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Analysis of aroma component changes and identification of irradiation markers in Luzhou-flavor liquor within one year after electron beam irradiation

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ABSTRACT

Irradiation-aging technology is still in the preliminary exploration stage worldwide. Therefore, in this study, we investigated the effects of high-energy electron beam irradiation on the aroma components and quality of Luzhou-flavor liquor irradiated with 2, 4, 6, 8, 10, and 12 kGy after storage for 30, 90, 180, 270, and 360 d. Using fold change analysis and *t*-test, eight possible irradiation markers were confirmed, including 2,3 butanediol (levulinic), 2,3 butanediol (endocyclic), propionic acid, isobutyric acid, ethyl propionate, dl-2-hydroxy-4-methyl valerate ethyl ester, hexyl hexanoate, and acetaldehyde. Acetaldehyde and caproic acid were confirmed as aging markers for liquor aged naturally for one year. The highest sensory scores were obtained with an irradiation dose of 4 kGy and 360 d of storage and an irradiation dose of 8 kGy and 90 d of storage. The findings of this study can provide a theoretical basis for enterprises to control the quality of irradiated liquor.

1. Introduction

Chinese liquor, one of the oldest distilled products globally, can be divided into 12 categories according to aromatic characteristics (Zeng et al., 2022). Among them, Luzhou-flavor liquor has unique attributes, including "mellow fragrance," "refreshing," and "sweet taste." It is especially fragrant after drinking with an endless aftertaste, and its output accounts for about 80 % of total liquor production in China (Hong et al., 2021). Liquors contain several components belonging to different chemical families, which play positive roles in contributing to the flavor of the liquor and reflect the quality of the liquor to a large extent (Xu et al., 2024). Many researchers have explored the changes in the volatile components of different types of liquor during the natural aging process and the prediction of the liquor age (Rudnitskaya et al., 2010).

Minimal research has been conducted on the key aroma compounds and age markers of Chinese and other liquors (Palassarou et al., 2017). Generally, liquor is stored for 2–3 years to improve its quality, increasing the distillery's storage costs. Therefore, manual aging technology has been applied in recent years to shorten the storage cycle of Chinese and other liquors (Gavahian et al., 2022).

Currently, eight methods are used to accelerate the aging of liquor, including electrochemical oxidation, ultrasound, microwave, light, magnetic field, high gravity, electron beam, and ^{60}Co γ-ray (Del Fresno et al., 2018; Liu, Loira, et al., 2016; Liu, Wei, et al., 2016). Electron beam irradiation is associated with higher energy utilization, and shorter irradiation times, and it can act vertically on the object to be processed (Pillai & Shayanfar, 2017). However, it is important to select a suitable irradiation vessel to maintain the aroma of the liquor. The principle by which electron beam irradiation accelerates the aging of liquor is that the rays generated by the electron beam interact with the aroma components and water, changing the proportion of the overall aroma

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components to improve the quality of the liquor. For example, one study reported that after the Luzhou-flavor liquor was irradiated with a dose of 8 kGy in a single circle, the volatile components of the liquor increased from 76 to 83 types, with esters rising from 36 to 40 types (Zhang et al., 2020). Another study found that electron beam irradiation significantly affects the quality of low-vintage Luzhou-flavor liquor. The longer the liquor is stored, the smaller the dose required to achieve the best aging effect (Zhang et al., 2014). However, there is no clear conclusion regarding the irradiation food markers of the irradiated liquor. The discovery of irradiation markers has great reference value for accelerating the aging of liquors using irradiation.

Some statistical methods can identify a subset of markers and contribute to the classification or discrimination based on a gas chromatography-flame ionization detector (GC-FID) or gas chromatography–mass spectrometry (GC–MS) fingerprint dataset, which is the most critical and core problem in the processing of a multivariate data matrix (Cheung et al., 2022). Common methods include principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA), orthogonal partial least squares discriminant analysis (OPLS-DA), random forest analysis (RFA), volcano diagram analysis (VDA), and upset plot analysis (UPA). PCA is an unsupervised multivariate statistical analysis method that can reduce the data dimensions and reflect the entire inter- and intra-group variability of samples (Pereira et al., 2016). OPLS-DA is a statistically supervised discriminant analysis (DA) method. Compared with PLS-DA, it can accurately screen for different variables between groups. The UPA can visually show overlaps, sets, and intersection numbers between different combinations, which provides a basis for obtaining characteristic components (Lex et al., 2014). Some statistical methods for the identification of activity and key compounds have been used successfully to study liquors. During the 17-year aging process of liquor, the key components causing the honey aroma of feng-flavor liquor were identified (Jia et al., 2022). Moreover, the key elements and their content variations in Niulanshan liquor after different storage periods were studied (Wang et al., 2022). In addition, the aroma differences of Luzhou-flavor liquor with varying ages of pit and positions were investigated (Ding et al., 2016). The abovementioned approaches help to identify the relevant markers for liquor from different perspectives.

The technology for aging liquor by irradiation is not mature, and enterprises are still limited in the actual production and application. Therefore, investigating the changes in the aroma components of irradiated liquor can provide a theoretical basis for enterprises to control the quality of irradiated liquor. Although the volatile components of liquor are altered while accelerating the aging of liquor via irradiation, the key components closely related to irradiation remain unclear.

This study aimed to determine the effects of different irradiation doses and storage times within one year of irradiation on the aroma components of the liquor and sensory evaluations, with a view to providing a reference for quality control of irradiated liquor.

2. Materials and methods

2.1. Liquor samples

Luzhou-flavor liquor samples (freshly distilled raw liquor) were supplied by Luzhou Laojiao Co., Ltd. (Sichuan, China), one of the leading manufacturers of Luzhou-flavor liquor in China. The liquor samples with an ethanol content of 73 % (*v*/v) were blended into 52 % (v/v) by pure water and stored at room temperature until further irradiation.

2.2. Selection of irradiation containers and sealing materials

To screen suitable irradiation containers and the sealing materials for liquor, different combinations were established: high borosilicate glass bottle and cork; high borosilicate glass bottle and liquor plug; high borosilicate glass bottle and silicone plug; high borosilicate glass bottle and plastic wrap; high borosilicate glass bottle and glass plug ; and partially open stainless steel and glass plug. The liquor samples (300 mL volumes) were placed in containers and closed the lid tightly. All combinations were sent to Sichuan Runxiang Irradiation Technology Co., Ltd. (Mei Shan, China) for high-energy electron beam irradiation (VF-PROACC-10/20, 20 kW, 10 MeV, Shandong Lanfu High Energy Physics Technology Co., Ltd., Shandong, China) with a 6 kGy irradiation dose. The liquid samples were irradiated at a beam intensity of 260 μA. These samples were driven by the conveyor belt to the rotary table with 8 m/min turntable speed for irradiation at room temperature (25 °C), which was also compared with the unirradiated liquor. Finally, the liquor samples were sent to Mianyang Fenggu Wine Co., Ltd. (Mianyang, China). National liquor judges evaluated six cups of liquor per round, and aroma comments were only recorded.

2.3. Liquor samples irradiated by different high-energy electron beam doses

The preliminary experiment found that the electron beam penetrated the stainless steel tank with a thickness of 4 cm. The liquor samples (300 mL volumes) were placed in a partially open stainless steel tank (size: 19.5 cm * 4.3 cm * 7.3 cm; volumes: 500 mL) resembling a cuboid covered tightly with a glass plug. Irradiation treatments were performed by Sichuan Runxiang Irradiation Technology Co., Ltd., equipped with a 20 kW/10 MeV electron accelerator. The irradiation doses of the liquor were 2, 4, 6, 8, 10, and 12 kGy. Using a silver dichromate dosimeter (Sichuan Nuclear Energy Institute, Sichuan, China) the absorbed doses were determined, and these were 2.29, 4.16, 6.07, 7.96, 9.97, and 12.33 kGy, respectively. All samples were prepared in triplicate ($n = 3$). The apparatus and procedures for irradiation are referred to in Section 2.2.

2.4. Determination of aroma components using GC-FID

Liquors irradiated with different doses were stored for one year and GC-FID studied the changes in their aroma components at different storage times (30, 90, 180, 270, and 360 d). Direct injection coupled with GC-FID (8890 A; Agilent Technologies, Santa Clara, CA, USA) was employed to identify the aroma components of the Luzhou-flavor liquor. The aroma components in the liquor were quantified using the internal standard method. A tested liquor sample (10 mL) was placed in a 50-mL volumetric flask. Subsequently, tertiary amyl alcohol, n-amyl acetate, and 2-ethyl butyric acid (0.1 mL; Aladdin Reagent Co., Ltd., Shanghai, China) were added as internal standards. After mixing, 1 μL of liquor sample was taken and analyzed with direct injection by GC-FID. The temperature of the GC injector was maintained at 240 °C. The initial column chamber temperature was maintained at 35 °C and held for 2 min, increased to 60 °C at 2 °C min^{-1}, then to 110 °C at 9 °C min^{-1}, and finally increased to 230 °C at 6 °C min^{-1} and held for 4 min. High-purity helium (≥99.99 %) was used as the carrier gas at a constant flow rate of 1 mL min^{-1}. The total aroma components (total acid, total ester, total alcohol, total aldehyde, and total ketone) in the irradiated liquor were compared with those in the control group. The quantitative method for the unknown component is mainly obtained by calculating the relationship between the peak area and the content of the standard component and the ratio of the peak area of the unknown element to that of the standard component.

2.5. Sensory evaluation of liquor

This study was approved by the moral license of the sensory evaluator. Ethical permission was provided by Xie Fei of Fenggu Wine Co., LTD. Oral informed consent was obtained from all the participants prior to the publication of this study. A liquor evaluation panel comprised 5 national liquor judges from Fenggu Wine Co., LTD., Mianyang City, Sichuan Province. At the same time, the liquor evaluation team conducted a dark evaluation and comparison score on the appearance, taste, aroma, and style of all Luzhou-flavor liquor samples by referring to the sensory standards of GB/T 10781.1–2021 and the China Liquor Industry Association (Table A.1). The liquor samples were irradiated. Their sensory scores were measured after storing for 30, 90, 180, 270, and 360 d, respectively.

2.6. Data processing and statistical analysis

Collation and summary of the data, calculation of the *t*-test (*p*-value), and fold change (FC) values were conducted using Microsoft Excel 2016 (Microsoft Corp., Redmond, WA, USA). OPLS-DA was performed using SIMCA software (version 14.0; Umetrics, Umea, Sweden). Statistical methods, including PCA, UPA, and heat maps, were created using Origin 2021 (OriginLab Corporation, Northampton, MA, USA).

3. Results and discussion

3.1. Selection of irradiation containers and sealing materials

Stainless steel tanks and glass stoppers are suitable liquid-irradiation containers and sealing materials. The sensory evaluation results of the different irradiated containers and sealing materials containing liquor before and after irradiation are presented in Table 1. In all the irradiated container combinations (except cuboid stainless steel tanks and glass stoppers), the liquor in the irradiated group had “mush” and “odor,” which may be due to the irradiated radiolysis of the materials inside the container, causing undesirable substances to enter the liquor body. Stainless steel tanks have the advantages of strong corrosion resistance and good sealing; therefore, the aroma after using them to contain liquor is normal (Xie et al., 2021). Some researchers have used comprehensive physical and chemical indices of baijiu after irradiation in white polyethene plastic bottles (Fu & Meng, 1994). The expert tasting scores show that when the dose is 2 kGy, the liquor body has a pure fragrance and is soft, harmonious, sweet, and clean. At a dose of 4 kGy, the irradiated liquor has a pungent aroma and a spicy and unpleasant taste.

3.2. Total aroma components of irradiated liquor

Irradiation had the greatest effect on the aldehyde content of the liquor, followed by the ketones, acids, and alcohols. The impact of different irradiation doses and storage times on the total aroma components of the liquor were studied using GC-FID (Fig. 1). The total acid content shown in Fig. 1 is only the sum of the detectable acid components, as are the total ester, alcohol, aldehyde, and ketone contents. However, more standard ingredients can quantify more aroma components.

The results showed five types of components: acids, esters, and alcohols, followed by aldehydes and ketones. Compared to the unirradiated liquor, the relative content of the total aroma components of the irradiated liquor increased with increasing irradiation dose within one year, except for the total esters and total ketones. Although the total ester content did not change significantly, some single esters changed significantly and could be used as irradiation markers (see Section 3.6). At 12 kGy of irradiation, the relative content of total aldehydes in the liquor stored for 270 d after irradiation increased from 7.66 % to over 20.00 %. The same trend was observed for the total acid content. Acids are responsible for fruity, fatty, and rancid notes and contribute significantly to the sensory characteristics of liquor (Villiers et al., 2004). Some unsaturated compounds containing carbon-carbon double or triple bonds may undergo oxidative fracture under irradiation and eventually produce carboxylic acids, such as isobutyric acid and propionic acid, as verified by data in Table A.3 (Fu & Meng, 1994). The relative content of total acid increased during the one year after irradiation. This corroborates the finding that the longer the liquor is stored, the more abundant the organic acids become (Jia et al., 2020 b). The relative content of total esters in the irradiated liquor remained almost unchanged. One study reported the decreasing trend of total esters in light-flavor Chinese liquor during the aging process, findings that were similar to ours (Xu, Yu, et al., 2017). In addition, the change in the total aroma components of the irradiated liquor samples was consistent with that in the unirradiated liquor samples with the extended storage time.

In addition, we found that the total ketone content of liquor after irradiation has an abnormal decrease behavior at a special time point and dose. The relative content of total ketones decreased from 14.15 % to 13.14 % when the liquor was irradiated by 6 kGy and stored for 360 d. Among all ketones, the contents of acetone, 2-butanone, 3-hydroxy-2-butanone, and 3-methyl-2-(5H) furanone decreased in some periods, and the decreases were up to 62.3 %, 42.13 %, 8.66 %, and 9.65 %, respectively. Some researchers have found that the ketones in Daqu liquor basically disappeared after irradiation (≥4 kGy), which reflects the effect of irradiation on the ketones in liquor to a certain extent (Zhang et al., 2018). Even the synergistic effects of volatilization, diffusion, and the storage environment also affects the change of the total ketone content.

Table 1
Effects of different irradiated containers and sealing materials on the quality of liquor before and after irradiation.

Combination	Sensory tasting	
	CK	Irradiation group
high borosilicate glass bottle (glass stopper)	normal aroma	mushy, unpleasant smell
high borosilicate glass bottle(silicone plug)	normal aroma	mushy, unpleasant smell
high borosilicate glass bottle(plastic wrap)	relatively normal aroma, with a green and stuffy taste	mushy, unpleasant smell
high borosilicate glass bottle(liquor stopper)	normal aroma	mushy, unpleasant smell
high borosilicate glass bottle(cork)	normal aroma	mushy, unpleasant smell
cuboid stainless steel tank (glass stopper)	normal aroma	normal aroma

3.3. Cluster heat map of aroma components of irradiated liquor

A total of 75 aromatic compounds were identified using GC-FID combined with a standard internal method, containing 10 series of acids, 32 esters, eight aldehydes, seven ketones, 16 alcohols, and two alkanes in the unirradiated and irradiated liquors. For quantitative analysis, detailed parameters, such as calibration curves and content ranges of the aroma components of the liquor, are summarized in Table A.2. Calibration curves were obtained by determining the ratio of the peak area and content of the internal standard and standard samples (Charapitsa et al., 2019). All aroma components in the content range achieved good linearity (correlation coefficients R^2 from 0.991 to 1.000). The limit of quantification for aroma components varied from 2.00 to 80.30 mg/100 mL, indicating good sensitivity.

To visualize the differences in the effect of different irradiation doses and storage times after irradiation on the concentration of chemical components of liquor, a heat map (Fig. 2) was generated and compared with the unirradiated liquor. Notably, eight aroma components are 0 mg/100 mL (sec-amyl alcohol, propyl acetate, isobutyl acetate, 2-heptanone, 3-ethyl-2-pentanol, benzaldehyde, 3-furan methanol, and nonanoic acid). The multivariate analysis did not include them (Zhang et al., 2021). The figure shows 67 aroma components.

The liquor components were divided into two categories, as shown in Fig. 2. The label “CK-days” represents unirradiated liquor (control). Category I contained 42 types of components, whereas Category II contained 25. Clustering into Category I or II indicated that the variation trends of the components before and after irradiation were similar. The total content of Category I components in the low-dose liquors (2–4 kGy) was lower than that in the high-dose liquors (6–12 kGy). The irradiation

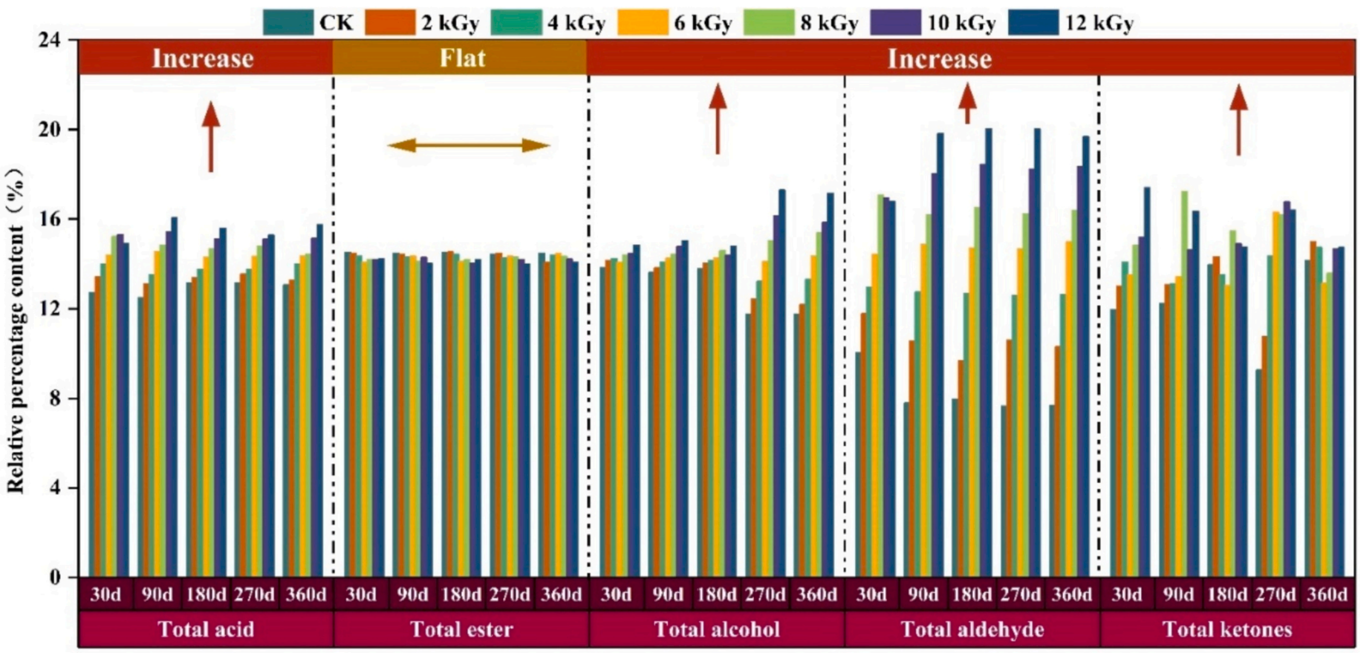

Fig. 1. Variations in the five types of volatile components of liquor according to different storage times and different irradiation doses.

dose affected the rate of oxidation, reduction, esterification, and hydrolysis reactions of the aroma components in the liquor, resulting in differences in the content of the aroma components in the liquor between the high- and low-dose irradiation group liquors (Jia et al., 2020).

In contrast, the total content of the components in Category II was reversed, which is due to the aromatic components' different chemical properties and characteristics. Changes in caproic acid, acetaldehyde, ethyl propionate, and other components may be largely due to the generation of free radicals by irradiation (Fu & Meng, 1994). The complexity of the chemical reaction is determined by the number of free radicals, which leads to different liquor components (Zhang et al., 2020). In addition, the content of liquor components changed with the extension of storage time after irradiation. Overall, both the irradiation dose and storage time after irradiation were key factors affecting the content of liquor components.

3.4. PCA analysis of aroma components of liquors

Clustering behavior was visualized by PCA to investigate the impact of irradiation dose and storage time after irradiation on the profiles of aroma components [Fig. 3(A), Fig. 3(B)]. Labelling by irradiation dose resulted in a random distribution of points in the PCA score plot, but labelling by storage time after irradiation resulted in a clear grouping. The first two principal components (PC1 and PC2) accounted for 49.3 % of the total variance (33.8 % for PC1 and 15.5 % for PC2). We found a clear separation between these groups, which were 30 d vs 90 d, 30 d vs 180 d, 30 d vs 270 d 30 d vs 360 d, 90 d vs 360 d, and 180 d vs 360 d. However, the rest of the groups overlapped. Considering all the aroma components is not a viable way to study irradiated liquors. Therefore, the identification of the key components related to irradiation requires the exclusion of other aroma components. Similarly, another study indicated that it is necessary to identify the key components associated with the liquor's aging time rather than taking all components into account (Zhang et al., 2021). These findings suggest that further research should be devoted to identifying the key components of irradiated liquor using supervised statistical methods.

In order to intuitively understand the changes of each aroma component with liquor irradiation dose and storage time after irradiation, we made Table A.3. In the analysis of variation of aroma components with dose, a total of 13 aroma components represented by dl-2-hydroxy-4-methylvaleric acid ethyl ester, 2,3-butanediol (L-racemic), 2,3-butanediol (meso-racemic), and isobutyric acid increased more, and the maximum increase is 25.483 times. The three components represented by glycerol 1,1-diethoxy-2-methylbutane, 1,1-diethoxy-3-methylbutane, and furfural were reduced more, and the reduction percentage was as low as 0.109. Moreover, with the extension of liquor storage time after irradiation, a total of six aroma components were detected to emerge from undetectable levels within 90 d to 360 d, and they are respectively acetone, 2-butanone, butyl butyrate, 3-hydroxy-2-butanone, propyl caproate, and diethyl succinate. The above conclusions can be combined with the content in Section 3.6.

3.5. Sensory evaluation results

The quality of the liquor irradiated at a low dose of 4 kGy was the best when stored for one year after irradiation. A radar map was generated to visualize the quality of Luzhou-flavor liquor treated with varying doses of irradiation one year after irradiation (Fig. 4). The corresponding sensory comments are listed in Table A.4. Within 30 d of storage after irradiation, the scores of all irradiated liquor were higher than unirradiated liquor, with a slight "aging flavor," which indicated that high-energy electron beam irradiation has a positive effect in accelerating the aging of liquor. The optimal irradiation dose for accelerating the liquor's aging was 8 kGy or 6 kGy during storage for 30 d after electron beam irradiation. Similarly, the optimal irradiation dose for accelerating the aging of Feng-flavor liquor was 5.9 kGy at storage for 40 d after γ-ray irradiation (Jia et al., 2020).

Notably, the taste of the liquor was poor for high-dose irradiated liquor storage for 180 d and 360 d after irradiation. The reason is that several free radicals produced by high-dose irradiation generated by increased irradiation time accelerate adverse chemical reactions and disturb the balance of aroma components of liquor (Aslanov et al., 2018; Bercu et al., 2017). Preliminary research from our laboratory and other research studies have reported that high-dose irradiated liquor and increasing irradiation frequency disrupt the dynamic balance in the natural aging process, resulting in poor taste (Jing et al., 2017; Zhang et al., 2020). Another study reported a similar reason for this phenomenon when high-vintage liquor was irradiated above a certain dose

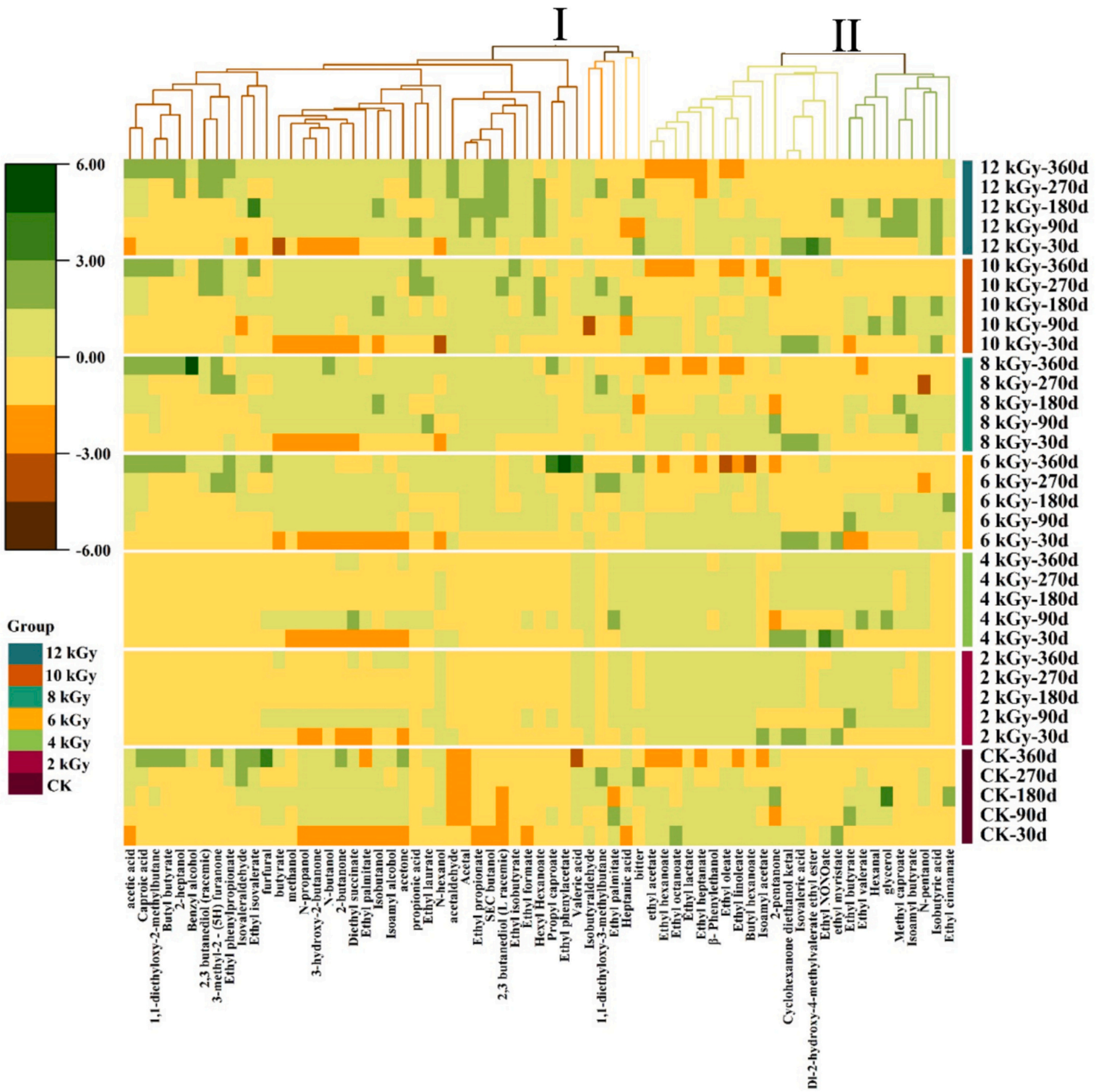

Fig. 2. Clustering heat map of the content of 67 types of volatile components of liquor according to different storage times and different irradiation doses.

(Zhang et al., 2014). When the liquor was stored for 360 d after irradiation, it had the highest score at a dose of 4 kGy. At this point, ethyl propionate and 2,3 butanediol (*meso*) levels significantly increased, enhancing the liquor's ester flavor and mellow sweetness.

3.6. Identification of irradiation markers of irradiated liquor

The main irradiation markers were short-chain fatty acids, ethyl esters, and alcohols. FC ($\geq$2 or $\leq$ 0.5) and *t*-test (p < 0.05) were employed to identify the differential components of irradiated liquors under different irradiation doses compared with unirradiated liquor. The UPE results based on the differential component dataset are shown in Fig. 5. The UPE plots show the common or unique components and intersections of diverse groups of liquors in storage for one year after irradiation. Eight possible markers of irradiated liquor, including ethyl propionate, dl-2-hydroxy-4-methyl valerate ethyl ester, isobutyric acid, acetaldehyde, propionic acid, hexyl hexanoate, 2,3 butanediol (levulinic), and 2,3 butanediol (endocyclc), increased significantly after irradiation.

3.6.1. Acid irradiation markers

Electron beam irradiation significantly increased isobutyric acid and propionic acid content. The taste of irradiated liquor can be improved by increasing the amount of acid (Xu et al., 2018). The role of propionic acid was also reflected in one study, which found that propionic acid (E) content in 5-year-old pure flavor liquor was significantly higher than in other vintages (Xu, Zhu, et al., 2017). Notably, isobutyric acid (C) was regarded as an irradiation marker for liquor stored for 30 d and 90

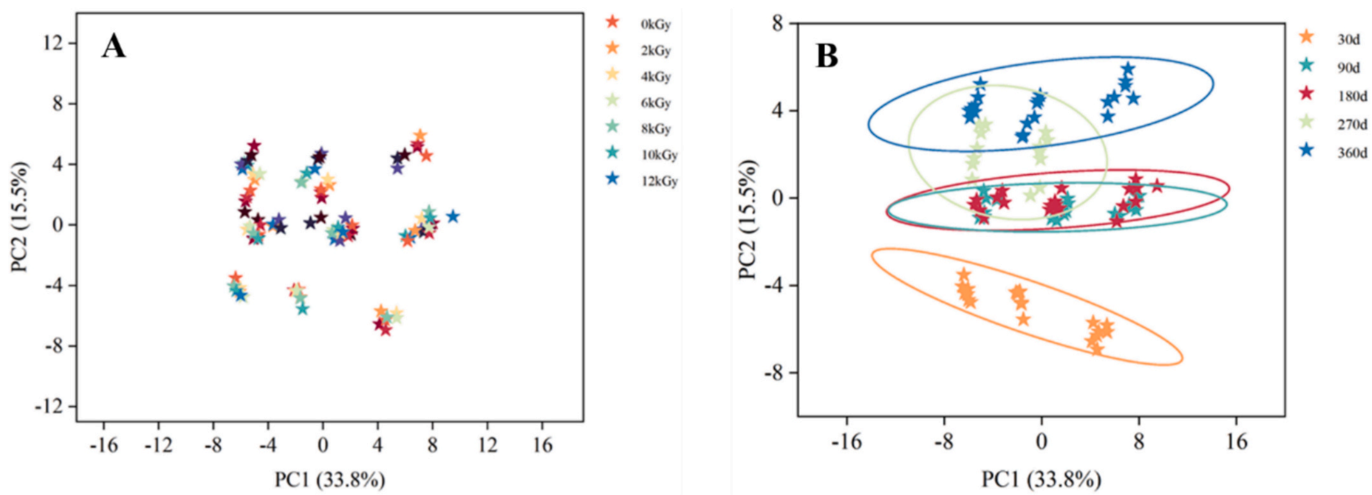

Fig. 3. (A) PCA of 67 aroma components of Luzhou-flavor liquors under different irradiation doses and (B) PCA of 67 aroma components of Luzhou-flavor liquors within storage for one year after irradiation.

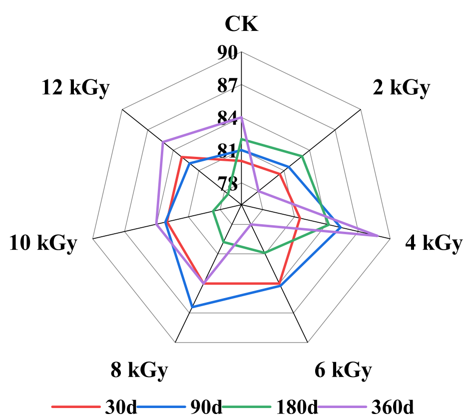

Fig. 4. Radar chart of sensory scores for liquor stored for different times after different doses of electron beam irradiation.

d after irradiation.

3.6.2. *Ester irradiation markers*

Among these, dl-2-hydroxy-4-methyl valerate ethyl ester was only an irradiation marker at storage for 30 d and 90 d after irradiation. Similarly, one study found that short−/medium-chain fatty acid esters may also be considered as age markers of liquor, especially for relatively older samples (> 2 years) (Zhang et al., 2021). Ethyl propionate, which was formed from acetic acid and n-propyl alcohol, can be used as a marker of the liquor for one year after irradiation. N-propanol is one of the components that provides astringent feelings in the taste of liquor. Too much N-propanol can produce pungent aromas and spicy tastes, affecting appetite (Zhu et al., 2020). At storage for 180 d and 270 d after irradiation, hexyl hexanoate was a marker of high-dose irradiation (≥ 10 kGy) with an apple aroma. A decrease in n-propyl alcohol and an increase in ethyl propionate and hexyl hexanoate can effectively improve liquor's taste and flavor.

3.6.3. *Aldehydes and alcohol irradiation markers*

As mentioned above, increased ethyl propionic acid and acetaldehyde content may be connected because of the free radicals generated by irradiation, which accelerate the oxidation and esterification reactions (Marin et al., 2019). Moreover, acetaldehyde can be an irradiation marker at an irradiation dose of more than 6 kGy. In comparison, 2,3 butanediol (levulinic) and 2,3 butanediol (endocyclic) can be irradiated markers of liquor at storage for 270 d and 360 d after irradiation. In addition, 2,3-butanediol isomers were found in the irradiated liquor, establishing a standard for identifying irradiated liquor (Yu et al., 2012). Notably, the propionic acid and valeric acid contents decreased significantly after storage for 180 d after 4 kGy irradiation, promoting the increase of esters. This is consistent with the results of the sensory evaluation of irradiated liquor.

3.7. *Identification of aging markers of natural aging liquor over one year*

The characteristic aroma components of the liquor differed with differing aging times. Four types of OPLS-DA models based on the aroma component dataset of two different aging times are shown in Fig. 6. Liquors with varying aging times could be distinguished, indicating significant differences in their aroma components. The related parameters for the four model types are listed in Table A.5. The model parameters were R^2_X (cum) = 0.981–0.994, R^2_Y (cum) = 0.999–1.000, and Q^2 (cum) = 0.987–0.998. The explanation rates, R^2_X (cum), R^2_Y (cum), and prediction rate Q^2 (cum), were close to 1, which indicated that they could better explain and predict the difference between the two groups of liquor samples. A permutation test ($n = 200$) was conducted to assess the degree of model fit (Song et al., 2019). The intercept values of R^2 and Q^2 in the permutation test demonstrated that the models did not overfit or meet the analysis requirements (Mullan et al., 2021). Different components of irradiated and unirradiated liquor were identified under different storage times after irradiation and quantified by FC (FC ≥2 or ≤ 0.5) and *t*-test results ($p < 0.05$) (Table A.6). The identification results are presented as volcano plots in Fig. 7.. The characteristic components of the naturally aging liquor over one year, identified by the three statistical methods, are summarized in Table A.7.

Acetaldehyde and caproic acid represented the half-year and one-year characteristic components of natural aging liquor in one year, respectively. Indeed, distinct components of natural aging liquor and irradiation marks of irradiated liquor differ. For example, acetaldehyde content in liquor significantly reduces with aging time (Xu, Yu, et al., 2017). This is consistent with the natural aging pattern of liquor, as the volatilization of aldehydes reduces the irradiation of liquor (Xu, Zhu, et al., 2017). The trends seen for acetaldehyde over one year are in contrast to those of irradiated liquor, but there is currently no evidence to explain this phenomenon. In addition, the increase in caproic acid could accelerate the formation of ethyl caproate and hexyl caproate, enriching the liquor's aroma. Previous research has indicated that some "fruity" compounds, namely ethyl butanoate, ethyl hexanoate, ethyl octanoate, ethyl pentanoate, and unsaturated long-chain fatty acids,

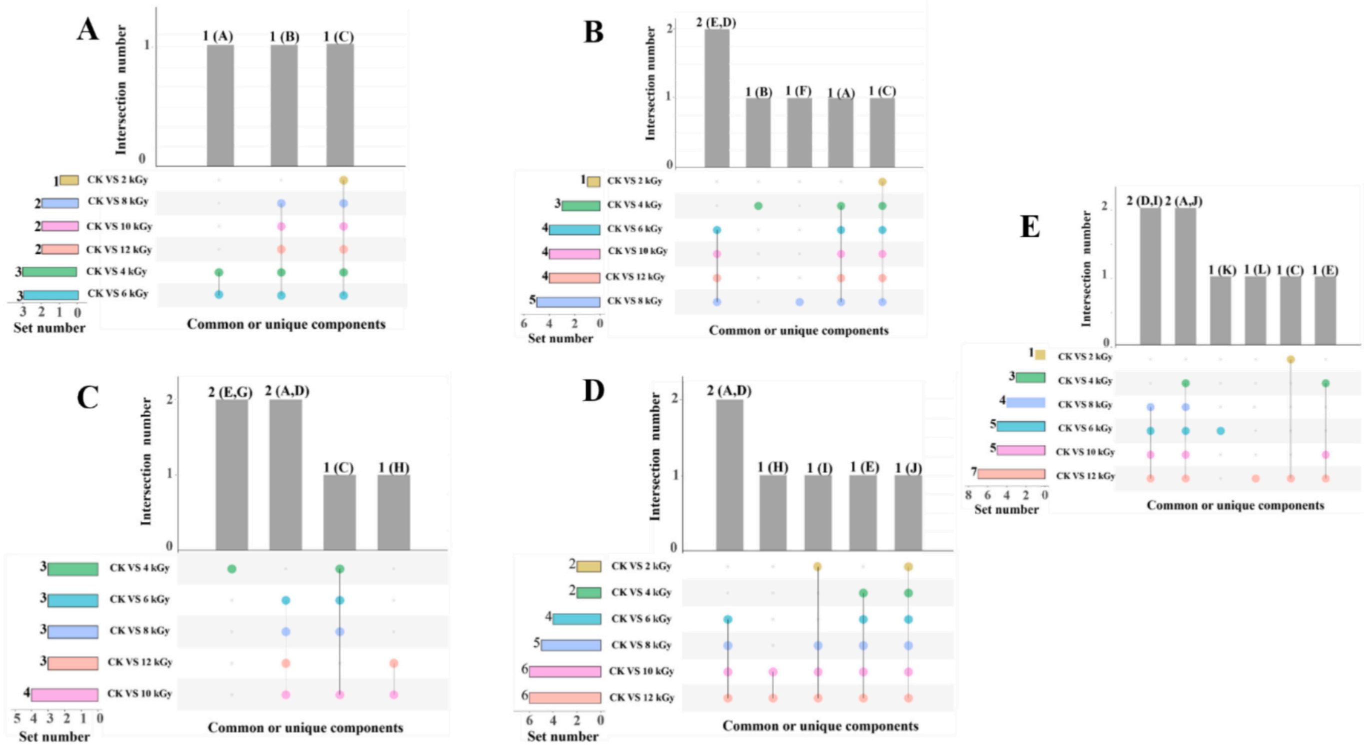

Fig. 5. Upset analysis of the different components of irradiated liquor and control liquor at different doses.

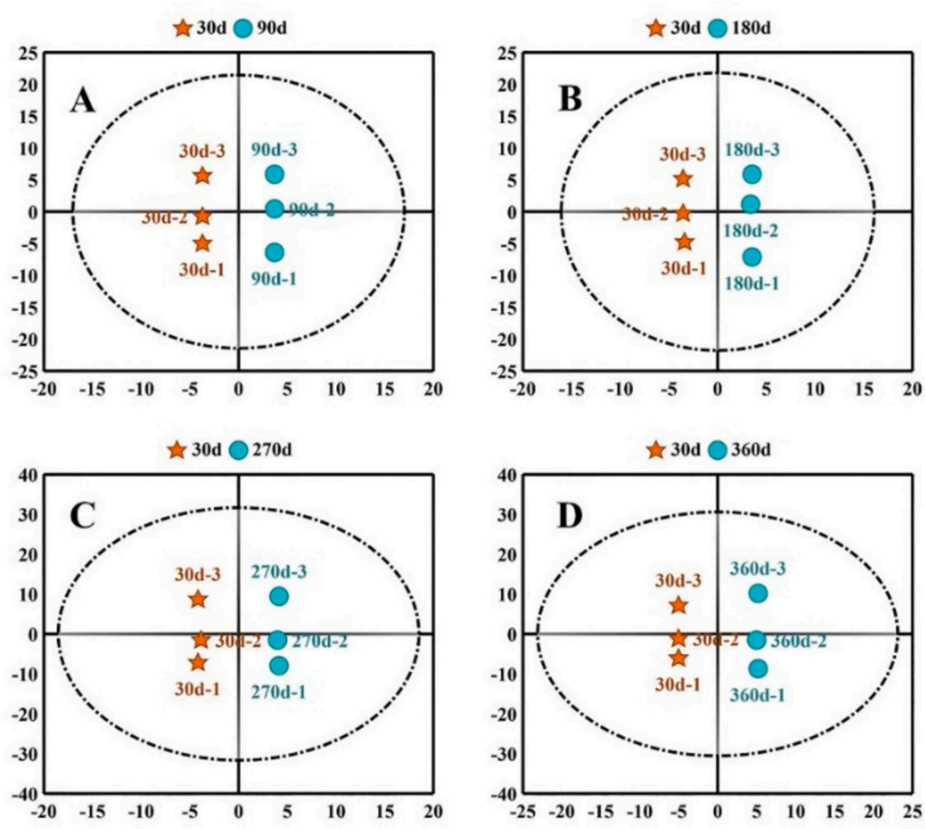

Fig. 6. OPLS-DA score plots of volatile components of liquors for different natural aging times.

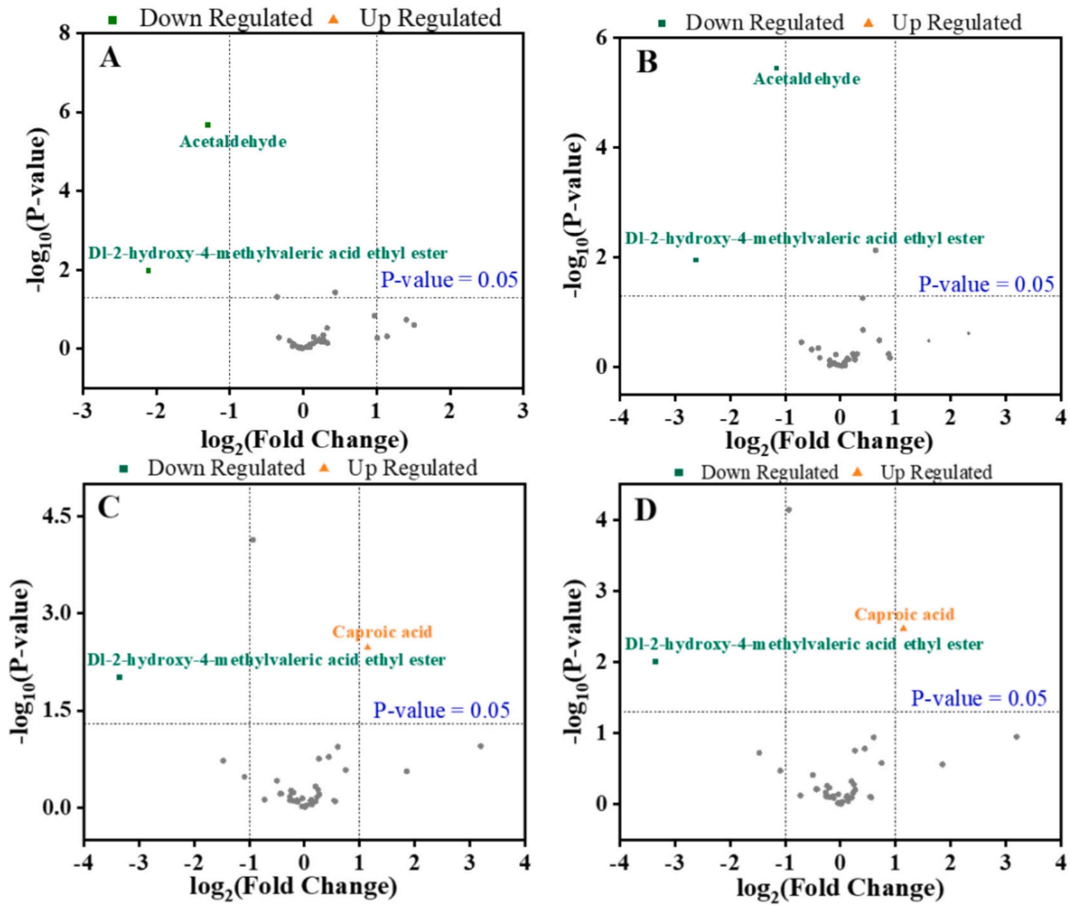

Fig. 7. Volcano plot analysis of the different natural aging times of liquors.

azelaic acid, and orthopaedic acid, are crucial to formulating the "aging" aroma (Zhu et al., 2020). These findings support our point that acetaldehyde and caproic acid are characteristic components in liquor that are aged naturally for one year.

This study had some limitations. The irradiation labels of Luzhou-flavor liquor of different manufacturers of Luzhou-flavor liquor and other flavor liquors have not been investigated. The sensory analysis method can further refine the aroma and taste evaluation to deepen the analysis of the effect of irradiation on the sensory quality of liquor. Moreover, this study lacks a correlation analysis between liquor flavor and markers.

4. Conclusions

This study screened a suitable combination of a stainless-steel tank and glass stopper-irradiated liquor through sensory taste evaluation. The content of aroma components in the liquor and the quality of the liquor were altered after high-energy electron beam irradiation of Luzhou-flavor liquor. The contents of most acids, alcohols, aldehydes, and ketones in the irradiated liquor increased with increasing doses of electron beam irradiation. Among them, the total aldehyde content increased the most with an increase in dose. Moreover, FC and *t*-test analysis confirmed eight types of potential irradiation markers for liquor irradiated by GC-FID, which mainly promoted the ester aroma and coordination of the liquor body. In addition, acetaldehyde and caproic acid were found in the naturally aged liquor after one year. The optimal irradiation dose for accelerating the aging of liquor ranged from a high dose (8 kGy) to a low dose (4 kGy), depending on the length of storage time after irradiation. Our findings can provide a theoretical basis for enterprises to control the quality of irradiated liquor. Future research should focus on the irradiation markers of irradiated liquors and investigate their effects on the quality of liquor through additional testing methods. Moreover, our ultimate goal is to find the common rules of flavor types and producers of liquors during long-term storage time after irradiation in aroma components, irradiation markers, and optimal irradiation dose by advanced methods.

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CRediT authorship contribution statement

Lili Zhang: Writing – original draft, Data curation. **Lina Pan:** Investigation, Funding acquisition. **Xiaoming Chen:** Writing – review & editing. **Defu Xu:** Conceptualization. **Xianbin Wang:** Methodology. **Rui Zhou:** Software. **Imran Ali:** Methodology. **Bensheng Wang:** Formal analysis. **Peng Gao:** Visualization. **Min Huang:** Resources. **Hao Chen:** Project administration. **Xiaoxue Dai:** Supervision. **Ruiqi Xue:** Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2025.102349.

Data availability

The data that has been used is confidential.

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