Progress in Analytical Chemistry
Volume 5

chemical analysis of the environment

and other modern techniques

edited by
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J. L. Lambert, and G. Zweig

PROGRESS IN ANALYTICAL CHEMISTRY
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CHEMICAL ANALYSIS OF THE ENVIRONMENT
AND OTHER MODERN TECHNIQUES

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PLENUM PRESS • NEW YORK–LONDON • 1973

Library of Congress Catalog Card Number 73-82575

ISBN 0-306-39305-0

A Division of Plenum Publishing Corporation
227 West 17th Street, New York, New York 10011

United Kingdom edition published by Plenum Press, London
A Division of Plenum Publishing Company, Ltd.
Davis House (4th Floor), 8 Scrubs Lane, Harlesden, London NW10 6SE, England

Printed in the United States of America

PREFACE

With the rise in general awareness of the effects of trace chemicals in the environment on man's health, it has been realized that traditional methods of analysis are often inadequate. Reliable analyses are needed in the fractional parts-per-million range of contaminants in condensed phases, and of the order of micrograms per cubic meter in air. Trying to get meaningful answers regarding such minute amounts raises cogent problems in all stages of an analysis.

It is most appropriate, therefore, that the 1971 Eastern Analytical Symposium should have four half-day sessions devoted to this general field. Two of these, entitled "Trace Metals in the Environment," were assembled by Dr. Kneip, one on "Pesticides in the Environment: Recently Discovered Analytical Problems," by Dr. Zweig, and one on "The Determination of Anions in Water," by Dr. Lambert. Together, these reports furnish a fairly complete picture of the present state of environmental analysis.

The remainder of this volume is devoted to pharmaceutical analysis, a diversified field in which nearly all analytical methods find a place. Partly because of this multiplicity of techniques, and partly due to the large number of samples which must be examined in connection with the manufacture, biological testing, and clinical application of pharmaceutical preparations, this area is particularly appropriate for the introduction of automation. The objective, broadly, is to speed up multiple analyses without the sacrifice of accuracy.

The 1971 Eastern Analytical Symposium was fortunate to be able to present two sessions in this field: "Current Topics in Pharmaceutical Analysis," under the chairmanship of Dr. Cohen, and "Automated Analysis," chaired by Dr. Ahuja. The Editors wish to take this occasion to thank the session chairmen and the individual authors for their contributions to this Symposium.

Galen W. Ewing

Ivor L. Simmons

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PITFALLS IN THE DETERMINATION OF ENVIRONMENTAL TRACE METALS

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INTRODUCTION

The growing realization of the importance of even extremely small amounts of metals in the environment has led to an ever increasing demand for determination of these metals at trace-level concentrations. The resulting flood of data has evoked a mixed response from members of the public, scientific and otherwise. Some accept the results unhesitatingly, particularly if in conformity with their prejudices, and make them the basis for legislative action, prosecution, indifference or panic. Others deny that quantities so small can be measured with any degree of meaning, while still others are selectively skeptical, or simply bewildered. In recognition of this state of affairs and of the importance of reliable and interpretable data in the many fundamental scientific and social problems related to the presence of trace metals in the environment, I would like to examine with you the present state of the art and its implications.

RELIABILITY OF TRACE METHODS

In trace level analysis we are dealing with concentrations no greater than the parts per million level and more often today with parts per billion or less. Our concern is with all phases of the environment: air, water, solid

earth and the biosphere, and includes indigenous metals as well as those deriving from pollution. In order to measure at the parts per billion (i.e., micrograms per kilogram) level, methods of high sensitivity and selectivity are needed. They must be applicable to real-world samples, accurate and reliable, and preferably they should also be convenient and economical. According to the literature there are several methods which meet all the essential requirements and indeed we find widespread adoption of atomic emission and absorption spectroscopy and colorimetry as well as significant use of neutron activation, electrochemical methods and mass spectrometry. The authors of many papers assure us that the necessary precision and accuracy (usually quoted as in the range of 5% at worst down to a few tenths of a percent under the most favorable conditions) is readily achieved in their laboratories, and we gain the impression that while minor adjustments may have to be worked out for applications to specific systems, the major problems have been identified and solved.

Now it is always prudent to be somewhat skeptical of broad claims made by enthusiastic authors. Such claims are, in general, made honestly, but not on the basis of particularly wide experience. In order to learn what a method might do for you, it is best to look at what it does do in the hands of a cross section of competent workers under circumstances where they have no idea of what the correct value might be. This is best accomplished by distributing portions of a carefully prepared and preserved unknown sample to a number of qualified analysts to run independently and report under code for comparison. A number of such studies have been made, particularly for the determination of trace metals in water, and it is rather instructive to look at some of the results.

In Table 1 is summarized some of the findings in a cooperative interlaboratory study of the determination of trace metals in water using conventional, widely accepted colorimetric methods (1). The 79 cooperating groups, which were all participating voluntarily, were professional water laboratories representing federal, state, municipal, academic, industrial and private organizations. Each had the same synthetic sample, which was run in triplicate, and the averages were used for comparisons between laboratories. Results which were clearly affected by some gross error, such as a factor of ten in dilution, were omitted from the

TABLE 1

STANDARD COLORIMETRIC TRACE METAL PROCEDURES FOR WATER
RESULTS OF INTERLABORATORY COMPARATIVE STUDY

Element	Labs	Added p.p.m.	Ave Found	Range p.p.m.	Std Dev %	Error %
Ag	14*	0.15	0.049	0.00-0.10	20	-67
Al	44	0.50	0.400	0.00-0.81	30	-20
Cd	44	0.05	0.053	0.02-0.11	20	+ 6
Cr	31	0.11	0.092	0.00-0.21	36	-16
Cu	25	0.47	0.514	0.26-0.72	19	+ 9
Fe	40	0.30	0.337	0.08-0.53	30	+12
Mn	33*	0.12	0.118	0.03-0.21	42	- 2
Pb	42*	0.07	0.076	0.00-0.20	43	+ 9
Zn	46	0.65	0.818	0.34-1.3	23	+26

comparisons, and an asterisk indicates the fact of one or more such omissions. The table gives the derived estimates of the precision and accuracy found for the single most commonly used colorimetric method for each of the elements in the sample. A limited amount of data for less commonly used colorimetric and other methods showed a similar pattern.

One is struck immediately both by the low precision of the results and the frequency of large absolute errors. The data on the ranges of values reported reveal that it was not an unusual event for a constituent to be missed entirely. In view of the fact that averages of triplicates should be more reliable than single values, and averages of 14 to 46 laboratories should be vastly more reliable than the observation of a single laboratory, one is forced to the conclusion that lacking supporting evidence, a single value reported by one laboratory under the conditions of this study carries very little weight indeed. This is a particularly disquieting thought in view of the fact that the vast majority of existing data on trace element distribution consists of single measurements by single laboratories without benefit of any cross comparisons.

In Table 2 is given some results on the determination of iron taken from a recent intercalibration study on trace elements in sea water conducted by Brewer and Spencer at the Woods Hole Oceanographic Institution (2). Thirteen

TABLE 2

INTERCALIBRATION STUDY: DETERMINATION OF IRON (µg/Kg) IN TWO SAMPLES OF SEA WATER

	SAMPLE A		SAMPLE B		RATIO
METHOD	MEAN	SD%	MEAN	SD%	B/A
AAS	8.6	3	14.7	7	1.7
AAS	6.7	27	7.9	39	1.2
AAS	7.4	-	15.1	-	2.0
AAS	5.87	4	9.74	6	1.7
AAS	4.3	4	7.05	13	1.8
NAA	9.7	19	15.3	10	1.6
NAA	7.28	71	4.0	6	0.6
NAA	22	-	22	-	1.0
NAA	5.7*	9	5.1	-	0.9
COL	11.7	5	17.0	6	1.5
COL	7.67	3	13.33	4	1.7
PAA	28.3	4	45.0	4	1.6
NR	31.6	48	32.7	4	1.0
MEAN	12.2		16.6		1.4
MEAN**	7.7		12.5		1.6

* Excludes one value
** Only replicated data with SD<20%

laboratories undertook to measure the iron content of three subsamples taken from two large primary samples of sea water, each laboratory using its own standard method. Five used chelation-solvent extraction followed by atomic absorption spectroscopy, four chose neutron activation analysis of dried sea salts, two colorimetric procedures, one coprecipitation with lanthanum hydroxide followed by atomic absorption, and one unreported. Again a striking lack of agreement is observed both in the absolute values obtained and in the precision of the data. The range of values reported was, for both primary samples, 3.7 to 47 µg/kg, and the ratio of the two sample concentrations ranged over more than a factor of three. Similar patterns were obtained for the determinations of cobalt, copper, lead, manganese, nickel and zinc.

The discovery of a situation such as this must necessarily come as a shock to anyone accustomed to accepting at face value typical published claims for the precision and accuracy of trace analytical methods. Lest it be assumed that the explanation is simply a particular ineptness on the part of water chemists, let me hasten to point out that the same mournful lack of consistency has appeared when geochemists have studied trace metals in standard rock samples, when industries have cross-checked control laboratory performance; and when clinical laboratories have collaborated in comparing unknown cholesterol samples. In actual fact, behavior of this sort is to some degree characteristic of all experimental measurements. Most investigations are done in such a way that the discrepances do not come to light, but when careful observations are made--especially with demanding operations such as trace metal analysis where the "signal to noise ratio" is unfavorable--there is no overlooking the effect. The path of the trace analyst is strewn with hidden pitfalls, to say nothing of a generous number of more obvious potholes, and it is profitable at this point to identify the more important ones.

SOURCES OF VARIABILITY

First, it must always be kept in mind that the analysis of real samples, the final result is the product of a multistage process, each step of which is an input channel for error. At the outset, one is faced with the problem of sample definition--what is the sample we are getting? Is it representative and/or homogeneous, and is it appropriate to answer the chemical questions which prompt its taking? Then there is the matter of physically taking the sample itself, sometimes no mean feat. Normally there is a period of storage, somewhere, in something, for some period of time. The sample will be handled in the course of treatment and it will often be measured in a quantitative subsampling step. There is often chemical treatment of one sort or another and there may be a separation and/or concentration process involved. The determinative step, chemical or physical, takes place and it must be coupled with some sort of analog-to-digital conversion, be it nothing more complicated than reading a buret. The information from a calibration operation must be fed in, and the final step of the process is the sometimes surprisingly subjective expression and interpretation of the result.

For evaluating the dependability of our results, we need information on the precision and accuracy of the overall analytical process under actual conditions of use. All too often the information in the literature is based on a shamefully unrealistic approach. The proud author of a new method is likely to have measured his reproducibility under completely artificial conditions, if indeed he has done more than demonstrate the repeatability of the determinative step on a known sample. With the best of intentions he may do everything in his power to avoid encountering the natural variability in his method, even to discarding some of his observations because "obviously something must have gone wrong with them." Data based on the repeatability of a method in the hands of a single person taking identical portions of a clean standard solution to measure all in one afternoon are irrelevant to the situation of the environmental chemist. Under supposedly identical conditions, a method will often give significantly different results on different days, at different times of the day with different batches of reagents, with presumably identical samples from different sources, and in the hands of different people. This is simply a consequence of the fact that the number of factors which affect a method or a measurement is enormous. The major ones are usually obvious, so we are aware of them and can make some effort to control or avoid them. Some factors vary so little or so rarely in our working environment that we overlook them, or else the trouble goes away before we have the time to figure out what is causing it. Many factors are actually quite significant, yet we are unaware of their influence simply because we have never set up a situation which would reveal their effects. When we do, we are likely to get results like those in the laboratory intercomparison studies I have just described.

We are accustomed to the idea that instrumental measurements are susceptible to physical factors such as temperature, but we tend to overlook or forget that there are so many such factors. I have at one time or another run across measurements which were unexpectedly but noticably responsive to magnetic fields, static charge, variations in line voltage and frequency, the intensity and spectral distribution of room lighting, humidity, the functioning of other not necessarily nearby instruments, the pressure in the water mains, vibration, the electrical conductivity of cooling water, the cycling of the central air conditioning system

and, literally, the phase of the moon. Chemical reactions have their own peculiarities many of which are even less predictable than those of instruments. It should be sufficient to point out that even the order in which the starting materials are added to a reaction mixture may affect not only the rate of formation and the purity but even the identity of the principal product.

Personal equation is a well recognized component in experimental differences. That some people have a knack for making instruments or procedures work, while others can't get the hang of it although both seem to be doing just the same things, is a phenomenon familiar to all of us. It emphasizes the fact that there are many unidentified factors involved in our operation which we sometimes adjust to quite unconsciously so we are able to do things successfully although we cannot explain how. Another important aspect of personal equation is the variation between individuals in reading instruments and estimation of final digits by interpolation. Gysel (3) in a study of the unconscious number preferences of technicians estimating the last significant figure in microchemical weighings found that the statistically predicted equal frequency of occurrence of the digits 0 to 9 was not even roughly approached. Instead, each individual showed a characteristic pattern of preferences in which the frequencies of appearance of some digits differed by factors as high as 5 or 6. These characteristic individual patterns sometimes showed remarkable stability and reproducibility from year to year. Figure 1 shows the frequency distribution of a set of 1050 last digit estimations taken from the laboratory notebooks of one of Gysel's technicians, and is quite typical. The probability of obtaining such a large deviation from the equal frequencies which should be observed in drawing from a uniform population is less than one in a million. Gysel found the same individual patterns of number preference in weighing, reading verniers, colorimeter and flame photometer scales, and in estimating the last digit in slide rule calculations. I have verified the reality of the effect by examining the last digit in buret readings recorded in student notebooks. Clearly this phenomenon can be a serious source of bias when one is straining to get the second figure in a two-significant figure result, and seems to be present—no matter how objective we think we are—in all of us.