Quantitative determination in three- way calibration strategies with hyphenated –data (chromatography-spectroscopy) of Polyherbal-herbomineral formulation

Jayanta kumar Maji, Shukla V.J, P .K. Prajapati

Abstract:

Chemometrics involved application of various three way calibration method, such as the generalized rank annihilation method (GRAM) and parallel factor analysis (PARAFAC) for drawing vital information from various complex and uncharacterized mixture. In this paper, theoretical and practical progression and overview of three way calibratio method from the flexible PARAFAC to Tucker-3, N-Partial Least square (N-PLS) have been discussed. The ability of three way analysis to uniquely deconvolve overlapped spectral signatures is harnessed to extract the analyte signal from an unknown and uncalibrated background prior to quantization with the help of appropriate algorithom. Calibration approaches PARAFAC can be used to analyze the data obtained from various instrument like NIR, ATR-FTIR, HPLC-DAD, Sensory Analysis, 2D-NMR. The technique has been used in the quality assurance and quality control of polyherbal&herbomineral formulation powder, capsule parametric test has also been discussed . It can be used easily multivariate environments like Ayurvedic formulation as a routine parameter.

Key words: Chemometrics, Three-way calibration, PARAFAC, Tucker, Polyherbal ,Herbo mineral

1. INTRODUCTION:

1.1 BACKGROUND INFORMATION:

In the past two decades, combining a chromatographic separation system on-line with a spectroscopic detector in order to obtain structural information on the analytes present in a sample has become the most important approach for the identification and confirmation of the identity of target and unknown chemical compounds. For most (trace-level) analytical problems in the research field of herbal medicines, the combination of column liquid chromatography or capillary gas chromatography with a UV-VIS or a mass spectrometer (HPLC-DAD, CE-DAD, GC-MS and LC-MS, respectively) becomes the preferred approach for the analysis of herbal medicines.

Chemometric techniques for calibration with three –mode signals are sufficiently developed for their use in routine analysis.

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The advantage of the second order property (the possibility of quantifying an analyte in the presence of interferents) together with the guarantee of the uniqueness of the decomposition, deconvolution , to extract the signal corresponding only to the analyte, make these calibration techniques especially useful for the quantification and identification of analytes in complex samples of interest. This review mainly focuses three way calibration strategies to evaluate the identification and quantification of poly herbal – herbo mineral formulation. The International Chemometric Society (ICS) gives a very simple definition of the term chemometrics: “Chemometrics is the science of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods” (ICS, 2006). In contrast to this simple definition, the field of chemometrics is almost universal, since the mathematical and statistical methods apply in very many situations. In the beginning of chemometrician researchers from around the world developing and applying mathematical and statistical methods to a wide range of problem in Chemistry.Chemometricians with analytical chemistry backgrounds were interested in such tasks as controlling or optimizing complicated analytical instruments, resolving spectra of complex mixtures into the spectra of pure components ,in general chemical information from quantitative measurement. Now a days the power and

complexity of instrumentation increases withthe number of "ways" the data is collected and treated [1]. This introduction will focus on a "rationale" for chemometrics and a brief description of the common chemometric techniques: Principal Component Analysis (PCA), generalized rank annihilation method (GRAM), Parallel Factor Analysis (PARAFAC), Partial Least Squares Regression (PLSR), and Multi-way Partial Least Squares Regression (N-way PLSR).

1.2 ASPECTS OF THE RATIONALE BEHIND CHEMOMETRICS:

Chemometrics has a holistic, exploratory approach to data and process modeling; none or only the barest minimum of a priori assumptions regarding data behavior ("distributions") are made in chemometrics prior to data analysis. The basic idea in chemometrics is to let the process or the data structures reveal their relations themselves. Chemometric data analysis often starts with far more parameters/variables than required to explain the phenomena under investigation. Consequently, chemometric methods are nearly always multivariate methods of which many are based on modeling and visualizing covariance structure among variables. This multivariate approach makes chemometrics suitable for process analyses and other structural characterization. Chemometrics allow monitoring schemes such as Multivariate Statistical Process Control (MSPC) to be based on latent structures in the process instead of single parameters. This has proved to be advantageous on many occasions such as .In polyherbal – herbomineral formulation of Ayurvedic system of medicine is composed of multiple herbs and minerals. During characterization of any polyherbal formulation with selective marker is now not key tone researcher [2], [3].On the other hand compound formulation is composed of multiclass compound (alkaloids, glycosides,tannin,streoidsetc) which is not easily evaluated as a single methods. On the contrary of Ayurvedic point of view drugs are explained as material level, in chemistry drugs are analyzed substance level. In that circumstances researcher are going to chemometrics measurement as a phytoequivalence to ensure the consistency herbal-herbomineral product. Now a day's some very sensitive, flexible instrument are available, easily captured data efficiently. If you collect data in multiway, applied various chemometrics models (PCA, PARAFAC, TURKER, N-way PLS), evaluated appropriate algorithoms (ALS, PLS, etc.), then mathematically solved this particular hurdles with calibration technique as a multi-component in polyherbal formulation. Trilinearity can be viewed as an extension of the bilinear relationship between variable and an independent one to a scenario with two independent variable and a dependent one. In this way, trilinearity could be seen as a natural extension of Lambert Beer's law to 2nd order data.

The analytical procedure, a precisely described operational sequence of action, in chemistry especially designed to obtain information about the composition of material. The improvement in the qualitative chromatographic information is a relevant issue, the possibility to obtain quantitative information is the most exploited and valuable aspect of the simultaneous analysis of several chromatographic runs. The main reason is the so called second –order advantage, which allows for the quantification of the analytes in the presence of unknown interferences [1]. Three way calibrations methods, such as the generalized rank annihilation method (GRAM) and Parallel factor analysis (PARAFAC), are becoming increasingly prevalent tools to solve analytical challenges. Analysis of such higher-dimension data matrix requires special data arrangement and multi-way methods. Multi-way modeling, such as MPCA, PARAFAC and Tucker3 models, can be used for decomposing the 3D data array directly [4], [5], [6].

2. MODEL & ALGORITHM

2.1 NOMENCLATURE

As a general note, we prefer to refer to chemical sample constituents rather than to components, because the latter word may imply abstract linear combinations of real constituents for some methodologies. It is also important to distinguish among technique, method, model, and algorithm, terms which are sometimes interchanged. In the context of calibration, an analytical technique is a procedure used to determine an analyte concentration, whereas an analytical method is more specific concerning the sample and measuring conditions. A model is a description of the data properties, and an algorithm is a detailed set of instructions for accomplishing a computational task. Therefore, the specific mathematical procedures for processing second- and higher-order data are all algorithms. They allow for data analysis based on a certain model, i.e., on certain assumptions concerning the properties of the data. Different algorithms may apply to the same model. The term method is employed in a more general sense and sometimes replaces the term algorithm [7].

2.2. ORDER OF THE SIGNAL AND CALIBRATION MODEL:

ZEROTH- ORDER DATA:

Sample with known concentration (calibration standard), the calibration curve is estimated which generally follows a linear relation fitted by means of least square regression. Total selectivity is needed; i,e a compete separation of the calibrated analyte. To quantify a problem sample, its signal is recorded and concentration is obtained from the estimated curve. With a univarite calibration, one cannot detect the presence of an interferent in a problem sample.(Table-1)

FIRST ORDER DATA:

Instrument response is a vector for each analyzed sample. Calibration model (PLS, PCR, etc).Conc. = f (signal). Each calibration sample (i=1… I) with diff. concn of the analyte, Yi, there corresponds a vector of dimension J (the number of scan

record) xi.These vectors are the rows of a matrix X, of dimension (I × J) which together with vector concentration Y, of dimension I, Constitute the calibration set. Using these experimental data, one constructs the calibration function. Assume that the data of the matrix X are centered by columns although this is not obligatory, it simplifies the formal explanation of the regression methods useful in calibration.

THE 2ND ORDER DATA:

In this case, the instrumental response is a matrix of numbers for each sample. For example, the matrix of numbers obtained for specific time interval, when the intensity at various wavelengths is recorded in high-performance liquid chromatography. By varying the sample, one has a set of data distributed in a cube, known as a tensor, of dimension I×J×K.

In HPLC-PDA run, 'I' is the number of samples, 'J' is the retention time and 'K' is number of wavelength at which the intensity was recorded. It is usual to name these ways by their chemical meaning. In our case, we have the sample way (relative concentration), the chromatographic way and the spectral way.

In that circumstance, we only describe the three –way regression methods with a response vector, (formed by the concentration of an analyte in the 'I' calibration samples), but there are suitable methods for the case in which the response is a matrix Y or a three way array Y [2].

The information provided by the second order signals together with an adequate decomposition of the three way set they generate enables one to identify the analyte with the guarantees required by current normative even in the presence of interferents not modeled in the calibration stage. This is known as the second order property.

In tensor notation, a scalar is a zeroth-order tensor, a vector is first order, a matrix is second order, a cube is third order, etc.

Table 1

Different arrays that can be obtained for a single sample or a set of samples.

Data order	Array		Calibration
	One sample	A sample set	
Zero	Scalar	One -way	Univariate
First	Vector	Two-way	Multivariate
Second	Matrix	Three-way	Multi-way
Third	Three way	Four way	Multi-way

2.3 ADDITIONAL REMARK:

Above explaining the calibration function has been related to the order of the signal .To build a calibration function from some experimental data is an attempt to decompose the response ,y, into two addends; the functional part, f(x), and the random part, e , such that y = f(x) + e. It is impossible to adequately model one of them independently of the other one. Further, the regression method to be used to estimate the calibration function depends on the supposed model for the random part. For example, the maximum likelihood method to estimate a linear function model is that of least squares when the residuals are normally distributed ,but the sum of the absolute values would have to be minimized instead (Laplace's method) if the residuals follow a double exponential distribution [8].

3. MULTI-WAY MODEL:

3.1 PARAFAC MODEL

The major component model for three way data is the Parafac model (Harshman, 1970; Harshman & Lundy, 1984c, 1984d). The same model was independently proposed in a different context by Carroll and Chang (1970) under the name Cande-Comp (canonical decomposition), but the name Parafac model is one of the generalizations of the singular value decomposition to three –way data. Several theoretical discussions about the nature of such generalization can be found in Denis and Dhrone (1988), Franc (1988), Yoshizawa (1987), and Kroonenberg (1989). The fundamental idea underlying Parafac model was first formulated by Cattell (1944) in the form of the principle of Parallel Proportional Profiles (explained in 1955.p.84; their italics; Cattell) assumption is that if the same factors are present in two samples under different conditions, then each factor in the first sample is expected to have the same pattern in the second sample but profiles of the factors will be scaled depending on the conditions (2) Another way of explaining the basic idea of PARAFAC is to use the same set of factors to describe the variation in several matrices of data simultaneously albeit with different weighting coefficients for each matrix [9]

There are six classes of three way data, and four of these classes can be appropriately modeled with the basic trilinear or PARAFAC (PARALLEL FACTOR) model, where the data cube is decomposed into N sets of triads ,$\hat{x}$,$\hat{y}$,and $\hat{z}$[10].

The trilinear model can be presented equivalently is statistical

$$\hat{R}_{ijk} = \sum_{n=1}^{N} \hat{X}_{ni} \hat{Y}_{nj} \hat{Z}_{nk} + E_{ijk} \quad \text{..... (1)}$$

Or mathematical forms

$$\hat{R}_{k} = \sum_{n=1}^{N} \hat{X}_{n} \hat{Z}_{nk} \hat{Y}_{n}^{t} + E_{k} \quad \text{..... (2)}$$

Here N refers to the number of factors employed by the model to describe the data cube, or the rank of the model. However, in problems with an underlying trilinear structure, when the proper number of factors is chosen for a trilinear model, the factors are accurate estimates of the true underlying factors. In other words, if a LC-UV/Vis DAS formed $\mathbb{R}$, then each $\hat{X}_n$ would correspond to one of the true N chromatographic profiles, each $\hat{Y}_n$ to one of the true spectroscopic profiles, $\hat{Z}_n$ and each to the relative concentrations in the K samples. Therefore, in three-way analysis, when, for an isolated chemical component (1) the true underlying factor in each of the three modes is

independent, except for scale, from the state of the other two modes; (2) the true underlying factor in any of the three modes cannot be expressed by linear combinations of the true underlying factors of other components in the same mode; (3) there is linear additivity of instrumental responses among the species present and; (4) the proper number of factors is chosen for the model, then the factors $\hat{x}$, $\hat{y}$, $\hat{z}$ and are unique to a scaling constant and are accurate estimates of the true under lying factors , x, y, and z. This is shown in graphically in fig-1 [11].

Parafac refers the parallel factorization of the data set R by equation (1), and (2) and to an alternating least square algorithm for determining X, Y, and Z, in the two equations. The ALS algorithm is known as PARAFAC, emanating from the work Kroonenberg [12], and as Cande-comp, for canonical decomposition, based on the work of Harshman [13].Two basic algorithoms are practically identical.

A full blown expose of the model, a more applied survey can be found in Harshman and Lundy (1994b), and a tutorial with a chemical slant in Bro (1997).The Parafac model has seen a large upsurge in both theoretical development and applications, when it realized that it corresponded to common physical models in analytical chemistry by Smilde et al.(2004). There are many other tensor decompositions, including INDSCAL, PARAFAC2, CANDELINC, DEDICOM, and PARATUCK2 as well as nonnegative vari-ants of all of the above. The N-way Toolbox, Tensor Toolbox, and Multilinear Engine are examples of software packages for working with tensors [14].

PARAFAC is a commonly used method for resolution of overlapping phenomena in three way data (or higher).In principle PARAFAC is simply an extension of PCA to higher order data. PCA is ideally suited for the analysis of bilinear data matrices produced by hyphenated chromatography – spectroscopic techniques. The principal component models are easy to construct, even when large or complicated data sets are analyzed.

Principal component Analysis:

Principle component analysis refers to a method of data analysis for building linear multivariate models of complex data .Developed using orthogonal basis vector (Eigen vector), usually called PCs.

In PCA a set of p correlated variables is transformed to a smaller set of uncorrelated hypothetical construct called principal component (PCs).

Empirical mathematical model:

$$A = T_k V_k^T + E$$

[T_K is the n×k matrix of Principal component scores.V_K is the m×k matrix of eigenvectors.E= residual error.]

The Eigen vector V_k is the orthonormal row basis vector for A. The column basis vector of T_k are called “scores” are mutually orthogonal but normalized.PCA is used as data reduction technique.

Multi-way methods, such as parallel factor analysis , promoted by Bro in the context of chemical problems, the generalized rank annihilation method(GRAM) [15],[16], [18], [19], [20] and direct trilinear decomposition (DTD) by Kowalski [17], [21] decompose these cubes of data into three matrices, which contain the elution profile(C) , the pure spectra (S) ,and quantitative information about the compounds in the different runs (Z). Parafac model can perform mathematical chromatography on mixture data enabling identification and quantification of specific analyte. The measurements of the mixtures are mathematically separated into pure-analyte information: estimated relative concentrations (scores) together with estimated spectra (loadings) and estimated retention time profiles (loadings) for each of the corresponding taken compounds.

Certain feature of Parafac model: Uniqueness, Noise, Missing data.

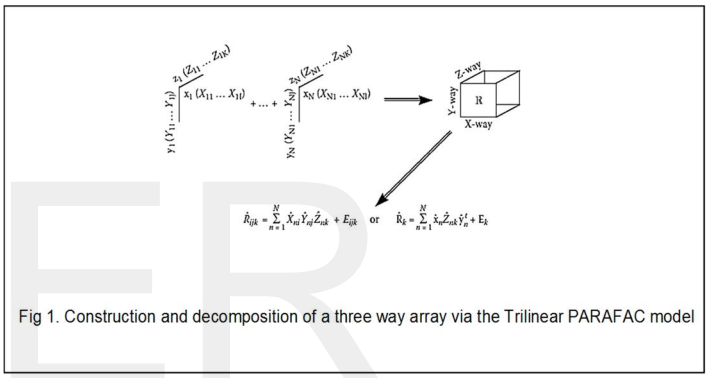

Fig 1. Construction and decomposition of a three way array via the Trilinear PARAFAC model

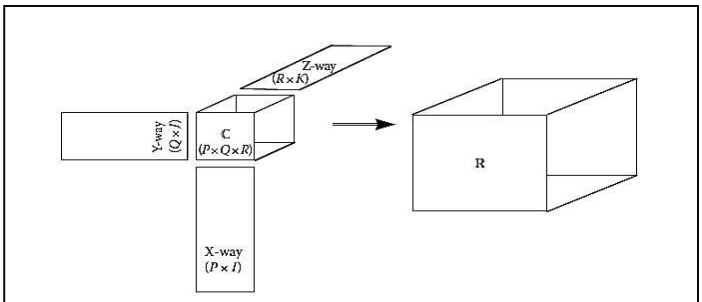

Fig 2. Construction of a three way array according to the unconstrained Tucker model.

3.2 TUCKER MODEL:

Three mode analysis as an approach toward analyzing three way data started with Ledyard Tucker's publications (Tucker, 1963) [22] about what he called three mode factor analysis, but it is now generally referred to as three-mode component analysis [23].This model now referred to as the Tucker 3 model.

The three way Tucker-3 model with (P, Q, R) component, matrices in the 1st, 2nd and 3rd mode may be formulated as in Eq. (3):

$$R_{ijk} = \sum_{p=1}^{P}\sum_{q=1}^{Q}\sum_{r=1}^{R} x_{ip}\, y_{jq} z_{kr} g_{pqr} + e_{ijk} \quad \text{..... (3).}$$

The Turker -3 model is best understood by viewing a graphical representation such as fig-2.A data cube,ℝ, is decomposed into three sets of factors,x̂,ŷ, and ẑ .But here constrained is not to be equal, 2ndly Turker 3 model employs a small core cube,© ,that governs the interactions among the factors. Third, the interaction in the Tucker 3 model makes it a nonlinear model. In addition, it also generates a core of reduced dimensions, C, from ℝ.

In the contrast to the PARFAC model, all Tucker model suffer from rotational ambiguity; by rotating the component matrices and counter rotating the core array, an infinite number of models with equal fit to ℝ can be obtained. In the N-way toolbox, the algorithoms have been implemented with an empirical scheme for the most efficient method for estimating the components in each of the mode [24].There are numerous applications of the Tucker3 model in Chemometrics[25], [26].

3.3 MULTI-LINEAR PARTIAL LEAST SQUARE (N-PLS):

Partial least squares regression is a method for building regression models between independent (called x) and dependent (called y) variables. For multiway calibration, multilinear PLS or simply N-PLS (Bro, 1996) is an extension of the ordinary regression model PLS, where the independent data are modelled in a way that emphasizes variation that is especially relevant for predicting the dependent variables.

The general terminology of N-PLS depend on the order of the data: a Greek prefix indicates the order of x and an Arabic suffix after PLS indicates the order of y .In tri-PLS1 , therefore, each calibration sample is characterized by a J × K matrix Xi , to build a cube of data X of dimension I×J×K, and for each sample there is a known measurement to be predicted by the independent variables, The values of which are collected in a general Y matrix of dimensions I×L×M. When measurement are concentrations, they are collected in a I×1 vector called y. If more than one variable is sought, these are collected in a matrix Y of dimensions I×L, where L is the number of different analytes (tri-PLS2, tri-PLS3, etc.).

For example, for trilinear PLS regression, a PARAFAC like trilinear structure of the independent data is used. These trilinear components are calculated such that the scores are predictive for the dependent variable(s) as in ordinary two-way regression .Successful applications can be found many types of application areas [27], [28], [29], [30], [31].Mostly, prediction quality is maintained or even improved, compared to two-way analysis. Multilinear models always are much simpler in interpretation and exploration.

4. TECHNIQUE & PHARMACEUTICAL APPLICATION:

Multiway analysis is the natural extension of multivariate analysis, when data are arranged in three or higher way arrays. Because this is in itself provides a justification for multiway methods. Multiway methods provide a logical and advantageous tool in many different situations.(Table-2).

a)Sensory analysis (sample x attribute x judge), b)Batch data (batch x time x variable), c)Time series analysis (time x variable x lag), d)Chromatography (sample x elution time x wavelength),e) Spectral data (sample x emission x excitation x decay), f) Storage problem (sample x variable x time) .

4.1 FLUORESCENCE SPECTROSCOPY:

Graciela M.Escandar, et al, explained property of second –order data in trilinerity form, equation (1) implies that the individual constituent signals are additive. The graphical intuitive display showing schematic representation of the parafac operation [32] fig-3, Renee D. Jiji et al, Parallel factor analysis (PARAFAC) is applied to three calibrations of a field portable, cuvette –based, single –measurement,excitation-emission matrix fluorometer. Here, PARAFAC is employed to deconvolve the fluorescence profiles of dissociated and complexed dye states. Calibration is performed based on the intnsity of dye –pesticide fluoresence[33].

4.2 HPLC (HIGH PERFORMANCE LIQUID CHROMATOGRAPHY):

The current method HPLC is used for the analysis of multi-component pharmaceutical formulation. In HPLC various kinds of injection and selective treatment are required for the analysis of samples. Data are collected in various dimension, one separation dimension (elution time), one identification dimension (Wavelength) & sample dimension with context of relative concentration. This data represent in a cube model. Collected data basically computed various algorithms (alternative least square, partial least square and least square algorithm).

HPLC-PDA signal is characterized by a concentration that follows a linear relationship with both wavelength and retention time profiles.Trilinearity assumes that the measured signal is the sum of the individual peaks of each analyte and that the profiles in each mode for the analytes are proportion in all samples.

Very recently, Vasough et al. [34] used PDS combined with PARAFAC algorithom to quantify four alfatoxins in extract of pistachio nuts by LC-DAD, in the presence of interferences, using standardization of solvent based calibration data ,was used as in the prediction step. Using these approaches, the cost per analysis was also reduced. HAL-LONG WU, MASAMI SHIBUKAWA et al., Using Moore-penrose generalized inverse with singular value decomposition as a alternating trilinear decomposition algorithom with application to calibration of HPLC-PDA for simultaneous determination of overlapped chlorinated aromatic hydrocarbons [13].

4.3 NIR SPECTRA:

NIR spectroscopy (nondestructive method) for monitoring processes by means of chemometric technique is now commendable position in Pharmaceutical industry. Vibrational spectra acquired in the NIR –region (780-2500nm) is characterized by broad and highly overlapping bands.

There are several ways to model data for quantitative purposes, curve resolution applied along with two-way and three way regression technique. The calibration strategy

Table 2
Different application of chemometric (Parafac) technique in pharmaceutical Sciences

Research envisaged	Instrumental technique	Chemometric analysis	References
TLC-Spectrodensitometric, and multivariate calibration methodsin pure form and in cough coldformulations	HPLC,TLC-Spectrodensitometric	Multivariate calibration methods	39
Structural characterization experiment: Commercial preparation of St.John'sWort.	HPLC-PDA-SPE-NMR-MS	Parallel factor analysis (PARAFAC)	40
Predicting the drug concentration in starch acetate matrix tablets from ATR-FTIR spectra using Multiway methods.	ATR-FTIR	Parallel factor analysis (PARAFAC) and multilinear partial least squares (N-PLS)	36
Spectrophotometric determination of food dyes in soft drinks by second order multivariate calibration of the absorbance spectra-pH data matrices	HPLC-PDA	PARAFAC & Bilinear Least Square/Residual bilinearization	41
Mathematicalchromatography solves the cocktail party effect in mixtures using 2D spectraand PARAFAC	2D-NMR	PARAFAC	42
PARAFAC: Adjustment for modeling consumer study covering probiotic and conventional yogurt	Sensory analysis	PARAFAC,PCA	37
Three-way principal component analysis applied to noodles sensory data analysis	Sensory analysis	TURKER- 3	43
Multiway Analysis of Alzheimer's Disease: Classification based on Space-frequency Characteristics of EEG Time Series	Electroencephalogram	PARAFAC	43
A novel strategy for solving matrix effect in three-way data using parallel profiles with linear dependencies	Fluorescence spectroscopy	PARAFAC,PARALIND	44
PARAFASCA: ASCA combined with PARAFAC for the analysis of metabolicfingerprinting data	NMR-spectroscopy	PARAFASCA	45
Metabolome Classification of Commercial *Hypericumperforatum* (St.John'sWort) Preparations via UPLC-qTOF-MS and Chemometrics	UPLC-Qtof-MS Hyphenated spectroscopy	PCA	46
Neonatal seizure localization using PARAFAC decomposition	Electroencephalography	PARAFAC	47
A Quality by Design approach to investigate tablet dissolution shift upon accelerated stability by multivariate methods	UV-Visible Spectroscopy	MPCA,ANOVA	48
Applying Parallel Factor Analysis models to HPLC diode array detector datasetsreveals strain dependent regulation of polyketide biosynthesis in *Fusariumgraminearum*, *Fusariumculmorum*and *Fusariumpseudograminearum*	HPLC-PDA	PARAFAC	49
Application of PARAFAC for calibration with excitation –emission matrix fluoresence spectra of three classes of enviormental pollutants.	EEM flurometer	PARAFAC	21

Single-Measurement Excitation/Emission MatrixSpectrofluorometer forDetermination ofHydrocarbons in Ocean Water. 2. Calibration andQuantitation of Naphthalene and Styrene	Spectroflurometer	PARAFAC	50

described in this work takes advantage of the synergic combination of temperature-induced spectral variation in Near Infrared (NIR) spectroscopy and the properties of tensor models. Rather than seeing spectroscopic temperature effects as artifacts that have to be circumvented or eliminated, a Parallel Factor (PARAFAC) model is used to extract and separate the relevant sources of information about the physical and chemical changes in a system. This information is highly related to the sources that provoke changes in the system as a function of temperature, but cannot be ascribed directly to them, mainly due to the nonlinearities induced in the spectra. For quantification purposes Multiple Linear Regression (MLR) is used to build a least squares calibration model from the PARAFAC sample scores.Ming Jing, Wrenching cai et al [35], using temperature effect on spectral data adding meaningful dimension can be modeled and predicted in a straightforward and highly effective way as a novel approach. Basically in this paper introduce a novel way of generating tensor data, which is more beneficial for interpretational and predictive point of view comparison to traditional chromatographic approach.

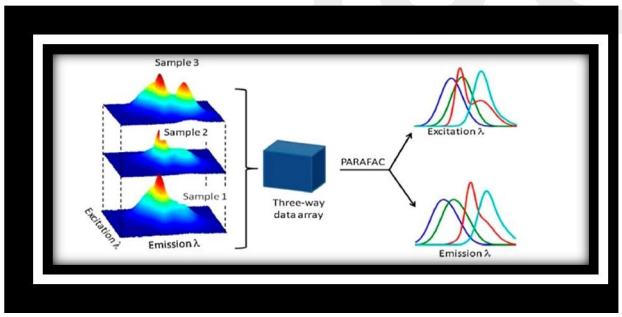

Fig 3. Schematic representation of the PARAFAC operation ,which builds a three way data array with the different data matrices, and then decomposes the array in both instrumental data modes (in this case excitation and emission fluorescence loadings as a function of wavelength,.sample scores are also produced, containing information relative to constituent concentrations.

4.4 ATR-FTIR MEASUREMENT:

The multi-way models together with ATR-FTIR spectra seemed to represent a useful method for the quantification and detection of drug and excipient distribution in a tablet during the release process. ATR spectra were measured over the wavenumber range of 2000-600cm-1 at a resolution of 1.0 cm-1.A multi-way data matrix for PARAFAC was constructed sample with different drug concentrations (one dimension) × Wavenumber (2nd dimension) × measurement point of parallel sample (third dimension).In that context Sanni et al. explored ATR-FTIR spectra using two multiway modeling techniques, Parallel factor analysis and multilinear partial least square (N-PLS),for the determination of drug and excipient distribution in a tablet. The N-PLS calibration method was more robust for accurate quantification of the amount of components in the sample whereas the PARAFAC model provided approximate relative amounts of components [36].

4.5 SENSORY ANALYSIS:

The parallel factor model (tool) was investigated complex food matrices on the consumer sensory acceptance data {I sample (probiotic/conventional) six yogurts × J attribute (aroma, flavor, taste, texture & overall liking) × K consumer (100)} in three way with the help of 9 –point hedonic hybrid scale. Resultant data are shown similar sensory acceptance towards probiotic and conventional Yogurts. Appearance and overall liking were the most significant attributes for the first two components PARAFAC model [37].

4.6 NMR DATA:

Rasmus Bro, et al applied three ways model (mathematical chromatography) from complex spectra is resolved into pure analyte information. Here just captured a series of diffusion – edited 2 D NMR spectra of mixture of glucose, maltose and maltotriose to demonstrate that it is possible to identify and to resolve individual components in highly overlapping 2D-NMR spectra. The measurements of the mixtures are mathematically separated into pure-analyte information: estimated relative concentrations (scores) together with estimated spectra (loadings) and estimated diffusion profiles (loadings) for each of the three compounds. However, Separation of analyte signals can be achieved even if the chemical analytes display near-identical NMR spectra and have self-diffusion coefficients of the same order of magnitude. It is the combined modulation of the chemical shift spectra and the diffusion profiles that allow PARAFAC to perform mathematical chromatography. The estimated concentrations need to be scaled to at least one sample to be absolute in specific molar units [38]

5.CONCLUSION:

The concept of phytoequivalence was developed in Germany in order to ensure consistency of herbal products. According to this concept, a chemical profile, such as a chromatographic fingerprint, for an herbal product should be constructed and

compared with the profile of a clinically proven reference product [9]. Chromatography offers very powerful separation ability, such that the complex chemical components in herbal extracts can be separated into many relatively simple sub-fractions. As a single herbal medicine may contain a great many natural constituents, and a combination of several herbs might give rise to interactions with hundreds of natural constituents during the preparation of extracts, the fingerprints produced by the chromatographic instruments, which may present a relatively good integral representation of various chemical components of herbal medicines .This article demonstrates the enormous scientific potential of using multi-way analysis for resolving complex data in systems biology. Applied researcher will appreciate the wealth of in-depth analyses of real –life data sets that convincingly demonstrate the additional benefits of adopting the three way view in the world. This review contain on data handling, model selection, and interpretation of results, which transcend the specific applications and nicely summarize "good practices" that will be useful in many discipline.

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REFERENCE:

[1] Esbensen, K.H., Wold, S., and Geladi, P., Relationships between higher-order data arrayconfigurations and problem formulations in multivariate data analysis, J. Chemom., 3, 33–48, 1988.
[2] A. De Juan, R.Tauler, Chemometrics applied to unravel multi- component processes and mixtures: revisiting latest trends in multivariate resolution. Anal.Chim .Acta 500, 195–210,2003.
[3] Y.Z. Liang, P.Xie, K.C.Chan, Quality control of herbal medicines, J. Chromatogr. B. 8, 12, 53–70, 2004.
[4] G.M. Escandar, N.M. Faber, H.C. Goicoechea, A. Mu˜noz de la Pe˜na, A.C. Olivieri, R.J. Poppi, Trends Anal. Chem. 26, 752–765, 2007.
[5]Tucker,L.R.,Some mathematical notes on three mode factor analysis. Psychometricka,31 ,279-311,1966.
[6] Jeroen J. Jansen, Rasmus Bro, Huub C. J. Hoefsloot, et al.," PARAFASCA: ASCA combined withPARAFAC for the analysis of metabolic fingerprinting data," Journal of Chemometrics, vol-22,114-221,2008.

[7] M.C. ORITZ, L. Sarabia et al., "Quantitative determination in chromatographic analysis based on n-way calibration strategies" , Journal of chromatography A, 1158, 94-100, 2007.
[8] N.Draper, H Smit, Applied Regression Analysis, third ed., Wiley, New York,P. 137, 1998.
[9] Christophe B.Y. Cordella, Riccardo Leardi, Douglas N. Rutledge., "Three-way principal component analysis applied to noodles sensory data analysis,"Chemometrics and Intelligent Laboratory Systems"106, pp-125-130, 2011.
[10] Booksh, K.S. and Kowalski, B.R., Calibration method choice by comparison of modelbasis functions to the theoretical instrument response function, Anal. Chim. Acta,348, 1–9, 1997.
[11] Paul Gemperline,.Practical Guide to Chemometrics.2nd ed.CRC Press Taylor & Francis Group ,page-478, 2006.
[12] Kroonenberg, P.M., Three-mode Principal Component Analyses: Theory and Applications, DSWO Press, Leiden, The Netherlands, 1983.
[13] Smilde, A.K., Tauler, R., Henshaw, J.M., Burgess, L.W., and Kowalski, B.R., Multicomponentdetermination of chlorinated hydrocarbons using a reaction based sensor, 3:medium-rank second-order calibration with restricted Tucker models, Anal. Chem., 66, 3345–3351, 1994.
[14] Tamara G. Kolda, Brett W. Bader., Tensor Decompositions and Applications, SIAM REVIEW; Society for Industrial and Applied Mathematics ,Vol. 51, No. 3, pp. 455–500, 2009.
[15] E. Sanchez, L.S. Ramos, B.R. Kowalski, J. Chromatogr.385, 151,1987.
[16] L.S. Ramos, E. Sanchez, B.R. Kowalski, J. Chromatogr. 385,165,1987.
[17]I. Garcia, L. Sarabia, M.C. Ortiz, J.L. Aldama, Anal. Chim. Acta 515, 55,2004.
[18] E. Sanchez, B.R. Kowalski, Anal. Chem. 58,496,1986.
[19] R.A.Gimeno, E. Comas, R.M. Marce , J. Ferre, F.X. Rius, F. Borrull, Anal .Chim. Acta. 498,47, 2003.
[20] M.Jalali – Heravi , M. Vosough, Anal. Chim. Acta 537,89,2005.
[21] E. Sanchez, B.R. Kowalski, J. Chemom. 4,29,1990.
[22]Tucker,L.R.(1963),Implications of factor analysis of three way matrices for measurement of change .In C. W. Harris (Ed.),Problems in measuring in change (pp. 122-137).Madison WI: University of Wisconsin Press.,.
[23] Anna de Juan, Roma Tauler, "Factor analysis of hyphenated chromatographic data Exploration, Resolution and quantification of multicomponent system", Journal of Chromatography A, 1158,184-195,2007.
[24] C.A. Andersson, R.Bro, Improving the speed of multi-wayalgorithoms: Part-1.Tucker3, Chemom.Intell. Lab. Syst.42,93-103, 1998.
[25] R.Boque, A.K. Smilde, Monitoring and diagnosing batch processes with multiway regression models, AIChE J.45,1504-1520,1990.
[26] P.J. Gemperline, K.H.Miller,T.L. West, J.E.Weinstein,J.C. Hamilton, J.T.Bray,Principal component analysis,trace elements, and blue crab shell disease, Anal. Chem. 64,

523A-532A, 1992.
[27] J.L. Beltran ,R. Ferrer, J. Guiteras, Multivariate calibration of polycyclic aromatic hydrocarbon mixtures fromm excitation-emissionfluoreseb=nce spectra, Anal. Chim. Acta 373,311-319,1998.
[28] R. Bro, H. heimdal, Enzymaticbrowing of vegetables, Calibration and analysis of variance by multiway methods, Chemom. Intell. Lab. Syst. 34,85-102,1996.
[29] J. Nilsson, E.J. Homan, A.K. Smilde, C.J. Grolet. al., Amultiway 3D QSAR analysis of a series of (S)-N- [(1-ethyl-2 pyrrolidinyl) methyl]-6-methoxy benzamides, J.Comput.-Aided Mol. Des.12 919980 81-93.
[30] R.E. Shaffer, S.L. Rose- Pehrsson, R.A. McGill, Multiway analysis of preconcentrator-sampled surface acoustic wave chemical tensor array data, Field Anal. Chem. Technol. 2, 179-192,1998.
[31] R. Boque, A.K. Smilde, Monitoring and diagnosing batch processes with multiway regression models, AIChE J.45,1504-1520,1999.
[32] Graciela M. Escandar, et.al. Second-and higher –order data generation and calibration: A Tutorial. Analytica ChimicaActa. 806,8– 26,2014.
[33]Renee D. JiJi, Greger G. Andersson etal.,Application of PARAFAC for calibration with excitation –emission matrix fluorescence spectra of three classes of Enviormentalpollutants., Journal Of Chemometrics; 14, 171-185, 2000.
[34] M. Vosough, M. Bayat, A. Salemi, Anal. Chim. Acta 663,11, 2010.
[35] Ming Jing ,Wernshengcai et al, Multiblock partial least square regression based on wavelet transform for quantitative analysis of near infrared spectra, Chemometric and Intelligent Laboratory Systems, Volume 100,Issue1,16 January, Page 22-27.
[36] M. Sanni, P. Jari, M. S. Anne et al., "Predicting the drug concentration in starch acetate matrix tablets from ATR-FTIR spectra using multi-way methods," Analytica ChimicaActa, vol. 595, no. 1-2, pp. 190–197, 2007.
[37] Adriano G. Cruz, Rafael S. Cadena , José A.F. Faria , Helena M.A. Bolini ,ClecioDantas et al.,"PARAFAC: Adjustment for modeling consumer study covering probiotic and conventional yogurt 'Food Research International,vol.45,pp-221-215,2012.
[38] Rasmus Bro, NannaViereck, Marianne Toft, Henrik Toft, Peter I. Hansen, Søren B. Engelsen; Mathematical chromatography solves the cocktail party effect in mixtures using 2D spectra and PARAFAC., Trends in Analytical Chemistry, Vol. 29, No. 4, 2010.
[39] M. Abdelkawy, F. Metwaly, N. E. Raghy, M. Hegazy, and N. Fayek, "Simultaneous determination of Ambroxol Hydrochloride and Guaifenesin by HPLC, TLC-Spectrodensitometric and multivariate calibration methods in pure form and in Cough Cold Formulations, "Journal of Chromatography," vol. 2, p. 112, 2011.
[40]Bonnie Schmidt,JerzyW.Jaroszewski,RasmusBro,Matthias Witt, and Dan Staerk,"Combining PARAFAC analysis of HPLC-PDA Profiles and Structural Characterization Using HPLC-PDA-SPE-NMR-MS Experiments: Commercial Preparation of St. John's Wort" Analytical Chemistry,Vol. 80,No.6.March 15,2008.
[41] Amjad H. El-Sheikh, Yahiya S. Al-Degs.,"Spectrophotometric determination of food dyes in soft drinks by second order multivariate calibration of the absorbance spectra-pH data matrices," Dyes and Pigment, vol-97,pp-330-339,2013.
[42] Rasmus Bro, NannaViereck, Marianne Toft, Henrik Toft, Peter I. Hansen, Søren B. Engelsen.,"Mathematical chromatography solves the cocktail party effect in mixtures using 2D spectraand PARAFAC" Trends in Analytical Chemistry," Vol. 29, No. 4, 2010.
[43] C.-F. V. Latchoumane, F. Vialatte, A. Cichocki,et al.,"Multiway Analysis of Alzheimer's Disease: Classification based on Space-frequency Characteristics of EEG Time Series,"Proceedings of the World Congress on Engineering 2008 "Vol II, WCE 2008, July 2 - 4, 2008, London, U.K.
[44] MortezaBahrama ,Rasmus Bro.," A novel strategy for solving matrix effect in three-way data using parallel profiles with linear dependencies," Analytica Chimica Acta, 584 ,pp-397-402, 2007.
[45]JERON J, Jonsen et al., PARAFASCA: ASCA combined with PARAFAC for the analysis of metabolic fingerprinting data., Journal of chromatography ., on line available 10 Jan (2008).
[46] Mohamed A.Frag, LudgerA.Wessjohann., " Metabolome Classification of Commercial Hypericumperforatum (St.John' sWort) Preparations via UPLC-qTOF-MS and Chemometrics, "Journal of Medicinal Plant and Natural Product Research," vol-78 .pp-488-496,2012.
[47] W. Deburchgraeve, P.J. Cherian, M. De Vos, R.M. Swarte et al.," Neonatal seizure localization using PARAFAC decomposition" Clinical Neurophysiology., 120 (2009) 1787–1796.
[48] Jun Huang, ChimanlallGoolcharran, KrishnenduGhosh., A Quality by Design approach to investigate tablet dissolution shift upon accelerated stability by multivariate methods." European Journal of Pharmaceutics and Biopharmaceutics,"vol-78, pp-141-150, 2011.
[49] Jens A. Andersson, Claus A. Andersson, et.al., Applying Parallel Factor Analysis models to HPLC diode array detector datasets reveals strain dependent regulation of polyketide biosynthesis in Fusariumgraminearum, Fusariumculmorum and Fusariumpseudograminearum., AnalyticaChimicaActa 647 (2009) 243–248.
[50] Karl S. Booksh,, Allen R. Muroski, and M. L. Myrick ., Single-Measurement Excitation/Emission MatrixSpectrofluorometer for Determination of Hydrocarbons in Ocean Water. 2. Calibration and

Quantitation of Naphthalene and Styrene, Anal.Chem.
1996, 68, 3539-3544.