

# A UNIFIED TREATMENT IN TEACHING OF INSTRUMENTAL AND CHEMICAL ANALYTICAL METHODS

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## INTRODUCTION

This report is a confession of some of the difficulties come across in teaching students the theory and practice of physical and instrumental methods of analysis, and examining them on the subject. An attempt made to overcome these difficulties is also reported.

The best way to acquaint a student with a branch of science is to show him its relationship to another branch which he has already studied. Therefore, because of their use in analytical practice, instrumental methods should be taken as a part of analytical chemistry and not of physical chemistry and not as a special subject. Likewise they should be taught on the same basis as the so-called classical methods of analysis, i.e. on the basis of separation and determination and not as separate techniques such as potentiometry, polarography, spectral analysis, chromatography, etc. When physical methods are taught separately, students are left with the impression that these methods are based on different principles from those of gravimetry, titrimetry, etc. It is often found that students think that mastering a technique such as potentiometry means knowing how to set up a cell containing the indicator electrode and how to turn the knobs on the potentiometer. They are ignorant of the properties of the electrode and the information it can provide about the reaction being used. The same is true for other methods such as conductometry or polarography.

On reflection one sees that apart from the modes of operation of the instruments, physical methods in no way differ in principle from the classical methods. In gravimetric analysis it is clear to every student that he can determine the constituents of the sample only after he has separated them from each other. In instrumental methods this separation of the constituents is not so obvious, but it can be found. Let us consider spectroscopic methods. We select from the emission spectrum of the sample those lines whose wavelengths characterize the elements present in the sample, and then determine the concentration of the elements from the density of the lines. Because every element has its own lines in the emission spectrum, we obtain by means of this property of the spectral lines the same result as if we had performed a physical separation of the constituents of the sample.

Again, the height of the absorption maximum in spectrophotometric methods gives the concentration of the absorbing substance and the wave length of maximum absorption identifies it.

The dropping mercury electrode permits both the separation and determination of the constituents of the sample. On the polarogram the wave heights show the concentrations of the constituents and the half-wave potentials show what the constituents are.

In the determination of concentrations of several ions together in aqueous solution from the measured potential of a suitable electrode we can attain "separation" of the ions by using electrodes which react selectively with only one ion. Thus we can determine, for instance, the activities of  $H^+$  or  $Cl^-$ .

In colorimetry we achieve separation of the constituents by successive formation of coloured compounds by addition of suitable reagents.

From this treatment it is clear that the concept of "separation" can be taken literally only in the case of gravimetry or chromatography, whereas in instrumental analysis it is used for the most part only figuratively.

### THE VALUE OF ANALYTICAL CHEMISTRY METHODS

From the foregoing it might be thought that every property of matter could be used with success in analytical chemistry. Experience shows, however, that the efficiency of methods of "separation" is not the same in all cases. Some properties of matter are very selective while with others it is impossible to achieve separation of the constituents of the sample. We can make use of the concept of an "analytical property" which can be defined as such a property of matter that its quality characterizes the substance and its magnitude has a certain and precisely defined relation to the amount (concentration) of the substance being determined.

Thus analytical properties include, for example, the ability of compounds to form complexes, the electrical or thermal conductivity, the index of refraction, the optical rotatory power, the electrode potential, the properties of polarographic waves, the properties of spectral lines or absorption bands, the coloration of a solution, the specific weight, the magnetic susceptibility, radioactive properties, and so on. Analytical methods, as our experience shows, are based on their use. By employing certain of them we can achieve both separation and measurement; this is determination. Several analytical properties are suitable only for separation of the constituents while others are applicable only for the determination of substances which have already been actually separated.

Now we must consider what we can expect from analytical methods and what requirements we can make of them.

### CRITERIA FOR THE COMPARISON OF ANALYTICAL METHODS

The chief requirements to be placed on a perfect analytical method can be summarised as follows. (1) The method should be as simple as possible; i.e. there should be as few operations as possible in the working procedure. (2) The method should be selective so that by a single operation we obtain the separation and determination of as many of the constituents of the sample as possible. (3) The method should be so precise and reproducible that on repeating the determination the deviations from the average value of the result should be as small as possible. (4) The method should be

sensitive such that it can be used also for the determination of traces of the substance.

The methods of emission spectroscopy come closest to our analytical ideal. If we choose suitable spectral lines, the methods are completely selective, very sensitive and with proper equipment very simple, since after placing the sample on the electrode and striking the arc we get the result. The measuring of the spectrogram can be compared with weighing.

The methods of absorption spectroscopy are nearly as good, because the positions and shapes of the absorption bands (over all spectral regions) give such a large number of combinations that it is very difficult to find two known substances which with differing composition would have the same absorption spectrum in all spectral regions.

Polarographic methods are somewhat farther from our ideal. In many cases they have a quite high selectivity and sensitivity, though not so high as that of the spectral methods. The precision is about the same as that of spectroscopic methods.

Methods based on chemical properties have the advantage of high selectivity, in that we can almost always find a reagent for a particular determination, but are not as rapid as spectroscopic methods since several operations are usually required.

Potentiometric methods in which we apply the Nernst equation to the potentials of electrodes specific for the ions to be determined are much less selective because of a lack of suitable electrode systems. We can determine  $[H^+]$ ,  $[Cl^-]$ , etc. in this way, but the applications of these methods are limited.

Radioactive properties can be widely used since they can be induced artificially in substances that are normally not radioactive, but they are not sufficiently selective unless special methods are used (gamma-ray spectroscopy, decay curves, and so on).

The use of the optical rotatory power is limited to the determination of single optically active substances since it is not possible to effect separation by its means. This almost complete lack of selectivity is offset by the simplicity and precision of the method when there is only one active species present in the sample.

Methods based on selective adsorption (or selective migration) are very efficient for the actual separation of the constituents and are called collectively chromatographic methods. Though they are very selective they cannot be used for the direct determination of the separated substances. For this purpose some other property must be made use of.

We can go on further treating a series of analytical properties; sometimes we meet ones which are in no way selective in the analytical sense. Methods based on electrical conductivity, refractive index and density are in no way selective. They are, however, sensitive and precise. We can therefore use them only for the quantitative determination of pure chemical substances, which we have previously separated by a method based on some selective analytical property. Their sensitivity in a quantitative determination is sometimes remarkably very high.

From the above it follows that a given analytical property on which the corresponding method is based is not influenced to the same degree by all

the substances which we wish with its aid to determine. The selectivity, sensitivity, and precision of each analytical property are different for each substance. Therefore, the dependence of the concentration of one substance on the value of a given analytical property cannot in general be transferred to a second substance.

The mutual comparison of the sensitivity of the various analytical properties is not easy, since the sensitivity is also dependent on the working procedure and on the equipment. It would seem that there is considerable room for improvement of the sensitivity of many analytical properties.

### THE USE OF ANALYTICAL PROPERTIES

Up to now we have restricted our consideration to the use of only one analytical property in analytical procedure. We need not, however, limit ourselves in this way. We can with advantage use one property for the separation of the constituents and then carry out the determination by means of another property which is the most sensitive for this purpose.

Thus, for example, traces of a metal which we wish to determine can be concentrated by electrolysis on an electrode (separation) and their determination can then be carried out by emission spectroscopy.

In colorimetric methods we use selection by means of chemical reagents. The interfering constituents of the unknown are first eliminated by complexing. The "intensity of coloration" is then measured by some physical property, e.g. either by a photocolormeter or by a spectrophotometer.

Similarly for increased selectivity in polarography we can again use complex formation to eliminate interferences and carry out the polarographic determination of the sought for ions without difficulty.

In a similar manner in electro-analytical methods we make use of chemical properties for the successive elimination of undesirable ions from the solution of the unknown. We can combine such reactions and work out a systematic procedure.

### ANALYTICAL PROPERTIES AS INDICATORS IN VOLUMETRIC ANALYSIS

Physical and physico-chemical properties are used with success as indicators for detection of the equivalence point in volumetric analysis. The actual analytical process is purely chemical but the equivalence point is made clear by some instrumental method. The indication of the equivalence point is successful even in those cases where the used property does not show a high sensitivity, since the sudden decrease of the concentration of the substance being determined in the vicinity of the equivalence point causes a strong change of this property.

The advantage of physico-chemical titrations rests on the fact that we can use various properties for the indication and so we can select for the determination of the equivalence point a property which shows it with the highest sensitivity and precision. Thus, for example, the conductometric titration of very weak acids is successful, because the change in the concentration of the anion of the weak acid is indicated by its mobility, which is markedly different from the mobility of  $\text{OH}^-$ . Potentiometric indication

is insensitive in this case, for it is based only on the change of pH, which is very low in a strongly hydrolysed solution.

Amperometric indication again permits the finding of the equivalence point by a reaction in which the ions under determination can polarize the indicating electrode. By this property they are distinguished from substances which would interfere in some other manner of indication.

### COMPARISON OF THE METHODS OF CLASSICAL ANALYSIS WITH THOSE OF INSTRUMENTAL ANALYSIS

If we want, we can draw a parallel between instrumental methods and those which we call classical ones. In all analytical methods we read off certain values of the analytical property on the scale of some instrument and from these we determine the amounts of the sought-for substance. Thus on the scale of the gas burette we directly read off the volume of gas. In volumetric analysis we read off on the burette the volume of titrant. In gravimetric analysis we determine the weight of the substance which we have separated by the addition of a reagent. Here the set of weights plays the rôle of a scale. Both the burette and the balance must first be set to a zero point. Further the burette and the set of weights must be calibrated just like the scale of any instrument.

The manner of using balances in analytical chemistry is the same as that for other physical instruments. The weight of the sought-for substance is compensated by the weight of the weights, while the fractions of it are determined by using a small scale at the pointer. The weight of the substance is completely non-selective; it is, however, an extremely sensitive analytical property. In gravimetric analysis it is therefore absolutely necessary to separate the components of the unknown by means of selective reagents and then to determine the components by the very sensitive gravitational property by means of a balance. From this it is evident that the methods of classical and instrumental analysis work on the same basis.

The scale of the instrument giving the value of some analytical property is frequently calibrated to give directly the amount (concentration) of the substance which we have to determine. We do this, for example, in the case of the potentiometer for measuring pH. A further typical example is the scale of saccharimeters in percentage of sucrose, for instance which can be a supplement to the circular scale of a polarimeter.

As this comparison shows the parallelism between instrumental analysis and classical chemical methods extends even to small details.

### CONCLUSION

Summing up, if we accept the idea of separating a sample into its constituents as the connecting link of all analytical methods, we have a common foundation on which it is possible to treat in a unified manner analytical methods based on the most various physical properties.

It is desirable to maintain the unity of treatment of all analytical methods so as to be able on the basis of a small number of principles to derive the foundation of all methods of analytical chemistry. For this reason it is advantageous to keep to the conception that there exists one Analytical

chemistry which has various branches based on various properties of matter and can use various means for its purpose.

The unified treatment of all analytical methods has a number of pedagogical advantages. It gives the students as well as the teacher a lever for generalising analytical rules to the whole field of Analytical chemistry. In addition it has a heuristic value, because even for the advanced student it lightens the task of applying experience gained in work with classical methods to the methods of instrumental analysis and vice versa. Further, it also makes it possible to master a method with a new and complicated instrument by comparing it with the known working procedure for another simple instrument.