

## PROBLEMS IN THE TEACHING OF ANALYTICAL CHEMISTRY

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Abstract - Because of the nature of analytical chemistry, those teaching it tend to be much more pragmatic in their approach than their colleagues in other branches of chemistry are, in designing lecture courses. Thus the main emphasis is on the employment of theory for attaining severely practical ends, rather than on theory for its own sake and interest. Further, because analytical chemistry utilizes any part of chemistry that will serve its purpose, it alone among the various branches of chemistry gives a unified picture of chemistry as a tool in the service of man. The application of analytical chemistry consists in effect of solving a series of problems presented by the nature of the material to be analysed, the equipment available, and the speed, accuracy, precision and information required. The teaching of the subject is therefore best done along the same lines, by presentation and solution of a series of problems, each of which is seen in the context of the analytical problem concerned (i.e. the technique and application), and of the chemistry that is used to solve it. These are the problems that are useful in teaching. There are many other problems for the teacher, however, many of them common to science teaching in general (such as inadequate preparation at lower levels of education) and some peculiar to analytical chemistry (such as lack of understanding of its aims and purpose even by other scientists). These are the problems we could well do without, though they can be instructive to students of the folly of mankind.

The original theme chosen for this lecture by the organizing committee was "The Renaissance in the Teaching of Analytical Chemistry". Now while it is true that there has been a resurgence in analytical chemical practice (as Professor Belcher will prove in his lecture at Birmingham in July), if there has been a renaissance in the teaching of the subject it exists only in the minds of analytical chemists, and has passed undetected by other kinds of chemist. The truth is, that analysis is still all too often regarded as not sufficiently academic to be fit for scholars to associate with. This attitude is, of course, completely contrary to the classical concepts of the university and of scholarship and is a condemnation, not of analytical chemistry, but of those who hold this view. On that score it is to be regretted. On the other hand, I find some consolation from the implication that analysis must in some way be inferior because of its close association with skilled practical work. I am glad of this implication because I believe that analysis is the most important and rewarding branch of chemistry simply because of its repeated emphasis on using theory to ensure that practice is correct, and its insistence on usefulness as a criterion of value. I once knew a Russian chemist who used to say "Those who do not work should not eat", and if we were to expand this by inserting "usefully" after "work" and adhere to the principle, there would be many academic chemists dying of starvation.

As with every generalization, there are exceptions, of course, and there are some countries, more enlightened than my own, where analysis is valued at its true worth and it is realised that without analysis not only chemistry but all our high technology would not have come into existence, and the guaranteed quality of the daily necessities of life, taken for granted by all of us, would disappear. In these countries analysis takes its rightful place in the academic spectrum.

Even so, there are certain problems, apart from that of recognition, that seem to be the same for all countries. From time to time these problems are discussed at conferences, as they were at Budapest two years ago, but such discussions usually show that there are as many opinions as teachers, and seldom end in agreement. It was for this reason that I asked to be allowed to change the topic to "Problems in the Teaching of Analytical Chemistry" in the hope of being able to put all the arguments into coherent form and to show that problems are the very lifeblood of the analytical chemist, rather than to say anything really new.

These problems can be qualitatively separated into three groups, under the headings of what to teach, when to teach it, and how to teach it. First, however, we should consider the objectives of higher chemical education in general, and then each group of problems in turn.

#### The objectives of chemistry teaching

The first problem is to define the objective of education in general - is it to be learning for its own sake, training for performance of some useful function, or both? Learning for its own sake is selfish and antisocial in the sense that it ignores the basic needs of society and if allowed to expand beyond a certain point can result in a self-perpetuating system which uses a large proportion of its product (the graduates) to do "research" and to teach the increasing number of students attracted by the apparent success of the system. The parallel with bureaucracy is obvious. Training purely for vocational purposes is much more sensible in terms of social need, but tends to cancel the basic requirement of any possession of an enquiring mind. There is an old story of the man who took his son to the Royal School of Mines in London to be taught to "do copper; nothing else, just copper", and that is vocational training narrowed to an absurdity. The ideal is a judicious mixture of training for the job and an understanding of the necessity to explore to the limit of one's ability.

Unfortunately, chemistry teaching often seems to have developed into the class of learning for its own sake, and often omits the "old-fashioned" rudiments in order to make room for the latest fads and fancies in research and in educational theory, and then complains (along with industry) when students are ignorant of things they have never been taught and could not be expected to know by instinct. As so often happens in life, the argument is that anything new must therefore be better, and the old must be scrapped. Although it has been shown time and again how fallacious this argument is, most people are no better than politicians when it comes to learning from experience. A look through the contents list of almost any journal devoted to publication of academic research will show that much of the work done is of very little use (or even none at all) to practical needs in a world that encompasses a range of development from stone age to high technology, has an expanding population and dwindling natural resources, and is inhabited by a species that lacks the ability (or perhaps the desire) to perceive its own predicament and work in harmony to deal with it. Nero fiddled while Rome burned, and we still all quote it as a joke.

#### What to teach?

Should we teach theory, or practice, or both? Not all chemists wish to be analysts, but practically all of them must use analytical results. If they are to do so sensibly, they must understand how analytical chemistry works, what its objectives are, and most important, not only what it can do but also what it can not do. This last is important because trying to do the impossible is not a very useful occupation, even though it is a possible solution to the problem of unemployment. Perhaps I should add here that enlarging the student population is one way of reducing unemployment by taking a steady-state population off the labour market, and is perhaps the politicians' reason for doing it.

First, we have to realise that the essential difference between analysis and other kinds of chemistry is that analysis must be quantitative. A synthetic chemist is not worried by a low or variable yield so long as he can obtain enough pure product for characterization and further work. It is not surprising that such chemists have little or no appreciation of the aims and methods of analytical chemistry. It is ironic that organic chemists discovered one of the methods of precipitation from homogeneous solution (recrystallization from aqueous alcohol) without realizing its analytical significance. Analytical chemistry is unique amongst the various branches of chemistry because it is the only one which provides a synthesis of all the others and relates all its theory to strictly practical ends. It is not for nothing that the dictionary defines analysis as "the determination of a substance; the report of the results of such a determination; a tracing of things to their source". It is this last definition that tells us what to teach, namely the analytical approach to problem solving, in which all aspects are examined and taken into account.

This begins with the nature and history of the material to be analysed, and the purpose of the desired analysis, which we need to know if we are to choose the correct method for sampling and the correct procedure. The nature of the material tells us the concentration levels of the constituent to be determined and of possible interferences. This means it decides the size of sample, the method of any decomposition needed, and the type of technique to be used for determination. The purpose of the analysis tells us the speed and precision required, and again indicates the techniques available for the job. The number of samples to be analysed per day and the cost of the work must also be taken into account.

Each of these steps itself poses problems. Is the sample homogeneous? If not, is it the average composition we want to know or the degree of segregation of material? Does the sample throughput demand automation? Is an instrumental method accurate enough? How fast is the method? Is the chemistry correct? Have all major sources of error been taken into account? And so on. These questions call into play a good general background of organic

and inorganic chemistry, materials science, economics, ergonomics and physical chemistry, and some knowledge of the principles of automation and computing, and the answers to them show how the analyst uses to the best advantage the tools at his disposal. Further, it can be shown from examples that sometimes nature still has surprises for us and new completely unexpected complications can arise which prevent the analyst from attaining the desired result until he has identified the cause of the trouble and learned how to deal with it. He then simply has one more tool in his outfit for problem solving. It is rather like trying to find why a motor car will not start - we first try the standard checks for petrol in the tank, engine not stolen in the night, ignition spark, petrol flowing to carburettor, no potato in the exhaust pipe or sugar in the petrol, etc. and if all these fail we search until the fault is found (perhaps a petrol-water clathrate frozen out in the carburettor) and then add this to the standard list of checks next time. A good example in chemistry is the discovery of the inert ligand-bridged binuclear complexes involving two different metals; these complexes may completely mask the metal of interest, or even worse, mask part of it (we then find the rest and imagine the result is correct). Another example arose during this meeting, when I was discussing with a colleague possible reasons for the failure of peroxide to oxidize completely traces of ferrous iron. It seemed to me that if the Haber-Weiss mechanism was operating, there could still be catalyst present (the ferrous iron) after all the peroxide had decomposed.

Finally, we must teach an appreciation of the magnitude and importance of errors. A biased error of 1% in the analysis of a material sold at a price fixed by the content of some component (e.g. iron or fertilizer) can be very expensive or very profitable, depending on whether the error favours the buyer or the seller. On the other hand, an error of 1% in the determination of mercury at the ppm level in water is quite without significance, as errors of several orders of magnitude can be produced by a bad choice of method or bad sampling. I should explain that ppm means parts per milliard, and I can see no excuse whatever for the continued use of the American billion to mean  $10^9$  when there is a perfectly respectable term - the milliard - that avoids the confusion with the European billion. The further problem of parts in  $10^{12}$  (parts per billion in Europe, parts per trillion in the USA, but a trillion is  $10^{18}$  in Europe and the abbreviation ppt is often used to mean parts per thousand!) could be resolved by using parts per 1000 milliard, or ng/kg or ng/litre. Quite simple calculations will show the relative size and importance of the errors. Similarly a simple calculation will often show whether a determination is worthwhile or not. Elemental microanalysis will certainly not differentiate between  $C_{30}H_{62}$  and  $C_{31}H_{64}$  for example (unless one follows the Bureau of Standards example and goes back to the old methods with 1 g of sample and an 8-hour combustion). Some knowledge of chemistry also sometimes helps - one organic chemist was upset by the very low carbon values for his research compounds, but on questioning revealed that these were fully halogenated flame-retardants, a fact he had not thought worth mentioning to the analyst. Students should also be told quite firmly that IUPAC ideas on nomenclature and units, though doubtless praiseworthy for their devotion to an ideal, are equivalent to imposition of a mental straitjacket, and strictly adhering to them is rather like being a Swiss but being able to speak only one language. Some of the SI units are far removed from everyday experience, and refer to unfamiliar concepts that need secondary explanation. Pressure is a good example - we can see what is meant by mm of mercury, but who has ever seen newtons or had a clear square metre of laboratory space to count them on? It is perhaps significant that almost without exception instruments are labelled in the commonly used non-SI units when there is a choice, and that authors generally prefer not to use them when writing papers.

Naturally there should be a supporting practical course to illustrate the various theoretical points made in the lecture course, so that the student can see for himself that analytical chemistry really works.

Ideally the course should begin by showing how the ideas of physical chemistry are combined to provide analytical techniques which are of broad application. This should be followed by showing how the analytical techniques are selected and modified according to the needs of the particular problem. We thus have a layered structure beginning with simple ideas and working up to quite complex ones.

There remains the problem of the total content and treatment of the course. We can think of it as a box of fixed capacity, which can be made wide in two dimensions and shallow in the third (like a drawer), or like a cube, or very narrow in two dimensions but very deep. In my opinion the dimensions must be comparable so that the knowledge imparted is not too narrow or too superficial, but both wide and deep.

#### When to teach it

In the early days of chemistry when analysis was still taught as the foundation stone of chemistry, it was dealt with right from the start of the course. Now that analysis has been placed on a firm theoretical foundation and is no longer purely descriptive, it should not be taught until the student has enough background knowledge of the other branches of chemistry to be able to understand what the lecturer is trying to tell him, without time being wasted in teaching him the rest of chemistry as well as analysis.

A problem here for the teacher is that it is necessary to know exactly what has been taught already, so that proper back-reference can be made and any errors or misunderstandings can be corrected. Students always seem to think that once they have passed an examination on some part of chemistry, they will never need that chemistry again, and can forget about it. They do not seem to realize that a university course is integrated, one part with another, and that none can really be done without, nor do they realize that recall of material is easier if there are more cross-links between sections, acting as additional memory-triggers.

In my opinion the student must at least have heard of the first and second laws of thermodynamics, the law of mass action, the Nernst equation, and a bit about kinetics. It does not matter if he has not fully understood it - the analyst can help him by providing examples showing the direct practical application of these concepts, and how abstract ideas can be made to do useful work. On this basis the student can first be taught the principles of gravimetric and titrimetric analysis, which in my opinion must come first in any analytical course because (i) they require the least expenditure on apparatus and instrumentation, (ii) they are inherently more precise than practically all instrumental methods and it gives a student much self-confidence if he can obtain closely agreeing results from different quantities of the same material, (iii) almost without exception, instrumental methods need calibration with standard reference materials, and these can be analysed accurately only by classical methods, (iv) almost all destructive methods need some solution chemistry, and skill in this can best be acquired by doing classical analysis.

This can be followed by a course on instrumental techniques, showing their completely different range of application, and their inherent special sources of error, which are too often ignored.

Finally, for the dedicated analysts, there should be a course on applications. This is conveniently split into two parts, with a certain amount of common ground. It is difficult to find short but adequate titles, but trace analysis and industrial analysis seem as good as any. In trace analysis the reasons for it may be given, and a survey of methods, cross-linked with a classification according to the field of application. Thus we might have trace analysis of water, foodstuffs, the atmosphere, pesticides, pharmaceuticals, plastics, ultrapure materials and so on, with an account of the problems and difficulties of sampling, contamination, adsorption or volatilization losses etc., and an examination of the real meaning and validity of the results. In industrial analysis, we can deal with both classical and instrumental methods as applied to both major and minor constituents and to traces, in both organic and inorganic materials, with critical appraisal of their usefulness and limitations. My own preference is for going through the periodic table, with discussion of the analytical reactions of the various groups of elements, and the various kinds of materials containing these species. Thus organic analysis can be dealt with along with carbon, with consideration of other elements such as hydrogen, the halogens etc. Silicate materials are dealt with when silicon is reached, together with a discussion of heteropoly acids. The metals can be taken in groups according to the type of industry, so we have iron and steel, including all the alloying elements, aluminium alloys, copper alloys, white metals, "space-age" metals (Zr, Ti, Ta etc.), nuclear reactor metals and so on. Then there are the heavy chemicals, petrochemicals, fertilizer, food, pharmaceutical and other industries, each with its own range of requirements. Throughout the course there should be adequate reference to the literature and instruction in its use, and also some training in the assessment of published work (i.e. a short course in refereeing).

In such a survey an important feature is showing how the analyst selects only those reactions which can be made to go practically 100% to completion, since these are the only ones generally suitable for his requirements. This is probably why analysis has come to be regarded as a part of inorganic chemistry, and not a branch of chemistry in its own right, simply because practically no organic reactions give quantitative or even reproducible partial yields (as any student can testify), whereas inorganic chemistry abounds in such reactions.

Given a course such as this, that develops as it goes and is close knit by cross-reference between the various sections, a student should be reasonably well equipped for industrial or academic research or quality control work. Of course, the student who is not a dedicated analyst will not and need not take the entire course, but at whatever level he stops he will have been exposed to the analyst's approach to the problems he is set.

#### How to teach it?

This must remain for each teacher to decide in terms of time and equipment available, the experience and interests of the staff etc. As a general guide, however, as analysis is in essence an exercise in problem-solving, it seems logical to try to teach it as a series of problems and their solutions. These can be considered in the order of the events in a chemical analysis.

#### Sampling

Sampling theory is not really well developed, largely because of the complexity of the problem; more use might be made of computers for tackling it. It is perhaps best to let

students invent their own methods of sampling very inhomogeneous samples such as a salt-sugar-sand mixture, and find out by analysis how good the methods are, and also that a biased sample may give unmeaningful results. The classic instance was the Customs office boy who took a sample of a packing case instead of the contents.

#### Decomposition

The opening out of a sample is a fruitful source of problems. The choice of decomposition technique will depend on both the nature of the sample and the analytical method to be used. Thus organic samples can be treated directly in suitable solvents when group analysis is to be done, but for elemental analysis an oxidative or a reductive decomposition is necessary. For metals the operative factors are (1) the redox potentials of the components and hence the choice of a non-oxidizing or an oxidizing acid, (2) the risk of loss of volatile compounds, (3) the effect of passivation or formation of protective coatings, (4) the possibility of alkaline attack for amphoteric metals, (5) use of complexing acids or both oxidation and complexation when the redox potential is very high. Note that "non-oxidizing" is a misnomer, because all acids are oxidizing if the hydrogen couple is involved in the reaction. For insoluble materials the cause of the insolubility is the key. Thus for sulphides we can treat the solubility product as the inverse of a stability constant and consider whether simple protonation of the sulphide ion will do, or whether oxidation to sulphur or sulphate is needed, or both oxidation of the sulphur and complexation of the metal ion. For carbonates and phosphates simple protonation is adequate. For silicates both alkaline attack and a complexation attack (Berzelius method with hydrofluoric acid and sulphuric acid) can be applied. It is useful to question students on the reasons for choice of method of attack, on the products, the effects of concentration and temperature (especially with oxidizing acids), the volumes necessary, the volumes of gas produced and so on.

At this stage the student can also be introduced to the notion that analysts never confine their thinking to one direction, but always try to see further applications, especially with a view to turning a drawback into an advantage. Thus the possible loss of volatiles can be turned into a means of separation and isolation; the adsorption effects that are undesirable in gravimetric work can be used to advantage in titrimetry with adsorption indicators; if A is a reagent for B, then B is equally a reagent for A.

#### Determination

Here the problems are mainly those of choice of classical or instrumental method, gravimetric or titrimetric, reaction type (acid-base, redox, complexometric), followed by choice of reaction conditions (pH, masking agents, aqueous or non-aqueous medium, etc.) All these are standard problems both for the student and the analyst, but with the difference that they are all new to the student and so have to be introduced to him first individually and then in combination. This itself is another problem, much the same as the problem of composing a paper such as this one, and arises whenever it is desired to compare and evaluate several ideas simultaneously. This can only be done once the ideas have been entered in the mind's memory banks, and the problem is to convey them to the audience without having some of them lost before the task is completed. In other branches of chemistry the student is seldom asked to comprehend more than one idea at a time, and even then in the context of highly simplified systems. A student beginning analytical chemistry has no experience of handling complex systems and so tends to get lost and to give up trying. The course is then said to be too difficult and the teacher is blamed, even though the ideas themselves are simple, the common currency of physical chemistry, and used over and over again in various analytical combinations and situations. The real trouble is that there is a tendency for other branches of chemistry to teach in terms of abstract theory without relating the consequences to practice, and sometimes to make statements without explanation. In classical analysis we are dealing with several competitive equilibria, and thus need to adjust the conditions so that the desired reaction takes place quantitatively, with exclusion of all competing or undesired reactions. There is great intellectual satisfaction to be gained from solving such problems, both for the student when he realises he can do it, and for the teacher when he sees he has managed to impart the analytical approach. Unfortunately many modern students seem to see problems as a nuisance and not as an intellectual challenge.

Further problems arise, of course, such as the questions of purity of reagents, tolerance limits on weights, volumetric apparatus, volumes of reagents to be added, etc., standardization, sources and magnitude of experimental error etc. and these or similar problems are common to both classical and instrumental methods.

#### Results and calculations

The first problem here is to get students to appreciate what is meant by precision and accuracy and how to express this in terms of significant figures. Since the advent of the cheap pocket calculator it is becoming increasingly difficult to find students who can (1) understand logarithms and their use, (2) do arithmetic quickly and accurately, (3) do enough mental arithmetic to be able to check quickly whether they have pressed the right buttons on their calculators, and (4) see how far and how soon to round off numbers. For myself I find calculators a waste of time because I usually do the calculation again by hand to check the calculator, and for some purposes the calculator is in fact slower. The student should

also be weaned away from the exclusive use of molarities in calculation and taught the importance of using normalities and equivalents as well.

It is difficult to persuade students to do any statistics on results and to attempt to assess experimental error, but an attempt should be made to get them to relate analytical results and errors to the economics of production plant, quality control etc. Thus they may be asked to calculate the cash saved by keeping the nickel content of steel in a lower quartile of the specification range and to suggest what the control band should be for check analyses. They can also be asked to work out the cash equivalent of a 1% relative error in iron determination when say  $10^4$  tons of iron ore are being bought at  $x$  cash units per % of iron per ton, and to assess their own results in these terms.

The student can further be introduced to the idea of cost effectiveness of various approaches to analysis, in terms of sample throughput, analysis time, labour costs, equipment costs (allowing for cost-accountancy ideas on depreciation) etc., so that he can form some idea of when automation is best and when a simple manual method will be best, fastest and cheapest (e.g. Cu in brass in 5 minutes, start to finish, Mn in steel in 7 minutes, Si in cast iron gravimetrically in 20 minutes). Doing this provides an excellent opportunity to present "case histories" of industrial analytical problems to give the student the "feel" of the subject.

#### Conclusion

I hope I have managed to convey adequately some of my thoughts on the problems we have to solve ourselves, and the problems we can ask students to solve, in the teaching of analytical chemistry. Naturally many will have ideas different from mine, but I think our cause is best served not by endless arguments over small points of detail but by reasoned and extended expositions of various points of view, followed by synthesis from what is generally acceptable.

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