

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ANALYTICAL REACTIONS AND REAGENTS*

**RECOMMENDATIONS FOR THE
USAGE OF SELECTIVE, SELECTIVITY
AND RELATED TERMS IN
ANALYTICAL CHEMISTRY**

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†Deceased 29 June 1982.

RECOMMENDATIONS FOR THE USAGE OF SELECTIVE, SELECTIVITY AND RELATED TERMS IN ANALYTICAL CHEMISTRY

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INTRODUCTION

The terms *selective* and *specific* and their substantives *selectivity* and *specificity* were originally introduced in analytical chemistry for the characterization of analytical reactions and determinations in solution with reference to the occurrence of interferences. Later, the terms have been adopted by analysts working in various fields of instrumental methods of analysis. Unfortunately, the terms are being used in different contexts, without precisely defined meanings. The same lack of definition applies to derivatives of the terms e.g. *selectivity coefficient* and to related terms such as *interference* and *resolution*. The aim of this paper is to provide guidelines for the use of these terms in order to prevent their further undefined usage. Furthermore it is hoped that the prevailing terminology will gradually be adapted to these guidelines in the various branches of analytical chemistry. It should be stressed that all terms discussed below and all propositions with respect to their use can only be applied to completely described methods of analysis, including sampling and data handling.

INTERFERENCE

There is no universally accepted definition of the term interference. A useful review of the problems arising on defining the term was given in 1974 by Wilson (1). Interference has to be defined in such a way that it applies to qualitative as well as to quantitative analysis. The following definition, along the lines proposed by Wilson (1) is recommended:

"An interfering substance for an analytical procedure is one that causes a predeterminate systematic error in the analytical result".

In the case of a qualitative method of analysis this means that the interferent either provides a positive test when the analyte is absent or a negative test when the analyte is present. The observation of the interference depends on the amount of the interferent and of the analyte in the sample. In the case of a quantitative method of analysis the allowable magnitude of the systematic error should be fixed beforehand in terms of the standard deviation of an individual determination of the analyte. Again, whether or not a substance interferes depends on the amount of the interferent and that of the analyte in the sample.

Furthermore it should be noted that the extent of an interference is not necessarily proportional to the concentration or the content of the interferent in a sample and that the effect of the presence of several interferents is not always additive. Synergistic as well as compensating effects may occur.

It has to be mentioned once more that in all cases in this paper the definitions and recommendations apply to completely described procedures. When it is e.g. possible to solve the problem of interference by a certain substance in a particular determination by proper data handling, this means that the substance is an interferent in a procedure which does not include this particular data handling and is a non-interferent in a procedure including it. Proposals have been made to make classifications of various types of interferences (e.g. in ref. 2). These classifications in most cases are closely related to the specific conditions which apply within a certain analytical technique and therefore cannot easily be generalized. For general purposes only a very general classification is considered to be potentially useful. For the moment only two types of interferences will be distinguished

- i SM-Interference is interference by a substance that produces a signal by a similar mechanism as the analyte, which in the given procedure (including the apparatus used) can not be distinguished from the signal given by the analyte. For example in a colour reaction with an organic ligand by also reacting with the ligand and producing a coloured compound absorbing at the same wavelength as the compound produced by the analyte or in an atomic spectrochemical analysis by absorbing or emitting at the same wavelength as the analyte.
- ii DM-Interference on the contrary would be interference in which the analytical signal is influenced by a different mechanism than the analyte, e.g. the formation of non-dissociating species in emission spectroscopy.

At least, one advantage of such a classification is that the influence of interferences of the SM-type on the analytical signal can be treated quantitatively in terms of the concentration of the interferent. The problem of classification of interferences is still in discussion

and will be dealt with in a future publication.

SELECTIVE, SELECTIVITY, SPECIFIC, SPECIFICITY

The terms selective, selectivity, specific, specificity, and derivatives of these terms have always been used by analytical chemists as means to express, either quantitatively or qualitatively, the extent to which the determination of a substance according to a given procedure is subject to interferences. A discussion on the usage of these terms will be separated into two parts, i.e. qualitative and quantitative.

1. Firstly the use of the terms in a qualitative sense will be considered, such as in expressions like selective determination, selective extraction, ion-selective electrode etc. Although there appears to be no unanimity in views most analytical chemists appear to agree on the use of the words in a qualitative sense, i.e. they are used to express whether other substances interfere. The same applies to the situation when the corresponding substantives are used as such, e.g. in "the selectivity of the determination of a certain substance according to a certain method is poor or good".

Kaiser (3) is the only author who has proposed the use of the words selectivity and specificity as numerical quantities. In his concept selectivity is connected with the possibility of the independent determination of all the constituents in a sample and the definition of the selectivity includes the whole system. It is a correct strictly mathematical model. Kaiser himself remarks at the end of his paper "in practice we will see whether this model will work". The answer must be that the model, though mathematically correct, is impracticable because it does not involve the mutual influence of different interferences.

It is therefore proposed to use the adjectives selective and specific and the substantives selectivity and specificity, when not followed by other substantives, as means to express, qualitatively the extent to which other substances interfere with the determination of a substance according to a given procedure. In this connection specificity is considered to be the ultimate of selectivity, it means that no interferences are supposed to occur. The same consideration applies to specific in its relation to selective.

According to these proposals it is perfectly correct to speak of a method being less or more selective than another method. It is not strictly correct to speak of a selective reagent because the terms under consideration only apply to completely described methods of analysis. However, it is perfectly clear for an analyst what the expression "EDTA is not a selective reagent" means. It means that in the titration of a particular metal ion with EDTA a lot of other metal ions will in general interfere.

2. Secondly the use of terms for the quantitative characterization of interferences will be discussed. In this connection only the word selectivity has to be considered. For a quantitative characterization of the selectivity of a procedure nearly always terms have been used such as selectivity constant, selectivity factor, selectivity coefficient, selectivity index, i.e. selectivity is used in conjunction with another substantive, clearly indicating that a quantity is meant, to which a numerical value can be attributed.

It is proposed to follow this practice and to restrict the quantitative use of selectivity to combinations of selectivity with another substantive. Unfortunately however, there appears to be some confusion in the usage of these quantitative terms. An attempt is now made to put order into this matter. Guidelines for the use of the substantives constant, coefficient, index, factor and number in conjunction with selectivity can be found in the Orange Book (4). The word "constant" should only be used for a universal constant, or a property of a material, such as dielectric constant. Hence, this word should be avoided in the present context. The word "index" should only be used for numerical values arising from ratios, e.g. refractive index. The dimension is unity ("dimensionless").

The expressions "number" and "factor" are satisfactory alternatives to index.

The term "coefficient" should only be used for numerical values which occur in equations of proportionality.

In view of the foregoing more detailed comments can be made on terms mentioned in literature, which combine selectivity (rarely also specificity) with one of the above

i Coefficient. The selectivity coefficient used in ion exchange nomenclature (5) is, according to the guidelines, not a coefficient but rather a factor. On the other hand the term potentiometric selectivity coefficient, $k_{A,B}^{pot}$ (6), used for ion selective electrodes, seems a proper term. It fulfils the requirement that a proportionality with the concentration of the interfering ion is involved. The interference of only one type of ion is described and the way in which the coefficient of proportionality has to be determined is precisely described so that no misunderstanding as to its practical meaning is possible. However, the smaller the value of $k_{A,B}^{pot}$, the stronger is the preference of the electrode for the principal ion A and hence the greater the selectivity, which is linguistically illogic. The term non-specificity coefficient, proposed by Pszonicki (7), seems a more logical expression, but a few objections can be raised. Firstly specificity is used where selectivity is to be preferred. Secondly the definition given is not unambiguous.

ii Index, number, factor. There is no need for further guidelines for the usage of selectivity in conjunction with any of the above words, as long as there is no contradiction with the general rules given earlier.

Only in the case of the term "selectivity index" proposals have been made for a definition

by Belcher and Betteridge (8,9,10,11) which have been commented upon by Wilson (12). No conclusion on this point has been reached. It is beyond the general scope of this paper to enter into this discussion.

RESOLUTION

Resolution is a term related to the words discussed so far. It is proposed to restrict the use of the word resolution to peak resolution as it is defined on several places in the Orange Book (13) and to distinguish it clearly from the concept of resolving power (14) which must be restricted to instruments. The resolving power of an instrument used in an analytical procedure may well have its impact on the selectivity of the overall procedure.

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