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ABSOLUTE METHODS IN ANALYTICAL CHEMISTRY

(Technical Report)

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Synopsis

There is an increasing tendency to obtain the analytical result on the basis of numerical calculations deriving from the theoretical model of the phenomena responsible for formation of an analytical signal. Such procedures where the calculations are based on universal quantities and fundamental physical constants only, may be termed absolute methods. There is a number of terms which refer to methods which do not need direct experimental calibration, which however cannot be named absolute. This project indicates also existing examples in various analytical techniques, where the term "absolute" is more or less justified.

1. Introduction

An analytical measurement is normally aimed at determining the amount of a given species (analyte) in a defined mass or volume of the sample. If the object (the analyte) cannot directly be counted or measured, then a macroscopic parameter should be found which is functionally related to the amount (concentration) of the analyte. The value of this parameter is the measure of the analytical signal.

Such a functional relationship can be formulated either on the basis of theoretical assumptions or experimental measurements. When the functional relationship can be completely described on the basis of physical constants and universal quantities, the method can be considered to be **absolute**. The numerical value of the proportionality factor between amount (concentration), x, and signal, y, is called **sensitivity** (dy/dx). The purely instrumental component of this factor may be denoted as the **instrument constant**. In the case of experimental measurements to determine the sensitivity, standard samples of various types are indispensable. Depending on the particular character of the analytical technique, standard samples may exhibit different degrees of similarity to the sample analyzed. Standard samples can be pure analytes, their solutions, or standards with matched matrices, as well as certified reference materials.

2. Absolute method of determination

Absolute methods are based on the evaluation of concentration (amount) with the use of fundamental physical constants and/or universal quantities only. For such methods the instrument constant should be evaluated using theoretical principles. Experimental conditions for the analysis must be chosen in such a way that they permit the prediction of the analytical signal.

Gravimetric, volumetric and coulometric methods, as well as those based on charged particle counting, can be regarded as absolute methods, under the condition that experimental conditions are chosen such that their efficiency is theoretically predictable (preferably 100% efficiency). This may create difficulties when several consecutive processes are involved in production of the final signal, as well as in the case of coupled (hyphenated) techniques (e.g., inductively coupled plasma-mass spectrometry).

Absolute methods are of particular practical relevance when they offer a result of the analysis with superior accuracy and precision than methods based on calibration.

Absolute methods were occasionally incorrectly called **standardless methods** or **calculable methods** [1]. Such terms may be used for procedures which are based on constancy, in given conditions, of physicochemical quantities determined experimentally in such conditions.

3. The analytical signal

The analytical signal depends on:

- the properties of the analyte species involved,
- the instrumental parameters of the particular equipment,
- the experimental conditions (mostly adjusted by the analyst), and
- the presence of accompanying substances.

3.1. *Properties of analyte species*

The following properties of analyte species which influence the analytical signal, or rather the proportionality factor (sensitivity), can be distinguished:

- **universal quantities** (molar mass, atomic number, stoichiometric factors);
- **physical (phenomenological) quantities.** These quantities are based on physical or chemical measurements (energy of excitation or ionization, atomic cross sections, electrochemical potentials, diffusion coefficients, molar absorptivities etc.). Many such data are collected in data bases;

Besides the proportionality factor usually includes also **fundamental physical constants** (Faraday constant, Avogadro constant etc.).

In practical analysis these quantities are mostly not considered separately, but combined to give one single numerical factor. The differences between such quantities for various species, and thus the numerical factors, are the basis of selectivity (specificity) of an analytical method. In many instances, evaluation of all parameters is complicated, if possible at all. This is why the vast majority of analytical procedures are based on experimental standardization.

3.2. *Instrumental parameters*

The effect of instrumental parameters such as electrode material and geometry, geometry involved in optical arrangements, characteristics of excitation sources, and detector parameters, can often be evaluated only by elaborate procedures. This is the reason why it is usually more advantageous and practical to determine the instrumental characteristics by experimental calibration. The instrumental parameters are often presented as combined parameters denoted as an **instrument constant.** Its value should be invariant in time, and independent of the nature of the determined species. This is not always the case, however, and experimental conditions used in a specific procedure for the determination of an analyte may modify the instrument constant. It may also change in time, or change when the instrumental set-up is rearranged. In such cases, frequent calibration of the instrument is required.

3.3. *Experimental conditions*

Experimental conditions such as temperature, pressure, type and concentration of buffer, gas atmosphere and possible side reactions affect the thermodynamic conditions and/or have influence on the kinetic behaviour of the system. Conditions are usually chosen in such a way that the system is easily and simply, but unambiguously, defined. In most cases this corresponds to conditions where 100% efficiency of the process is guaranteed. This is not the case when there are several signal generating coexisting species which may, or may not, be in equilibrium. The recorded signal is then composed of the contributions of these species.

3.4. *Presence of accompanying compounds*

Very often the magnitude of the analytical signal is influenced by accompanying compounds (interferents). These effects may have different origins as they may arise from the same or different signal generating mechanisms and may be specific or non-specific [2]. There are numerical procedures to eliminate the effect of the accompanying species [e.g.,3]. In exceptional cases, the effect of interferents may be expressed in terms of universal quantities related to the specific interferent. Such corrections usually require the knowledge of the type of interferent and its concentration, which is rarely available *a priori*.

3.5. *Internal standardisation*

Internal standardization is one way of compensating for the effects of instrumental, and sometimes also experimental, parameters not readily calculated on a theoretical basis. Such relative measurements have been used for many years in various analytical methods. Isotope dilution mass spectrometry is an important example of a technique giving relative measurements which therefore exhibits extremely high accuracy. The analytical result is obtained from the masses of sample and added material (spike) and on the measurement of the atomic fraction of the isotopes. Such a procedure can form the basis of a definitive method (see below).

4. Definitive methods

Definitive methods are methods that are based on a valid and well-described theoretical foundation, which has been experimentally validated so that the reported results have negligible systematic errors and have high levels of precision [4]. They are usually not absolute methods, they require highly skilled personnel and are time consuming as well as expensive.

5. Reference methods of analysis

Reference methods of analysis may have an empirical basis but should have good accuracy certified by comparison with a definitive method or be based on (certified or standard) reference materials.

6. Attempts to create absolute methods of analysis

Contemporary analytical problems are mostly related to the complexity of samples. This complexity apparently increases in terms of the variety of compounds, or when methods are used which allow the detection of species at extreme low concentration levels. The lack of standard reference materials for all possible kinds of samples, on the one hand, and a deeper knowledge of principles of existing analytical methods, on the other hand, have stimulated the tendency to develop analytical methods, which, if not strictly speaking absolute, are at least less dependent on the experimental conditions and the composition of the matrix. There are numerous examples dealing with various experimental techniques in which their authors to various degrees approach the concept of absolute methods. Some representative publications describe attempts in the fields of X-ray fluorescence spectrometry [5-9], atomic emission spectrometry [10], atomic absorption spectrometry [11-19], spark-source mass spectrometry [20], glow-discharge mass spectrometry [21], neutron activation analysis [22-25], direct potentiometry [26-27] and in chromatography [28,29]. The authors use different terms to describe the methods as "absolute", "truly absolute", "standardless", "without standard reference samples", "fundamental parameter technique". In some cases a very sophisticated choice of experimental conditions enables the analyte content to be calculated, but for practical reasons experimental calibration is usually necessary.

7. Misuse of the term "absolute method of analysis"

The above cited examples indicate that there are some types of analytical procedures which have been improperly named "absolute", In most methods, in spite of describing the analyte signal through fundamental parameters, the instrumental parameters and experimental conditions are so complex and so difficult to define that for practical reasons empirical calibration is necessary. This type of calibration is sometimes expressed in the form of an instrument constant. Such a constant may be valid independent of the species determined but often depends on particular conditions of determination, for example when the sensitivity of the detector varies with the wavelength. Of course, the term "without calibration curve" should refer to cases where the analytical result is evaluated on the basis of a functional relationship, but not through graphical form.

To some extent most of the methods mentioned above can be considered as **interference-free (matrix effect free)** because the signal of the analyte is independent of the presence of accompanying substances. As the number of potential interferents is practically unlimited, and it is impossible to test them all and it is better to speak of **apparently interference-free** methods. Such methods are tested only for the effect of species which are likely to occur in the type of analytical samples for which the method is developed. The term interference-free method does not mean that the method is absolute!

The term **pseudo-absolute** method may be used when the instrumental parameters can be evaluated experimentally and do not change with time.

In such a case it should be possible for calibration to be made with model samples, containing pure analyte, instead of samples closely resembling the analyzed material in composition and/or physical properties.

8. Perspectives for the absolute methods of analysis

In spite of all the efforts to create truly absolute methods of analysis, which would be more valuable than semi-quantitative determinations, it has not been possible to develop such methods except in special cases. As a criterion of utility for such methods, a comparison of the accuracy of an absolute method with a method based on empirical calibration should be made. Such procedures are mainly promoted by practical analysts, whereas the absolute method approach is developed mainly by physical chemists. Progress in this field can result from a better knowledge and more precise descriptions of the theoretical fundamental phenomena responsible for generation of the analytical signal, and from development of instrumentation with perfectly reproducible and/or theoretically described characteristics.

An intermediate step is the development of interference-free (matrix independent) methods which should significantly decrease the need for exactly matched standard reference materials for a vast diversity of analytical problems.

9. References

1. **ISO Guide 32.**
2. G. den Boef and A. Hulanicki, *Recommendations for the usage of selective, selectivity and related terms in analytical chemistry,* Pure Appl. Chem., **55,** 553 (1983).
3. L. Pszonicki,*The standard addition and successive dilution method for evaluation and verification of results in atomic absorption analysis,* Talanta, **36**, 1265 (1989).
4. G.A. Uriano and C.C. Gravatt, *The role of reference materials and reference methods in chemical analysis*, CRC Crit. Rev. Anal. Chem., **6**, 361 (1977).
5. J. Sherman, *The theoretical derivation of fluorescent X-ray intensities from mixtures,* Spectrochim. Acta, **7**, 283 (1955).
6. T. Shiraiwa and N. Fujino, *Theoretical calculation of fluorescent X-ray spectrochemical analysis*, Jpn. J. Appl. Phys., **10**, 886 (1966).
7. Fei He and P.J. Van Espen, *General approach for quantitative energy dispersive X-ray fluorescence analysis based on fundamental parameters,* Anal. Chem., **63**, 2237 (1991).
8. H. Sakata, I. Yamamoto, M. Sone and M. Matsubara, *Quantitative analysis of metal elements in leaves by XRF using the fundamental parameter technique,* Poster 2P642, ICAS 91, Chiba, Japan.
9. T. Ui, M. Kataoka, M. Kato and E. Asada, *XRF determination of iron with absorption correction using Compton scattering,* Bunseki Kagaku, **37**, 538 (1988).
10. L. De Galan, *The possibility of a truly absolute method of spectrographic analysis*, Anal. Chim. Acta, **34**, 2 (1966).
11. B.V. Lvov, *Electrothermal atomization - the way towards absolute methods of atomic absorption analysis,* Spectrochim. Acta, **33B**, 153 (1978).
12. B.V. Lvov, V.G. Nikolaev, E.A. Norman, L.K. Polzik and M. Mojica, *Theoretical calculation of the characteristic mass in graphite furnace atomic absorption spectrometry,* Spectrochim. Acta, **41B**, 1043 (1986).

13. W. Slavin and D.C. Manning, *Reduction of matrix interferences for Pb determination with the Lvov platform and the graphite furnace,* Anal. Chem., **51,** 261 (1979).
14. D.C. Baxter and W. Frech, *Temperature gradients as a limiting factor for absolute analysis by graphite furnace atomic absorption spectrometry,* Spectrochim. Acta, **42B**, 1005 (1987).
15. Z. Grobenski and B. Welz, *Graphite furnace atomic spectroscopy on the way towards an absolute method of analysis,* Chem. Anal.(Warsaw), **35,** 141 (1990).
16. G. Torsi, P. Reschiglian, F. Fagioli and C. Locatelli, *Absolute analysis in electrothermal atomization atomic absorption spectroscopy - an atomization system for confining all the atoms injected in the optical beam,* Spectrochim. Acta, **48B,** 681 (1993).
17. Yansheng Zhang and Xingguang Su, *Application of standardless analysis in graphite furnace atomic absorption spectrometry: Determination of chromium,* Talanta, **40,** 347 (1993).
18. Yansheng Zhang and Xingguang Su, *Analyses without calibration curve for determination of indium in sediment and geochemical samples,* Mikrochim. Acta, **112,** 237 (1994).
19. B. Magyar, *Problems involved in the calculation of theoretical sensitivities of flame absorption measurements,* Mikrochim. Acta, **111,** 1 (1993).
20. G.I. Ramendik, *Elemental analysis without standard reference samples: The general aspect and the realization in SSMS and LMS,* Fresenius J.Anal. Chem., **337,** 772 (1990).
21. W. Vieth and J.C. Huneke, *Relative sensitivity factors on glow discharge mass spectrometry*, Spectrochim. Acta, **B**, (1991).
22. F. De Corte, A. Simonits, A. De Wispelaere and J. Hoste, *Accuracy and applicability of the k_0 standardization method*, J.Radioanal. Nucl. Chem., **113**, 145 (1987).
23. A. Simonits, F. De Corte, A. De Wispelaere and J. Hoste, *Nuclear data measurements for zirconium isotopes used for activation analysis and neutron metrology*, J.Radioanal. Nucl. Chem., **113**, 187 (1987).
24. R. Dams, *Radiochemical and instrumental neutron activation analysis - recent trends,* Fresenius J. Anal. Chem., **337**, 492 (1990).
25. F.De Corte, *The traceability of the neutron activation analysis k_0-* ***standardization method****,* J. Trace Microprobe Tech., **5**, 115 (1987).
26. R. Dohner, D. Wegmann, W.E. Morf and W. Simon, *Reference electrode with free-flowing free-diffusion liquid junction*, Anal. Chem., **58**, 2585 (1986).
27. G.G. Rumpf, L.F.J. Duerselen, H.W. Buehler and W. Simon, *Opportunities and limitations in the use of ISEs in clinical analysis: Assays without calibration?,* in Contemporary Electroanalytical Chemistry, Ed. A. Ivaska, A. Lewenstam, R. Sara, Plenum Press, New York 1990, p.305.
28. G. Torsi, G. Chiavari, C. Laghi, A.M. Asmundsdottir, F. Fagioli and R. Vecchietti, *Determination of the absolute number of moles of an analyte in a flow-through system from peak-area measurements*, J. Chromatogr., **482**, 207 (1989).
29. G. Torsi, A.M. Gioacchini and N. Gandini, *Absolute analysis method applied to the dansyl derivatives of aminoacids in HPLC. Stability of aminoacids in 6N HCl*, Ann. Chim., **83**, 345 (1993).