

Supporting information for
Elucidating metal ions-regulated flavour formation mechanism in the
aging process of Chinese distilled spirits (Baijiu) by electrochemistry,
ICP-MS/OES, and UPLC-Q-Orbitrap-MS/MS

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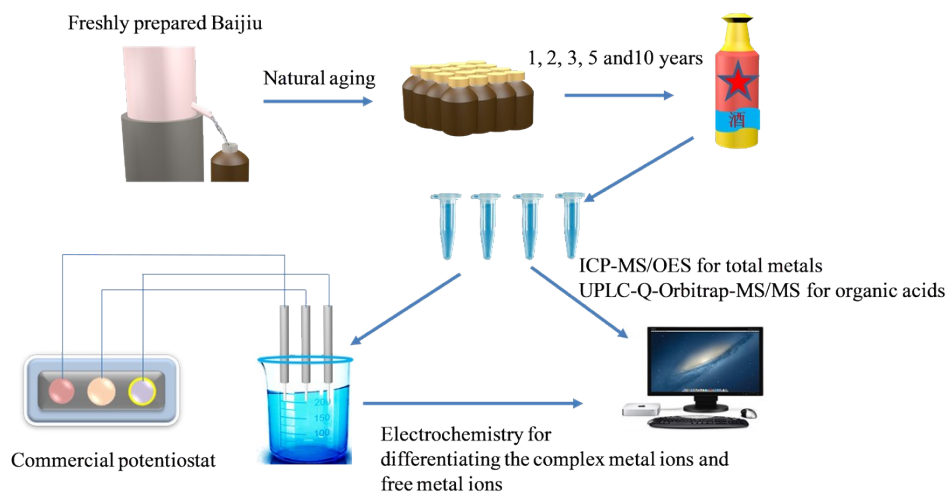


Figure S1. The schematic representation of the flow diagram of the methods.

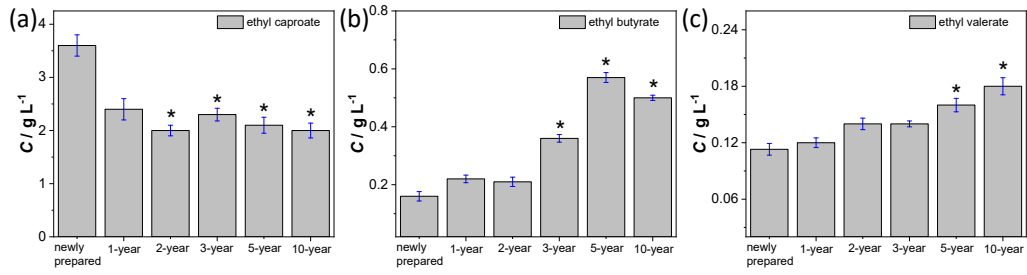


Figure S2. The contents of ethyl caproate, ethyl butyrate, and ethyl valerate in liquors with different aging times, measured by gas chromatography using reference standards. Samples were analyzed in triplicate and the data were presented as the mean value of these measurements ($n = 3$, $*P < 0.05$, compared with the control).

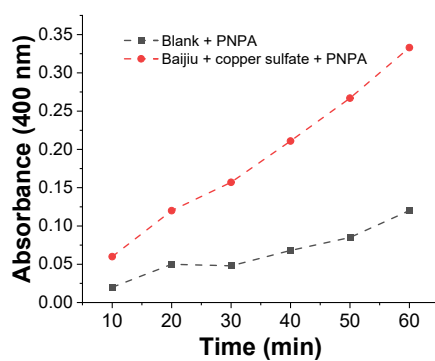


Figure S3. Plots of UV-vis absorbance vs. time for ester hydrolysis, 0.5 mM PNPA as substrate.

Ester hydrolysis was monitored using p-nitrophenyl acetate (PNPA) as the substrate according to the reference.¹ The hydrolytic product of PNPA was 4-nitrophenol with an absorption peak at 400 nm, so the hydrolysis reaction can be monitored by recording the absorbance at 400 nm with an UV-visible spectrophotometer.

PNPA hydrolysis was done in a quartz cuvette containing 200 μL of Baijiu, 500 μM PNPA, 500 μM copper sulfate.

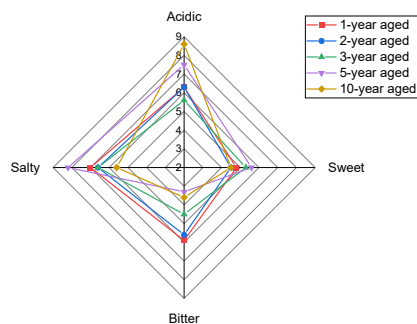


Figure S4. The mean taste values for aged Baijiu (1, 2, 3, 5, and 10 years) obtained from the electronic tongue.

The taste values of the aged Baijiu (1, 2, 3, 5, and 10 years) were determined by electronic tongue. Four basic taste values (acidic, sweet, bitter, and salty) were determined with the aid of standards (citric acid, sucrose, quinoline hydrochloride, and sodium chloride).^{2, 3} The radar plot was performed to visualize the mean taste values obtained from the electronic tongue (Fig. S4). As seen, Baijiu with different aging times present different taste values. It should be noted that the acidic taste value for 10-year aged Baijiu was larger than that for other Baijiu, which may be related to the change of organic acids content in the aging process.

Table S1. Metal concentrations in aged Baijiu (1, 2, 3, 5, and 10 years). All concentrations expressed in $\mu\text{g L}^{-1}$.

Metal	1 year	2 years	3 years	5 years	10 years
Al	40.80	53.47	85.07	98.06	100.32
Ba	29.81	49.93	72.20	70.32	72.68
Ca	82.88	85.63	101.02	100.75	108.68
Cu	34.92	57.09	56.66	68.35	75.85
Fe	52.02	83.24	95.04	96.65	113.14
Mg	70.45	80.86	95.76	98.36	112.88
K	31.20	32.86	34.92	35.35	38.68
Na	20.63	23.47	25.35	28.32	28.95
Ni	1.12	2.36	3.35	3.38	5.72
Cr	0.32	0.65	0.85	0.86	0.93
Ag	0.012	0.015	0.021	0.018	0.023
Cd	0.002	0.006	0.005	0.008	0.009
Li	0.021	0.08	1.26	2.36	5.23
Pb	0.002	0.012	0.036	0.055	0.12
Ti	0.07	0.26	0.39	0.42	0.55
Zn	1.23	1.96	3.62	5.36	8.74
Eu	0.001	0.001	0.002	0.002	0.002
La	0.032	0.036	0.021	0.031	0.025

Reference

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2. F. Tang, W. Cai, C. Shan, Z. Guo, Q. Hou, Z. Zhang and Y. Dong, Dynamic changes in quality of jujube wine during fermentation, 2020, **44**, e14704.
3. L. Zhu, X. Wang, X. Song, F. Zheng, H. Li, F. Chen, Y. Zhang and F. Zhang, Evolution of the key odorants and aroma profiles in traditional Laowuzeng baijiu during its one-year ageing, *Food Chem.*, 2020, **310**, 125898.