

Environmental chemical analysis

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Preface

There is a very real need both to teach analytical chemistry in relation to the jobs it has to do, and also to show how chemical analysis can yield reliable data which are valuable to other scientists. There is also a need to explain the difficulties facing the analyst, and to show how he chooses methods and techniques appropriate to the situation. The methods developed and the results obtained by analytical chemists will be used by many other scientists, and some background knowledge and appreciation of the subject is a prerequisite to avoiding possible pitfalls and errors.

I hope that teachers in universities, technical colleges and even schools will find in this book the inspiration to try a new approach to teaching analytical chemistry. When the coverage of this text falls short of what they need, the references will guide them to the specialist literature. Senior undergraduates should be encouraged to follow up some of these references, but younger students should find the text reasonably complete in itself.

The book would be little more than a seedling still had it not been for the generous and enthusiastic assistance and encouragement of my colleague Malcolm Cresser. After eleven years of teaching analytical chemistry to undergraduates and postgraduates in a university Soil Science department, he was as convinced as I was that this text would meet a real need. Our fields of experience have been largely complementary, and the balance has improved greatly under his influence. The final text, however, has been very much a combined effort.

There are of course still areas outwith our experience, and we have not hesitated to ask friends and experts for assistance—help has always been willingly and generously given, and to these people we owe special thanks. We would like to mention here Steve Black (art work), David Bullock (lead in blood), Bob Chalmers (prompt answers to all sorts of awkward questions), Brian Clark (environmental impact analysis), Peter Brown, Ian Davidson and Sam Frazer (costing of analytical services), Dieter Klockow and Jan Slanina (analysis of air and rain), Eric Lachowski (electron microscopy), Jim Marr (X-ray diffraction), Andrew Morrison (LIDAR), Alistair Smith (GC/MS of fatty acids), Gunther Tölg (problems in ultra-trace analysis), Richard Weddle (analysis of food) and various commercial firms mentioned in the text. Many students deserve thanks too, for trying out all the experi-

ments as well as many more besides. Finally, we wish to thank our respective wives Eva and Louise, who have both waited patiently a very long time for alterations to kitchens to be completed, and the publishers, who have also been very patient and given much encouragement.

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I.L.M.

Factors are of course intertwined with our science, and we have not hesitated to ask friends and experts for assistance. Help has always been willingly and generously given, and to these people we owe special thanks. We would like to mention here Steve Black (now at David Bullock Head), Harold Bob Chapman (prompt answers to a series of awkward questions), Joan Clark (environmental impact analysis), Fred Brown, Ian Davidson, and Sam Frazier (ecology of analytical ecology), Peter Klohn, and Jan Storer (analysis of air and water), Eric Larkin (selection microscopy), Jim Mair (X-ray diffraction), Andrew Morrison (DARL Aftersmith), and Mrs. J. Mair (analysis of chemical data), and various other friends mentioned in the text. Many students have also helped in various ways, and all the experts

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1 The nature and scope of environmental chemical analysis

1.1 Introduction

Almost everybody has some idea of what is involved in environmental chemical analysis. Indeed, other people's preconceived notions might well come to be regarded by the environmental analyst as one of the main occupational hazards of his work. Mere mention of an association with soils or plants as an analyst can all too quickly prompt the typical response: "Oh, how interesting! You must come and look at my gooseberry bushes. I'm sure there's something wrong with the soil as they've all gone a funny colour." On the other hand, if you admit to working in a laundry, rarely does someone say: "Oh, how interesting! You must come and help me with my dirty washing." So to the general public the environmental analyst, like the doctor or veterinary surgeon, is a potential source of highly valuable knowledge and information—in short, he holds the key to many of life's little mysteries.

To the analyst, on the other hand, the general public, and indeed even those members of it who might be expected to know better, often appear to have a surprisingly naïve concept of environmental analysis. While the gooseberry bushes may well be exhibiting symptoms of some deficiency or toxicity in the soil, it is equally likely that they may be under attack from any one of a number of pests or diseases or a neighbour's stray herbicide. In this instance, chemical analysis of a soil sample, however careful and comprehensive, will take up a good deal of time but may throw no light at all upon the malaise of the bushes. Chemical analysis in isolation, then, should never be regarded as a panacea, but rather as a powerful tool which may be used to provide the answer to highly specific questions. In many instances the analyst has a reasonable idea of what chemical species he is likely to find in his samples and what their approximate concentrations are likely to be before he starts any laboratory work. Analysis is then used to confirm or refute a diagnosis. Although in some instances he may be confronted by a complete "unknown", fortunately such events are rare.

Nevertheless the general public's concept of an analysis and that of the analytical chemist would, if reduced to terms of fundamental definitions, probably lead to similar end products. Qualitative analysis is the name given to the identification of elements or compounds which are present in a sample, while quantitative analysis is the process of measurement of the amount or

concentration of any one or more of the species present in a sample. In practice this division into qualitative and quantitative analysis, whilst convenient, does not stand up to close scrutiny. The analyst may well establish that a particular species is present, but he cannot normally establish its absence. Rather, he shows that, if it is present, it is at a level below that which may be detected by the particular test he has used to look for its presence. This level may be considered as totally insignificant and therefore effectively zero, but in as many other cases the low level which may still just be detected lies well above those levels which may occur in the environment and give rise for concern. It might therefore be more satisfactory to develop concepts of quantitative and semi-quantitative analysis, which would at least save the environmental scientist from having to face the apparently miraculous appearance and disappearance of elements in ecological systems. In practice, by far the greater part of the analyst's work is quantitative.

The curious may wonder why the authors should feel the need to stress that environmental analytical chemistry is capable only of answering very specific questions. The reason is that all too often the scientist requesting the analysis may do so in very vague terms: "The fish are dying at a fish farm north of here. We think it's something in the water. Do you think you can tell us what it is?" A very reasonable question—or is it? Are the fish disease-free? Is their diet adequate? Have the deaths suddenly started? Has there been a change in the diet recently? Is the food from a reasonable supplier? Is any pollution suspected and is it likely to be organic or inorganic? Is there any reason to suspect a change in the level of pollution? And so on.

Note that the analyst does not need to be an expert in fish husbandry. The questions he is asking are commonsense, but if he gets satisfactory answers he may at least have some clues as to what to start looking for. At least he would have a rational basis for deciding if dead (and live) fish, or water, or the fish food would be the most suitable sample to commence work on. Note also that, unless he has much experience of a particular type of sample, chemical analysis may tell him nothing at all. He must first establish suitable reference levels, for example, for the composition of the fish which were, until taken for analysis, swimming about quite happily. It may be, of course, that the person posing the problem has sufficient knowledge and experience to interpret the numerical results of particular analyses, in which case the analyst's problem is alleviated to some extent.

It is worth considering here a further example of a problem associated with obtaining suitable reference levels for comparative purposes. Suppose soil analyses are to be carried out to ascertain the levels of zinc and cadmium contamination in the vicinity of a smelter. With the wisdom of hindsight it is easy to suggest that soil samples should have been collected and either analysed or stored under suitable conditions before the smelter became

operational. Because soil is very variable in composition, collecting samples a few kilometres away does not provide a satisfactory alternative. In this instance it may be necessary to collect samples from under old buildings in the hope that they will have been protected from contamination, and will therefore provide natural background levels for zinc and cadmium in the area.

In this example, the analyst is answering a specific question, namely, "What are the total levels of zinc and cadmium contamination in the soils?" He provides the answer by determining the total levels of the two elements in contaminated and uncontaminated soil (note, by the way, that we speak of the elements as being *determined* and the soil as being *analysed*). He could equally well have been asked; "Are these elements in a form in which they can be taken up by vegetables grown in the area, to reach a dangerous level?" This is a different question altogether, and would require different analyses to be done to provide the answer. When selecting a method of analysis, it is important that the analyst be quite clear about the precise question he is being asked and is trying to answer.

It would be quite misleading to create the impression that *every* analysis completed by a competent analyst will have involved a substantial amount of painstaking interrogation and detective work before the start of the laboratory investigation. This approach is necessary when some particular one-off problems have to be solved, it is true, but much of the everyday work of the environmental analytical chemist may involve the determination of the same species in a number of samples on a routine basis, i.e. by the same analytical procedure. In this case much original thought may go into the selection and specification of procedures for sample collection and analysis, but the final procedure, once established as reliable, becomes simple routine—much like following instructions in a cookery book. Environmental analyses in this category generally fall under one of two broad headings: quality control, or routine testing.

In *quality-control* analysis the analyst is answering the question, "Is the customer receiving a product whose chemical and/or physical composition falls within clearly defined limits?" This may involve establishing that a metal alloy does not contain levels of impurities which would weaken its strength, or that a pharmaceutical preparation does contain a certain minimum level of active ingredient. It may involve checking the protein content of a food product or confirming that a fertilizer will give a farmer at least as much of a specified plant nutrient element as the bag indicates. Sometimes it may involve checking that undesirable elements are present only at levels below some extremely low specified concentration, as is often the case in the semiconductor industry.

In most of the examples cited, the determinations do not need to be

completed with great precision, but there are instances where even a small error in the result of a determination may be important. In the case of nuclear fuels or precious metals, for example, quite a small error could correspond to a very substantial financial loss (or enough plutonium going "missing" to make a small nuclear weapon).

In *routine testing* on the other hand, the analyst compares samples with suitable control standards to provide a quantitative evaluation of the extent of a problem, and possibly of the extent of the treatment which is necessary to rectify the problem. This may sound complicated, but is really very simple. He is answering questions such as, "How much fertilizer does this soil need?" or, "Does the analysis of this patient's blood or urine indicate that he is suffering from lead poisoning?" or, "Is the zinc level in these apple tree leaves so low as to suggest that zinc deficiency may be a problem in the orchard they came from?" Routine testing, then, is concerned with providing the answer to specific problems, and not with guaranteeing the quality of a marketable product.

This division is rather arbitrary, since the same method of analysis may be applied in routine testing, in quality control, and in solving one-off problems. It is, however, useful in that it gives an indication of the vital role played by the analytical chemist in so many spheres of human activity. Sometimes analytical procedures are borrowed directly (or after slight modification) from quality control or routine testing laboratories in order to solve one-off problems. Is the sliver of glass in the pocket of the arrested man really from a beer glass, as he suggests, or could it be from the broken window at the scene of a crime? Do the levels of phosphorus in soil samples taken from the archaeological excavation indicate the type or extent of human activity on the site? Can we tell from looking at the scrapings of paint on bits of wreckage from this aircraft exactly how it broke up? These three questions all pose a further question to the analyst, namely, "What determination will give the most useful information?" Once answered, the resulting method is likely to be drawn from an appropriate routine procedure as used in the glass industry, in agriculture, or in the paint industry.

1.2 A typical environmental study—lead in the environment

One aspect of environmental chemical analysis makes it rather different from many of the examples just quoted: one is dealing with the environment as a whole, the ecosystem. One of the reasons for carrying out chemical analysis of environmental samples is to be able to understand biological pathways or cycles, particularly those involving harmful materials. This assists the environmental health specialist in deciding what levels can be tolerated, what levels exist, and whether the materials are in a form which makes them readily

available to plants and animals. These analyses may be followed by others to see whether man accumulates the harmful substances or simply excretes them, possibly without change. This should become clearer if we look at a specific example. Figure 1.1 shows some data for daily lead throughput for a

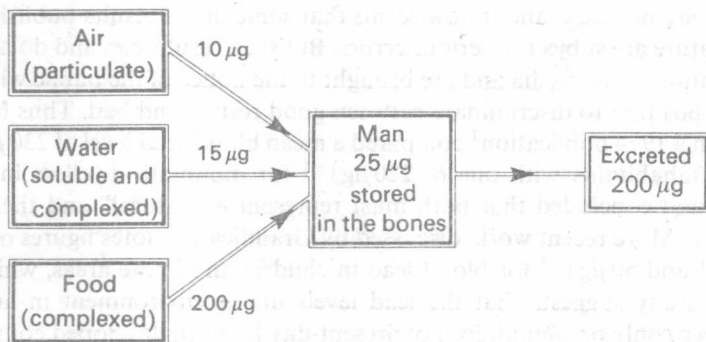


Figure 1.1 Daily lead balance for a typical city dweller.

typical urban dweller in a developed country.¹ It shows why it is essential to investigate many different components of the environment before attempting to draw conclusions from the results. In this case samples of air, airborne dust, drinking water and a large variety of foods must be analysed for their lead content, care being taken to determine the total lead, not just the water-soluble species. From the individual results it will then be possible to estimate the lead content of the "weekly shopping basket" and interpret that in terms of the total burden in the diet per person.

It is clear that any two sets of results for these analyses will probably show large discrepancies, depending on where and when the samples were collected, so very many samples from many sources will have to be analysed at many times over a prolonged period so as to make it possible to construct the simple diagram shown in Fig. 1.1. Indeed, one might argue that such gross bulking of analytical data (applicable perhaps to the 1971 average Scottish man with 0.83 of a wife and 1.20 children) does not make any sense, and that one should rather subdivide the population into groups living, say in the towns and in the country, or in areas with hard or soft water, and then make comparisons between these groups.

Having arrived at figures such as those shown in Fig. 1.1, one would then ask where the body stores the lead accumulating at 25 μg per day, and to answer this many different parts of the body will have to be analysed. Blood and urine are easily obtained from living people, and most surveys are based on analyses of the former. But there is reason to believe that the lead is stored

in the bones, and is only released into the blood in times of stress. So do blood-lead levels give a true picture? Other workers have analysed teeth extracted by dentists from live patients, and others have analysed milk teeth lost by children. How do these results fit in?

It is particularly unfortunate that in the case of lead in the environment the analyses are not easy, and it now seems that some of the results published in the literature are subject to serious errors. But such results can and do attract the attention of the media and are brought to the notice of the public who are not in a position to discriminate between good results and bad. Thus results quoted in a 1974 publication¹ compared a mean blood-lead level of $230 \mu\text{g l}^{-1}$ for UK inhabitants with one of $220 \mu\text{g l}^{-1}$ for mountain dwellers in New Guinea and concluded that both must represent a "natural" and therefore safe value. More recent work, discussed by Grandjean² quotes figures of only $30 \mu\text{g l}^{-1}$ and $50 \mu\text{g l}^{-1}$ for blood-lead in children in remote areas, while yet another study suggests that the lead levels in the environment in ancient Egypt were only one-hundredth of present-day levels in developed countries. This ties in with the changes of lead concentration found at varying depth in polar ice corresponding to atmospheric deposition from different historical periods, the levels increasing significantly at depths laid down since the beginning of the industrial revolution 200 years ago (see p. 53).

Possibly even more difficult than the chemical analyses are the sociological and psychological surveys which are needed together with the chemical work to show at what levels the lead in the various sections of the environment begins to present a hazard. It is therefore not surprising that one report concluding that current levels of lead exposure in the UK do not present a significant health hazard³ should be followed a year later by one finding that there is a definite correlation between blood-lead level and intelligence in children at school.⁴

However difficult it may be to carry out these investigations with sufficient care and skill to be able to obtain reliable results and to be able to draw significant conclusions from them, it does not take much effort to show that a problem does indeed exist. Just as one can attempt to draw up a mass-balance for lead in the ordinary citizen, so one can try to do it for the whole country. The annual demand for lead in the UK is around 4×10^5 tonnes, of which some 10 000 tonnes are consumed as additives in petrol, and therefore find their way into the air and on to the land near our roads and cities. The high levels of lead in airborne street dust (around 0.1 % or more, see 3.7.10) are then not very surprising.

More surprising are the claims that swans are being killed by lead poisoning arising from lead weights lost in rivers and lakes by anglers, amounting in the UK to some 250 tonnes per year. The lead pellets are swallowed by the swans as they scavenge for food in the sediments of the