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Modern Analytical Chemistry

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The supply of analytical chemists has been of concern to the Royal Society of Chemistry (RSC) for some years now. In 1980, the RSC published a report¹ of a working party which, amongst other courses of action, recommended that: “(a), improvements are made in the education of analytical chemists; and (b), educational establishments should be encouraged to pay more attention to the coherent teaching of analytical chemistry (both theoretical and practical) within the over-all chemistry course.”

More recently the RSC's activities in the production of indicative registers of chemists with particular types of expertise has been discussed in the Society's *Professional Bulletin*.^{2,3} The most recent of these stated “The work of professional chemists extends over a broad and diverse range of activities, fields and specialisms, many of which involve responsibilities to maintain standards of quality and safety in the public interest—sometimes (and increasingly) under legislative requirements” and went on to announce that “The Society has already identified several specific groupings of chemists where there is both a need and a demand for a register—a need by the public for a means of identifying competent practitioners in a given field, and a demand for the services that members can provide. We have already reached an advanced stage in developing proposals for indicative registers in two areas—analytical chemistry and health and safety.”

The introduction of such a register of analytical chemists has implications for the provision of analytical chemistry teaching in the UK. Almost certainly, following a transition period in which existing practitioners are registered, entry to the register will be open only to those professional members of the Society who have satisfied the requirements of an appropriate study guide. As the register will only be open to Members and Fellows, it seems likely that the contents of the study guide will resemble more closely the contents of an MSc course rather than the recently introduced ACOL programme,⁴ a distance learning scheme at the senior technician level.

It is difficult to assess accurately the current provision of analytical chemistry teaching in British universities and polytechnics, as no detailed survey has been made since 1979.¹ A superficial survey⁵ of the present-day level of activity in universities compared with that of the early 1970s suggests that there has been a considerable decline. That the UK is considerably out of step with the rest of Europe is shown in the results of a survey⁶ conducted by the Working Party on Analytical Chemistry (WPAC) of the Federation of European Chemical Societies (FECS). The questionnaires from 45 UK and 2 Turkish institutions were returned after the results for

159 institutions from 20 member countries had already been returned and analysed by WPAC. Institutions were divided into two groups, those with and those without a separate chair of analytical chemistry. When the results for the UK institutions were included, the average number of hours spent on all analytical topics fell from 599 to 579 for the former category and from 456 to 367 for the latter category.

The UK institutions⁷ consisted of almost exactly two-thirds university and one third polytechnic chemistry departments. Of these, only 17 were able to identify a person with over-all responsibility for the teaching of analytical chemistry and many indicated difficulty in completing the questionnaire as analytical chemistry was incorporated into areas of organic, inorganic and physical chemistry and thus could not be distinguished as a separate undergraduate discipline.

At least 20% of the UK's professional chemists are employed in analytical work in one capacity or another⁸ and many vacancies for graduates are, as the advertisement pages of *Chemistry in Britain* show, analytical in nature. It may thus be important for institutions to demonstrate that their graduates have indeed covered many of the topics necessary to satisfy the requirements of the study guide for entry to the indicative register of analytical chemists. This may not be too difficult, if indeed analytical topics are taught but not co-ordinated as the responses to the FECS questionnaires seemed to suggest.

The purpose of this article is to propose a framework within which analytical material may be viewed and thus to enable the analytical content of any undergraduate programme to be regarded as a co-ordinated set of topics.

The Underlying Philosophy of Analytical Chemistry

Analytical chemistry covers such a wide range of topics and underpins so many areas of science that it is difficult to provide a concise accurate definition for it. However, the underlying major theme is that analytical chemists provide information about the chemical composition of materials in order that a decision may be taken. The over-all analytical method can be considered to be built up of a number of individual stages, as shown in the first line of Fig. 1. Linking each stage in the method is a procedure such as is shown in line two of Fig. 1. The task facing the analytical chemist is to choose the most appropriate procedures in order that the desired information about the particular material of interest can be provided. To be able to do this, the analytical chemist must firstly have a working knowledge of the characteristics of the available

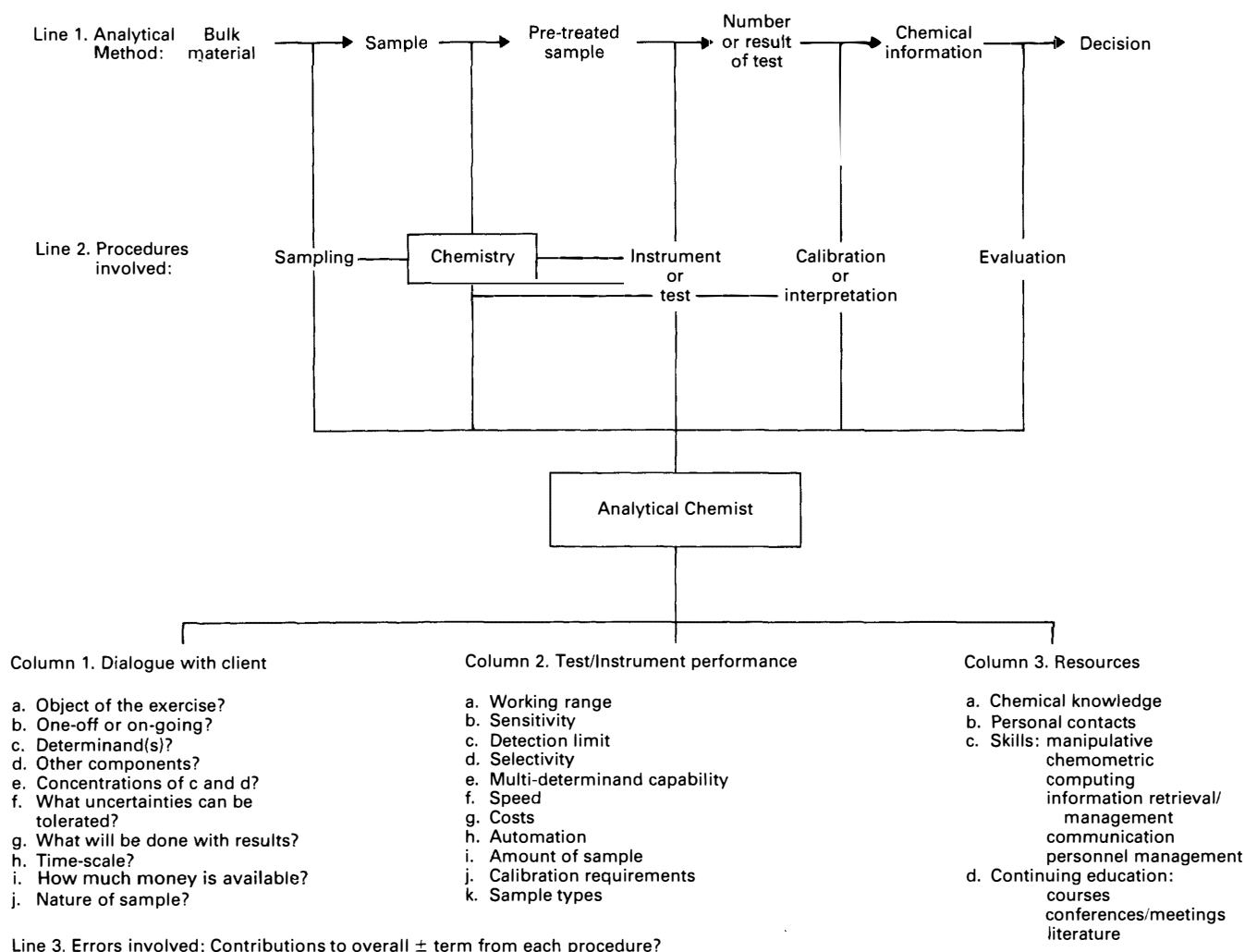


Fig. 1. The analytical chemist at work

procedures, and secondly enter into a dialogue with the end-user of the information. This latter activity is necessary to ascertain under what constraints the method must operate, and will involve the topics listed in column 1 in Fig. 1. As the majority of analytical methods involve an instrumental technique it is important that an appropriate one is chosen. The relevant performance criteria are listed in column 2. It may well be that the most appropriate instrument for the method is a burette or balance. Thus, in this view of analytical chemistry, there is no division between the so-called "classical" and "instrumental" methods. All instruments, *i.e.*, devices which produce a number related to the chemical composition of the pre-treated sample, are considered to be part of the analytical chemist's range of techniques, whether they are based on the measurement of volume or of mass-to-charge ratio.

In addition to a knowledge of the relevant performance criteria of various instrumental techniques, the analytical chemist makes use of a number of other resources in deciding on or devising an analytical method. It has been said that the most efficient method of devising an analytical method for a problem not previously encountered is to telephone someone who has already dealt with the problem. The problem then becomes one of knowing whom to telephone. The role of personal contacts and how they are made (through various continuing education and professional society activities) is not to be underestimated, as the majority of analytical chemists nearing the end of their careers now will be using techniques which did not feature in courses of study 30–40 years ago.

The final procedure is possibly the most important of all, as without an indication of the reliability of the chemical

information produced, no decision should be taken. Line 3 in Fig. 1 summarises the evaluation procedure. In order to assign an uncertainty to a numerical value, usually in the form of a "plus or minus" term, the analytical chemist has to be able to assess the uncertainty of each of the procedures involved in a particular method. This involves a knowledge of sources of random and systematic error and of how they will propagate through the method. Thus, the analytical chemist must be conversant with the appropriate chemometric techniques for the calculation and manipulation of uncertainties. Depicting the analytical method as progress through a sequence of procedures underlines the cumulative effect of the errors involved and the view of this effect as "no chain can be stronger than its weakest link" is readily appreciated. The weakest link may turn out to be a gross blunder, and analytical chemists should be watchful for transpositions (or worse) during calculations. Nothing should be taken for granted, including the concentrations of the standards, and calculations should always be independently checked.

In general, in devising and using an analytical method there will be three sorts of decision to be made. The first and second concern the method itself and are decisions about (a) does the method work, *i.e.*, does it meet the requirements of the client, and (b) once in use, is the method performing satisfactorily. Answering these questions requires a knowledge of strategies for method validation and quality control and of the implications in terms of time and cost of the proper implementation of such strategies. Clients are often reluctant to accept the extra costs of good quality control, but the failure to implement properly such procedures has been demonstrated, by many

reports in the literature, to lead to large uncertainties in results. A recent example of such a report⁹ and the subsequent correspondence generated, illustrate these points nicely. It is important to communicate clearly to the customer the consequences of skimping on the quality control procedures, namely cheaper analyses but less reliable results. Of course, it is important to use analytical procedures appropriate to the customer's requirements. The third sort of decision concerns the use to which the chemical information generated is to be put, and again the appropriate chemometric procedures will have to be invoked if a degree of confidence is to be assigned to the correctness of the decision taken.

Many analytical chemistry text-books quite properly stress the importance of being able to assess the over-all uncertainty in a method and include discussions of sampling errors, problems of loss and/or contamination during pre-treatment and of various interference effects in instrumental techniques, but ignore the uncertainties introduced by the calibration procedure adopted. Many chemical instruments are calibrated by recording the off-null registrations of the instrument to the concentration of a discrete number of standards. A calibration function is then constructed by a curve-fitting algorithm of some sort. Linear regression procedures for both straight lines and curves and some commonly used micro-computer based methods introduce considerable errors.^{10,11}

The Role of the Instrument

Instrumental techniques occupy a central position in the procedures of an analytical method both literally and metaphorically. In order to be able to assess the suitability of a technique for a particular method, according to the criteria set out in column 2 in Fig. 1, to adopt appropriate pre-treatment and calibration procedures and to be able to assess the instrument's contribution to the over-all uncertainty, it is necessary for the analytical chemist to understand how the instruments work. Most chemical instruments can be considered to consist of the internal functions, shown in Fig. 2, that are seen when the "lid is taken off the black box".

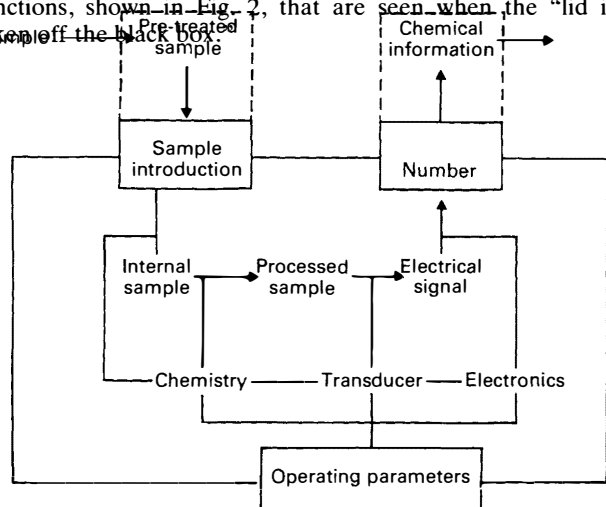


Fig. 2. Taking the lid off the black box

There are two main functions inside the instrument, chemical and electronic. These interface at the transducer, the device which converts information in the chemical and physical domains into information in the electrical domain. The analytical chemist needs to know how the transducer works, how reliable it is, what factors affect its reliability as well as what is done to the electrical signal before it appears as a number in the digital domain. Some instruments, of course, are not designed to produce a single piece of information in the digital domain but to record the variation of signal (analogue or

digital) level with time (which may be related to some other physical parameter, such as wavelength). In this latter instance, the conversion of the instrument output to chemical information will involve interpretation rather than calibration; for example, the success of a partial elucidation of a molecular structure by infrared absorption spectrometry depends on the accuracy with which the wavenumbers and relative intensities of various peaks in the spectrum may be assigned. It is also important that, to avoid the introduction of easily avoidable errors, the analytical chemist knows how changes in the operating parameters affect the working of the instrument.

The Role of Chemistry

It can be seen from Fig. 1 (line 2) and Fig. 2 that chemistry occurs in a number of distinct locations. Firstly, it is bound up with the sampling procedure. A knowledge of the chemical properties of the determinands and of the other components of the bulk material is necessary if an appropriate sampling procedure is to be devised. Secondly, a wide variety of chemical procedures are involved in pre-treatment: these range from preservation or fixing at the scene of sampling, through dissolution, pre-concentration and matrix isolation, to the addition of appropriate reagents. Most of the latter procedures are performed on the bench in the laboratory. It should be noted that a sample which arrives in a laboratory for analysis will probably be sub-sampled before the method continues.

The third location of chemistry in an analytical method is inside the instrument. Many instrumental techniques in use in laboratories today perform extensive chemistry on the sample components. Consider, for example, the internal processes of an atomic absorption spectrometer or a gas-liquid chromatograph. A knowledge of chemistry is required to understand the basis of a number of interference effects and to compensate for these by the design of appropriate instrument operating conditions or calibration procedures.

Many interpretation problems concern interpretation of "chemical shifts." This terminology is widely used in, for example, nuclear magnetic resonance and X-ray photoelectron spectroscopies, but the same principle is involved in interpretation of the results produced by molecular ultraviolet-visible absorption, fluorescence and infrared absorption spectrometries. In these techniques, no chemical reactions occur inside the instrument as part of its basic operation, but the chemical nature of the sample material influences the behaviour of the transducer.

In some techniques the transducer converts information directly from the chemical domain into the electrical domain as, for example, with ion-sensitive electrodes.

Throughout the method, up to the point at which the information required is encoded as an electrical signal, chemistry is involved in assessing the risks of contamination of the sample material, either with the determinand species or interfering species, and a loss of the determinand species.

There is thus no diminution in the amount of chemistry in analytical chemistry, and scientists who wish to pursue a career in this area must have a substantial chemical education (arguably to degree level). Developments in instrumentation have meant that chemistry is performed in locations other than reaction vessels on the laboratory bench, but this has not decreased the requirement for chemical knowledge.

Role of Sampling

Although it is widely recognised that providing a representative sample from a bulk material for laboratory analysis is not a trivial problem,¹² and that errors introduced at this stage cannot be compensated for later on, it is often overlooked that the material for analysis may be sub-sampled several times before the chemical information is encoded in the electrical domain. Take, for example, the analysis of a solid material for

a trace element by a method which uses flame atomic absorption spectrometry as the instrumental technique. Once the material for analysis has arrived in the laboratory a sub-sample will be dissolved, a further sub-sample may be taken for pre-treatment and a further sub-sample loaded into a cup in the auto-sampler tray. The auto-sampler selects a sub-sample, which is further sub-sampled by the nebuliser and spray chamber. As the beam of radiation from the hollow cathode lamp passes through a restricted volume of the flame, the resulting population of vapour phase species is further sub-sampled before the photomultiplier tube converts light intensity into electrical current.

It should also be borne in mind that sampling is very much part of electrical signal processing. Inappropriate sampling in, for example, analogue to digital conversion procedures, can give rise to problems of aliasing if a regular waveform is being sampled, or errors in peak height and peak area measurements, if single transient events are being monitored.

Practice, Teaching and Research and Development

Fig. 1 summarises the practice of analytical chemistry and it might be argued that, as many scientists make use of information provided by analytical chemists, all scientists should be aware of the contents of Fig. 1 and, in particular, of the constraints under which analytical chemists operate. It is also necessary for such scientists to appreciate why information will be qualified by a statement about its reliability, that uncertainties can be large and that the reduction of uncertainty can be an expensive and time-consuming business.

Chemistry students who will possibly enter employment as analytical chemists need not only to appreciate the underlying philosophy of Fig. 1 but to have the appropriate knowledge and skills outlined in column 3 (Fig. 1), as well as a knowledge of instrument performance criteria (column 2, Fig. 1) and of instrument function as illustrated in Fig. 2.

Research and development in analytical chemistry may be viewed as efforts to improve the performance of analytical methods by improving the performance of the various procedures involved. The criteria set out in column 2 of Fig. 1 provide a suitable check-list against which to evaluate the success of such efforts. At present many such efforts are being

directed at extending the boundaries of the instrument, as shown by the dotted lines in Fig. 1, so that (a) sample pre-treatment procedures are carried out within the instrument (ideally they would be rendered redundant by developments in internal chemistry and transducer function), and (b) evaluation and calibration procedures are part of the instrument function.

The latter development means that it is increasingly important that analytical chemists (or anyone who uses such an instrument) have the necessary knowledge of how the instrument has produced its chemical information in order to assess its reliability.

These are the views of an academic, but it is time that employers of analytical chemists made their views of training requirements known.

References

1. "Supply of and Demand for Analytical Chemists. Report of an Investigation by a Working Party of the Royal Institute of Chemistry," Royal Society of Chemistry, London, July, 1980.
2. *Royal Society of Chemistry Professional Bulletin*, No. 80, December, 1985.
3. *Royal Society of Chemistry Professional Bulletin*, No. 82, July, 1986.
4. ACOL Project Office, Thames Polytechnic, Wellington Street, Woolwich, London SE18 6PF.
5. Tyson, J. F., *Anal. Proc.*, 1988, **25**, 111.
6. Kellner, R., and Pungor, E., *Trends Anal. Chem.*, 1985, **4**, v.
7. In the UK, the survey was co-ordinated by the Education and Training Group of the Analytical Division of the RSC. The Honorary Secretary, Dr. L. A. Gifford, provided a brief analysis of the UK returns at a committee meeting in September, 1985.
8. "Remuneration Survey, 1986," Royal Society of Chemistry, London, 1986.
9. Sherlock, J. C., Evans, W. H., Hislop, J., Kay, J. J., Law, R., McWeeny, D. J., Smart, G. A., Topping, G., and Wood, R., *Chem. Br.*, 1985, **21**, 1019.
10. Miller, J. C., and Miller, J. N., "Statistics for Analytical Chemistry," Second edition, Ellis Horwood, Chichester, 1988, pp. 102-115.
11. Bysouth, S. R., and Tyson, J. F., *J. Anal. At. Spectrom.*, 1986, **1**, 63.
12. Smith, R., and James, G. V., "The Sampling of Bulk Materials," Royal Society of Chemistry, London, 1981.