J. Assoc. Publ. Analysts, 1978, **16**, 39–44

The Relevance of Reliable Reactions to Analytical Practice

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The substance of a talk given by Dr Stephen at the Annual Conference of the Association of Public Analysts at York on 22 April 1977.

It may well be that a better title would be "The scope of chemical reactions in analytical practice", but the purpose of this talk is to restore some of the imbalance which black-box analysis has brought to analytical chemistry.

The oldest reaction we know which utilises an organic reagent was used by Pliny the Elder in the first century A.D. to establish the adulteration of copper sulphate with iron sulphate. Pliny used, as his reagent, an extract of gall-nuts from the oak, *Quercus infectoria* and impregnated papyrus with a solution of his sample. The result was the first recorded spot test using an organic compound.

The reaction between tannin or gallotannic acid and iron salts is well-known to you all. I like to think of it as the original Stephen's Blue-Black—as writing ink, an article of commerce once advertised on the walls of every little village shop throughout the length and breadth of this country.

This reaction has withstood the greatest test of all, that is, of time. I wish the same could be said of many other chemical reactions which have been used or recommended for analytical purposes. I do not propose to spend any time on ill-conceived or misunderstood chemistry. Instead, in the time available to me, let me show you how the analytical chemist can use the reaction of chemical substances for his own ends, i.e. chemical analysis.

There are many ways of considering the reaction

$$A + B \rightarrow C + D.$$

The analyst looks at this as a means to detect or determine *A*, *B*, *C* or *D*. And it is this simple way of looking at chemical analysis which has provided us with many interesting and useful methods. Let me give one or two examples from the field of masking and demasking, so essential to the improvement of selectivity in analytical processes.

The detection and determination of nickel is best achieved by precipitation with one of the dioximes of vicinal diketones, for example, dimethylglyoxime, which in neutral or alkaline solution gives that characteristic scarlet precipitate first observed by Chugaev in 1905 and containing covalently bound nickel. In the presence of appreciable amounts of cobalt, however, the nickel complex is obscured by the more soluble cobalt complex. The difficulty is easily over-

0004–5780/78/020039+06 $01.00/0 © 1978 The Association of Public Analysts

come as shown by Feigl and Kapulitzas. Sufficient cyanide is added to form the cyanocomplexes, $Ni(CN)_4^{2-}$ and $Co(CN)_4^{2-}$, followed by hydrogen peroxide to oxidise Co(II) to Co(III). Of course, addition of dimethylglyoxime at this stage gives no precipitate. But if a solution of formaldehyde is now added, the free cyanide necessary to maintain the nickel complex in the tetracyano form is removed as glycolic nitrile as is the cyanide arising from the dissociation of the metal complex. This leads to the production of free nickel ions which react at once with the reagent to give the red precipitate. The much more stable hexacyanocobaltate(III) ion (cobalticyanide) is not affected by the formaldehyde. There is enough chemistry in this overall process to make it the subject of several separate discussions, but as a chemical test for traces of nickel in cobalt salts, it is beautiful in its conception.

The development of the aminopolycarboxylic acids as analytical reagents principally by Schwarzenbach and his co-workers almost 30 years ago has given the analytical chemist a powerful new means of achieving the requisite selectivity in the separation and detection of metal ions. Take the classical example of the alkaline earths. I will not describe in detail the several alternatives for the chemical separation of barium, strontium and calcium. This is a problem to which the Midlands Association for Qualitative Analysis has given much attention over the years. The problem is exacerbated by the possible presence of lead, if all these ions are to be separated as their sparingly soluble sulphates. Consider for present purposes, barium and lead in mixtures as the sulphates. These ions have much in common, and without extensive treatment such as fusion with sodium carbonate, they cannot easily be separated. Traces of one may interfere with the detection of the other in tests using chromate or rhodizonate as reagent. However, both sulphates dissolve readily in ammoniacal EDTA from which barium sulphate only can be reprecipitated by adding a solution of magnesium sulphate. Lead and magnesium EDTA are both much stronger complexes than barium EDTA, which can no longer survive under these conditions and which reforms the sparingly soluble barium sulphate. Addition of dilute sulphuric acid, after removal of the barium sulphate, reprecipitates the lead sulphate. A simple solution to a knotty problem.

Most of you will know of the Malaprade reaction—involving oxidation of vicinal dihydroxy compounds such as glycerol, etc. with periodic acid. The result of such a reaction is that the IO_4^- is reduced to IO_3^-. Under normal circumstances, the excess periodate is determined and is the means for the measurement of the periodate consumed by the organic material. However, this does not allow the more favourable equivalence that the determination of the iodate would confer on the determination. Iodometrically, each iodate ion can produce 6 equivalents of iodine. But, of course, under the same conditions, each periodate ion produces 8 equivalents of iodine. The problem reduces to that of determining iodate in the presence of periodate. Not easy, you say. The ions are so similar. But are they? Periodic acid exists mainly as *para*periodic acid, H_5IO_6, a weak dibasic acid. Like phosphoric acid, it readily forms heteropoly acids with molybdate and tungstate. In fact, the Frenchman, Burnel, described the 6-molybdoperiodic acid, $H_2(H_3IO_6.6MoO_3)$

or $H_2(H_3I(MoO_4)_6)$, in 1965. Such complex acids no longer have the oxidising power of the uncomplexed periodic acid. Thus, in the presence of molybdate ions, iodate can be determined by the advantageous amplification process without interference from periodate. We can go one stage further. Oxalic acid is not oxidised by permanganate in the presence of molybdate ions. This indicates how strongly the oxalate is bound in the molybdeno-oxalic acids. If oxalate is added to the molybdeno-periodic acid, the periodate is released and can be determined iodometrically. Thus, the analysis of a mixture of iodate and periodate is not so difficult to achieve, providing the right reactions are used.

There are numerous other examples one could quote from this subject of masking and demasking in which chemical reactions are used simply and elegantly to achieve particular analytical objectives.

But, having mentioned amplification, I would like to show you how multiplication of reactions can provide more favourable conditions for measurement of particular species.

The classical amplification is that of iodine. Reduced to iodide and oxidised to iodate with bromine water, six times the original iodine is then liberated by reaction with an acid iodide solution:

$$I_2 \xrightarrow{SO_3^{2-}} 2I^- \xrightarrow{Br_2} 2IO_3^- \xrightarrow{I^-,H^+} 6I_2.$$

Vieböck used this type of favourable equivalence in his modified Zeisel alkoxyl determination. The alkyl iodide is reacted with bromine in glacial acetic acid to form iodine bromide. This in turn forms iodate when diluted with water so an iodometric finish to the determination gives 6 equivalents of thiosulphate for every methoxyl group in the organic compound.

A similar situation exists in Untersaucher's method for the direct determination of oxygen in organic compounds. The carbon monoxide formed by pyrolysis of the organic material is led over heated iodine pentoxide and the liberated iodine is oxidised to iodate.

An old but not so well-known method for phosphorus in steel depends on the conversion of the conventional ammonium molybdophosphate precipitate into lead molybdate. As the final weighing form, this is interesting in that it contains none of the element being determined but is about 140 times the weight of the original phosphorus. Each phosphorus atom is equivalent to 12 molecules of lead molybdate.

You are all familiar with cobaltinitrite as a precipitant for potassium. This ion is easily formed from Co(II) ions by oxidation with nitrous acid. If the hexa-amminocobaltic ion is added to it, a precipitate of the cobaltinitrite is formed. This can be filtered off, destroyed with acid to form 2 cobalt ions for each original cobalt ion present. The process can be repeated as often as practicable. Repeating it 10 times would give over 1 gram of cobalt from an original 1 mg.

Well, again these examples serve only to indicate the wealth of chemical reactions which can be classified as amplification reactions.

I should like now to turn to some aspects of trace analysis and to illustrate how a basic chemical reaction can be exploited in several ways. The fact that mercury(II) chloride is only very slightly dissociated has, of course, been used in the mercurimetric determination of the chloride ion. It is not really surprising that organo-mercury halides, such as phenylmercury(II) chloride, are also covalent in character. Not so compounds like phenylmercury(II) nitrate which is completely ionised in aqueous solution. Thus, treatment of a dilute chloride solution with phenylmercury(II) nitrate allows the corresponding chloride to form which can be removed from its aqueous solution by extraction with chloroform. All the chloride is now present in the organic solvent and a variety of methods is now available for its determination. Perhaps the most favoured is gas–liquid chromatography. The thermal stability and volatility of phenylmercury(II) chloride are quite sufficient to allow chromatography to occur at temperatures around 175°C. The sensitivity of the method is dependent on the nature of the compound and the type of detector. With flame ionisation, for example, 10–15 ng of chloride can be detected. With an electron-capture detector this is improved some 10,000 times, when a solvent such as benzene or toluene is used.

The great advantage of gas–liquid chromatography is that useful separations can also be achieved. Mixtures of chloride, bromide and iodide can be resolved and simultaneously determined.

Solution spectrophotometry can also be used for the final measurement. The chloroform solution of phenylmercury(II) chloride can be treated with a solution of sodium diethyldithiocarbamate and the resultant phenylmercury complex absorbs strongly at 297 nm. This procedure will not differentiate between chloride, bromide and iodide and gives only the total halide present. A third method requires the phenylmercury(II) halide to be removed from the aqueous solution with a non-halogen solvent; propyl acetate is quite effective. The organic solution is then vaporised in an atomic absorption machine and the mercury content thus determined.

This type of solvent extraction-gas chromatography process can be applied also to the determination of metals in trace amounts. The environmentally significant metals such as beryllium and chromium can be determined in amounts of 10^{-12} gramme or even lower. In 1920, Morgan and Drew in a paper on certain acetylacetonates stated rather figuratively that "acetylacetone has given wings to the metals, for certain of these compounds are volatile without decomposition". In this same paper, the authors suggest the term "chelate" to describe the caliper-like groups which lead to the binding of a central metal atom in a stable complex ring structure. These chelate compounds find very wide application in analytical chemistry through the participation of organic reagents with metal ions. The β-diketones, of which acetylacetone is the best known example, readily form metal complexes of a chelate character, molecules with no overall charge and with largely covalent properties. Beryllium and chromium acetylacetonates can be distilled without decomposition, such is their volatility, but enhanced characteristics can be imparted to the resultant metal chelates by using appropriately substituted β-diketones. Thus, trifluoro- and hexafluoroacetylacetone give more volatile chelates and thus are more

suited to gas chromatographic methods than the parent acetylacetonates. As with the halides, separations and individual determinations are possible. The conventional β-diketones are not so useful for divalent transition metals for various reasons. But the coordination chemistry of these ions suggests that ligands containing sulphur may produce more useful chelate structures. Monothioacetylacetone, in which one of the keto-oxygens of the parent β-diketone is replaced by sulphur, is a more effective ligand and monothiotrifluoroacetylacetone is better still. Thus, nickel, palladium and platinum can easily be separated on a column heated to little more than 180°C. The determination of nickel is possible in a variety of materials, such as alloy steels, fats and oils, and instant tea powder. The last mentioned is interesting in that the tea plant tends to concentrate metal ions in the young growing leaves. Foreign ions such as nickel may be assimilated by the plant from fungicidal sprays containing nickel dithiocarbamates. Analysis of several samples has shown them to contain about 12 p.p.m. of nickel. The gas chromatographic method seems preferable to the atomic absorption method (AAS), in giving a lower standard deviation.

The exploitation of chemical reactions in this way promises much in the way of useful analytical methods, particularly for the analysis of troublesome combinations of metals, such as potassium and rubidium, niobium and tantalum, zirconium and hafnium and much work is being done to provide more effective ligands for these particular mixtures of metals.

I want to conclude this rather brief account of reaction chemistry with a comment on the usefulness of nephelometric methods. Precipitation reactions especially as applied to conventional gravimetric analysis are considered as rather a bore. Gravimetry is tedious, troublesome and, above all, demands a high degree of experimental ability. Although most precipitants used in gravimetry are of sufficiently low solubility to allow quantitative analysis, solubility effects can be serious especially during the isolation and purification of the precipitate. The determination of the sulphate ion as barium sulphate is a good example. Tractable precipitates are obtained only by adequate digestion and ageing of the precipitate in the mother liquor. If, however, one wishes to determine small amounts of sulphate ion by nephelometry, that is, by measurement of the light scattering of the suspended particles of barium sulphate, then quite different considerations apply in the formation of the precipitate. It needs to be as uniform as possible with a particle size of about 0·5–1·0 microns in diameter. The precipitate should not age rapidly or aggregate readily. It should be the ideal suspension and in very dilute solution this is sometimes difficult to obtain, especially with purely inorganic ionic precipitates.

But there are many advantages to the use of precipitation reactions in this way. It is no longer necessary to remove, isolate and purify the precipitate. Precipitation is generally favourably influenced by the continued presence of the excess of precipitant—the Common Ion Effect—and the full sensitivity of the precipitation reaction can be utilised in a way which is difficult with the gravimetric operation.

Organic precipitants generally give precipitates which are often easier to

handle, and two reagents, amino-chlorodiphenyl and 2-aminoperimidine, show the ease with which nephelometric measurements of low sulphate concentrations can be made.

An interesting method for the determination of traces of mercury in various materials, but particularly in laboratory dusts, depends on a conventional wet digestion of the sample followed by reduction, and volatilisation of the mercury in a stream of air. This is absorbed in dilute nitric acid and a new reaction is used to convert the mercury into a suitable form of suspension for nephelometric measurement. In aqueous solution, mercury(II) ions readily form diphenylmercury, $C_6H_5HgC_6H_5$, on reaction with an aqueous solution of phenylboric acid, $C_6H_5B(OH)_2$. The finely-divided organo-mercury compound is insoluble in water and forms an ideal type of suspension. The method is somewhat less sensitive than AAS but is simple and easily adapted for routine purposes at the p.p.m. level.

Other environmentally significant metals such as zinc, cadmium and lead are equally amenable to this sort of nephelometric process, thus providing useful alternatives to the more costly flame spectrometric methods.

I have tried in the brief time at my disposal to emphasise the role of chemical reactions in the continuing development of sound analytical methods. There are many who say that there is little or no chemistry remaining in modern analytical practice. I am one who thinks it will be a very sad day if and when that happens. In my own work I shall continue to pursue the fascinating subject of analytical reaction chemistry.