

Tribute to Alan Walsh from the analytical chemistry group at Imperial College, London, 1963–1975[☆]

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1. Introduction

I am indebted to the editors of this special edition of *Spectrochimica Acta B* in honour of the late Sir Alan Walsh, FRS, for the invitation to make a personal contribution in relation to his influence on my own work and that of the staff and postgraduate students of the research school of Analytical Chemistry at the Imperial College of Science and Technology of the University of London. Alan's enormously significant contribution to the development of a laboratory technique for measuring atomic absorption during the early-to-mid-1950s had a profound effect on my thinking about how the new research team I was about to set up there in late 1963 could best make a worthwhile contribution to the determination of traces of metal ions and to the training of postgraduate students in relevant modern techniques.

[☆] Dedicated to the memory of Sir Alan Walsh and published in this Memorial Issue.

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2. Trace metal analysis before the Walsh era

To set this out logically it is necessary, first of all, to review the current technology of the time and to follow this with a brief account of what we were doing just before Alan's seminal contribution of atomic absorption spectroscopy (AAS) to the scene. At that time there was generally no simple way of determining traces of metal cations in solution. In most cases the analytical procedures that could be used demanded many laboratory operations before the desired analyte could be presented to the measuring instrument. The whole process was fraught with the possibility of contamination and loss of sample and was, in modern parlance — though we did not think so then — generally time-consuming and labour intensive.

The principal technique used in most laboratories of those days was molecular absorption spectrometry. It relied on the use of chelate complexes formed by the metal cations with reagents such as dithizone and oxine, and the selective extraction and preconcentration of these com-

plexes into organic solvents such as chloroform. Spectral measurements were made in mainly crude ‘absorptimeters’ which relied on optical filters to isolate the necessary wavebands from a continuum light source. The gradual introduction of more sophisticated spectrometers using prisms and gratings in the late 1940s to early 1950s scarcely improved matters.

The problem was that the metallochromic absorption spectra were invariably overlaid with those of the reagents and were rather broad, covering at least 100–200 nm, so that the spectral effect of chelate formation was not capable of being used efficiently. These reagents were extremely unselective in their reactions with metal cations. Sometimes masking agents such as cyanide ion could bind some interfering ions, e.g. Zn and Cd in the determination of Cu, sufficiently to prevent them from reacting with the metallochromic agent. Demasking of Cd was possible subsequently by adding an excess of hydroxylamine, which by cyanhydrin formation removed the cyanide ion from some of the more weakly bound cyano-complexes, e.g. Cd, so that the liberated metal cation could now react with the metallochromic agent. Various other clean-up/preconcentration techniques such as adsorption chromatography, ion exchange, adsorption–flotation and even, on the odd occasion, distillation were used in addition to solvent extraction as precursors to the final analytical operation.

Another spectral technique much used by laboratories which carried out large numbers of repetitive analyses on mainly fixed major matrices, such as steels and other alloys, was emission spectrography using electric arcs and sparks between carbon electrodes, first with photographic plates and subsequently with photomultiplier arrays. It was an extremely empirical technique, but worked well in certain restricted areas. Flame emission spectrometry (FES), using the nebulisation of solutions (adopted subsequently in AAS), was useful for the alkali metals and the alkaline earths and, though also prone to matrix effects, it too was quite widely used in some areas. Flames generally were insufficiently energetic to excite most elements other than those.

Variations using ‘total consumption’ burners and air–acetylene flames extended the range of metals that could be determined by flame emission. Flame emission was largely replaced in due course by inductively coupled plasma emission spectrometry (ICPES) which was developed principally by Velmer Fassel in the USA and Stan Greenfield in the UK. ICPES, like AAS, is much used at the present time. Other spectroscopic techniques very much in vogue at present such as spark source mass spectrometry were also undergoing development during the early 1960s.

It is not particularly relevant to this discussion, but I feel that I should mention the electrochemical technique of polarography devised by Heyrovsky and which subsequently won him the Nobel Prize. It was quite widely used at the point when AAS was undergoing development and, in its various DC-, AC-, square wave-, Tast- and other forms, is still used today though not nearly so widely on the inorganic scene as AAS. It strikes me as sadly ironic that those of us who drew Alan Walsh’s development of the AAS technique to the attention of more than one Nobel Prize Committee were unable to win a similar accolade for him.

3. Pre-AAS at Birmingham University

As a newly appointed lecturer at the University of Birmingham in 1955 I had become intensely interested in Schwarzenbach’s technique of complexometry and was more particularly interested in the metallochromic indicators, largely *o,o'*-dihydroxyazo phenyl and naphthyl dyestuffs which he used to detect the disappearance of the last traces of free metal cations in solution as he approached the end-point of his EDTA titrations. It appeared to me that this was a possible source of metallochromes for the absorptometric determination of traces of metals. The problem with these, which we set out to resolve, was that they were very unselective. Just before AAS hove on the scene, we had attained a considerable degree of success by developing ‘Calcichrome’, a

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