PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Introduction

J. M. Thomas

Phil. Trans. R. Soc. Lond. A 1982 **305**, 471-473
doi: 10.1098/rsta.1982.0044

Phil. Trans. R. Soc. Lond. A **305**, 471–473 (1982)
Printed in Great Britain

Introduction

BY J. M. THOMAS, F.R.S.
Department of Physical Chemistry, University of Cambridge, Lensfield Road,
Cambridge CB2 1EP, U.K.

From its inception this Society has been keenly interested in the techniques and results of analytical chemistry. Many of its distinguished fellows, notably Boyle, Hooke, Priestley and Davy, made direct contributions to the subject. Others, such as Faraday, Stokes, Rutherford, Aston and the Braggs, laid down the foundations of methods now extensively used for automatic analytical purposes. If, as is often argued, chemistry is the language of experimental science, it must surely be agreed that analytical chemistry constitutes the grammar. The need to know which chemical elements are present in a given specimen, and the nature of their combination, is fundamental. Moreover, efforts to improve the sensitivity and versatility of analytical techniques never cease.

Until a few decades ago the stoichiometry and structure of nominally pure materials could not readily be established, with the techniques then available, if quantities of the substance to be analysed were in the milligram range. Nowadays, as some of the papers to be presented at this Discussion Meeting will reveal, the situation is very different. Femtogram (10^{-15} g) quantities or less can be identified or characterized by X-ray emission or energy-loss spectroscopic methods by using a fine pencil of high-energy electrons as primary beams. Moreover, gas chromatography can now be so automated, and so strategically deployed, as the paper by Purnell describes, that mixtures of several dozen components of chemically similar species may be routinely separated and identified. Technological achievement has transformed the subject, and many traditional methods are no longer suitable or appropriate.

Some important techniques are not covered in this meeting partly because of the exigencies of time and partly because they require fuller discussions than would be appropriate here. One of these is fast atom bombardment mass spectrometry, developed recently by Barber & Sedgwick (Barber *et al.* 1981*b*, *c*). As Barber, Sedgwick and others have shown, this technique enables the structure of complicated, biologically important materials such as the enkephalins (Barber *et al.* 1981*a*), oligopeptides (Barber *et al.* 1981*e*) and glycoside antibiotics (Barber *et al.* 1981*d*), as well as organometallics (Barber *et al.* 1981*c*), to be accomplished without conversion of these materials into their volatile derivatives. This work of Barber has already made a major impact in biochemistry and in wider fields of enquiry. It renders possible the rapid sequence assignment of peptides.

Our knowledge of solid surfaces, as the comprehensive review paper here by Rivière shows, has also been greatly elucidated. The presence of adsorbed or constitutional species at levels of less than a thousandth of a monolayer of a single crystal surface (i.e. *ca.* 10^{12} atoms cm^{-2}) can now be detected. There are indications (W. J. Jones, personal communication 1981) that certain nonlinear optical techniques and rather esoteric Raman amplification spectroscopic methods may be able to achieve levels of detectability involving no more than 10^9 atoms cm^{-2}, at interfaces exposed to a gas or submerged in a liquid. Moreover, these could, in principle, be applied under robust conditions, unlike the majority of present-day sensitive techniques for surface analysis where ultra-high vacuums are usually required.

Quite apart from its practical importance to the research scientist and the technologist, analytical chemistry, more so perhaps than most other branches of natural science, possesses a touch of the romantic. Its impact in the study of the objects of antiquity as well as in the field of forgeries in the visual arts, not to mention its role in forensic science, has been immense. It is evocative to recall that some of the early ferruginous objects of the ancient Egyptians were shown by spectrochemical analyses to be of meteoritic rather than terrestrial origin. (It may be significant that the hieroglyphic for iron means 'the metal that fell from heaven'.) Elementary techniques of analytical chemistry were at one time adequate to prove that the pottery and porcelain produced in the nineteenth century in many European factories along the lines of those made earlier in Florence and Orvieto were false: all that was required was a few reliable colour or spot tests for chemical impurities. Nowadays, however, to establish the authenticity of a painting when it might have been created by an errant genius like Hans van Meegeren rather than by Jan Vermeer, more sophisticated techniques are required (Keisch 1970; Fleming 1975). Stylistic analysis, being subjective, yields to and is therefore supplanted by the objective authority of the analyst. Thus, in its raw form as a blue pigment, lapis lazuli from Afghanistan, which until the nineteenth century was the only source of ultramarine, has a quite different relative abundance of sulphur isotopes from the more recently mined lapis lazuli of the Chilean Andes. Again, a recent fake of a seventeenth century Dutch painting might well be characterized by lead white impurity levels of: Ag $\leqslant$ 10 μg g^{-1}, Zn $\geqslant$ 15 μg g^{-1}, Cr $\leqslant$ 40 μg g^{-1}, whereas an authentic work would register (Fleming 1975): Ag $\geqslant$ 18 μg g^{-1}, Zn $\leqslant$ 1 μg g^{-1}, Cr $\geqslant$ 200 μg g^{-1}. Likewise, the work of the forensic analyst, notwithstanding the human tragedies and vice upon which it often impinges, frequently conjures up a feeling of awe and admiration for the technical virtuosity of twentieth-century man (see Curry 1977). To be able to specify, as the forensic scientist now can on the basis of the variation of arsenic content along a length of a human hair and the known growth rate of hair, precisely when a poison was administered, is no mean achievement. Whether the analyst, knowing the characteristics of ^{14}C decay (Baxter & Walton 1971), and given the appropriate access, will be able to establish if the Turin shroud is genuine or the work of some ingenious mediaeval forger, remains to be seen.

My colleagues Professor Belcher and Dr West and I were conscious at the outset that we could not do justice in this short meeting to all the important activities of the modern analyst. We have been deliberately selective; and we recognize that our personal predilections have meant that many topics have been omitted. We are confident, however, that this publication fairly reflects some of the highlights of modern analytical chemistry.

REFERENCES (Thomas)

Barber, M., Bordoli, R. S., Garner, G. V., Gordon, D. B., Sedgwick, R. D., Tetler, L. W. & Tyler, A. N. 1981*a* *Biochem J.* **197**, 401.
Barber, M., Bordoli, R. S., Sedgwick, R. D. & Tyler, A. N. 1981*b* *J. chem. Soc. chem. Commun.*, p. 325.
Barber, M., Bordoli, R. S., Sedgwick, R. D. & Tyler, A. N. 1981*c* *Nature, Lond.* **293**, 270.
Barber, M., Bordoli, R. S., Sedgwick, R. D., Tyler, A. N. & Bycroft, B. W. 1981*d* *Biochem. biophys. Res. Commun.* **101**, 632.

Barber, M., Bordoli, R. S., Sedgwick, R. D., Tyler, A. N. & Whalley, E. T. 1981*e* *Biomed. Mass Spectrom.* **8**, 337.

Baxter, M. S. & Walton, A. 1971 *Proc. R. Soc. Lond.* A **321**, 105.

Curry, A. S. 1977 *Proc. R. Soc. Lond.* B **199**, 189.

Fleming, S. J. 1975 *Authenticity in art: the scientific detection of forgery*. London: Institute of Physics.

Keisch, B. 1970 *Application of science in examination of works of art*, vol. 2. Boston: Museum of Fine Art.

Morris, H. R., Pancio, M., Barber, M., Bordoli, R. S., Sedgwick, R. D. & Tyler, A. N. 1981 *Biochem. biophys. Res. Commun.* **101**, 623.