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Views and criticism

On the expression "external calibration" in atomic spectrometry

Tibor Kántor

Geological Institute of Hungary, Stefánia Ave 14, 1143 Budapest, Hungary

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Abstract

The expressions "calibration" and "external calibration" appear together in the present literature of atomic spectrometry resulting in a dilemma of understanding and correct use. It is examined how the IUPAC can provide a guidance to the solution of this problem by recalling the definitions of related terms of optical, mass and X-ray atomic spectrometry techniques. The introduction and definition of these expressions in widely used text books are investigated and statistically evaluated for the articles published during the last 30 years in the periodical Spectrochimica Acta Part B. For the elimination of the literary difficulties with the use of the term "calibration", attributes are proposed to express the degree of matrix matching of standards and samples.

Keywords: Terminology; Calibration; Optical atomic spectrometry; Plasma mass spectrometry; X-Ray fluorescence spectrometry

1. A rising terminology dilemma

When writing or reviewing scientific papers difficulties may arise about the acceptability or correct use of certain scientific expressions and terms. As it will be shown below, both the expressions *calibration* and *external calibration* appear together in the recent literature of atomic spectrometry, while the tendency is in favor of *external calibration*. It is clear that the use of two terms for the same meaning may lead to confusions unless it is declared that the two terms are synonyms (alternatives in use). On the other hand, if these two expressions have different meanings, this must be clearly understood and their use is to be recommended accordingly.

In this presentation of a potentially open discussion, a consultation with the appropriate IUPAC (International Union of Pure and Applied Chemistry) publications will be followed by the citations of terms from some widely read textbooks of atomic spectrometry. The "analytical" type of papers which appeared in the last 30 years in the periodical Spectrochim. Acta Part B will be evaluated for the frequency of use of the two terms and their closely related alternatives. It will be analyzed, how the terminology dilemma discussed here is connected with the limitations of clearly composed terms to the procedures that are existing in the practice of spectrochemical analysis. Finally, modifications of terms will be proposed for approaching a more unambiguous and simpler understanding.

E-mail address: kantib@t-online.hu.

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2. IUPAC recommendations to overall analytical chemistry and chromatography

For a most comprehensive overview of the terms relevant to the overwhelming body of analytical chemistry, the "compellation" of IUPAC publications may be recommended [1]. In *Chapter 18* (Quality assurance of analytical processes) the following statement is found: "The source paper is not yet published for calibration and standardization." The text of this Chapter contains, however, the terms *calibration function* and *calibration curve* with corresponding explanations.

In *Chapter 9* (Analytical separation methods) and more specifically in *Subsection 9.2.* (Chromatography) the following terms are defined.

2.1. Internal standard

"A compound added to a sample in known concentration to facilitate the qualitative identification and/or quantitative determination of the sample components."

2.2. External standard

"A compound present in a standard sample of known concentration and volume which is analyzed separately from the unknown sample under identical conditions. It is used to facilitate the qualitative identification and/or quantitative

determination of the sample components. The volume of the external standard (standard sample) need not to be known if it is identical to that of the unknown sample."

It is interesting to observe that *external standard* is a recommended term in chromatography, and this applies also logically to the term *external standardization*, and its synonym form *external calibration*. The possible influence of these terms to the nomenclature of atomic spectrometry will be examined below (Section 5).

Comparing the principal characteristics of chromatography and spectroscopy with regard to qualitative analysis it is known that *chromatography is less analyte specific*, as the retention parameters (time or volume) are strongly influenced by the instrumental conditions. On the other hand, *spectroscopy is highly analyte specific* as the value of spectral parameter (wavelength, mass/charge, etc.) is not affected by the instrumental conditions. The accuracy of signal identification is, however, dependent on the resolving power of the spectroscopic instrument. Clearly, the combinations of spectroscopic and chromatographic instrumentation have been introduced for the sake of minimizing the above limitations of the two techniques in signal identification. The characteristic difference as above may be, however, a reason for a deviation in the terminology of the two disciplines (see below).

3. IUPAC recommendations to spectrochemistry

The *Chapter 10* of the Compilation [1], entitled "Spectrochemical method", encompasses the optical and X-ray spectrometry methods, while "Mass spectroscopy" is dealt with separately (*Chapter 12*). In *Chapter 10*, the terms *calibration* and *external calibration* are completely lacking. Related terms mentioned are: *reference solutions*, *analytical curve technique*, *internal reference line*, *reference element* and *analytical addition technique*. For a more detailed indexing of the terms used in spectrochemistry, the reader is directed to a separate publication, entitled "Cumulative index" [2].

In this cumulative index further expressions related to *calibration* and *standardization* can be found with references to the original IUPAC publications, such as *analytical calibration curve*, *analytical calibration function*, *analytical concentration range*, *analytical curve*, *reference-element technique*, *reference intensity* and *reference material*.

It is interesting to observe that some basically important terms, such as (line) *intensity*, *internal reference* and its synonym *internal standard* were defined in the first IUPAC publication on spectrochemistry nomenclature (Pure and Applied Chemistry, 1972) [3]. Also in this pioneering publication, the specific meaning of *external standard* is explained and mentioned amongst the non-recommended expressions in spectrochemical publications. The definitions of these terms are as follows.

3.1. Intensity

"In (spectrochemical) practice it is often unnecessary to consider what radiant quantity is really measured, or to refer to the particular radiant property of the light source (radiance or radiant intensity)… Intensity of a spectral line or of the background in a spectrum is then a loose relative expression referring to the radiant quantity measured by the receiver. This intensity has unit dimension."

As a consequence of this definition the addition of the supplement "in arbitrary unit" to the "Intensity" scale of a coordinate is not required (which is still not always obeyed in the present literature).

3.2. Internal reference

"The relative nature of intensity is explicit when internal reference lines in the spectrum are used. Then accidental variations in the physical conditions of the experiment (especially in the light source) are generally without harmful effect, since one measures the intensity I, of the spectral line of the analysis element in relation to the intensity I, of a line of a suitably selected reference element. Ideally both the analysis element line intensity and the reference element line intensity should respond to changes in the experimental conditions in the same way and rate (Gerlach's homologous lines)."

3.3. Internal standard and external standard (as not recommended terms)

These terms are in part connected with the use of photographic photometry, which is nowadays an obsolete technique of intensity measurement. Therefore a short explanation might be useful to be offered here. When the photographic characteristics of the emulsion is different for the analysis and reference lines (due to a relatively large wavelength difference), an intensity bridge is required to set up a *generalized* (usable for more than a single emulsion) calibration curve. The intensity ratio of the two "bridge pillar" (the one close of the analysis line and the other close to the reference line in wavelength) is determined in each photographic plate and used for normalization of the intensity ratio calculable directly from the emulsion calibration curves, which are determined separately at the two wavelengths. For the purpose of set up an "intensity bridge" either continuum spectra of standard radiation sources (as mentioned in the cited text below) or line spectra of stabilized discharges (e.g. d.c. iron-arc) have been applied.

"An intensity bridge ratio can be derived from a spectrum with known spectral distribution of intensities. Examples are: the spectrum of a standard d.c. graphite arc or of a tungsten ribbon lamp etc. This idea of an intensity bridge is usually implicit in the term external standard. But the use of this term is discouraged since it is not clearly defined and might wrongly be considered as the opposite of internal standard, a term that in the future should be replaced by reference element or reference intensity."

Accordingly, in the earlier spectrochemical literature the expressions *external standard* and *external standardization* were not unknown, but these expressions were related to the technique of intensity measurement and were not related directly to concentration determination, i.e. to *analytical calibration*. It is not likely, however, that the spreading use of *external standardization* or *calibration* is originating from this old term of spectrochemistry.

Another important conclusion from the above IUPAC definition is to be emphasized with respect of *internal standard* and *internal*