

# Recent Advances in Environmental Analysis

Edited by  
Roland W. Frei  
The Free University, Amsterdam

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CURRENT TOPICS IN ENVIRONMENTAL  
AND TOXICOLOGICAL CHEMISTRY

VOLUME TWO

# Recent Advances in ENVIRONMENTAL ANALYSIS

*Edited by*

R. W. FREI

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RECENT ADVANCES IN  
ENVIRONMENTAL ANALYSIS

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CURRENT TOPICS IN ENVIRONMENTAL AND TOXICOLOGICAL  
CHEMISTRY

This is a series of books based on papers from the two journals, *International Journal of Environmental Analytical Chemistry* and *Toxicological and Environmental Chemistry Reviews*

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Volume 1 ANALYTICAL ASPECTS OF MERCURY AND OTHER  
HEAVY METALS IN THE ENVIRONMENT

*Edited by R. W. Frei and O. Hutzinger*

Volume 2 RECENT ADVANCES IN ENVIRONMENTAL  
ANALYSIS

*Edited by R. W. Frei*

## Preface

With the exception of four contributions, this book contains selected papers which have been presented at the 8th Annual Symposium on the Analytical Chemistry of Pollutants, held in Geneva, Switzerland in April 1978. They have appeared in issues of *International Journal of Environmental Analytical Chemistry* and *Toxicological and Environmental Chemistry Reviews*. Since the contributions are interspersed in different issues and not readily available to a large segment of readers interested in this subject, it was thought useful to collect them in this volume.

The content is therefore not as homogeneous as one would prefer, although the papers have been arranged according to the two major subjects—air pollution and water pollution analysis. Inorganic and organic pollutants work has also been grouped together as far as possible within the two major subject areas and papers of a more general overview or review nature are preceding the more specific subjects.

Obviously this book is not intended as a comprehensive overview in environmental analysis, but it gives an up-to-date account of the state-of-the-art in several more specific subject areas as they have been presented within a recognized and established symposium series on pollutants analysis. The advanced instrumentation used is discussed by reputable experts. Sampling and monitoring problems receive good attention. Applications of a more specialized type or data from small geographical areas are discussed in some papers but still permit workers in other areas to draw broader conclusions. While multielement techniques seem to be gaining more attention in inorganic trace analysis, it is speciation which comes very much into focus for organic pollutants as well as their metabolites. Automation, computerized structure elucidation and fingerprinting techniques very much set the tone in today's analytical world and this is also reflected in several papers here.

Briefly, this volume might give some ideas and valuable information to many researchers active in this area and can be of interest to a wide segment of workers in government laboratories, regulation agencies and applied interdisciplinary groups in industries and universities which have a stake in environmental problem solving.

R.W.F.

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## AIR POLLUTION



# Advanced Techniques in Air Pollution†

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*(Received May 19, 1978; in final form November 22, 1978)*

Specific usage of neutron activation analysis, charged particle analysis,  $\gamma$  photons analysis, G.C.M.S. coupling, stable isotope dilution techniques, are discussed.

Dust collected on filters, oxygenated compounds in exhaust gases from car engines, nitrogen oxides, have thus been determined.

Special calibration methods for ozone, and remote detection by Lidar Raman are also described.

**KEY WORDS:** Air pollution, activation analysis, charged particle analysis, Lidar Raman, analysis of nitrogen oxides, ozone, exhaust gases, dust particles.

## INTRODUCTION

Advances in analytical techniques have been such during the past decades that competition between them has become very close.

We no longer live at a time when to perform a given analysis—say  $O_2$  or  $N_2$  is a gas—a single technique and a single apparatus was available on the market. Now problems have to be defined much more precisely in order to get a correct solution and it is appropriate to point out a number of essential parameters (see Table I) that should always be discussed when describing analytical procedures, in order to make intercomparisons possible or easy.

a) Specific aim of the work—Element (or molecules) to which the technique can be applied.

Many papers are obviously the result of work planned merely to extend the range of a technique. It is the duty of the author to state if, provided

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†Paper presented at the 8th Annual Symposium on the Analytical Chemistry of Pollutants, April 78 Geneva, Switzerland.

the equipment exists, it may be used, for other purposes than the one it was originally intended for, but it is also up to him to inform the reader whether, for the new purpose, this technique is the preferred one or not.

TABLE I  
Essential parameters that should always  
be discussed when describing analytical  
procedures

---

- SPECIFIC AIM
- CONCENTRATION RANGE
- ABSOLUTE QUANTITIES INVOLVED
- PRECISION
- ACCURACY - CALIBRATION METHOD
- LIMITING FACTOR
- RESPONSE TIME
- POSSIBILITY FOR CONTINUOUS - REMOTE - AUTOMATIC ANALYSIS
- COMPARISON WITH OTHER METHODS

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- b) Concentration range within which the technique can be used, and particularly detection limits.

These should be expressed *both* in concentration *and* total amount of matter detectable. Too often only one of these two quantities is stated and the weight or volume of samples to be handled is not often mentioned.

- c) Precision and accuracy of the method

Attention should be given to make clear whether calibration involves using known reference samples or not, and if so how they are procured.

- d) Limiting factors, such as possible interferences, surface contamination, sample inhomogeneity, should always be quoted.
- e) Other characteristics such as the time it takes to analyse samples, the amount of work it requires, the cost, are often interesting.
- f) Akin to these one should mention, when relevant, the possibility of adapting the method to continuous or to remote or automatic analysis.
- g) Finally comparison of the merits of the advocated methods with the more heavily competing ones should always be attempted.

Unfortunately I cannot follow this plan of discussion rigorously and must give only partial information on the many methods to be dealt with; interested readers can apply for further details.

## I—ANALYSIS OF AIR DUST COLLECTED ON FILTERS

Specific aim: analyse collected particles on filters.

The use of activation or charged particle analysis is investigated, because of the following possibilities of the methods.

- a) non destructive analysis of the dust that avoids chemical treatment, thus eliminating sources of error.
- b) low detection limits for some elements, enabling small absolute quantities to be analysed.
- c) easy calibration of the results without reference samples.
- d) possibility of analysing simultaneously, or in rapid succession, a number of filters.

### I—1 Neutron activation analysis

Filters located at “strategic” points in the Paris area are routinely analysed by the “*Laboratoire Central de la Préfecture de Police*”. Amounts of dust corresponding to the filtration of 30 to 60 cubic meters are collected, the weight is a few hundred micrograms.

The elements Cd and Pb are measured by the Laboratoire Central using atomic absorption.

Neutron activation can provide supplementary data on:

Al, Au, Br, Ca, Cd, Cl, Co, Cr, Eu, Fe, K, La, Mn, Na, Cu, Sb, Sc, V, Zn.

—Absolute quantities necessary for detection range from 0.05 ng (Eu) to 150 ng (Co), Iron is less sensitive (36  $\mu\text{g}$  are necessary). Total sample as small as required by these absolute quantities can be analysed.

—Precision is  $\pm 10\%$ .

—Accuracy is of the same order of magnitude.

—Calibration is obtained by activation of pure elements or salts.

—Response time is tied with the necessary irradiation length, which is often thought to be of the same order of magnitude as the half-life.

Although the above mentioned elements have half lives from 2 minutes to 243 days, the irradiation time can be chosen either 5 minutes or 2 hours. The possibility exists also to analyse simultaneously many samples with little need of operator time, this brings down the expected cost of analysis to amounts comparable with that of other methods.

Comparison of results for Cadmium and Lead by activation and conventional methods are given in Table II.

Discussion: Neutron analysis is adapted to many analysis of a few elements. Accuracy is good, especially when results correspond to the bulk analysis of the sample (Cadmium determination).

TABLE II

Analysis of air dust collected on filters  
Comparison of results for Cadmium and Lead by activation and conventional methods

FILTER	CADMIUM (ng/m <sup>3</sup> )		LEAD (μg/m <sup>3</sup> )		
	SACLAY (neutron activation)	PARIS	SACLAY		PARIS
			(γ, n)	(α, X)	
H1	< 1,5	2,9	1,3	1,3	0,9
H2	13,8 ± 0,3	5,9	1,8	1,7	1,8
H3	2,6 ± 0,3	4,1	0,5	1,0	0,9
V1	4,7 ± 0,5	3,7	1,1	1,0	1,4
V2	1,3 ± 0,1	4,7	2,0	1,7	1,6
V3	5,6 ± 0,6	3,3	0,5	0,9	0,9
GRATING N° 1	< 3	0,6			1,0
GRATING N° 2		0,2	0,6		0,8
GRATING N° 3	≤ 0,8	0,8	2,6		1,8
GRATING N° 4		15,0	5,3		5,1
GRATING N° 5		0,8	0,7		0,6

NOTE : LOSSES PROBABLY WERE CAUSED BY CUTTING THE FILTERS

H<sup>3</sup> AND V<sup>3</sup> FOR (γ, n) ANALYSIS

## I—2 Charged particle analysis<sup>1</sup>

Although differences in techniques are considerable, the use of He ions produced by a several MeV accelerator to induce X-ray fluorescence has much the same advantages as neutron activation.

In addition

I—2.1. It applies also conveniently to elements such as Lead, Titanium, Sulphur.

The response time is negligible, as results are obtained during the irradiation itself.

I—2.2. Samples can be irradiated in series, in very rapid succession (one to ten minutes analysis time per sample).

Figure 1 shows the irradiation chamber enabling 24 samples to be irradiated in succession.

Figure 2 shows an overall view of the experiment.

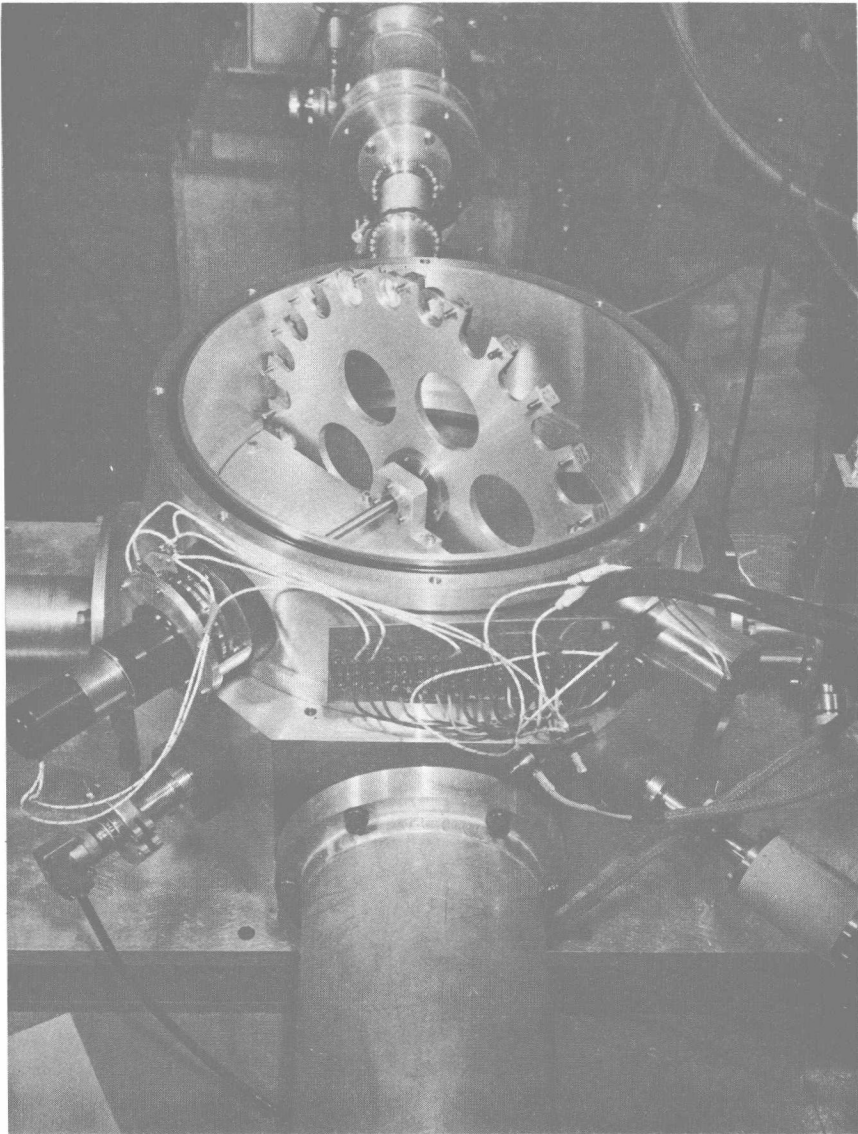


FIGURE 1 Analysis by charged particle induced X-ray fluorescence: target chamber.

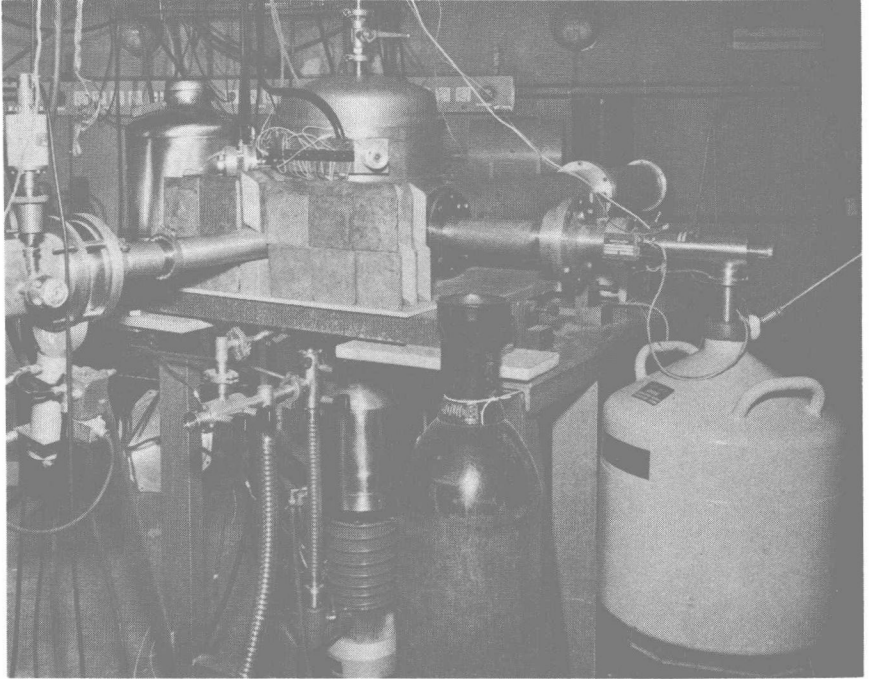


FIGURE 2 Analysis by charged particle induced X-ray fluorescence: Overall view of the experiment.

Figure 3 shows how the intensity of the Selenium  $K\alpha$ -ray, or the Gold  $L\alpha$ -ray, varies with the energy of protons or  $\alpha$  particles.

Figure 4 shows an X-ray spectrum obtained on a filter sampling bombarded by 1.5 MeV protons.

Table III shows the result of the analysis of a filter after sampling of a marine atmosphere, obtained by activation analysis by charged particles.

### I—3 Activation by $\gamma$ photons

$\gamma$  produced by bremsstrahlung of energetic electrons on heavy element targets can provide also multielement analysis. Characteristics of the method are closely related with that of charged particles use with the following differences.

Granulometry of samples that may have to be taken into account in the former is no factor to be considered here.

Heavy elements such as Lead can be analysed with good detection limits ( $10^{-3}$   $\mu\text{g}$ ) and specificity but require several hours irradiation time.



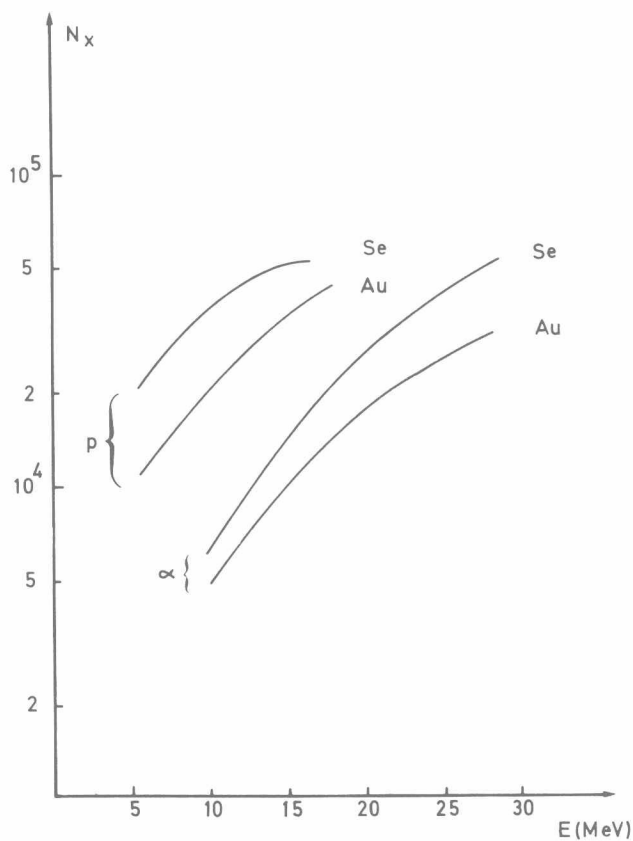


FIGURE 3 Variation of the Se K $\alpha$ -ray and Au L $\alpha$ -ray intensity with the energy of protons or  $\alpha$  particles.