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Detection of Dextrin Content in Milk Powder Based on Dynamic Nonlinear Chemical Fingerprint Method

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Abstract: A nonlinear chemical fingerprint method for determining the content of dextrin in milk powder was developed. Firstly, the content of dextrin in milk powder was rapidly determined by using the dynamic nonlinear chemical fingerprint method. Using sulfuric acid, manganese sulfate, acetone and sodium bromate as reaction system, the dextrin with different contents was added into milk powder as milk powder standard samples. The nonlinear chemical fingerprints of milk powder standard samples were obtained, and there was a linear relationship between inductive time or undulatory end time and the content of dextrin in milk powder standard samples, respectively. Then, the content of dextrin in milk powder was calculated by the least square method. The results showed that within 0 ~ 30% of mass fraction of dextrin, there was a good linear relationship between the content of dextrin in milk powder and inductive time or undulatory end time, the determination coefficient was 0. 997 2 ~ 0. 999 1, the recovery was 94. 00% ~ 104. 89%, the relative standard deviation was 0. 17% ~ 1. 17%, the determination range of dextrin content in milk powder was 0 ~ 30%, and the detection limit of $1.3 \times 10^{-3} \sim 4.7 \times 10^{-3}$ mg/g was obtained. The developed method was a practical and feasible method for determining the content of dextrin in milk powder, and it had advantages of good accuracy, low cost, simple operation and no sample pretreatment. In addition, the method can be used to determine the dextrin content in different batches of the same brand of milk powder or different brands of milk powder, it can also be used as an approach for the determination of other components in other complex samples.

Key words: milk powder; dextrin; linear regression method; dynamic nonlinear chemical fingerprint

0 Introduction

Milk and dairy products are important sources of nutrients for humans. The consumption of dairy products is increasing year by year. Infant formula milk powder is the most important source of nutrition for non-breastfed babies, and it is a product with fast growth in the consumption of dairy products[1]. Dextrin is a kind of food additive, is mainly used for thickening, preserving and stabilizing food structure, improving the flavor of foods. Dextrin is polymerized from several to dozens of glucose groups and is intermediate of starch decomposition products, and its molecular formula is $(C_6H_{12}O_5) \cdot 2H_2O$, but the length of carbon chain is different[2]. About milk powder with artificially added dextrin, GB10765 - 2010 "infant formula food" clearly stipulates that the appropriate amount of prepaste starch (including dextrin) added is allowed, but the excess of such substance in products is limited through lactose accounted for the total amount of carbohydrates. For 6 ~ 36 months older infants, the amount of lactose limited in the standard is not required, but the nutrient content of products must be consistent with the provisions of the standard products. Prepaste starch (including dextrin) is allowed to be added into the infant formula from the

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Codex Alimentarius, and its addition amount shall not exceed 30% of the total carbohydrates. European Union on the requirements of the prepaste starch in infant food is consistent with the provisions of the Codex Alimentarius. In United States, Canada, Australia and other countries, the use of prepaste starch has no clear provisions, as long as the content of each nutrient in infant formula meets the requirements of the product standard. Therefore, dextrin added in milk powder is not allowed to excess, but it must meet the product standards. However, due to the low price of dextrin, some manufacturers add a lot of dextrin into infant formula with no added or less added dextrin in order to obtain high profits. Excess dextrin added may increase the proportion of carbohydrate of milk powder and reduce the content of protein in milk powder. Once infants and young children eat this kind of milk powder, which can lead to children's protein intake too little, malnutrition and affect their growth and development. Based on the above discussion, it is necessary for the determination of dextrin content in milk powder.

At present, detection methods of dextrin in dairy products have color rendering method, absorbance method, hydrolysis method of reducing sugar, spectrum method, test paper method, etc. Pretreatment of these methods is complicated, and the operation is cumbersome. Thus, it is necessary to explore a simple and low-cost method without separate and purify of samples for determining dextrin in milk powder.

Nonlinear chemical fingerprinting, as a new type of fingerprint technology, is a kind of dynamic full spectrum with abundant qualitative and quantitative information because of its dynamic characteristics. Its reactions include chemical turbulence, chemical oscillation, chemical wave and chemical pattern. The reactions phenomena have attracted the attention of many scholars [3-12]. Nonlinear chemical fingerprinting technology is used to identify the authenticity of the samples and to evaluate the quality of the products, which is few reported abroad, and most of the studies have been found in China. The proposed technology can be used to identify and evaluate complex samples, such as drugs and foods. The method is easy to operate, and has great advantages in the selection of materials and technological process. Up to now, using "sulfuric acid – manganese sulfate – acetone – sodium bromate" as reaction system, many research results have been reported by nonlinear chemical fingerprint technique, such as studying on the detection conditions, characteristics and application of nonlinear chemical fingerprint technology[3], identification of goat, cow's milks and their origins by nonlinear electrochemical fingerprint technique[13], simultaneous determining content of cow and mare milks mixed with goat milk[14] and determining calcium content in milk powder[15]. Meanwhile, there is no nonlinear chemical fingerprint reported in analysis of dextrin in milk powder.

Therefore, in this study, using "sulfuric acid – manganese sulfate – acetone – sodium bromate" as reaction system, a quantitative evaluation model is established between dextrin content in milk powder and the characteristic parameters by nonlinear chemical fingerprint technique and least square method. Quantitative analysis and quality evaluation of dextrin in infant formula is studied by using this model.

1 Materials and methods

1.1 Reagents and instruments

Sulfuric acid (1.00 mol/L), acetone (1.00 mol/L), sodium bromate (0.80 mol/L), manganese sulfate (0.08 mol/L) and dextrin were used. All the chemicals used were of analytical reagent grade. Double distilled water was used throughout. In this work, three brands of milk powder provided by the Institute of Product Quality Supervision and Inspection in Shaanxi Province were referred to as milk powder 1#, milk powder 2# and milk powder 3#, respectively. The different batch of the same brand of milk powder 3# was referred to as milk powder 4#.

Preparation of standard milk powder samples: a brand of seven standard milk powder 1# samples was spiked with known levels of dextrin, namely, dextrin content in milk powder 1# samples was 0, 5%, 10%, 15%, 20%, 25% and 30%, respectively. The total dosage of each mixed milk powder sample was 1.0 g. Preparations of standard milk powder 2# sample, 3# and 4# are consistent with standard milk powder 1# sample.

A nonlinear chemical fingerprint instrument (Model

MZ-1B-2) developed by Central South University and Xiangtan Ltd. was used. A Type 217 calomel electrode was used as reference electrode and a Type 213 platinum electrode was used as working electrode (both were purchased from Shanghai Precision & Scientific Instrument Co., China). Electronic balance (Model BS 224S) was purchased from Shanghai Precision & Scientific Instrument Co., China.

1.2 Experimental method

1.2.1 Measurement of quantitative information of standard samples and the establishment of regression model

Totally seven standard milk powder 1# samples were detected, respectively. The total dosage of each mixed milk powder sample was 1.0 g. The nonlinear chemical reaction mixture was prepared by mixing of 25 mL of sulfuric acid, 12 mL of manganese sulfate, 15 mL of acetone, 10 mL of double distilled water and 1.0 g of milk powder sample. All components of reaction mixture was added into the reactor. The reactor cover with two injection holes, the electrodes and a thermometer was closed. The instrument was then turned on, with temperature and stirring rate adjusting to 50℃ and 800 r/min, respectively. After stirring for 3 minutes, 5 mL of sodium bromate solution was injected into the reactor. Electric potential-time ($E-t$) curve was immediately obtained and finished as soon as the potential oscillation disappeared. Quantitative parameter of nonlinear chemical fingerprint of milk powder such as inductive time, maximum amplitude and undulatory end time were determined by Matlab software, and a linear regression model was established between dextrin content in milk powder and quantitative parameter by using the least square method.

1.2.2 Determination of unknown sample

1.0 g milk powder sample was accurately weighed and added to the reactor, according to Section 1.2.1 experiment method, the fingerprint of milk powder was obtained. Inductive time and undulatory end time were determined by Matlab software, and dextrin content was calculated through a linear regression model established.

2 Analysis principle of nonlinear chemical fingerprinting technique

2.1 Experimental principle

According to the principle of chemical oscillation, in the acidic medium and under the closed condition, acetone, BrO_3^- and Mn^{2+} are organic substrate, the oxidant and the catalyst, respectively, which forms a stable "H_2SO_4—CH_3COCH_3—$MnSO_4$—$NaBrO_3$" oscillation system. $HBrO_2$ has a self catalytic effect in the reaction process, and its formation and disappearance affect the change of BrO_3^- further reduction product Br^- and metal ion oxidation product Mn^{3+} concentration. When the consumption of Br^- concentration and accumulation of Mn^{3+} concentration achieve a certain value, a series of oxidation-reduction reaction can be caused in the system. When the accumulation of Br^- concentration and consumption of Mn^{3+} concentration achieve a certain value, a series of oxidation-reduction reaction also can be caused in the system. Thus, the periodic variation of the redox value in the system is formed[16]. In the closed system, the oscillation will eventually stop when the energy in the system is constantly dissipated without external energy supplement. Due to differences of compositions and content of different brands of milk powder, compositions of the reaction substrate are changed when milk powder is added to this oscillation system, which will play a role in promoting or inhibiting the oscillation system. Because of the differences oxidation reduction of chemical composition in different brands of milk powder, effect of promotion or inhibition the oscillation system is different. Therefore, the shape and the quantitative information of nonlinear chemical fingerprint in the corresponding milk powder are different.

2.2 Basic information and reproducibility of nonlinear chemical fingerprint of milk powder

Nonlinear chemical fingerprint contained abundant intuitive information and quantitative information. Intuitive information contained inductive curve, oscillatory curve, wave crest shape and potential drift curve, etc. Quantitative information was also the characteristic parameter, which included inductive time (t_{ind}), oscillatory start potential (E_{uns}), canyon potential (E_{can}), canyon time (t_{can}), peak top potential (E_{pet}), peak top time (t_{pet}), oscillatory end potential (E_{une}), undulatory end time (t_{une}), equilibrium potential (E_{equ}), equilibrium time (t_{equ}), fluctuation range (ΔE_{und}), maximum amplitude (ΔE_{max}), wave number (n_{wav}), undulatory period (τ_{und}), undulatory life (t_{und}), etc[14-15]. The 0.9 g of milk powder 1# sample without dextrin was added to the reactor, according to Section 1.2.1 experiment method, the fingerprint of milk powder 1# sample was obtained. As shown in Fig. 1 the $e-f$ segment was named as inductive curve, and the $f-g$ segment was named as fluctuation curve. The e and h were the start and end points of reaction, respectively[15]. All of them were described in detail in the literature [3]. Influence of the substances and their concentration in the reaction system on nonlinear chemical fingerprint was reported in the literature [15].

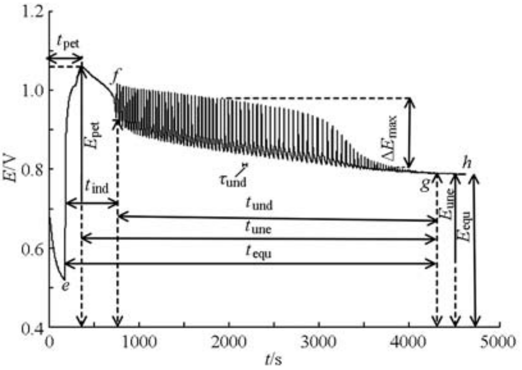


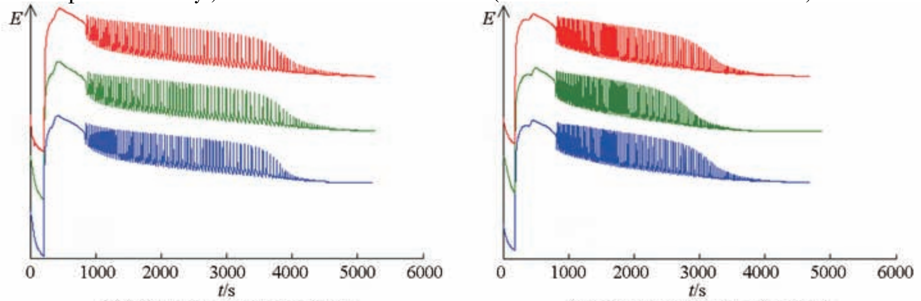
Fig. 1 Basic characteristic information of nonlinear chemical fingerprint of milk powder 1

In the same test conditions, according to Section 1.2.1 experiment method, nonlinear chemical fingerprints of milk powder 1# without dextrin and milk powder 1# with artificially added 15% dextrin were obtained, andthree repeated measurements of each sample were carried out. The nonlinear chemical fingerprints of two kinds of milk powder had good characteristics and reproducibility, and it could be seen from Fig. 2. Because of difference of species and concentration in milk powder, their fingerprints show corresponding differences. When differences of composition and concentration of milk powder are greater, differences of characteristic information of corresponding fingerprints are also greater. On the contrary, differences of corresponding fingerprints are smaller. Based on this, characteristic difference of nonlinear chemical fingerprint is only related to species and concentration of milk powder.

If adulterations in milk powder exist, the content of original constituents in milk powder is changed, which results in difference of corresponding fingerprint. It was obvious from Fig. 2a that the concave at left side for inductive curve of nonlinear chemical fingerprint of milk powder 1# without dextrin was smaller. In comparison, Fig. 2b indicated that the concave at left side for inductive curve of nonlinear chemical fingerprint of milk powder 1# with artificially added 15% dextrin was larger than the former. Therefore, milk powder 1# without dextrin and milk powder 1# with artificially added 15% dextrin could be distinguished from characteristic differences of their nonlinear chemical fingerprints. At the same time, good reproducibility and characteristics of nonlinear chemical fingerprint provided necessary conditions for quantitative analysis of adulterated milk powder.

2.3 Quantitative determination of dextrin content in milk powder

Due to difference of species and concentration in different brands of milk powder, the fingerprint of milk powder showed the corresponding differences when different amounts of dextrin were added to milk powder. According to the actual samples, a linear relationship might be established between dextrin content in milk powder and quantitative information (such as inductive time, undulatory end time,



(a) Milk powder 1# without dextria

(b) Milk powder 1# with15% dextria

Fig. 2 Reproducibility and characteristic difference of nonlinear chemical fingerprints of milk powder 1 undulatory period or maximum amplitude), which was decided based on determining kinetic information of nonlinear chemical reaction of samples by using nonlinear chemical fingerprint. In this paper, milk powder 1# samplewas analyzed by nonlinear chemical fingerprint method. There was a good linear relationship between dextrin content in milk powder and inductive time when dextrin content was in the range of 0 ~ 30%. It could be seen from the curve a in Fig. 3. When dextrin content exceeded 30%, it could lead to deviation from the linear relationship. It could be seen from the curve b in Fig. 3.

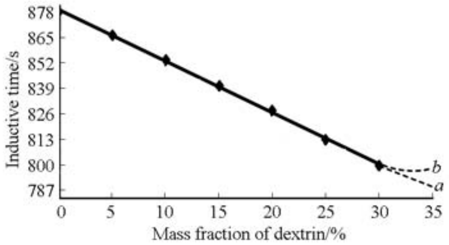


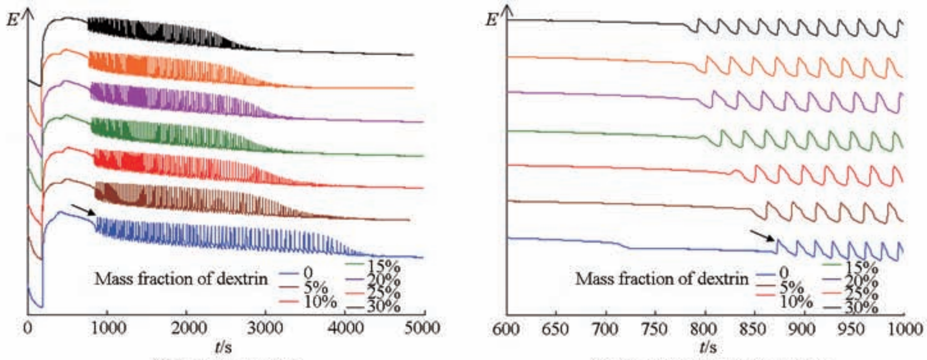
Fig. 3 Effects of dextrin content in milk powder 1 on inductive time of nonlinear chemical fingerprint

Fingerprint characteristics of mixed milk powder and characteristics of pure milk powderwere significantly different when milk powder with different content of dextrin. Therefore, in this study, nonlinear chemical fingerprints of milk powder with artificially added dextrin were obtained, and the corresponding milk powder was distinguished and evaluated by using the linear regression model between dextrin content in milk powder and characteristic parameter.

3 Results and discussion

3.1 Effect of different amount of additive on characteristic information of nonlinear chemical fingerprint of milk powder

According to Section 1.2.1 experiment method, 1.0 g of milk powder 1# samples were prepared and analyzed. Effects of dextrin content on characteristic information of nonlinear chemical fingerprint of milk powder 1# were shown in Fig. 4. The position of induction time for each fingerprint was indicated by a black arrow. Fig. 4b was the local inductive and undulatory curve of corresponding nonlinear chemical fingerprint in milk powder 1# in the range of 600 ~ 1 000 s. With the increase of dextrin content, induction time of corresponding fingerprint was gradually shortened. At the same time, different first peak time of each fingerprint was different. Due to the increase of dextrin content, the composition of reaction substrate was changed. Effect of dextrin content on inhibition of nonlinear chemical reaction was gradually weakened, which led to the different corresponding induction time.



(a) Integral graphics (b) Corresponding local graphics

Fig. 4 Effects of dextrin content on inductive time of nonlinear chemical fingerprint of milk powder 1

Alinear relationship between dextrin content in milk powder 1 # and inductive time was obtained when dextrin content was in the range of 0 ~ 30% (Fig. 5). The information provided necessary condition for determination of dextrin content in milk powder.

3.2 Determination of dextrin content in milk powder by nonlinear chemical fingerprint method

In this study, the experimental method of 1.2.1 was used, and nonlinear chemical fingerprints of milk powder 1# with artificially added dextrin were obtained by nonlinear chemical fingerprint method. Mass fraction C of dextrin in milk powder could be calculated on the basis of the linear relationship between dextrin content in milk powder and inductive time through the corresponding fitting equations in Fig. 5, and the results were showed in Tab. 1.

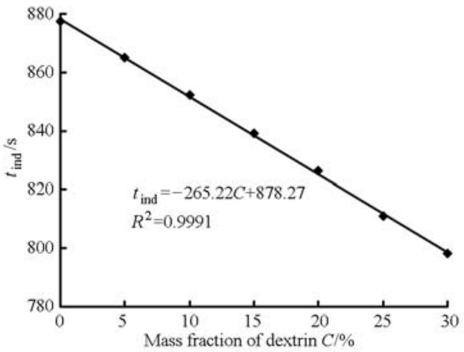


Fig. 5 Linear relationship between dextrin content in milk powder 1 and inductive time of nonlinear chemical fingerprint

As observed from Tab. 1, the relative standard deviation (RSD) of all samples was less than or equal to 1.17%, indicating a higher precision. The recovery rate was between 94.00% and 104.89%, and it indicated that the method had better accuracy. The results confirmed that the method could be applied to detection of dextrin in milk powder and further indicated that it provided the basis for evaluation and detection of other components in samples.

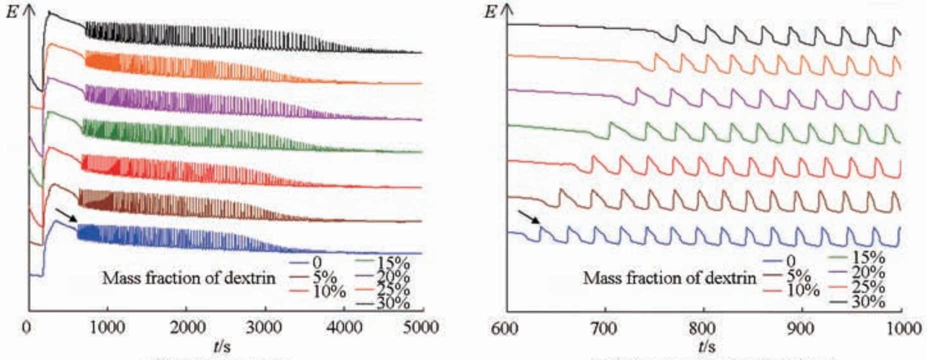
Tab. 1 Results of dextrin content in milk powder 1 by nonlinear chemical fingerprint method

Samples No.	t_{ind}/s	Regression equation	Found/%	Actual value/%	RSD/%	Recovery/%	Evaluation results
1	878.15	$t_{ind}=-265.22C+878.27$	0.045	0	0.29		Pure milk powder
2	876.64		0.610	0.60	0.38	101.67	Pure milk powder
3	875.79		0.940	1.00	0.95	94.00	Pure milk powder
4	830.66		17.950	18.00	0.59	99.72	17.95% dextrin
5	821.99		21.220	21.00	1.17	101.05	21.22% dextrin
6	800.38		29.370	28.00	1.01	104.89	29.37% dextrin

3.3 Verification experiment

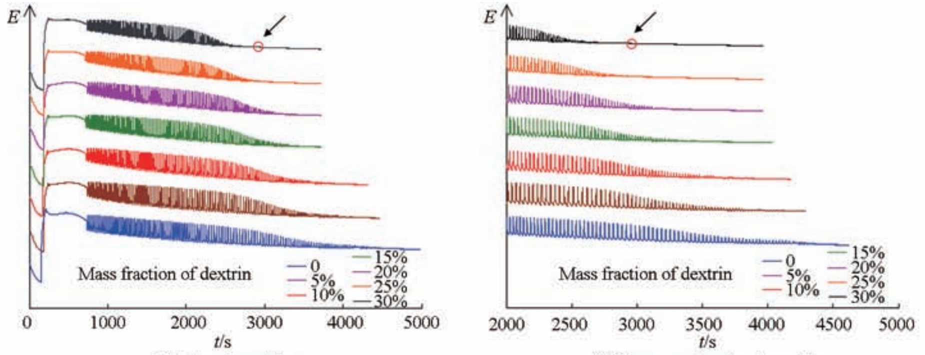
To further verify the feasibility and reliability of the proposed method, milk powder 2#, milk powder 3# and milk powder 4# were spiked with different content of dextrin, namely, dextrin content added in corresponding milk powder was 6%, 13% and 22%, respectively. The experimental method of Section 1.2.1 was used, and the experiments were carried out in triplicate. The total dosage of each mixed milk powder sample was 1.0 g. Effects of dextrin content on characteristic information of nonlinear chemical fingerprint of milk powder 2# and milk powder 3# were shown in Fig. 6 and Fig. 7, respectively. The linear relationships between dextrin content in corresponding milk powder and inductive time, undulatory end time were shown in Fig. 8 when dextrin content in milk powder 2# and milk powder 3# were in the range of 0 ~ 30%. The regression equations were $t_{ind}=513.22C+631.93$ and $t_{une}=-5\,583C+4\,572.9$, respectively. The coefficients of determination R^2 were 0.997 2 and 0.998 1, respectively. Dextrin content in milk powder 2#, milk powder 3# and milk powder 4# was calculated by corresponding regression equations, respectively, which was shown in Tab. 2.

The results showed that the proposed method was feasible for determining dextrin content in milk powder. At the same time, the regression equation established was applied as a permanent calibration model for the same brand of milk powder. Dextrin content in different batches of the same brand of milk powder could be calculated as long as characteristic parameter of corresponding milk powder was determined under the same experimental condition by using corresponding regression equation, and milk



(a) Integral graphics (b) Corresponding local graphics

Fig. 6 Effects of dextrin content on inductive time of nonlinear chemical fingerprint of milk powder 2



(a) Integral graphics (b) Corresponding local graphics

Fig. 7 Effects of dextrin content on undulatory end time of nonlinear chemical fingerprint of milk powder 3

powder quality could be analyzed and identified. For example, undulatory end time of milk powder 4# with artificially added 6%, 13% and 22% dextrin was obtained by nonlinear chemical fingerprint method, respectively, and they were substituted into the fitting equation of milk powder 3#, namely, $t_{une} = -5\,583C + 4\,572.9$. The results were shown in Tab. 2. Nonlinear chemical fingerprints of corresponding milk powder 4# were shown in Fig. 9, respectively. The results indicated that the method could be applied to detection dextrin content in different batches of the same brand of milk powder.

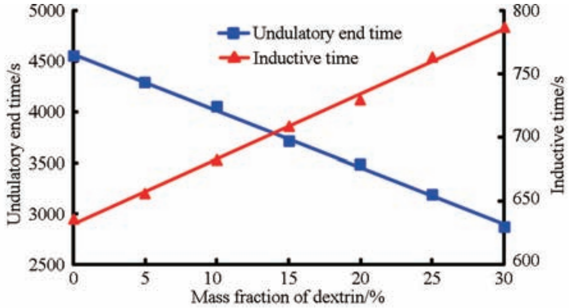
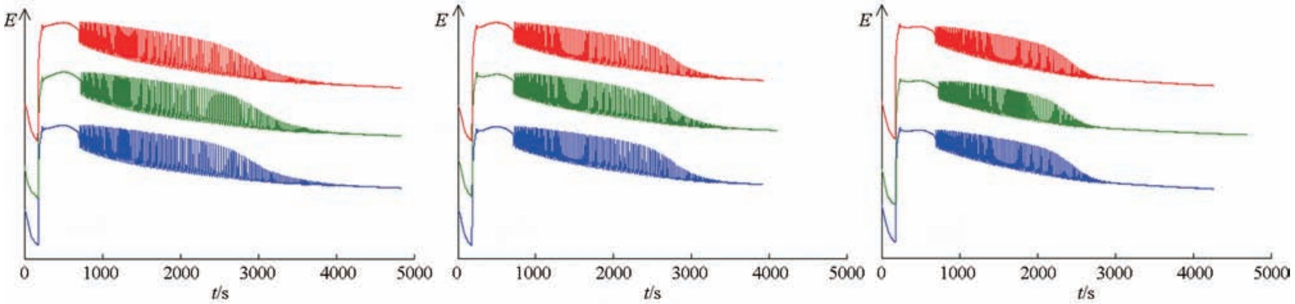


Fig. 8 Linear relationship between dextrin content in milk powder and quantitative information of nonlinear chemical fingerprint

Tab. 2 Results of dextrin content in milk powder by nonlinear chemical fingerprint method

Sample	t_{ind}/s	Found/%	Actual value/%	RSD/%	Recovery/%	Evaluation results
Milk powder 2#	662.66	5.99	6.00	0.38	99.83	5.99% dextrin
	693.31	11.96	13.00	0.67	99.67	11.96% dextrin
	746.27	22.28	22.00	0.81	101.27	22.28% dextrin
Milk powder 3#	4242.60	5.92	6.00	0.23	98.67	5.92% dextrin
	3867.86	12.63	13.00	0.95	97.15	12.63% dextrin
	3340.59	22.07	22.00	0.17	100.32	22.07% dextrin
Milk powder 4#	4222.85	6.27	6.00	0.77	104.50	6.27% dextrin
	3840.97	13.11	13.00	0.30	100.85	13.11% dextrin
	3361.95	21.69	22.00	0.29	98.59	21.69% dextrin



(a) Milk powder 4# with 6% dextrin (b) Milk powder 4# with 13% dextrin (c) Milk powder 4# with 22% dextrin

Fig. 9 Effects of dextrin content on nonlinear chemical fingerprints of milk powder 4

3.4 Detection range and limit of detection of dextrin content in milk powder

The amount of dextrin in milk powder is generally not more than 20% in the market, namely, per 100 g of milk powder is not more than 20 g. In this study, mass fraction of dextrin is in the range of 0 ~ 30%, namely, per 100 g of milk powder with dextrin of 0 ~ 30 g can be detected. According to the calculation method of detection limit[17-20], in this study, milk powder 1#, milk powder 2# and milk powder 3# were analyzed, and eight repeated measurements of each sample were carried out. Detection limits of three kinds of milk powder were shown in Tab. 3. As observed from Tab. 3, the detection limits for milk powder with artificially added dextrin were greater than or equal to 1.3×10^{-3} mg/g, and determined results had high confidence level. In fact, the amount of dextrin in milk powder is generally more than 10 mg/g in the market[21]. Therefore, milk powder is referred to pure milk when the amount of dextrin in milk powder is less than or equal to 10 mg/g. Based on the above discussion, the proposed method was feasible for quantitative analysis and quality evaluation of milk powder with artificially added dextrin by using nonlinear chemical fingerprint method, and had high accuracy and precision. The detection range was in the range of 0 ~ 30%, and detection limit was 1.3×10^{-3} ~ 4.7×10^{-3} mg/g. In addition, the method also provided a basis for detection of milk powder with artificially added dextrin.

Tab. 3 Detection limits of dextrin content in milk powder

Sample	Temperature/℃	Dextrin content in the lowest concentration/mg	Mean value of response signal/s	Standard deviation	Detection limit/($mg \cdot g^{-1}$)
Milk powder 1#	50	1.00	878.28	0.75	2.6×10^{-3}
Milk powder 2#	50	1.00	633.98	0.99	4.7×10^{-3}
Milk powder 3#	50	1.00	4577.80	1.91	1.3×10^{-3}

4 Conclusions

(1) Milk powder with artificially added dextrin was quantitative analyzed by using "sulfuric acid-manganese sulfate-acetone-sodium bromate" reaction system. A quantitative relation was established between dextrin content in milk powder and quantitative parameters of nonlinear chemical fingerprint of corresponding milk powder (such as inductive time and undulatory end time), and dextrin content in milk powder could be detected by firstly established regression equation.

(2) Experimental results showed that the proposed method had higher precision and accuracy. The method could not only be used to determine dextrin content in different brands of milk powder or different batches of the same brand of milk powder, but also be used to determine the content of other substances in complex samples. At the same time, the established regression equation was applied as a permanent calibration model instead of the long-term preservation of standard milk powder sample. Dextrin content in different batches of the same brand of milk powder could be calculated as long as characteristic parameter of corresponding milk powder was determined by using corresponding regression equation, and milk powder quality could be analyzed and identified.

(3) In the study, the proposed method had the advantages of simple operation, without sample pretreatment and low cost. The method provided a kind of new approach for detecting dextrin content in milk powder.

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基于动态指纹图谱的奶粉中糊精添加量检测方法

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摘要： 采用动态非线性化学指纹图谱法对奶粉中添加的糊精进行定量分析。利用“硫酸-硫酸锰-丙酮-溴酸钠”为振荡体系，先向奶粉中添加不同量的糊精，配成掺杂糊精的奶粉标样。通过非线性化学指纹图谱法对奶粉标样进行测定，运用最小二乘法，分别拟合其诱导时间和停波时间相对于奶粉中添加糊精含量之间的一元线性关系，可求出奶粉中添加的糊精含量。实验表明，当奶粉中添加的糊精质量分数在0~30%范围内时，糊精含量与诱导时间及停波时间线性关系良好，决定系数 R^2 为0.997 2~0.999 1，回收率为94.00%~104.89%，相对标准偏差为0.17%~1.17%，检测范围为0~30%，检出限为 $1.3\times10^{-3}\sim4.7\times10^{-3}$ mg/g。方法准确度高，操作简单，是一种切实可行的测定奶粉中添加糊精的方法，也可作为复杂样本中其他成分定量分析借鉴的方法。

关键词： 奶粉；糊精；线性回归法；动态非线性化学指纹图谱

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Detection of Dextrin Content in Milk Powder Based on Dynamic Nonlinear Chemical Fingerprint Method

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Abstract: A nonlinear chemical fingerprint method for determining the content of dextrin in milk powder was developed. Firstly, the content of dextrin in milk powder was rapidly determined by using the dynamic nonlinear chemical fingerprint method. Using sulfuric acid, manganese sulfate, acetone and sodium bromate as reaction system, the dextrin with different contents was added into milk powder as milk powder standard samples. The nonlinear chemical fingerprints of milk powder standard samples were obtained, and there was a linear relationship between inductive time or undulatory end time and the content of dextrin in milk powder standard samples, respectively. Then, the content of dextrin in milk powder was calculated by the least square method. The results showed that within 0~30% of mass fraction of dextrin, there was a good linear relationship between the content of dextrin in milk powder and inductive time or undulatory end time, the determination coefficient was 0.997 2~0.999 1, the recovery was 94.00%~104.89%, the relative standard deviation was 0.17%~1.17%, the determination range of dextrin content in milk powder was 0~30%, and the detection limit of $1.3\times10^{-3}\sim4.7\times10^{-3}$ mg/g was obtained. The developed method was a practical and feasible method for determining the content of

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dextrin in milk powder, and it had advantages of good accuracy, low cost, simple operation and no sample pretreatment. In addition, the method can be used to determine the dextrin content in different batches of the same brand of milk powder or different brands of milk powder, it can also be used as an approach for the determination of other components in other complex samples.

Key words: milk powder; dextrin; linear regression method; dynamic nonlinear chemical fingerprint

引言

乳及乳制品是人体重要的营养来源，乳品的消耗在逐年增加，尤其婴幼儿配方奶粉，它是非母乳喂养婴儿最重要的营养来源[1]，已成为我国乳制品消费中增长速度较快的产品。糊精是食品添加剂的一种，主要用于增稠、保型、稳定食物结构、改善食物风味等。它由几个至几十个葡萄糖基聚合而成，是淀粉的中间分解产物，分子通式为$(C_6H_{12}O_5)\cdot 2H_2O$，但是碳链长短不一定相同[2]。在奶粉中添加糊精，GB10765—2010《婴儿配方食品》中明确规定，允许适量添加预糊化淀粉（包括糊精），但通过对乳糖占碳水化合物总量的要求来限制产品中该类物质的过量添加，针对 6 ~ 36 月龄较大婴幼儿，标准中没有对乳糖限量作出要求，但规定产品各营养成分含量必须与产品标准的规定一致。国际食品法典规定婴儿配方中允许添加预糊化淀粉（包括糊精），加入量不超过总碳水化合物的 30%。欧盟关于婴幼儿食品中预糊化淀粉的添加要求，与国际食品法典的规定相一致。美国、加拿大和澳大利亚等国家则对于预糊化淀粉的使用没有明确规定，婴幼儿配方食品中各营养成分含量符合产品标准的要求即可。因此，在奶粉中对于糊精的添加或者不允许过量添加，必须符合产品标准。然而，由于糊精价格低廉，于是一些厂家为了谋求高额利润，在一些不应该添加或者应该少添加糊精的配方乳粉中加入了大量糊精，而过量的糊精添加会增加奶粉中碳水化合物的比例，从而降低奶粉中蛋白质的含量，如果婴幼儿长期食入这种奶粉，会导致幼儿蛋白质摄入过少，从而导致营养不良，影响其生长发育。基于此，对奶粉中糊精含量的测定是非常必要的。

目前乳品中糊精的检测方法主要有显色法、吸光度法、水解测还原糖法、光谱法和试纸法等，这些方法前期预处理复杂、操作繁琐。为此，探索一种既简单、低成本，又无须分离和提纯的奶粉中添加糊精测定方法十分必要。

非线性化学指纹图谱作为一种新型的指纹图谱技术，因其具有动力学的特性，是一种含有丰富定性定量信息的动态全谱，其反应包括化学湍流、化学振荡、化学波和化学斑图等，已受到众多学者的关注[3-12]，但采用非线性化学指纹图谱技术鉴别样本真伪和评价产品质量，国外鲜有报道，多数应用研究见于国内。此技术可以用来鉴别和评价像药品和食品这类复杂的样本，并且操作简单，在材料选用和工艺流程等方面具有很大的优越性。目前，采用非线性化学指纹图谱技术，利用“硫酸-硫酸锰-溴酸钠-丙酮”为振荡体系，已报道了许多研究成果，如对非线性化学指纹图谱的检测方法、条件、特点和应用的研究[3]，采用非线性电化学指纹图谱技术鉴别羊奶和牛奶及其产地[13]，羊奶中同时掺杂的牛奶和马奶含量的测定[14]，以及奶粉中钙含量的测定等[15]，但采用该振荡体系来检测奶粉中添加的糊精鲜有报道。

本文以“硫酸-硫酸锰-溴酸钠-丙酮”为振荡体系，采用动态指纹图谱技术，即非线性化学指纹图谱方法，利用最小二乘法建立特征参数与掺杂糊精含量之间的定量评价模型，对婴幼儿配方奶粉中添加的糊精进行定量分析和质量评价。

1　材料与方法

1.1　试剂和仪器

1.00 mol/L 硫酸、1.00 mol/L 丙酮、0.80 mol/L 溴酸钠、0.08 mol/L 硫酸锰溶液和糊精。以上试剂均为分析纯，水为二次蒸馏水。所用某品牌奶粉（以下简称“奶粉”）由陕西省产品质量监督检验研究所提供。3 种品牌奶粉样品分别为 1 号、2 号、3 号，其中与 3 号奶粉同品牌不同批次的奶粉以下简称为 4 号奶粉。

奶粉标准样品系列配制：取 7 份 1 号奶粉，分别加入 0、5%、10%、15%、20%、25%、30% 的糊精，配成掺杂糊精的奶粉标样，每份标样的总量为 1.0 g。2 号奶粉、3 号奶粉和 4 号奶粉添加糊精的奶粉标样的配制方法同 1 号奶粉。

MZ－1B－2 型非线性化学指纹图谱测定仪，湖南尚泰测控科技有限公司；217 型复合甘汞电极和 213 型金属铂电极，上海精密科学仪器有限公司；BS 224 S 型电子天平，上海精密科学仪器有限公司。

1.2　实验方法

1.2.1　标样定量信息测定与回归方程模型建立

取 1.0 g 上述 1 号奶粉 7 个标样于反应器中，分

别加入 25 mL 硫酸、12 mL 硫酸锰溶液、15 mL 丙酮和 10 mL 蒸馏水。盖好带注射孔和电极的反应器盖。打开恒温系统调节反应器，温度设为 50℃，恒速搅拌转速设定为 800 r/min，点击菜单采集数据，搅拌到 3 min 时用注射器迅速加入 5.00 mL 溴酸钠溶液。记录 $E-t$ 曲线至电位 E 不再随时间 t 变化为止。奶粉指纹图谱的定量参数如诱导时间、最大波幅和停波时间等由 Matlab 软件导出。采用最小二乘法来建立定量参数与添加糊精含量之间的一元线性回归模型。

1.2.2　未知试样的测定

准确称取 1.0 g 奶粉样品于反应器中，按照 1.2.1 节的实验方法，测定指纹图谱，利用 Matlab 软件导出所测奶粉指纹图谱的诱导时间和停波时间，通过所建立的一元线性回归模型计算奶粉中添加的糊精含量。

2　非线性化学指纹图谱技术的分析原理

2.1　实验原理

根据化学振荡原理，在酸性介质中，在封闭条件下，丙酮为有机底物，BrO_3^- 为氧化剂，Mn^{2+} 为催化剂，构成稳定的 $H_2SO_4-CH_3COCH_3-MnSO_4-NaBrO_3$ 振荡体系。在反应过程中，$HBrO_2$ 具有自催化作用，它的生成与消失影响着 BrO_3^- 的进一步还原产物 Br^- 和金属离子氧化产物 Mn^{3+} 浓度的变化，随着 Br^- 浓度消耗和 Mn^{3+} 浓度累积至一定值，能引发体系一系列氧化-还原反应的发生，当 Br^- 浓度累积和 Mn^{3+} 浓度消耗至一定值时，同样引发体系一系列氧化-还原反应的发生，于是形成体系氧化还原值的周期性变化[16]。在封闭体系中，没有外界能量的补充，随着体系内能量不断耗散，振荡最终停止。由于不同品牌的奶粉组成成分和含量不同，当将其加入到此振荡体系时，使反应底物的组分发生改变，从而对振荡体系会起到促进或抑制作用。不同品牌奶粉因其化学成分的氧化还原性存在差异，其促进或抑制作用不同，因此所得相应奶粉的非线性化学指纹图谱的形状和可量化信息存在差异。

2.2　奶粉非线性化学指纹图谱的基本信息和重现性

非线性化学指纹图谱拥有丰富的直观信息和可量化信息，其直观信息中包含诱导曲线、波动曲线、波峰形状和电位漂移曲线等；而可量化信息即特征参数包含诱导时间 t_{ind}、起波电位 E_{uns}、峰谷电位 E_{can}、峰谷时间 t_{can}、峰顶电位 E_{pet}、峰顶时间 t_{pet}、停波电位 E_{une}、停波时间 t_{une}、平衡电位 E_{equ}、平衡时间 t_{equ}、波动幅度 ΔE_{und}、最大波幅 ΔE_{max}、波数 n_{wav}、波动周期 τ_{und} 和波动寿命 t_{und} 等[14-15]，按照 1.2.1 节的实验方法，称取 0.9 g 未加糊精 1 号奶粉样品与反应器中，测得其非线性化学指纹图谱如图 1 所示。图中 $e \sim f$ 段为诱导曲线，$f \sim g$ 段为波动曲线，e 和 h 分别为非线性化学反应的起点和终点[15]。各种特征参数的含义参照文献[3]。反应体系中各物质及其浓度对非线性化学指纹图谱的影响参照文献[15]。

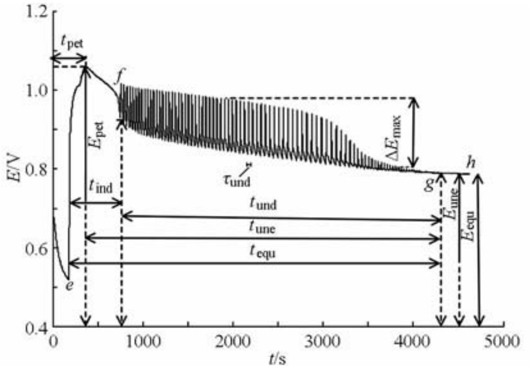


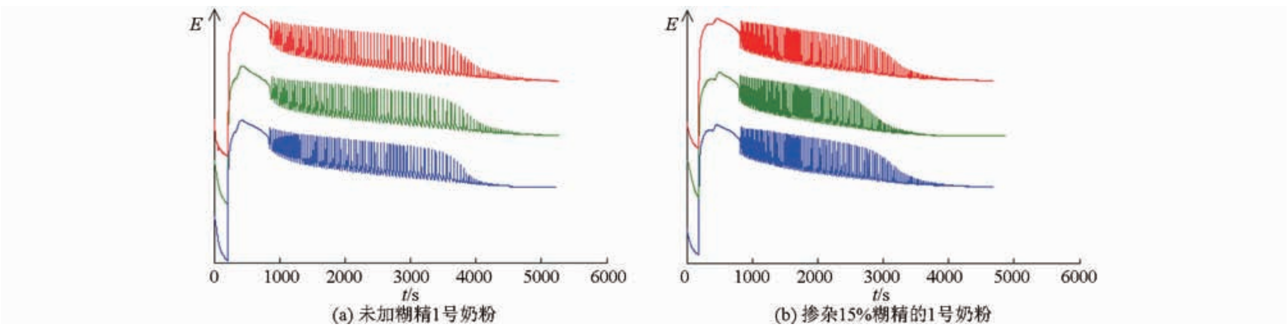
图 1　未加糊精 1 号奶粉非线性化学指纹图谱的基本特征信息

Fig. 1　Basic characteristic information of nonlinear chemical fingerprint of milk powder 1

在同一检测条件下，按 1.2.1 节的实验方法，测定了未加糊精 1 号奶粉和添加糊精 15% 的 1 号奶粉的非线性化学指纹图谱，各样本平行测定 3 次。图 2 表明，2 种奶粉非线性化学指纹图谱均有很好的特征性和重现性。奶粉因其成分的种类和浓度差异，其指纹图谱表现出相应的差异。奶粉的成分及其浓度的差异越大，其指纹图谱特征信息的差异就越大；反之，相应指纹图谱的差异就越小。基于此，利用非线性化学指纹图谱技术所测得的指纹图谱特征差异性，仅与奶粉的成分种类和含量有关。如果奶粉中存在掺杂成分，则改变了奶粉原有的成分含量，从而导致相应的指纹图谱存在一定的差别。由图 2a 可知，未加糊精 1 号奶粉的诱导曲线轮廓左端下凹现象较小；相比较而言，由图 2b 可知，添加糊精 15% 的 1 号奶粉的诱导曲线轮廓左端下凹现象较前者大。因此，直接利用这些指纹图谱明显的直观特征差异就可将未加糊精 1 号奶粉与添加糊精 15% 的 1 号奶粉区别开，同时其良好的重现性和特征性为掺杂定量分析提供了必要条件。

2.3　奶粉添加糊精定量测定

由于不同品牌奶粉的成分种类和含量存在差异，当添加不同量糊精时，相应的奶粉指纹图谱表现出相应的差异。其定量信息如诱导时间、停波时间、波动周期或最大波幅等与奶粉中糊精含量之间可能呈线性关系，这要根据实际样品，利用非线性化学指纹图谱技术测定其非线性化学反应的动力学信息之后来决定。本文以 1 号奶粉为检测样本进行实验，



(a) 未加糊精1号奶粉　　(b) 掺杂15%糊精的1号奶粉

图 2　1 号奶粉的非线性化学指纹图谱的重现性和特征差异

Fig. 2　Reproducibility and characteristic difference of nonlinear chemical fingerprints of milk powder 1

实验结果表明，当糊精质量分数在 0～30% 时，1 号奶粉指纹图谱的定量参数诱导时间与糊精含量呈良好的线性关系，如图 3 中的曲线 *a*。当糊精质量分数超过 30% 时，就不呈线性，如图 3 中曲线 *b* 所示。

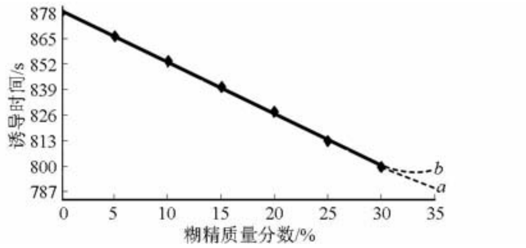


图 3　1 号奶粉中添加的糊精含量对非线性化学指纹图谱诱导时间的影响

Fig. 3　Effects of dextrin content in milk powder 1 on inductive time of nonlinear chemical fingerprint

当奶粉和不同含量的糊精互掺时，其混合奶粉指纹图谱特征与纯品的特征明显不同。为此，本文通过向奶粉中添加不同含量的糊精，测定混合奶粉的指纹图谱，利用这些指纹图谱的特征参数与混合奶粉中糊精含量之间的线性回归关系模型，对相应奶粉进行鉴别和定量评价。

3　实验结果分析

3.1　不同添加量对奶粉指纹图谱特征信息的影响

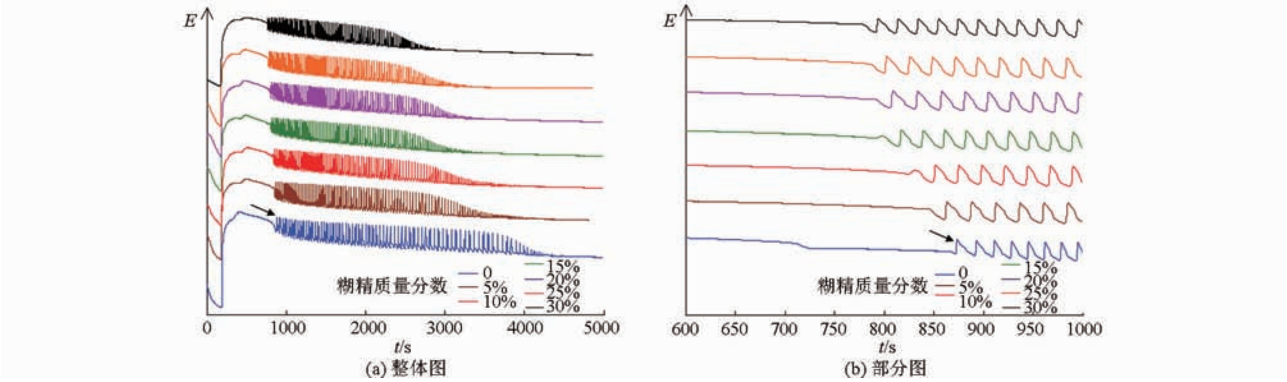
准确称量 1.00 g 的 1 号奶粉 7 个标样，按 1.2.1 节的实验方法测定其指纹图谱。1 号奶粉中糊精添加量对指纹图谱特征信息的影响见图 4，图中箭头表示诱导时间的位置。图 4b 是图 4a 相应指纹图谱分别在 600～1 000 s 时的部分诱导曲线和波动曲线图，由图 4b 可知，随着糊精量的增加，相应的指纹图谱的诱导时间在逐渐缩短，同时每个图谱第 1 个出峰时间是不同的，如箭头所示。这是因为随着糊精添加量的增加，反应底物组分发生改变，糊精含量对非线性化学反应的抑制作用在减弱，从而导致相应的诱导时间存在差异。

当奶粉中添加的糊精质量分数在 0～30% 范围时，1 号奶粉的非线性化学指纹图谱的特征参数诱导时间与相应奶粉中添加糊精的含量之间呈良好的线性关系，如图 5 所示，这些信息为测定奶粉中添加的糊精含量提供了必要条件。

3.2　非线性化学指纹图谱法测定奶粉中添加的糊精含量

利用非线性化学指纹图谱法，按照 1.2.1 节的实验方法，测定了 1 号奶粉添加不同量糊精的非线性化学指纹图谱，根据混合奶粉非线性化学指纹图谱的特征参数诱导时间与相应奶粉中添加的糊精含量之间所呈线性关系，通过图 5 中相应的拟合方程，可求出相应奶粉中添加的糊精质量分数 *C*，实验结果见表 1。

由表 1 可知，测定结果的相对标准偏差在



(a) 整体图　　(b) 部分图

图 4　糊精含量对 1 号奶粉非线性化学指纹图谱诱导时间的影响

Fig. 4　Effects of dextrin content on inductive time of nonlinear chemical fingerprint of milk powder 1

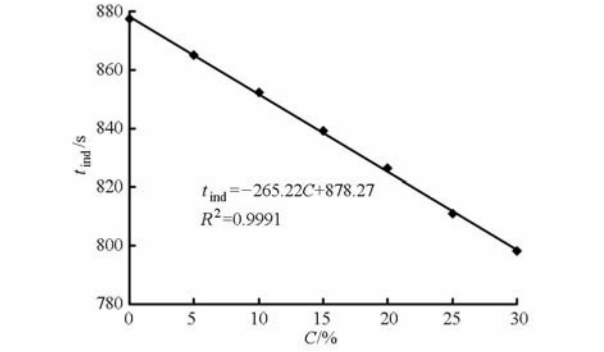


图 5　1 号奶粉中添加的糊精含量与诱导时间之间的线性关系

Fig. 5　Linear relationship between dextrin content in milk powder 1 and inductive time of nonlinear chemical fingerprint

1.17%以内，说明该方法的精确度较好，回收率在94.00%~104.89%之间，说明该方法的准确度较高。此方法完全可用于奶粉中糊精含量的检测，其方法可行，同时还可以为样品中其他添加物质的含量测定提供依据。

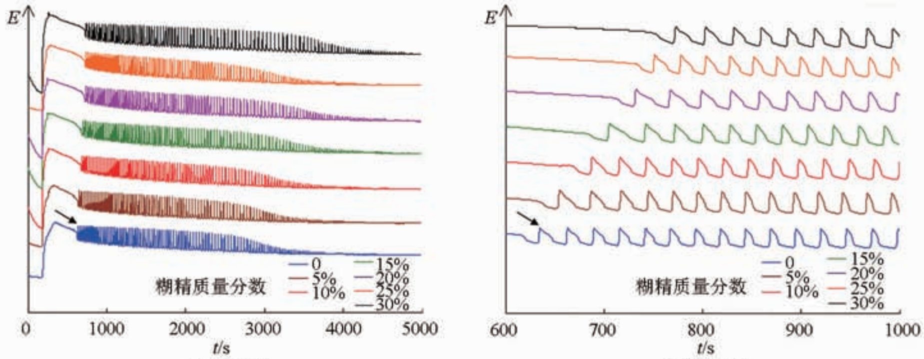
3.3　验证实验

为了进一步验证实验的可行性和可靠性，分别取 2 号奶粉、3 号奶粉和 4 号奶粉各 3 份，人为向奶粉中分别加入 6%、13% 和 22% 的糊精，每份奶粉标样的总量为 1.0 g，按照 1.2.1 节的实验方法，每个样品平行测定 3 次。2 号奶粉和 3 号奶粉中糊精添加量对指纹图谱特征信息的影响分别见图 6 和图 7。当2号奶粉和3号奶粉分别添加糊精含量在

表 1　非线性化学指纹图谱法测定 1 号奶粉中添加糊精含量的结果

Tab. 1　Results of dextrin content in milk powder 1 determined by nonlinear chemical fingerprint method

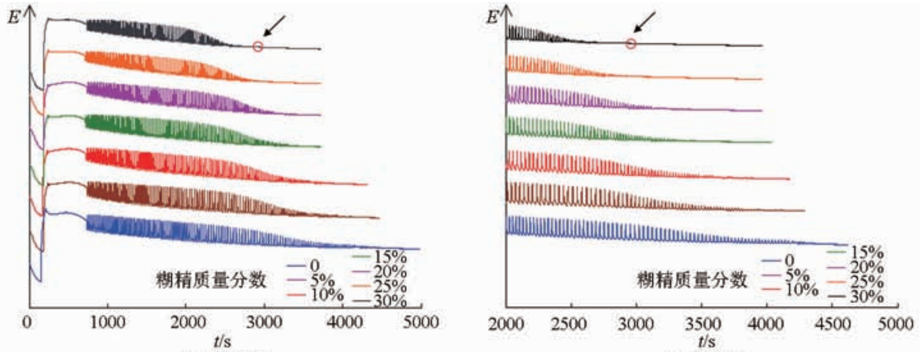
样本编号	诱导时间/s	线性回归方程	测定值/%	实际值/%	相对标准偏差/%	回收率/%	鉴定评价结果
1	878.15	$t_{ind} = -265.22C + 878.27$	0.045	0	0.29		纯奶粉(未加糊精)
2	876.64		0.610	0.60	0.38	101.67	纯奶粉(未加糊精)
3	875.79		0.940	1.00	0.95	94.00	纯奶粉(未加糊精)
4	830.66		17.950	18.00	0.59	99.72	掺杂 17.95%
5	821.99		21.220	21.00	1.17	101.05	掺杂 21.22%
6	800.38		29.370	28.00	1.01	104.89	掺杂 29.37%



(a) 整体图　　(b) 部分图

图 6　糊精的含量对 2 号奶粉非线性化学指纹图谱诱导时间的影响

Fig. 6　Effects of dextrin content on inductive time of nonlinear chemical fingerprint of milk powder 2



(a) 整体图　　(b) 部分图

图 7　糊精的含量对 3 号奶粉非线性化学指纹图谱停波时间的影响

Fig. 7　Effects of dextrin content on undulatory end time of nonlinear chemical fingerprint of milk powder 3

0～30%范围时，相应诱导时间、停波时间与糊精含量之间的线性关系如图 8 所示，回归方程分别为 $t_{\text{ind}} = 513.22C + 631.93$ 和 $t_{\text{une}} = -5\,583C + 4\,572.9$，决定系数 R^2 分别为 0.997 2 和 0.998 1。利用相应的回归方程，对 2 号奶粉、3 号奶粉和 4 号奶粉中添加的糊精进行检测，结果如表 2 所示。

由验证实验可知，利用非线性指纹图谱法测定奶粉中添加糊精的含量，其方法可行，同时此方法用回归方程代替长期保存的奶粉标样，当检测与奶粉标样同品牌不同批次的奶粉时，只要利用非线性化学指纹图谱法测出该品牌奶粉的图谱信息，代入相应拟合的方程，就可以对该奶粉的质量进行分析鉴定。如与 3 号奶粉同品牌不同批次的 4 号奶粉，人为向其中分别加入 6%、13%和 22%的糊精，利用非线性化学指纹图谱法测出相应添加糊精的 4 号奶粉的停波时间，将其代入 3 号奶粉的拟合方程 $t_{\text{une}} = -5\,583C + 4\,572.9$ 中进行验证，检测结果见表 2，其非线性化学指纹图谱分别如图 9 所示。由实验结果可知，该方法可以用来测定同品牌不同批次的奶粉中添加的糊精含量。

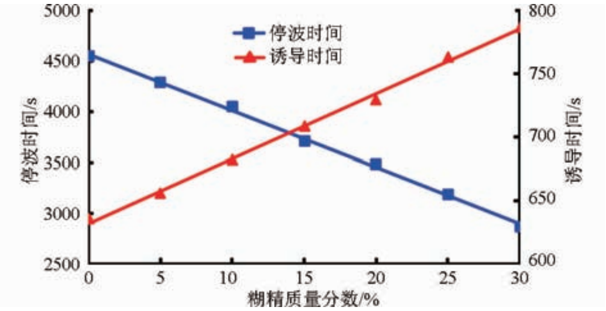


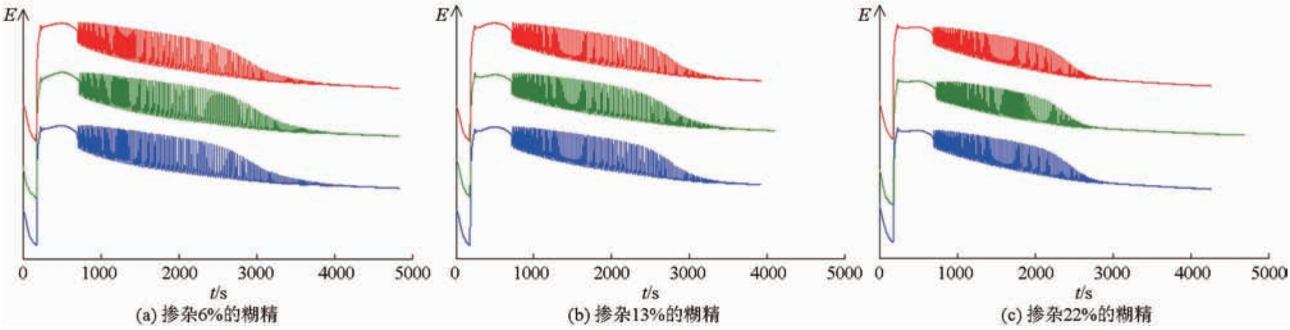
图 8　奶粉中添加的糊精含量与定量信息之间的线性关系

Fig. 8　Linear relationship between dextrin content in milk powder and quantitative information of nonlinear chemical fingerprint

表 2　非线性化学指纹图谱法测定奶粉中添加糊精含量的结果

Tab. 2　Results of dextrin content in milk powder determined by nonlinear chemical fingerprint method

样本	诱导时间/s	测定值/%	实际值/%	相对标准差/%	回收率/%	鉴定评价结果
2 号奶粉	662.66	5.99	6.00	0.38	99.83	掺杂 5.99%
	693.31	11.96	13.00	0.67	99.67	掺杂 11.96%
	746.27	22.28	22.00	0.81	101.27	掺杂 22.28%
3 号奶粉	4 242.60	5.92	6.00	0.23	98.67	掺杂 5.92%
	3 867.86	12.63	13.00	0.95	97.15	掺杂 12.63%
	3 340.59	22.07	22.00	0.17	100.32	掺杂 22.07%
4 号奶粉	4 222.85	6.27	6.00	0.77	104.50	掺杂 6.27%
	3 840.97	13.11	13.00	0.30	100.85	掺杂 13.11%
	3 361.95	21.69	22.00	0.29	98.59	掺杂 21.69%



(a) 掺杂6%的糊精　(b) 掺杂13%的糊精　(c) 掺杂22%的糊精

图 9　糊精含量对 4 号奶粉非线性化学指纹图谱的影响

Fig. 9　Effects of dextrin content on nonlinear chemical fingerprints of milk powder 4

3.4　奶粉中添加糊精含量的检测范围和检出限

市场上乳粉中糊精的添加量一般不超过 20%，即每 100 g 乳粉中不超过 20 g，而本研究中糊精质量分数在 0～30%范围内，即每 100 g 乳粉中含有 0～30 g 糊精时，均能检测出来。

根据检出限的计算方法[17－20]，本研究中以 1 号、2 号和 3 号奶粉为例，每个样品平行测定 8 次，3 种奶粉检出限值如表 3 所示。由表 3 可知，计算所得检出限范围为奶粉中添加糊精 1.3×10^{-3} mg/g 以上时，测定结果具有较高置信度。实际上，市场上乳粉中糊精的添加量一般在 10 mg/g 以上[21]，因此，当奶粉中添加糊精在 10 mg/g 以下时，将该奶粉作为纯奶粉处理。基于此，利用非线性化学指纹图谱法对奶粉中添加糊精进行定量分析和质量评价，检测范围为 0～30%，检出限为 $1.3 \times 10^{-3} \sim 4.7 \times 10^{-3}$ mg/g，方法可行，并且有较高的准确度和精密

度。另外本方法也为配方乳粉中添加糊精含量的检测提供了依据。

表3 奶粉中添加糊精的检出限

Tab.3 Detection limits of dextrin content in milk powder

样品	温度/℃	糊精最低浓度时质量/mg	响应信号平均值/s	标准偏差	检出限/（mg·g^{-1}）
1号奶粉	50	1.00	878.28	0.75	2.6×10^{-3}
2号奶粉	50	1.00	633.98	0.99	4.7×10^{-3}
3号奶粉	50	1.00	4 577.80	1.91	1.3×10^{-3}

4 结束语

利用“硫酸-硫酸锰-丙酮-溴酸钠”组成的非线性化学反应体系对奶粉中添加的糊精进行定量分析。奶粉中添加的糊精含量与相应混合奶粉非线性化学指纹图谱的定量参数（如诱导时间和停波时间）之间存在定量关系，利用奶粉标样非线性化学指纹图谱信息拟合的线性回归方程，可以测定奶粉中添加的糊精含量。实验结果表明，提出的非线性化学指纹图谱法具有较高的精密度和准确度，不仅可以用来测定不同品牌或同品牌不同批次的奶粉中添加的糊精含量，而且还可以用于复杂样品中其他物质含量的测定。同时此方法用回归方程代替长期保存的奶粉标样，当检测与奶粉标样同品牌不同批次的奶粉时，只要利用非线性化学指纹图谱法测出该品牌奶粉的图谱信息，代入相应拟合的方程，就可以对该奶粉的质量进行分析鉴定。该方法具有操作简单、样品不用预处理和分析成本低廉的优点，同时为乳粉中添加的糊精含量测定提供了一种新方法。

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