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Quantitative Analysis of Routine Chemical Constituents of Tobacco Based on Thermogravimetric Analysis

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Cite This: *ACS Omega* 2022, 7, 26407−26415

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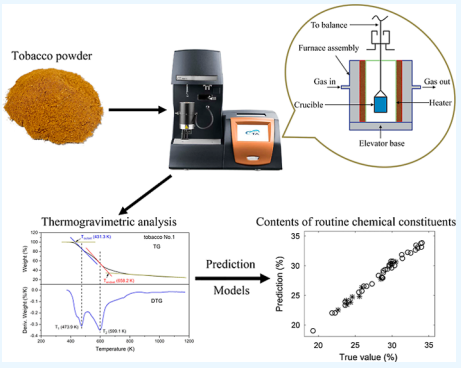
ABSTRACT: As the most basic indexes to evaluate the quality of tobacco, the contents of routine chemical constituents in tobacco are mainly detected by continuous-flow analysis at present. However, this method suffers from complex operation, time consumption, and environmental pollution. Thus, it is necessary to establish a rapid accurate detection method. Herein, different from the ongoing research studies that mainly chose near-infrared spectroscopy as the information source for quantitative analysis of chemical components in tobacco, we proposed for the first time to use the thermogravimetric (TG) curve to characterize the chemical composition of tobacco. The quantitative analysis models of six routine chemical constituents in tobacco, including total sugar, reducing sugar, total nitrogen, total alkaloids, chlorine, and potassium, were established by the combination of TG curve and partial least squares algorithm. The accuracy of the model was confirmed by the value of root mean square error for prediction. The models can be used for the rapid accurate analysis of compound contents. Moreover, we performed an in-depth analysis of the chemical mechanism revealed by the result of the quantitative model, namely, the regression coefficient, which reflected the correlation degree between the six chemicals and different stages of the tobacco thermal decomposition process.



1. INTRODUCTION

As a special lignocellulose biomass, the chemical composition of tobacco is complex.[1,2] In addition to hemicellulose, cellulose, and lignin, the three structural substances that constitute the cell wall, there are also large amounts of extractives.[3] Among these extractives, the contents of routine chemical constituents, including the total sugar, reducing sugar, total nitrogen, total alkaloid, chlorine, and potassium, are the most basic indexes to evaluate the quality of tobacco for the formulation design,[4] quality monitoring,[5] and classification of cigarette products.[6] At present, the contents of these routine chemical constituents in tobacco are mainly detected by continuous-flow analysis. Unfortunately, this method suffers from complex operation, time consumption, and environmental pollution caused by the consumption of a large amount of organic reagents in the testing process.[7] Therefore, developing rapid accurate quantitative analysis of routine chemical constituents in tobacco is necessary for quality assurance of cigarettes.

With the rise and development of chemometrics methods, the coupling of chemometrics with spectroscopy which can characterize the chemical information of sample has been widely used in quantitative and qualitative analyses of complex system.[8,9] In the quantitative analysis of tobacco chemical composition, previous studies were mainly focused on the use of near-infrared (NIR) spectroscopy due to its high efficiency and nondestructive characteristic.[10−12] For example, Wei et al. found that NIR spectroscopy combined with deep transfer learning enabled rapid and accurate analysis of moisture, starch, protein, and soluble sugars in tobacco.[10] Zhou et al. proposed an ensemble partial least squares (PLS) algorithm based on variable clustering for quantitative analysis of nicotine in tobacco by NIR spectroscopy.[11]

Apart from NIR, which directly characterizes the composition of tobacco through the molecular vibration of tobacco endogenous substances,[13] we propose an indirect method, thermogravimetric analysis (TGA). TGA is an important method to characterize the pyrolysis reaction characteristics of tobacco, reflecting the chemical composition of tobacco from the perspective of chemical reaction.[14,15] The shape of the TG curve was comprehensively determined by the physical and chemical properties of tobacco, including substance composition, complex cross-linking structure between compounds, microscopic pores of tobacco, and so on.[16] Moreover, chemical quantitative prediction model based on TG curve can reflect

Received: April 11, 2022
Accepted: July 1, 2022
Published: July 21, 2022

https://doi.org/10.1021/acsomega.2c02243
ACS Omega 2022, 7, 26407−26415

the correlation degree between the detected chemical indexes and the thermal decomposition reaction process of different chemical substances corresponding to different temperature ranges, so as to reveal the possible synergistic, coupling, catalytic, and other interaction effects of quantitatively analyzed chemical substances such as potassium, chlorine, glucose, and so forth with other compounds in tobacco during the pyrolysis process. In the process of cigarette smoking, pyrolysis is the main stage of the generation of nicotine, aroma components, and other volatile and semi-volatile compounds. Therefore, the exploration of pyrolysis reaction mechanism can provide theoretical guidance for cigarette quality evaluation, tar, and damage reduction but still remains a grand challenge. The quantitative analysis model of chemical constituents in tobacco based on the TG curve can reveal pyrolysis reaction mechanism from the perspective of data analysis, which is difficult to be achieved by the quantitative analysis model based on NIR. However, to the best of our knowledge, quantitative analysis of tobacco chemical substances based on the TG curve has not yet been reported due to the complexity.

Herein, we proposed for the first time to use the TG curve to characterize the chemical composition of tobacco and established the quantitative analysis model of routine chemical substances. This method is different from the ongoing researches that mainly chose NIR as the information source for quantitative analysis of chemical components in tobacco. By the combination of TG curve and chemometrics, we established quantitative analysis models of six routine chemical constituents of total sugar, reducing sugar, total nitrogen, total alkaloids, chlorine, and potassium in tobacco, with contents of 19.22−34.10, 17.18−30.82, 1.63−2.42, 1.48−3.27, 0.07−1.10, and 1.36−2.89%, respectively, in the samples used in this work, as shown in Table S1 in the Supporting Information. Due to the differences in testing principles, the response mechanism and intensity of TG curve to chemical information are different from that of NIR, which may provide a new idea for qualitative and quantitative analyses of tobacco. In addition, the numerical results of the quantitative analysis model based on the TG curve are deeply analyzed to deepen our understanding of the pyrolysis reaction mechanism revealed by the model.

2. EXPERIMENTAL SECTION

2.1. Materials. 49 single-grade flue-cured tobaccos used in this work were obtained from the Technology Center of China Tobacco Zhejiang Industrial Co., Ltd. (Hangzhou, China). Before usage, the tobacco was ground into powder. The powder that passed through 40-mesh but was trapped on a 60-mesh sieve was collected in a sealed valve bag for subsequent measurements. The size of tobacco particles ranged from 0.250 to 0.425 mm.

In order to understand the chemical composition characteristics of the special lignocellulosic biomass of tobacco, the results of the ultimate and proximate analyses, as well as the content of hemicellulose, cellulose, lignin, and extractives, were commonly provided for five representative samples, as shown in Tables S2 and S3 in the Supporting Information. The proximate analysis of the tobacco samples was determined according to the People's Republic of China (PRC) national standard, GB/T 28731-2012 (GB/T: Chinese abbreviations of recommended national standards in PRC). The ultimate analysis was carried out using an elemental analyzer (VARIO ELIII, Elementar Analysensysteme GmbH, Germany). The contents of structural carbohydrates and lignin in tobacco were determined according to a National Renewable Energy Laboratory procedure.[17]

2.2. Pyrolysis Experiment. The weight-loss characteristics of the samples were analyzed in a TG analyzer (Discovery, TA). In a typical run, 5.5 mg of sample was used. The sample was heated from room temperature to 373 K at a rate of 10 K/min, followed by incubation at 373 K for 30 min to remove free water completely. The sample weight was regarded as 100% after dehydration pretreatment. We heated the sample to 1173 K at a rate of 10 K/min and recorded the weight loss of the sample during the temperature-programmed process. During the whole tests, the flow rates of the carrier gas (high-purity N_2) and protective gas (high-purity N_2) were set at 50 mL/min and 30 mL/min, respectively. Each test was repeated three times under the same conditions.

2.3. Chemical Analysis of Six Routine Constituents of Tobacco. The contents of total sugar, reducing sugar, total nitrogen, total alkaloids, chlorine, and potassium in 49 tobacco powder samples were determined by a continuous flow analyzer (Alliance-Futura), according to Tobacco Industry Standards YC/T159-2002, YC/T 161-2002, YC/T 468-2013, YC/T 217-2007, and YC/T 162-2011, respectively. Specifically, the detection principle of sugars, including total sugar and reducing sugar, is that the sugar in tobacco extract reacts with 4-hydroxybenzoic acid hydrazide, producing a yellow azoic compound in the alkaline medium at 85 °C. The maximum absorption wavelength of this compound is 410 nm and can be detected by a colorimeter. The analysis principle of total nitrogen is that the organic nitrogen-containing compounds are digested and decomposed by strong heat under the action of concentrated sulfuric acid and catalyst. The nitrogen is converted to ammonia, which was oxidized into ammonium chloride by sodium hypochlorite and then reacted with sodium salicylate to produce an indigo dye. The content of this kind of dye can be determined by the colorimetric method at 660 nm. The quantitative analysis of total alkaloids mainly depends on its reaction with sulfanilic acid and cyanogen chloride. The products obtained can be detected by a colorimeter at 460 nm. The detection of chlorine is mainly through the reaction of chlorine in tobacco extract with mercuric thiocyanate and the release of thiocyanate ion. Thiocyanate ion reacts with ferric to form a complex compound that can be determined by the colorimetric method at 460 nm. The analysis principle of potassium is that during the combustion of tobacco extract, the peripheral electrons of potassium absorb energy and transition from the ground state to the excited state. The electrons are unstable in the excited state and release energy to return to the ground state. The released energy can be detected by the photoelectric system. When the concentration of potassium is in a certain range, its radiation intensity is proportional to the concentration.

2.4. PLS Modeling. Before modeling, the data set was randomly divided into a calibration set (39 samples) and a test set (10 samples). The PLS method was used to build a calibration model. Fivefold cross validation was performed to the calibration set to calculate the RMSECV value. An F test based on the result of cross-validation was used to select the optimal number of latent variables (LVs). The significance level was set to 0.25 as previously suggested.[18] Prior to building the PLS model, all data were mean-centered.

2.5. Evaluation. The root mean square error (RMSE) is used as a measure of model performance. RMSE for calibration

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ACS Omega 2022, 7, 26407−26415

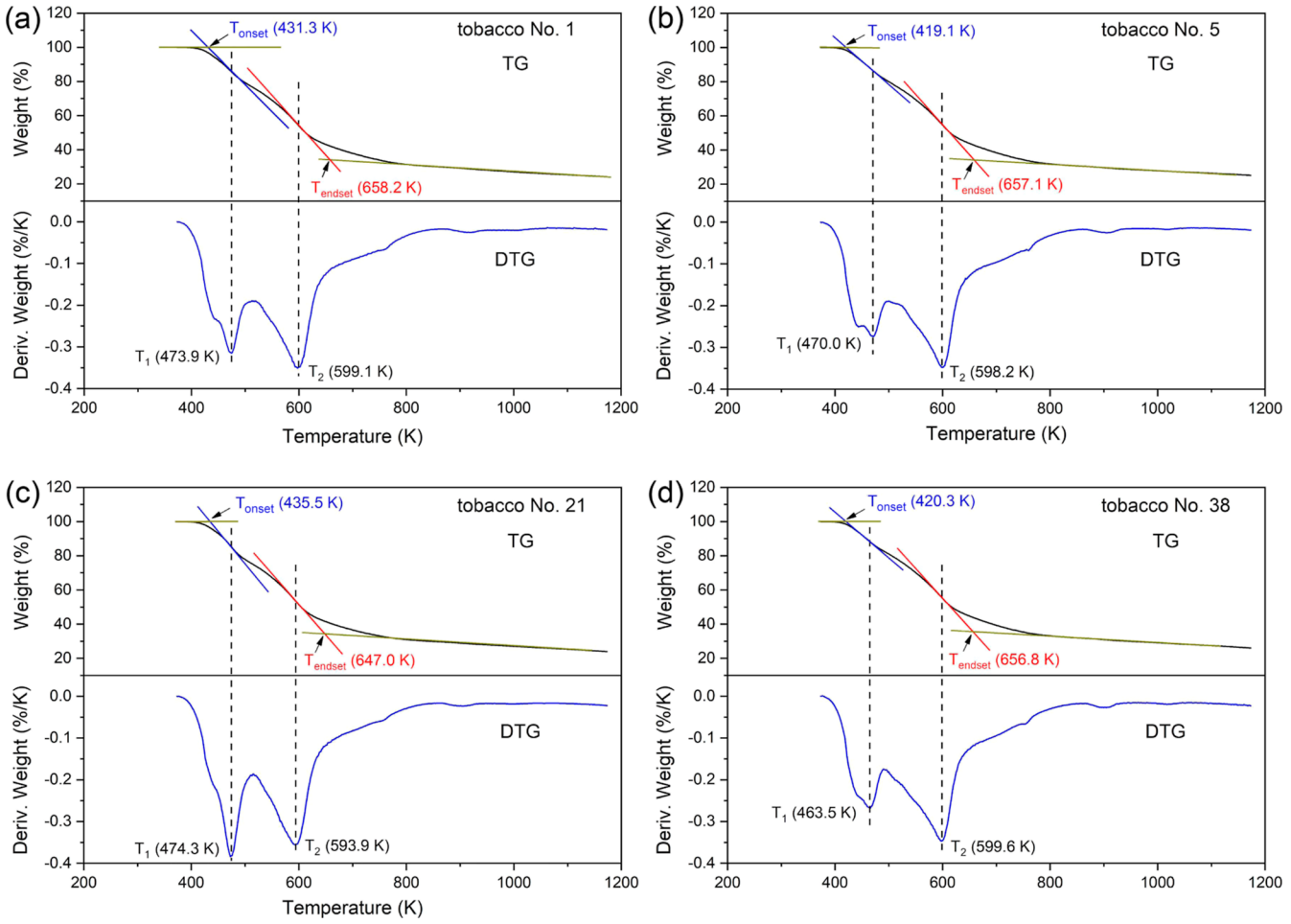

Figure 1. TG and DTG curves of tobacco (a) no. 1, (b) no. 5, (c) no. 21, and (d) no. 38.

(RMSEC), RMSE for cross-validation (RMSECV), and RMSE for prediction (RMSEP) are defined as follows

$$\mathrm{RMSEC} = \left(\frac{1}{N_C} \sum_{i=1}^{N_C} (y_{\mathrm{exp}}^{(i)} - y_{\mathrm{pred}}^{(i)})^2 \right)^{1/2} \quad (1)$$

$$\mathrm{RMSECV} = \left(\frac{1}{N_{CV}} \sum_{i=1}^{N_{CV}} (y_{\mathrm{exp}}^{(i)} - y_{\mathrm{pred}}^{(i)})^2 \right)^{1/2} \quad (2)$$

$$\mathrm{RMSEP} = \left(\frac{1}{N_P} \sum_{i=1}^{N_P} (y_{\mathrm{exp}}^{(i)} - y_{\mathrm{pred}}^{(i)})^2 \right)^{1/2} \quad (3)$$

where $y_{\mathrm{pred}}^{(i)}$ is the predicted value, and $y_{\mathrm{exp}}^{(i)}$is the experimental value. N_C, N_{CV}, and N_P are the numbers of calibration, cross-validated, and test set samples, respectively.

2.6. Computation. Computations were performed in MATLAB 7.14 (Mathworks, Inc., Natick, MA, USA). All of the programs were written in-house and run on a personal computer with a 3.20 GHz Intel Core i5 processor, 8 GB RAM, and Windows 7 operating system.

3. RESULTS AND DISCUSSION

3.1. Analysis of TG Curves. Figure S1 in the Supporting Information shows the TG and derivative TG (DTG) curves of 49 tobacco samples during the thermal decomposition process. Overall, TG curves of 49 tobaccos were similar in shape. According to DTG curves, tobacco mainly has two rapid weight-loss stages at about 470 and 600 K, respectively. For different tobacco samples, there were few differences in the temperature corresponding to the two maximum weight-loss rates, namely, the peak temperature. The difference mainly lies in the relative weight loss of these two stages, which can be seen from the ratio of DTG peak area around 470 and 600 K, as shown in Figure S1. In order to compare the pyrolysis properties of different tobaccos in detail, we randomly selected four types of tobacco samples, namely, no. 1, no. 5, no. 21, and no. 38. We calculated their pyrolysis characteristic temperatures, including the extrapolated onset temperature (T_{onset}), the endset temperatures (T_{endset}), and two peak temperatures, T_1 and T_2. T_{onset} and T_{endset} were determined by a tangent method.[19] As shown in Figure 1, the differences of T_{onset} among these four tobaccos were most obvious. Tobacco no. 38 had the lowest T_1 at 463.5 K, whereas no. 21 had the lowest T_2 and T_{endset}. Hence, the shape of DTG curve and characteristic temperatures, especially T_{onset}, of different tobacco samples were not identical.

We conducted a general analysis of the correlation between the contents of six routine chemical constituents and TG curves of 49 tobaccos. The contents of these constituents were detected by a continuous flow analyzer. The correlation was analyzed based on the Pearson correlation coefficient, which is an index used to measure the degree of linear correlation between two variables.[20,21] In general, the absolute value of Pearson coefficient ranging from 0.9 to 1.0 represents a strong

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ACS Omega 2022, 7, 26407−26415

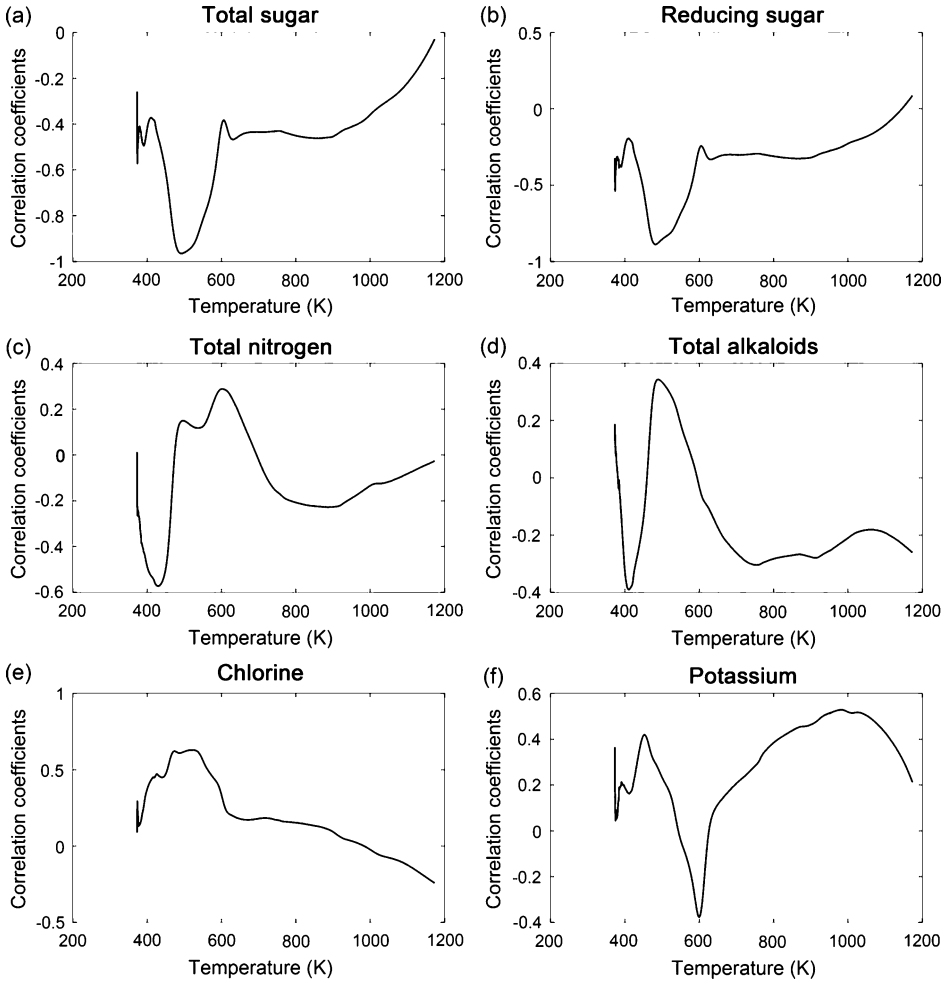

Figure 2. Pearson correlation coefficients between TG curves and the contents of six routine chemical constituents of (a) total sugar, (b) reducing sugar, (c) total nitrogen, (d) total alkaloids, (e) chlorine, and (f) potassium. The contents of these constituents were detected by a continuous flow analyzer.

linear correlation. The range from 0.7 to 0.9 represents a strong linear correlation. The range from 0.5 to 0.7 represents a moderate linear correlation. Absolute values below 0.5 indicate a weak or even negligible correlation between the two variables.[22,23]

Figure 2a,b reflects the linear correlation degree between total sugar, reducing sugar, and TG curve. Total sugar and reducing sugar were mainly composed of water-soluble reducing sugars such as glucose and fructose in tobacco. The contents of these components have a highly linear correlation with the TG curve at approximately 473 K. Specifically, the coefficients for total sugar and reducing sugar reached 0.95 and 0.89, respectively. The correlation may be derived from the Maillard reaction. According to previous studies, the reaction occurring around 473 K mainly comprises the release of Maillard products and the volatilization of nicotine during the thermal decomposition process of tobacco.[24,25] The TG curve represents the remaining mass of the sample after the release of volatile products. As an important reactant of Maillard reaction, the higher the content of water-soluble reducing sugar, the faster the release rate of products, resulting in less remaining mass of the sample. Therefore, the contents of total sugar and reducing sugar were negatively correlated with the TG curve at approximately 473 K.

As shown in Figure 2c, a negative linear correlation between total nitrogen and TG curve appeared at about 423 K, reaching 0.56. This phenomenon may also be attributed to the Maillard reaction. As the main components of nitrogenous compounds in tobacco, amino acids and proteins are also another reactant of Maillard reaction besides water-soluble sugars.

There was a moderate positive linear correlation (0.60−0.65) between the chlorine content and TG curve in the temperature range of 450−530 K (Figure 2e). As such, chlorine was detrimental to the Maillard reaction. This was also consistent with previous studies that reported high chlorine content worsens the sensory quality of cigarettes, possibly because chlorine inhibits the release of aromatic components such as Maillard products.[26,27]

The linear correlation of both total alkaloid and potassium contents with the TG curve was weak within the whole temperature range, where the absolute values were lower than 0.5, as shown in Figure 2d,f. In this case, the relationship between the contents of these two compounds and TG curve was relatively complex.

For clarity, we briefly summarized the correlation of chemical constituents and TG curves based on Pearson correlation coefficients. The contents of total sugar, reducing sugar, and total nitrogen were negatively correlated with the TG curve at ∼473, ∼473, and ∼423 K, respectively, which may

https://doi.org/10.1021/acsomega.2c02243
ACS Omega 2022, 7, 26407−26415

be caused by the Maillard reaction. These three substances showed different degrees of linear correlation with the TG curve. Among them, total sugar and reducing sugar were strongly correlated with the TG curve, while total nitrogen was moderately correlated with the TG curve. A moderate positive linear correlation between the chlorine content and TG curve occurred in the temperature range from 450 to 530 K. The direct linear correlations of both total alkaloid and potassium contents with TG curves were rather weak in the whole temperature range, indicating that the mathematical relationships between these two compounds and TG curves were relatively complex. It may be necessary to carry out principal component extraction of TG curve and find the linear combination of TG values at different temperature points as a new variable to associate with total alkaloid and potassium contents, so as to improve the correlation between the TG curve and these two chemical constituents.

3.2. Establishment of the Calibration Model. From Section 3.1, it was roughly proven that there was a certain correlation between TG curves and constituents content. In order to establish a quantitative analysis model, the specific mathematical relationship between them was further analyzed. The detailed procedure to establish the quantitative analysis models is illustrated in Figure S2 in the Supporting Information. Specially, the 49 tobacco samples were numbered from 1 to 49 and randomly divided into 39 calibration samples and 10 test samples according to the ratio (8:2) of calibration set to test set.[28] PLS algorithm written by MATLAB software was used to correlate the contents of six routine chemical constituents in 39 calibration samples with the corresponding TG curves. The quantitative analysis models of six routine chemical constituents of tobacco based on the TG curve were finally established via RMSEC and RMSECV. The TG curves of 10 samples in the test set were input into the calibration model to predict the contents of corresponding chemical constituents and then compared with the measured values obtained by the continuous flow analyzer. The accuracy of the model was evaluated and verified by calculating RMSEP.

Table 1 shows the number of LVs, RMSEC, RMSECV, and RMSEP of the model. The mean values [mean (Y)] of six routine chemical constituents for 49 tobacco samples are also listed in Table 1. RMSEP of total sugar, reducing sugar, and total nitrogen were 0.46, 1.06, and 0.05, respectively, which were relatively small compared with the corresponding values of mean (Y), indicating high accuracy of the quantitative analysis models of total sugar, reducing sugar, and total nitrogen. RMSEC and RMSEP of total alkaloids were 0.15 and 0.26, respectively, which were relatively high with respect to mean (Y). Therefore, the prediction of the current model for the total alkaloid content was less accurate than that for sugar models. The contents of chlorine and potassium in tobacco were so low that the comparison of relative deviation was not meaningful. Here, RMSEP values of 0.12 and 0.20 can guarantee the accuracy of prediction of these two indicators in an acceptable range.[29] The predicted contents of routine chemical constituents in calibration and test samples obtained by the quantitative analysis model were compared with the actual values, as shown in Figure 3. Therefore, the established model can be used for accurate quantitative analysis of six conventional chemical substances including total sugar, reducing sugar, total nitrogen, total alkaloids, chlorine, and potassium.

Table 1. Prediction Result of the Calibration Model[a]

routine chemical constituents	LV	RMSEC (%)	RMSECV (%)	RMSEP (%)	mean (Y) (%)
total sugar	6	0.40	0.60	0.46	28.92
reducing sugar	6	0.76	1.14	1.06	26.10
total nitrogen	6	0.05	0.06	0.05	1.97
total alkaloids	10	0.15	0.24	0.26	2.27
chlorine	11	0.03	0.06	0.12	0.37
potassium	10	0.05	0.11	0.20	2.02

[a]LVs: latent variables; RMSEC: root mean square error for calibration; RMSECV: root mean square error for cross-validation; RMSEP: root mean square error for prediction; mean: the mean values of six routine chemical constituents for 49 tobacco samples.

In summary, the quantitative analysis models established by PLS has a strong ability to predict the contents of total sugar, reducing sugar, and total nitrogen. Their ability to predict the content of total alkaloids is relatively weak. It may be necessary to further increase the number of samples to optimize the model and improve the accuracy of the quantitative analysis model for total alkaloids. Based on the established models, the contents of routine chemical components in any unknown tobacco could be determined efficiently and quickly via its TG curve, thus avoiding the tedious operation process and environmental pollution caused by the conventional chemical analysis method.

3.3. Analysis of Model Results from the Perspective of Chemical Reaction Mechanism. We tried to explore the pyrolysis mechanism of tobacco through the results of the quantitative model established in Section 3.2. For tobacco samples, the ordinate value [weight (%)] corresponding to each abscissa [temperature (K)] of the TG curve represents an independent variable of the sample, while the chemical content of the sample is the dependent variable. From a mathematical point of view, the establishment of the model aims to find a coefficient corresponding to each independent variable. The dot product of the coefficient and independent variable is equal to the dependent variable. This coefficient is named as the regression coefficient, which can reflect the unique contribution of each independent variable.[30,31]

Figure 4 shows the regression coefficients of the quantitative analysis models of six routine chemical constituents based on TG curves in the whole pyrolysis temperature range. As shown in Figure 4a,b, the contents of total sugar and reducing sugar exhibited a strong negative correlation with the TG curve at about 473 K, which may be attributed to the Maillard reaction, also consistent with the conclusion in Figure 2. The correlation between total nitrogen and TG curve mainly existed before 673 K (Figure 4c). According to previous studies, the temperature range between 373 and 473 K of TG curve mainly corresponded to the release of Maillard reaction products and the volatilization of nicotine. The temperature range between 523 and 623 K was mainly attributed to the pyrolysis process of glucose, pectin, hemicellulose, cellulose, and other saccharides.[25,32,33] The results showed that there was a strong correlation between the content of total nitrogen and these reactions. The thermal decomposition of nitrogen-containing compounds in tobacco occurred only when the temperature was above 673 K.[25,34] There was no obviously strong correlation between total nitrogen and this temperature range, indicating that the current model mainly applies to the quantitative analysis of nitrogen-containing compounds

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ACS Omega 2022, 7, 26407−26415

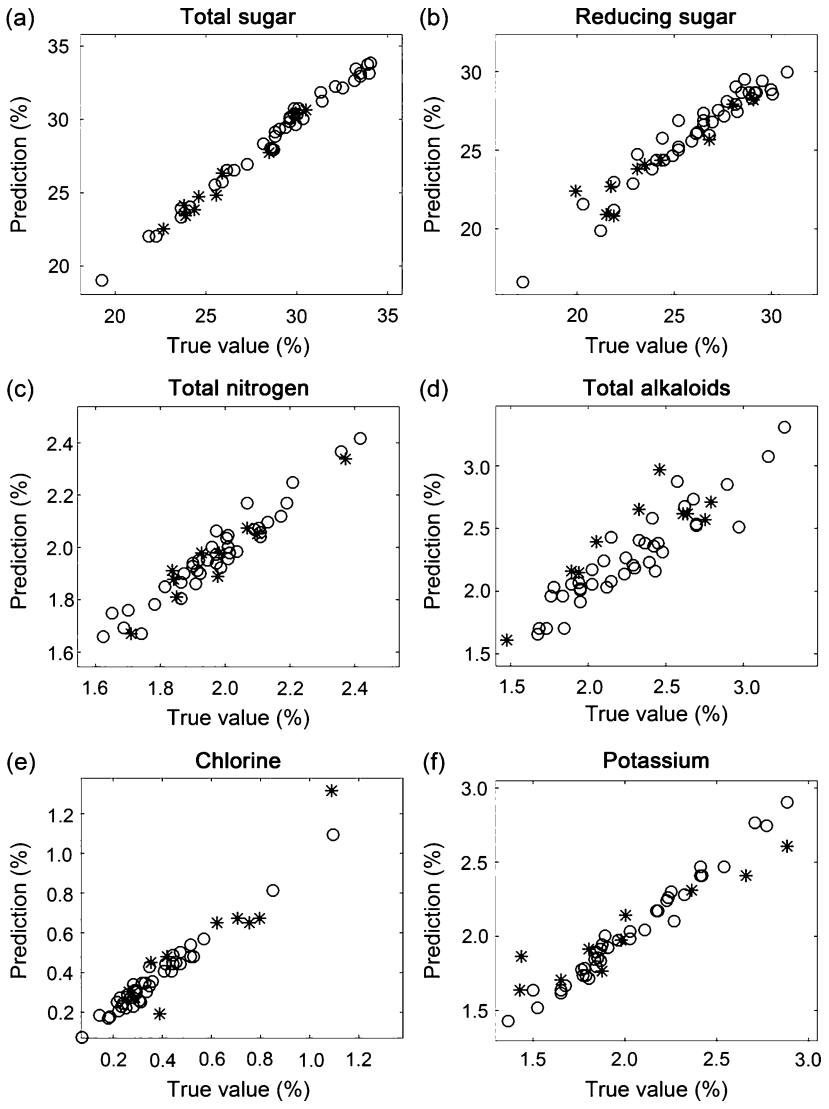

Figure 3. Correlation between the predicted content obtained by the quantitative analysis models and the actual one detected by continuous flow analyzer of (a) total sugar, (b) reducing sugar, (c) total nitrogen, (d) total alkaloids, (e) chlorine, and (f) potassium. o represents calibration set data, * represents test set data.

through Maillard reaction, nicotine volatilization, and the thermal decomposition process of sugar rather than their own pyrolysis process.

The positive and negative correlations between total nitrogen and TG curve were opposite to that of total sugar in the whole temperature range. TG curve records the relative percentage content of chemical substance consumed rather than the absolute mass. The content of total sugar in tobacco (approximately 30%) was much higher than that of total nitrogen (less than 2%). The higher the relative content of sugar, the lower the relative content of total nitrogen.

There was a strong positive correlation between total alkaloids and TG curve at about 520 K, as shown in Figure 4d. This phenomenon is out of our expectation because more than 90% of total alkaloids in tobacco were composed of nicotine, which was mainly volatilized at 473−573 K. Accordingly, the higher the nicotine release amount, the less the residual mass corresponding to the TG curve. In other words, the nicotine content and TG curve should theoretically be negatively correlated. We hypothesize that this phenomenon is also affected by the correlation between sugar and TG curve, just similar to total nitrogen.

Based on regression coefficient, the numerical relationship between the chlorine content and TG curve was relatively complex (Figure 4e), although chlorine has a significant positive linear correlation with TG in the temperature range of 450−530 K from the perspective of Pearson correlation coefficients as shown in Figure 2e. This may be because the Maillard reaction and the thermal decomposition of sugars are in essence a complex multi-step reaction process. The influential mechanism of chlorine on different elementary reaction steps occurring at different temperature ranges varies. Therefore, the response mode and intensity of TG curve to chlorine content at different temperature points are also different.

There was a strong negative correlation between the potassium content and TG curve at about 600 K, as shown in Figure 4f. This temperature range mainly corresponded to the pyrolysis process of hemicellulose, pectin, and water-soluble carbohydrates such as glucose and fructose, indicating that potassium was conducive to the pyrolysis reaction of these

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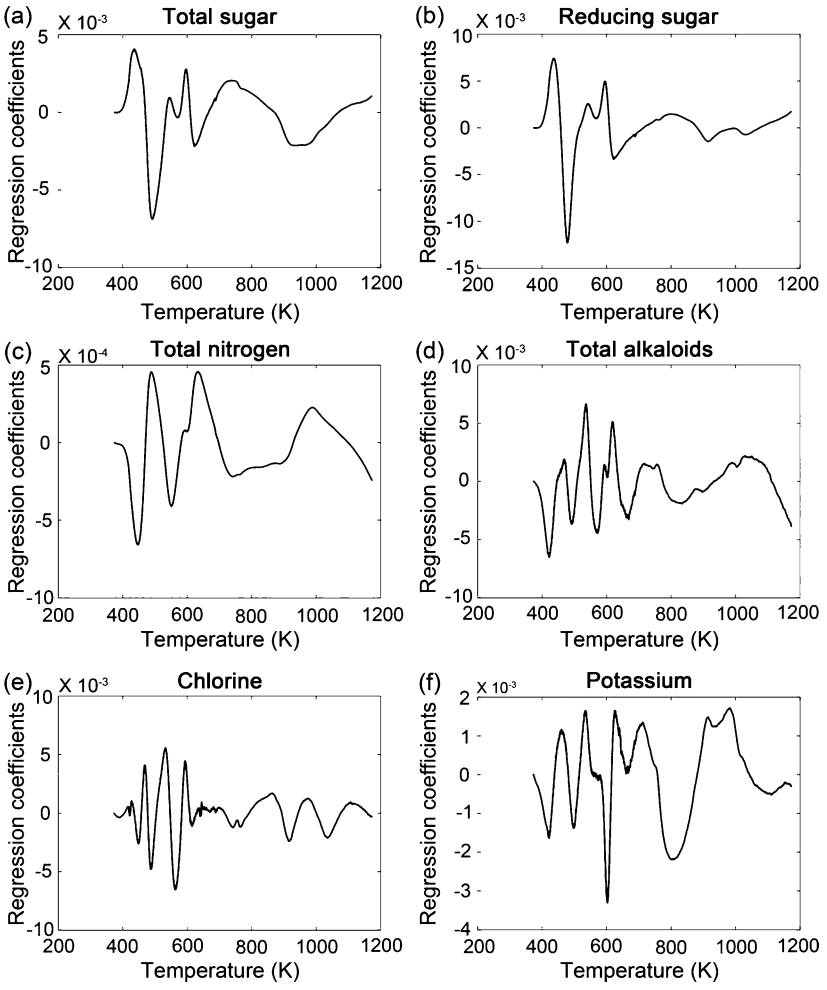

Figure 4. Regression coefficients of the quantitative analysis models of (a) total sugar, (b) reducing sugar, (c) total nitrogen, (d) total alkaloids, (e) chlorine, and (f) potassium based on TG curves.

substances. This was also consistent with previous studies that potassium salt has a catalytic promoting effect on the degradation of oxygen-containing organic functional groups of carbohydrates in tobacco.[35]

From the analysis of the regression coefficients, we found that the quantification of total sugar and reducing sugar mainly depended on the Maillard reaction in which carbohydrate compounds participate. The correlation of total nitrogen and total alkaloids with TG curves in the whole temperature range was affected by total sugar. Although chlorine is detrimental to Maillard reaction in general, it has different effects on the different elementary steps of the Maillard reaction. Potassium can promote the thermal decomposition of hemicellulose, pectin, and water-soluble carbohydrates such as glucose. In the process of cigarette smoking, most of the aroma components and harmful substances in cigarette smoke are generated through pyrolysis reaction. Therefore, the study on the pyrolysis mechanism of tobacco has an important guiding significance for the design and development of new tobacco products with less harm. However, due to the complexity of pyrolysis reaction, the understanding of thermal decomposition process of tobacco is still limited. The regression coefficient of the quantitative analysis model established in this study can reveal the synergistic, coupling, catalytic, and other interaction effects of different compounds in tobacco during pyrolysis, so as to shed light on the pyrolysis mechanism.

In conclusion, we achieved quantitative analysis models of routine chemical constituents of tobacco based on the TG curve and explained the results of the models from the perspective of pyrolysis mechanism. However, we have to realize that this work is only based on a limited number of tobacco samples, namely, 49. In order to improve the accuracy of the model and ensure that the regression coefficient of the model has a higher universality, it is necessary to increase the number of samples studied and continuously optimize the model. On the other hand, a series of experimental analysis methods, such as TG−Fourier transform infrared, TG−mass spectrometry (MS), and Py-gas chromatography/MS, should be adopted to track and monitor the thermal decomposition process of tobacco, so as to deeply explore the pyrolysis mechanism revealed by the model results, which is also the focus of our future research.

4. SUMMARY AND CONCLUSIONS

In this work, for the first time, quantitative analysis models of total sugar, reducing sugar, total nitrogen, total alkaloids, potassium, and chlorine in tobacco based on the TG curve were established, realizing the rapid and accurate determination of the contents of these six routine chemical constituents. The PLS method was adopted to realize the establishment of the quantitative analysis model. The accuracy of the model was confirmed by the value of RMSEP. We

https://doi.org/10.1021/acsomega.2c02243
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performed an in-depth analysis of the chemical mechanism revealed by the result of the quantitative model, namely, the regression coefficient which reflected the correlation degree between the six chemicals and different stages of tobacco thermal decomposition process.

We believe that this quantitative analysis model of chemical constituents in tobacco based on the TG curve can not only be used for the accurate analysis of compound content but also provide enlightenment for the study of pyrolysis reaction mechanism from the perspective of data analysis, which is of great significance for quality control, tar, and damage reduction of cigarette. In fact, the quality evaluation of tobacco involves multiple procedures such as purchasing and processing, cigarette product design and maintenance, and so forth. How to comprehensively and rapidly monitor tobacco quality is of pivotal importance to the tobacco industry. In addition to the routine chemical composition detection, the quality characterization of tobacco has many other dimensions, including aroma, sensory quality evaluation, and so forth, which were mainly carried out by artificial suction. However, artificial suction has the disadvantage of strong subjectivity and is difficult to be quantified. According to this work, it can be concluded that TG curves can effectively reflect the characteristics of different tobaccos. Therefore, it has great potential to use TG curves to predict and characterize various quality dimensions of tobacco, including sensory quality. This method can reduce the manual workload and effectively promote the transformation of tobacco quality evaluation from experience to fundamental understandings. Moreover, this work can be extended to the digital quality detection and control of other industrial systems such as crops and food. On the other hand, this method can also be used as a strategy for the study of chemical reaction mechanism, that is, mathematical analysis methods can be adopted to reveal the objective laws of chemical reactions hidden behind large amounts of data.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02243.

Contents of six routine chemical constituents in the 49 tobacco samples; ultimate and proximate analyses; chemical compositions; TG and DTG curves of tobacco samples; and detailed procedure to establish quantitative analysis models (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Science Foundation of China Tobacco Zhejiang Industrial (grants no. ZJZY2021A009 and ZJZY2021A013).

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https://doi.org/10.1021/acsomega.2c02243
ACS Omega 2022, 7, 26407−26415