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THEORETICAL ASPECTS OF GRAVIMETRIC ANALYSIS

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Abstract

An attempt has been made to build a revised and logical concept of the univariate analytical calibration in qualitative and quantitative analysis. It focuses on the terms of real (virtual) and model (practical) calibration functions and their similarity as a condition for correct calibration leading to a reliable analytical result. The similarity of both functions depends on the extent to which the random and systematic measurement changes, so-called uncontrollable analytical effects, are eliminated and/or compensated. It is assumed that the model function is able to be formulated exclusively with the use of calibration standards, which can be not only chemical but also mathematical, biological or physical in nature. On the basis of the developed concept it has been proved that every method of qualitative and quantitative analysis requires analytical calibration. It was justified using the example of analytical methods commonly regarded as absolute or standardless ones.

Key words- Univariate analytical calibration, Calibration principles, Calibration function, Measurement errors, Absolute methods.

INTRODUCTION

Analytical calibration is the basic issue combining analytical chemistry as a science with chemical analysis understood as a practical examination of the qualitative and quantitative chemical composition of matter. The generally accepted division of analytical calibration includes univariate and multivariate calibration. The latter is based on chemometric methods and its goal in analytical chemistry is to develop multivariate models that can be used to predict the composition of matter from the measured properties of the chemical system. In analytical practice, however, univariate calibration is much more often used, mainly due to the fact that it is simpler and more accessible in terms of mathematics and interpretation. Without this process, which accompanies millions of analyzes performed every day around the world, it is impossible to obtain correct information about the type and amount of components that make up matter.

The content of a given element or ion in a substance is usually found in gravimetric analysis, from the weight of a precipitate formed when the element or ion is converted into an insoluble compound. Gravimetric analysis by weight is the process of isolating and weighing an element or a definite compound of the element in as pure a form as possible. I separated the element or compound from the weighed portion of the substance which is to be examined. A large proportion of determinations in gravimetric analysis is concerned with the transformation of the element or radical to be determined into pure stable compound, which can be readily converted into a form suitable for weighing. Then the weight of the element or radical can readily be calculated from the knowledge of the formula of the compound and atomic weights of the constituents' elements. Separation of element or compound containing it may be affected in several ways.

i) Volatilisation method

ii) Precipitation method

iii) Electroanalytical method and

iv) Miscellaneous physical method

Out of these, the precipitation method is the most important. Moreover, in the present work, the precipitation method has been employed throughout. So, an elaborate discussion regarding various aspects of precipitation will serve the purpose.

PRECIPITATION METHODS:

I precipitated the constituent being determined from a solution in a form which is so slightly soluble that no appreciable loss occurs when the precipitate is separated by filtration and weighed. The precipitate must be so insoluble that no loss occurs when it is collected by filtration. In practice, this usually means that the quantity remaining in solution does not exceed the minimum detectable by the ordinary analytical balance i.e., 0.1mg another important factor which requires discussion is the physical nature of the precipitate which must be such that it can be readily separated from the solution by filtration and can be washed free of soluble impurities. The conditions require that the particles are of such size that they do not pass though the filtering medium and that the particle size is unaffected by washing. The third factor that must be borne in mind is the precipitate, which must be convertible into a pure substance of definite chemical composition. I can affect this either by ignition or by a simple chemical operation, i.e., evaporation with a suitable liquid.

3.REQUIREMENT FOR PRECIPITATE:

If the precipitated from undergoes any chemical changes on ignition, then not the precipitate but some other compound is weighed. In this condition, we must make the necessary alteration in calculation. Whatever be the substance that is weighed as ultimate result is called weighed form.

The most important requirement of the weighed form is that its composition should correspond exactly to its chemical formula, so that calculation can be made easily. Moreover, the weighed form should have adequate chemical stability. If it is sensitive to moisture, absorption of CO_2 Oxidation or reduction, then analysis would be difficult and the results obtained will be incorrect. Another requirement of the weighed form is that the content of the element to be determined in the precipitate should be as low as possible. Under the circumstances, if at all error has been committed during the determination, has less effect on the final result.

They contaminate if precipitate with extraneous ions or ion of precipitant, then washing removes these impurities partly. Moreover, if these are volatile, then further ignition causes them to go off. In certain case i.e. Cu^{+2} forms $Cu(OH)_2$, then MH_4OH should not be used as insufficient addition will cause incomplete precipitation while slight excess of NH_4OH will cause a dissolution of $Cu(OH)_2$. In such cases, KOH or NaOH solution will serve the purpose of precipitation.

4.PROBLEMS WITH CERTAIN PRECIPITATE:

The problems which arise with certain precipitates include the coagulation or flocculation of a colloidal dispersion of a finely divided solid to permit its filtration and to prevent its repatriation on washing the precipitate.

5.THE COLLOIDAL STATE:

A certain range of particle size distinguishes this state of matter as a consequence of which certain properties become apparent. Substances of particle size ranging between 0.1m and 1m i.e. : 10^{-4}mm and 10^{-6}mm. Ordinary exhibit colloidal properties. Ordinary quantitative filter paper will retain particles up to a diameter of about 10^{-2}mm or 10m, so that colloidal solutions behave in this respect. Like correct solutions (size of molecule is of the order of 0.1m or 10^{-8} cm).

Correct solution i.e. those with particles of molecular dimensions, do not exhibit the Tyndall Effect and are said optically empty. Another important consequence of the smallness of the size of the particles is that the ratio of surface area to the weight is extremely large. The phenomenon of adsorption," which depends on the size of the surface, will therefore play an important part with substances in the colloidal state. The characteristic properties of the most type of colloidal particles" encountered in inorganic analysis are: (I) They exhibit Tyndall Effect' when viewed with proper illumination (II) they may be separated from true solutions by means of collodion or parchment membrane i.e. by the process of dialysis, (III) they may be regarded to posses electrical charge since they migrate under the influence of suitable potential gradient and (IV) they posses a very large surface area. I have divided colloids into two dominant classes; - Lyophobic and lyophilic colloids. The sols of the former are less viscous, easily coagulable by the minute electrolytes, possess an electric charge of definite sign and reveals Brownian's movement, while sole of the latter are more viscous, coagulable by large electrolytes, possess positive charge in acidic medium and negative charge in alkaline medium and only a diffused light can be viewed under ultra microscopic examination.

The gradual development of a crystalline particle with some amorphous substances by suitable treatment or digestion with hot water or the addition of electrolyte is called ‘again"; Alternatively, the process for disappearing a gel or flocculated solid to form a solution is called pectisation. It is the reverse of coagulation. Salvation stabilises lyophilic solution. The charge on the ions added is responsible for the precipitation of colloidal.

Solution. According to Hardy and Schulze’s law" “higher the valence of the active ion, greater is its precipitating power”. The minimum amount of an electrolyte, which is able to cause an observable decrease in decrease in degree of dispersion, is called coagulation value. Pectisation is of great importance in quantitative analysis. The absorptive property of the colloids finds a number of applications in analysis, especially in the use of adsorption indicator in qualitative detection and colorimetric determination of elements and radicals with many organic reagents.

SUPERSATURATION AND PRECIPITATE FORMATION

The usual definition of solubility is valid only for the particles of size greater than 0.01mm. Solubility depends largely by the particle size. When particle size decreases 0.01mm in diameter, the solubility increases owing to the increasing role played by the surface effect. A supersaturated solution is one that contains a greater concentration of solute that corresponds to the equilibrium solubility at the temperature under consideration. It is therefore an unstable state which may be brought to a state of stable equilibrium by seeding, the solution or by some other substance or by mechanical means such as shaking or stirring.

According to Von Weimern (1913), 1925), supersaturation plays an important part in determining the particle size of a precipitate. He suggested that initial velocity of precipitation is proportional to (0-5/5) where Q - total concentration of the substance, that is to precipitate and 5 = equilibrium solubility. (Q-5) will denote the supersaturation at the moment, when precipitation commences. The above expression is valid only when Q is largest than S. Von Weimar accumulated many data, which evidently showed that particle size of the precipitate decreases whenConcentration of the reactants is increased for the production of crystalline precipitate for which the adsorption errors will be the least and filtration will be the easiest (Q-S/S) should limit to reducing (Q-S /S) by making q very small, since for a precipitation to be of value in analysis, it must be complete in a comparatively short time and the volumes of the solution involved must not be too large. Freundlich suggested that decreases in the Zest potential leading to precipitation is brought about by the adsorption of lions of opposite to that of the colloid particles. The applications of the above conception are to be found in following recognised procedures in gravimetric analysis:

THE PURITY OF THE PRECIPITATE ANDCO-PRECIPITATION:

When a precipitate separates from the solution, they contaminate it with impurities depending on the nature of the precipitate and the condition of precipitation. The contamination of the precipitate by the substances, which are normally soluble in the mother liquor, is termed co- precipitation. Thus, out of two types of co - precipitation, one is concerned with adsorption at the surface of the particles exposed to the solution and another relates to the occlusion of foreign substances during the process of crystal growth from the primary particles. in regard to surface adsorption, this will in general be greatest for gelatinous precipitates and lest for those of pronounced microcrystalline character. Precipitate with ionic lattices appear to conform to the Paneth - Fajan - Hahns adsorption rule, which states that the ion which is the most strongly adsorbed by an ionic substance (Crystal lattice), is that ion which forms the least soluble salts. The deformability of the absorbed ions and the electrolytic dissociation of the adsorbed compound also have a considerable influence, the smaller the dissociation of the compound, the greater is the adsorption". The second type of coprecipitation may be visualised as occurring during the building up of the precipitate from the primary particles. The latter will be subject to a certain amount of surface adsorption and during their coalescence the impurities will either be partially eliminated if large single crystals are formed and the process takes place slowly, or if coalescence is rapid, large crystals composed of loosely bound small crystals may be produced and some of the impurities may be entrained within the walls of the impurities may be entrained within the walls of the large crystals. If the impurity is isomorphous or forms a solid solution with the precipitate, the amount of co- precipitation may be very large, since there will be no tendency for elimination during the ageing process. It is a source of error in gravimetric analysis. The process is of special interest in co-precipitation of micro component increasing selectivity and improving experimental condition in analysis.

CONCLUSIONS

The vision of the basis of analytical calibration presented in this paper is based on the observation of the essence of analytical research. The aim of the analyst's work is to look deep into the matter and determine the type or quantity of components contained in it. In other words, every chemical analysis is, in a sense, a quest for the objective truth that the surrounding reality conceals. This goal can never be fully achieved, but it can be approached as closely as possible with the tools created by the analyst. Chemical analysis is thus a confrontation between what is unattainable (true, theoretical) and what can be created and achieved in practice.

REFERENCES

1. Vogel, A.1. :“A text Book of Quantitative Inorganic Analysis, Longman, Green and Co Ltd; P 104 (1962)

2. Allexeyev, V. :“Quantitative Analysis, Publishers Moscow, USSR, P-66. Mir

3. Vogel, A.I. :“A text Book of quantitative Inorganic Analysis, Longman, Green and Co. Ltd: P-105 (1962).

4. Kryt, M. R. :Colloid Science, Ed. Elservier Publishing Co Amsterdam (1952)

5. Mc Bain, J. W.: Colloid Science, D. C. Heath, Boston, (1950)

6. Kayser, H: Ann. Physik, 14, 451 (1881)

7. Glasstone, S :Text Book of Physical Chemistry, Mecmillan and Co. Ltd. London, P 1237 (1962), Proc. Roy. Soc. 66A, 110 (1900), : J. Pr. Chem. 25, 431 (1882).