solution, is not an absolute proof of the goodness of a method. For the analysis of lower formaldehyde concentrations as encountered in industrial atmospheres and in diffuse emissions, in earlier work the DNPH method was not showing any negative bias and had an overall uncertainty below 30 %. The most suitable method for determination of formaldehyde in emission gases is absorption in water and spectrophotometrical analysis with pararosaniline according to EPA Method 316. This method had acceptable accuracy and precision in the laboratory, and this was confirmed by consistent results from different labs on industrial plant emissions.

References

1. Extractive FTIR method for the measurement of emissions from the mineral wool and wool fiberglass industries, EPA Method 318, 1999
2. Sampling and Analysis of Formaldehyde Emissions from Stationary Sources in the Mineral Wool and Wool Fiberglass Industries, EPA Method 316, 1999
3. Sampling for selected aldehyde and ketone emissions from stationary sources, EPA Method 0111 Revision 0, 1996
4. Measurement of formaldehyde emissions from natural gas fired stationary sources – Acetyl acetone derivatization method, Conditional Test Method 37 (CTM-037), 2001
5. J. Frederic Walker. "Formaldehyde". 3rd Edition. Reinhold Publishing Corporation. New York 1967
6. E. Goelen, M. Lambrechts, F. Geyskens, Sampling Intercomparisons for Aldehydes in Simulated Workplace Air, Analyst 1997, Vol. 122 (411-419)