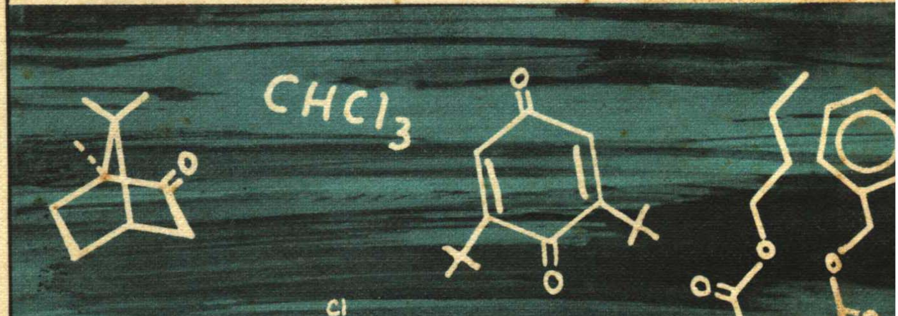
Lawrence H. Keith

Advances in the Identification & Analysis of Organic Pollutants in Water Volume 1



ANN ARBOR SCIENCE

Advances in the Identification & Analysis of Organic Pollutants in Water

Volume 1

Edited by
Lawrence H. Keith

ANN ARBOR SCIENCE
PUBLISHERS INC /THE BUTTERWORTH GROUP

230 Collingwood, P.O. Box 1425, Ann Arbor, Michigan 48106

Library of Congress Card Catalog Number 81-68031
ISBN 0-250-40397-8

Manufactured in the United States of America

Butterworths, Ltd., Borough Green, Sevenoaks, Kent TN15 8PH England

PREFACE

Five years ago the first book on identification and analysis of organic pollutants in water was published. The genesis of that book was primarily a symposium of the same title held during the First Chemical Congress of the North American Continent in Mexico City. In the ensuing years, advances in the identification and analysis of organic pollutants in water have continued at an accelerated pace. Thus, it was only natural that the second symposium on this subject be held during the Second Chemical Congress of the North American Continent in Las Vegas, Nevada.

As in the initial publication, all but a few of the chapters in this book were contributed by the many distinguished authors who participated in that symposium. These scientists represent the leading analytical and environmental chemists on the North American continent and abroad. The advances described in these volumes represent the current state-of-the-art methodology for analysis of organic compounds, often at trace levels, in all types of water samples ranging from the very pure (drinking water) to the extremely "dirty" (untreated industrial wastewaters).

Knowledge of specific organic pollutants in water has increased exponentially over the past five years. This has been largely due to the methodology that has enabled these analyses to be conducted efficiently, scientific and governmental interest in the subject, and the fact that knowledge of the subject area five years ago was minimal. Despite intense work over the past five years, little "brand new" methodology has been introduced for analyzing trace levels of organic pollutants in water. However, refinements of the techniques then in use have made these methods even better and more efficient and have contributed significantly to our current methodology. Solvent extractions, resins or gas purging techniques are still the primary methods used to concentrate organics from water, and gas or high-pressure liquid chromatography with various detectors (including mass spectrometers) are still used to identify and quantify them. One new method, using tandem mass spectrometers (MS/MS), offers promise of analyzing for specific compounds in a complex matrix without the tedious and expensive concentration and separation requirements of conventional instrumental analyses. At present, however, MS/MS is quite expensive and still in its initial stage of exploration and exploitation.

One significant difference in the direction of environmental analyses today, as compared to five years ago, is the emphasis on improving both accuracy and reliability of quantitative data. This is being accomplished through more stringent quality assurance/quality control programs and the use of numerous and more sophisticated quantitative methods such as the use of multiple internal standards, often isotopically labled. Five to ten years ago, compounds identified in water often were not even quantified. Two driving forces appear to be the primary reason for this change of emphasis: (1) legal and regulatory ramifications and (2) the realization that adverse effects of all organic pollutants are related to their concentration in water.

Predictably, environmental analyses seem to be moving increasingly into the lawyer's domain. This makes life more complicated for analytical environmental chemists, who have the sometimes difficult problem of explaining that 18 and 24 parts per billion are really the same number (within experimental error), or that it is not a worthwhile environmental goal to try to reduce the pH of water to near zero. Nevertheless, the overall effect of these legal and regulatory pressures on scientists is a positive one. It requires an emphasis on careful work and on improving the accuracy and precision of measurements that are often pushed to their limits. But, past history has shown that growth and improvement in most disciplines increase more rapidly when pressure is applied.

Another significant difference in the direction of environmental analyses today is an emphasis on automation. Analyses of organic pollutants in water are becoming more prevalent as a result of new regulations and modifications of old ones (e.g., the National Pollutant Discharge Elimination System industrial wastewater discharge permits). The result is an increasing competitiveness and pressure to produce large numbers of analyses for decreased costs. This, of course, is a natural and healthy trend as long as the pressure for cheap analyses does not compromise accuracy and precision, and it is realized that not all objectives can be met using cheap analyses for a "laundry list" of pollutants.

There still remains much to be learned about the kinds of pollutants in water and the chemistry involved. Until we have the correct methodology for analyzing organic compounds, we will continue to miss some even though they may be literally right under our noses. An example is the recent discovery that dihaloacetonitriles are apparently a new class of anthropoaqueous pollutants in drinking water. Despite the fact that countless chemists have been analyzing for trihalomethanes in drinking water these past five to six years, the fact was missed that dihaloacetonitriles are also probably present in many of those same samples. Why? Because the methodology being used was not conducive for the analysis of dihaloacetonitriles.

I think we have reached the stage in the evolution of analysis of organic pollutants in water where the easy methods and the easy compounds have been exploited. Now we will have to work harder and be more clever to produce newer and better methodology with which to uncover the more difficult organic pollutants. Is this necessary? I think so. How can one make an intelligent decision until the pertinent facts are known?

Five years ago, I said, "much still remains to be done. We have only begun to learn and to apply what we have learned to provide a better and cleaner environment." I think we have applied what we have learned very well over the past five years. We know a great deal more about the prevalence, distribution and concentrations of organic pollutants in water now than we did then. However, much still remains to be done. Now we must refine our techniques, verify our quantitative accuracy and turn our attention to developing new methodology for analysis of the more elusive and difficult organic pollutants.

L H Keith

L. H. Keith

Lawrence H. Keith's current technical interests continue to center around analyses of organic pollutants in the environment, with emphasis on developing new methods or improving on old ones. Techniques for the safe handling of carcinogenic and/or extremely toxic materials are also an important aspect of Dr. Keith's current research efforts.

Dr. Keith was formerly involved with the selection of many of the initial U.S. Environmental Protection Agency's 129 Priority Pollutants, and he also helped to formulate some of the initial methodology for analyzing for these pollutants. He is presently involved in the selection of representative compounds and methodologies for the Appendix C Priority Pollutants and for the synfuel industry.

A member of the American Chemical Society's Division of Environmental Chemistry Executive Committee, Dr. Keith has served as secretary, alternate councilor, program chairman and chairman of the division. He is also a past chairman of the Central Texas Section of the American Chemical Society and past secretary and councilor of the Northeast Georgia Section of the American Chemical Society.

In other professional activities, Dr. Keith served as Vice-Chairman of the Gordon Research Conference on Environmental Sciences: Water, and is currently a delegate of the U.S. National Committee to the International Association of Water Pollution Research. He is also a member of the National Research Council Committee on Military Environmental Research.

Dr. Keith and his wife, Virginia, reside in Austin, Texas.

Ronald G. Webb was born in Weatherford, Oklahoma, and began his college studies at the Central Christian College in Oklahoma City (1957–1959). He completed his BA at David Lipscomb College in Nashville, Tennessee (1961), and then went on to earn his PhD at the University of Georgia in Athens in 1968. After graduation, Ron stayed in Athens and began his professional career at the Southeast Water Laboratory which was then a part of the U.S. Department of the Interior. This laboratory changed names several times and finally became one of the regional research laboratories when the U.S. Environmental Protection Agency was created in 1970.

Ron is probably best known for his work with the chromatographic separation and identification of many of the individual isomers comprising Arclor (polychlorinated biphenyl) mixtures. He was also involved in developing methodology for extracting and concentrating organic pollutants from water in the latter years of his short career. Thus, it was natural that Ron, early on, became involved with helping to develop methodology for extracting, concentrating and chromatographing the moderately volatile Priority Pollutants after they had been chosen. For his part Ron received the EPA Silver Medal for Superior Service "In recognition of outstanding accomplishment in developing a new and technically sound approach for identifying and measuring priority toxic pollutants in industrial wastes to establish Best Available Technology guidelines."

However, chemistry only occupied one segment of Ron's busy life. With his wife, Gretchen, and his two sons, they maintained an active participation in the membership and affairs of the Church of Christ. And, as long as he was able, Ron also was an active member of the Society for the Preservation and Encouragement of Barbershop Quartet Singing in America.

Ron loved to sing, and he and Gretchen kept a positive outlook on life even though the cancer that eventually took his life was discovered back when he was still in graduate school. Ron and I shared an office for many years while we were together at the Athens Environmental Research Laboratory. I am proud to have known and worked with him there; he was one of the bravest men I have ever known.

It is with a deep sense of loss for a friend and a colleague that this volume is dedicated to the memory of Ron Webb and to his optimism and everlasting courage.

ACKNOWLEDGMENTS

As in the previous book, most, but not all, of the chapters were derived from a symposium sponsored by the American Chemical Society (ACS) Division of Environmental Chemistry. The editor is grateful for the support of the ACS and the division for providing the forum from which this book is primarily derived. The many authors who have diligently written these chapters are leading scientists in their fields and, without their work, ideas, and contributions, these books could never have been produced.

The editor is also very grateful for the help and support from his wife, Virginia, who did most of the work compiling the extensive index. This index is the heart of these volumes when they are used as reference books, and thus, helps make these books unique in their field. No other works of this kind meld analytical methodologies with specific organic pollutants that have been identified in water. It is, in fact, this dual purpose of providing a single source for both the identification and the methods for analysis of organic pollutants in water that has proven to be so useful to workers in the field of environmental chemistry.

CONTENTS

Section 1: Protocols

Section 2: High-Resolution Gas Chromatography

Section 3: Stable Labeling

Section 4: Microextraction

Section 5: Resin Adsorption

Section 6: High-Performance Liquid Chromatography

Section 7: Derivatization

CHAPTER 1

VALIDATION AND PRIORITY POLLUTANT ANALYSIS

R. O. Kagel
Environmental Quality
Dow Chemical USA
Midland, Michigan

The modern analytical chemist has become so proficient in detecting compounds at such trace concentration levels that, under certain circumstances and with particular compounds, he might expect to find everything in anything. This was, in fact, pointed out several years ago by Donaldson [1], for wastewater analysis:

> the number of compounds detected in a sample of water is related to the detection level. As the detection level decreases an order of magnitude, the number of compounds detected increases an order of magnitude. Based on the number of compounds detected by current methods, one would expect to find every known compound at concentration 10^{-12} g/l or higher.

More recently, quantitative results for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in a variety of matrices were reported at the subpart-per-trillion level [2], which approaches Donaldson's 10^{-12} g/L. The finding that TCDD is ubiquitous would reinforce Donaldson's observation. Priority pollutant analyses in wastewaters have routinely been reported in the 10^{-8}- to 10^{-9}-g/l range and below. Donaldson notes that for drinking water, the ability of an analyst to detect compounds is marginal at 10^{-8} g/L, and a higher detection limit would probably be selected for wastewater effluents where the constituents are generally more concentrated and matrix effects more severe.

The first question we should ask ourselves involves the validity of an analytical measurement performed near the limit of detection, or for that matter, any analytical measurement involving a sample complicated by gross matrix effects. These situations are typically encountered in priority pollutant analyses. It behooves us as analytical chemists to know what we are doing and how we are doing it, for as other scientific disciplines learn more about the effects of chemicals in the environment, there is an ever-increasing demand for lower detection limits and for technology transfer from one sample matrix to another.

In this chain of events, Wessel [3] notes: "Analytical methodology tends to be one of the sciences at the very forefront of many environmental disputes." Wessel, a well-known environmental attorney, who is concerned with translating science to a language easily understood by the general public, goes on to say:

> Understandably, therefore, there are differences of opinion among chemists as to just what is involved [in data interpretation]. One, using so-called "thin layer chromatography," will see a signal which he considers to be that of a particular compound for which he is searching; a second, examining precisely the same chromatogram, will be unable to totally distinguish what he sees from a whole host of other signals which are "noise," or the routine, ordinary background emanations of compounds which are omnipresent in the environment. Each will describe what he sees, and let others examine the evidence for themselves. Where there is no scientific consensus, the issue as to what is in fact present must be resolved by whoever the arbiter may be and ultimately, as in all socio-scientific disputes, by the public. The public certainly will not be able to understand all of what each of these analytical chemists has done, but it can be made to appreciate just how difficult it is to find trace concentration quantities at these extremely low levels.

In Wessel's case, the arbiter in all socioscientific disputes is ultimately the general public. However, this is not necessarily true in the case of priority pollutant analyses. A more immediate arbiter is almost certainly the courts. If the general public has a problem understanding analytical data, imagine what the magnitude of the problem must be within the legal profession! At least one other attorney has come to grips with the problem of data validity, and argues, on constitutional grounds, a case for methods validation [4].

So, once we have answered our first question regarding what constitutes methods validation, we should concern ourselves with the legal aspects of this subject. It is almost a foregone conclusion that methods validity will be a central issue in future litigation when effluent guidelines for the priority pollutants are issued.

The scientific and legal aspects of methods validation are the two subjects to which my remarks will be addressed.

SCIENTIFIC VALIDATION

Validation of an analytical procedure, of course, involves the statistical treatment of data to determine precision, accuracy, sensitivity and reproducibility of the procedure from laboratory to laboratory or even from analyst to analyst within a laboratory. In the jargon of the field, a validated analytical procedure is an analytical method. Validation provides a common denominator for agreement on just what an analytical result really means. We expect the civil and criminal sanctions for noncompliance with priority pollutant effluent limitations to be severe; therefore, there must be unequivocal methodology for analyzing effluents.

The question of unequivocal measurement methodology is by no means a new one. In fact, it is an age-old issue with implications much more serious than mere civil and criminal sanctions. The issue, in truth, is a moral issue, and the first known set of guidelines to deal with it are found in Proverbs 11:1: "A false balance is abomination to the Lord: But a just weight is his delight." These are words for environmental analytical chemists to live by.

Over the years, other criteria have been developed that are generally recognized as either necessary or highly desirable to assure that results will be accurate and, it is to be hoped, precise. Rogers [5] has detailed several criteria necessary for methods validation:

1. Sampling: The sampling step is crucial. Unless precautions are taken to assure that a sample is representative, even the most careful analysis will be misleading. Sample handling, including storage and transporation, is critical to minimizing errors from contamination or loss. A well-designed sampling program must be part of the validation protocol.
2. Independent Analysis: Different portions of the same sample should be analyzed using at least two procedures that are as nearly independent as possible. This criterion cannot always be followed because of sample size limitations, and at times there is no other equivalent procedure available, especially when state-of-the-art technology is used. In these cases, one must rely on two or more physical properties, such as gas chromatographic retention time or use of two or more different column packings.
3. Material Balance: This criterion is useful for major component analysis, but is not relevant when dealing with trace analysis.

4. Recovery: There are a number of ways to determine recovery. In trace analysis, the method of "standard addition" is commonly used. Here, a known amount of the material of interest is added to a real sample. The sample is analyzed before and after the addition. The difference of the two results provides an estimate of the amount originally present. The "internal-standard" method involves addition of an isotopically labeled species. Isotopic dilution is a third method.
5. Interferences: The number of interfering species increases as the concentration of the material of interest decreases. To minimize interferences, it is desirable to use highly selective steps to remove interfering species before measurement. It is also desirable to use a highly discriminating measurement technique.
6. Replicate Analysis: Replicate analysis lends confidence to a result when the analysis is performed by an expert who is using an already proven method. The number of replicates is an important factor in estimating the confidence level of the results.
7. Interlaboratory Reproducibility: Two or more laboratories applying the same procedures should obtain precise results with confidence limits that overlap to a large degree.
8. Limits of Detection (LOD)/Limits of Determination (LD). Rogers did not include LOD or LD in his original list of criteria. LOD and LD are tied to precision, accuracy and reproducibility, and define the working limits of an analytical procedure.

Methods validation for priority pollutant analyses has been debated since 1975. In 1977 the Chemical Manufacturers Association's Environmental Monitoring Task Group (CMA/EMTG) developed a validation protocol for the U.S. Environmental Protection Agency (EPA) Effluent Guidelines Division (EGD). The protocol was based on the EPA Environmental Monitoring and Support Laboratory (EMSL) procedure [6].

The EGD also recognized the need for validation in its protocol [7]:

> None of the methods are known to work in all of the effluent types presently being studied. Therefore, all procedures that are utilized will have to be validated.

Along with the Section 304h Compliance Methods [8], EMSL also published quality control/quality assurance procedures which involved validation protocol for gas chromatography/mass spectrometry (GC/MS).

All of these efforts, however, lacked uniformity. National and even international agreement is needed on what constitutes a valid environmental