

DFG Deutsche Forschungsgemeinschaft

Analyses of Hazardous Substances in Air

Volume 8

 **WILEY-VCH**

DFG Deutsche Forschungsgemeinschaft

Analyses of Hazardous Substances in Air

Volume 8

edited by Antonius Kettrup
Working Group Analytical Chemistry

江苏工业学院图书馆
藏书章

Commission for the Investigation of Health
Hazards of Chemical Compounds in the
Work Area
(Chairman: Helmut Greim)



WILEY-VCH GmbH & Co. KGaA

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Deutsche Bibliothek Cataloguing-in-Publication Data:

Analyses of hazardous substances in air / DFG, Dt. Forschungsgemeinschaft; Comm. for the Investigation of Health Hazards of Chem. Compounds in the Work Area. – Weinheim; New York; Chichester; Brisbane; Singapore; Toronto: Wiley-VCH

Erscheint unregelmäßig. – Aufnahme nach Vol. 1 (1991)

Vol. 1 (1991) –

ISBN 3-527-27793-5

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Composition: ProSatz Unger, Weinheim

Printing: betz-druck gmbh, Darmstadt

Bookbinding: Litges & Dopf Buchbinderei GmbH, Heppenheim

Printed in the Federal Republic of Germany.



Analyses of Hazardous
Substances in Air

Preface

In response to the worldwide demand for methods for the determination of hazardous compounds in the air of work areas, the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area of the Deutsche Forschungsgemeinschaft (DFG) is publishing contemporaneously with the German edition “Analytische Methoden zur Prüfung gesundheitsschädlicher Arbeitsstoffe“, the English international series “Analyses of Hazardous Substances in Air”. Since the beginning of the nineties, when the first volume appeared, seven other volumes have been published until the beginning of the year 2003.

The structure of this new volume – Volume 8 of “Analyses of Hazardous Substances in Air” – is similar to that of the other volumes in this series and it comprises sixteen new analytical methods for determining hazardous compounds in the air of work areas. In this publication new methods for the determination in air of acetamide, alkali metal hydroxides and alkaline earth hydroxides, alkanolamines, atrazin, lacquer aerosols (three methods), PAH (two methods), PCB, etc. are described. Additionally, the method for the determination of benzotriazoles represents an important contribution for monitoring the air of work areas during the exposure to cooling lubricants.

Each chapter includes a short evaluation of the method, a brief listing of the reliability criteria and general information on the chemical compound to be tested, i.e. its industrial importance, toxicity and its limit value at the workplace. This is followed by a detailed description of the preparatory and analytical steps, discussion of the reliability and a reference list.

It is a satisfaction for me, as chairman of the Deutsche Forschungsgemeinschaft’s Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, to ascertain the progress that we have made to our goal concerning the protection of workers against risks from chemical agents in work areas.

For this reason I would like to express my gratitude to Professor A. Kettrup, who has headed the Working Subgroup “Analyses of Hazardous Substances in Air of Work Area” of the “Analytical Chemistry” Working Group for many years, for his successful work. Similarly, I wish to acknowledge the contribution made by the authors and examiners of these methods, as well as the accurate work of the translators of this volume. Particular thanks goes to the secretariat of the commission – Dr. M.R. Lahaniatis and Dr. R. Schwabe – for their successful work and great personal engagement.

H. Greim
Chairman of the Commission for the
Investigation of Health Hazards of Chemical
Compounds in the Work Area

Foreword

We are pleased to present the eighth volume in the series “Analyses of Hazardous Substances in Air”, which contains sixteen new analytical methods suitable for routine use by quantitative determination of hazardous compounds in the air of work areas. Research and development of such methods is a long-term objective of the Working Subgroup “Analyses of Hazardous Substances in Air of Work Areas” in line with the objectives of the Working Group “Analytical Chemistry” of the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area of the Deutsche Forschungsgemeinschaft (DFG).

The methods chosen for publication in this volume, which is the result of in-depth work carried out by the experts of the Working Subgroup “Analyses of Hazardous Substances in Air of Work Areas”, have been tested and confirmed by at least one examiner regarding their reliability and reproducibility.

It is important to highlight the fact that this volume contains three methods for the determination of lacquer aerosols in the workplace area. In these procedures the main emphasis is on the simultaneous sampling of the particles and free solvent vapour together with that released during drying. Furthermore, two other important methods for the determination of polycyclic aromatic hydrocarbons (PAH) are also included in this volume. Three PAH compounds which are among the PAH with high carcinogenic potential – benzo[a]pyrene, dibenz[ah]anthracene and benzo[ghi]perylene – can be determined by using the methods described here. Additionally, the method “Alkali metal hydroxides and alkaline earth hydroxides” permits the determination of sodium hydroxide and calcium hydroxide, when present as particles in a concentration range of 0.1 to 2 times the actual valid threshold limit values, and of lithium hydroxide and potassium hydroxide in the same concentration range. The method for determining the pentachlorophenol and lindane concentrations bound to particles, and at the same time those not deposited on the filter, first appeared in June 2000 as guideline VDI 4301 Part 2. It contains instructions for measuring the concentrations of these substances in the air inside buildings.

Without going into details, besides the sixteen analytical methods, this volume comprises a list of the members and guests of the Working Subgroup, as well as a list of compounds (according to their CAS number) for which analytical methods can be found in the series “Analyses of Hazardous Substances in Air”.

We would like to thank the members and guests of the Working Subgroup, without whose voluntary services this collection of methods would not have been possible. We thank the Deutsche Forschungsgemeinschaft for financial and organisational help in the development of our activities.

Our thanks are also extended our publishers and Dr. Eva E. Wille of the Wiley-VCH Verlag, with whom we have enjoyed long-standing and efficient collaboration. We also wish to thank Mrs. Handwerker-Sharman for translation.

J. Angerer
Chairman of the Working Group
“Analytical Chemistry” of the
Commission for the Investigation
of Health Hazards of Chemical
Compounds in the Work Area

A. Kettrup
Chairman of the Working Subgroup
“Analyses of Hazardous Substances in Air
of Work Areas”

Working Group “Analytical Chemistry” of the Commission of the Deutsche Forschungsgemeinschaft for the Investigation of Health Hazards of Chemical Compounds in the Work Area

Organization

The Working Group “Analytical Chemistry” was established in 1969. Under the chairmanship of Prof. Dr. J. Angerer at the present it includes two Working Subgroups:

“Air Analyses”

(Leader: Prof. Dr. A. Kettrup)

“Analyses of Hazardous Substances in Biological Materials”

(Leaders: Prof. Dr. J. Angerer and Chem.-Ing. K. H. Schaller).

The participants, who have been invited to collaborate on a Working Subgroup by the leaders, are experts in the field of technical and medical protection against chemical hazards at the workplace.

A list of members and guests of “Analyses of Hazardous Substances in Air” is given at the end of this volume.

Objectives and operational procedure

The two analytical subgroups are charged with the task of preparing methods for the determination of hazardous industrial materials in the air of the workplace or to determine these hazardous materials or their metabolic products in biological specimens from the persons working there. Within the framework of the existing laws and regulations, these analytical methods are useful for ambient monitoring at the workplace and biological monitoring of the exposed persons.

In addition to the working out the analytical procedure, these subgroups are concerned with the problems of the preanalytical phase (specimen collection, storage, transport), the statistical quality control, as well as the interpretation of the results.

Development, examination, release, and quality of the analytical methods

In its selection of suitable analytical methods, the Working Group is guided mainly by the relevant scientific literature and the expertise of the members and guests of the Working Subgroup. If appropriate analytical methods are not available they are worked out within the Working Group. The leader designates an author, who assumes the task of developing and formulating a method proposal. The proposal is examined experimentally by at least one other member of the project, who then submits a written report of the results of the examination. As a matter of principle the examination must encompass all phases of the proposed analytical procedure. The examined method is then laid before the members of the subgroups for consideration. After hearing the judgement of

the author and the examiner they can approve the method. The method can then be released for publication after a final meeting of the leader of the Working Group "Analytical Chemistry" with the subgroup leaders, authors, and examiners of the method.

Under special circumstances an examined method can be released for publication by the leader of the Working Group after consultation with the subgroup leaders.

Only methods for which criteria of analytical reliability can be explicitly assigned are released for publication. The values for inaccuracy, imprecision, detection limits, sensitivity, and specificity must fulfil the requirements of statistical quality control as well as the specific standards set by occupational health. The above procedure is meant to guarantee that only reliably functioning methods are published, which are not only reproducible within the framework of the given reliability criteria in different laboratories, but also can be monitored over the course of time.

In the selection and development of a method for determining a particular substance the Working Group has given the analytical reliability of the method precedence over aspects of simplicity and economy.

Publications of the working group

Methods released by the Working Group are published in the Federal Republic of Germany, by the Deutsche Forschungsgemeinschaft as a loose-leaf collection entitled "Analytische Methoden zur Prüfung gesundheitsschädlicher Arbeitsstoffe" (WILEY-VCH Verlag, Weinheim, FRG).

The collection at present consists of two volumes:

Volume I "Luftanalysen"

Volume II "Analysen in biologischem Material".

These methods are also to be published in an English edition. Volume 1 to 7 of "Analyses of Hazardous Substances in Biological Materials" have already been published. The work at hand represents the eighth English issue of "Analyses of Hazardous Substances in Air".

Withdrawal of methods

An analytical method that is made obsolete by new developments or discoveries in the fields of instrumental analysis or occupational health and toxicology can be replaced by a more efficient method. After consultation with the membership of the relevant project and with the consent of the leader of the Working Group, the subgroup leader is empowered to withdraw the old method.

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Analytical Methods

Acetamide

Method number	1
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	May 1998

Summary

The method described permits the determination of acetamide in the workplace air using personal air sampling or static sampling [1, 2]. It is quick and simple to perform. Measured air volumes are drawn through activated carbon sampling tubes. Acetamide is desorbed with methanol and quantitatively determined with an NP detector after gas chromatographic separation and external calibration.

Concentration range: 0.002–0.2 mg/m³ acetamide in air

Precision:

Table 1. Standard deviation (relative) s and mean variation u , at a concentration of 20.6 µg acetamide per m³ air and $n = 7$ determinations.

Temperature °C	Humidity (relative) %	Standard deviation (relative) s %	Mean variation u %
22	30	1.4	3.4
35	80	2.4	5.9

Limit of quantification: 2 µg acetamide per m³ air with a sampled air volume of 500 L

Recovery: $\eta = 102\%$ at 22 °C and 30% relative humidity
 $\eta = 98\%$ at 35 °C and 80% relative humidity
 at a concentration of 20.6 µg acetamide per m³ air

Sampling recommendation: Sampling time: 8 hours
 Sampled air volume: 500 L

Acetamide [CAS No. 60–35-5]

Acetamide is a colourless, crystalline substance (molecular weight 59.07, melting point: 82.3 °C, boiling point: 221.2 °C at 1013 hPa, density: 1.1590 g/mL at 20 °C, dipole moment: $12.4 \cdot 10^{-30}$ Cm, dissociation constant: $3.2 \cdot 10^{-11}$), which hydrolyses readily in the presence of acids and bases. The aqueous solution has amphoteric character. Acetamide dissolves readily in ethanol, water, chloroform and glycerol, it is barely soluble in ether. Melted acetamide serves as solvent for numerous organic and inorganic compounds. Another area of use is as solubilizer for substances barely soluble in water.

Acetamide is classed in carcinogen category 3B in the List of MAK and BAT Values [1].

Authors: *S. Herramhof, H. Malissa*

Examiner: *M. Hennig*

Acetamide

Method number	1
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	May 1998

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1 General principles

With a pump, measured air volumes are drawn through an adsorption tube filled with activated carbon [2–4]. The acetamide collected is desorbed with methanol and determined after capillary gas chromatography with an NP detector [5–10]. Quantitative evaluation is carried out by means of external calibration.

2 Equipment, chemicals and solutions

2.1 Equipment

Battery-operated pump for personal air sampling, e.g. Dräger, Accuro Constant, No. 6400380

Adsorption tube filled with activated carbon, e.g. type NIOSH, adsorption agent: coconut carbon, adsorption phase: 100 mg, break-through section: 50 mg, length: 70 mm, internal diameter: 4.2 mm (e.g. Dräger, Order No. 6728631)

Laboratory centrifuge, at least 5000 rpm

1 mL, 10 mL and 100 mL Volumetric flasks

5 mL Bulb pipette, class AS, ± 0.015 mL

10 mL Bulb pipette, class AS, ± 0.02 mL

250 μ L Microlitre syringe

5 μ L GC Injection syringe

Semimicro balance

Magnetic stirrer

PTFE magnetic stirring rod (about 12 mm \times 4.5 mm)

Aluminium weighing boat

Soap bubble meter

Disposable filters made of PTFE reinforced with polypropylene, 0.45 μ m pore size

2.2 Chemicals

Methanol, analytical grade

Acetamide, analytical grade (e.g. from Merck, Darmstadt)

Helium, purity: 99,999%

Hydrogen, purity: 99,999%

Nitrogen, purity: 99,999%

Synthetic air, purity: 99,999%

Helium, purity: 99,996%

2.3 Calibration standards

Acetamide concentrate solution:

100 mg acetamide ($\pm 5\%$) is weighed exactly to ± 0.1 mg into a weighing boat, transferred to a 10 mL volumetric flask and the flask is filled to the mark with methanol. The solution contains 10 mg acetamide/mL and can be stored at a temperature of $+4^\circ\text{C}$ for at least 4 months.

Acetamide stock solution:

With a microlitre syringe, 100 μL is transferred to a 100 mL volumetric flask and the flask is filled to the mark with methanol. The solution contains 10 μg acetamide/mL and must be freshly prepared for each analytical series.

Acetamide calibration solution:

The calibration solutions are prepared by diluting the stock solution with methanol according to the following pipetting scheme:

Table 2. Preparation of the calibration solutions for determining the working range.

Volume of the stock solution mL	Final volume of the calibration solution mL	Concentration of the calibration solution $\mu\text{g/L}$
0.10	10.00	0.10
0.50	10.00	0.50
1.00	10.00	1.00
5.00	10.00	5.00

The exact concentrations of the calibration solutions, and the number of significant figures, depend on the exact amount weighed and the precision of the volume measuring equipment used.

3 Sample collection

To adjust for the flow resistance of the adsorbent during calibration, first of all an adsorption tube is attached to the inlet of the pump. The flow rate is adjusted to 1050 mL/min (± 63 L/h) using a soap bubble meter. With an internal diameter of the sampling tube of exactly 4.2 mm this results in a linear flow rate of 1.25 m/s. Strict observance of this flow rate guarantees that the particulate components are collected as the inhalable fraction [11, 12].

For personal air sampling, a sampling tube is opened at both ends by cutting the ends with a glass cutter and breaking them off. On the inlet side the whole of the lumen must be opened. The pump is connected at the inlet to the sampling tube with a piece of tubing about 20–30 cm long and attached to the person in such a way that the tube is