Electronic Supplementary Information

1 Sample preparation of PbI_2-tea

Another sample was prepared to calculate the limit of detection (LoD) of Pb in tea. Here, PbI_2 reagent (p-OLED, China) with purity > 99.99% was used to prepare a PbI_2 solution with a concentration of 0.001 g/mL. And Tieguanyin tea powder was mixed with the PbI_2 solution, referred to as PbI_2-tea samples, which was used to calculate the LoD of Pb element. The sample pre-treatment process is shown in Fig. S1. Firstly, 0.001 g/mL PbI_2 solution (heated to 100℃ in water bath) was prepared and diluted in different degrees. Then, six parts of 4 g tea powders were weighed to prepare a solid-liquid mixture with Pb content of 1, 10, 50, 100, 1000 and 10000 ppm, respectively. In order to mix tea powder and PbI_2 solution fully and evenly, the mixture was shaken in an ultrasonic cleaner (SK1200H, Kudos, China) for 10 minutes, and then dried in a drying oven (DHG-9146A, Jing Hong, China) at 120℃ for 8 hours. After drying, the sample was crushed into powder again, and 2 g powder was pressed into pellet.

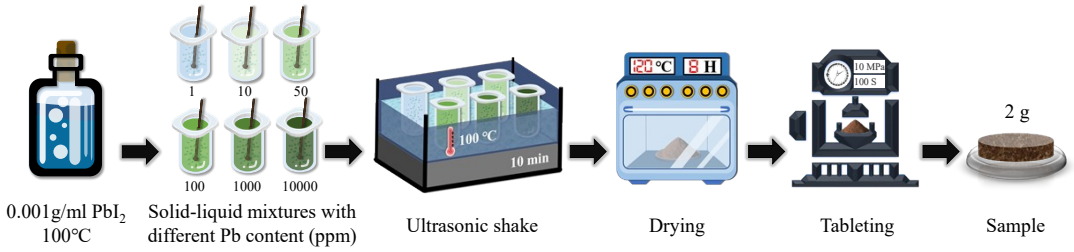


Fig. S1 Schematic diagram of LCG-tea samples pre-treatment process.

2 LIBS spectra and elemental analysis

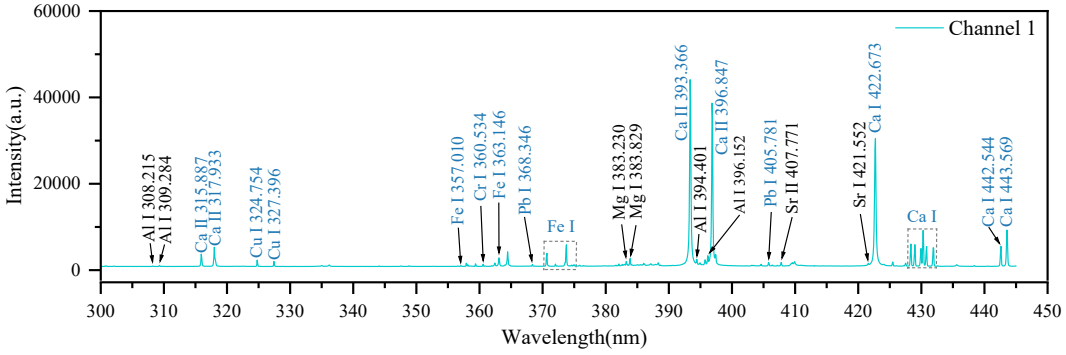
Table S1. All characteristic lines selected in Fig. 3.

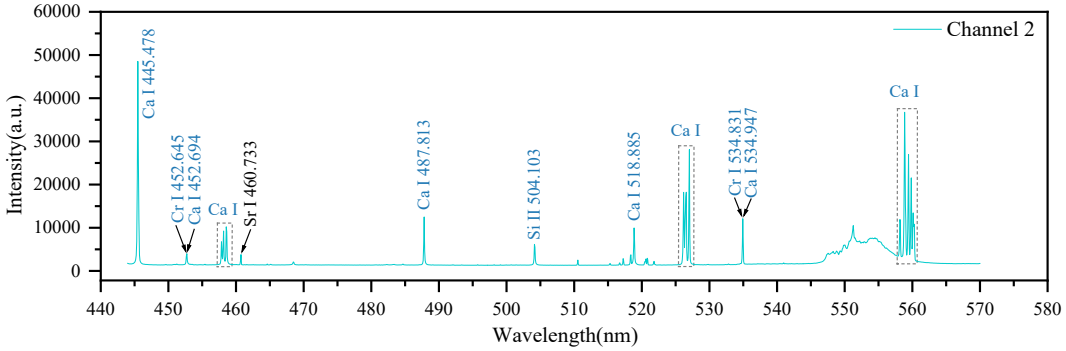
Elements	Wavelength (nm)
Ca I	422.722, 428.342, 428.969, 429.942, 430.289, 430.843, 431.880, 457.849, 458.084, 458.554, 487.818, 585.756, 610.317, 612.263, 616.263, 643.965, 645.015, 646.298, 647.229, 649.436, 650.015, 657.280
Ca II	315.916, 317.992, 393.369, 396.848, 849.759, 854.195, 866.290
Si I	390.628
Si II	504.127
Sr I	421.588, 460.739
Sr II	407.788
O I	777.277, 777.549, 844.679
N I	742.454, 744.329, 746.882, 818.580, 818.896, 820.053, 821.102, 821.731, 822.359, 824.343, 856.836, 859.461, 863.034, 868.099, 868.384, 870.373, 871.222, 871.975, 873.009

H I	656.361
Na I	589.002, 589.625
Mg I	383.241, 383.860, 516.697, 517.239, 518.320
Al I	308.255, 309.304, 394.430, 396.169
Fe I	357.014, 363.085, 370.683, 373.772
Mn I	403.133, 403.355, 403.504
K I	766.592, 769.940
Cu I	324.783, 327.431
Pb I	368.375, 405.799
Cr I	360.583, 425.473, 452.653

Table S2. Selected CN and CaO radical characteristic lines in Fig. 3.

Free radical	Wavelength (nm)
CN	357.908, 358.152, 385.098, 386.178, 387.179, 388.331, 415.217, 415.794, 416.729, 418.093, 419.737
CaO	596.822, 598.427, 600.399, 603.350, 605.923, 606.657, 620.726, 622.408, 623.128, 624.805





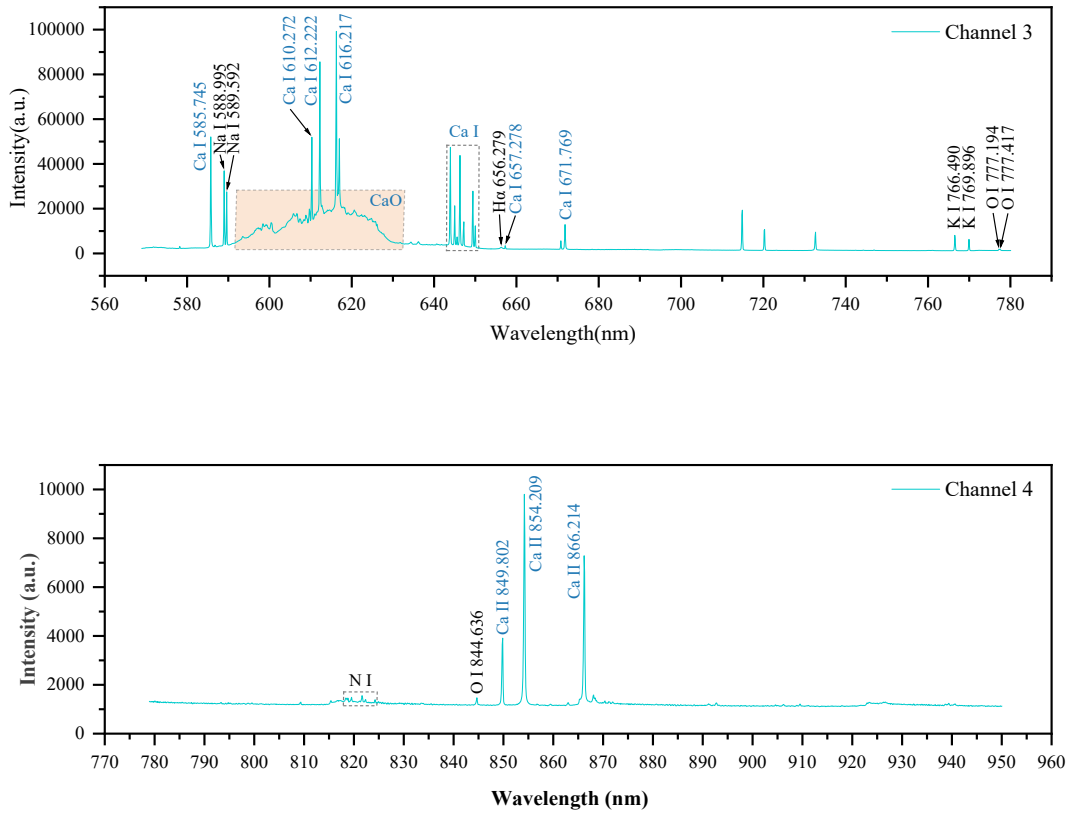


Fig. S2 LIBS spectra of lead chrome-green powder.

3 PCA models

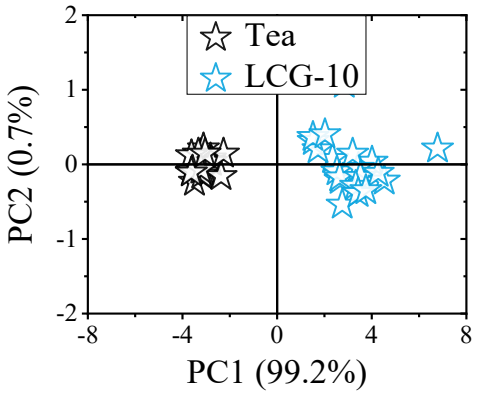


Fig. S3 PCA model based on CN radical characteristic spectral lines.

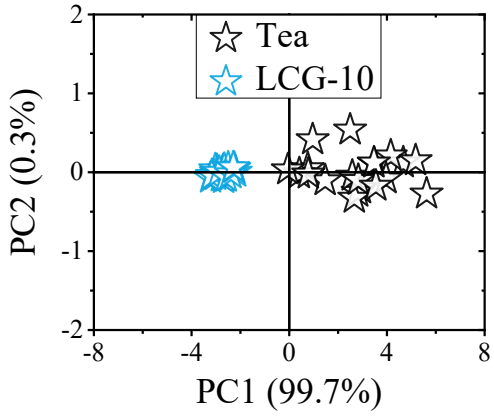


Fig. S4 PCA model based on CaO radical characteristic spectral lines.

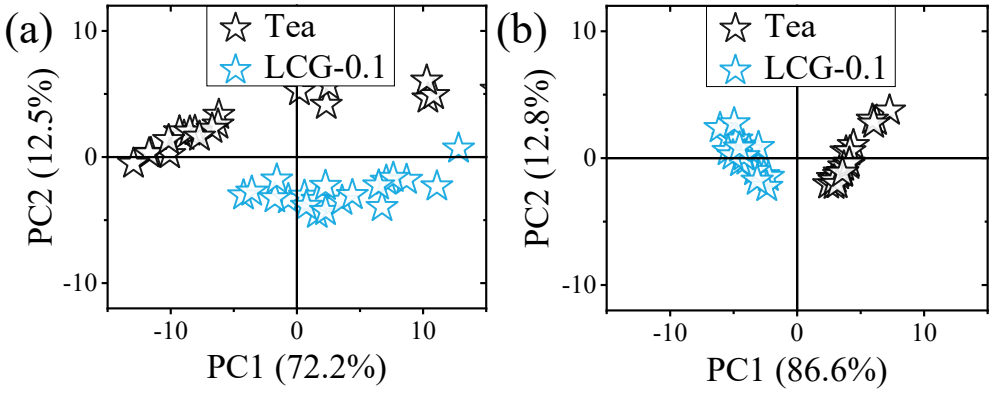


Fig. S5 PCA model based on (a) all characteristic spectral lines (b) CN and CaO radical characteristic spectral lines.

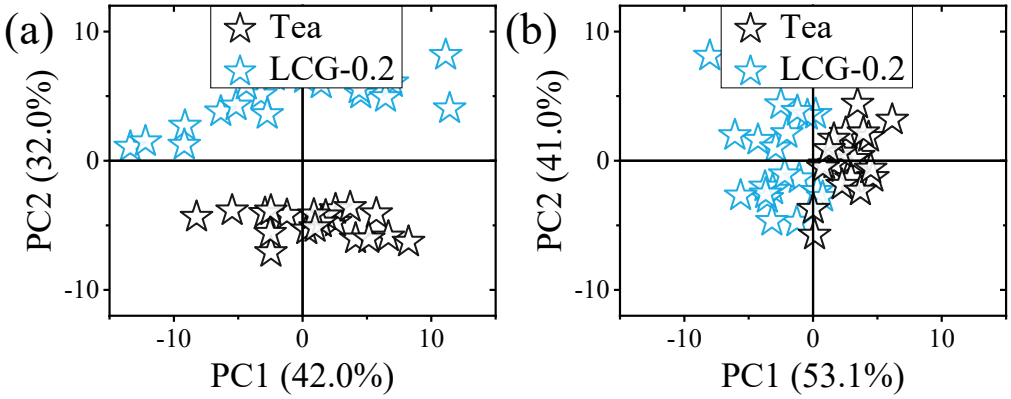


Fig. S6 PCA model based on (a) all characteristic spectral lines (b) CN and CaO radical

characteristic spectral lines.

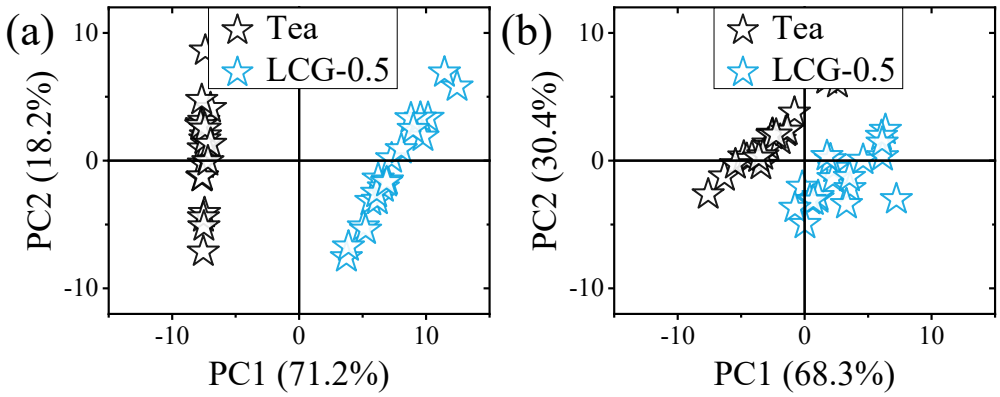


Fig. S7 PCA model based on (a) all characteristic spectral lines (b) CN and CaO radical characteristic spectral lines.

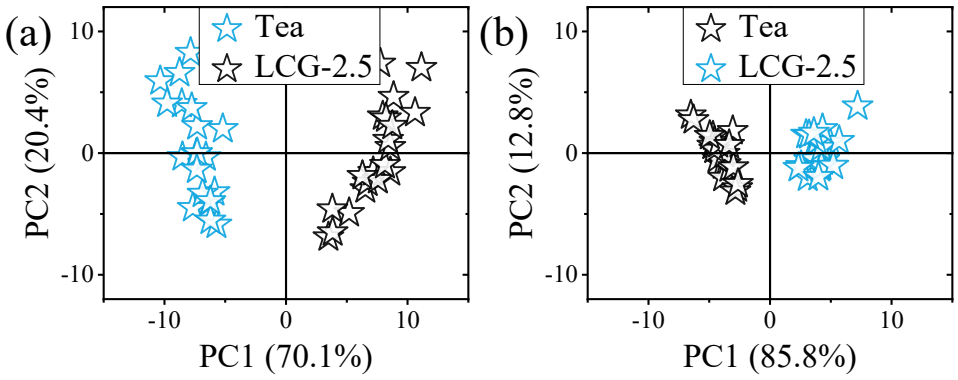


Fig. S8 PCA model based on (a) all characteristic spectral lines (b) CN and CaO radical characteristic spectral lines.

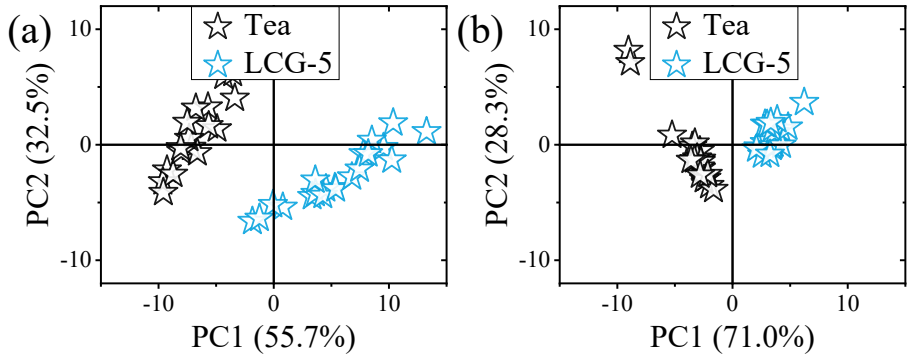


Fig. S9 PCA model based on (a) all characteristic spectral lines (b) CN and CaO radical characteristic spectral lines.

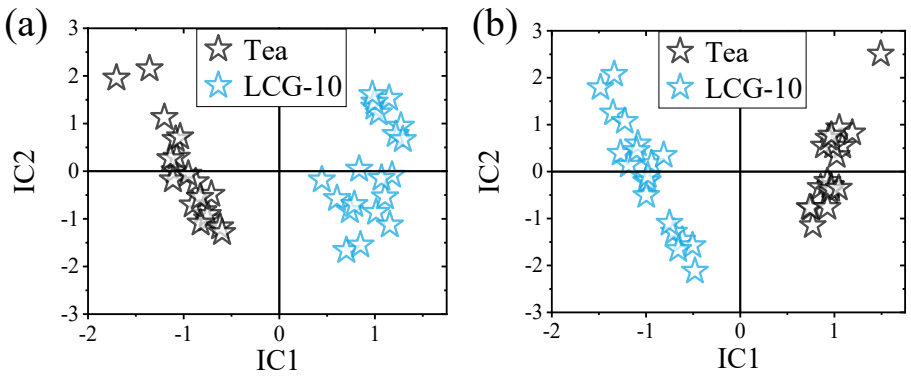


Fig. S10 ICA model based on (a) all characteristic spectral lines, (b) CN and CaO characteristic spectral lines.

Table S3. Coefficient matrix of PC1 and PC2 scores in Fig. 5(a).

Elements and Wavelength (nm)		PC1	PC2	Elements and Wavelength (nm)		PC1	PC2
Al I	308.255	0.11666	0.08776	Mg I	518.32	0.11561	0.09066
Al I	309.304	0.11577	0.08921	Ca I	585.756	-0.11655	0.0817
Ca II	315.916	-0.11014	0.08746	Na I	589.002	0.10272	0.08581
Ca II	317.992	-0.1054	0.09743	Na I	589.625	0.10209	0.07776
Cu I	324.783	-0.11748	0.07364	Ca I	610.317	-0.11957	0.06502
Cu I	327.431	-0.11902	0.06986	Ca I	612.263	-0.12069	0.06354
Fe I	357.014	0.11723	0.06641	Ca I	616.263	-0.12053	0.06782
Cr I	360.583	0.01276	0.18841	Ca I	643.965	-0.11796	0.08453
Fe I	363.085	-0.1136	0.10879	Ca I	645.015	-0.11771	0.07701

Pb I	368.375	0.02465	0.21542	Ca I	646.298	-0.11813	0.08233
Fe I	370.683	-0.07215	0.17224	Ca I	647.229	-0.11476	0.08501
Fe I	373.772	0.00533	0.2156	Ca I	649.436	-0.11556	0.0895
Mg I	383.241	0.12107	0.06865	Ca I	650.015	-0.10901	0.10475
Mg I	383.86	0.12042	0.07253	H I	656.361	0.12269	0.05114
Si I	390.628	0.11824	0.08011	Ca I	657.28	0.11405	0.07898
Ca II	393.369	0.06591	0.17977	N I	742.454	0.12404	0.04255
Al I	394.43	0.11718	0.08088	N I	744.329	0.12431	0.04097
Al I	396.169	0.11724	0.08524	N I	746.882	0.12417	0.04226
Ca II	396.848	0.0422	0.20732	K I	766.592	0.11267	0.06493
Mn I	403.133	0.11797	0.07861	K I	769.94	0.10665	0.078
Mn I	403.355	0.11566	0.08826	O I	777.277	0.12419	0.04245
Mn I	403.504	0.11698	0.08434	O I	777.549	0.12397	0.04347
Pb I	405.799	0.03463	0.20817	N I	818.58	0.12386	0.03844
Sr II	407.788	0.11084	0.10131	N I	818.896	0.1239	0.03609
Sr I	421.588	0.11734	0.08507	N I	820.053	0.12061	0.05874
Ca I	422.722	0.01354	0.21432	N I	821.102	0.12251	0.04906
Cr I	425.473	-0.04688	0.17107	N I	821.731	0.12421	0.03187
Ca I	428.342	-0.1139	0.11143	N I	822.359	0.12368	0.0407
Ca I	428.969	-0.11523	0.10593	N I	824.343	0.12392	0.03385
Ca I	429.942	-0.11437	0.10904	O I	844.679	0.12417	0.03986
Ca I	430.289	-0.10856	0.12779	Ca II	849.759	-0.09513	0.16134
Ca I	430.843	-0.10583	0.13626	Ca II	854.195	-0.05316	0.2203
Ca I	431.88	-0.11394	0.11029	N I	856.836	0.12355	0.03774
Cr I	452.653	-0.08156	0.18669	N I	859.461	0.12409	0.03883
Ca I	457.849	-0.10123	0.13852	N I	863.034	0.12433	0.0347
Ca I	458.084	-0.1067	0.12844	Ca II	866.29	-0.05231	0.22445
Ca I	458.554	-0.11279	0.10674	N I	868.099	0.1246	0.03531
Sr I	460.739	0.08539	0.14111	N I	868.384	0.12413	0.03923
Ca I	487.818	-0.081	0.17913	N I	870.373	0.12379	0.04277
Si II	504.127	-0.10131	0.14359	N I	871.222	0.12412	0.03903
Mg I	516.697	0.11792	0.08404	N I	871.975	0.12398	0.03472
Mg I	517.239	0.1156	0.0911	N I	873.009	0.1181	0.04069

Table S4. Coefficient matrix of PC1 and PC2 scores in Fig. 5(b).

Free Radical and Wavelength (nm)		PC1	PC2
CN	357.908	0.21441	0.1698
CN	358.152	0.21983	0.20232
CN	385.098	0.21964	0.20497
CN	386.178	0.21991	0.20076
CN	387.179	0.21968	0.20345
CN	388.331	0.21962	0.2048
CN	415.217	0.21911	0.20312
CN	415.794	0.2186	0.21403
CN	416.729	0.2181	0.22431
CN	418.093	0.21769	0.22786
CN	419.737	0.21825	0.22482
CaO	596.822	-0.21746	0.23515
CaO	598.427	-0.2174	0.23502
CaO	600.399	-0.2173	0.23731
CaO	603.35	-0.21728	0.23884
CaO	605.923	-0.21783	0.2274
CaO	606.657	-0.21791	0.22672
CaO	620.726	-0.21799	0.22535
CaO	622.408	-0.21827	0.22043
CaO	623.128	-0.21813	0.22143
CaO	624.805	-0.21808	0.22211

4 LIBS spectra of three different brands of Tieguanyin tea

Except for the Wuhu brand Tieguanyin, we purchased two different brands of Tieguanyin tea, Zhongminhongtai and Changxiangyi, also from Anxi County, Quanzhou City, Fujian Province. The new brands of tea were pressed into pellets and tested, and the LIBS spectra were compared with Tieguanyin of Wuhu brand. Three brands of Tieguanyin tea were simply referred to as W Sample, Z Sample and C Sample. And the LIBS spectra of the three samples were shown in Fig. S11.

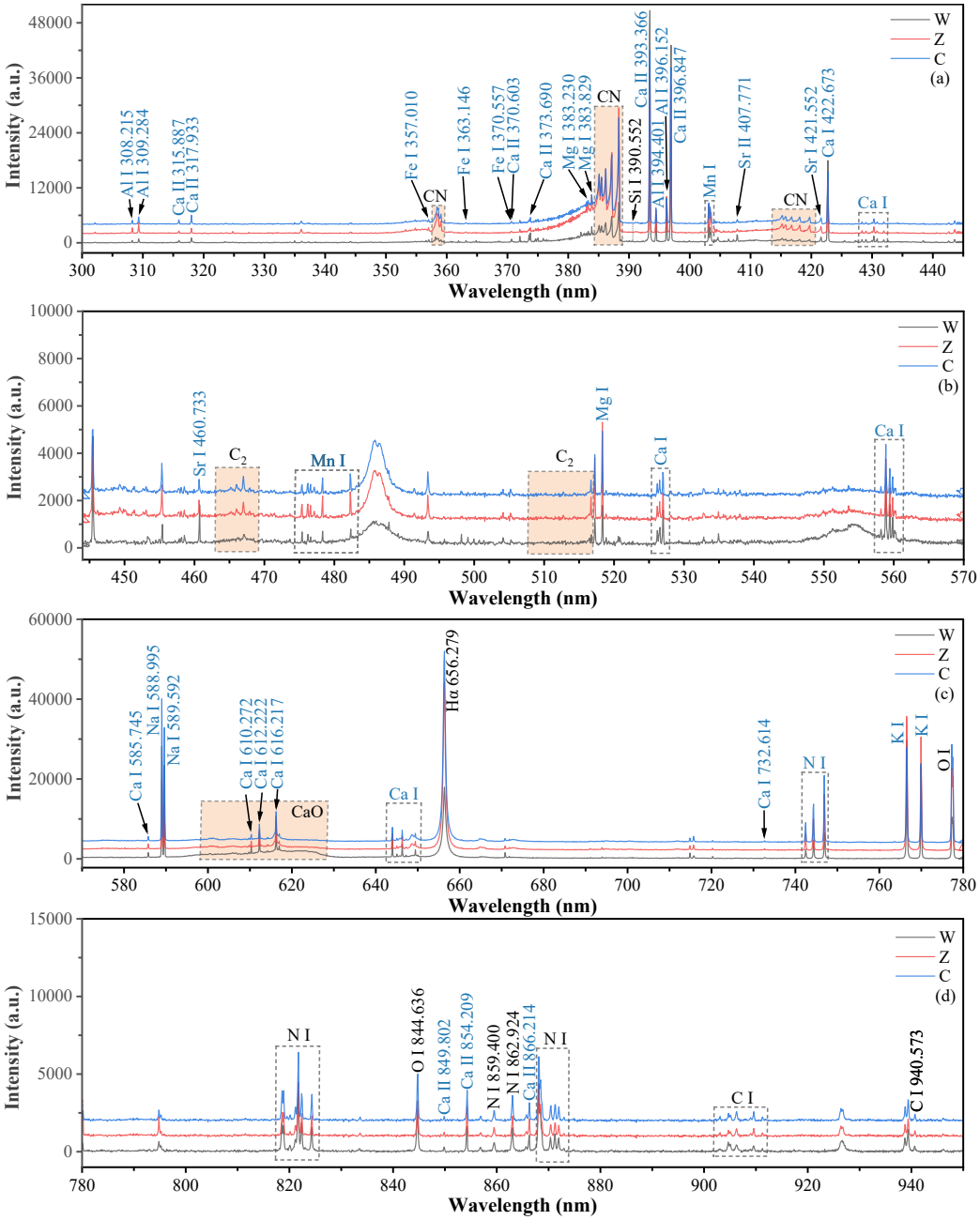


Fig. S11 LIBS spectra of three different brands of Tieguanyin tea.

5 Results of ICP-OES

Table S5. Test results of ICP-OES.

Sample	Element	Content (ppm)
Tieguanyin tea	Ca	14873.1
	Cr	8.9

	Pb	0.2
□	□	
	Ca	16614.3
LCG-5	Cr	18.1
	Pb	38.3
□	□	
	Ca	419000.0
LCG	Cr	280.3
	Pb	1094.5

6 Plasma parameter

Table S6. The electron density (Ne) and plasma temperature (T) of LCG-tea samples.

Sample	T (K)	N_e (10^{17} cm^{-3})
Tieguanyin tea	8159.7	1.44103
LCG-0.1	9018	2.8378
LCG-0.2	9125.23	2.95197
LCG-0.5	9019.16	2.80142
LCG-2.5	8819.65	2.35454
LCG-5	8457.27	1.88431
LCG-10	8026.06	1.0796
LCG	7266.4	0.981364

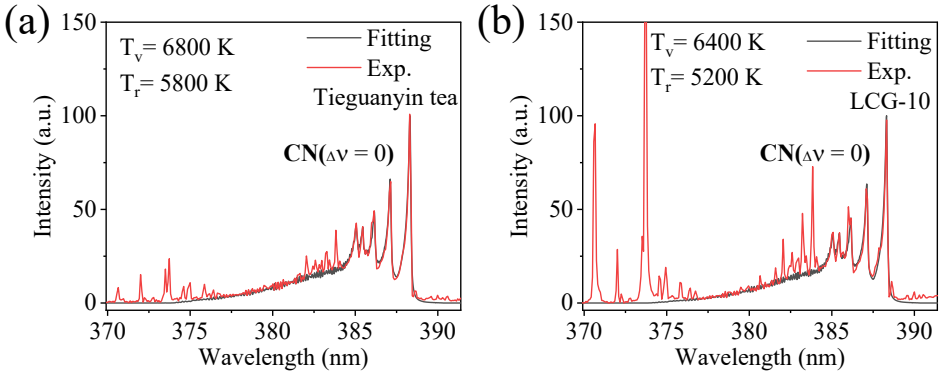


Fig. S12 Fitting spectral lines CN (Δv = 0) of Tieguanyin and LCG-10 by LIFBASE.

7 Calculation the LoD of Pb with PbI_2

During the growth of tea trees, Pb and Cr elements will be enriched in leaves. If the local air, water or soil pollution is serious, the Pb content in tea may exceed the food safety requirements.[1] Therefore, the detection limit of Pb element obtained by LIBS technique has important reference value. LCG is a mixture of lead chrome yellow and iron blue or phthalocyanine blue,[2] and the exact ratio is unknown. Moreover, the proportion of LCG attached to tea leaves was unknown, so the

content and the detection limit of Pb element cannot be obtained by using LCG. In order to obtain the detection limit of Pb element, tea with different Pb content were obtained by preparing PbI_2 solutions with different concentrations.

In order to quantitatively calculate the detection limit of Pb element, the known Pb content and the corresponding Pb I 405.781 nm spectral line intensity are used to construct the calibration curve which is the relationship between the intensity and the concentration of the element. [3, 4]

The detection limit is defined as:[5]

$$\alpha_{LOD} = \frac{3\sigma}{S} \quad (1)$$

In the formula, σ is the standard deviation of background signal intensity in the spectrum, and S is the slope of the calibration curve of the target element.

Fig. S13(a) shows the Pb I spectral lines of PbI_2-tea with different Pb contents. The spectral line intensities of Pb I (368.346 nm and 405.781 nm) weakened with the decrease of Pb content. When the Pb content decreased to 10 ppm or below, the spectral line of Pb I was almost not observed. Fig. S13(b) shows the calibration curve of Pb I 405.781 nm spectral line in the PbI_2-tea. The contents of Pb element used to establish calibration curves were 50, 100, 1000 and 10000 ppm respectively, and RSDs of Pb I 405.781 nm were 3.39%, 2.80%, 2.52% and 2.88%, respectively, which were lower than 5%. The determination coefficient R^2 of the fitting curve was 0.994, indicating that the calibration curve fitting result was good. According to the equation (1), the detection limit of Pb was 39 ± 1.4 ppm, which was better than 48.4 ppm reported by other research groups.[1]

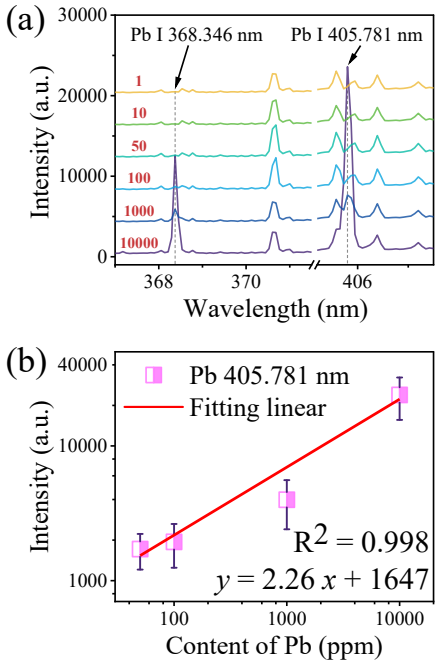


Fig. S13 (a) Pb I spectral lines of PbI_2-tea with different Pb contents (ppm), (b) calibration curve of Pb I 405.781 nm in PbI_2-tea.

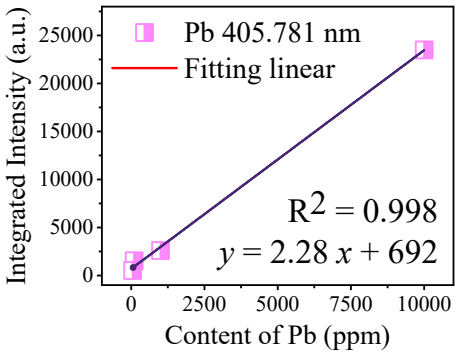


Fig. S14 Calibration curve established using the integrated intensity of Pb I 405.781 nm.

Reference

1. X. Lu, Y. Z. Liu, Q. H. Zhang and L. Li, Laser Phys. Lett., 2020, **17**(1), 8.
2. L. Y. Chen, C. Y. Lu and X. Liu, Tropical Agricultural Engineering, 2008, **32(1)**, 38–40, 44.
3. M. A. Gondal, Y. B. Habibullah, U. Baig and L. E. Oloore, Talanta, 2016, **152**, 341-352.
4. F. Yang, L. Jiang, S. M. Wang, Z. T. Cao, L. Liu, M. M. Wang and Y. F. Lu, Opt. Laser Technol., 2017, **93**, 194-200.
5. X. S. Wang, S. S. Wan, Y. G. He, S. L. Qiu, X. Ma, N. Wazir, R. B. Liu and Y. X. Tian, Spectroc. Acta Pt. B-Atom. Spectr., 2021, **178**, 106123.