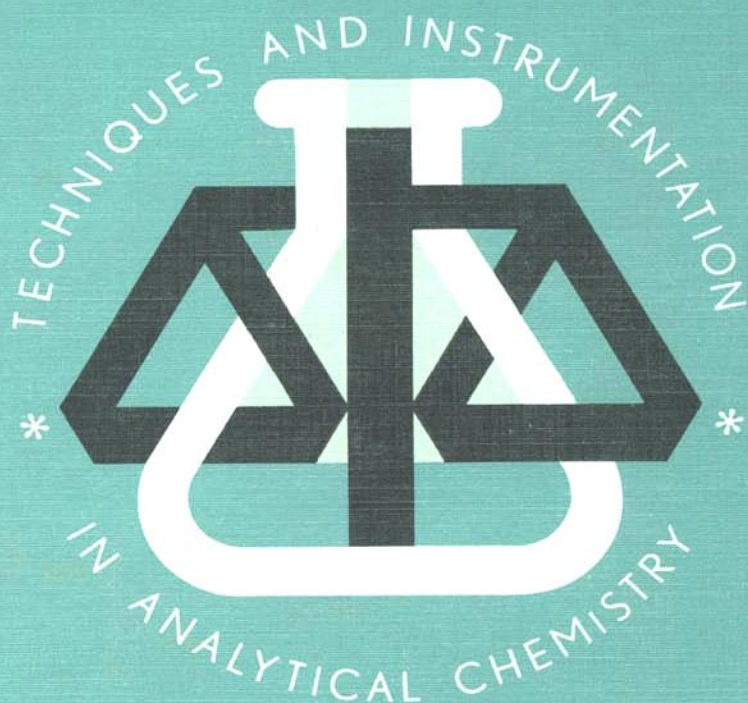


1



# **EVALUATION AND OPTIMIZATION OF LABORATORY METHODS AND ANALYTICAL PROCEDURES**

A Survey of Statistical and Mathematical Techniques

**D.L. Massart, A. Dijkstra and L. Kaufman**

with contributions by S. Wold, B. Vandeginste and Y. Michotte

**ELSEVIER SCIENTIFIC PUBLISHING COMPANY**

**TECHNIQUES AND INSTRUMENTATION IN ANALYTICAL CHEMISTRY – VOLUME 13**

# **ENVIRONMENTAL ANALYSIS**

**TECHNIQUES, APPLICATIONS AND  
QUALITY ASSURANCE**

## **TECHNIQUES AND INSTRUMENTATION IN ANALYTICAL CHEMISTRY**

- Volume 1 **Evaluation and Optimization of Laboratory Methods and Analytical Procedures. A Survey of Statistical and Mathematical Techniques**  
by D.L. Massart, A. Dijkstra and L. Kaufman
- Volume 2 **Handbook of Laboratory Distillation**  
by E. Krell
- Volume 3 **Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials. Compendium and Atlas**  
by H.L.C. Meuzelaar, J. Haverkamp and F.D. Hileman
- Volume 4 **Evaluation of Analytical Methods in Biological Systems**  
**Part A. Analysis of Biogenic Amines**  
edited by G.B. Baker and R.T. Coutts  
**Part B. Hazardous Metals in Human Toxicology**  
edited by A. Vercruysse  
**Part C. Determination of Beta-Blockers in Biological Material**  
edited by V. Marko
- Volume 5 **Atomic Absorption Spectrometry**  
edited by J.E. Cantle
- Volume 6 **Analysis of Neuropeptides by Liquid Chromatography and Mass Spectrometry**  
by D.M. Desiderio
- Volume 7 **Electroanalysis. Theory and Applications in Aqueous and Non-Aqueous Media and in Automated Chemical Control**  
by E.A.M.F. Dahmen
- Volume 8 **Nuclear Analytical Techniques in Medicine**  
edited by R. Cesareo
- Volume 9 **Automatic Methods of Analysis**  
by M. Valcárcel and M.D. Luque de Castro
- Volume10 **Flow Injection Analysis – A Practical Guide**  
by B. Karlberg and G.E. Pacey
- Volume11 **Biosensors**  
by F. Scheller and F. Schubert
- Volume12 **Hazardous Metals in the Environment**  
edited by M. Stoepler
- Volume13 **Environmental Analysis. Techniques, Applications and Quality Assurance**  
edited by D. Barceló

TECHNIQUES AND INSTRUMENTATION IN ANALYTICAL CHEMISTRY – VOLUME 13

# ENVIRONMENTAL ANALYSIS

TECHNIQUES,  
APPLICATIONS AND  
QUALITY ASSURANCE

Edited by

**D. Barceló**

*Department of Environmental Chemistry, C.I.D. (C.S.I.C.), Jordi Girona, 18-26,  
08034 Barcelona, Spain*



**ELSEVIER**

**Amsterdam — London — New York — Tokyo 1993**

ELSEVIER SCIENCE PUBLISHERS B.V.  
Sara Burgerhartstraat 25  
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

First printing 1993  
Second impression 1996

Library of Congress Cataloging-in-Publication Data

Environmental analysis: techniques, applications and quality assurance / edited by Damià Barceló.  
p. cm. -- (Techniques and instrumentation in analytical chemistry; vol. 13)  
Includes bibliographical references and index.  
ISBN 0-444-89648-1  
1. Environmental protection. 2. Environmental chemistry.  
3. Organic water pollutants--Analysis. I. Barceló, Damià.  
II. Series: Techniques and instrumentation in analytical chemistry: v. 13  
TD193.E54 1993  
628.5--dc20

93-28296  
CIP

ISBN: 0-444-89648-1

© 1993 Elsevier Science Publishers B.V. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the written permission of the Publisher, Elsevier Science Publishers B.V., Copyright and Permissions Department, P.O. Box 521, 1000 AM Amsterdam, The Netherlands.

Special regulations for readers in the USA. - This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the USA. All other copyright questions, including photocopying outside of the USA, should be referred to the publisher.

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

This book is printed on acid-free paper.

# CONTENTS

## Preface

<i>by D. Barceló</i> .....	xi
----------------------------	----

## FIELD SAMPLING TECHNIQUES AND SAMPLE PREPARATION

### CHAPTER 1. SAMPLING TECHNIQUES FOR AIR POLLUTANTS

*by R. Niessner*

1.1. Introduction.....	3
1.2. Sampling without suction, with deposition.....	4
1.3. Sampling with suction, without deposition.....	6
1.4. Sampling with suction, with deposition.....	13
1.5. Conclusion.....	17
References.....	18

### CHAPTER 2. SAMPLE HANDLING STRATEGIES FOR THE ANALYSIS OF ORGANIC COMPOUNDS FROM ENVIRONMENTAL WATER SAMPLES

*by M.-C. Hennion and P. Scribe*

2.1. Introduction.....	24
2.2. Sample handling of non-volatile organic compounds.....	26
2.3. Sample handling of volatile organic compounds.....	63
2.4. Conclusion and further developments.....	71
References.....	72

### CHAPTER 3. EXTRACTION, CLEAN-UP AND RECOVERIES OF PERSISTENT TRACE ORGANIC CONTAMINANTS FROM SEDIMENT AND BIOTA SAMPLES

*by D.E. Wells*

3.1. Introduction.....	80
3.2. Recovery.....	81
3.3. Pre-extraction treatment.....	83
3.4. Extraction.....	85
3.5. Comparative extraction studies.....	90

3.6. Clean-up.....	95
3.7. Automation .....	100
3.8. Multi-residue schemes .....	104
3.9. Direct methods .....	105
References .....	105

## APPLICATION AREAS

### CHAPTER 4. CURRENT DEVELOPMENTS IN THE ANALYSIS OF POLYCHLORINATED BIPHENYLS (PCBS) INCLUDING PLANAR AND OTHER TOXIC METABOLITES IN ENVIRONMENTAL MATRICES

*by D.E. Wells*

4.1. Introduction.....	113
4.2. Sources of error .....	114
4.3. Compound selection.....	114
4.4. Detection .....	118
4.5. Interpretation.....	119
4.6. Chromatographic separation .....	126
4.7. Group separation .....	129
4.8. Clean-up.....	135
4.9. Extraction .....	141
4.10. Chlorobiphenyl metabolites .....	141
Acknowledgements.....	145
References .....	145

### CHAPTER 5. OFFICIAL METHODS OF ANALYSIS OF PRIORITY PESTICIDES IN WATER USING GAS CHROMATOGRAPHIC TECHNIQUES

*by D. Barceló*

5.1. Priority lists of pesticides.....	149
5.2. General considerations about analytical methods.....	159
5.3. EPA methods of analysis.....	160
5.4. SCA methods of analysis .....	169
5.5. Other GC methods.....	175
5.6. Conclusions.....	178
References .....	178

### CHAPTER 6. COUPLED-COLUMN REVERSED PHASE LIQUID CHROMATOGRAPHY AS A VERSATILE TECHNIQUE FOR THE DETERMINATION OF POLAR PESTICIDES

*by E.A. Hogendoorn and P. van Zoonen*

6.1. Introduction to pesticide residue analysis .....	181
6.2. Coupled chromatographic techniques .....	185

6.3. Column-switching rplc in pesticide residue analysis.....	192
6.5. Recent developments in coupled-column RPLC.....	204
6.6. Conclusion and trends.....	217
Acknowledgement .....	221
References .....	221

## **CHAPTER 7. LIQUID CHROMATOGRAPHIC DETERMINATION OF PHENOLS AND SUBSTITUTED DERIVATIVES IN WATER SAMPLES**

*by G.A. Marko-Varga*

7.1. Introduction.....	225
7.2. Column liquid chromatographic separation .....	226
7.3. Sample handling techniques.....	230
7.4. Detection .....	234
7.5. Applications .....	241
7.6. Characterization of lignin and its breakdown products.....	246
Acknowledgements.....	267
Appendix: List of abbreviations .....	267
References .....	267

## **CHAPTER 8. HPLC METHODS FOR THE DETERMINATION OF MYCOTOXINS AND PHYCOTOXINS**

*by J.F. Lawrence and P.M. Scott*

8.1. Introduction.....	273
8.2. Mycotoxins .....	274
8.3. Phycotoxins.....	289
References .....	304

## **CHAPTER 9. DETERMINATION OF RADIONUCLIDES IN ENVIRONMENTAL SAMPLES**

*by V. Valkovic*

9.1. Introduction.....	311
9.2. Radionuclides in the environment.....	312
9.3. Pathways and samples of interest.....	317
9.4. Collection and preparation of samples .....	320
9.5. Counting.....	324
9.6. Gamma spectrometry.....	329
9.7. Beta particle spectrometry .....	332
9.8. Alpha particle spectrometry .....	333
9.9. Liquid scintillation measurement method .....	337
9.10. Radiochemical analyses .....	339
9.11. Rapid methods .....	342
9.12. Analytical quality control.....	344
9.13. Non-radiometric methods.....	350
9.14. Conclusions.....	353
References .....	353



## QUALITY ASSURANCE AND REFERENCE MATERIALS

### CHAPTER 10. QUALITY ASSURANCE IN ENVIRONMENTAL ANALYSIS

*by W.P. Cofino*

10.1. Introduction.....	359
10.2. Environmental management and the need for information.....	360
10.3. Total quality management of environmental information .....	362
10.4. Quality systems for chemical analysis.....	364
10.5. A closer look into quality assurance in the laboratory .....	367
10.6. Inter-laboratory studies and their feedback .....	374
References .....	378

### CHAPTER 11. CERTIFIED REFERENCE MATERIALS FOR THE QUALITY CONTROL OF MEASUREMENTS IN ENVIRONMENTAL MONITORING

*by E.A. Maier*

11.1. Particular aspects of environmental analysis.....	383
11.2. Reliability of data .....	384
11.3. The need for accuracy .....	384
11.4. How to achieve accuracy.....	385
11.5. Use of CRMs.....	390
11.6. Requirements for certified reference materials.....	393
11.7. CRMs for environmental monitoring .....	396
11.8. Conclusion .....	399
References .....	399

### CHAPTER 12. STANDARD REFERENCE MATERIALS FOR THE DETERMINATION OF TRACE ORGANIC CONSTITUENTS IN ENVIRONMENTAL SAMPLES

*by S.A. Wise*

12.1. Introduction.....	403
12.2. NIST SRMs for organic contaminants .....	405
12.3. Uses of environmental SRMs.....	444
Acknowledgement .....	444
References .....	444

## EMERGING TECHNIQUES

### CHAPTER 13. APPLICATION OF FLUORESCENCE SPECTROSCOPIC TECHNIQUES IN THE DETERMINATION OF PAHS AND PAH METABOLITES

*by F. Ariese, C. Gooijer and N.H. Velthorst*

13.1. Introduction.....	449
-------------------------	-----

13.2. Fluorescence spectroscopy .....	451
13.3. Applications .....	459
13.4. Conclusions.....	478
References .....	479

## **CHAPTER 14. CHARACTERIZATION OF SURFACTANTS IN WATER BY DESORPTION IONIZATION METHODS**

*by F. Ventura*

14.1. Introduction.....	481
14.2. Characterization of surfactants.....	483
14.3. Environmental applications of desorption ionization methods .....	504
14.4. Conclusions.....	517
References .....	517

## **CHAPTER 15. LC-MS INTERFACING SYSTEMS IN ENVIRONMENTAL ANALYSIS: APPLICATION TO POLAR PESTICIDES**

*by M.H. Lamoree, R.T. Ghijsen and U.A.Th. Brinkman*

15.1. Introduction.....	521
15.2. LC-MS interfaces.....	522
15.3. Applications .....	527
15.4. Conclusions.....	543
Acknowledgement .....	546
Appendix: List of abbreviations .....	547
References .....	547

## **CHAPTER 16. HYPHENATED TECHNIQUES APPLIED TO THE SPECIATION OF ORGANOMETALLIC COMPOUNDS IN THE ENVIRONMENT**

*by O.F.X. Donard and R. Ritsema*

16.1. Introduction.....	550
16.2. Flow injection analysis.....	552
16.3. Volatilization reactions, cryogenic trapping, chromatographic separation and atomic spectrometry detection .....	554
16.4. Separation by gas chromatography .....	562
16.5. Separation by liquid chromatography .....	579
16.6. Conclusion .....	600
Appendix: List of abbreviations .....	601
References .....	601

## **CHAPTER 17. THE POTENTIAL OF CAPILLARY ELECTROPHORESIS IN ENVIRONMENTAL ANALYSIS**

*by M.W.F. Nielen*

17.1. General introduction .....	607
----------------------------------	-----

17.2. CE techniques .....	609
17.3. Instrumentation for capillary electrophoresis .....	612
17.4. Trace enrichment in capillary electrophoresis .....	614
17.5. Environmental applications .....	622
17.6. Conclusion and future developments .....	631
References .....	632
<b>Subject Index</b> .....	<b>635</b>

## PREFACE

This book treats three different aspects of environmental analysis: the use of various analytical techniques, the applications to trace analysis of pollutants, mainly organic compounds, and the quality assurance aspects, including the use of certified reference materials for quality control of the whole analytical process. The need for more selective and sensitive analytical methods to help solve the numerous trace analysis problems in complex environmental samples is undisputed. The tremendous growth of environmental analysis in the last few years is due to the assessment of the quality of our environment being dependent on the availability of reliable analytical data as scientific conclusions and political decisions on environmental issues are based on their interpretation. Consequently, the development of analytical methods for pollutants has gone hand in hand with the adoption of regulations controlling their release into the environment.

One of the key elements of effective quality assurance is the availability of analytical techniques which can generate reliable data and their appropriate application. Obviously, the number and variety of these techniques currently in use in environmental analysis is so vast that their complete coverage in one book is impossible.

The book is organized in four sections. The first describes field sampling techniques and sample preparation in environmental matrices: air, water, sediment and biota. It provides a critical review of air monitoring sampling, the development of solid-phase extraction principles including on-line precolumn technologies for trace enrichment of organics in water, the sample handling of volatile organic compounds and the various aspects of the extraction and clean-up procedures for the more persistent organic compounds in sediment and biota matrices.

The second section covers the application of robust analytical techniques to the characterization of environmental target compounds included in many priority lists. The recent developments in the analysis of PCB congeners are discussed and the different official methods of analysis of pesticides in water using gas chromatography are reviewed. Various liquid chromatographic techniques, including coupled columns and pre- and post-column derivatization, used for the determination of phenolic compounds, polar pesticides and mycotoxins and phycotoxins, respectively, are covered. The final chapter in this section covers the use of liquid scintillation and radiochemical analyses for the determination of radionuclides in environmental samples.

Validation and quality assurance is one of the key parameters in all analytical measurements. These aspects are described in the third section of the book, and comprise a general discussion about quality assurance and the use and preparation of certified reference materials in environmental analysis. This is a very important issue since without quality assurance, questionable data can be obtained which can result in questionable conclusions.

The last section of the book deals with the newest techniques applied to the field of environmental analysis. Shpol'skii and synchronous fluorescence spectroscopy, and mass spectrometric approaches including the use of desorption ionization methods such as fast atom bombardment, are described for the characterization of PAHs and detergents, re-

spectively. The development of different interfacing systems in LC-MS, hyphenated techniques and various CE approaches such as CZE, electrokinetic capillary and isotachopheresis in environmental analysis, are also considered.. Although some of these techniques are not widely used at present, with only a few specialized laboratories currently using them on a routine basis, their inclusion in the book is to give some future perspectives to this continuously changing field.

By the nature of its content and written as it is by experienced practitioners, the book is intended to serve both as a general reference for post-graduate students as well as a practical reference for environmental chemists who need to use the analytical techniques for environmental studies and analytical chemists needing information on the complexity of environmental sample matrices and interferences. Each chapter includes sufficient references to the literature to serve as a valuable starting point for a more detailed investigation. The broad spectrum of the book, with its description of novel techniques, its many applications to the analysis of a variety of compounds, including applications to the analysis of metabolites from pesticides, PAHs and detergents, and the focus on quality assurance, makes it unique in many ways.

I thank the authors for their time and effort in preparing their chapters. Without their cooperation and engagement this volume would certainly not have been possible.

Barcelona, May 5, 1993

D. Barceló

## Field sampling techniques and sample preparation

This Page Intentionally Left Blank

## Chapter 1

# Sampling techniques for air pollutants

Reinhard Niessner

*Technical University of Munich, Institute of Hydrochemistry, Marchioninistrasse 17,  
D-8000 München 70, Germany*

## CONTENTS

1.1. Introduction .....	3
1.2. Sampling without suction, with deposition.....	4
1.3. Sampling with suction, without deposition.....	6
1.4. Sampling with suction, with deposition.....	13
1.4.1. Discontinuous sampling .....	13
1.4.2. Continuous sampling.....	17
1.5. Conclusion.....	17
References .....	18

## 1.1. INTRODUCTION

Monitoring of air constituents has become an important task for many scientists. Whether they are interested in meteorology, atmospheric physics, or chemistry, all have the same problem: "How can I describe the air compartment in the right way"?

Air constituents include not only gas molecules, but also finely dispersed materials of a homogeneous or heterogeneous nature. The problem of describing air exhaustively using physical or chemical techniques is often limited by two properties of the aerosols: first, they consist of multi-phase particle systems (such as the model aerosol particles shown in Fig. 1.1) and, secondly, the mass of a typical particle encountered in such an aerosol is in the ultratrace range (for example, the mass of one 100-nm particle is estimated to be of the order of femtograms).

Considering the fact that each particle has a different microstructure, adlayers, etc., one can imagine the impossibility of exhaustively describing air. So, in general, we measure only the averaged properties of a highly dynamic particle distribution and gas mixture.

From the analytical point of view, this means that we have to apply analytical techniques of the highest sensitivity and selectivity. To deal with the inherent dynamics of the system an on-line capability is also imperative. At present, for most problems this is still nearly impossible. Table 1.1 lists the most relevant analytes presently of interest in emission monitoring, together with the necessary detection limits. The figures originate from various governmental clean air acts. Of course the list is incomplete but it is intended to represent those analytes which are most relevant. For immission monitoring, a much lower detection limit (up to a factor of 10 000) has to be achieved. These limits can only be achieved by using a considerable enrichment prior to the intended analytical technique.



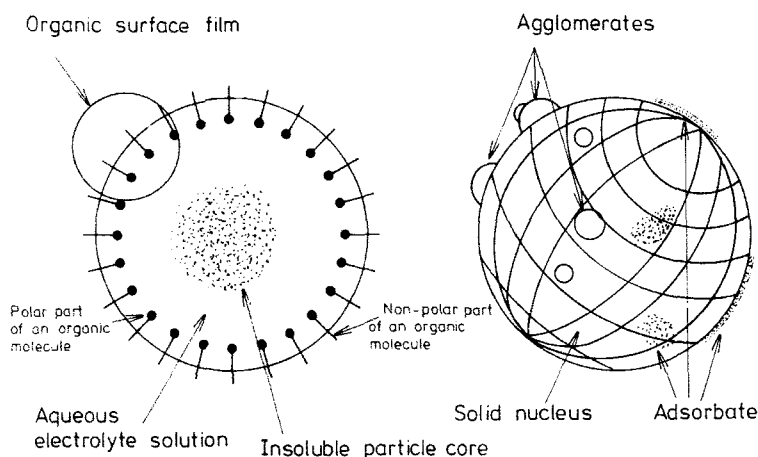


Fig. 1.1. Possible microstructure of particles.

The problem to be discussed in this chapter is how one can transfer the components of interest, without changes in the physical and chemical states, to the analytical process. This means that any artifact formation during sampling has to be avoided.

In order to evaluate the different possible strategies, we divide sampling techniques as follows:

- sampling without suction, with deposition;
- sampling with suction, without deposition;
- sampling with suction, with deposition;
  - (a) discontinuous sampling;
  - (b) continuous sampling.

We discuss existing sampling principles that may be suitable for an application in the above-mentioned sense, but also cover new potential solutions and developments. The discussion concentrates mainly on particle-related analytical techniques.

## 1.2. SAMPLING WITHOUT SUCTION, WITH DEPOSITION

The typical method of “passive sampling” is the accumulation of material towards a natural or artificial sink. Very commonly in gas sampling one uses diffusion tubes with coated inner walls (e.g. using Tenax for organic vapors [1]). Other well known sampling techniques for air monitoring use more or less open coated beakers or adhesive tape samplers [2]. The same principle is used for fog sampling, in mimicry of a spider’s web [3].

It is obvious that this technique cannot be used for concentration measurements. The samplers generally produce a temporally and spatially unknown mass flux. Consequently, the deposited mass of substances reflects only the quality of such an artificial or natural sink and the forces acting on the air constituents during the sampling period.

Forces that remove particles and gases from an air volume are condensation, impaction, diffusion, thermophoresis and diffusiophoresis. Other mechanisms are sedimentation and turbulent transfer. The properties of the receptor and the removed substances (reactivity, humidity, solubility, size, charge, roughness, alkalinity, etc.) will determine the deposition efficiency achieved. These facts make a theoretical treatment extremely difficult. We have to conclude that all published and recommended sampling techniques based on passive sampling will produce results that are valid only for the special type of collector and receiver used. The results will be only comparable to those from other collectors in very favorable circumstances. The same holds for other types of concentration measurements.

A very interesting new sampling scheme, presented by Steen [4], was based on a simultaneous, isokinetic sampling of both particulate and gaseous air constituents. The collector is shown in Fig. 1.2. Isokinetic sampling conditions (which means that there is no particle separation caused by different sampling velocities around the inlet and inside the duct of a sampler) are established by the use of Venturi nozzles and a weather-vane suspension for the collector tube. During sampling, the axis of the cylinder is oriented parallel to the flow lines and the aerosol is sucked in isokinetically through the inlet nozzle. A coaxially fixed field emission electrode, held at a high electrical potential at the inlet puts a unipolar charge on all particles. The meteorological conditions (wind speed

TABLE 1.1

## TARGET SUBSTANCES OF INTEREST IN AIR MONITORING (EMISSION SITUATION)

Most interesting analytes		Necessary detection limit
Gas phase	Hydrogen chloride	< 60 ppb
	Nitric acid	< 10 ppm
	Hydrogen sulfide	< 10 ppm
	Sulfur trioxide	< 50 ppb
	Mercury	< 10 ppb
	Benzene, toluene, xylene	<100 ppb
	Nicotine	< 70 ppb
	Organic aromatic amines	No threshold limit recommended
Aerosol phase	Sulfuric acid	< 50 $\mu\text{g m}^{-3}$
	Diesel exhaust	No threshold limit recommended
	Asbestos fibers	No threshold limit recommended
	Polycyclic aromatic hydrocarbons	No threshold limit recommended
	Nickel	No threshold limit recommended
	Polychlorinated biphenyls	<500 $\mu\text{g m}^{-3}$
	Polychlorinated dibenzodioxins and dibenzofurans	<100 $\text{pg m}^{-3}$
	Chromium trioxide	<100 $\mu\text{g m}^{-3}$
	Cadmium	< 40 $\text{ng m}^{-3}$
	Zinc	<100 $\mu\text{g m}^{-3}$

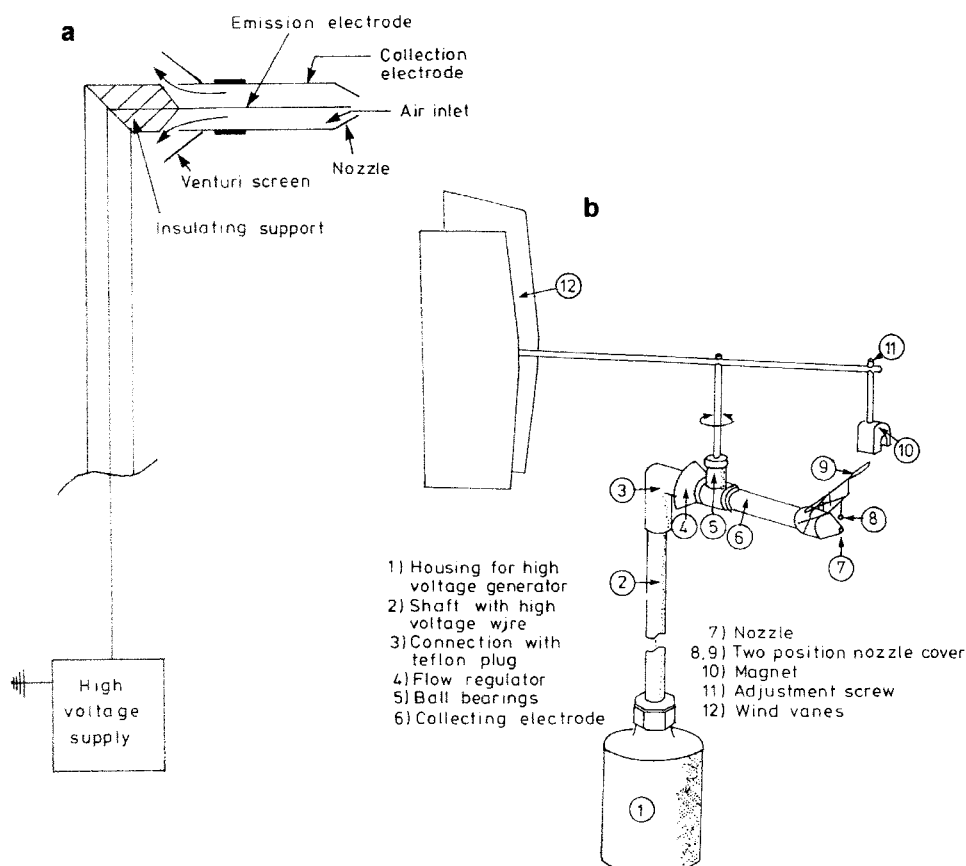


Fig. 1.2. (a) Schematic diagram of the basic isokinetic electrostatic particle sampler. (b) Sampler with wind vane control of nozzle cover for wind-directed measurements.

and wind direction) act as driving forces for the sampling by causing an underpressure across the venturi nozzles. The only limitations result from the varying charging efficiencies for incoming particles of different diameter and the receptor quality of the inner wall. Unfortunately, this system has never become popular, but would seem to be worth developing further.

### 1.3. SAMPLING WITH SUCTION, WITHOUT DEPOSITION

In this chapter, we recognize the great advantage of this sampling philosophy, because sampling with suction and without deposition is identical to in-situ and on-line sampling. Historically, on-line and in-situ sampling were a response to the increasing demand for fast signal generation and acquisition, which are required by modern control and regulation technologies, e.g. of combustion processes. However, producing a traditional off-line measurement signal for a trace constituent often involves the enrichment of hundreds of

cubic meters of air. This may lead to serious sampling artifacts, since the dispersed state of matter is changed by deposition on a very small surface such as a membrane filter, or by concentration into a very small volume, for example as a condensate. Extensive reaction between all possible reaction partners is a not unexpected result.

Which artifacts are possible? Table 1.2 shows some known artifacts reported during recent years. These artifacts can occur, but are not consequently induced by the sampling process. Whether an artifact is produced during enrichment depends on many variables, and one can only optimize sampling with respect to the analyte of interest. We must keep in mind that the method applied may be the worst solution for another compound.

There is sometimes disagreement about the existence of artifacts, mainly on the assumption that the presumed reactions would have happened earlier, in the atmosphere. This sounds reasonable but holds true only in well-mixed, aged air, and not in populated

TABLE 1.2

## POSSIBLE ARTIFACTS DURING SAMPLING OF AIR CONSTITUENTS

Artifact (caused by)	Example
<b>Gaseous air constituents</b>	
Memory effects in transfer lines and gas/particle separation means (adsorption of dipolar molecules)	Adsorption of HNO <sub>3</sub> , HCl or HF within stainless steel tubing [5], filter holders and membrane filters [6,7]
Production of acidic or alkaline gases (HCl, HNO <sub>3</sub> , NH <sub>3</sub> ) (acid/base reaction within sampled aerosols)	Topochemical interaction of strong acidic aerosol (H <sub>2</sub> SO <sub>4</sub> , HSO <sub>4</sub> <sup>-</sup> ) with already deposited particles (MeNO <sub>3</sub> , MeCl) [8,9]; catalytic formation on deposited particles (SO <sub>x</sub> ) [10–18]
<b>Particulate material (aerosols)</b>	
Decomposition of originally solid particulates or liquid droplets (due to temperature change or change of saturation pressure in ambient air with respect to substance of interest)	NH <sub>4</sub> NO <sub>3</sub> (l) ⇌ HNO <sub>3</sub> (g) + NH <sub>3</sub> (g) [19–25] PAH(adsorbed) ⇌ PAH(g) [26–31]
Interaction of reactive gases with particulate material	2NH <sub>4</sub> NO <sub>3</sub> (s) + H <sub>2</sub> SO <sub>4</sub> (l) → 2NH <sub>4</sub> HSO <sub>4</sub> (l) + 2HNO <sub>3</sub> (g) [6,8,9] NH <sub>3</sub> (g) + H <sub>2</sub> SO <sub>4</sub> (l) → NH <sub>4</sub> HSO <sub>4</sub> (s) [32,33] 2NH <sub>4</sub> Cl(s) + H <sub>2</sub> SO <sub>4</sub> (l) → (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (s) + 2HCl(g) [6,8,9] NO <sub>x</sub> + HNO <sub>3</sub> + PAHs → Nitro-PAHs [34–41]
Change of particle size distribution (due to electrostatic deposition or volatilization)	O <sub>3</sub> + π-electron rich systems, e.g. PAHs, terpenes [42–45] Strong losses of charged particles in PVC tubing; loss of liquid droplets in slightly heated tubing (e.g. tobacco aerosol)

areas such as cities. In an urban environment, a rapid mixing during the sampling period cannot be expected, due to the presence of a large number of diffuse emission sources (cars, chimneys, factories, etc.) and extremely complicated air streaming conditions. Many problems with distinct odor emissions testify to this. Another well-known example is that acidic aerosols and high concentrations of ammonia were found to co-exist in large cities. Chemically one might not expect this, but one explanation may be that there is a complicated source pattern, for which the different aerosol systems need a considerable time to reach a final thermodynamic equilibrium mixture.

The best way to avoid artifact formation is to use in-situ sampling, where the relevant substance is determined in its natural state of suspension. Such in-situ measurement techniques are at an early stage of development and only a few, but very promising, applications have been reported. The most prominent techniques with their reported detection limits are summarized in Tables 1.3 and 1.4.

Many of the listed techniques are based on laser light sources. One reason for this selection is that the sensor signal (pressure in photo-acoustic spectroscopy, light emission in the case of LIBS, fluorescence and Raman spectroscopy, and light scattering in the case of LIDAR) is proportional to the exciting light intensity. An excellent example of an experimental technique for the in-situ measurement of individual aerosol particles using Raman scattering is given by Fung and Tang [83]. A schematic diagram for the single-particle Raman spectrometer is shown in Fig. 1.3. The particle cell consists of an electrodynamic suspension trap. Two electrodes provide the necessary levitating DC-potential for the charged particle and an AC-potential applied to the ring-electrode keeps the parti-

TABLE 1.3

## HIGHLY SENSITIVE IN SITU GAS MONITORING TECHNIQUES

Detection principle	Analyte (detection limit)	References
<b>Light absorption</b>		
Photo-acoustic spectroscopy	Mercury (100 ppt)	[46]
	1,3-Dichloropropane (250 ppb)	[47]
	Ammonia (2 ppb)	[48,49]
Fourier transform infrared spectroscopy	Nitric acid: (4 ppb)	[50]
IR tunable-diode laser spectroscopy	Nitric acid: (100 ppt)	[51]
<b>Light emission</b>		
Fluorescence spectroscopy (laser-induced)	Nitric acid (100 ppt)	[52,53]
	Anthracene (10 ppb)	[54]
Laser-induced breakdown spectroscopy	Chlorine (8 ppm)	[55–58]
Chemiluminescence	Nitrogen dioxide: (5 ppt)	[59]
<b>Physical properties</b>		
Ion mobility	Nitroglycerine (180 ppt)	[60–63]
	Hydrogen chloride (1 ppb)	
Aerosol ionization	Sulfur dioxide (200 ppb)	[64]

TABLE 1.4

## HIGHLY SENSITIVE IN SITU AEROSOL MONITORING TECHNIQUES

Detection principle	Analyte (detection limit)
<b>Light absorption</b>	
Photo-acoustic spectroscopy	Carbon or diesel aerosol ( $300 \text{ ng m}^{-3}$ ) [65–68]
Optothermally induced light scattering	Sulfate ( $5 \mu\text{g m}^{-3}$ ) [69,70]
Optothermally induced particle charging	Carbon ( $<1 \mu\text{g m}^{-3}$ ) [71,72]
<b>Light emission</b>	
Laser-induced, time-resolved fluorescence	e.g. Perylene ( $<10 \text{ ng m}^{-3}$ ) [73–75]
Laser-induced breakdown spectroscopy	Cadmium ( $20 \mu\text{g m}^{-3}$ ) [76,77]
Analysis by ICP-atomic emission spectroscopy	Cu, Ti, Mg (LOD not given) [78–81]
Analysis by Raman spectroscopy	Sulfate, nitrate (single particle analysis) [82–87]
IR laser back-scattering	Sulfuric acid ( $<1 \text{ g m}^{-3}$ ) [88,89]
<b>Analysis by measurement of electrons, ions or ionized particles</b>	
Photoelectron spectroscopy for chemical analysis	Iodide (LOD not given) [90]
Mass spectrometry	4,4'-Dibromobiphenyl ( $10^{-13} \text{ g abs.}$ ) [91,92]
Aerosol photoemission	e.g. Benzo[a]pyrene ( $1 \mu\text{g m}^{-3}$ ) or nickel oxide ( $250 \text{ ng m}^{-3}$ ) [93–101]
<b>Analysis by observation of hygroscopic properties</b>	
Aerosol mobility chromatograph	Sulfuric acid ( $1 \text{ ng m}^{-3}$ ) [102]
Condensation on monodispersed aerosols	Sulfuric acid ( $<1 \mu\text{g m}^{-3}$ ) [103,104]
<b>Analysis by chemical identification reactions</b>	
Selective stoichiometric reaction and observation of the products	Sulfuric acid ( $0.2 \mu\text{g m}^{-3}$ ) [105] Hydrochloric acid aerosol ( $800 \mu\text{g m}^{-3}$ ) [106]

cle in the center of the cell. Such arrangements open new possibilities for studying the chemical behavior of particulate materials without any artifact formation.

An on-line PAH measurement system based on laser-induced and time-resolved fluorescence is shown in Fig. 1.4. It consists of a fast ( $\lambda_p = 300 \text{ ps}$ ) nitrogen laser as light source and a fast digital storage oscilloscope in addition to connecting quartz fiber optics, monochromator, mirror and beam trap. Preliminary results yielded a detection limit of some  $100 \text{ ng pyrene/m}^3$ . Work is currently in progress on deconvolution algorithms for the interpretation of superimposed fluorescence decay processes and emission spectra of several PAHs adsorbed on one particle [107]. The use of laser scanners should make a three-dimensional screening of air volumes possible within the near future. This would be of considerable importance for finding the sources of aerosol emission (e.g. in clean rooms or for fire detection).

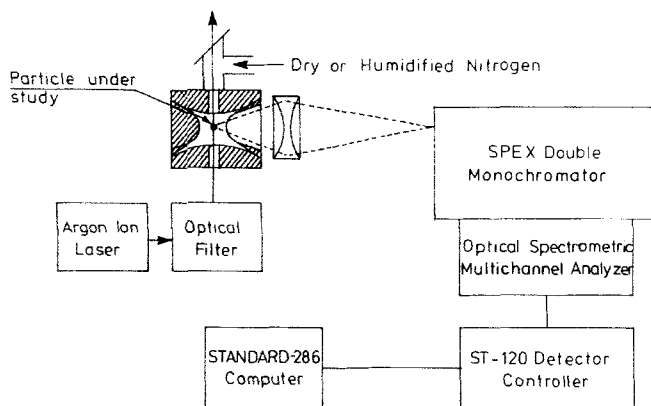


Fig. 1.3. Experimental set-up for single-particle Raman spectroscopy.

Great interest has arisen in light-absorbing particles since a change in the world's climate has been noticed, and there has been speculation about a possible influence of soot particles on the total radiation budget [108]. Up to now, photo-acoustic spectroscopy has offered the only available approach for on-line, in-situ measurement of the absorption of radiation by ultrafine airborne particles. A new detection technique, using a high-power laser working in the infrared spectral region ( $I_p \sim 1$  W), is depicted in Fig. 1.5. The advantage of such a laser diode, compared with other high-power lasers in the visible region, is its emission wavelength of 800 nm, the small size of the laser, and the possibil-

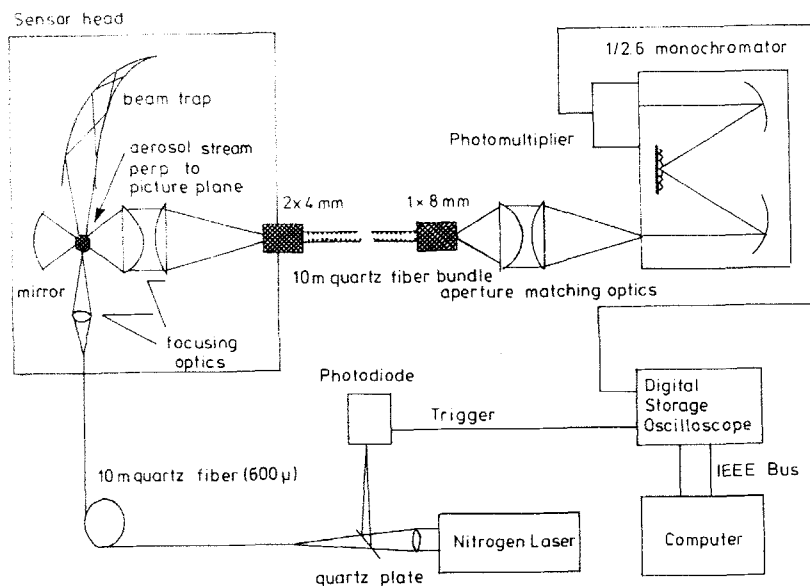


Fig. 1.4. Experimental set-up for on-line aerosol fluorescence detection of particle-bound PAHs.

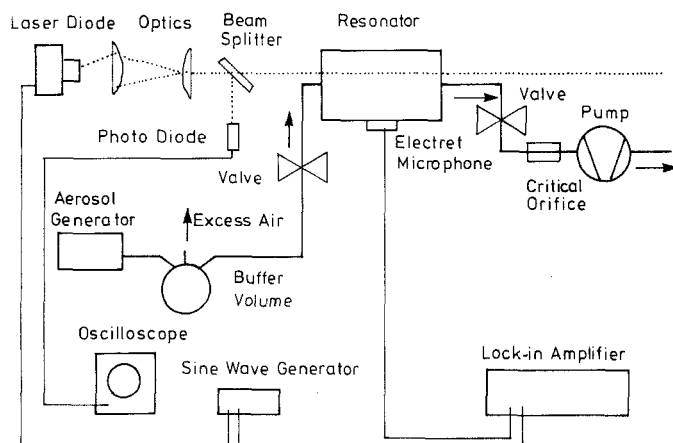


Fig. 1.5. General scheme of experimental set-up for the generation and photo-acoustic detection of carbonaceous aerosol.

ity of electronic intensity modulation of the light instead of modulation by a mechanical chopper. This results in a decreased background signal and an extended modulation frequency range. By using a resonant photo-acoustic cell, a detection limit of  $10 \mu\text{g m}^{-3}$  of carbon in a free flowing aerosol stream has been achieved [68].

One special application of the photoelectric aerosol sensor (PAS) as a detector for particle-bound PAHs in diesel exhaust is given in Fig. 1.6. The photoelectric aerosol sensor consists of the detection system, the aerosol sampling head, and the measuring system. With the dilution air controlled by the mass flow controller, 1, in the dilution system, the exhaust aerosol is mixed with particle-free air at the entrance of the sampling head. The system allows dilution ratios up to 1:32. With this dilution system, the PAS can be used to monitor PAHs in an undiluted car exhaust. Within the measuring system, the aerosol is stripped of the charged particles in an electrostatic filter. The neutral particles then enter the illumination section, where a PAH mass-related particle photocharging takes place (at a wavelength of 185 nm). Only surface-enriched molecules with an extended  $\pi$ -electron-system show a high photoelectric quantum yield. The PAS signal was correlated with the PAH-content determined by sampling on a parallel filter and GC determinations. The measurements indicated that the photoelectric signal is influenced by photoelectrically inactive paraffins adsorbed on the diesel particles. In this case, it was possible to correct the PAS signal for the true PAH content. The results shown in Fig. 1.7 are valid for various types of engines and loading conditions.

In our opinion, sampling with suction but without deposition is a most promising analytical tool for the future. A large number of classical optical techniques can be applied to the air constituents, avoiding many possible artifacts. However, there is a major restriction for particulate or particle-bound analytes because only a few of these techniques are really mass-related, most of them being surface-sensitive.



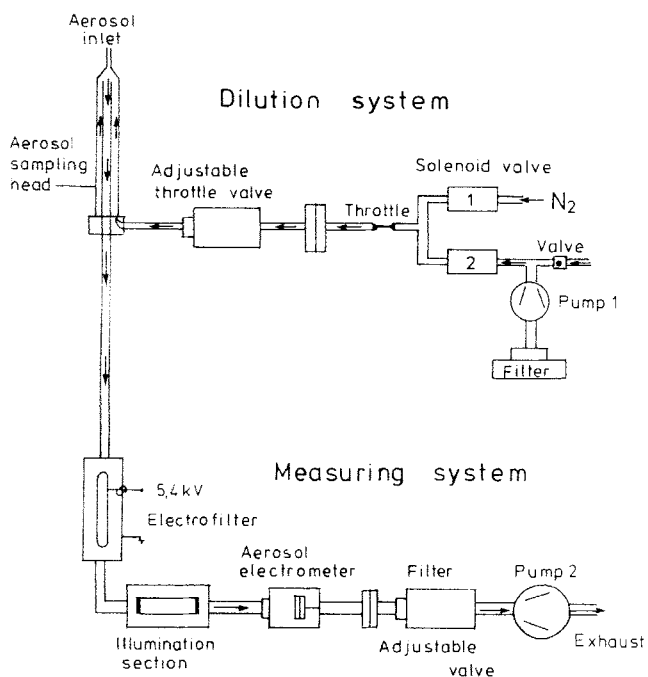


Fig. 1.6. Set-up for on-line detection of particle-bound PAHs in diesel exhaust with the photoelectric aerosol sensor (PAS).

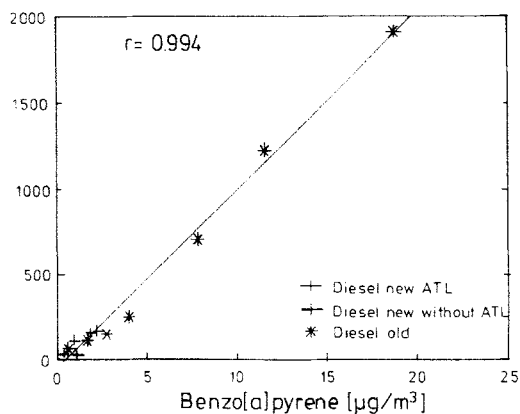


Fig. 1.7. Correlation between PAS signal (convoluted with the total volatile hydrocarbon content) and the wet-chemically determined total PAH content of various diesel engines at different loads and speeds.

## 1.4. SAMPLING WITH SUCTION, WITH DEPOSITION

### 1.4.1. Discontinuous sampling

A typical technique for the sampling of unstable species is cryo sampling [109], where the species is frozen or condensed within a protective matrix. The condensate is then chemically analyzed and the volume of air sampled is computed by measuring the volume of water collected and assuming the air is totally stripped of water. Open questions relate to the collection of particles by thermophoretic and diffusiophoretic forces which act during condensation. Gases are sampled referentially, especially the soluble ones. A certain drawback is the small volume of water sampled. Some applications are reported in connection with balloon-borne investigations of radicals or pesticides. One recent example is the sampling of herbicide traces by condensing atmospheric water and water-soluble gaseous atrazine [110]. Although only a few microliters of aqueous sample are obtained, the use of an ultrasensitive determination technique, such as an enzyme-linked immunosorbent assay (ELISA) for atrazine, allows the measurement of enriched volatilized pesticide at the stagnant boundary layer for the first time. Extreme absolute sensitivity is the prerequisite for such sampling and analysis (in the given example 100 fg of atrazine is the absolute detection limit). As can be seen from Fig. 1.8, an enrichment of condensable atrazine, a wide-spread herbicide, is observed near the inversion layer. One can conclude that contamination of remote and non-contaminated areas is predominantly influenced by such air-freight processes.

An improved aqueous scrubber (see Fig. 1.9) for collection of soluble atmospheric trace gases, such as  $\text{NH}_3$ ,  $\text{HCl}$  or  $\text{SO}_2$ , consists of a combination of an aerosol generator and water condenser [111]. During sampling, air is drawn through a nebulizing nozzle, thereby aspirating the absorber solution and forming a "trace catcher" aerosol. The resulting mist sprays upwards through a reaction chamber until it impinges on a hydrophobic

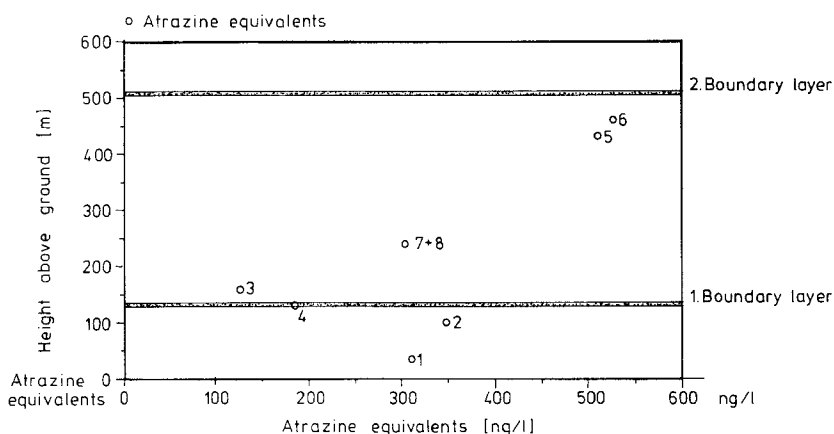


Fig. 1.8. Results of balloon-borne investigation of condensable atrazine traces as a function of height above ground.

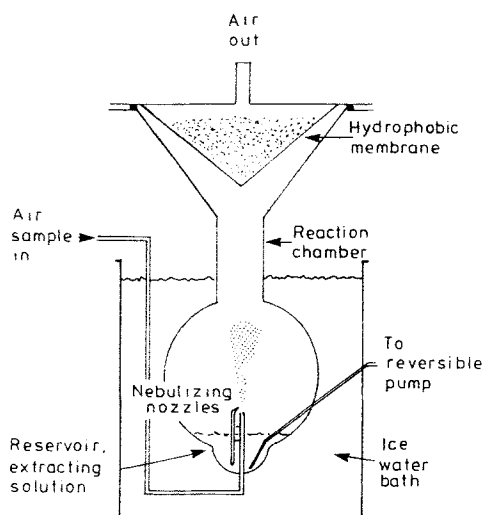
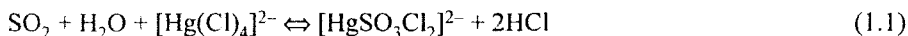


Fig. 1.9. Schematic representation of nebulization-reflux concentrator.

membrane that virtually blocks the passage of droplets but not the gas flow. After a preselected concentration period, the extracting solution containing the analyte can be withdrawn for analysis. A similar application for the determination of chlorine was published by Isacson and Wettermark, who observed the chemiluminescence when a luminol aerosol was reacted with the oxidant [112].

Another example of sampling of highly volatile and unstable aerosol constituents, such as tobacco aerosols or fog droplets has been reported by Keith [113]. He proposed co-condensation or micro-encapsulation of the aerosol under study, using the vapor of methyl cyanoacrylate monomer. During sampling, the monomer starts the polymerization reaction and the whole sampling ends with micro-encapsulated, deposited aerosol particles. This technique seems very advantageous for postcollection inspection by FTIR techniques since the encapsulation is IR-transparent. Similar intentions are seen in the work of Bächmann, in which single rain droplets were allowed to fall through liquid nitrogen vapor and were immediately frozen. Using spot analysis techniques, the single frozen droplets can be chemically characterized [114].

Stabilization of reactive air constituents to avoid artifact formation was attempted by different groups for sulfuric acid aerosols [6,115]. Amine vapors were admitted to the aerosol stream, yielding an amine sulfate that was no longer reactive towards halides. Unfortunately, it was never possible to separate the amine sulfates from other sulfates, such as ammonium salts. Another classical example of a protection step in gas sampling is the well-known West-Gaeke technique, where stabilization is obtained by forming a tetrachloromercurate complex



The use of a proton buffer allows complete preservation of sulfur dioxide against oxidative attack [116].

Gases are usually sampled by chemisorption and/or physisorption. Very often, pre-filters are recommended for removal of particulate material. As discussed in the previous chapter, one has to check carefully that such discrimination does not lead to artifact formation (e.g. by volatilization of already sampled particles, gas/particle interaction or by irreversible adsorption on the filter matrix). Capacity problems have to be considered also, especially in solid sorbent sampling, such as that of organic vapors on charcoal or on materials like Tenax. The subsequent desorption step can also be a source of serious problems due to irreversible adsorption or chemical reactions on the sorbent. Critical testing of the whole sampling procedure (sample transfer through tubing, preconcentration, desorption and determination) with suitable test gases or aerosols is strongly recommended.

Perhaps the most powerful technique for gas/particle separation is diffusion sampling by means of denuder tubes. A known volume of air containing the analyte is drawn through a tube or tube-like arrangement, called a denuder. The inner walls of a denuder are coated with a trapping agent suitable for the gaseous analyte. Gas/particle separation is obtained as the aerosol is drawn through the denuder, since gaseous constituents have a considerably higher diffusion coefficient than even ultrafine particles. This is exemplified in Fig. 1.10, where the relative change of diffusion coefficient as a function of particle size is plotted.

Diffusion tubes have a long tradition. Even in 1900, Townsend estimated the diffusion coefficient of ions in moist gases using denuder tubes [117]. Today a large variety of gaseous and particulate air constituents can be determined using denuder sampling technologies. A comprehensive review on this subject has been published by Slanina et al. [118]. We can categorize these sampling procedures as follows:

- I. Deposition of a gas without any analytical determination
  - use of a wall coating as a sink with limited capacity [119–121]
  - deposition of a gas on a continuously renewed sink [122]
  - catalytic destruction of a gas at the wall coating [123]

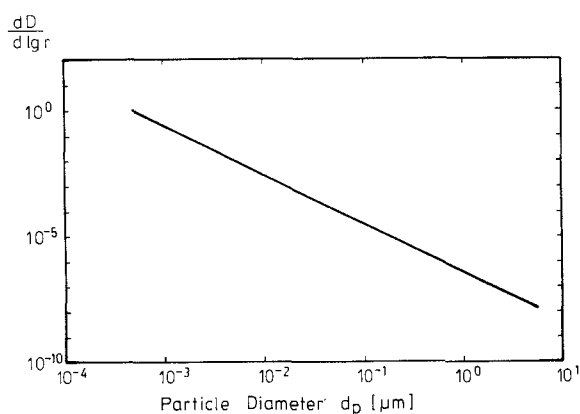


Fig. 1.10. Relative change of diffusion coefficient as a function of particle size.

- II. Deposition of a gas with subsequent analytical determination
  - one-time sampling and analytical determination after elution of the wall coating [124–145]
  - thermodesorption of the adsorbed gas from a reversibly acting sink, with subsequent analytical determination of the gas [146–150]
  - liberation of a new, stoichiometrically formed substance; determination of the deposited gas by analysis of the newly formed compound [105,106,151]
  - determination by parallel sampling with and without a diffusion sampler, (difference determination) [121,152]
  - deposition of a gas on a continuously renewed liquid sink and continuous analytical determination of the adsorbed species [153–157]

Within recent years, a clear trend has been observed in the application of highly selective sink materials. Immobilization of enzymes [158] and the application of antibodies for specific trapping of deposited antigens can be expected in future “super-denuders”.

Diffusion sampling may also help (in favorable cases) in size-related particle/particle sampling:

- I. Diffusion batteries for particle/particle separation
  - in situ determination of particle size distribution (combination with particle counters) [117,159–177]
  - combination of size-fractionating aerosol sampling with deposition and subsequent analysis [178–185]
- II. Thermodiffusion denuder for separation of labile aerosol systems
  - one-time sampling and determination after elution of wall coating [128,130,186]
  - thermodesorption of deposited particulate material from a reversibly usable sink with subsequent chemical analysis [187–191]
  - liberation of a new, stoichiometrically formed compound; determination of the deposited particulate material via analysis of the new compound [128,192,193]
  - determination by parallel sampling, with and without a thermodenuder [194–197]
- III. Separation based on different diffusion coefficients
  - separation of molecules by means of artificially established boundary layers (e.g. membrane or screen) [198–202]
- IV. Separation by change of state (accompanied by drastic change of diffusion coefficient)
  - use of selective gas phase reaction for particle production
  - initiation of particle nucleation by means of electromagnetic radiation
- V. Separation by means of different sinks
  - application of sequentially arranged diffusion tubes of different sink quality [130]

Common to all these diffusion samplers is the principle that proper sampling requires diffusion as the only driving force. In the meantime, many solutions have been published: simple cylindrical tubes, annular denuder, parallel plate denuder, coiled denuder, thermodenuder and solution-based denuder. Of particular note are annular denuders, which have become quite popular. They offer a high operational flow rate and hence a short sampling time for a given minimum amount of enriched material. A drawback compared to the simple straight denuder tube is the large volume required for complete extraction

(because of the extended wall surface of the annular space). This is often a limitation, because of higher blank values. A second serious drawback of all denuder constructions which do not have a straight tube design is associated with an increased particle deposition. Zhang et al. [155] have presented results on particle losses in 8 different denuder configurations, ranging from a simple tube to an annular design. The results clearly indicate a particle loss averaging 3.2–14.7% for a straight denuder tube (particle size range 0.1–2.99  $\mu\text{m}$ ;  $Q = 5 \text{ l min}^{-1}$ ) and of 16.7–19.7% for a glass annular denuder (particle size range 0.6–2.99  $\mu\text{m}$ ;  $Q = 5 \text{ l min}^{-1}$ ).

#### 1.4.2. Continuous sampling

In addition to in-situ sampling (and determination) which has already been mentioned, the quasi-continuously (or even better, continuously) working techniques are of considerable importance, especially for emission control. For many purposes, an on-line measurement (as achieved with optical techniques) is a prerequisite for a self-regulating, and thus optimized, process. A good example is in combustion monitoring where an oxygen sensor is used to establish optimum combustion. For gases, more or less all applicable chemical sensors may be combined. For aerosol monitoring, the continuous transfer of representative ambient aerosol samples, or stack samples containing particles and/or droplets, can give rise to serious technical problems, even at the sampling point, for example using anisokinetic sampling. Anisokinetic sampling leads inevitably to large losses, especially of larger particles with high mass. Since all monitoring of emission sources is governed by mass concentrations (threshold limits), the loss of only a few large particles containing the analyte of interest will yield a false determination.

Simultaneous sampling and analytical determination is used in the total-suspended-dust monitors which work with the  $\beta$ -absorption of the membrane-filter-collected material. Further speciation of the sampled material is not possible here. Another direct total mass recording system uses a piezo-electric quartz sensing element. Deposited material changes the mechanical properties of the quartz crystal, thus changing the resonance frequency in an oscillator circuit.

### 1.5. CONCLUSION

Sampling is surely the most critical step within the total scheme of air analysis. Because of the arbitrary and complex dynamic nature of air, in terms of the temporal and spatial fluctuations of gaseous and particulate analytes, many sampling problems still exist. Considerable improvements have been achieved within the last decades but with increasing insight into atmospheric aerosol systems, we also see an increased need for faster and more selective sampling techniques which are free of major artifacts. The main conclusion is to avoid sampling (if possible), and to try to exploit the in-situ measurement systems.

A blank space on the map of aerosol sampling and characterization can still be identified easily, i.e. the monitoring of bio-aerosols and microstructured particles.

## REFERENCES

- 1 E. Palmes, A. Gunnison, J. DiMattio and C. Tomczyk, *Am. Ind. Hyg. Assoc. J.*, 37 (1976) 570.
- 2 M. Diem, *Staub*, 20 (1960) 278.
- 3 W. Jäschke, Workshop on Sampling and Chemical Analysis of Fog Water with Respect to the Micro Physics of Fog, Kleiner Feldberg, Frankfurt/Main, Germany, 1985.
- 4 B. Steen, *Atmos. Environ.*, 11 (1977) 623.
- 5 J. Bowermaster and R. Shaw, *J. Air Pollut. Control Assoc.*, 31 (1981) 787.
- 6 R. Niessner, Ein neuer Weg zur Bestimmung starker Säuren und ihrer Salze in der Atmosphäre, Dissertation, Universität Dortmund, 1981.
- 7 J. Auffarth, Katalytisch-kinetische Mikrospurenbestimmung von Fluorid in Umweltmatrices, Dissertation, Universität Dortmund, 1979.
- 8 D. Klockow, B. Jablonski and R. Niessner, *Atmos. Environ.*, 13 (1979) 1665.
- 9 R. Niessner, *VDI-Ber.*, 500 (1983) 105.
- 10 D. Klockow, *Fresenius' Z. Anal. Chem.*, 282 (1976) 269.
- 11 J. Notholt, J. Hjorth and F. Raes, *Atmos. Environ.*, 26A (1992) 211.
- 12 B. Finlayson-Pitts and S. Johnson, *Atmos. Environ.*, 22 (1988) 1107.
- 13 D. Hitchcock, L. Spiller and W. Wilson, *Atmos. Environ.*, 14 (1980) 165.
- 14 C. Spicer and P. Schumacher, *Atmos. Environ.*, 13 (1979) 543.
- 15 W. Pierson, W. Brachaczek, T. Konrisky, T. Truex and J. Butler, *J. Air Pollut. Control Assoc.*, 30 (1980) 30.
- 16 B. Appel, S. Wall, Y. Tokiwa and M. Haik, *Atmos. Environ.*, 13 (1979) 319.
- 17 J. Forrest, R. Tanner, D. Spandau, T. D'Ottavio and L. Newman, *Atmos. Environ.*, 14 (1980) 137.
- 18 L. Laskus, D. Bake, M. Möller, J. Kura and T. Möhlmann, *Staub-Reinhalt. Luft*, 51 (1991) 277.
- 19 C. Richardson and R. Hightower, *Atmos. Environ.*, 21 (1987) 971.
- 20 R. Harrison and C. Pio, *Tellus*, 35B (1983) 155.
- 21 L. Hildemann, A. Russell and G. Cass, *Atmos. Environ.*, 18 (1984) 1737.
- 22 T. Larson and G. Taylor, *Atmos. Environ.*, 17 (1983) 2489.
- 23 G. Doyle, E. Tuazon, R. Graham, T. Mischke, A. Winer and J. Pitts, *Environ. Sci. Technol.*, 13 (1979) 1416.
- 24 A. Stelson, S. Friedlander and J. Seinfeld, *Atmos. Environ.*, 13 (1979) 369.
- 25 I. Tang, *Atmos. Environ.*, 14 (1980) 819.
- 26 J. Peters and B. Seifert, *Atmos. Environ.*, 14 (1980) 117.
- 27 U. Knecht and J.-J. Woitowitz, *Fresenius' Z. Anal. Chem.*, 331 (1988) 8.
- 28 R. Coutant, L. Brown, J. Chuang, R. Riggan and R. Lewis, *Atmos. Environ.*, 22 (1988) 403.
- 29 P. Leinster and M. Evans, *Ann. Occup. Hyg.*, 30 (1986) 481.
- 30 A. Miguel, J. de Andrade and S. Hering, *Int. J. Environ. Anal. Chem.*, 26 (1986) 265.
- 31 D. Grosjean, *Atmos. Environ.*, 17 (1983) 2565.
- 32 L. Newman, *Atmos. Environ.*, 12 (1978) 113.
- 33 D. Hayes, K. Snetsinger, G. Ferry, V. Overbeck and N. Farlow, *Geophys. Res. Lett.*, 7 (1980) 974.
- 34 D. Grosjean, K. Fung and J. Harrison, *Environ. Sci. Technol.*, 17 (1983) 673.
- 35 J. Chuang, S. Hannan and L. Slivon, *Chemical Characterization of Polynuclear Aromatic Hydrocarbon Degradation Products from Sampling Artifacts*, U.S. Environmental Protection Agency, Publ. EPA/600/4-87/039, 1987.
- 36 R. Bradow, R. Zweidinger and F. Black, Sampling diesel engine particle and artifacts from nitrogen oxide interactions, SAE Paper 820182, 1982, p.13.
- 37 A. Lindskog, E. Brorström-Lundéu, I. Alfheim and I. Hagen, *Sci. Total Environ.*, 61 (1987) 51.
- 38 A. Hartung and H. Kies, Artefakt-Bildung während der Sammlung von Dieselpartikeln, Forschungsber. Nr. FMT 8406 V/5 der Volkswagen AG, Wolfsburg, Germany, 1984.

- 39 D. Schuetzle and J. Frazier, in N. Ishinishi, A. Koizumi, R. McClellan and W. Stöber (Editors), *Carcinogenic and Mutagenic Effects of Diesel Engine Exhaust*, Elsevier, Amsterdam, 1986, p. 41.
- 40 D. Schuetzle and J. Perez, *J. Air Pollut. Control Assoc.*, 33 (1983) 751.
- 41 Z. Guo and R. Kamens, *J. Atmos. Chem.*, 12 (1991) 137.
- 42 J. Pitts, H.-R. Paur, B. Zielinska, J. Arey, A. Winer, T. Ramdahl and V. Mejia, *Chemosphere*, 15 (1986) 675.
- 43 W. de Raat, G. Bakker and F. de Meijere, *Atmos. Environ.*, 24A (1990) 2875.
- 44 C. Davis, R. Caton, S. Guerin and W. Tam, in M. Cooke and A. Dennis (Editors), *Polynuclear Aromatic Hydrocarbons*, Battelle Press, Columbus, OH, 1986, p. 337.
- 45 E. Brorström, P. Grennfelt and A. Lindskog, *Atmos. Environ.*, 17 (1983) 601.
- 46 J. Patterson, *Anal. Chim. Acta*, 164 (1984) 119.
- 47 D. Bicanic, H. Jalink, H. Sauren, P. Torfs, W. Kunze, J. Lloyd, L. Tuinstra and A. Roos, *Rev. Roum. Phys.*, 34 (1988) 1007.
- 48 A. Solyom, A. Miklos, G. Angeli and A. Lörincz, *Acta Chim. Hung.*, 128 (1991) 877.
- 49 P. Meyer and M. Sigrist, *Rev. Sci. Instrum.*, 61 (1990) 1779.
- 50 E. Tuazon, R. Graham, A. Winer, R. Easton, J. Pitts and P. Haust, *Atmos. Environ.*, 12 (1978) 865.
- 51 G. Mackay and H. Schiff, in *Proc. 1987 EPA/APCA Symp. on Measurement of Toxic and Related Air Pollutants*, US Environmental Protection Agency, Publ. EPA 600/9-87-010, 1987, p. 366.
- 52 T. Papenbrock and F. Stuhl, *J. Atmos. Chem.*, 10 (1990) 451.
- 53 S. Colson, The detection and study of molecular species using time resolved laser spectroscopy, Report, US Army Research Office, ARO-22 561.10, Order No. AD-A 198 482, 1988.
- 54 L. Jandris and R. Force, *Anal. Chim. Acta*, 151 (1983) 19.
- 55 D. Cremers and L. Radziemski, *Anal. Chem.*, 55 (1983) 1252.
- 56 N. Bonifaci and A. Denat, *IEEE Trans. Electr. Insul.*, 26 (1991) 610.
- 57 T. Loree and L. Radziemski, *Plasma Chem. Plasma Process.*, 1 (1981) 271.
- 58 M. Casini, M. Harith, V. Palleschi, A. Salvetti, D. Singh and M. Vaselli, *Beams*, 9 (1991) 633.
- 59 D. Kley and M. McFarland, *Atmos. Technol.*, 12 (1980) 63.
- 60 M. Cohen, R. Wernlund and R. Stimac, *Nucl. Mater. Manage.*, 13 (1984) 220.
- 61 J. Preston, F. Karasek and S. Kim, *Anal. Chem.*, 49 (1977) 1746.
- 62 D. Blyth, in *Proc. Int. Symp. Prot. Chem. War. Agents*, Stockholm, Sweden, 1983, p. 65.
- 63 G. Eiceman, C. Leasure and V. Vandiver, *Anal. Chem.*, 58 (1986) 76.
- 64 H.-J. Grosse, H.-R. Döring and F. Gleisberg, *Staub-Reinhalt. Luft*, 42 (1982) 197.
- 65 K. Adams, *Appl. Opt.*, 27 (1988) 4052.
- 66 K. Adams, L. Davis, S. Japar and W. Pierson, *Atmos. Environ.*, 23 (1989) 693.
- 67 C. Bruce and N. Richardson, *Appl. Opt.*, 23 (1984) 13.
- 68 A. Petzold and R. Niessner, *SPIE*, 1716 (1992) 510.
- 69 A. Campillo and H.-B. Lin, US Patent 4.415.265, 1983.
- 70 A. Campillo, C. Dodge and H.-B. Lin, *Appl. Opt.*, 20 (1981) 3100.
- 71 R. Niessner, H. Schröder, W. Robers and K. Kompa, *J. Aerosol Sci.*, 19 (1988) 491.
- 72 W. Robers, H. Schröder, K. Kompa and R. Niessner, *Z. Phys. Chem. (Munich)*, 159 (1988) 129.
- 73 F. Beretta, A. Cavaliere and A. D'Alessio, *Combust. Sci. Technol.*, 27 (1982) 113.
- 74 R. Niessner, W. Robers and A. Krupp, *Fresenius' J. Anal. Chem.*, 341 (1991) 207.
- 75 R. Niessner and A. Krupp, *Part. Part. Syst. Charact.*, 8 (1991) 23.
- 76 M. Essien, L. Radziemski and J. Sueddon, *J. Anal. Atomic Spectrom.*, 3 (1988) 985.
- 77 L. Radziemski, T. Loree, D. Cremers and N. Hoffman, *Anal. Chem.*, 55 (1983) 1246.
- 78 P. Pfannerstill, J. Creed, T. Davidson, J. Caruso and K. Willeke, *J. Anal. Atomic Spectrom.*, 5 (1990) 285.
- 79 W. van Borm and J. Broekart, *Anal. Chem.*, 62 (1990) 2527.



- 80 W. van Borm, J. Broekart, R. Klockenkämper, P. Tschöpel and F. Adams, *Spectrochim. Acta*, 46B (1991) 1033.
- 81 T. Graule, A. van Bohlen, J. Broekart, E. Grallath, R. Klockenkämper, P. Tschöpel and G. Tölg, *Fresenius' Z. Anal. Chem.*, 335 (1989) 637.
- 82 K. Fung and I. Tang, *Appl. Spectrosc.*, 45 (1991) 734.
- 83 K. Fung and I. Tang, *Appl. Spectrosc.*, 46 (1992) 159.
- 84 M. Buehler, T. Allen and E. Davis, *J. Colloid Interface Sci.*, 146 (1991) 79.
- 85 G. Hoffmann, B. Oelichmann and B. Schrader, *J. Aerosol Sci.*, 22 (Suppl. 1) (1991) 427.
- 86 J. Carls, G. Moncivais and J. Brock, *Appl. Opt.*, 29 (1990) 2913.
- 87 A. Serpengüzel, J. Swindal, R. Chang and W. Acker, *Appl. Opt.*, 31 (1992) 3543.
- 88 H. Mudd, C. Kruger and E. Murray, *Appl. Opt.*, 21 (1982) 1146.
- 89 M. Wright, J. Pollack and D. Colburn, *NBS Spec. Publ. (US)*, 464 (1977) 301.
- 90 E. Janssen and A. Goldmann, *J. Aerosol Sci.*, 22 (1991) S 841.
- 91 J. Stoffels, *Int. J. Mass Spectrom. Ion Phys.*, 40 (1981) 217.
- 92 M. Sinha and S. Friedlander, *Chemical Characterization of Aerosol Particles by Mass Spectrometry. Aerosols: Formation and Reactivity*, Pergamon, Oxford, 1986, p. 875.
- 93 R. Niessner, *J. Aerosol Sci.*, 17 (1986) 705.
- 94 R. Niessner, *Fresenius' Z. Anal. Chem.*, 329 (1987) 406.
- 95 R. Niessner, W. Robers and P. Wilbring, *Anal. Chem.*, 61, (1989) 320.
- 96 R. Niessner and G. Walendzik, *Fresenius' Z. Anal. Chem.*, 333 (1989) 129.
- 97 R. Niessner, B. Hemmerich and U. Panne, *Fresenius' Z. Anal. Chem.*, 333 (1989) 704.
- 98 R. Niessner, B. Hemmerich and U. Panne, *Fresenius' Z. Anal. Chem.*, 335 (1989) 728.
- 99 A. Zajc, E. Uhlig, H. Hackfort and R. Niessner, *J. Aerosol Sci.*, 20 (1989) 1465.
- 100 R. Niessner and F. Lutz, *Polycyclic Aromatic Compounds*, 2 (1991) 49.
- 101 M. Bäcker, N. Pelz and R. Niessner, *Fresenius' J. Anal. Chem.*, (1993) submitted.
- 102 B. Liu, D. Pui, K. Whitby, D. Kittelson, Y. Kousaka and R. McKenzie, *Atmos. Environ.*, 12 (1978) 99.
- 103 R. Niessner, B. Däumer and D. Klockow, *Aerosol Sci. Technol.*, 12 (1990) 953.
- 104 R. Niessner and C. Helsper, *J. Aerosol Sci.*, 16 (1985) 201.
- 105 R. Niessner and D. Klockow, *Int. J. Environ. Anal. Chem.*, 8, (1980) 163.
- 106 D. Seebacher, R. Bendura and D. Wornom, *Atmos. Environ.*, 14 (1980) 543.
- 107 U. Panne, F. Lewitzka and R. Niessner, *Analisis*, 20 (1992) 57.
- 108 O. Preining, *Atmos. Environ.*, 25A (1991) 2443.
- 109 J. Farmer and G. Dawson, *J. Geophys. Res.*, 87 (1982) 8931.
- 110 R. Niessner, *VDI Berichte*, 1059 (1993) 33.
- 111 W. Cofer, V. Collins and R. Talbot, *Environ. Sci. Technol.*, 19 (1985) 557.
- 112 U. Isacson and G. Wettermark, *Anal. Chim. Acta*, 83 (1976) 227.
- 113 C. Keith, *Beitr. Tabakforsch. Int.*, 11 (1982) 123.
- 114 K. Bächmann, I. Haag, U. Sprenger, K.-H. Steg, B. Bastian and A. Röder, *Fresenius' J. Anal. Chem.*, 340 (1991) 548.
- 115 R. Snyder, M. Tonkin and A. McKissick, *Evaluation of Methodology and Prototype to Measure Atmospheric Sulfuric Acid*, US Environmental Protection Agency, Publ. EPA-600/2-79-168, 1979.
- 116 D. Klockow and A. Teckentrup, *Int. J. Environ. Anal. Chem.*, 8 (1980) 137.
- 117 J. Townsend, *Philos. Trans. R. Soc. London Ser. A*, 193 (1900) 129.
- 118 J. Slanina, P. de Wild and G. Wyers, in J. Nriagu (Editor), *Gaseous Pollutants: Characterization and Cycling*, Wiley, New York, 1992, p. 129.
- 119 D. Kaplan, D. Himmelblau and C. Kanaoka, *Environ. Sci. Technol.*, 15 (1981) 558.
- 120 J. Durham, W. Wilson and E. Baker-Bailey, *Atmos. Environ.*, 12 (1978) 883.
- 121 R. Shaw, R. Stevens, J. Bowermaster, J. Tesch and E. Tew, *Atmos. Environ.*, 16 (1982) 845.
- 122 P. Dasgupta, *Atmos. Environ.*, 18 (1984) 1593.
- 123 R. Niessner and C. Helsper, DE-Patent 3409932, 1984.
- 124 M. Pack, A. Hill, M. Thomas and L. Transtrum, *Soc. Testing Mater., Spec. Tech. Publ.*, 281 (1959) 27.