Analytical Aspects Of Environmental Chemistry

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PREFACE

The objective of this volume when it was first being organized was to highlight analytical techniques that would become increasingly important in solving environmental chemistry problems primarily associated with increasing the specificity with which a quantitative analysis can be performed. In the period that has passed, additional developments have been completed and many of these methods have become more and more widely used.

Many early environmental studies focused on elemental concentrations. The developments reported here permit the identification and quantification of specific compounds. The importance of these improvements is that they permit us to obtain a much more detailed understanding of the complex chemistry that takes place in environmental systems. Since the effects of various elements are intimately related to their chemical speciation, it is the ability to determine the amounts of specific compounds that permits a better estimation of the effects of discharges of various elements such as lead, tin, mercury, and arsenic.

With the improvements in chromatographic techniques, very complicated mixtures, typical of the environment, can be separated and the components identified using mass spectrometry. The broad spectrum of natural and anthropogenic compounds possibly present in a sample makes this ability to separate and identify essential to the understanding of the system under study, whether it be photochemical smog, the chlorination of wastewater effluents, or the weathering of spilled oil.

Another of the important new aspects of environmental analysis has been the study of surfaces. The ability to closely examine the chemical nature of a surface or to scrutinize individual particles substantially increases our knowledge of the species present at the point of contact with the environment. Not only can we examine the elemental concentrations of single particles but we can examine the structure of the particle as we peel away the surface, identifying changes in composition with depth into the particle. The ability to identify different chemical states of an element in a particle and to compare those results with bulk analysis techniques

indicates that what is commonly found by such bulk analyses is not really what is present in the particle or that the surface concentration is much higher than the apparent bulk concentration. All this detailed information gives us a much better understanding of the chemistry of the environment.

Finally, environmental chemists have realized that it is often difficult to even identify all of the quantities that need to be measured in order to characterize an environmental system. Yet we have methods that produce sets of data so large that it is difficult for an individual to directly extract information from them. The application of various statistical techniques then becomes a valuable tool to interpret the processes that are occurring. These techniques also can be a valuable part of a quality assurance program to identify outliers and examine the data for systematic biases. It must be realized, however, that the techniques require someone knowledgeable about the physical and chemical processes of the real world to ensure that these interpretations are realistic.

We wish to thank the authors who have contributed to this volume for their patience and diligence in seeing it through to completion. Thanks are particularly due to Barbara Cummins for assisting in the preparation of several of these manuscripts.

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CHEMICAL SPECIATION

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1.   CHEMICAL SPECIATION

1.1.   Introduction

The term "speciation" has come into a certain degree of use in the past few years in connection with environmental analysis. As applied, the term means identification of inorganic, organometallic, or organic compounds actually present in the environment. This is not always an easy (or even a possible) task, as will be developed later. The term speciation really draws attention to the distinction between measuring the total concentration of an element and measuring the concentration of each of its chemical forms.

Chemists have, of course, been measuring the concentration of specific chemical compounds or ions for many years, if not from the very start of chemical analysis. Some of the first and most widely known examples of chemical analyses on environmental samples provide a "speciation." Particularly there comes to mind the water analyses for NO_3^-, NO_2^-, NH_4^+, and "amine type nitrogen" in which nitrogen is reasonably well divided into its most important environmental forms, if not all the specific molecular forms present. In air we have the CO, CO_2, and "total hydrocarbon" type analyses, which are also speciation to some extent for carbon. Gas chromatographic analyses for specific organic compounds is speciation of a type, and many thousands of applications have been made.

This chapter is not intended to be an exhaustive discussion of environmental analysis methods that have a speciation capability realized or implied. What is intended is to discuss the problem of determining low concentrations of specific metal complexes or organometallic forms of elements of current interest. Included will be some general comments on this type of analytical problem and air and water analyses as specific problems followed by a review of some specific elements of interest.

1.2.   Importance of Speciation Studies

With the advent of x-ray fluorescence spectroscopy, improved emission spectroscopy, neutron activation analysis, much improved multiele-

ment emission spectroscopy, and atomic absorption spectroscopy, the collection of total element data has been so much facilitated that these methods have been widely used in environmental analyses. As a result, total element data dominate the literature, at least for the metallic and semimetallic elements. Maximum permissible concentrations of various elements are given in terms of total element concentrations. Most of the data on total element composition has been used with reasonably good effects in environmental studies or in monitoring. It is certain that total element concentration data are sufficient for some elements—perhaps, eventually, for all except a very few when pollution monitoring is involved. Nevertheless, this has drawn attention away from studying the activities of specific forms of elements in the environment, which is an unfortunate state of affairs that has only recently been corrected.

Speciation studies are important for several reasons. The biological activity, for example, toxicity, of an element can vary widely from compound to compound, and it is important to know if and how toxic forms are produced or handled in biological systems. Because of differences in the important physical properties of volatility and solubility for various chemical forms of an element, one or several may dominate physical exchanges in global geochemical cycles. Similarly, chemical properties may strongly affect rates of decomposition and rates of local transportation of various elements (important in cases of pollution) as well as rates of transportation on a global scale.

A matter that has been given less attention here than it deserves is the need for monitoring on a global basis in nonpolluted locations the specific forms of elements—especially those having reasonably toxic and environmentally mobile forms. Almost no data of this type exist on most elements. Elements suggested as most important to study are sulfur (well known to be mobile), arsenic, mercury, and selenium, but other likely biologically active elements such as tin, lead, tellurium, and antimony should be added to the list. What must be determined is whether the several forms of these elements remain in more or less constant ratio to each other, indicating an approximate equilibrium condition in global cycles, or if any form is increasing versus the others on a local or on a global basis, a situation that could have rather grave consequences.

A related and similar speciation problem is the study of specific "point type" pollution sources for speciation type of information. Point sources here could be physically large-sized areas such as traffic systems, sanitary landfill areas, estuaries, and embayments.

Despite the transport of pollution from sources, by the wind in the case of air pollution or by river flow in the case of water pollution, there may be sufficient time for pollutants to interact with the biological and physical systems present and possibly come to a degree of equilibrium, a situation that usually means the buildup of a localized concentration of one or several forms of an element. Other examples of localized conditions are air entrapped in meteorological inversions and air partially trapped under woodland canopies. Isolated lakes are good examples where aqueous–sediment interface equilibria can be established. The anaerobic waters of certain marine areas such as the Curacau trench and embayments exhibiting poor tidal flushing are good examples of isolated saline waters. Although these localized areas can hardly be considered in an equilibrium state of the kind considered in global cycle modeling, nevertheless, they could approach equilibrium if chemical exchanges and reactions proceed at rates greater than losses to the exterior of the affected area. It would be instructive to determine whether a material balance of transported forms of an element can be made based on appropriate analyses.

The study of these isolated systems should prove interesting when compared to nonpolluted or nonisolated locations. A different speciation ratio of a particular element compared to that of the same element in ambient locations will probably be found depending on the prevailing pE and pH. In aqueous systems the pE (oxidation potential is really simply a factor related to the dissolved oxygen concentration) as well as the pH may be substantially different from that of nonisolated locations, for example, open ocean or ecologically "well-balanced" (nonentrophied) freshwater lakes.

Obviously, chemical forms of many elements are susceptible to oxidation and reduction reactions in the limits of conditions available in the environment. In the case of air, the range of pE values is limited because oxygen is omnipresent. A range of surface pH values is available. The chemical nature of air samples depends on the input of a certain compound or group of compounds from pollution sources if present.

Speciation studies and compositional type models such as pE–pH diagrams compliment each other. Results of environmental studies aid in better describing the real aqueous system present. This leads to a better interpretation of the pE–pH diagrams, which are, in fact, nothing more than intelligent guesses of what should be present.

Speciation studies are needed in several specific circumstances. Par-

ticularly important is their use in preparing environmental impact statements. When chemical pollution is involved, total element values may not be sufficient to indicate potential toxicity problems. In addition, when extrapolating from existing data and applying the results to a proposed new location being studied, the chemical, physical, and biological makeup of the new areas (i.e., pE, pH, water composition, temperature, hydrology, and biology) must be considered. If the overall chemical environment of the new area is only somewhat different from that of the prior study, the speciation could be radically different. Where environmentally mobile elements are important, speciation studies should be carried out prior to the completion of an environmental impact statement.

Speciation studies can influence the selection of environmental monitoring equipment. In some cases it may be more useful to test for a single compound than to obtain a total element value. This could be true, for example, if total element analyses are different because conversion of a particulate solid phase form into an analyzable form is difficult and requires complicating steps in the analysis procedure.

1.3. Strategy in Speciation Studies

Even in the instance of some elements for which reasonably good analytical methods exist, the determination of only total element present in a sample can be time-consuming and expensive. The prospect of analyzing for every determinable form of every element is simply not feasible.

The best compromise between knowing nothing about the chemistry of a particular element in the environment and trying to do the impractical is to do studies on a case-by-case basis and monitor by using the easier total element analyses where available. Thus it should suffice to analyze once for the several forms of arsenic in a lake being polluted (perhaps by an organic arsenical), in the air above the lake, and in the adjacent area, sediments, soil, plants, and other biota. After this, total element analysis of lake water and perhaps also of the air should suffice for monitoring.

Speciation studies may be partially repeated over long intervals after the first round to determine if any significant shifts in the ratio of chemical forms are occurring. In this regard, seasonal variations in speciation may be observed as a result of changes in temperature, degree of sunlight, ground cover, and biological activity.

The speciation of an element will probably be the same for locations

that have approximately the same types of pollution and makeup of the
ambient area. This can serve to guide the selection of appropriate ana-
lytical methods. For example, the range of sulfur compounds found near
paper mills should be the same no matter where the mills are located,
and a similar environmental pollution profile should be found.

1.4. Nature of Speciation as an Analytical Problem

The analytical problems encountered in environmental studies are, as
in other areas of analytical chemistry, tied to the objective of the intended
study. Use of the data obtained governs the analyses needed. A quick
survey may require an analytical method having a 10 ppb limit of de-
tection and only for some empirically selected fraction of the element
present—such as "soluble element" defined as in water samples that pass
a 0.45-μm filter. A carefully done biological impact assessment could
require a 0.5-ppb limit of detection of the same element with some in-
dication of its organometallic forms present.

Unless analytical work has been done on a similar problem, the en-
vironmental researcher may find the progress of his or her work limited
by the need for analytical methods development. This is not a very pleas-
ing situation especially for those who are much given to making and fol-
lowing research plans in an orderly fashion. Particularly upsetting is the
need often found to spend large amounts of time developing analysis tech-
niques and proving their reliability and accuracy in field operations or in
analyses of real samples.

Generally, the analytical speciation problem has the following char-
acteristics. (1) Samples are a complex mixture of compounds often in-
cluding elemental forms. (2) Part or all of the mixture can be sensitive to
air oxidation or chemical reduction during ordinary sampling and sample
processing. (3) Part or all of the mixture can be sensitive to pH changes.
(4) The range of volatility of the chemical forms of an element can be
from that of a solid to that of a gas. (5) Polymers and complexes may be
present. (6) Total analyte is likely to be less than 1 μg per sample taken
and often less than 1 ng for a convenient sample size. (7) Sometimes the
presence of the components sought has not been proven in real environ-
mental samples despite a lot of intelligent speculation or opinion and even
good laboratory model chemical systems work. (It is particularly at this
point that the analytical chemist working on environmental chemistry

finds himself crossing fields of scientific discipline.) (8) Finally, there may be few or no good ways to verify the analytical method since the one just developed is the only one available.

The usual logical process in developing an analytical method involves first a statement of the analysis needed followed by application of the properly selected analytical procedure. Unfortunately, in speciation work the statement of the problem is the major part of the problem. One often finds oneself restating the problem during its study. This is a common phenomenon in science but certainly one that again underlies the fact being emphasized here: Analyses for speciation studies are not routine and should not be treated as such by anyone, analytical chemists or scientists of other persuasions.

The balance of this chapter on speciation will concern itself with first general approaches to speciation in air and in water. This will be followed by a review of speciation of selected elements that have caught the interest of researchers in recent times.

2. SPECIATION IN AIR ANALYSIS

2.1. Optical Absorption Methods

No studies on the environmental distribution of the several forms of a particular element have been reported using optical absorption methods in either aqueous or gas samples. The very low concentrations of compounds encountered in the environment simply cannot be detected by the several types of instruments now available or under study. Nevertheless, considerable progress is being made and a review of current capabilities is in order.

Optical absorption methods do have the potential advantage of good selectivity for individual molecules particularly in the IR region of the spectrum. They also possess the obvious advantage of not requiring a chemical modification or physical transfer (e.g., a separation or chemical reaction) prior to analysis. Of all the air analysis sample acquisition techniques, optical absorption methods have the highest collection efficiency (100%) and perturb the nature of the sample the least.

A very substantial amount of interest has gone into developing optical absorption methods of analysis for trace materials in the environment.

Applications have included stack monitoring, long path infrared monitoring using ordinary sources, and analysis and monitoring using laser sources. For more background, the reader is referred to the book on air pollution analytical methods edited by Stevens and Herget (1) and a book on laser monitoring by Hinkely (2).

Early laser devices were of the fixed wavelength type without much capability of wavelength selectivity. The availability of tunable lasers has greatly enhanced both selectivity and ability to perform multicomponent analysis. Hinkley (3) has compared the capabilities of the several type of tunable lasers. Typical applications have been to the detection of specific important pollutants. Table 1A, with data from Hinkley and Calawa (4) illustrates current detection limits attainable with a diode laser instrument albeit over a 2-k path length. Table 1B data from Pitts and co-workers (5, 6) give detection limits for a He–Ne laser source, Michelson interferometer–computer type instrument. The interferometer approach, which is in part a Fourier transform infrared spectrometer, has the ad-

TABLE 1.   Detection Limits for Laser Source Optical Absorption Analysis Systems

Compound	λ (μm)	Sensitivity (ppb)[a]
A. Diode Laser (4)		
CO	4.74	0.3
O_3	4.75	3.0
NO	5.31	1.5
SO_2	8.88	15
C_2H_4	10.54	0.8
B. He–Ne Laser, FT–IR (5, 6)		
NH_3	931 (μm^{-1})	4[b]
HCHO	2779	6
HCOOH	1110.3	2
HNO_3	896	6
HNO_2	853	4
O_3	1055	10
PAN	1162	3
H_2O_2	1250	8
CH_3OH	1033	2

[a] Path length is 2 km.
[b] Path length is 0.9 km.

vantage of a short wavelength scanning time. A computer is needed to convert the interferogram to its Fourier transform, a conventional IR spectrum. The need for a computer is not a disadvantage; the computer will be needed for resolution of data obtained from mixtures of compounds also. Green and Steinfield (7) have studied the use of a CO_2 laser for monitoring mixtures of organic vapors in air. Minimum detectable concentrations were in the parts-per-million range for a 10-m pathlength. Some typical values are: benzene, 25 ppm; t-butanol, 14 ppm; vinyl chloride, 6.4 ppm; d-chloridifluoromethane, 1 ppm; and ethyl acetate, 4.2 ppm. These are concentrations at which a 20% error in measured absorption is observed for the single compound alone. When a mixture of compounds is to be analyzed, a multiple wavelength measurement technique is used. A computer programmed least-squares analysis of the data is used to resolve the mixture.

In summary, it appears that long path optical absorption methods do not yet demonstrate sufficient sensitivity for any analysis purposes at ambient concentrations below parts per billion. Nevertheless, good applications have been made to analyses of individual pollutants with detection limits approaching this. Through the use of multiple wavelength measurements and computer programmed solution of simultaneous equations, the capability of multiple component analysis exists. It is a virtual certainty that if detection limits are reduced to below 1 ppb by state-of-the-art advances, more speciation applications will become possible but at the cost of a greatly increased complexity of detected sample components.

2.2.   Preconcentration, Separation, and Detection

2.2.1.   Cryogenic and Cold Trapping

Air components in vapor form often are present in concentrations well below those that permit direct analysis. Cold trapping and cryogenic trapping (which is simply cold trapping with liquid air, oxygen, or nitrogen) can be used to collect these volatile compounds. The usual approach is to cool a tube packed with some suitable solid material and draw air through the tube by means of a pump. A number of problems occur with this type of sampling, the chief of which are water removal and accuracy of determining sample air volume. Ten liters of air at 25°C will contain 0.25 mL of water at 100% relative humidity. If more than a few liters of

air are to be sampled, a water-removing pretrap or a large drying tube is needed to avoid plugging the cold sampling trap with ice. The trapping of water with the sample can obstruct the air flow through the sampling tube, an effect that changes with sampling time. This makes the accurate determination of the sampled air volume difficult. The use of an in-line wet test meter is suggested.

Another difficulty with cryogenic trapping is the rapid absorption of major air components, CO_2 and O_2, onto the solid surface of the absorbent used. High surface area solid sorbents such as Chromosorb 102 absorb the most. Two effects result from this: The absorption of air onto the solid surface can be so rapid at first as to produce a greater than pumped flow rate into the cooled absorption device. Upon warming, the liquidified gases produce a very high flow rate out of the sampler, sometimes physically expelling the frozen analyte as an aerosol or particulate spray. These problems probably limit the wide application of cold trapping in field analysis or monitoring especially when 10–20 L of air or more must be processed. Altshuller (8) has reviewed cryogenic trapping methods.

Cryogenic trapping has often been used to concentrate comparatively small sample volumes, 50–500 mL, prior to analysis by gas chromatography (9–11). Cryogenic trapping is required for preconcentration of the light hydrocarbons. Even so, there can be problems. This writer has found that methane (b.p. $-164°C$) was not even quantitatively absorbed out of a He carrier gas stream at 100 mL/min on glass beads at liquid nitrogen temperatures. A high surface area sorbent (Chromosorb 102) was needed to obtain quantitative trapping of methane.

Physical absorption onto solid sorbents of a variety of types has been used for preconcentration of vapors out of air prior to analysis. Physical absorption at ambient temperatures avoids water absorption problems and can provide good preconcentration. Analysis procedures usually consist of sample absorption, rapid heating of the sorbent cartridge in a GC carrier gas feed stream followed by separation and analysis in the usual fashion. Rapid and quantitative desorption is the key to good results. It is probably best to desorb from a high surface area trap into a small surface cryogenic trap followed by separation and analysis. This technique reduces the size of the sample volume and thus improves separation.

A reasonably large number of solid sorbents have been studied for preconcentration of vapors out of air at ambient temperatures. In every case where physical absorption is the cause of preconcentration, chro-