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# CONCEPTS AND APPLICATIONS OF THE TERM “DIMENSIONALITY” IN ANALYTICAL CHEMISTRY

## (IUPAC Technical Report)

Prepared for publication by

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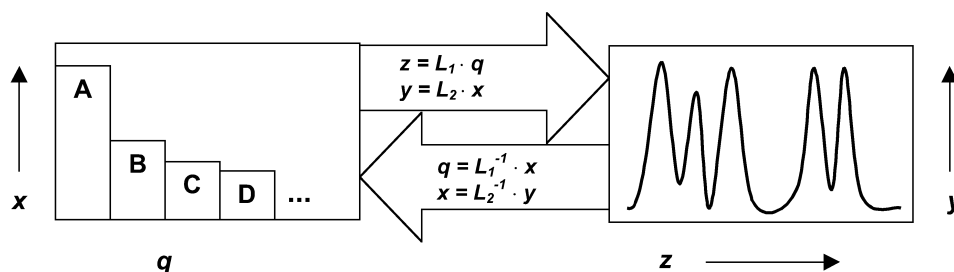
# Concepts and applications of the term “dimensionality” in analytical chemistry

## (IUPAC Technical Report)

*Abstract:* The term “dimensionality” has been used by the analytical chemistry community with several meanings. On different occasions, analysts speak about “two-dimensional” analytical methods, for example, 2D nuclear magnetic resonance spectroscopy, 2D thin-layer chromatography, “two-dimensional” or “three-dimensional” analytical information [1], “two-dimensional” or “three-dimensional” images in surface analytical chemistry, and of “ $m$ -dimensional” analytical data [2] obtained, for example, as a result of multicomponent analyses. These examples show that the use of the term “dimensionality” is at times contradictory. This confused position does not promote the unequivocal application of the term “dimensionality” in analytical chemistry. The aim of this document is to provide a concept for the use of the term “dimensionality” as it is related to analytical information.

### 1. INTRODUCTION

The chemical measurement process [3] can be understood as a defined transformation (coding) of analytical information in the sample domain (chemical domain),  $x = f_1(q)$ , see Fig. 1, left, into analytical information in the signal domain,  $y = f_2(z)$ , see Fig. 1, right. Evaluation of analytical measurements represents then the back-transformation (decoding) of a signal (function) into chemical information.



**Fig. 1** Relation of the analytical function (sample composition)  $x = f_1(q)$  and the measured function (signal function)  $y = f_2(z)$ , according to [4].

For this general transformation,

$$x = f_1(q) \Leftrightarrow y = f_2(z) \quad (1)$$

transformations have to be carried out using the information on chemical species in the sample,  $q_i$ , into signals  $z_i$ , and on their amounts (contents),  $x_{q_i}$ , to give signal intensities as indicated in the arrows in Fig. 1. ( $L$  is, in general, a linear operator.)

The analytical function  $x = f_1(q)$  represents a two-dimensional pattern of the sample composition, viz. certain types of chemical species (analytes)  $q_i$  and their amounts  $x_{q_i}$ . The projection of this into the signal domain results in the (likewise, two-dimensional) pattern of signals with their different intensities (the signal function or measured function), see Fig. 1.

From the above point of view, one can consider the dimensionality of chemical measurements, measured functions (signal functions), and, therefore, of analytical information. On this basis, a concept for the use of the term “dimensionality” in analytical chemistry is provided.

## 2. DIMENSIONALITY OF ANALYTICAL INFORMATION

General axiom: The dimensionality of a functional relationship is determined by the number of dependent and independent variables in such a function.

Examples: Functions of the type  $a = f(b)$  are two-dimensional, of the type  $a = f(b_1, b_2)$  three-dimensional, and such of the type  $a = f(b_1, b_2, \dots, b_n)$  are  $(n + 1)$ -dimensional. The representation of only one variable is one-dimensional.

Dimensionality in analytical chemistry comprises different types of dimensions spread by different sorts of variables, which can be discrete or continuous:

- **Physical dimensions:** time and space, characterized by the variables time, latitude, longitude, and altitude
- **Chemical dimensions:** number and amounts of analytes (i.e., distinct chemical species)
- **Measuring dimensions (signal-theoretical dimensions):** signal position (i.e., signal energy or time characteristic) and signal intensity
- **Statistical dimensions:** number of variables (intrinsic or latent) taken into account in evaluation. Statistical dimensions define the type of data handling and evaluation, e.g., univariate, bivariate, multivariate

These different types of dimensions are applied for the characterization of analytical information in combination.

As a result of chemical measurements, signal quantities are obtained, in the case of instrumental analytical measurements signal successions or signal functions,  $y = f(z)$ , respectively. The record of the signal intensity  $y$  as a function of the signal position  $z$ , Fig. 2, represents a two-dimensional signal function that can be back-transformed into two-dimensional analytical information,  $x = f(q)$ .

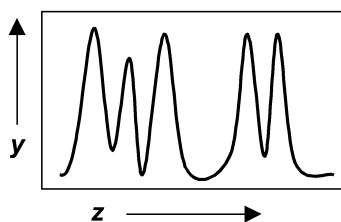
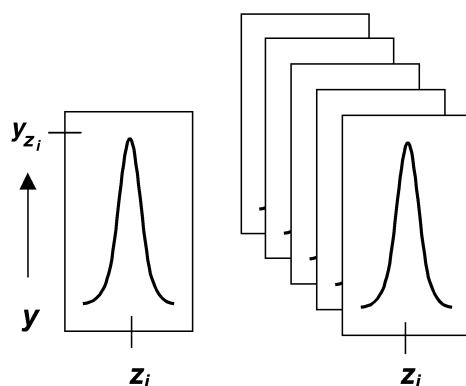


Fig. 2 Two-dimensional analytical information in form of a signal function.

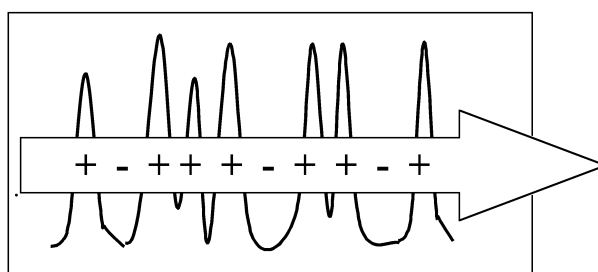
The abscissa may represent an energy or energy-related scale, e.g., wavelength-, frequency-, or mass/charge coordinates of spectrometers or time coordinates of chromatograms [4]. The evaluation of the signal function is as a rule carried out in both dimensions.

An evaluation of only one of the two quantities, either the intensity  $y_{z_i}$  of a given signal  $z_i$  (that is characteristic for a certain species in the sample, see Fig. 3, left-hand side) or the appearance of certain signals that indicate the presence of the corresponding species in the sample (Fig. 4) represent typical one-dimensional analytical information.

One-dimensional analytical information corresponds to the quantitative analysis of one given analyte by typical single-element methods like atomic absorption spectrometry (AAS), as shown in Fig. 3 (left side).



**Fig. 3** One-dimensional information (in  $y$ -direction; quantitative signal evaluation of one given analyte  $z_i$ )  $y_{z_i}$ , left-hand side, and quasi-multidimensional information on several analytes (sequence of one-dimensional information), right-hand side.



**Fig. 4** One-dimensional information (in  $z$ -direction; qualitative signal evaluation, signal identification).

Quasi-multidimensional information as shown in Fig. 3 (right side) can be obtained in different ways, for example,

- by sequential changing detecting channels, thus, measuring one analyte after another (e.g., spectrophotometry)
- by sequential changing excitation sources (e.g., hollow cathode lamps in AAS)
- by sequential measurement of the same element, which is temporally separated in different species (e.g., GC-AAS)

In analytical practice, one-dimensional information according to Fig. 4 corresponds to qualitative analysis (testing of presence of certain components, e.g., by optical emission spectroscopy) the basis of which is only the exceedance of critical values,  $x_{z_i} > x_C$  [3].

The most frequent case in analytical chemistry is the evaluation of two-dimensional analytical information in the form of spectra, chromatograms, thermograms, current-voltage curves, etc. Additional dimensions can be given by

- successive separation steps, e.g., in two-dimensional chromatography (two-dimensional thin-layer chromatography) that result in three-dimensional analytical information  $y = f(z_1, z_2)$ , as shown in Fig. 5
- two-dimensional excitation experiments (two wavelengths excitation in fluorescence spectroscopy or two frequency experiments in 2D-NMR) generate also three-dimensional information  $y = f(z_1, z_2)$

- coupled (hyphenated) analytical techniques of a separation method and a method of analytical determination, e.g., GC-MS, see Fig. 6
- time-dependent analytical measurements, which give three-dimensional information of the type  $y = f(z, t)$ , schematically shown in Fig. 7. The same characteristic holds for distribution analysis in one spatial direction, i.e., line scans,  $y = f(z, l)$

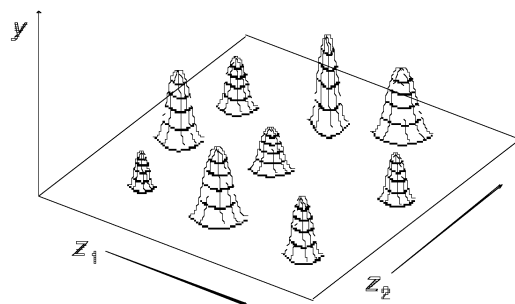


Fig. 5 Three-dimensional analytical information of two-dimensional analytical techniques.

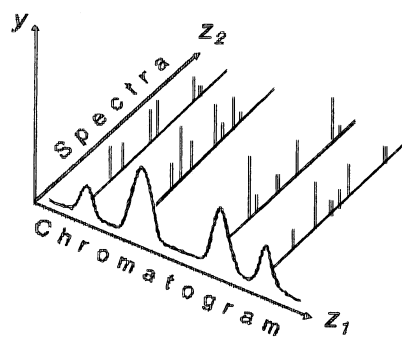


Fig. 6 Three-dimensional analytical information of coupled techniques, e.g., GC-MS.

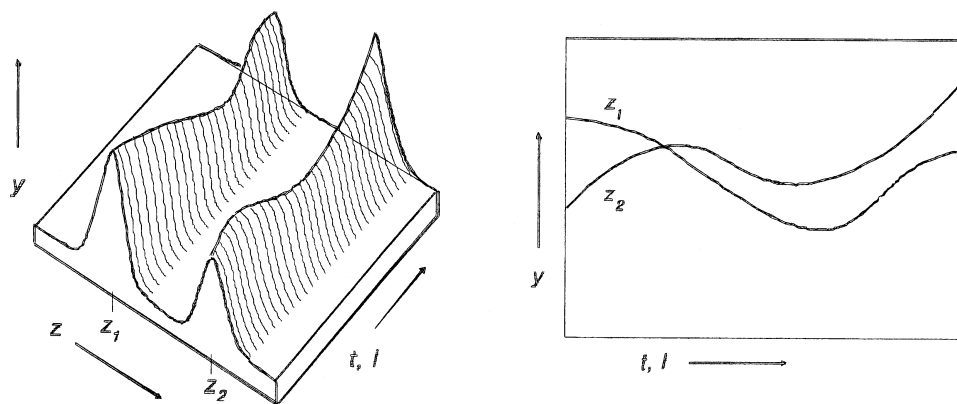
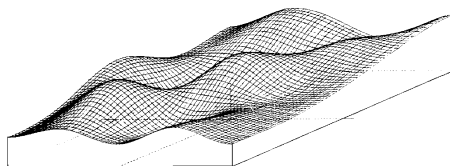


Fig. 7 Temporally or spatially dependent analytical measurements, e.g., a line scan of electron microprobe analysis as three-dimensional analytical information represented in different ways



**Fig. 8** Surface scan of an analyte (Mn distribution in iron on a surface area measured by laser micro optical emission spectrometry).



**Fig. 9** Surface scan of one element (Si distribution in a binary eutectic Al-Si alloy measured by electron microprobe).

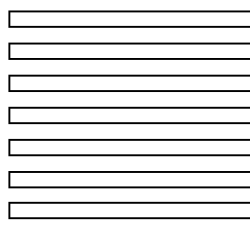
- distribution-analytical investigations in which spatial directions of the sample represent additional variables such as
  - line scans of microprobes  $y = f(z, l_x)$  for several analytes giving images like that represented in Fig. 7
  - surface scans of microprobes  $y = f(z, l_x, l_y)$  for a given analyte, see Fig. 8
  - component images  $z = f(l_x, l_y)$  for one or two analytes by black and white representations like Fig. 9, for more components by colour images
  - so-called “3D” images of SIMS (secondary ion mass spectrometry), which in fact represent four- or five-dimensional analytical information depending on the actual function  $y = f(z, l_x, l_y)$ ,  $y = f(l_x, l_y, l_z)$ , or  $y = f(z, l_x, l_y, l_z)$ , respectively

### 3. ALTERNATIVE CHARACTERIZATION OF THE DIMENSIONALITY OF ANALYTICAL FUNCTIONS AND INFORMATION

The SIMS example shows that the dimensionality of analytical information and of measured functions follow occasionally other principles than given in paragraph 2, where the dimensionality of a functional relationship is determined by the number of dependent and independent variables in such a function. In contrast with this, in signal theory the dimensionality of signal functions is frequently determined only by the number of independent variables. The dependent quantities are ignored. Therefore, a signal curve representing the dependence of the signal intensity from a given independent variable (mostly time) is characterized as one-dimensional. Also, in analytical practice such a characterization of analytical functions is sometimes used, especially in relation to analytical images. So, spectra are considered as one-

dimensional images and analytical element distributions like those given in Figs. 8 and 9 as two-dimensional element images.

*Note:* From the most general point of view, the theory of fractals, one-, two-, three-,  $n$ -dimensional figures are only borderline cases [6]. Only a straight line is strictly one-dimensional, an even area strictly two-dimensional, and so on. Curves such as in Fig. 7 may have a fractal dimension of about 1.1 to 1.3 according to the principles of fractals; areas such as in Fig. 8 may have the fractal dimension of about 2.25 and the figure given in Fig. 10 drawn by one line may have the dimension of about 1.9 [6]. Fractal dimensions in analytical chemistry may be of importance in materials characterization and problems of sample homogeneity [7].



**Fig. 10** Line with a fractal dimension of nearly 2.

Analytical functions of different dimensionality have been listed in some detail by Danzer et al. [5]. The most important analytical functions of practical relevance are given in Table 1.

**Table 1** Selection of analytical functions [5] and their dimensionality.

Analytical function	Information	Dimension
$z_{y,l_x,l_y,l_z,t}$	Qualitative average analysis ( $l_x, l_y, l_z, t = \text{const}$ ) for several components, e.g., by a sequence of spot tests	1
$y_{z,l_x,l_y,l_z,t}$	Quantitative average analysis ( $l_x, l_y, l_z, t = \text{const}$ ) for one given component, e.g., by gravimetry or AAS	1
$y = f(z)_{l_x,l_y,l_z,t}$	Quantitative average analysis ( $l_x, l_y, l_z, t = \text{const}$ ) for several components, e.g., by ICP-OES <sup>a</sup>	2
$y = f(l_x)_{z,l_y,l_z,t}$	Line analysis: determination of the variation (distribution) of the amount of one component (given $z$ ) along a line $l_x$ across the sample, e.g., by EPMA <sup>b</sup>	2
$z = f(l_x, l_y)_{l_z,t}$	Surface analysis: qualitative representation of the presence (distribution) of several components across a surface area, see Fig. 9 obtained by EPMA <sup>b</sup>	3
$y = f(l_x, l_y)_{z,l_z,t}$	Surface analysis: quantitative representation of the variation (distribution) of the amount of a given component across a surface area, see Fig. 8 obtained by micro spark OES <sup>c</sup>	3
$y = f(l_x, l_y, l_z)_{z,t}$	Volume distribution of one given component: SIMS <sup>d</sup> data; representation mostly by categorial $y$ (color-coded)	4

(continues on next page)

**Table 1** (Continued)

Analytical function	Information	Dimension
$y = f(z, l_x)_{l_y, l_z, t}$	Line analysis of several components: determination of the variation (distribution) of the amounts of along $l_x$ , see Fig. 7, e.g., by EPMA <sup>b</sup>	3
$y = f(t)_{z, l_x, l_y, l_z}$	Quantitative process analysis: recording the amount of one given component ( $z$ ) in dependence of time, e.g., by flow techniques	2
⋮	⋮	⋮
$y = f(z, l_x, l_y, l_z, t)$	Quantitative determination of several components in dependence of space and time (spatial-resolved dynamic quantitative multicomponent analysis), e.g., by a series of 3D-SIMS <sup>d</sup> images for several elements and at different times	6

<sup>a</sup> Inductively coupled plasma optical emission spectrometry

<sup>b</sup> Electron probe micro analysis

<sup>c</sup> Optical emission spectrometry

<sup>d</sup> Secondary ion mass spectrometry

#### 4. DIMENSIONALITY OF ANALYTICAL DATA

The dimensionality of analytical data must be distinguished from the dimensionality of analytical information and of measuring functions. Measured and/or analytical data are represented mostly in the form of data sets and data matrices

$$X = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1m} \\ x_{21} & x_{22} & \cdots & x_{2m} \\ \vdots & \vdots & & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{nm} \end{bmatrix} \quad (2)$$

where  $m$  is the number of components (distinct chemical species, constituents) determined in  $n$  objects (samples). Matrix (1) has the dimension  $n \times m$ , and the related data set is called  $m$ -dimensional. It is the endeavor of multivariate data analysis to reduce the dimensions of data sets (matrices) by finding redundant variables in form of correlated components. If  $k$  of  $m$  components are found correlated with the remainder, the dimension of the data set is reduced to  $m-k$  corresponding to the number of independent components. The aim of data analytical methods like factor analysis and principal component analysis (PCA) [8] is to reduce the dimensions in such a way that the relation between the  $n$  objects (samples) can be represented by minimum dimensional displays, usually in two or three dimensions.

Details of how to achieve reduction of dimensionality in data sets are available in the chemometrical literature [2,8,9].

#### REFERENCES

1. K. Eckschlager and K. Danzer. *Information Theory in Analytical Chemistry*, Wiley, New York (1994).
2. I. E. Frank and R. Todeschini. *The Data Analysis Handbook*, Data Handling in Science and Technology, Vol. 14, B. G. M. Vandeginste and S. Rutan (Eds.), Elsevier, Amsterdam (1994).
3. L. A. Currie. IUPAC Commission on Analytical Nomenclature, "Nomenclature in evaluation of analytical methods including detection and quantification capabilities", *Pure Appl. Chem.* **67**, 1699 (1995).



4. K. Danzer and L. A. Currie. IUPAC Commission on General Aspects of Analytical Chemistry, “Guidelines for calibration in analytical chemistry. Part 1. Fundamentals and single component analysis”, *Pure Appl. Chem.* **70**, 993 (1998).
5. K. Danzer, K. Eckschlager, D. Wienke. *Fresenius’ Z. Anal. Chem.* **327**, 312 (1987).
6. B. B. Mandelbrot. *Fractals—Form, Chance, and Dimension*, Freeman, San Francisco (1977).
7. K. Danzer and L. Kuechler. *Talanta* **24**, 561 (1977).
8. M. A. Sharaf, D. L. Illman, B. R. Kowalski. *Chemometrics*, Wiley, New York (1986).
9. D. L. Massart, B. G. M. Vandeginste, S. N. Deming, Y. Michotte, L. Kaufman. *Chemometrics—A Text-book*, Elsevier, Amsterdam (1988).