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The following is the Silver Medal lecture delivered by Dr. J. F. Tyson, the Fourteenth SAC Silver Medallist, at the Research and Development Topics in Analytical Chemistry Meeting of the Division held on July 8th and 9th, 1987, at the University of Strathclyde, Glasgow.

A Judicious Mixture of Reaction Chemistry and Instrumentation

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I chose a general title for this lecture for several reasons. Firstly, as about 13 or 14 scientific meetings in 1987 already featured my name amongst the list of speakers and there were, no doubt, several members of the audience who must have felt they had attended all of them, I wished to say something different in this lecture. Secondly, as atomic spectroscopists have featured prominently as Silver Medal lecturers, I wished to avoid atomic spectroscopy. Thirdly, as it is well known in educational circles that the attention span of an audience is about 20 min, I wished to present three 20-min lectures on somewhat different topics. However, they are linked by the common underlying theme of "time and the philosophy of analytical chemistry."

The title of the lecture is, in fact, a quotation,¹ which in full reads, "The study of chemical reactions is necessary for the future chemist to learn what chemistry is, in the same manner as learning about laboratory instruments shows him how to apply them. The use of properly chosen reactions in conjunction with an appropriate instrument gives perhaps an ideal connection of theory with practice. For these reasons, modern teaching of analytical chemistry should contain a judicious mixture of reaction chemistry and instrumentation." Anyone aspiring to the title of analytical chemist should read reference 1, as it contains much thought-provoking material. In this paper I wish to extend the definition given and argue that all of analytical chemistry—the teaching of, research in, and practice of—can be summarised as a "judicious mixture of reaction chemistry and instrumentation."

Analytical Chemistry—The Present

The entire philosophy of analytical chemistry is summarised in Fig. 1, which shows the processes involved in providing

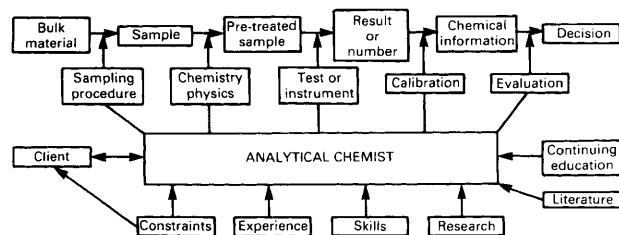


Fig. 1. The analytical chemist at work

information about the chemical composition of a bulk material, together with an indication of the quality of that information (the \pm term to go with a quantitative result). The analytical chemist uses the resources available to decide on the most appropriate way of building up an over-all method given the constraints imposed by the client, availability of equipment,

etc. The teaching of analytical chemistry involves the processes whereby students become conversant with the various procedures available to progress from "bulk material" to "decision" and acquire the ability to evaluate critically the merits of such procedures. Also, research in analytical chemistry involves the generation of improvements in one, some or all of the stages involved or, indeed, the generation of suitable over-all procedures for analytical problems which have, hitherto, remained unsolved.

In order to appreciate fully the role of chemistry in the processes shown in Fig. 1, the role of the instrument in a procedure involving a quantitative measurement is examined in more detail in Fig. 2. It can thus be seen that a variety of chemical processes take place inside the instrument (e.g., an atomic absorption spectrometer with a graphite furnace electrothermal atomiser or a high-performance liquid chromatograph), in addition to a variety of physical and electronic processes. It is important that the analytical chemist understands each of these processes and how an over-all uncertainty in the chemical information is produced from the uncertainties in each of the stages involved both inside and outside the instrument.

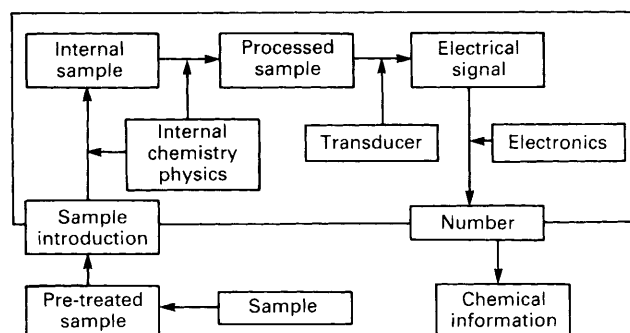


Fig. 2. Taking the lid off the black box

Analytical Chemistry—The Future

Many areas of scientific endeavour (including medical diagnoses, forensic science and industrial manufacture) are underpinned by analytical chemistry and therefore a continued supply of analytical chemists is needed.

However, the major source of such analytical chemists is under threat. For some years now, analytical chemistry within universities has been in decline: a decline that has accelerated since the University Grants Committee's (UGC) cuts of 1981, which have resulted in the non-replacement of staff who have left or retired from Chemistry Departments which were traditionally strong in analytical chemistry (such as Aberdeen,

Birmingham, Chelsea, Exeter, Imperial College and Salford). The untimely death of senior staff at Strathclyde and UMIST and, as yet, their non-replacement has been a further blow. Although the emergence of one or two strong schools of analytical chemistry in polytechnics (notably Sheffield and Plymouth) and the establishment of groups at Hull University and Birkbeck College may have partly off-set the general decline, the national picture is still one of diminished activity compared with the situation in the early 1970s. The effects of the most recent UGC cuts have yet to be fully felt, but the news will not be good for analytical chemistry as the revised levels of funding to universities took account of the results of the UGC's "selectivity in research" exercise. Of the chemistry departments currently research active in analytical chemistry, only one was judged "above average," two were "average" and six were "below average."

On top of all this, an even more serious crisis for analytical chemistry may be imminent. The UGC has selected chemistry² as the next subject to undergo an "Oxburgh" style review.^{3*} Before this can get under way, the Advisory Board for Research Councils (ABRC) has proposed that instead of conducting such reviews subject by subject, whole institutions should be placed into one of three categories.⁴ The top 15 would be fully funded for research, the same number in the next category would be doing some high-level research in less costly areas and the remainder would be teaching at undergraduate and master's level with little real research. At this early stage it is not clear what criteria are to be applied in deciding into which category a Department or University (depending on whether the UGC or ABRC review is implemented) will be placed, but it is almost certain that the UGC's own selectivity in research ranking list(s) will be involved.

The future for analytical chemistry can hardly be said to be bright; and when, in the not too distant future, (a) the supply of graduates with analytical skills has decreased, (b) the numbers of higher graduates with MScs and PhDs in analytical chemistry has dwindled and (c) there are no active research groups to provide consultancy or short- or long-term research facilities for industry and government, don't say you weren't warned!

Analytical Chemistry Research

Returning to the present, for the moment, another way in which research in analytical chemistry can be viewed is illustrated in Fig. 3. As this represents a cost spectrum, it is perhaps not surprising that the majority of research within academic institutions in the UK falls to the left-hand end of this spectrum. Two such low-cost research areas will be described, each of which exploits the measurement of time as part of the quantitative measurement.

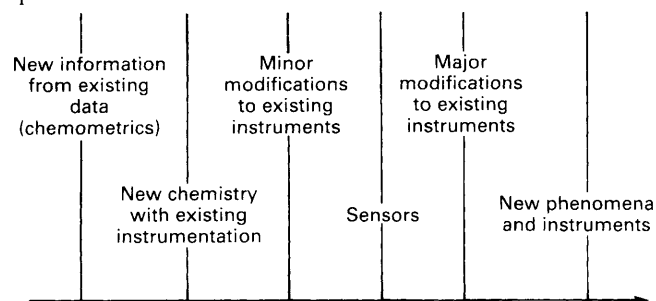


Fig. 3. A spectrum of analytical chemistry research

* Professor R. Oxburgh is the Chairman of a UGC group reviewing Earth Sciences in Universities. The group's recommendations are to divide the existing 51 departments into three categories. The top group, of 12-15 institutions, would be funded to carry out teaching and research to doctoral level and beyond. The middle group, 15+, would be able to teach at master's level and the remainder would only offer undergraduate courses. This third group would be recommended to stop maintaining separate departments and to run courses through service teaching from other departments.

Diffusion-controlled Reactions

At an electrode surface

When an electroactive material arrives at a plane electrode under conditions of semi-infinite linear diffusion, the current which flows is proportional to the number of moles diffusing per unit time per unit electrode area, which, in turn, is proportional to the concentration gradient at the electrode surface, *i.e.*,

$$i = nFaD_o \left(\frac{dC}{dx} \right)_{0,t} \quad \dots \quad (1)$$

where *i* is the current flowing at time *t*, *n* is the number of electrons involved in the electrode reaction, *F* is the Faraday constant, *a* is the electrode area, *D_o* is the diffusion coefficient of the oxidised species (*i.e.*, the species diffusing towards the electrode) and $(dC/dx)_{0,t}$ is the concentration gradient at zero distance from the electrode surface at time *t*. As

$$\left(\frac{dC}{dx} \right)_{0,t} = C_o^b / (\pi D_o t)^{1/2} \quad \dots \quad (2)$$

where *C_o^b* is the bulk concentration of the oxidised species, then

$$i = nFaC_o^b (D_o/\pi t)^{1/2} \quad \dots \quad (3)$$

Taking equation (3) as a starting point, it can be shown⁵ that if the reduced species is monitored by a light beam passing normally through the electrode, the absorbance, *A*, is given by

$$A = \epsilon_R 2 (D_o t/\pi)^{1/2} C_o^b \quad \dots \quad (4)$$

where ϵ_R is the molar absorptivity of the reduced species (it is assumed that ϵ_o , the molar absorptivity of the oxidised species, is zero at the wavelength in question). When equation (4) is compared with the Beer's law relationship

$$A = \epsilon b C \quad \dots \quad (5)$$

it can be seen that the behaviour at the electrode surface may be modelled by the movement of a boundary out into the solution to give a path length *b* of $2(D_o t/\pi)^{1/2}$ up to which the concentration is *C_o^b* and beyond which it is zero. Although equation (4) provides, in principle, the quantitative basis of an analytical technique, a simple calculation shows that for typical values of *D_o* ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and reasonable time scales the path lengths are too short to be analytically useful.

However, if the light beam is rotated through 90° and passed at grazing incidence along the electrode surface, as shown in Fig. 4, the path length term becomes $2(D_o t/\pi)^{1/2} b/h$, *i.e.*, the path length is increased by a factor *b/h*, where *b* is the length of the electrode surface and *h* is the thickness of the light beam.

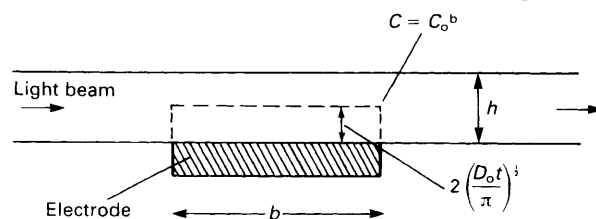


Fig. 4. Grazing incidence spectroelectrochemical configuration

Values of *b/h* of several tens are possible and the sensitivity enhancement gives the configuration of grazing incidence the basis for useful analytical measurements. The full equation is given by

$$A = (\epsilon_R - \epsilon_o) [2(D_o t/\pi)^{1/2} b/h] C_o^b \quad \dots \quad (6)$$

where ϵ_o is the molar absorptivity of the oxidised species.

Not only is absorbance directly proportional to concentration (measured at a fixed time after the start of the experiment), but $At^{-1/2}$ is also proportional to concentration, so the slope of the plot of A versus $t^{1/2}$ can be used as a quantitative analytical parameter. Thus, the working range of the technique may be increased as for more concentrated solutions, if the absorbance value measured goes off-scale, there will still be sufficient data available to calculate a value of $At^{-1/2}$. It has been found⁶ that a linear relationship exists for both quantitative parameters, not only for simple homogeneous redox reactions (such as the reduction of polyphosphomolybdate) but also when a chemical reaction following the electrochemical reaction is monitored (such as the reaction of starch with iodine produced by the oxidation of iodide).

Although the technique removes some of the kinetic restrictions often associated with conventional spectrophotometric methods, allows the working range to be extended and offers interesting possibilities in the design of chemical and electrochemical reactions for analytical purposes, there is no improvement in detection limit compared with the conventional technique (the concentration in the light beam cannot be greater than the bulk concentration). Also, the technique is intrinsically slow, as the absorbance - time characteristics are governed by the diffusion of the electroactive species up to the electrode surface (diffusion in liquids is a slow process).

The sensitivity of the technique can be improved by introducing a pre-concentration stage whereby a metal is electrodeposited on the electrode surface before stripping into a solution containing a colorimetric reagent. Silver has been determined⁶ by anodic dissolution into an *o*-phenanthroline-tetrabromofluorescein reagent after pre-concentration for 15 min. The characteristic concentration (concentration for absorbance 0.0044) obtained was 0.38 p.p.b., which compares favourably with a typical value for flame atomic absorption spectrometry of 50 p.p.b.

To speed up the production of an analytical signal based on a diffusion-controlled process, the concentration gradient responsible for the diffusion must be made steeper. This is the basis of the increased sensitivity of pulsed voltammetric techniques (detection limits are improved as greater discrimination between Faradaic and non-Faradaic processes may be achieved). This approach has yet to be tried for the spectroelectrochemical studies outlined here.

Combination with laminar flow

If the experiment is designed so that the concentration gradients generated by laminar flow in a narrow circular tube are used as the driving force, diffusion-controlled chemistry on short time scales may be exploited for analytical purposes. This concept is the basis of the single-line flow injection manifold, in which a discrete volume of sample is injected into a continuously flowing reagent carrier stream and the reaction product is monitored at a downstream detector. The early stages of the experiment are shown in Fig. 5. There is difficulty in giving an accurate representation of a flow injection experiment in diagrams of this type because, firstly, if the typical values of tube diameter and volume injected of 0.5 mm and 50 μ l, respectively, are taken, whatever scale is used in the diagram the length of the injected slug should be 500 times the diameter of the tube (*i.e.*, the sample occupies a length of 25 cm). Secondly, at the typical flow-rate of 1 ml min^{-1} (33 μ l s^{-1}) the central stream line (which in laminar flow is moving at twice the average linear velocity) is moving at 170 mm s^{-1} , so the lower diagram in Fig. 5 shows the shape of the boundary approximately 0.009 s after injection. Molecules on the leading boundary diffuse from faster to slower moving stream-lines, as shown by the arrows, whereas molecules on the trailing boundary diffuse from slower to faster moving stream-lines. Hence the entire sample zone is transported down the tube to the detector, during which time the zone is mixing with the carrier stream. Under the conditions normally employed

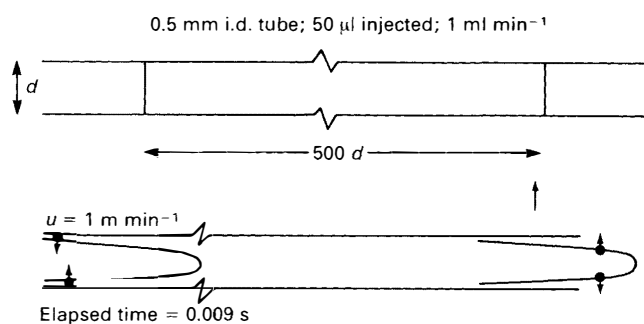


Fig. 5. Initial stages of dispersion by laminar flow in a straight tube

flow injection analysis, no analytical solution of the diffusion-convection equations is possible⁷ and one approach to predicting the shapes of the peaks produced is to model the dispersion process.

One very simple model is the single well stirred tank (WST) model, the basis of which is that all dispersion is modelled by the passage of a discrete slug through a single well stirred tank. This model produces exponential-shaped peaks and the concentrations at the peak of sample (injected), C_p^S , and reagent, C_p^R , (in the carrier stream) are given by

$$C_p^S = C_m^S [1 - \exp(-V_i/V)] \quad \dots \quad (7)$$

$$C_p^R = C_m^R \exp(-V_i/V) \quad \dots \quad (8)$$

respectively, where C^S and C^R are the steady-state concentrations of sample and reagent, respectively, and V_i and V are the volume injected and tank volume, respectively. The extent of dispersion is normally quantified by the dispersion coefficient, D , at the peak, where D is given by

$$D = C_m/C_p \quad \dots \quad (9)$$

Transforming equations (7) and (8) by the appropriate substitutions for D and D^R (sample and reagent dispersion, respectively) produces the relationship

$$D = D^R/(D^R - 1) \quad \dots \quad (10)$$

It can be shown that this relationship holds at all points on the rise and fall curves and indeed is independent of the dispersion model used.⁸

If only physical dispersion is considered (see upper diagrams in Fig. 6), the peak width, Δt , at any concentration C' of the injected sample material is, on the basis of the WST model, given by

$$\Delta t = (V/u) \ln[(C_m^S/C') - 1] - (V/u) \ln(D - 1) \quad \dots \quad (11)$$

where u is the volumetric flow-rate. Equation (11) indicates that peak-width measurement has potential as the basis of a quantitative method as Δt is a logarithmic function of the injected concentration. However, the presence of C' in the logarithmic expression means that to use the relationship, when in practice instrument response, H , as a function of time is measured, the concentration corresponding to the measurement level must be found from a separate experiment. If the approximation $C_m^S/C' \gg 1$ is made,⁸ equation (11) reduces to

$$\Delta t = (V/u) \ln C_m^S - (V/u) \ln C'(D - 1) \quad \dots \quad (12)$$

This equation is valid regardless of the relationship between the response of the instrument; all that is necessary is that the response is stable with time. Thus, the working range of the instrument may be extended, as has been shown⁹ for flame atomic absorption spectrometry, by several orders of magnitude.

When chemical reaction occurs and the reaction product is monitored, two possible situations arise as shown in Fig. 6. If the dispersion characteristics are such that the reagent is always in excess (left-hand diagrams in Fig. 6), the product profile will match the sample profile and equation (11) will describe the peak width. However, if the dispersion characteristics are such that the sample is in excess in the profile centre (right-hand diagrams in Fig. 6) then a doublet product peak is formed. For a 1 : 1 reaction (the situation illustrated in Fig. 6), the points at

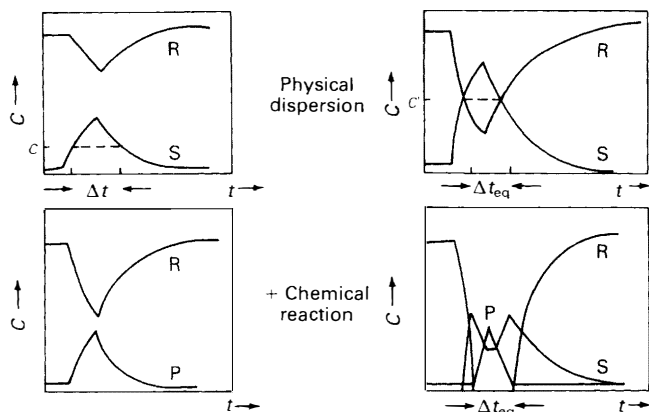


Fig. 6. Physical dispersion and chemical reaction in a single-line flow injection manifold

which the sample and reagent profiles intersect are the equivalence points to the flow injection "titration" on the leading edges and on the trailing edges of the dispersed profiles. If the concentration at the equivalence point is C_{eq} , substitution for the appropriate values of D and D^R at these points into equation (10) gives

$$C_{eq} = C_m^R C_m^S / (C_m^R + C_m^S) \quad \dots \quad (13)$$

and substitution of C_{eq} given by equation (13) for C' in equation (11) gives

$$\Delta t_{eq} = (V/u) \ln C_m^S - (V/u) \ln C_m^R (D - 1) \dots \quad (14)$$

showing that the time interval between the equivalence points, Δt_{eq} , is a simple logarithmic function of the injected concentration.

The use of equation (14) is illustrated in Fig. 7, which shows the calibration obtained for the determination of OH^- over the range 5×10^{-5} to 5 M . The reagent was an acidified solution of bromothymol blue and good approximations to exponential peaks were obtained from a "gradient tube" $52 \text{ mm} \times 1.5 \text{ mm}$ i.d.

As the response of the detector only has to be stable with time, it is suggested that an inexpensive detector could be constructed for such measurements based on light-emitting

diodes and photodiodes and making use of simple digital logic circuitry to measure time (via a clock chip) between two peaks. As this is peering into the future to some extent, perhaps such an instrument, making quantitative measurements in the time domain, should be known as an analytical chemistry time machine.

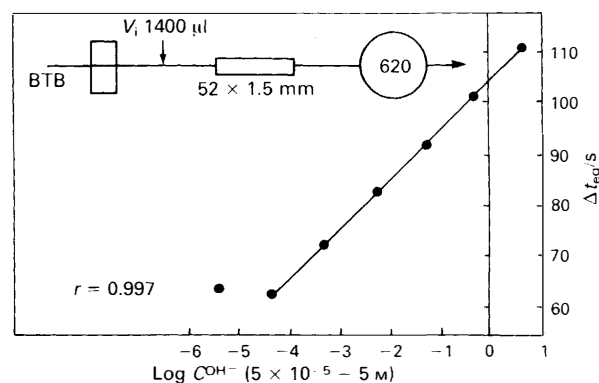


Fig. 7. Determination of OH^- by a peak-width flow injection method

Conclusion

In acknowledging the help and guidance of several groups of people, I would like to recall the opening theme of this paper as I was undoubtedly influenced to pursue a career in analytical chemistry by my experiences as an undergraduate at Aberdeen University. Thus Bob Chalmers along with Professor Tom West, my PhD Supervisor, and my present colleagues at Loughborough University, particularly Professor Jim Miller, must take some responsibility for my contributions to analytical chemistry and I thank many other members of the Analytical Division for being such supportive professional colleagues. Several overseas governments have sponsored research workers, for which I am grateful, as I am to both the SERC and the Trustees of the Analytical Division Trust Fund for financial support over several years.

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