

Principle of nonlinear chemical fingerprint by using dissipative components in samples as well as calculation and evaluation of similarity

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Under the conditions of constant temperature and pressure, different influences of samples with different chemical components on the mechanism of nonlinear chemical reaction will cause different changes of the potential-time relationship curve of the nonlinear chemical reaction system. Using it as the character, and using the B-Z nonlinear chemical system to use acetone and substrates in samples as main dissipative substances qua an example, the principle of nonlinear chemical fingerprint has been researched and discussed in detail. At the same time, the general method for calculating the system similarity about nonlinear chemical fingerprint was also put forward, and similarities of nonlinear chemistry fingerprints of different batches of Guhan Yangshengjing and 18 sorts of other samples were calculated by Euclidean distance, correlation coefficient, included angle cosine and system similarity, at the same time, the various similarities were analyzed. The results showed that, both of correlation coefficient and included angle cosine are unable to be used as the criterion for quantitatively evaluating the similarity of nonlinear chemistry fingerprint; as non-parametric similarity, Euclidean distance can accurately reflect the feature differences in the fingerprints, but as parametric similarity, sometimes, Euclidean distance can not accurately reflect the relative extent of characteristic difference in the nonlinear chemical fingerprints; system similarity can most truthfully reflect the characteristic difference in the nonlinear chemical fingerprints, and is the best evaluating method among the four ones. Therefore, system similarity can be used to quantitatively calculate the similar extent between the nonlinear chemical fingerprints. An economical, simple and convenient, easy pushing and effective method for identifying and evaluating complicated samples has successfully been put forward.

dissipative components, nonlinear chemical fingerprint, principle, system similarity, identification, evaluation, sample

1 Introduction

The discovery of B-Z (Belousov & Zhabotinsky) oscillatory reaction started the era of investigating nonlinear chemical reaction [1], and the research on the application of nonlinear chemical reaction also becomes popular gradually [1–6]. The phenomena of the reaction include chemical oscillation, chemical turbulence, chemical pattern and chemical wave,

etc, and the mechanisms to bring the phenomena and their applications have been investigated for a long time. Especially, the reaction mechanism [1, 2, 7–15] and application [1–6] of chemical oscillation qua the most familiar phenomenon of nonlinear chemistry have been investigated more widely and thoroughly by the domestic and foreign scholars. However, the study on the applications of the different nonlinear chemical reactions such as chemical oscillation, chemical turbulence, chemical pattern and chemical wave in the identification and quality evaluation of such complex samples as food and Chinese traditional medicine,

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etc has not been reported abroad, and just started at home [16–19]. So nonlinear chemical fingerprint technique is a new one based on the principle of non-equilibrium chemistry for identifying and evaluating the samples. Samples containing different chemical components have different influences on the mechanism of nonlinear chemical reaction so as to cause different changes of shape of potential-time relationship curve (namely $E-t$ curve) in the nonlinear chemical reaction of the system. In this work, by taking the B-Z nonlinear chemical reaction to use acetone and some components in a food as its dissipative substances qua an example, and taking the abovementioned phenomenon qua the reaction character, the principle of nonlinear chemical fingerprint without pretreatments such as separation and purification, etc and suitable for the through characterization of components of each complicated sample was studied and discussed in detail. At present, the fingerprint techniques of chromatogram and spectrum have been reported largely [20–43], and in the main methods for evaluating the similarities of the fingerprints, there are overlapping-peak [44], distance-coefficient [45], correlation-coefficient [46], included-angle-cosine [47] and synthesizing-criterion [48, 49], etc. Because of its kinetic property, the formation principle and information of nonlinear chemical fingerprint are different from those of chromatographic and spectral fingerprints, so the methods suitable for evaluating similarities of chromatographic and spectral fingerprints are not always suitable for nonlinear chemical fingerprint. Therefore, on investigating nonlinear chemical fingerprint, the method suitable for calculating its similarity must be put forward at the same time. On the basis of the research work of earlier stage [16, 17], the authors have discussed the computational method of systemic similarity based on similarity system theory and its application [18]. However, the computational model is only suitable for the systemic similarity between the fingerprints based on congeneric nonlinear chemical reactions, and on the computation, only an eigenvalue is used for each similar element; moreover, the model is not suitable for calculating the systemic similarity between the fingerprints based on non-congeneric nonlinear chemical reactions such as turbulent reaction and oscillatory reaction, etc. Therefore, in this paper, the authors will in depth discuss the method for computing the systemic similarity between the fingerprints based on non-congeneric nonlinear chemical reactions and its application in the identification of food. At the same time, the similarities of the nonlinear chemical fingerprints of 19 sorts of samples were calculated by four methods, and were compared with each other. The result showed that systemic similarity can best reflect the difference in samples and may be used to quantitatively evaluate the similarity between the nonlinear chemical fingerprints, and is highly significant for identifying samples rapidly and accurately. The nonlinear chemical fingerprint technique for identifying and evaluating complicated samples have been proposed successfully.

2 Experimental

2.1 Main apparatus, reagents and materials

Main apparatus: Analytical instrument of non-linear chemical fingerprint (Model MZ-1A, developed by Central South University and Xiangtan Ltd. for Making Whole Set Instruments and Meters, Hunan, China)

Main reagents and materials: sulfuric acid (1.00 mol L^{-1} ; acetone ($0.0250 \text{ mol L}^{-1}$, prepared by $1.00 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$); sodium bromate (0.800 mol L^{-1}); MnSO_4 (0.0800 mol/L , prepared by $1.00 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$); glucose. The solutions were prepared with analytical grade reagents. Bi-distilled water was used. The solutions above were placed in a constant temperature trough (37.0°C) for standby. Besides Guhan Yangshengjing from Ziguang Guhan Jituan, Hengyang, Hunan, all food samples were bought from WalMart Supermarket in Changsha, Hunan.

2.2 Procedure

An appropriate dosage of solid or liquid samples, 25.00 mL of the H_2SO_4 , 20.00 mL of acetone and 12.00 mL of MnSO_4 were added into the reactor, and the reactor cover with the electrodes, an injection hole and a thermometer was closed. Then the instrument was turned on, and the temperature in the reactor was adjusted to a constant temperature (37.0°C), and the stir rate was adjusted to 850 r min^{-1} and the timing for stir starts. When the constant rate stir just continues for 5.0 min , 3.00 mL of the sodium bromate solutions are injected into the reactor, and the menu was immediately dotted for plotting the $E-t$ curve, until the potential diversification disappeared.

3 Results and discussion

3.1 Basic principle of nonlinear chemical fingerprint

By taking the B-Z oscillatory system using acetone and glucose qua its dissipative substances as the example, the basic principle of the nonlinear chemical fingerprint will be discussed from three aspects, namely the general relationship between the relative electrode potential (E) and the time (t) in a nonlinear oxidation-reduction reaction, the basic mutative courses of the reaction system and their expression of $E-t$ relationship, as well as the different influences of chemical components in different samples on the curve of the $E-t$ relationship.

(1) General relationship between the electrode potential and the time in nonlinear oxidation-reduction reaction. As mentioned in ref. [19], on being designed into a primary cell, any spontaneous oxidation-reduction reaction may be divided into reduction and oxidation half-reactions. The potentials (φ_{R} and φ_{O}) of the electrodes responding the reduction and oxidation half-reactions may be expressed as

follows, respectively,

$$\varphi_R = \varphi_R^\circ + \frac{RT}{nF} \ln \frac{a_{O_1}^{n_1} \cdots}{a_{R_1}^{n'_1} \cdots} \quad (1)$$

$$\varphi_O = \varphi_O^\circ + \frac{RT}{nF} \ln \frac{a_{O_2}^{n_2} \cdots}{a_{R_2}^{n'_2} \cdots} \quad (2)$$

For a definite chemical system, the normal electrode potentials φ_k° ($k = R, O$) in constant temperature eqs. (1) and (2) do not vary. Because of the difficulty to determine the absolute value of an electrode potential, the potential is actually the electromotive force (E) of the relevant working cell, namely the indication-electrode potential relative to the reference electrode. It is noticeable that the working cell is not the primary cell of the relevant oxidation-reduction reaction because its electromotive force does not equal zero generally when that of this primary cell equals zero. Under the condition of constant temperature, the potential (φ_{ref}) of the reference electrode is invariable, therefore, it is obvious from eqs. (1) and (2) that the expressions of the relative potentials of the electrodes responding the reduction and oxidation half-reactions may be expressed as follows, respectively,

$$\begin{aligned} E_R = \varphi_R - \varphi_{\text{ref}} &= \varphi_R^\circ + \frac{RT}{nF} \ln \frac{a_{O_1}^{n_1} \cdots}{a_{R_1}^{n'_1} \cdots} - \varphi_{\text{ref}} \\ &= K_R + \frac{RT}{nF} \ln \frac{a_{O_1}^{n_1} \cdots}{a_{R_1}^{n'_1} \cdots} \end{aligned} \quad (3)$$

$$\begin{aligned} E_O = \varphi_O - \varphi_{\text{ref}} &= \varphi_O^\circ + \frac{RT}{nF} \ln \frac{a_{O_2}^{n_2} \cdots}{a_{R_2}^{n'_2} \cdots} - \varphi_{\text{ref}} \\ &= K_O + \frac{RT}{nF} \ln \frac{a_{O_2}^{n_2} \cdots}{a_{R_2}^{n'_2} \cdots} \end{aligned} \quad (4)$$

In a nonlinear oxidation-reduction reaction, the extrema of the activities of the reactants and resultants may appear because the activities are all the nonlinear functions of the time (t). The extrema of the activities may result in the extremum of the electrode potential, so the potential is also the nonlinear function of the time. Therefore, on responding the reduction half-reaction or oxidization one, respectively by the relevant electrode, the general relationship between the relative potential and the time may be expressed as follows, respectively,

$$E_R(t) = K_R + \frac{RT}{nF} \ln \frac{(a_{O_1}(t))^{n_1} \cdots}{(a_{R_1}(t))^{n'_1} \cdots} \quad (5)$$

$$E_O(t) = K_O + \frac{RT}{nF} \ln \frac{(a_{O_2}(t))^{n_2} \cdots}{(a_{R_2}(t))^{n'_2} \cdots} \quad (6)$$

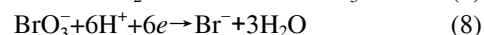
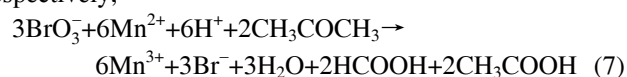
Obviously, whatever the oxidization half-reaction or the reduction ones is responded by the relevant electrodes, the E - t relationships of different nonlinear chemical reactions

are of different specific expressions. For the different courses in one nonlinear chemical reaction, such as the inductive and oscillatory courses, etc, the specific expressions of their E - t relationships are also different because the times happening the relevant reactions, the numbers of the electrons transferred in the oxidation-reduction reactions, the sorts and stoichiometric numbers of reactants and resultants, as well as the function relationships between the activities of the substances and the time t , etc are different. For the same courses in different nonlinear chemical reactions, such as the inductive or oscillatory course in the reactions joined by the chemical components of different samples, the specific expressions of the E - t relationships are also different due to the differences of the numbers of the electrons transferred in the oxidation-reduction reactions, the sorts and stoichiometric numbers of reactants and resultants, especially the function relationships between the activities of the substances and the time t , e and so on. Because of the space limitation of publication, only the expression of E - t relationship relating to the reduction half-reaction will be discussed here.

(2) Basic process in B-Z nonlinear chemical reaction and its E - t relationship expressions

The mechanism of the B-Z reaction to use H^+ , BrO_3^- , Mn^{2+} , acetone and glucose, etc as the reaction substrates will be discussed qua an example. Although the mechanism of the B-Z reaction involves dozens of elementary reactions [2], the elementary reactions may still be generalized into two major reactions, namely inductive and oscillatory reactions [2, 14].

From the literature [19] we know that the inductive reaction may be divided into two irreversible courses A and B; the expressions of the inductive reaction and its reduction half-reaction may be obtained from eqs. (2), (3) and (4), eq. (5) in the literature, and expressed with eqs. (7) and (8), respectively,

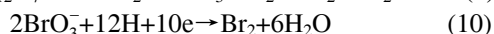


It is obvious from eq. (7) that Br^- comes into being in the inductive reaction. When the concentration of Br^- in the reaction system is higher than the critical concentration $[Br^-]_{\text{crit}}$, the B-Z oscillatory reaction will be initiated by Br^- . It is obvious from eqs. (7)–(15) in the ref. [19] that the oscillatory reaction may be divided into three irreversible courses, namely courses C, D and E.

When the $[Br^-]$ in the system $>$ the $[Br^-]_{\text{crit}}$, course C accumulating Br_2 and consuming Br^- will immediately take place; The Br^- is consumed in course C. When the $[Br^-]$ in the system is lower than $[Br^-]_{\text{crit}}$, the course D accumulating Mn^{3+} and $HOBr$ will take place; When the substance able to reduce Mn^{3+} to Mn^{2+} exists in the reaction system, the course E reducing the catalyst manganese and regenerating Br^- will be initiated because the Br_2 and Mn^{3+} , $HOBr$ are

accumulated, respectively in courses C and D. When the $[\text{Br}^-]$ is higher than the $[\text{Br}^-]_{\text{crit}}$ due to the regeneration of Br^- , course C is initiated again. In this way, courses C, D and E move in cycles so as to form the oscillatory reaction. In the oscillatory reaction, the intermediate HBrO_2 operates in the switch from course C to course D.

From eqs. (7)–(15) in the ref. [19], it is obvious that the total reaction of the oscillatory course and its reduction half-reaction may be expressed by equation (9) and equation (10), respectively,



For the inductive and oscillatory reactions of the B-Z system, the general expressions of the relationships between the relative potentials (namely $E_{\text{R}}(t)_{\text{ind}}$ and $E_{\text{R}}(t)_{\text{osc}}$) of the indicating electrode responding the reduction half-reaction and the time may be written out by utilizing eqs. (5), (8) and (10), and the expressions are eqs. (11) and (12), respectively.

$$E_{\text{R}}(t)_{\text{ind}} = K_{\text{R ind}} + \frac{RT}{6F} \ln \frac{(a_{\text{BrO}_3^-}(t)) \cdot (a_{\text{H}^+}(t))^6}{(a_{\text{Br}_2}(t))} \quad (11)$$

$$E_{\text{R}}(t)_{\text{osc}} = K_{\text{R osc}} + \frac{RT}{10F} \ln \frac{(a_{\text{BrO}_3^-}(t))^2 \cdot (a_{\text{H}^+}(t))^{12}}{a_{\text{Br}_2}(t)} \quad (12)$$

In principle, according to the elementary reactions in FKN mechanism [7] of the B-Z oscillation course, the differential equations of the reaction velocities may be written out by using law of mass action, and then, the specific expression of the nonlinear relationship between the activities of every substances in eqs. (11) and (12) and the time may be confirmed by carrying out relevant mathematizations to the differential equations. Hereby, the particular expressions of eqs. (11) and (12) may also be acquired. The E - t curves in the inductive and oscillatory courses of the B-Z reaction are thus the image-descriptions of the particular expressions. The combination of the E - t curves of the inductive and oscillatory courses (see curves (e)–(g) and (g)–(h) in Figure 1(b) in the ref. [19], respectively) thus forms the E - t curve of the entire process of the B-Z nonlinear chemical reaction. Because the potential of the indicating electrode is the nonlinear function to the time, the electrode potential does not always vary monotonously with time in the inductive and oscillatory reactions, and the potential extrema may appear, so as to cause the gurgitation of the E - t curve. From the FKN mechanism in the ref. [19], it is obvious that all of the intermediates and reactants except acetone and glucose can form “dissipation-regeneration” cycle in the oscillatory reaction, that is, their concentrations or activities can vary in gurgitation with the time. The activities of BrO_3^- , Br_2 and H^+ , etc in the system can also vary in gurgitation. As a result, the electrode potential expressed by eq. (12) in the oscillatory reaction can also vary in gurgitation. In addition, in the oscillatory reaction, the activities of the reactants such as

acetone and glucose (CH_3COCH_3 and $\text{C}_6\text{H}_{12}\text{O}_6$) become less and less, and contrarily, the activities of the resultants restraining the reaction, such as acetone bromide and gluconic acid ($\text{BrCH}_2\text{COCH}_3$ and $\text{C}_6\text{H}_{12}\text{O}_7$) become larger and larger. Therefore, the rate of the oscillatory reaction becomes slower and slower. The exhibition is that the period of the gurgitation becomes longer and longer till the end of the reaction (see the curve (g)–(h) in Figure 1(b) of the ref. [19]). From the beginning of the nonlinear chemical reaction to the ending, namely in the relevant time from point e to point h in Figure 1(b) of the ref. [19], the potential of the indicating electrode may be denoted by the potential of the electricity pair relating to the relevant reduction half-reaction, as shown by eqs. (11) and (12). Because BrO_3^- has not been added into the reactor before the time to which point e corresponds, the relevant segment of E - t curve is actually the reflection of the change of the reduction potential relating to the oxygen electricity pair in the solution with the time. The potential decreases monotonously with the time, which may be the result of the reaction of the dissolved oxygen with reducible substances such as the reducible sample-components existing in the solution. In this experiment, an indicating platinum electrode was used as the positive electrode, and its electrode potential relative to a reference electrode was determined. Although a platinum electrode may be used not only as the electrode responding the oxidation half-reaction of the primary battery but also as one responding the reduction half-reaction, the two electrodes of the working battery in this experiment are a platinum electrode and a reference electrode, respectively. Therefore, the potential responded by the indicating platinum electrode is the potential of the electricity pair with higher potential in the solution, namely that of the electricity pair concerning the reduction half-reaction.

(3) Influences of components in samples on the E - t curve of non-linear chemical system and non-linear chemical fingerprints. The nonlinear chemical system is sensitive to foreign chemical substances. Many chemical substances, such as microelement, alkaloid, surfactant, organic acid, amino acid, polypeptide, vitamin, enzyme, hormone, ketone, ether, hydroxide and so on, are able to influence greatly the forms (for example, the forms of inductive curve, undulatory curve, period wave, etc.) and the quantifiable parameters (such as inductive time, undulatory period, undulatory life, etc) (see “Essential information of nonlinear chemical fingerprint”) of E - t curve of nonlinear-chemical-reaction system. The significances of the influence to the application research of nonlinear chemical reaction have been introduced in many papers [1, 12, 15–18]. Different samples usually contain different substrates (include dissipative substances) necessary for nonlinear chemical reaction and many of the abovementioned different sorts of micro- and even macro-chemical substances coexisting in samples. Different substrates will bring different nonlinear chemical reactions, and the other substances coexisting with the sub-

strates will also have different influences on the nonlinear chemical reactions. The influences not only include the influence on the physical properties (such as viscosity, ionic strength, dielectric constant, interfacial tension, equivalent conductivity, osmotic pressure, etc) of the reaction solution, but also include the influence on the chemical mechanism of the nonlinear chemical reaction due to the reactions of the other chemical substances with the reactants or intermediates in the system [12]. The influences not only result in the changes of the quantifiable parameters such as inductive time, undulatory period, undulatory amplitude, undulatory life, etc (this can be seen by the comparison of $E-t$ curves in Figure 1(b) and 1(c) in the ref. [19]), but also result in the changes of the quantitative relationships (eqs. (11) and (12)) between the potential and the time in the inductive and oscillatory courses (including the changes of the substance sorts, power indexes, activities and their nonlinear relationships with the time in the relationship expressions), namely resulting in the changes of the intuitionistic shapes of the inductive curve, undulatory curve, period wave, and even whole $E-t$ curve, etc. For different samples, even if the substance sorts, power indexes, etc in the general expressions (eqs. (11) and (12)) of the $E-t$ relationships concerning the inductive and oscillatory reactions joined by them are the same, the final specific expressions of the quantitative relationships and their shapes are different (Figures 1, 2 and 3) because the differences of the thermodynamic and kinetic influences of components in different samples on the nonlinear chemical reaction can result in the change in the relation function $a_i(t)$ (i is the i th substrate) between the activity of each substrate and the time in eqs. (11) and (12). The influencing law is of the most important significance for the identification and quality evaluation of samples. Because of the differences in the chemical substances or their contents, different sorts or qualities of products added into the reactor will result in different nonlinear chemical mechanisms so as to result in different specific $E-t$ relation expressions, that is, the $E-t$ curves with different shapes and information parameters may be determined for different samples. For example, when the reducing agent glucose in the above pure B-Z system is changed into a food sample containing many components with reducing property, some of the reducing components will replace the reducing reagents in the reactions [19], $\text{Br}_2 + \text{CH}_3\text{COCH}_3 \rightarrow \text{BrCH}_2\text{COCH}_3 + \text{Br}^- + \text{H}^+$ and $2\text{Mn}^{3+} + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \rightarrow 2\text{Mn}^{2+} + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$ in the inductive and oscillatory courses, or will compete with the reducing reagents, so as to change the chemical mechanisms of the inductive and oscillatory reactions, or make the mechanisms become more complex. The change of the reaction mechanism will also result in the changes of the reaction rates, the changes of the rates will result in those of the functional relationships of the activities of the reactants with the time again. And all the changes will finally result in the change of the specific expression of the relationship between the potential and the time (namely $E-t$ relationship,

eq. (5)), so as that the $E-t$ curve of the sample (Figure 1(c) in the ref. [19]) not only are different from the $E-t$ curve of the steady system " $\text{H}^+ + \text{Mn}^{2+} + \text{BrO}_3^- + \text{acetone}$ " (Figure 1(a) in the ref. [19]), but also are obviously different from that of the pure B-Z system (Figure 1(b) in the ref. [19]). From Figure 1 in the ref. [19], it is obvious that the intuitionistic information (such as the shapes of the inductive curve, undulatory curve and period wave) and the quantifiable information (such as the peak-top potential, canyon potential, equilibrium potential, inductive time, undulatory life, undulatory period, wave number) in the $E-t$ curve of the sample have various extents of differences from the relevant messages in one of the pure B-Z system, so as that the shapes of the two curves are totally different. As before mentioned, because of the different reducing components existing in different samples, the mechanisms, complexities, rates, etc of the relevant nonlinear chemical reactions are obviously different, therefore, the specific expressions of $E-t$ relationships concerning the respective reactions are also obviously different, namely different $E-t$ curves may be determined for different samples (Figures 1, 2 and 3). By comparing the $E-t$ curves in Figures 1, 2 and 3, it can be seen that the different changes of shapes of $E-t$ curves determined after adding different samples into the reactor make the relevant $E-t$ curves completely different from that of the pure B-Z system under the same determination condition, and it is more important that the changes embody the characters of the internal chemical species of different samples. In other words, the $E-t$ curve obtained by adding a sample into the reactor may be looked upon as the throng characterization of the chemical species or active components in the sample, and its information may be used to analyze the whole character of the chemical species in the sample. Consequently, the sort and quality of the sample may be identified and evaluated by such $E-t$ curve. Therefore, the repeatable $E-t$ curve obtained after adding a sample into the proper chemical system may be named the nonlinear chemical fingerprint of the sample due to its functions of identifying and evaluating the sample. In this paper, the B-Z system using acetone and the relevant reducing components in food samples as its main dissipative substances is used to investigate the nonlinear chemical fingerprints of samples.

3.2 Essential information of nonlinear chemical fingerprint

According to "Procedure", the nonlinear chemical fingerprint was determined by adding 1.000 g of solid Kafu fruit drink with grape flavor into the reactor, the fingerprint was shown in Figure 1(c) in the ref. [9]. It is obvious from the figure that the essential characteristic information of nonlinear chemical fingerprint mainly includes: (1) inductive time (t_{ind}), namely the time interval from the wink when the last substrate (that in the experiment was NaBrO_3) is just added into the reactor to the start of oscillatory or turbulent

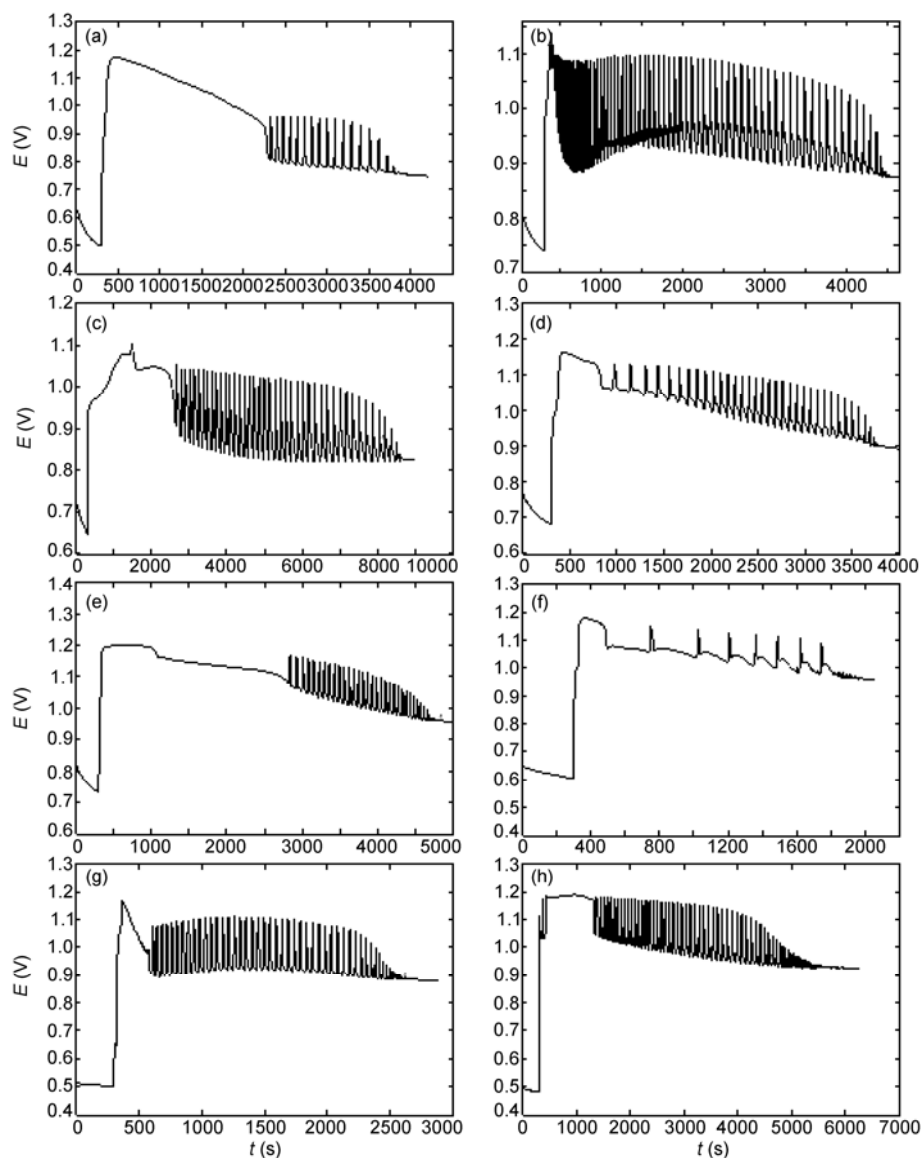


Figure 1 The nonlinear chemical fingerprints of some foods determined according to “Procedure” and based on oscillatory reaction (left) and turbulent reaction (right). (a) Walnut milk; (b) Huiyi Yoghourt; (c) Malays soy milk; (d) Liziyuan corn juice; (e) Naiqi corn juice; (f) Guliguli corn juice; (g) solid Kafu fruit drink with grape flavor (the dosage: 1.0000 g); (h) Kangshifu Tieguanyin tea (the dosage: 11.00 mL). (a)–(f): The dosages were all 13.00 mL, but the NaBrO_3 solution was changed into 5.00 mL.

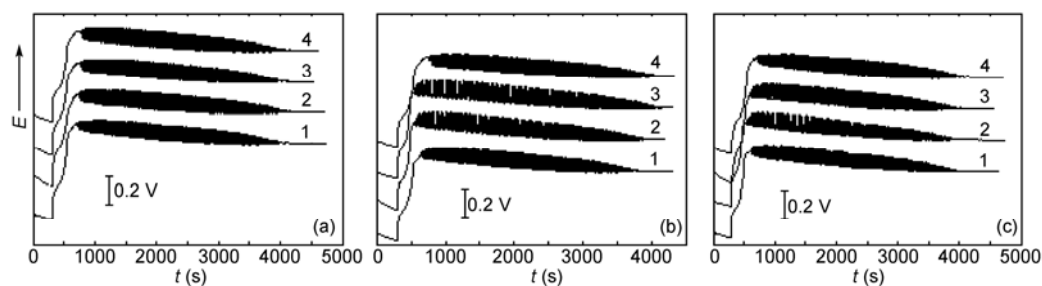


Figure 2 According to “Procedure”, the determined nonlinear chemical fingerprints of Guhan Yangshengjing from the production batch 10236 ((a); 1, 2, 3 and 4 are the serial numbers of the parallel determinations) and different production batches ((b) and (c)). The dosages of (a) and (b) were all 1.30 mL; the production batches of 1, 2, 3 and 4 in (b) and (c) were 10027, 10093, 10158 and 10236, respectively; the dosages of 1, 2, 3 and 4 in (c) were 1.25, 1.28, 1.35 and 1.31 mL, respectively.

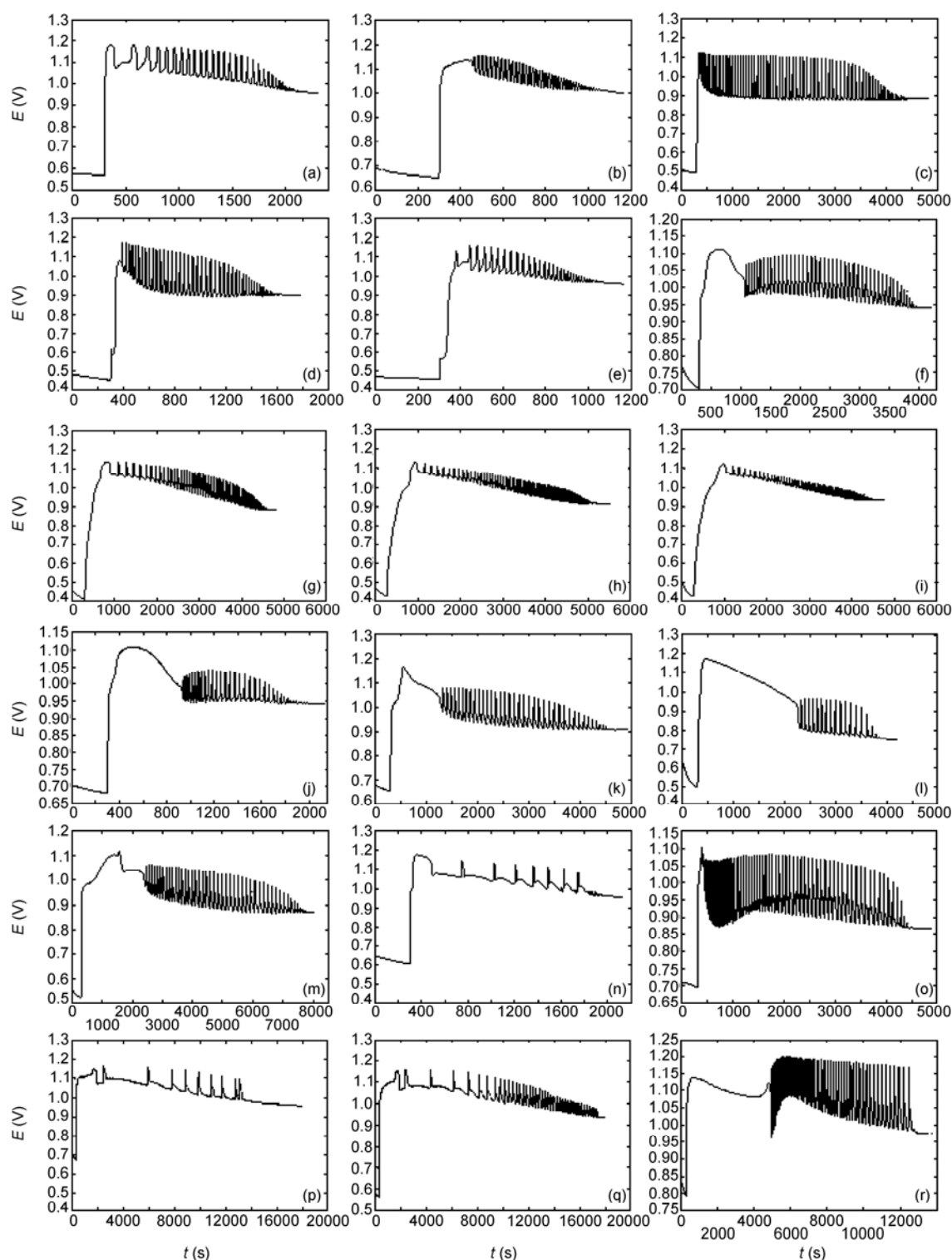


Figure 3 The nonlinear chemical fingerprints of some different foods. (a) Wang Laoji herb tea; (b) Pepsi-Cola without sugar; (c) Yang Guifei apple vinegar; (d) 100c Lemon juice; (e) Dole apple juice; (f) Yili yoghourt; (g) Nestle coffee; (h) Meishi-Yaha coffee; (i) Naikajingxuan-Yaha coffee drink; (j) Mengniu yoghourt; (k) Yang Xiecheng soy milk; (l) Walnut milk; (m) Malays soy milk; (n) Guliguli corn juice; (o) Huiyi yoghourt; (p) Yili whole milk; (q) Mengniu whole milk; (r) Nine system citrus drink.

reaction; (2) oscillatory period, namely the interval between two adjacent potential peaks (the positive or negative peaks) in the oscillatory curve; (3) oscillatory life, namely the time

for which the oscillation lasts; (4) canyon potential (E_{can}) and canyon time (t_{can}), namely the potential and time to which each canyon in the inductive curve corresponds; (5)

peak top potential (E_{pet}) and peak top time (t_{pet}), namely the potential and time to which each peak top in the inductive curve corresponds; (6) oscillatory start potential, namely the potential corresponding to the start of the oscillation; (7) oscillatory end potential and oscillatory end time, namely the potential and time at the wink when the oscillation just ends; (8) equilibrium potential (E_{equ}) and equilibrium time (t_{equ}), namely the potential and time at the wink when the system is just in the thermodynamic equilibrium state, and on fixing the determination conditions, it does not change with time, moreover, it is not always equal to the end potential; (9) oscillatory amplitudes, namely the difference values of the neighbouring positive potential peaks and negative ones in the oscillatory course; (10) maximum oscillation amplitude, namely the maximum one in oscillatory amplitudes of an oscillatory curve; (11) oscillatory wave number, namely the fluctuation times of oscillatory curve; (12) inductive curve, namely the part corresponding to the inductive time in the E - t curve; (13) oscillatory curve, the curve of the potential-time gurgitation with constant or basically constant periods due to the oscillatory reaction, namely the part corresponding to the oscillatory life in the E - t curve (Figure 1(c) in the ref. [19]); (14) oscillatory period wave, namely the shape of the part curve corresponding to each oscillatory period in the E - t curve based on oscillatory reaction; (15) oscillatory end curve, namely the part from the oscillatory end to the potential excursion end in the E - t curve; (16) equilibrium curve, namely the part after the potential excursion end in the E - t curve (in some nonlinear chemical fingerprints, the oscillatory end potential are the same as the equilibrium potential so as that there are no the oscillatory end curve). In addition, there still be the other messages such as (17) turbulent curve, the curve of the potential-time gurgitation with non-constant periods due to the turbulent reaction, namely the part corresponding to the turbulent life in the E - t curve (for example, all of the fingerprints in Figure 4 comprise the turbulent curves; Strictly speaking, the section of E - t curve ((g) and (h)) in Figure 1(b) of the ref. [19] is a turbulent curve, therefore, its specific expression of E - t relationship is more complicated than an oscillatory curve), and both of turbulent curve and oscillatory one may be called undulatory curve; (18) turbulent life, namely the time for which the turbulence lasts, as shown in Figure 4, and both of turbulent life and oscillatory life may be called undulatory life (t_{und}); (19) turbulent amplitude, namely the difference value between the neighbouring positive potential peak and negative one in the turbulent curve, and both of turbulent amplitude and oscillatory amplitude may be called undulatory amplitude (ΔE_{und}); (20) maximum turbulence amplitude, namely the maximum one in turbulent amplitudes of a turbulent curve, and both of maximum turbulence amplitude and oscillatory amplitude may be called maximum undulatory amplitude (ΔE_{mau}); (21) turbulent wave number, namely the fluctuation times of the turbulent curve, and both of turbulent wave number and oscil-

latory wave number may be called wave number (n_{wav}); (22) turbulent period, namely the interval between two adjacent potential peaks (positive or negative peaks) in the turbulent curve, the change of the turbulent period are usually very large (Figure 4), and both of turbulent period and oscillatory period may be called undulatory period (τ_{und}); (23) turbulence times (m), namely the times of the apparent turbulence reactions observable from the fingerprint (for example, it is obvious from the fingerprints in Figure 4 (right) that the times of the apparent turbulence reactions are 2, and the turbulence to which the arrowhead points is the first one); (24) turbulent intermission time (t_{tui}), namely the intermission time between the neighbouring apparent turbulences (Figure 4 (right)); (25) turbulent start potential, namely the potential corresponding to the start of the turbulence of the system, and both of turbulent start potential and oscillatory start potential may be called undulatory start potential (E_{uns}); (26) turbulent end potential and turbulent end time, namely the potential and time at the wink when the turbulent reaction of the system just ends, both of turbulent end potential and oscillatory end potential may be called undulatory end potential (E_{une}), and both of turbulent end time and oscillatory end time may be called undulatory end time (t_{une}); (27) turbulent end curve, namely the part from the turbulent end to the potential-excursion end in the E - t curve, and both of turbulent end curve and oscillatory end curve may be called excursion end curve; (28) turbulent period wave, namely the shape of part curve corresponding to each turbulent period in the E - t curve based on turbulent reaction, in general, the form change of turbulent period wave is very large, that of oscillatory period wave is very small, and both of turbulent period wave and oscillatory period wave may be called period wave; (29) oscillatory fingerprint, namely the fingerprint based on the oscillatory reaction (Figure 1 (left)); (30) turbulent fingerprint, namely the fingerprint based on the turbulent reaction (Figure 1 (right)). A whole nonlinear chemical fingerprint generally consists of the inductive curve, undulatory curve, excursion end curve and a part of equilibrium curve.

3.3 Reproducibility of nonlinear chemical fingerprint

Under definite condition, the determined nonlinear chemical fingerprint has very reproducibility for each sample. For example, according to "Procedure", added 13.00 mL of Huiyi Yoghourt, 10.00 mL of Nestle coffee and 11.00 mL of Kangshifu Tieguanyin tea into the reactor, and their nonlinear chemical fingerprints were determined by 3 times of parallel mensuration. The results are shown in Figure 4. It is obvious from Figure 4 and Table 1 that, for the same sort of samples with the same source, all of the information indexes in their fingerprints determined under the same condition are basically the same because the components and their contents in the samples are the same, and the RSDs of the determination $\leq 2.1\%$. Therefore, nonlinear chemical fin-

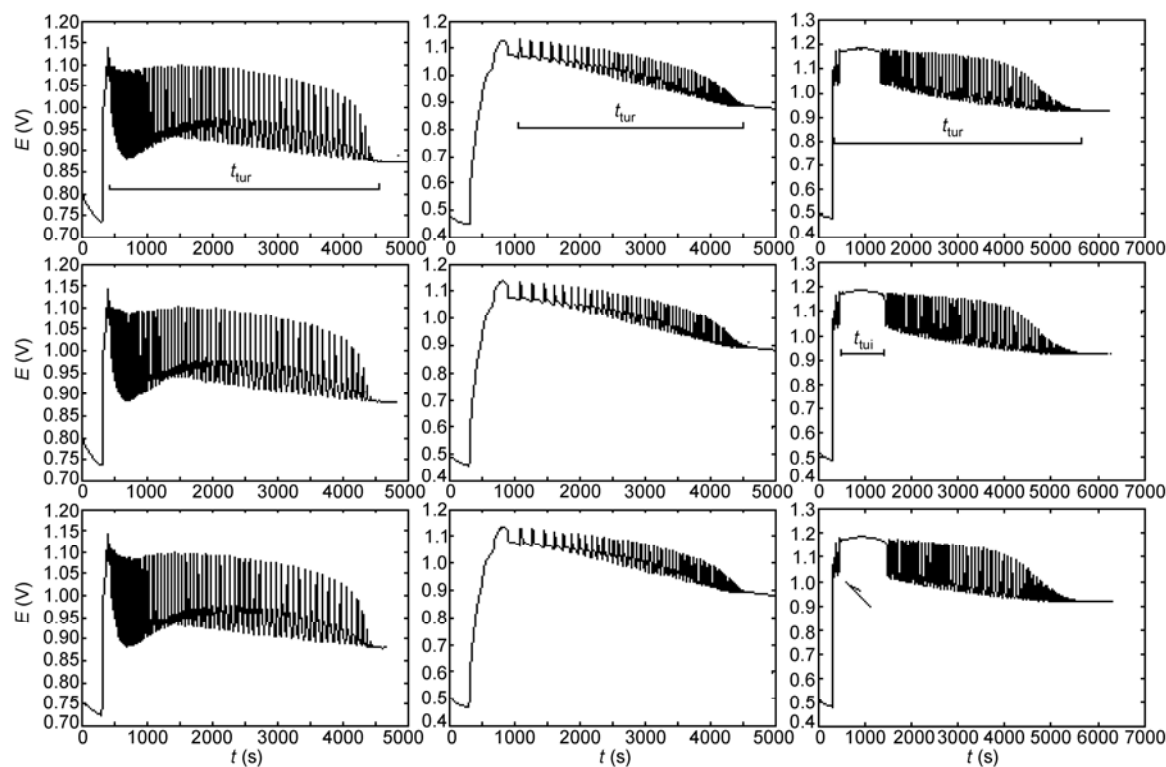


Figure 4 The nonlinear chemical fingerprints of Huiyi Yoghourt (left), Nestle coffee (middle) and Kangshifu Tieguanyin tea (right) obtained by 3 parallel determinations.

Table 1 The reproducibilities of the information indexes in the nonlinear chemical fingerprints of Huiyi Yoghourt, Nestle coffee and Kangshifu Tieguanyin tea^{a)}

| Sample and deviation | Eigenvalue | X ^{b)} | | | | | | | | | | | | | | |
|----------------------------|------------|--------------------------------|--------------------------------|-----------------------------|-----------------------------|--------------------------------|--------------------------------|----------------------------------|--------------------------------|-------------------------|-----------------------------|--------------------------------|-----------------------------|--------------------------------|----------|--------------------------------|
| | | <i>t</i> _{ind} (s) | <i>E</i> _{uns} (V) | <i>E</i> _{une} (V) | <i>t</i> _{uns} (s) | <i>E</i> _{equ} (V) | <i>t</i> _{equ} (s) | Δ <i>E</i> _{mau} (V) | <i>t</i> _{und} (s) | <i>n</i> _{wav} | <i>E</i> _{can} (V) | <i>t</i> _{can} (s) | <i>E</i> _{pet} (V) | <i>t</i> _{pet} (s) | <i>m</i> | <i>t</i> _{tui} (s) |
| Huiyi Yoghourt-1 | | 103 | 1.073 | 0.875 | 4485 | 0.847 | 4590 | 0.208 | 4082 | 74 | 0.735 | 300 | 1.139 | 393 | 1 | |
| Huiyi Yoghourt-2 | | 102 | 1.078 | 0.882 | 4486 | 0.850 | 4590 | 0.209 | 4084 | 73 | 0.736 | 300 | 1.146 | 392 | 1 | |
| Huiyi Yoghourt-3 | | 104 | 1.072 | 0.884 | 4486 | 0.869 | 4591 | 0.207 | 4082 | 73 | 0.719 | 301 | 1.142 | 394 | 1 | |
| RSD (%) | | 0.97 | 0.31 | 0.54 | 0.02 | 1.4 | 0.015 | 0.48 | 0.030 | 0.97 | 1.3 | 0.24 | 0.31 | 0.25 | 0 | |
| Nestle coffee-1 | | 770 | 1.068 | 0.891 | 4469 | 0.884 | 4676 | 0.103 | 3399 | 61 | 0.452 | 301 | 1.137 | 804 | 1 | |
| Nestle coffee-2 | | 772 | 1.066 | 0.892 | 4575 | 0.885 | 4681 | 0.106 | 3503 | 60 | 0.457 | 300 | 1.135 | 806 | 1 | |
| Nestle coffee-3 | | 776 | 1.069 | 0.909 | 4472 | 0.901 | 4678 | 0.107 | 3396 | 60 | 0.453 | 300 | 1.138 | 808 | 1 | |
| RSD (%) | | 1.2 | 0.15 | 1.1 | 0.90 | 1.1 | 0.054 | 2.0 | 1.8 | 1.2 | 0.58 | 0.24 | 0.14 | 0.25 | 0 | |
| Kangshifu Tieguanyin tea-1 | | 34 | 1.028 | 0.930 | 5621 | 0.921 | 5672 | 0.201 | 5287 | 3+68 | 0.478 | 300 | 1.080 | 313 | 2 | 1099 |
| Kangshifu Tieguanyin tea-2 | | 35 | 1.030 | 0.926 | 5617 | 0.925 | 5669 | 0.200 | 5282 | 3+67 | 0.483 | 301 | 1.066 | 314 | 2 | 1091 |
| Kangshifu Tieguanyin tea-3 | | 34 | 1.022 | 0.920 | 5619 | 0.930 | 5671 | 0.201 | 5285 | 3+68 | 0.479 | 301 | 1.067 | 312 | 2 | 1102 |
| RSD (%) | | 2.1 | 0.41 | 0.55 | 0.036 | 0.49 | 0.012 | 0.35 | 0.048 | 1.0 | 0.55 | 0.23 | 0.70 | 0.32 | 0 | 0.52 |

a) τ_{tur} and ΔE_{tur} were elided due to their too much eigenvalues; both of t_{can} and t_{pet} comprise about 300 s of dead time before the nonlinear chemical reactions start; b) information parameters.

gerprint is of very good reproducibility.

3.4 Characteristic of nonlinear chemical fingerprint

The obvious characteristics of nonlinear chemical fingerprints are shown in Figure 1, 2 and 3. It can be seen from

the figures that, under the same determination conditions, both of the quantifiable information and the intuitionistic shapes of the nonlinear chemical fingerprints concerning different samples are different from each other, due to the differences in the components and their contents in the samples. Therefore, nonlinear chemical fingerprint is of

very good characteristic.

3.5 Analysis of kinetic factor to affect the determining time of nonlinear chemical fingerprint

It is obvious from Figure 1, 2 and 3 that, not only the characteristic shapes of the fingerprints of different samples are different, but also the determining time of the fingerprints varies in the larger range from more than ten minutes to several hours. The larger difference in the determining time results consequentially in the larger difference of the quantifiable messages such as inductive time, undulatory life, undulatory period, etc, in the fingerprints, which is propitious to show the intuitionistic difference in the fingerprints and to facilitate the identification and evaluation of samples. Because of the ultra-complexity of nonlinear chemical reaction, the reasons begetting the larger difference of the determining time are also very complex, but the main reasons among them may be discussed from the perspective of chemical kinetics. There are numerous elementary reactions in a nonlinear chemical reaction, and the time for accomplishing the whole nonlinear chemical reaction, namely the time for determining the fingerprint will be decided by the slowest elementary reaction among them. As the classical theory of chemical kinetics described, not only the concentrations of reaction particles influence the reaction rate, but also under the same conditions of temperature and concentration, the rates of different elementary reactions are different because the activation energies of the reactions are different so as to result in the differences in the effective collision frequencies. For different samples, not only the components influencing nonlinear chemical reactions are different, but also the substrates or dissipative substances in the relevant reaction vary with the samples. These consequentially lead the differences in the elementary reactions of the nonlinear chemical reactions, and then the slowest elementary reactions controlling whole nonlinear chemical reaction course are also different. Of course, the rates of the nonlinear chemical reactions are also different, even have larger differences. These finally lead the difference in the time required to complete the whole nonlinear chemical reaction. In addition, even in rare cases, the substrates or dissipative substances from different samples are the same, but their concentrations are usually different, and the other chemical substances coexisting with them, namely chemical environments are also usually different. These will also influence the rates of the elementary reactions, even influence the time required to complete whole nonlinear chemical reaction, namely the time required for the emergence of a part of equilibrium curve in the test curve.

However, the larger differences in the times required to determine the fingerprints of different samples do not foreclosed the actual application of the fingerprint technique. For example, the times required to determine chromatographic fingerprints of different samples often vary in the

larger range from more than ten minutes to several hours, too, however, it is well known that the larger differences in the determining times do not the actual application of chromatographic fingerprint technique. Moreover, to see just from the timesaving aspect, the nonlinear chemical fingerprint technique has more advantages than the chromatographic one. In determining the chromatographic fingerprint, the time-consuming and cumbersome pretreatment must often be carried out for samples, especially solid samples such as Chinese traditional medicines, natural medicines, foods, agricultural products, etc. Therefore, the completion of several parallel determinations of one sample usually spends a long time. Moreover, the determination of the nonlinear chemical fingerprint is generally without the pretreatment for the sample, even on determining natural medicine and other insoluble solid samples, the sample may be determined after being ground into powder only in minutes. Most of the times required to determine nonlinear chemical fingerprints are less than 2 h, and some are only a few or more than ten minutes (Figures 1, 2 and 3). For the case to spend a longer time, the determining time may be decreased by increasing the rate of the nonlinear chemical reaction by rising the determining temperature. The reason is that, the higher the temperature, the larger the average energy in the system, the higher the collision frequency, the higher the effective collision ratio, the rapider the rate of each elementary reaction. Eventually, the whole nonlinear chemical reaction is speeded, and the time required to determine the fingerprint is shortened (see Figure 4 in the ref. [19]). The reason to shorten the determining time consumed by properly rising the temperature has been expatiated in Section 3.2(5) of the ref. [19].

3.6 General calculation method of system similarity of nonlinear chemical fingerprint

According to the similarity system theory [50, 51], the system similarity between systems A and B may be divided into product system similarity Q_p and average system similarity Q_a [18]. The product system similarity Q_p is the product of the relevant number similarity Q_n and the degree similarity Q_d :

$$Q_p = Q_n \times Q_d \quad (13)$$

While the average system similarity may be expressed by the average value Q_a of the number similarity Q_n and the degree similarity Q_d :

$$Q_a = (Q_n + Q_d) / 2 \quad (14)$$

According to statistic principle, $Q_p \leq Q_a$, namely, only when both of Q_n and Q_d are close or equal to 100%, $Q_p \approx Q_a$ or $Q_p = Q_a$. When both of Q_n and Q_d are less than 100%, or one of them is less than 100%, Q_p is less or far less than Q_a . Obviously, the degree of the characteristic difference of systems A and B can be reflected better by the product system similarity Q_p . The number similarity in the product system sim-

ilarity may be expressed as:

$$Q_n = n / (K + L - n) \quad (15)$$

While the degree similarity may be expressed as:

$$Q_u = \frac{1}{n} \sum_{i=1}^n q(u_i) \quad (16)$$

Therefore, eq. (13) may be expressed as:

$$Q_p = \frac{1}{K + L - n} \sum_{i=1}^n q(u_i) \quad (17)$$

Among the similar elements of systems A and B, each pair of similar elements a_i and b_i ($i = 1, 2, 3 \dots n$) composes a similar cell u_i . The value of the i th similar cell may be expressed by $q(u_i)$. It is obvious from eq. (17) that, the product system similarity Q_p is a multivariate function of the numbers (K and L) of the composition elements of systems A and B, the number n of the similar elements, namely the elements with the same attribute between the two systems and the value $q(u_i)$ of each similar cell. The value $q(u_i)$ can reflect the similarity of each pair of similar elements, and similarly, it may be expressed by the product of its number similarity $q(u_i)_n$ and degree similarity $q(u_i)_d$:

$$q(u_i) = q(u_i)_n \times q(u_i)_d \quad (18)$$

Suppose that, the numbers of the eigenvalues possessed by similar elements a_i and b_i of the i th similar cell u_i are l_i and m_i respectively, and there are o_i pairs of comparable eigenvalues a_{ij} and b_{ij} ($i = 1, 2, 3 \dots n; j = 1, 2, 3 \dots o_i; o_i$ is equal to the smaller in l_i and m_i), whereupon, the number similarity of the i th similar cell may be expressed as:

$$q(u_i)_n = o_i / (l_i + m_i - o_i) \quad (19)$$

Suppose that, the relevant ratio coefficients of o_i pairs of comparable eigenvalues and their feature weights are r_{ij} and d_{ij} ($i = 1, 2, 3 \dots n; j = 1, 2, 3 \dots o_i$) respectively, whereupon, the degree similarity of the i th similar cell may be expressed as:

$$q(u_i)_d = \frac{1}{o_i} \sum_{j=1}^{o_i} d_{ij} \cdot r_{ij} \quad (20)$$

And then eq. (18) may be written as:

$$q(u_i) = \frac{1}{l_i + m_i - o_i} \sum_{j=1}^{o_i} d_{ij} \cdot r_{ij} \quad (21)$$

Here, $r_{ij} = S_{ij}/B_{ij}$, S_{ij} and B_{ij} are the smaller value and the bigger one in the j th pair of comparable eigenvalues a_{ij} and b_{ij} of the i th similar cell between systems A and B, respectively. So eq. (17) may be changed into:

$$Q_p = \frac{1}{K + L - n} \sum_{i=1}^n \frac{1}{l_i + m_i - o_i} \sum_{j=1}^{o_i} d_{ij} \cdot \frac{S_{ij}}{B_{ij}} \quad (22)$$

Speaking to nonlinear chemical fingerprint, K and L in the equation are the numbers of the sorts of quantifiable information parameters in fingerprints A and B, respectively. For example, in fingerprint A or B, there are the sorts of quantifiable parameters, such as canyon potential (E_{can}), canyon time (t_{can}), peak top potential (E_{pet}), peak top time (t_{pet}), inductive time (t_{ind}), undulatory start potential (E_{uns}),

undulatory end potential (E_{une}), undulatory end time (t_{une}), equilibrium potential (E_{equ}), equilibrium time (t_{equ}), undulatory amplitude (ΔE_{und}), maximum undulatory amplitude (ΔE_{mau}), undulatory life (t_{und}), undulatory period (τ_{und}), wave number (n_{wav}), turbulent intermission time (t_{tui}), turbulence times(m), etc. The n in the equation is the number of the sorts of the comparable information parameters between fingerprints A and B due to their same attribute. Each feature weight d_{ij} in the equation may be 1. The information parameters may be considered as the composition elements or similar ones of systems A and B, namely fingerprints A and B, and their values may be considered as their eigenvalues. Different sorts of composition elements or similar elements may possess different numbers of eigenvalues.

For different-sample fingerprints based on the same category of nonlinear chemical reactions, the numbers (K and L) of the sorts of the quantifiable information parameters and the number n of the similar elements are the same generally, however, the numbers of the eigenvalues of the similar elements are not always the same. For example, in the two systems shown in Figure 1(a) and 1(c), namely in the fingerprints of walnut milk and Malays soy milk, both of the numbers of sorts of the quantifiable information parameters and the number of the similar elements are the same, namely $K = L = n$. Because both of the fingerprints are ones based on oscillatory reactions, namely the nonlinear chemical reactions consisting of inductive and oscillatory processes, both of their quantifiable-information-parameter-sort number, namely the composition-element-sort number of the two systems are fifteen, namely $K = L = n = 15$. Concretely speaking, the parameter sorts include canyon potential, canyon time, peak top potential, peak top time, inductive time, undulatory start potential, undulatory end potential, undulatory end time, equilibrium potential, equilibrium time, undulatory amplitude, maximum undulatory amplitude, undulatory life, undulatory period and wave number. However, the numbers of the eigenvalues of the similar elements are not always the same. For example, the eigenvalue numbers of the similar elements such as the inductive times, undulatory start potential, undulatory end potential, undulatory end time, equilibrium potential, equilibrium time, maximum undulatory amplitude, undulatory life and wave number are the same, and all equal 1; however, the eigenvalue numbers of the similar elements such as canyon potential, canyon time, peak top potential, peak top time, undulatory amplitude and undulatory period are not always the same. For example, the eigenvalue numbers of the canyon potential, peak top potential, canyon time and peak top time in Figure 1(a) are all 1 (it is noteworthy that, the number of eigenvalue is not eigenvalue itself, for example, the eigenvalues of the canyon potential and canyon time are 0.490 and 300, respectively), while the eigenvalue numbers of the canyon potential, peak top potential, canyon time and peak top time in Figure 1(c) are all 3; the eigenvalue number of the undulatory period in Figure 1(a) are 18, while that of the

undulatory period in Figure 1(c) are 43; the number of the undulatory amplitude in Figure 1(a) are 36, while that of the similar element in Figure 1(c) are 86. The computational model of the system similarity of the two fingerprints was actually obtained by simplifying eq. (22):

$$Q_p = \frac{1}{n} \sum_{i=1}^n \frac{1}{l_i + m_i - o_i} \sum_{j=1}^{o_i} d_{ij} \cdot \frac{S_{ij}}{B_{ij}} \quad (23)$$

Eq. (23) is suitable for calculating the similarity of the fingerprints base on the same category of nonlinear chemical reactions under the conditions of different chemical environments, namely different samples.

For different-sample fingerprints based on different category of nonlinear chemical reactions, the sort numbers of their composition elements, namely information parameters are generally different. Therefore, the number n of their similar elements is usually not equal to the number K or L of the composition elements. Besides the eigenvalue numbers of their similar elements are not always the same, the number n of the similar elements comparable between the two fingerprints are generally less than the number (K or L) of the composition elements, as shown in Figure 1(a) and (f). The figure (a) is a fingerprint based on an oscillatory reaction, while the figure (f) is that based on a turbulent reaction with two turbulences in which both of the differences of the turbulent amplitudes and the turbulent periods are very large. The former includes 15 sorts of composition elements such as canyon potential, canyon time, peak top potential, peak top time, inductive time, undulatory start potential, undulatory end potential, undulatory end time, equilibrium potential, equilibrium time, undulatory amplitude, maximum undulatory amplitude, undulatory life, undulatory period and wave number, namely $K=15$. While the latter includes 17 sorts of composition elements such as canyon potential, canyon time, peak top potential, peak top time, inductive time, equilibrium potential, equilibrium time, undulatory start potential, undulatory end potential, undulatory end time, undulatory amplitude, maximum undulatory amplitude, undulatory life, undulatory period, wave number, turbulence times and turbulent intermission, namely $K = 17$. The similar elements are the same category of composition elements between two systems, namely two fingerprints, therefore, there are 15 sorts of similar elements between the figures (a) and (f), namely fingerprints a and f. They are canyon potential, canyon time, peak top potential, peak top time, inductive time, undulatory start potential, undulatory end potential, undulatory end time, equilibrium potential, equilibrium time, undulatory amplitude, maximum undulatory amplitude, undulatory life, undulatory period and wave number, namely $n = 15$. In this case, the similarity between the fingerprints may be calculated by eq. (22). From the comparison of eq. (22) with eq. (23), it is obvious that the similarity between different-sample fingerprints based on different category of nonlinear chemical reactions will be less than that of the fingerprints based on the same category

of nonlinear chemical reactions.

For the fingerprints of the same samples from an source or an production batch, because of the same chemical environment and the determination condition based on the same nonlinear chemical reaction, the sort numbers (K and L) of the composition elements are completely the same as the number n of the similar elements (as shown in Figure 4), namely $K=L=n$. Besides, the eigenvalues of the similar elements and their numbers are also the same completely in theory, namely $l_i=m_i=o_i$. In this case, the similarity of the fingerprints may be calculated by eq. (24).

$$Q_p = \frac{1}{n} \sum_{i=1}^n \frac{1}{o_i} \sum_{j=1}^{o_i} d_{ij} \cdot \frac{S_{ij}}{B_{ij}} \quad (24)$$

Because $K+L-n \geq n$ and $l_i+m_i-o_i \geq o_i$, it is obvious from comparing eqs. (22), (23) and (24) that, among the above three cases, the system similarity of the fingerprints of the same samples with the same source or production batch and base on the same nonlinear chemical reaction is the largest, the similarity of the different-sample fingerprints based on different category of nonlinear chemical reactions is the smallest, and that of the different-sample fingerprints based on the same category of nonlinear chemical reactions is between the both. Generally, the similarity of the nonlinear chemical fingerprint determined in each case may be calculated by eq. (22), namely the general formula for calculating the system similarity. In this experiment, the general calculation program for the system similarity was written according to eq. (22).

3.7 Nonlinear chemical system required to determine the fingerprint

When the nonlinear chemical fingerprints of different samples are determined, the relevant nonlinear chemical reactions with different reaction substrates and/or in different chemical environments must often be utilized, and the mechanisms of various nonlinear chemical reactions are generally very complex. For example, there may be dozens of elementary reactions [7, 8] in the process of the B-Z reaction to use H^+ , BrO_3^- , Mn^{2+} , acetone and the reducing substances (including the dissipative substance) in the sample as its substrates. In the entire process of nonlinear chemical reaction, the relationship between the potential (E) and the time (t) varies in nonlinear manner. For example, the $E-t$ curve of nonlinear chemical system consisting of H^+ , BrO_3^- , Mn^{2+} , acetone and solid Kafu fruit drink with grape flavor was shown in Figure 1(c) in the ref. [19]. From the inductive and oscillatory curves in the figure, it is obvious that the B-Z nonlinear chemical reaction consists of the relevant inductive and oscillatory reactions. In this experiment, the non-steady-state system consisting of H^+ , BrO_3^- , Mn^{2+} , acetone and sample components was selected as the system for determining the nonlinear chemical fingerprints of samples.

3.8 Determination of nonlinear chemical fingerprints of the same category of samples from different sources or production batches

The intuitionistic shape and quantifiable information of a nonlinear chemical fingerprint associate not only with the sort of the sample, but also with the contents of the sample components. In all fingerprint techniques, on evaluating the qualities of the same category of samples from different sources or production batches, there must be differences in the fingerprints, especially the quantitative messages in them; however, on identifying the authenticity of samples, the fingerprints of the same samples from different sources or production batches must be the same or very similar. Therefore, in the nonlinear chemical fingerprint technique, according to the functional relationship between the whole content of sample components and the quantitative information [16, 17], and under other constant determining conditions, the fingerprints with different quantitative messages of the whole contents may be obtained by using the same determining dosage for the same sort of samples from different sources or production batches, and the qualities of the samples may be evaluated with the fingerprints. However, on identifying the authenticities of samples, the same or very similar fingerprints with high similarity may be obtained by suitably changing the dosage for the same sort of samples from different sources or production batches. This is one of the advantages of nonlinear chemical fingerprint technique. For example, the research showed that not only there are quantitative relationships between the oscillatory lives, namely undulatory lives of the fingerprints of Guhan

Yangshengjings and the total contents of the active components, but also there are the very good linear relationships in the range of the determining dosage from 0.60 mL to 1.60 mL (Figure 5). It is obvious from Figure 5 that, although in the production of different batches of Guhan Yangshengjings, the changes of the sources of raw materials or the fluctuations of the process conditions may result in the change of the slope of the quantitative linear relationship, there are very good linear relationships between the undulatory lives in the fingerprints of all batches of samples and the whole contents of the components all the time. If according to the relevant linear quantitative relationships respectively, the fingerprints of different batches of Guhan Yangshengjings were determined by adjusting the dosage suitably, there will be very high similarity between the determined fingerprints. For example, according to the above method, the fingerprints of four batches of Guhan Yangshengjings were determined by using 1.30 mL of constant dosage, the results were shown in Figure 2(b); by using the linear relationships shown in Figure 5, the dosages of Guhan Yangshengjings, whose batch numbers are 10027, 10093, 10158 and 10236 respectively, were changed into 1.25, 1.28, 1.35 and 1.31 mL, respectively, and then the relevant fingerprints were determined, the results were shown in Figure 2(c). It is obvious from Figure 2(a) that, for the parallel determination of Guhan Yangshengjing from the same source and production batch, the determined fingerprints are almost the same completely because both of the sorts of the chemical components and their contents are the same. According to the fingerprints in Figure 2(b) and the linear relationship between their undulatory lives and

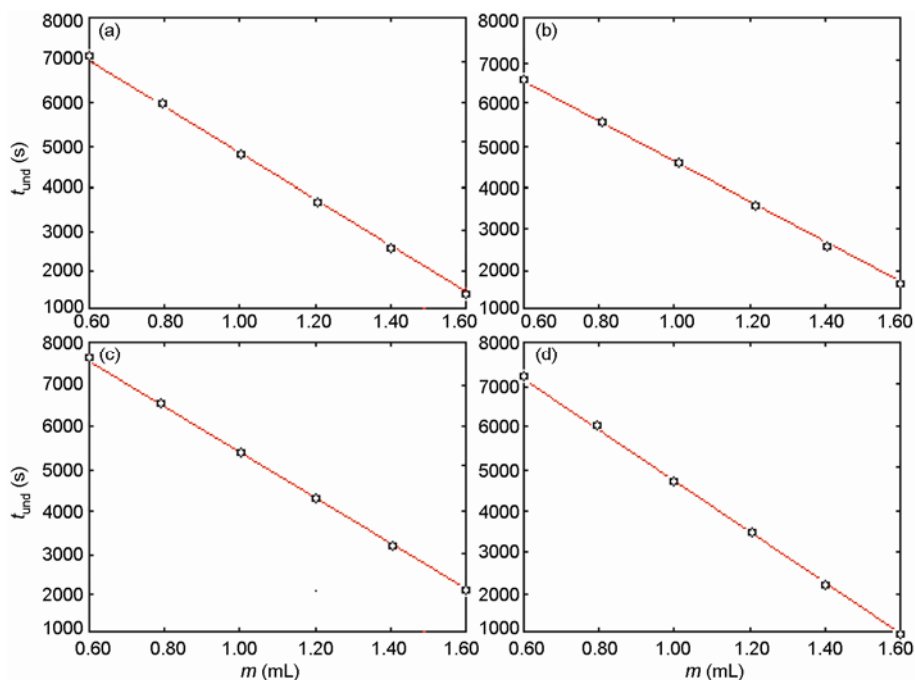


Figure 5 The influence of the determining dosage (m) on the undulatory lives of the fingerprints of Guhan Yangshengjings from different batches. The production batch number: (a) was 10027, (b) was 10093, (c) was 10158 and (d) was 10236.

the whole content of the sample components, the relative whole contents of the components of the 4 batches of Guhan Yangshengjings may be estimated easily. The order of the whole contents of the components of the Guhan Yangshengjings is:

batch number 10027 > batch number 10093 > batch number 10236 > batch number 10158

Visibly, the quality of the sample may be evaluated by the quantitative information in the nonlinear chemical fingerprint. It is obvious from Figure 2(c) that, under the conditions of true raw materials, strict compatibility and standardized production process, the fingerprints determined by suitably changing the dosages of Guhan Yangshengjings from different sources or different batches will be of very high similarity between each other. The method for determining the fingerprint is propitious to standardize the characteristic of the fingerprint, and also makes for identifying samples with similarity.

3.9 Parameter information in nonlinear chemical fingerprints of different samples

According to "Procedure", added new batches of Wang Laoji herb tea, Pepsi-Cola without sugar, Yang Guifei apple vinegar, 100c Lemon juice, Dole apple juice (11.00 mL, respectively), Nine system citrus drink (4.00 mL) and appropriate amounts of Guhan Yangshengjings (see the note of Figure 2) into the reactor, respectively; on changing the volume of NaBrO₃ solution into 5.00 mL, added Yang Xiecheng soy milk, walnut milk, Malays soy milk, Guliguli corn juice, Huiyi yoghurt, Mengniu yoghurt, Yili yoghurt (13.00mL, respectively) and Nestle coffee, Meishi-Yaha coffee, Naikajingxuan-Yaha coffee drink (10.00 mL, respectively) into the reactor, respectively; on changing the volume of NaBrO₃ solution into 10.00 mL, added 11.00 mL of Mengniu whole milk and Yili whole milk, respectively. Then, the nonlinear chemical fingerprints were determined, the results are shown in Figures 2 and 3. All of the fingerprints were determined repeatedly 4 times, and their average values were used as the parameter values to calculate the similarities of the fingerprints of the samples. All of the parameter values were listed in Table 2. It is obvious from the data in Table 2 that, All of the differences in the values of the same parameters in the fingerprints of a sort of samples are smaller generally, while those in the values of the same parameters in the fingerprints of different sorts of samples are all larger generally.

3.10 Calculation and analysis of similarity of nonlinear chemical fingerprints

In order to find a method which can be used to reasonably evaluate the similarity of nonlinear chemical fingerprint, by using the data in Table 2, the fingerprints (Figure 3) of some samples were compared with the mutual model of the fin-

gerprints (Figure 2(c)) of Guhan Yangshengjings from different batches (including the comparison of the repeatedly determined fingerprints (Figure 2(a)) of one batch of Guhan Yangshengjing), and the values of the Euclidean distance, correlation coefficient, included angle cosine and system similarity of 19 sorts of samples were calculated. It is obvious from Table 3 that, all the correlation coefficients of the fingerprints of different samples are greater than 0.931, and all the included angle cosines are greater than 0.946. Therefore, both of correlation coefficient and included angle cosine can not be used to evaluate the similarity of the nonlinear chemical fingerprint. All the Euclidean distances of the nonlinear chemical fingerprints of Guhan Yangshengjings from 4 batches are less than 253, and ones between the fingerprints of 18 sorts of other samples and Guhan Yangshengjing are all greater than 425.7. However, the largest difference in the Euclidean distances between the fingerprints of the identical sort of samples are 232.3, and the smallest difference in ones of different samples are only 173.4, therefore, sometimes, the degrees of the intuitionistic characteristic differences of nonlinear chemical fingerprints can not be reflected correctly by Euclidean distance, as explained in the ref. [18]. The system similarities of the repeatedly determined fingerprints of the identical batch of Guhan Yangshengjing are all greater than 0.971, and those of Guhan Yangshengjings from 4 batches are all greater than 0.920, while the system similarities between the fingerprints of 18 other samples and one of Guhan Yangshengjing are all less than 0.595. Therefore, the sorts of samples and degrees of the differences between their fingerprints can be reflected most truly by the system similarity. So, the method for calculating system similarity is the best one among the above four methods, and may be used to calculate the similarity of nonlinear chemical fingerprint and to identify samples quickly, easily and accurately by combining with the intuitionistic information. The reason may be explained by analyzing the theoretical formulas for calculating the relevant similarities.

At present, many of similarity-calculation software have been used in the investigation on fingerprints. However, several application software recommended by Chinese national pharmacopoeia committee are ones developed by Central South University and Zhejiang University, respectively. In the software developed by the former, the correlation coefficient is used as the index for evaluating the similarity, and in that developed by the latter, the included angle cosine is used as the index. The both of software were directly written with the relevant mathematical models introduced in some literatures about higher mathematics. However, whether the similarities calculated with the mathematical models can effectively reflect the characteristic difference between the fingerprints, which was not considered carefully in writing software. Two different types of data may be use to calculate fingerprint similarities. One is the parameter information in fingerprints, such as the areas, heights

Table 2 The parameter information in nonlinear chemical fingerprints of 19 sets of samples (the average values of the parameters in the fingerprints obtained by 4 parallel determinations)^{a)}

| Sample ^{b)} | Element | t_{idu} (s) | E_{uns} (V) | E_{unc} (V) | t_{unc} (s) | E_{equ} (V) | t_{equ} (s) | ΔE_{mau} (V) | t_{und} (s) | n_{wav} | E_{can} (V) | t_{can} (s) | E_{pet} (V) | t_{pet} (s) | m | t_{tui} (s) |
|---------------------------------|---------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------------|-------------------------|------------------|-------------------------|-------------------------|----------------------|-------------------------|-----|-------------------------|
| Guhan No. 10236-1 | | 450 | 0.997 | 0.908 | 3802 | 0.888 | 3897 | 0.108 | 3052 | 149 | 0.432 | 300 | 1.053 | 723 | | |
| Guhan No. 10236-2 | | 456 | 0.999 | 0.916 | 3870 | 0.886 | 3928 | 0.118 | 3114 | 145 | 0.429 | 300 | 1.051 | 734 | | |
| Guhan No. 10236-3 | | 461 | 1.012 | 0.907 | 3829 | 0.890 | 3906 | 0.112 | 3068 | 151 | 0.443 | 300 | 1.051 | 739 | | |
| Guhan No. 10236-4 | | 457 | 1.016 | 0.910 | 3847 | 0.887 | 3913 | 0.112 | 3090 | 147 | 0.421 | 300 | 1.052 | 752 | | |
| Guhan No. 10027 | | 314 | 1.022 | 0.906 | 3501 | 0.871 | 3693 | 0.110 | 2887 | 139 | 0.439 | 300 | 1.060 | 655 | | |
| Guhan No. 10093 | | 247 | 1.010 | 0.914 | 3400 | 0.875 | 3668 | 0.115 | 2853 | 128 | 0.434 | 300 | 1.068 | 508 | | |
| Guhan No. 10158 | | 309 | 0.976 | 0.903 | 3424 | 0.890 | 3711 | 0.118 | 2815 | 141 | 0.423 | 300 | 1.067 | 576 | | |
| Guhan No. 10236 | | 471 | 1.012 | 0.908 | 3608 | 0.887 | 3975 | 0.112 | 2837 | 146 | 0.416 | 300 | 1.051 | 673 | | |
| Wang Laoji herb tea | | 107 | 1.105 | 0.962 | 1516 | 0.960 | 1957 | 0.132 | 1109 | 31 | 0.565 | 301 | 1.180 | 351 | 1 | |
| Pepsi-Cola without sugar | | 143 | 1.129 | 1.007 | 1054 | 0.900 | 1136 | 0.090 | 611 | 42 | 0.645 | 299 | 1.147 | 437 | | |
| Yang Guifei apple vinegar | | 71 | 1.017 | 0.884 | 4395 | 0.878 | 4471 | 0.237 | 4024 | 75 | 0.488 | 300 | 1.131 | 337 | | |
| 100c Lemon juice | | 81 | 1.064 | 0.896 | 1637 | 0.900 | 1747 | 0.231 | 1256 | 49 | 0.459 | 300 | 0.631 | 306 | | |
| | | | | | | | | | | | 0.575 | 336 | 1.077 | 378 | | |
| Dole apple juice | | 85 | 1.078 | 0.963 | 1075 | 0.965 | 1185 | 0.131 | 690 | 32 | 0.561 | 309 | 0.142 | 373 | | |
| Yili yoghurt | | 775 | 0.976 | 0.940 | 3783 | 0.939 | 3992 | 0.122 | 2708 | 48 | 0.699 | 302 | 1.113 | 646 | | |
| Nestle coffee | | 772 | 1.066 | 0.892 | 4575 | 0.885 | 4681 | 0.106 | 3503 | 60 | 0.457 | 300 | 1.135 | 806 | 1 | |
| Meishi-Yaha coffee | | 854 | 1.075 | 0.925 | 4956 | 0.927 | 5189 | 0.0745 | 3802 | 81 | 0.432 | 299 | 1.141 | 956 | 1 | |
| Naikajingxuan-Yaha coffee drink | | 898 | 1.064 | 0.938 | 4570 | 0.935 | 4572 | 0.0365 | 3372 | 68 | 0.430 | 300 | 1.102 | 978 | 1 | |
| Mengniu yoghurt | | 655 | 0.959 | 0.970 | 1753 | 0.939 | 1987 | 0.0984 | 798 | 31 | 0.678 | 300 | 1.115 | 573 | | |
| Yang Xiecheng soy milk | | 1023 | 0.981 | 0.911 | 4523 | 0.918 | 4611 | 0.140 | 3200 | 41 | 0.652 | 300 | 1.163 | 549 | | |
| Walnut milk | | 2014 | 0.808 | 0.756 | 3765 | 0.752 | 3996 | 0.181 | 1451 | 19 | 0.491 | 300 | 1.173 | 471 | | |
| | | | | | | | | | | | 0.529 | 299 | 1.104 | 1342 | | |
| Malays soy milk | | 2149 | 0.904 | 0.825 | 7694 | 0.871 | 7795 | 0.201 | 5245 | 44 | 1.100 | 1485 | 1.128 | 1481 | | |
| | | | | | | | | | | | 1.035 | 1693 | 1.049 | 1995 | | |
| Guliguli corn juice | | 427 | 1.058 | 0.959 | 1927 | 0.959 | 2087 | 0.125 | 1200 | 20 | 0.603 | 300 | 1.179 | 368 | 2 | 21 |
| Huiyi yoghurt | | 104 | 1.072 | 0.884 | 4486 | 0.869 | 4591 | 0.207 | 4082 | 73 | 0.719 | 301 | 1.142 | 394 | 1 | |
| Yili whole milk | | 1713 | 1.074 | 0.990 | 13052 | 0.966 | 16288 | 0.127 | 11043 | 9 | 0.660 | 303 | 1.161 | 15890 | 1 | |
| Mengniu whole milk | | 1733 | 1.068 | 0.936 | 17191 | 0.946 | 17453 | 0.124 | 15158 | 42 | 0.561 | 300 | 1.162 | 15755 | 1 | |
| Nine system citrus drink | | 4662 | 0.954 | 0.979 | 12504 | 0.976 | 13016 | 0.218 | 7542 | 59 | 0.789 | 301 | 1.141 | 693 | 1 | |
| | | | | | | | | | | | 1.079 | 4003 | 1.125 | 4903 | | |

a) Because of the space limitation, the eigenvalues of τ_{und} and ΔE_{und} are elided due to too much, only the numbers of their eigenvalues are listed in the table; both of t_{can} and t_{pet} include 300 s of dead time before the beginning of the nonlinear chemical reaction; on calculating the correlation coefficients, included angle cosines and Euclidean distances, only the average values were used for the parameters (or elements) with multiple eigenvalues, and both of parameters m and t_{tui} were not adopted. b) No.: Batch number; Guhan: Guhan Yangshengjing.

and retention times of the peaks in a chromatogram as well as the inductive time, undulatory periods, undulatory amplitudes, undulatory life, peak top potentials, canyon potentials, etc in a nonlinear chemical fingerprint. And the other is the relative intensity information in fingerprints, such as the relative electrical signal at each datum collection point in a chromatographic or nonlinear chemical fingerprint. The fingerprint similarity calculated by the former is intitled parametric similarity, and that calculated by the latter is intitled nonparametric similarity. Both of the two types of similarity may be calculated by correlation coefficient r , included angle cosine $\cos\alpha$ and Euclidean distance $d(x,y)$, and the computational models are expressed by eqs. (25), (26) and (27), respectively.

$$r = \frac{\sum_{i=1}^n [(x_i - \bar{x})(y_i - \bar{y})]}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}} \quad (25)$$

$$\cos\alpha = \frac{\sum_{i=1}^n x_i y_i}{\sqrt{\sum_{i=1}^n x_i^2 \sum_{i=1}^n y_i^2}} \quad (26)$$

$$d(x,y) = \sqrt{\sum_{i=1}^n (x_i - y_i)^2} \quad (27)$$

On calculating parametric similarity, the n in the computational models denotes the number of comparable parameters between two fingerprints, such as the number of the comparable peak areas between chromatographic fingerprints or that of types of such comparable parameters as inductive times, peak top potentials, canyon potentials, maximum undulatory amplitudes, undulatory periods, undulatory lives, etc between nonlinear chemical fingerprints. The x_i and y_i denote the values of the i th pair of comparable parameters between fingerprints X and Y, respectively. On calculating nonparametric similarity, the n denotes the number of datum collection time points in the fingerprint, and x_i and y_i

denote the relative signal intensities at the i th datum collection point of compared fingerprints X and Y, respectively, such as the relative values of electrical signals in the two chromatograms or nonlinear chemical fingerprints. It can be seen from the analyses about eqs. (25) and (26) that, both of the correlation coefficients and included angle cosines calculated respectively by eqs. (25) and (26) for the repeatedly determined fingerprints of one sample can be close to 100%, however, both of the computational models do not contain " $x_i - y_i$ ", namely the calculation factor able to express the difference value of each pair of comparable parameters or relative signal intensities in fingerprints. The only difference between the methods for calculating the two similarities is that, on calculating correlation coefficient, the difference ($x_i - \bar{x}$ or $y_i - \bar{y}$; $i = 1, 2, 3 \dots n$) between the datum (x_i or y_i) and its average value (\bar{x} or \bar{y}) must be calculated firstly, and on calculating included angle cosine, besides replacing $x_i - \bar{x}$ and $y_i - \bar{y}$ with x_i and y_i respectively, the computational method is almost the same as that for calculating correlation coefficient. The differentiation treatment is only to calculate differences between data contained in the same fingerprint and their average value, such as the differences between x_i and \bar{x} as well as those between y_i and \bar{y} , and does not deal with the difference de-

grees ($x_i - y_i$) of the comparable data between two fingerprints. However, the difference degree between overall characteristics of fingerprints may effectively be reflected only by the result of statistical treatment of difference values ($x_i - y_i$) between their comparable parameters or relative signal strengths at each datum collection point. Therefore, both of correlation coefficient and included angle cosine are not sensitive to the difference between the characteristics of fingerprints, and can't effectively express the difference degree between the characteristics of fingerprints. It can also be seen from the data in Table 3 that the both are very insensitive to the characteristic difference.

Euclidean distance is calculated directly with statistical treatment carried out by the difference values ($x_i - y_i$) of comparable parameters between fingerprints, therefore, as a similarity, it can better reflect the characteristic difference between fingerprints. It is obvious from eq. (27) that, the higher the overlap ratio between messages of fingerprints, namely the smaller the difference values ($x_i - y_i$) between the comparable parameters or signal strengths at each datum collection point, the smaller the Euclidean distance between the fingerprints, the higher the similarity. Therefore, the similarity between sample fingerprints or between sample fingerprints and their mutual model may be evaluated according Euclidean distance. It is worth mentioning that, on

Table 3 The results of calculating similarities of 19 sorts of samples

| Sample name (batch number) | Euclidean distance | Correlation coefficient | Included angle cosine | System similarity |
|-----------------------------------|---------------------|-------------------------|-----------------------|-------------------|
| Guhan Yangshengjing (No. 10236-1) | 51.46 | 0.9999 | 0.9999 | 0.9712 |
| Guhan Yangshengjing (No. 10236-2) | 57.49 | 0.9999 | 0.9999 | 0.9763 |
| Guhan Yangshengjing (No. 10236-3) | 41.81 | 0.9999 | 0.9999 | 0.9868 |
| Guhan Yangshengjing (No. 10236-4) | 20.03 | 0.9999 | 0.9999 | 0.9815 |
| Guhan Yangshengjing (No. 10027) | 60.70 | 0.9999 | 0.9999 | 0.9560 |
| Guhan Yangshengjing (No. 10093) | 190.26 | 0.9993 | 0.9995 | 0.9204 |
| Guhan Yangshengjing (No. 10158) | 68.01 | 0.9999 | 0.9999 | 0.9527 |
| Guhan Yangshengjing (No.10236) | 252.3 | 0.9989 | 0.9991 | 0.9234 |
| Wang Laoji herb tea | 2740 | 0.9974 | 0.9978 | 0.4019 |
| Pepsi-Cola without sugar | 4133 | 0.9434 | 0.9571 | 0.3457 |
| Yang Guifei apple vinegar | 931.3 | 0.9919 | 0.9934 | 0.4874 |
| 100c Lemon juice | 3319 | 0.9982 | 0.9985 | 0.4254 |
| Dole apple juice | 4139 | 0.9602 | 0.9694 | 0.4078 |
| Yili yoghourt | 622.2 | 0.9955 | 0.9965 | 0.5534 |
| Nestle coffee | 531.5 | 0.9979 | 0.9984 | 0.5942 |
| Meishi-Yaha coffee | 1209 | 0.9981 | 0.9985 | 0.5476 |
| Naikajingxuan-Yaha coffee drink | 425.7 | 0.9967 | 0.9975 | 0.5341 |
| Mengniu yoghourt | 3263 | 0.9670 | 0.9752 | 0.4298 |
| Yang Xiecheng soy milk | 661.2 | 0.9919 | 0.9936 | 0.5183 |
| Walnut milk | 1957 | 0.9313 | 0.9461 | 0.4034 |
| Malays soy milk | 5422 | 0.9911 | 0.9932 | 0.3468 |
| Guliguli corn juice | 3027 | 0.9934 | 0.9951 | 0.3322 |
| Huiyi yoghourt | 904.0 | 0.9925 | 0.9938 | 0.4209 |
| Yili whole milk | 1.300×10^5 | 0.9812 | 0.9847 | 0.2515 |
| Mengniu whole milk | 1.787×10^5 | 0.9966 | 0.9973 | 0.2844 |
| Nine system citrus drink | 1.081×10^5 | 0.9575 | 0.9681 | 0.2557 |

calculating parametric similarity of chromatographic fingerprints, such as peak area similarity, all of the peak areas are comparable, even the area of a non-mutual peak in one chromatogram and that of a missing peak at the same retention time in another chromatogram are also comparable each other on regarding the area of the missing peak as zero; however, as mentioned above, for nonlinear chemical fingerprints, when the compared fingerprints were determined based on different types of nonlinear chemical reactions such as oscillatory and turbulent reactions, the non-comparable elements often exist in the fingerprints, and the numbers of the eigenvalues of the same sort of comparable elements are not always equal to 1 or are the same. Therefore, the factors must be considered firstly when the similar degree between fingerprints is quantitatively evaluated by similarity. It is obvious from eq. (35) that, on being as non-parametric similarity, Euclidean distance can effectively reflect the differences between fingerprint characteristics because only the difference $(x_i - y_i)$ between relative signal intensities at each datum collection point must be considered in its calculation. However, on calculating parametric similarity between nonlinear chemical fingerprints, besides considering the differences between the values of the comparable parameters, the difference of types of parameters in two fingerprints and that between numbers of eigenvalues of the same type of the comparable parameters must also be considered at the same time. One of the reasons is that the parameters with different definition are not comparable each other, for example, any parameter in a fingerprint based on oscillatory reaction and the turbulent intermission time in one based on a turbulent reaction is not comparable each other. The other reason is that, in two fingerprints based on the same type of nonlinear chemical reactions, such as those based on oscillatory reactions, the sort numbers (K and L) of the parameters and the number (n) of comparable parameters are the same generally, however, for the oscillatory fingerprints of different samples, the numbers of the eigenvalues of the same comparable parameters are not always the same, for instance, the numbers of their oscillatory amplitudes or oscillatory periods are generally different. However, on calculating the parametric similarity of the fingerprints by eq. (27), it is unable to consider all of the factors at the same time. Therefore, sometimes, Euclidean distance can't correctly reflect the difference degree between the fingerprint characteristics.

Eq. (22) is the computational model of system similarity as parametric similarity. We can see from eq. (22) and its derivation that, system similarity is calculated by directing against the differences between fingerprints of samples. Comparing with correlation coefficient, included angle cosine and Euclidean distance, system similarity can express the characteristic differences between the fingerprints fully, directly or more effectively, namely can express the various differences between the fingerprints, including the type difference of the parameters, the number difference of the

comparable parameters and that of the eigenvalues of the same comparable parameters, etc. Therefore, system similarity is most suitable for quantitatively describing the difference degree between characteristics of fingerprints, especially suitable for calculating and evaluating the similarity between nonlinear chemical fingerprints.

3.11 Relationship between degrees of intuitionistic characteristic difference of nonlinear chemical fingerprint and system similarity

From Figures 2 and 3, it is obvious that there all are evident intuitionistic characteristic differences between the fingerprints of various samples. Figure 2 still shows that the change trends of the inductive and oscillating curves in fingerprints of the 4 batches of Guhan Yangshengjing are the same, and the relevant parameter values are also close to each other. From the data of Table 3, it is obvious that the system similarities of the fingerprints of different batches of Guhan Yangshengjing are all larger than 0.920, while those between the fingerprints of other samples and the fingerprint of Guhan Yangshengjing are all less than 0.595. This shows that the similarities between fingerprints of the same sort of samples are all higher, while those between fingerprints of different sorts of samples are all lower. From the fingerprints in Figures 2, 3 and the data in Table 3, it is obvious that the values of the system similarities very coincide with the difference degrees of intuitionistic characteristics of the nonlinear chemical fingerprints, that is, the larger the difference of the intuitionistic characteristic, the smaller the system similarity, and vice versa.

Summing up the above, in the methods for evaluating the similar property of nonlinear chemical fingerprint, system similarity excels Euclidean distance, and more excels the other evaluating methods. Therefore, system similarity was chosen to evaluate the similar degree of nonlinear chemical fingerprints quantitatively.

4 Conclusion

(1) Under definite determination condition, different samples have different influences on the nonlinear chemical reaction due to differences in the chemical components and their contents of the samples, resulting in the difference in the relationships of the system potentials and the time in the reaction processes. The influences not only include those on physical properties of the reaction solution, but also include those on the chemical mechanisms of nonlinear chemical reactions. They not only result in the changes of quantifiable parameters in the $E-t$ curves of nonlinear chemical reactions, but also result in those of the intuitionistic shapes of the $E-t$ curves.

(2) Not only can different changes of the shapes of the $E-t$ curves due to adding different samples into the reactor

make the relevant $E-t$ curves themselves completely vary from the $E-t$ curve of a relative simple nonlinear chemical system, namely a pure B-Z system under the same determining condition, but more importantly, they can reflect the whole characters of chemical substances in different samples. In other words, the $E-t$ curve obtained by adding a sample into the reactor may be regarded as the through characterization of the chemical components or effective components of the sample, namely the non-linear chemical fingerprint.

(3) Correlation coefficient and included angle cosine are very insensitive to the characteristic difference between nonlinear chemical fingerprints, so they are not suitable for evaluating the similarity between nonlinear chemical fingerprints. The Euclidean distance as nonparametric similarity can correctly reflect the characteristic difference between fingerprints, however, sometimes the Euclidean distance as parametric similarity can't correctly reflect the relative degree of characteristic difference between nonlinear chemical fingerprints.

(4) System similarity can correctly reflect the difference between the component characteristics of samples, and can be used to identify the sorts, sources and production batches of samples. The value of system similarity very coincides with the intuitionistic difference between nonlinear chemical fingerprints, can correctly reflect the similar degree between fingerprints, and the result to evaluate a sample by it accords with the reality of the sample.

(5) On evaluating the qualities of a sort of samples from different sources or production batches by the component quantitative information, the fingerprints with different quantitative messages of whole component contents may be obtained by the nonlinear chemical fingerprint technique, while on identifying the authenticities of samples by fingerprint similarity, the same or similar fingerprints of the samples may be obtained by adjusting their determining dosages properly. This is propitious for the standardization of fingerprint characteristic, and is very useful for the sample identification by similarity.

(6) nonlinear chemical fingerprint not only has very good reproducibility, but also contains abundant quantifiable information and intuitionistic information. They may be used to analyze the chemical components of the sample as a whole in order to identify and evaluate the sample.

(7) The nonlinear-chemical-fingerprint technique is an economical, simple and convenient, easy popularizing and effective method for identifying and evaluating complex samples. And it will play a very important role in material selection, raw recipes, standardization of production process, product quality control, crackdown on shoddy products, and so on.

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