Title

A RECOMMENDATION FOR COMBINING THE STANDARD ANALYTICAL METHODS FOR THE DETERMINATIONS OF FORMALDEHYDE AND TOTAL ALDEHYDES IN AIR

Authors

Miksch, R.R.
Anthon, D.W.

Publication Date

1981-08-01

LBL-13194
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

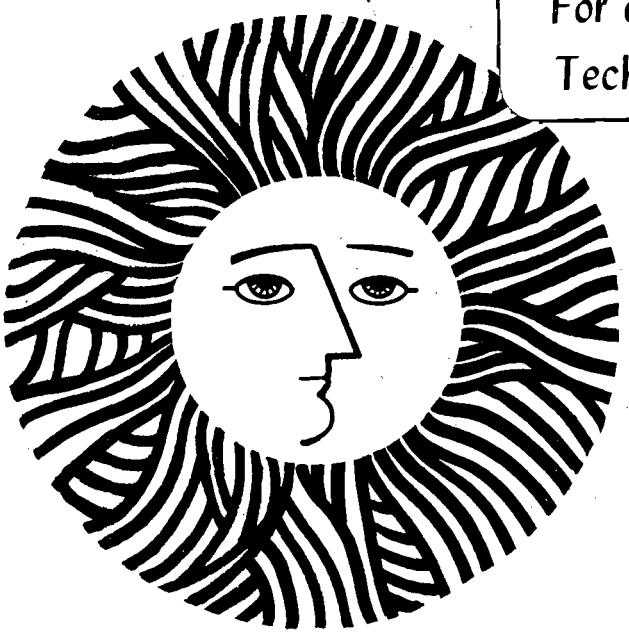
ENERGY & ENVIRONMENT
DIVISION

Submitted to the Journal of the American
Industrial Hygiene Association

A RECOMMENDATION FOR COMBINING THE STANDARD ANALYTICAL METHODS FOR THE DETERMINATIONS OF FORMALDEHYDE AND TOTAL ALDEHYDES IN AIR

R.R. Miksch and D.W. Anthon

August 1981



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

To be submitted to the
Journal of American
Industrial Hygiene Association

LBL-13194
EEB-Vent 81-33

A Recommendation for Combining the Standard Analytical Methods for the Determinations of Formaldehyde and Total Aldehydes in Air

R.R. Miksch and D.W. Anthon

Building Ventilation and Indoor Air Quality Program
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

August 1981

This work was supported by the Director, Office of Energy Research, Office of Health and Environmental Research, Human Health and Assessments Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

abstract

For determining formaldehyde, the Intersociety Committee of the American Public Health Association recommends a method using chromotropic acid (CA), and for determining total aliphatic aldehydes a method using 3-methyl-2-benzothiazolone hydrozone (MBTH). In field studies, the use of these separate methods involves performing many tasks in parallel and in duplicate. Inspection of the chemistry underlying the MBTH method suggested that the CA method might be successfully applied to MBTH-containing samples, provided that MBTH did not act as an interferent. We applied the recommended CA method to water and 0.05% MBTH impinger solutions from parallel sampling trains at six field sites, and found the mean formaldehyde levels to differ on the average by 5%. Having established that a single MBTH sample can yield both the formaldehyde and total aliphatic aldehyde contents of a sampled atmosphere we devised a combined method with improved techniques that streamlined laboratory analysis by maximizing procedural overlap.

A recommendation for combining the standard analytical methods for the determinations of formaldehyde and total aldehydes in air.

Robert R. Miksch, Ph.D. and Douglas W. Anthon

Building Ventilation and Indoor Air Quality Program, Energy and Environment Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

Keywords: chromotropic acid, MBTH, 3-methyl-2-benzothiazolone hydrazone

introduction

The Intersociety Committee of the American Public Health Association (APHA) recommends a Chromotropic Acid Method[1] for determining formaldehyde in air and a MBTH Colorimetric Method[2] for determining total aldehydes in air. Chromotropic acid (CA) reacts specifically with formaldehyde in concentrated sulfuric acid to form a chromophore, allowing formaldehyde solutions from 0.25 to 5 μg/mL to be quantified. MBTH (3-methyl-2-benzothiazolone hydrazone) reacts generally with aliphatic aldehydes and yields a chromophore after subsequent oxidation. Formaldehyde solutions from 0.03 to 0.7 μg/mL can be quantified by the MBTH method.

At the Lawrence Berkeley Laboratory we have been measuring formaldehyde and total aldehyde levels in energy-efficient residences and buildings as part of a program to determine the relationship between indoor air quality and the implementation of energy conservation strategies[3]. In following the recommended methods we found ourselves performing many tasks in parallel and in duplicate. By examining the reactions that occur in the MBTH method, we realized that the two methods could be partially merged and thereby streamline application of the APHA procedures. A combined method in which a single MBTH sample yields both the formaldehyde and total aldehyde contents of sampled air is described below.

standard methods for the determination of formaldehyde and total aldehydes in air

In brief the CA and MBTH procedures recommended by APHA for the determination of formaldehyde and total aldehydes in air are as follows:

1. CA: 20 mL of distilled water are placed in each of two all-glass samplers with coarse-fritted tube inlets in series.

   MBTH: 35 mL of 0.05% MBTH absorbing solution is placed in an all-glass sampler with a coarse-fritted tube inlet. The MBTH absorbing solution is prepared by dissolving 0.5 g of MBTH in distilled water, diluting to 1 L, and filtering by gravity if turbid.

2. CA: A measured volume of air is drawn through the sampler at a rate of 1 sLpm (standard liter per minute) for 24 h, or a shorter time appropriate to the estimated formaldehyde concentration.

   MBTH: A measured volume of air is drawn through the sampler at a rate of 0.5 sLpm for 24 h, or a shorter time appropriate to the estimated total aldehyde concentration.

3. CA: The sampling solution is transferred to a 50 mL graduate and the volume is noted.

   MBTH: The sampling solution is transferred to a 50 mL graduate, diluted to 35 mL with distilled water, and allowed to stand for 1 h.

4. CA: A 4 mL aliquot of the sampling solution is transferred to a glass-stoppered test tube and 0.1 mL of 1% chromotropic acid reagent is added.

   MBTH: A 10 mL aliquot of the diluted sampling solution is transferred to a glass-stoppered test tube. A blank containing 10 mL of MBTH solution is also run.

5. CA: 6 mL of concentrated sulfuric acid is pipetted slowly and cautiously to the solution (with evolution of heat) with mixing.

   MBTH: 2 mL of oxidizing reagent is added to the solution. The oxidizing reagent is prepared by dissolving 1.6 g of sulfamic acid and 1.0 g of ferric chloride in distilled water and diluting to 100 mL.

6. CA: After cooling to room temperature, the absorbance is read at 580 nm using a 1 cm cell.

   MBTH: After standing for at least 12 min, the absorbance is read at 628 nm using a 1 cm cell.

7. CA: The sample is compared against a calibration line prepared from standardized formaldehyde solutions covering the range 0.25 to 5 μg/mL. Standardization is accomplished by iodimetric titration.

   MBTH: The sample is compared against a calibration line prepared from standardized formaldehyde solutions diluted with 0.05% MBTH solution to cover the range 0.03 to 0.7 μg/mL. Standardization is accomplished by iodimetric titration.

8. CA: The concentration of formaldehyde in the sampled atmosphere is calculated using the following equation, assuming standard conditions are taken as 760 Torr and 25 °C.

$$\text{ppm (volume)} = \frac{C \times A \times 24.47}{V \times M.W.}$$

where

V = liters of air sampled.

C = µg of formaldehyde in aliquot.

A = aliquot factor (sampling solution volume/aliquot volume).

M.W. = molecular weight of formaldehyde (30.03).

24.47 = mL of formaldehyde gas in one millimole at 760 Torr and 25 °C.

No correction factor is included for the collection efficiency of two samplers in series which is reported to be approximately 95%.

MBTH: The concentration of total aliphatic aldehyde, expressed as equivalents of formaldehyde, in the sampled amosphere is calculated using the following equation.

$$\text{ppm (volume)} = \frac{C \times 35 \times 24.45}{V \times M.W. \times E}$$

M.W., 24.45 = same as above.

C = µg/mL of formaldehyde in sampling solution. (Since each sample is diluted to 35 mL, this figure must be multiplied by 35 to give the total micrograms in sampling solution.)

E = correction factor for collection efficiency (0.84 is used for a single sampler with coarse-fritted tube inlet).

discussion

Use of these two methods in our field studies required the use of two bubbler sampling trains at each location, one bubbler containing distilled water and the other 0.05% MBTH absorbing solution. During subsequent laboratory analysis, some operations overlapped (e.g., standardization of a stock formaldehyde solution) but, in general, the two methods were conducted independently.

The difference between the field samples generated by these two methods is that the MBTH sample contains 0.05% MBTH. Inspection of the MBTH-formaldehyde adduct present in the MBTH sample[4] shows that it could revert to starting materials under the harsh acidic conditions of the CA method. If the formaldehyde is indeed recovered then the CA method should proceed normally provided the MBTH is not an interferent.

We began applying the APHA-recommended CA method to MBTH containing field samples. Indoor air was sampled at six field sites using refrigerated bubbler sampler trains. A sample inlet of teflon tubing was teed immediately ahead of two trains, one containing distilled water and the other containing 0.05% MBTH absorbing solution. The MBTH sample was analyzed using both the APHA-recommended methods, and the results were compared with the analysis by CA of the distilled water sample.

The results of the two CA analyses compare very favorably, as shown in Table I. If the data from the Medford 2 pre-retrofit site is deleted, the differences between the mean equivalents of formaldehyde determined average 5%. This precision is comparable to that of the laboratory analysis, and is certainly better than that of the individual mean determinations, which are primarily defined by environmental fluctuations.[3,5] The total aliphatic aldehyde levels determined by the MBTH method are greater in every case than the formaldehyde levels determined with CA showing that, indeed, other aldehydes are present, though formaldehyde is the major constituent.

Having established the ability of a single MBTH sample to yield both the formaldehyde and the total aliphatic aldehyde content of an air sample we devised a single method of analysis combining the features of the APHA recommended CA and MBTH methods. Attention was given to minimizing the number of solutions to be prepared, maintaining cognizance of the difference in sensitivity between CA and MBTH, and incorporating other improvements. Calibration lines prepared according to the combined procedure described below are identical within experimental error to lines prepared previously according to the APHA recommended method,[3] as shown in Table II.

A recommendation for a combined chromotropic acid and 3-methyl-2-benzothiazolone hydrazone method for determining formaldehyde and total aliphatic aldehydes in air

The procedural steps involved in our combined method are as follows:

1. A measured volume of air is drawn through a bubbler sampling train at a rate of 1 sLpm for 24 h, or a shorter time appropriate to the sensitivity of the CA method and the estimated formaldehyde concentration. The bubbler sampling train consists of two bubblers placed in series, each containing 20 mL of 0.05% MBTH absorbing solution.

2. The sample is diluted to a volume of 50 mL using 0.05% MBTH solution. A 5 mL aliquot is further diluted with 20 mL of 0.05% MBTH solution in a 50 mL beaker. A blank containing 25 mL of MBTH solution is also run. The solutions are allowed to stand for 1 hr.

3. CA: A 4 mL aliquot of the diluted to volume sampling solution is transferred to a test tube and 0.1 mL of 1% chromotropic acid reagent is added, followed cautiously by 6 mL of concentrated sulfuric acid and vortex mixing.

   MBTH: 5 mL of oxidizing reagent is pipetted into the 50 mL beaker containing the further diluted sample. The oxidizing reagent is prepared by dissolving 1.6 g of sulfamic acid and 1.0 g of ferric chloride in distilled water, and diluting to 100 mL.

6. CA: After cooling to room temperature, the absorbance is read at 580 nm using a 1 cm cell.

   MBTH: After standing for at least 12 min the absorbance is read

at 628 nm using a 1 cm cell.

7. The absorbances are compared against calibration lines prepared as follows:

   a. A stock solution of approximately 4 mg/mL formaldehyde is prepared by refluxing paraformaldehyde and standardizing the resultant solution using a sulfite-pH titration technique.(3)

   b. One mL of the stock solution is diluted to 250 mL in a volumetric flask.

   c. In 100 mL volumetric flasks are placed 0, 0.5, 1.0, 2.0, 3.0, 5.0, 15.0 and 25.0 mL of the diluted stock solution. The flasks are filled to the mark with 0.05% MBTH solution and allowed to stand for 1 h.

   d. CA: 4 mL aliquots of the flasks containing 0, 2.0, 5.0, 15.0, and 25.0 mL of the diluted stock solution are analyzed in the same manner as the field samples.
   MBTH: 25 mL aliquots of the flasks containing 0, 0.5, 1.0, 2.0 and 3.0 mL of the diluted stock solution are analyzed in the same manner as the field samples.

8. The concentrations of formaldehyde and total aliphatic aldehydes (as equivalents of formaldehyde) in the sampled atmosphere are calculated using the following equation, assuming standard conditions to be 760 Torr and 25 °C.

$$\text{ppm (volume)} = \frac{C \times A \times 24.46}{V \times 30.06 \times 0.95}$$

where

V = liters of air sampled.

C = μg/mL of formaldehyde in MBTH or CA sampling solution.

A = effective sampling solution volume, equal to 50 mL for CA and 250 mL for MBTH.

30.03 = molecular weight of formaldehyde.

24.46 = mL of formaldehyde gas in one millimole at 760 Torr and 25 °C.

0.95 = correction factor for collection efficiency of two bubblers in series.

The advantages of this combined method are:

1. Because only a single sampling train is required to determine the formaldehyde and total aliphatic aldehyde contents in the sampled atmosphere, efficiency and is increased the costs of field measurements are reduced.
2. By maximizing the overlap of procedures and incorporating improved techniques, subsequent laboratory analysis is simplified and streamlined.

Acknowledgement

The assistance of Leah Fanning, Nils Peterson and Linda Jencks is gratefully acknowledged.

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Energy Research and Development, Building Systems Division of the U.S. Department of Energy under contract no. W-7405-ENG-48.

references

1. Tentative Method of Analysis for Formaldehyde Content of the Atmosphere (Colorimetric Method). Method 116: p. 303 in Methods of Air Sampling and Analysis. APHA Intersociety Committee, Second Edition, edited by Morris Katz, American Public Health Association, Washington, DC 20036 (1977).

2. Tentative Method of Analysis for Formaldehyde Content of the Atmosphere (MBTH-Colorimetric Method-Application to Other Aldehydes). Method 117: p. 308, Ibid.

3. Miksch, R.R., D.W. Anthon, L.Z. Fanning, C.D. Hollowell, K. Revzan and J. Glanville: Modified Pararosaniline Method for the Determination of Formaldehyde in Air, Anal. Chem., in press (1981).

4. Sawicki, E., T.R. Hauser, T.W. Stanley and W. Elbert: The 3-Methyl-2-Benzothiazolone Hydrazone Test. Anal. Chem. 37:679 (1961).

5. Leidel, N.A., K.A. Bush, and J.R. Lynch: NIOSH Occupational Exposure Sampling Strategy Manual, U.S. Department of Health, Education and Welfare, USDHEW (NIOSH) Publication No. 77-173, U.S. Government Printing Office, Washington, DC (1977).

TABLE I

Formaldehyde and Total Aliphatic Aldehyde Levels Measured in Indoor Air at Residential Field Sites[a]

Site	Number of Measurements	Mean Equivalents of Formaldehyde, ppb[b]		
		Chromotropic Acid Method	MBTH Sample Analyzed by Chromotropic Acid Method	MBTH Total Aldehydes Method
Cranbury, NJ	15	19.3 ± 5.1	20.2 ± 5.5	29.1 ± 9.5
Wild River,	20	91.8 ± 14.2	97.4 ± 14.6	158.0 ± 59.0
Medford 1, OR Pre-Retrofit	13	53.2 ± 9.2	52.5 ± 10.8	84.5 ± 11.7
Medford 1, OR Post-Retrofit	12	52.5 ± 5.0	57.2 ± 4.4	84.9 ± 7.4
Medford 2, OR Pre-Retrofit	11	61.9 ± 13.5	48.5 ± 11.8	94.1 ± 15.8
Medford 2, OR Post-Retrofit	13	54.1 ± 11.5	57.2 ± 8.2	70.6 ± 11.7

[a]Air was sampled for 24 hour periods using refrigerated bubbler sampling trains. A sample inlet of teflon tubing was teed immediately ahead of two trains, one containing distilled water (for chromotropic acid) and one containing 0.05% MBTH absorbing solution.

[b]Errors expressed as relative standard deviation from the mean. Outdoor levels determined simultaneously were all less than 10 ppb.

TABLE II
Reproducibility of Chromotropic Acid, MBTH/Chromotropic Acid and MBTH Methods for Formaldehyde Determination

	Number of Calibration Lines	Calibration Line			
		Slope $AUmL\mu g^{-1}$	Intercept AU	Blank AU	R
Chromotropic Acid[a]	7	0.233 ± 0.006	0.051 ± 0.007	0.030 ± 0.004	0.9990
MBTH/Chromotropic Acid[b]	8	0.230 ± 0.005	0.047 ± 0.009	0.038 ± 0.006	0.9993
MBTH	8	1.49 ± 0.03	0.074 ± 0.011	0.072 ± 0.009	0.9997

[a]Data taken from Miksch et al(3)

[b]Formaldehyde standards containing MBTH analyzed by chromotropic acid according to the combined procedure described in the text.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720