

INSTRUMENTAL ANALYSIS OF POLLUTANTS

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Edited by

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Foreword

ENVIRONMENTAL MANAGEMENT SERIES

The current expansion of both public and scientific interest in environmental issues has not been accompanied by a commensurate production of adequate books, and those which are available are widely variable in approach and depth.

The *Environmental Management Series* has been established with a view to co-ordinating a series of volumes dealing with each topic within the field in some depth. It is hoped that this Series will provide a uniform and quality coverage and that, over a period of years, it will build up to form a library of reference books covering most of the major topics within this diverse field. It is envisaged that the books will be of single, or dual authorship, or edited volumes as appropriate for respective topics.

The level of presentation will be advanced, the books being aimed primarily at a research/consultancy readership. The coverage will include all aspects of environmental science and engineering pertinent to management and monitoring of the natural and man-modified environment, as well as topics dealing with the political, economic, legal and social considerations pertaining to environmental management.

J. CAIRNS and R. M. HARRISON

Preface

This book originated out of my own need for rapid access to basic information on the uses and limitations of a variety of instrumental techniques for the analysis of environmental pollutants. The complexity of environmental problems, the multiplicity of pollutants of current concern and the variety of media that must be investigated ensure that the practising environmental chemist must be at least familiar with a very wide range of analytical methods. Such information can, of course, be found in many excellent textbooks but these generally cover only one of the techniques commonly used for pollutant analysis. What appeared to be lacking was a single volume covering the principal methods in common use. Here, we attempt to describe these, with particular emphasis on their application to the analysis of environmental pollutants.

The first chapter by Casimiro Pio and Aristides Hall from the University of Aveiro, Portugal, gives a very detailed account of the methods used to collect samples from the environment, highlighting the major problem areas of contamination and representativeness. It includes a comprehensive literature review of over two hundred references, allowing easy referral to original research. Subsequent chapters describe various instrumental methods of analysis: Kevin Jones, Linda Owen and Ed Peace from the University of Lancaster discuss chromatography, Iain Marr and Malcolm Cresser from the University of Aberdeen optical spectroscopy and Ronald Mitchum from Battelle mass spectrometry. X-ray methods are described by Rene Van Grieken of the University of Antwerp and Andrzej Markowicz of the Academy of Mining and Metallurgy, Cracow, radiochemical methods by Alastair MacKenzie of the Scottish Universities Research and Reactor Centre, and electroanalytical techniques by Steve de Mora of the University of Auckland. The final chapter is by Stuart

Black of the US Environmental Protection Agency's Environmental Monitoring Systems Laboratory and describes methods of data analysis and presentation.

This international field of authors has been selected on the basis of their reputations in environmental chemistry and on their clarity of presentation. I hope the book fulfills its objective as a general source of information on the instrumental methods of analysis most commonly used for the determination of pollutants in the environment and that a wide range of readers will find it useful.

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Chapter 1

Sampling Methods

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1.1 INTRODUCTION

Pollution is said to exist when the concentration of a contaminant is large enough to interfere with the normal use of the environment and the well-being of biota, especially Man. In order to quantify the effects of these contaminants measurements of their concentrations have to be made. In some cases it is possible to make measurements directly within the environmental reservoirs themselves by deployment of appropriate probes, but more frequently a sample of that compartment will have to be isolated and adequately processed before a final measurement can be made. A knowledge of pollutant levels may help to trace the origin of contaminants and to follow their decay processes and effects in the environment. Sampling may also be necessary to ensure the enforcement and adequacy of control measures on emissions.

1.2 SAMPLING OF GASES AND AEROSOLS

1.2.1 Introduction and sampling considerations

Use of the olfactory organ is the most direct means Man has to evaluate the degree of air pollution and through smell the identification of several common atmospheric contaminants is possible. Unfortunately the method is non-quantitative and furthermore many compounds are odourless or

* Sadly Aristides Hall passed away during the preparation of this book.

toxic at levels lower than the olfact detection limit. Other methods are therefore necessary to evaluate air quality. For the majority of air contaminants, because of the low levels present even in polluted atmospheres the existent analytical techniques are not sensitive enough for direct measurement. Usually it is necessary to collect a sample from the atmosphere, with separation of the pollutant under consideration from other air constituents, producing a much more concentrated sample. After separation the mass of pollutant collected is evaluated by physical or chemical analytical methods and the concentration in the atmosphere calculated from the volume of air sampled, which should be measured with accuracy.

The air sample is not collected instantaneously but over a determined period, which can vary from some seconds to several weeks. The minimum period of sampling is frequently limited by the pump capacity, or by the efficiency of the pollutant/air separation process. To collect a mass of pollutant sufficient for analysis, various combinations of sampling time and flow rate are possible. The best choice takes into account the capacity of the pumping system and the objective of the measurement. Shorter sampling periods give more information about ambient level variations with time than longer periods, but as the work involved is proportional to the number of samples taken the shortest sampling period possible is not always the best choice.

A system for air pollutant sampling is generally formed, as shown in Fig. 1.1, by an air entry, a concentration unit, where the pollutant is concentrated and separated from other air components, a pump and a unit to measure the volume of sampled air.

The sampling of gases and particles can be performed without any tube entry by placing the collecting media on open filter holders. When this is not feasible tubing length should be as short as possible to reduce the residence time in the inlet line. Important chemical reactions for O_3 and NO_x in inlet tubing have been observed when the residence time was longer than 5 s.¹

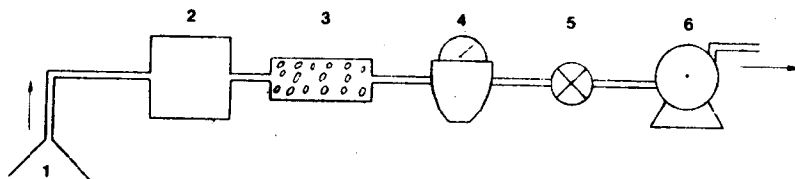


Fig. 1.1. Schematic figure showing a system for air pollutants sampling: 1, air entry; 2, separation and concentration; 3, pump protection; 4, air volume measurement; 5, flow control; 6, pump.

Interferences during passage through the inlet line are due to pollutant removal by physical or chemical sorption on tube walls, or therein deposited aerosols and humidity,² or to the release of chemical gaseous interferences from tube walls.³

Inlet interferences are much more probable for very reactive gases, such as HNO_3 . Depending on the pollutant to be measured the choice of tubing material will be different; generally glass is better than stainless steel and polyethylene, other plastic materials and Teflon better than glass.

Physical adsorption is important during sampling of very low gaseous concentrations. In these conditions even Teflon is not inert. To diminish adsorption the preconditioning of tubing material to the pollutant of concern before sampling is recommended. Physical adsorption is frequently reversible and desorption can take place when the concentration in the sampled air decreases, or an increase in temperature or a variation in relative humidity occurs.

1.2.2 Sampling of gaseous pollutants

1.2.2.1 Absorption by bubbling

One important fraction of air pollutants is present as gases or vapours. The separation and concentration of gaseous pollutants can be done by several techniques, of which absorption in a liquid solution, or hygroscopic solid, is one of the most common. Absorption is a solubility phenomenon controlled by the equilibrium partial pressure of the dissolved gas over the liquid surface and can be improved if the absorbed species undergoes an irreversible chemical reaction which produces a non-volatile compound.

The period of time necessary to produce stable compounds is a very important factor in the absorption of gaseous pollutants and the kinetics of the gas/liquid transfer is frequently the limiting mechanism in the absorption process. It is possible to reduce kinetic limitations by extending the period of contact between the sampled air and the absorbing solution, or by increasing the gas/liquid contact interface. This can be accomplished by changing the absorption geometry and/or lowering the sampling flow rate. Increasing the concentration and the volume of the absorbent solution will produce a similar effect.

To improve absorption efficiency a variety of bubblers with different formats have been used and recommended. The most simple and inexpensive are open bubblers, for example, the Dreschell bottle, which although less efficient for the collection of some pollutants, permit high flow rates with little pressure fall. Standard impingers, or absorbers with fritted glass diffusers, allow an enhanced efficiency due to an increase in the

air/liquid contact surface area, resulting from the formation of finely dispersed bubbles. These absorbers either introduce a large fall in pressure, limiting the maximum flow rate of sampling, or are difficult to clean and are expensive.

To measure air pollutant concentrations total absorption is desirable but not necessary. Measurement is still possible in cases of incomplete removal if the absorption efficiency is known and constant, or if two or more absorbers are used together and the air is sampled sequentially through each absorber. Atmospheric concentration can be calculated, from the volume of air sampled and the masses of pollutants collected in each absorber, through a very simple equation.⁴ For two absorbers in series the equation takes the form

$$C = M_1^2 / (M_1 - M_2) V$$

where C is the atmospheric concentration, V the volume of sampled air, and M_1 and M_2 the masses of pollutant collected in the first and second absorbers, respectively. This type of equation is only valid if the collection efficiency (relation between the mass of pollutant collected and the mass of pollutant in the gaseous phase prior to absorption) remains constant for each collector. Frequently, when sampling very low concentrations, this does not happen and the efficiency decays with the concentration.⁵

Collection by bubbling has been used for measuring a variety of inorganic and organic pollutants in source, industrial hygiene and ambient atmospheres. Sulphur dioxide has been sampled by absorption in hydrogen peroxide,⁶ with later analysis by titrimetry,⁷ or spectrophotometry as sulphate,⁸ in tetrachloromercurate,⁹ formaldehyde¹⁰ and oxaldi-hydroxamic acid.¹¹ The tetrachloromercurate/pararosaniline is still nowadays the reference method for the measurement of atmospheric SO_2 in the USA and EEC. NO_2 sampling has been accomplished by the Saltzman method,¹² absorption in guaiacol,¹³ triethanolamine/guaiacol¹⁴ and sodium arsenite.¹⁵ Ozone and other oxidants have been collected in KI solutions, with spectrophotometric analysis of produced iodine,¹⁶ or in indigodisulphonate.¹⁷ An ensemble of other absorption methods exist for the collection of most atmospheric pollutants, such as H_2S ,¹⁸ reduced sulphur,¹⁹ formaldehyde,^{20,21} isocyanates,²² chlorine,^{23,24} mercury vapours,²⁵ etc.

1.2.2.2 Impregnated filters

Sorption of atmospheric gaseous contaminants can be achieved by passage through a filter material impregnated with a chemical reagent which, by

reaction, removes and concentrates the pollutant. Collection with impregnated filters presents several advantages in comparison with bubbling/absorption. The material is less fragile and heavy to transport, occupies less volume, there are no problems of solution evaporation, automatization is easier and several pollutants can frequently be collected simultaneously by sequential filtration through different impregnated filters.

Generally, sampling is performed by forcing the air through a previously impregnated filter, placed in a proper filter holder. A suitable design is shown in Fig. 1.2. If no problems of collection efficiency exist, it is possible to use impregnated filters with high volume sampling, permitting measurements with shorter sampling periods, or of lower atmospheric levels.²⁶

Co-collection of aerosol particles can interfere with gaseous pollutant measurement if the adsorbed chemical product also exists in the particulate form. Prior removal of particulates by filtration eliminates this problem. The pre-filter material needs to be efficient in the removal of even the smallest particles and inert to the pollutant in question. Some filter substrates adsorb reactive pollutants. For example, glass fibre filters collect SO_2 and HNO_3 with high efficiency at low atmospheric levels.²⁷ Nylon filters are perfect absorbers of HNO_3 ,²⁸ and also efficiently absorb HCl .²⁹

Filter collected particles can also be a source of interference by reaction

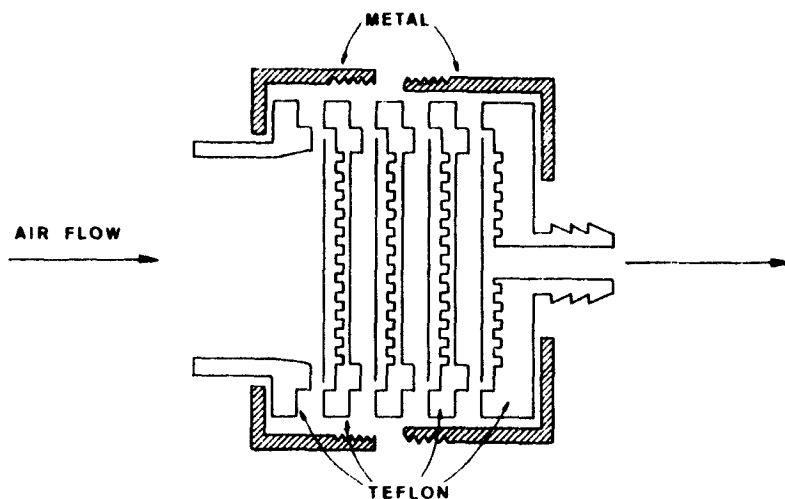


Fig. 1.2. Holder for sampling with impregnated filters.

with the gaseous pollutant, or volatilization of particulate compounds, an example of which is the volatilization of NH_4NO_3 aerosols and reaction of HNO_3 with basic particles during nitric acid sampling.³⁰

The efficiency of impregnated filters is frequently a problem when sampling atmospheric gaseous contaminants. Sampling efficiency is dependent on both the air velocity across the filter and gaseous phase concentration of the pollutant. Furthermore, the capacity of impregnated filters is generally limited: if sampling continues after exhaustion of the impregnated reagent, sorption efficiency is reduced drastically.³¹

Humidity can have a great influence on the performances of impregnated filters. Generally absorption efficiency decreases substantially for low RH (relative humidities): collection of SO_2 with filters impregnated with KOH , or K_2CO_3 , was reduced strongly for $\text{RH} < 30\%$.^{31,32} The efficiency of NaCl impregnated filters in HNO_3 sampling decreased from 80–90%, in the range 50–90 RH, to 50%, at 25% RH. Impregnated filters have been applied to the collection of a variety of gaseous atmospheric pollutants, such as HCl ,³³ H_2S ,³⁴ volatile arsenic,³⁵ HF ,³⁶ HNO_3 ,³⁷ acidic gases,³⁸ NO_2 ,³⁹ NH_3 ,⁴⁰ and SO_2 .⁴¹

Some filter materials can be used to collect gaseous pollutants without impregnation. Nylon filters have been extensively used for the sampling of HNO_3 and HCl . Nylon filters are efficient in the removal of acidic gases because they contain reactive centres formed by alkaline amino and amide groups.²⁸ Nylon filters exhibit retention efficiencies $> 90\%$ and loadings up to $30 \mu\text{g}/\text{cm}^2$ of HNO_3 , at RH 50–100%.⁴² Filter efficiency decreases to 50%, at 25% RH.²⁶

1.2.2.3 Denuder systems

Due to the presence of aerosol particles a number of interferences arise during the sampling of atmospheric gaseous contaminants. Prior removal of particulate constituents by filtration resolve some of these problems, but several interfering reaction processes can take place on the filter substract, such as sorption of reactive gases by the filter material, or deposited particles, and loss of collected volatilizable particle-phase compounds.^{30,43,44} Sampling with denuders overcome many of these aerosol interference problems. A denuder sampler consists usually of a narrow cylindrical long tube, through which the air sample is sucked. The tube internal walls have a chemical composition that make them an efficient sink for the pollutant molecules, which are sorbed on the surface along the tube length. So long as there is laminar flow inside the tube, the system permits gaseous pollutant collection without appreciably removing the suspended

aerosol particles. Under these conditions transport to the tube walls is achieved by diffusion mechanisms; the gaseous compounds, having high diffusion coefficients, are transported much more efficiently than aerosol particles which possess lower Brownian diffusivities.^{45,46}

Denuder sampling is highly sensitive and free from interferences but drawbacks are that impregnation and extraction processes are labour intensive, and that low laminar flow rates are usually needed to obtain efficient removal and separation. To obviate repetitive arduous coating and extraction processes the so-called denuder difference technique was developed. The method has been extensively applied to the sampling and differential analysis of nitric acid and particulate nitrates, and consists of parallel filtration of the air sample through two nylon or impregnated filters, in which both particles and gaseous compounds are collected together. One of the total collecting filters is preceded by a denuder, where the gaseous component is removed, and collects the particulate phase only. The other filter samples air directly from the atmosphere, removing particulate plus gaseous contaminants. The mass and concentration of the gaseous pollutant can be calculated, by difference, from the analysis of the two filter deposits.^{43,47}

Denuder techniques have been used to collect and remove a variety of gaseous atmospheric contaminants. Denuder tubes coated with tungstic acid or tungstic oxide,⁴⁸ $\text{Al}_2(\text{SO}_4)_3$,⁴⁹ or MgO ,^{43,44} or lined with nylon sheets,⁵⁰ were employed to sample HNO_3 . SO_2 was absorbed in denuder systems impregnated with PbO_2 ,⁵¹ K_2CO_3 ,⁵² or tetrachloromercurate.⁵³ NH_3 was collected in tubes covered with oxalic or phosphoric acids,⁴⁵ or ion exchange membrane liners.⁵⁴ Denuder methods have also been applied to the measurement of HCl ,⁵⁵ HF ,⁵⁶ organic vapours,⁵⁷ NO_2 ,⁵⁸ ethylsulphates,⁵⁹ aniline⁶⁰ and nitrous acid.⁶¹

In the last few years great emphasis has been given to the utilization of annular denuders in gaseous air pollutant sampling. Annular denuders are formed by two concentric tubes, maintained in place by proper spacers, the air circulating in the annular space between the internal and external tubes. The outer surface of the internal tube and the inner surface of the external tube are coated with reactive chemicals and both serve as sinks to the gaseous pollutant in consideration. Annular denuders are more efficient than single tube configurations, as has been demonstrated theoretically,⁶² permitting sampling at higher flow rates and therefore shorter sampling periods. Examples of typical annular denuder configurations are shown in Fig. 1.3.

Denuder methods have been employed to pre-remove gaseous

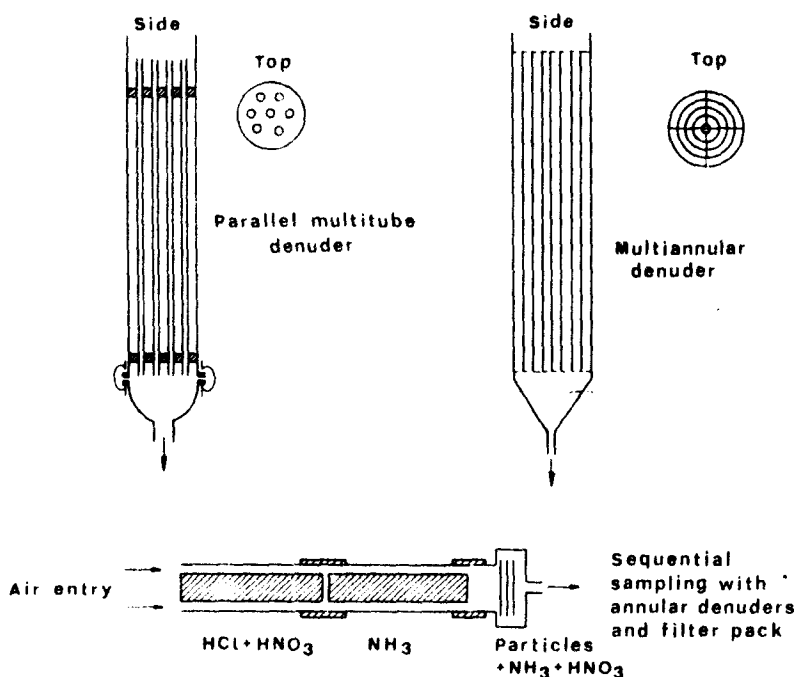


Fig. 1.3. Examples of multitube, annular and multiannular denuders.

interferences during atmospheric particulate sampling. A denuder, where the gaseous interferent is adsorbed without aerosol concentration and composition modification, can be placed ahead of the particle collector or analyser. The principle has been applied to the sampling of acid particles.⁶³ A denuder coated with oxalic acid served to remove NH_3 , prior to acidic particle collection in a low volume impactor, with the aim of eliminating acidity neutralization during sampling.⁶⁴ A similar system was employed in the sampling of sulphate aerosol with a virtual impactor.⁶⁵

1.2.2.4 Adsorption

Adsorption is a surface phenomenon consisting of the concentration and bonding of gas molecules on the surface of a solid substance. Gaseous pollutant sampling by adsorption has increased in recent years with the development of gas chromatographic techniques, being presently the most commonly used method for the collection of atmospheric organic gases and vapours.