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Influence of ^{60}Co-γ Irradiation on the Components of Essential Oil of Curcuma

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Abstract: The gas chromatography–ion mobility spectrometry (GC-IMS) method is a new technology for detecting volatile organic compounds. This study was carried out to evaluate the effects of volatile aroma compounds of Curcuma essential oils (EOs) after ^{60}Co radiation by GC-IMS. Dosages of 0, 5, and 10 kGy of ^{60}Co were used to analyze EOs of Curcuma after ^{60}Co irradiation (named EZ-1, EZ-2, and EZ-3). The odor fingerprints of volatile organic compounds in different EOs of Curcuma samples were constructed by headspace solid-phase microextraction and GC-IMS after irradiation. The differences in odor fingerprints of EOs were compared by principal component analysis (PCA). A total of 92 compounds were detected and 65 compounds were identified, most of which were ketones, aldehydes, esters, and a small portion were furan compounds. It was found that the volatile matter content of 0 kGy and 5 kGy was closer, and the use of 10 kGy ^{60}Co irradiation would have an unstable effect on the EOs. In summary, it is not advisable to use a higher dose when using ^{60}Co irradiation for sterilization of Curcuma. Due to the small gradient of irradiation dose used in the experiment, the irradiation dose can be adjusted appropriately according to the required sterilization requirements during the production and storage process of Curcuma to obtain the best irradiation conditions. GC-IMS has the advantages of GC's high separation capability and IMS's fast response, high resolution, and high sensitivity, and the sample requires almost no pretreatment; it can be widely used in the analysis of traditional Chinese medicines containing volatile components. It is shown that irradiation technology has good application prospects in the sterilization of traditional Chinese medicines, but the changes in irradiation dose and chemical composition must be paid attention to.

Keywords: Curcuma; essential oils; chemical compounds; ^{60}Co irradiation; GC-IMS

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1. Introduction

Curcuma is widely used in traditional Chinese medicine. It is often used to promote the flow of qi, eliminate blood stasis with strong effect, and relieve pain by removing the stagnation of undigested food [1]. The pharmacological effects of essential oils (EOs) in Curcuma mainly include anti-tumor, anti-inflammatory analgesic, and antiviral effects, as well as protection of the cerebral tube, influence on the nervous system, protection of the kidneys, antioxidation, termination of pregnancy and prevention of early pregnancy, liver protection, cytotoxicity effects, antidepressant effects, and anti-diabetic effects [2–5]. In particular, the anti-tumor effect has attracted the attention of many researchers and has been widely used in clinical practice. It can be seen that Curcuma, as a commonly used clinical traditional Chinese medicine in the ginger family, has great medicinal value and is worthy of our in-depth development and utilization.

An efficient and rapid sterilization method, ^{60}Co irradiation is the use of high-energy rays produced by γ-ray ionizing radiation to produce powerful physical and biological effects in the process of energy transfer to achieve insecticidal effect, sterilization, and inhibition of physiological processes. The principle is mainly to destroy the DNA and RNA in microbial cells so that the damaged DNA and RNA are degraded, and the synthetic protein and genetic functions are lost to achieve the effect of killing cells [6]. Chinese medicine is highly susceptible to microbial contamination because of its complex composition. ^{60}Co irradiation sterilization has become more popular in the traditional pharmaceutical industry because it has the characteristics of cold treatment, strong penetration, simple operation, and continuous operation [7]. However, some traditional Chinese medicines have changed their chemical composition after irradiation, such as Gentianae macrophyllae Radix, Gentianae Radix et Rhizoma, Asteris Radix et Rhizoma, Bambusae concretio Silicea and Physalis calyx seu Fructus.

The GC-IMS method is a new technology for detecting volatile organic compounds. Here, the substances are further separated in the IMS drift tube. Analysis of IMS as a detector for GC can achieve two-dimensional separation of volatile organic substances [8]. It has the advantages of GC's high separation capability and IMS's fast response, high resolution, and high sensitivity, and the sample requires almost no pretreatment [9]. It is used in the analysis of foods containing volatile components.

In previous studies, the volatile oil of turmeric was extracted by steam distillation and irradiated with ^{60}Co rays of different intensities (dosages of 0, 5, and 10 kGy). The results showed that 97 volatile components were detected in turmeric volatile oil and 64 components were identified by database retrieval. With the change in irradiation intensity, the volatile components in the three turmeric volatile oil samples were similar but there were significant differences in peak intensities. In general, different doses of ^{60}Co irradiation can affect the content of volatile substances in turmeric volatile oil. As the irradiation dose increases, the peak area decreases, so the best irradiation dose is 5 kGy/min.

The essential oil of Curcuma, as its bioactive ingredient, is rich in chemical constituents. However, there are almost no reports in the literature of a study of the chemical constituents of Curcuma essential oil after ^{60}Co radiation by GC-IMS. We describe here for the first time the chemical components of the essential oils of Curcuma by GC-IMS. The purpose of this work is to determine the changes in essential oil composition under different irradiation intensities of ^{60}Co and to select an appropriate irradiation dose using GC-IMS.

2. Results

2.1. GC-IMS Analysis of EOs in Curcuma

The data generated by the instrument constitute a three-dimensional spectrogram (retention time, migration time, and peak intensity), as shown in Figure 1, from which the differences in volatile organic compounds in different samples can be intuitively seen. However, because of the inconvenience of observation, the following top view is taken for comparison of differences.

A two-dimensional top view of the compounds in Curcuma essential oils was generated using the Reporter plug-in, as shown in Figure 2. It consists of drift time, retention time, and ion signal intensity. The background of the whole figure is blue and the red vertical line at the abscissa at 1.0 is the RIP (reactive ion peak, normalized). The ordinate coordinate represents the retention time(s) of gas chromatography and the abscissa represents the ion migration time (normalization process). Each point on either side of the RIP represents a volatile organic compound. The color represents the concentration of the substance; white indicates a lower concentration, red indicates a higher concentration, and a darker color indicates a greater concentration.

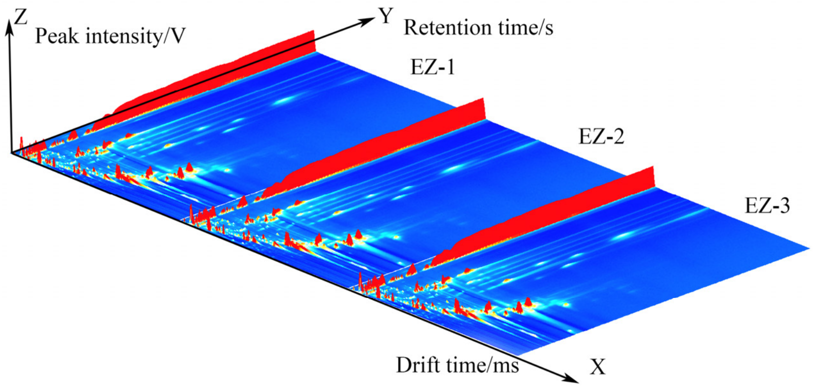

Figure 1. A comparison of the GC-IMS 3D spectra.

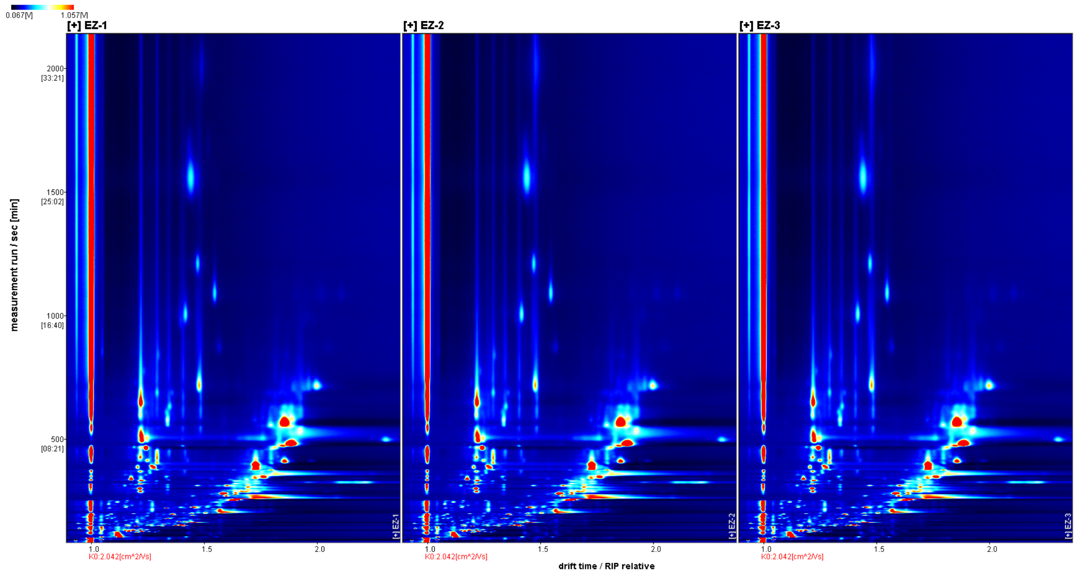

Figure 2. GC-IMS chromatograms of samples.

We use the Reporter plug-in to obtain a GC-IMS difference plot of the sample, as shown in Figure 3. We use EZ-1 as a reference and the rest of the spectra to subtract the signal peaks in EZ-1 to obtain a difference spectrum of the two. Regions with fewer points indicate that the substance is lower than EZ-1 in this sample and regions with more points indicate that the substance is more than EZ-1 in this sample. Similarly, the darker is the color, the greater is the difference.

2.2. EO Fingerprint Comparison of Samples

To visually and quantitatively compare EO differences between different samples, using the Gallery Plot plug-in, we obtain a Gallery Plot of the sample, as shown in Figure 4. Each row in the figure represents all the signal peaks selected in a sample. Each column in the figure represents the signal peak of the same volatile organic compound in different samples. Some of the substances are followed by _M and _D, which are monomers and dimers of the same substance, and the numbers are unidentified peaks. The complete EO information for each sample and the differences between EOs between samples can be seen from Figure 4.

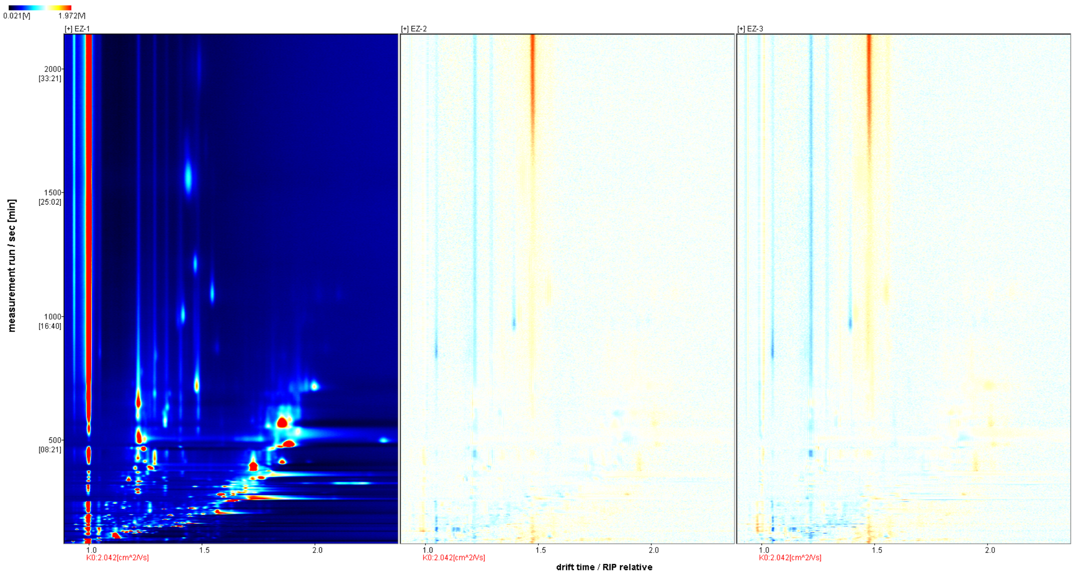

Figure 3. Difference analysis of GC-IMS of samples.

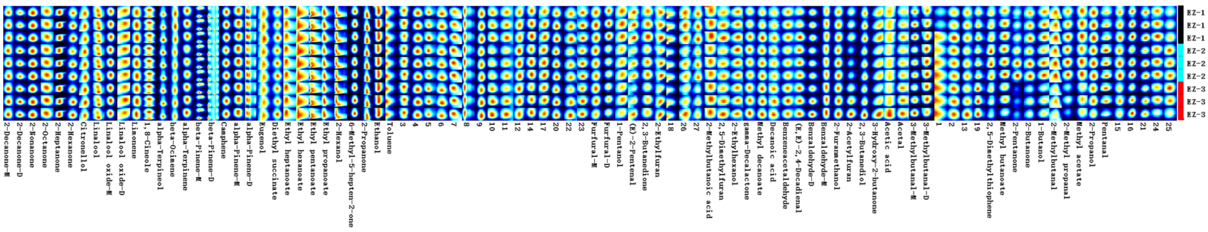

Figure 4. Gallery Plot of selected essential oil compounds by GC-IMS.

2.3. *PCA of EOs in Samples*

PCA is a multivariate data analysis tool for analyzing cubes with quantitative variables [10]. By using several main component factors to represent many other complex and hard-to-find variables in the original sample, we compare the differences between different samples. PCA of Curcuma essential oils was performed, and the results are shown in Figures 5 and 6. It can be seen from the figure that the composition of the essential oil after the treatment of the three methods is not the same, among which EZ-1 and EZ-2 are slightly more similar and EZ-3 is quite different from the other samples.

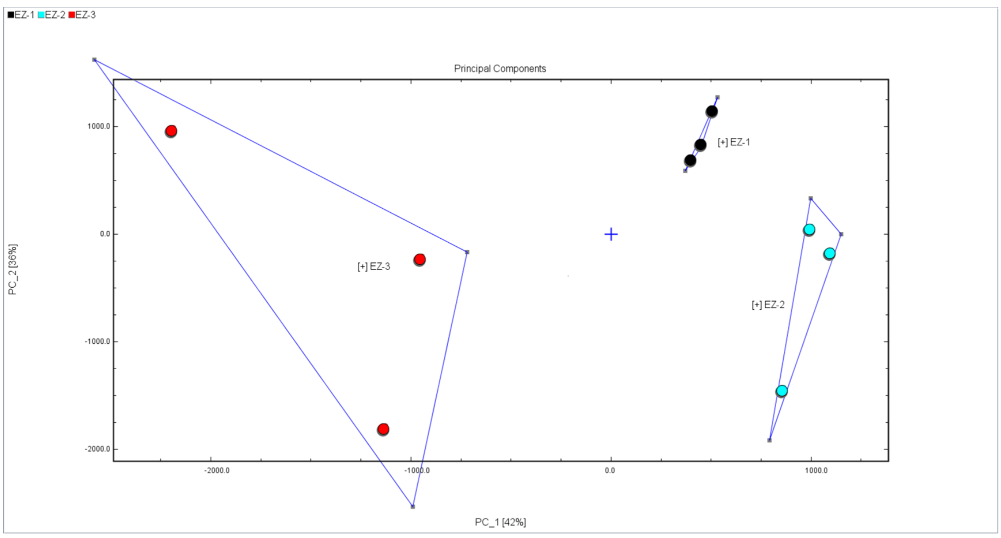

Figure 5. PCA analysis plot of the sample.

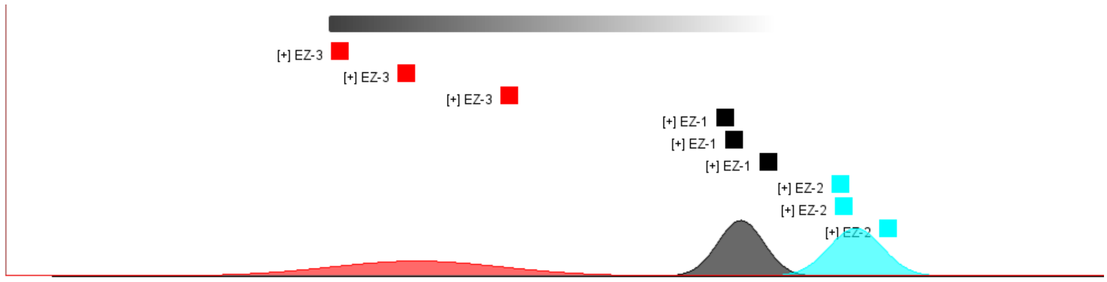

Figure 6. Sample's nearest neighbor–Euclidean distance map. (The closer the distance, the higher the similarity.)

2.4. Chemical Composition of the EOs

Using the NIST database and IMS database built into VOCal software(Version 0.4.03, GAS Deutschland, Dortmund, Germany) and other plugins (Reporter plugin, Gallery Plot plugin, Dynamic PCA plugin), we can qualitatively analyze the substance. A total of 65 chemical components have been identified from Curcuma essential oils after ^{60}Co irradiation and the composition identification results are shown in Table 1. Because of the higher dimer content of compounds such as 2-decanone, linalool oxide, and beta-pinene, two peaks were present; these correspond to monomers and dimers. As can be seen from Tables 1 and 2, the main chemical components of Curcuma essential oil include esters, aldehydes, terpenes, alcohols, ketones, and acids.

Table 1. Results of component analysis of Curcuma essential oils.

Count	Compound Name	CAS	RI	Molecular Formula	Rt/s	Dt/ms (RIPrel)	Comment
1	gamma-Decalactone	C706149	1598.5	$C_{10}H_{18}O_2$	1209.228	1.47454	-
2	Methyl decanoate	C110429	1508.0	$C_{11}H_{22}O_2$	1079.39	1.54878	-
3	(E,E)-2,4-Decadienal	C25152845	1454.2	$C_{10}H_{16}O$	1002.04	1.42077	-
4	Decanoic acid	C334485	1360.2	$C_{10}H_{20}O_2$	867.201	1.57124	-
5	Eugenol	C97530	1341.6	$C_{10}H_{12}O_2$	840.393	1.29711	-
6	2-Decanone	C693549	1256.7	$C_{10}H_{20}O$	718.508	1.48226	Monomers
7	2-Decanone	C693549	1255.1	$C_{10}H_{20}O$	716.197	1.99783	Dimers
8	alpha-Terpineol	C98555	1206.8	$C_{10}H_{18}O$	646.87	1.22248	-
9	Diethyl succinate	C123251	1234.7	$C_8H_{14}O_4$	686.937	1.29422	-
10	Citronellol	C106229	1197.5	$C_{10}H_{20}O$	633.591	1.34963	-
11	Linalool	C78706	1106.9	$C_{10}H_{18}O$	503.438	1.2229	-
12	Ethyl heptanoate	C106309	1122.5	$C_9H_{18}O_2$	525.872	1.9311	-
13	2-Nonanone	C821556	1091.9	$C_9H_{18}O$	481.9	1.88944	-
14	Linalool oxide	C60047178	1080.6	$C_{10}H_{18}O_2$	465.66	1.24616	Monomers
15	Linalool oxide	C60047178	1081.0	$C_{10}H_{18}O_2$	466.245	1.8138	Dimers
16	1,8-Cineole	C470826	1027.6	$C_{10}H_{18}O$	389.61	1.73145	-
17	beta-Ocimene	C13877913	1054.5	$C_{10}H_{16}$	428.22	1.21822	-
18	Benzeneacetaldehyde	C122781	1045.1	C_8H_8O	414.765	1.2491	-
19	Limonene	C138863	1025.6	$C_{10}H_{16}$	386.685	1.20792	-
20	alpha-Terpinene	C99865	1015.0	$C_{10}H_{16}$	371.475	1.22263	-
21	6-Methyl-5-hepten-2-one	C110930	990.5	$C_8H_{14}O$	339.885	1.17704	-
22	beta-Pinene	C127913	976.0	$C_{10}H_{16}$	327.6	1.21969	Monomers
23	beta-Pinene	C127913	976.0	$C_{10}H_{16}$	327.6	1.64175	Dimers
24	Camphene	C79925	944.9	$C_{10}H_{16}$	301.275	1.21822	-
25	alpha-Pinene	C80568	931.8	$C_{10}H_{16}$	290.16	1.22116	Monomers
26	alpha-Pinene	C80568	931.1	$C_{10}H_{16}$	289.575	1.67557	Dimers
27	2-Ethylhexanol	C104767	1018.3	$C_8H_{18}O$	376.21	1.79856	-
28	Ethyl hexanoate	C123660	1007.5	$C_8H_{16}O_2$	360.735	1.81595	-
29	2-Octanone	C111137	999.2	$C_8H_{16}O$	348.832	1.7651	-
30	Benzaldehyde	C100527	959.8	C_7H_6O	313.914	1.15225	Monomers

Table 1. *Cont.*

Count	Compound Name	CAS	RI	Molecular Formula	Rt/s	Dt/ms (RIPrel)	Comment
31	Benzaldehyde	C100527	959.4	C_7H_6O	313.517	1.47206	Dimers
32	Ethyl pentanoate	C539822	901.2	$C_7H_{14}O_2$	264.315	1.71158	-
33	2-Heptanone	C110430	891.6	$C_7H_{14}O$	256.379	1.62862	-
34	2-Furanmethanol	C98000	873.3	$C_5H_6O_2$	246.856	1.1188	-
35	2-Acetylfuran	C1192627	911.1	$C_6H_6O_2$	272.648	1.45333	-
36	2,5-Dimethylthiophene	C638028	856.5	C_6H_8S	238.127	1.07866	-
37	Furfural	C98011	828.3	$C_5H_4O_2$	223.446	1.08401	Monomers
38	Furfural	C98011	826.7	$C_5H_4O_2$	222.652	1.3329	Dimers
39	2-Methylbutanoic acid	C116530	827.5	$C_5H_{10}O_2$	223.049	1.46938	-
40	2-Hexanol	C626937	793.1	$C_6H_{14}O$	205.193	1.56974	-
41	2-Hexanone	C591786	791.9	$C_6H_{12}O$	204.546	1.50912	-
42	2,3-Butanediol	C513859	778.3	$C_4H_{10}O_2$	198.14	1.3627	-
43	1-Pentanol	C71410	760.5	$C_5H_{12}O$	190.908	1.25055	-
44	Acetal	C105577	748.9	$C_6H_{14}O_2$	186.155	0.96913	-
45	(E)-2-Pentenal	C1576870	747.3	C_5H_8O	185.535	1.36062	-
46	3-Hydroxy-2-butanone	C513860	733.1	$C_4H_8O_2$	179.749	1.33778	-
47	2,5-Dimethylfuran	C625865	739.9	C_6H_8O	182.503	1.0218	-
48	Methyl butanoate	C623427	716.5	$C_5H_{10}O_2$	172.993	1.15331	-
49	Ethyl propanoate	C105373	695.4	$C_5H_{10}O_2$	164.398	1.44128	-
50	2-Pentanone	C107879	686.6	$C_5H_{10}O$	161.106	1.37552	-
51	2-Ethylfuran	C3208160	674.9	C_6H_8O	157.998	1.3211	-
52	2-Methylbutanal	C96173	663.8	$C_5H_{10}O$	155.072	1.40387	-
53	3-Methylbutanal	C590863	650.6	$C_5H_{10}O$	151.597	1.4118	Dimers
54	1-Butanol	C71363	656.2	$C_4H_{10}O$	153.06	1.37552	-
55	3-Methylbutanal	C590863	645.1	$C_5H_{10}O$	150.134	1.20319	Monomers
56	2-Butanone	C78933	591.7	C_4H_8O	136.053	1.24854	-
57	2-Methyl propanal	C78842	555.1	C_4H_8O	126.36	1.28596	-
58	2-Propanol	C67630	565.4	C_3H_8O	129.104	1.22814	-
59	2,3-Butanedione	C431038	582.1	$C_4H_6O_2$	133.493	1.18732	-
60	Acetic acid	C64197	565.4	$C_2H_4O_2$	129.104	1.16918	-
61	2-Propanone	C67641	502.4	C_3H_6O	112.462	1.11816	-
62	Ethanol	C64175	476.1	C_2H_6O	105.513	1.12723	-
63	Methyl acetate	C79209	550.9	$C_3H_6O_2$	125.263	1.20319	-
64	Toluene	C108883	772.7	C_7H_8	195.852	1.01046	-
65	Pentanal	C110623	693.6	$C_5H_{10}O$	163.667	1.18165	-

Table 2. Area of Curcuma volatile oil.

No	Compounds	Molecular Formula	Comment	[+] EZ-1	[+] EZ-2	[+] EZ-3
1	gamma-Decalactone	$C_{10}H_{18}O_2$	-	2912.16	3431.98	3369.21
2	Methyl decanoate	$C_{11}H_{22}O_2$	-	3341.36	3892.70	4013.00
3	(E,E)-2,4-Decadienal	$C_{10}H_{16}O$	-	2973.06	3282.99	3434.15
4	Decanoic acid	$C_{10}H_{20}O_2$	-	547.35	633.02	734.73
5	Eugenol	$C_{10}H_{12}O_2$	-	1281.77	1241.07	1233.21
6	2-Decanone	$C_{10}H_{20}O$	Monomers	6027.45	6303.08	6420.79
7	2-Decanone	$C_{10}H_{20}O$	Dimers	5086.61	5864.29	5719.93
8	alpha-Terpineol	$C_{10}H_{18}O$	-	11,283.16	11,913.89	11,295.72
9	Diethyl succinate	$C_8H_{14}O_4$	-	1309.52	1346.32	1390.25
10	Citronellol	$C_{10}H_{20}O$	-	1096.75	1081.54	1118.81
11	Linalool	$C_{10}H_{18}O$	-	9174.36	8964.94	9084.55
12	Ethyl heptanoate	$C_9H_{18}O_2$	-	8358.19	8392.94	8400.00
13	2-Nonanone	$C_9H_{18}O$	-	17,585.94	17,143.82	17,310.05
14	Linalool oxide	$C_{10}H_{18}O_2$	Monomers	4690.67	4701.49	4740.07
15	Linalool oxide	$C_{10}H_{18}O_2$	Dimers	1377.23	1291.99	1354.36
16	1,8-Cineole	$C_{10}H_{18}O$	-	12,249.16	12,122.78	12,239.11

Table 2. *Cont.*

No	Compounds	Molecular Formula	Comment	[+] EZ-1	[+] EZ-2	[+] EZ-3
17	beta-Ocimene	$C_{10}H_{16}$	-	1694.48	1418.96	1385.90
18	Benzeneacetaldehyde	C_8H_8O	-	907.73	843.63	960.16
19	Limonene	$C_{10}H_{16}$	-	1129.65	1087.89	1100.73
20	alpha-Terpinene	$C_{10}H_{16}$	-	918.33	753.93	883.22
21	6-Methyl-5-hepten-2-one	$C_8H_{14}O$	-	2011.42	1931.01	1962.76
22	beta-Pinene	$C_{10}H_{16}$	Monomers	2522.96	2519.12	2598.67
23	beta-Pinene	$C_{10}H_{16}$	Dimers	5057.77	4934.82	4995.13
24	Camphene	$C_{10}H_{16}$	-	2191.88	1963.45	1998.16
25	alpha-Pinene	$C_{10}H_{16}$	Monomers	1366.07	1343.20	1351.68
26	alpha-Pinene	$C_{10}H_{16}$	Dimers	3062.82	2762.18	2848.96
27	2-Ethylhexanol	$C_8H_{18}O$	-	570.80	651.25	626.41
28	Ethyl hexanoate	$C_8H_{16}O_2$	-	6863.47	6978.71	7043.41
29	2-Octanone	$C_8H_{16}O$	-	2915.13	2853.83	2942.25
30	Benzaldehyde	C_7H_6O	Monomers	221.68	219.65	238.90
31	Benzaldehyde	C_7H_6O	Dimers	473.44	415.37	483.78
32	Ethyl pentanoate	$C_7H_{14}O_2$	-	20,873.63	20,994.98	20,390.77
33	2-Heptanone	$C_7H_{14}O$	-	7475.55	7083.04	7137.75
34	2-Furanmethanol	$C_5H_6O_2$	-	388.76	373.74	385.81
35	2-Acetylfuran	$C_6H_6O_2$	-	235.13	147.71	235.75
36	2,5-Dimethylthiophene	C_6H_8S	-	373.28	428.12	347.52
37	Furfural	$C_5H_4O_2$	Monomers	179.78	171.41	169.89
38	Furfural	$C_5H_4O_2$	Dimers	301.64	223.43	233.77
39	2-Methylbutanoic acid	$C_5H_{10}O_2$	-	296.69	266.89	276.09
40	2-Hexanol	$C_6H_{14}O$	-	7430.20	7138.66	7364.58
41	2-Hexanone	$C_6H_{12}O$	-	453.71	389.56	391.78
42	2,3-Butanediol	$C_4H_{10}O_2$	-	847.31	685.55	654.67
43	1-Pentanol	$C_5H_{12}O$	-	120.72	108.34	108.60
44	Acetal	$C_6H_{14}O_2$	-	113.23	112.71	135.34
45	(E)-2-Pentenal	C_5H_8O	-	79.52	61.97	58.52
46	3-Hydroxy-2-butanone	$C_4H_8O_2$	-	467.65	377.73	358.13
47	2,5-Dimethylfuran	C_6H_8O	-	45.71	46.97	51.40
48	Methyl butanoate	$C_5H_{10}O_2$	-	74.38	79.05	70.13
49	Ethyl propanoate	$C_5H_{10}O_2$	-	1540.94	1377.37	1423.45
50	2-Pentanone	$C_5H_{10}O$	-	113.31	125.79	49.42
51	2-Ethylfuran	C_6H_8O	-	225.15	186.35	177.51
52	2-Methylbutanal	$C_5H_{10}O$	-	744.68	675.02	583.69
53	3-Methylbutanal	$C_5H_{10}O$	Dimers	788.51	732.97	689.25
54	1-Butanol	$C_4H_{10}O$	-	398.41	379.24	285.82
55	3-Methylbutanal	$C_5H_{10}O$	Monomers	299.34	222.36	229.26
56	2-Butanone	C_4H_8O	-	253.22	227.04	159.78
57	2-Methyl propanal	C_4H_8O	-	161.44	153.49	88.17
58	2-Propanol	C_3H_8O	-	1192.77	1087.52	1045.79
59	2,3-Butanedione	$C_4H_6O_2$	-	391.70	358.15	347.32
60	Acetic acid	$C_2H_4O_2$	-	718.70	654.59	652.46
61	2-Propanone	C_3H_6O	-	9466.58	8838.34	8918.75
62	Ethanol	C_2H_6O	-	2438.91	2048.25	2256.04
63	Methyl acetate	$C_3H_6O_2$	-	364.86	337.56	295.63
64	Toluene	C_7H_8	-	498.55	426.60	460.66
65	Pentanal	$C_5H_{10}O$	-	94.88	126.62	106.95

3. Discussion

This study used GC-IMS to analyze the essential oils of Curcuma under different doses of irradiation. In the obtained three-dimensional, two-dimensional, and differential comparison spectra, it was clearly observed that there were differences in the content of volatile components among the three irradiation dose components. To confirm the conclusion, a PCA differential analysis model was established and the Euclidean distance between samples was calculated to reduce the dimensionality of the data for visualization [11,12]. It can be more intuitively understood that the volatile components of EZ-1 and EZ-2 samples are closer, while EZ-3 samples have significant differences from the other two components when they are far apart, and the three samples between groups are also relatively dispersed; the dosage of 10 kGy has a significant and unstable impact on the volatile component content of the essential oil from Curcuma. Qualitative analysis was conducted on the volatile components in the essential oil of Curcuma and a total of 92 compounds were detected. Among them, 65 compounds were able to be identified and 27 compounds were temporarily unable to be confirmed due to incomplete databases. The confirmed compounds include 11 ketones, 10 aldehydes, 9 esters, 6 terpenoids, and a small amount of acid compounds.

It can be seen from the fingerprint that the contents of furfural, 1-pentanol, E-2-pentenal, 2,3-butanedione, 2-ethylfuran, and other substances are higher in EZ-1. The contents of methyl 2,5-dimethylthiophene, methyl butyrate, 2-pentanone, 2-butanone, 1-butanol, 2-methylbutyral, methyl acetate, 2-propanol, valeraldehyde, and other substances in EZ-2 are higher. The contents of γ-caprolactone, methyl caprate, capric acid, phenylacetaldehyde, (E, E)-2,4-decadienoal, benzaldehyde, 2-furanmethanol, 2-acetylfuran, 2,3-butanediol, 3-hydroxy-2-butanone, acetic acid, acetal, and other substances in EZ-3 are higher. If there are specific requirements for the selection of the content of a certain component, the appropriate irradiation dosage is recommended.

This is somewhat different from the volatile oil of Curcuma detected using GC-MS technology [13–16]. The possible reason is that more small molecule substances are detected.

Modern pharmacology has shown that Curcuma has anti-tumor effects, anti-inflammatory effects, and anticoagulant effects, as well as improving liver and kidney function [17–23]. It has very high medicinal value, and most of the component analysis of Curcuma is carried out using GC-MS technology. This study uses GC-IMS technology to analyze the volatile oil of Curcuma, which can better detect substances with lower thresholds, it can provide a more detailed report for the pharmacological study of effective substances in the volatile oil of Curcuma. At the same time, it also provides a certain selection basis for the dosage standard of ^{60}Co radiation sterilization used in the production and storage of traditional Chinese medicinal materials of Curcuma, which has high research significance.

^{60}Co irradiation is a high-energy ray produced by γ-ray ionizing radiation, which is used for efficient and rapid sterilization. The principle is to destroy DNA and RNA in microbial cells, thereby killing cells. The source of traditional Chinese medicine is complex and it is extremely polluted by microorganisms and some harmful pests. When other sterilization methods such as high temperature destroy the ingredients of traditional Chinese medicine, irradiation sterilization becomes a good method, and it is easy to operate and has strong penetrating power. But some traditional Chinese medicines have changed their chemical composition after irradiation, such as Gentianae macrophyllae Radix, Gentianae Radix et Rhizoma, Asteris Radix et Rhizoma, and Physalis calyx seu Fructus. So, the changes in irradiation dose and chemical composition must be paid attention to.

4. Materials and Methods

4.1. Plant Material

Curcuma (the rhizome of *Curcuma wenyujin* Y. H. Chen et C. Ling) was gathered from Baise, China and identified by Prof. Zhaoming Xie at the Hunan Academy of Traditional Chinese Medicine. A voucher specimen (HNATCM2021-012) was deposited in the herbarium of the Hunan Academy of Traditional Chinese Medicine.

4.2. Isolation of the EOs

The sample (50 g) was subjected to hydro-distillation in a Clevenger-type apparatus for 5 h in accordance with the Pharmacopoeia of China (2020). In brief, a sample was added to 300 mL of distilled deionized water in a 1.0 L round-bottomed flask and heated to boiling, after which the essential oil was evaporated together with water vapor and finally collected in a condenser. The essential oil layer was separated, preserved in a sealed sample tube, and then stored in the dark (away from light) at 4 °C for analysis. The yield of extraction was 2.2% (*w*/*w*) based on the weight of sample.

4.3. ^{60}Co Irradiation

The resulting Curcuma EOs were dehydrated with anhydrous Na_2SO_4 and then divided into three equal parts for ^{60}Co irradiation (store in 1.5 mL sealed vials), radiation source intensity 2.96×10^{16} Bq, irradiation method: dynamic stepping. Dose rates were 0, 5, and 10 kGy/min; irradiation time was 6 h. The ^{60}Co γ radiation source (^{60}Co class I radioactive source irradiation equipment, Huangshi, China) was located at Hunan Radiological Technology Application Research Center (Changsha, China).

4.4. GC-IMS Analysis

The GC-IMS analysis was performed using GC coupled with an ion mobility spectrometry instrument (Flavourspec®-G.A.S., Dortmund, Germany). The sample enters the instrument with the carrier gas, first through the initial separation of the gas chromatography column and then into the ion migration tube. After the ionization of the molecule to be measured, under the action of the electric field and the reverse drift gas, it migrates to the Faraday disc for detection to achieve secondary separation.

We take 50 µL of sample, load it into a 20 mL headspace flask, heat the headspace vial at 80 °C for 10 min, and incubate it at 500 rpm. Automatic headspace injection volume is 100 µL and the temperature of the injection needle is 85 °C for headspace injection analysis.

GC conditions: The column is an MXT-5 column (15 m × 0.53 mm × 1 µm), the column temperature is 60 °C, and the carrier gas is N_2. The carrier air velocity program is initially 2.0 mL/min, which is held for 2 min, linearly increased to 100.0 mL/min at 2 min to 20 min, and maintained at a flow rate of 100.0 mL/min for 20 min to 40 min. Flow is then stopped for a total running time of 40 min.

IMS conditions: drift gas is N_2 and drift gas velocity is 150 mL/min.

4.5. Statistical Analysis

Using the NIST 17 database, we identified compounds in the GC-IMS data by comparing the linear retention indices and mass spectra. The GC-IMS data were examined using the special software including LAV (from G.A.S., Dortmund, Germany version 2.0.0), Reporter, Gallery Plot, and GC-IMS Library Search. Using NIST Library and IMS database retrieval software from G.A.S., we determined the detected EOs by combining the retention index (RI) and drift time (Dt).

5. Conclusions

The experimental results showed that irradiation with 0, 5, and 10 kGy on the volatile oil of Curcuma does not produce new substances, but it can change the content of its volatile substances and the effects on different substances are inconsistent. Using GC-IMS for qualitative analysis of volatile compounds, a total of 92 compounds were detected, most of which were ketones, aldehydes, and esters, and a small portion were furan compounds. GC-IMS detection has more efficient separation ability and sensitive response speed, and can detect small molecule compounds without sample pretreatment, making it more effective for analyzing the differences in volatile components among different samples. By analyzing the GC-IMS fingerprint, PCA, and adjacent Euclidean distance map of the sample, it was found that the volatile matter content of 0 kGy and 5 kGy was closer, and the use of 10 kGy ^{60}Co irradiation would have an unstable effect on the EOs. In summary, it is not advisable to use a higher dose when using ^{60}Co irradiation for sterilization of Curcuma. Due to the small gradient of irradiation dose used in the experiment, the irradiation dose can be adjusted appropriately according to the required sterilization requirements during the production and storage process of Curcuma to obtain the best irradiation conditions. The results indicated that irradiation has a certain effect on the composition of Curcuma EOs; with the increase in irradiation dose, some composition of Curcuma EOs changed. This study provides a sound basis for the use of ^{60}Co-γ ray irradiation sterilization technology during the preparation of medicinal herbs for the effective destruction of mycotoxin contamination.

It shows that irradiation technology has a good application prospect in the sterilization of foods and traditional Chinese medicine containing volatile components, but the changes in irradiation dose and chemical composition must be paid attention to. GC-IMS has the advantages of simple operation, strong separation ability, short detection cycle, and the ability to preserve the original taste of samples to the greatest extent, and can be successfully applied to foods and traditional Chinese medicine.

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