Selectivity in Analytical Chemistry

Recommendations for its Use

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*The correct use of the term **selectivity** and its clear distinction from the term specificity are discussed. Selectivity is promoted.*

Evolution of the terminology

The use of the term **selectivity** has evolved in parallel with the development of more sensitive and discriminating methods that can quantify analytes with less interference from other components than earlier methods were able to do. Modern methods often comprise several strategies that introduce their own selectivity to reduce interferences. In this way, highly selective methods can be obtained.

Useful interactions

Several kinds of interactions are used in the selectivity-generating steps leading to the final measurement.

Typical interactions are, e.g.,

chemical reactions

associate formation

adsorption to surfaces

inclusion phenomena

absorption of radiation

biochemical (immunochemical or enzymatic), or

electrochemical (redox) principles

Selectivities in methods

Current analytical methods are based on multistage separation and detection principles.

Metals are often determined with methods based on ***detection selectivity***, e.g, atomic emission spectrometry.

Separation techniques for all types of species rely on selectivity in the separation process, ***separation selectivity***.

Hyphenated techniques, like LC-MS, combining selectivities with respect to detection and separation, are applied when the demands for selectivity are especially high. The addition of tandem mass spectrometry, LC-MS-MS, yields a selectivity that is rarely compromised and often required in legal situations.

Selectivities in methods (cont.)

Responses from combinations or arrays of sensors with different degrees of selectivities have in recent years been evaluated in the mathematical domain, often called "***computational selectivity***". The handling of near infrared spectra using the whole spectrum over a wavelength range is a good example, where otherwise important information would not have been possible to extract. The spectroelectrochemical detector represents a single sensor with incorporated multimode selectivities that overcomes interferences.

Semantic aspects

Selectivity has its origin in ***seligo***, which is Latin for "**to choose**" or "**to select**".

Thus selective can mean "**tending to choose carefully**" and selectivity, "**the state or quality of being selective**".

By combining these two expressions, a useful concept can be found for what actually **selectivity** is all about viz, "***Selectivity is the state of choosing carefully***". This expression very well fits the principles by which modern analytical methods are constructed.

Expressing selectivity

In the current analytical literature, selectivity is very often expressed in combination with words such as adjustment, tuning, optimization, predetermined, enhancement, and coefficients, as well as selective enrichment.

These expressions indicate that **selectivity** is regarded as something that can be graded. Methods have often been described in qualitative terms, such as having good selectivity or even high, excellent, or extreme selectivity. *This qualitative use of the term has been discouraged.*

Calculations of degree of selectivity

Some attempts have been made in the literature to quantify selectivity (and even specificity). One of the first treatments was made by Kaiser. He also distinguished between the use of **specificity** for single analyte analysis and **selectivity**, when several analytes were involved.

Very demanding procedures have been proposed for calculations where a sensitivity factor matrix, K, is involved with *n* sensor responses for *m* components. An approach that will be helpful for the practicing analytical chemist with a complex sample still has to be developed.

Selectivity or specificity

The terms selectivity or specificity are in many cases used interchangeably. As specificity is considered as an absolute term, it cannot be graded. IUPAC has earlier stated that "*specificity is the ultimate of selectivity*".

The desire to avoid the term specificity has been expressed as "*Sometimes the term specificity is used. This usage suggests that no component other than the analyte contributes to the result. Hardly any method is that specific (sic!) and, in general, the term should be avoided*".

The frequent use of selectivity in prestigious journals reflects this situation but nowhere is a recommendation in "Notice for authors"found.

Provisional Recommendation

1. **That the term Selectivity be promoted**
   Selectivity is the recommended term in analytical chemistry to express the extent of interferences. To avoid confusion, the use of the term specificity is to be discouraged, as it is incorrect. A method is either specific or not. Few, if any, methods are specific.
2. **Definition of Selectivity**

   Selectivity refers to the extent to which a method can determine particular analytes in mixtures or matrices without interferences from other components.

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