

# Implementation of a single quadrupole mass spectrometer for fingerprint analysis: *Venenum bufonis* as a case study

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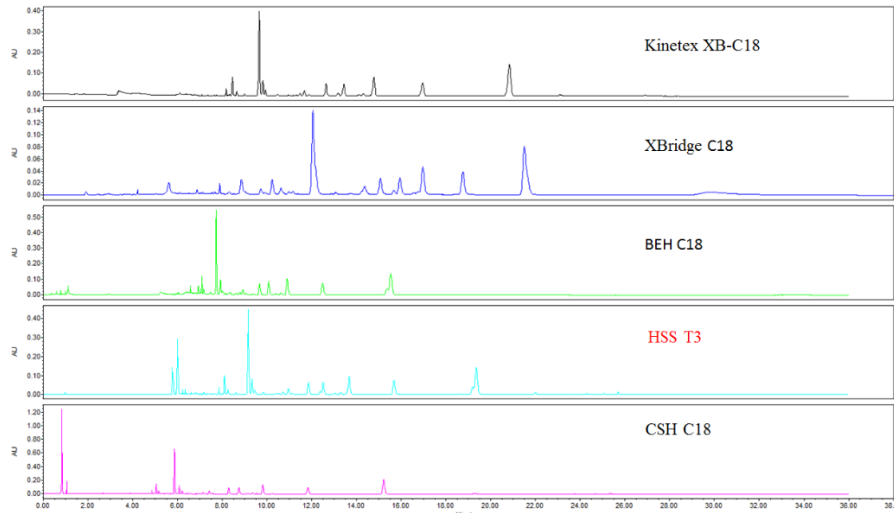
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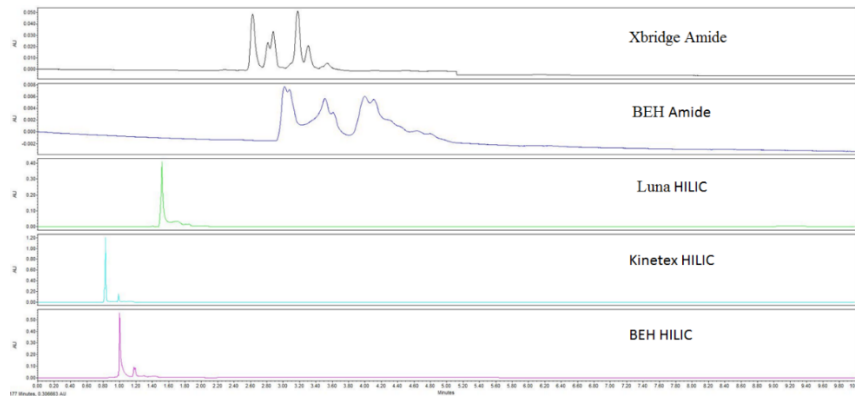
## Supporting Information

### Mass Spectrometry conditions of Q-TOF-MS and QQQ-MS

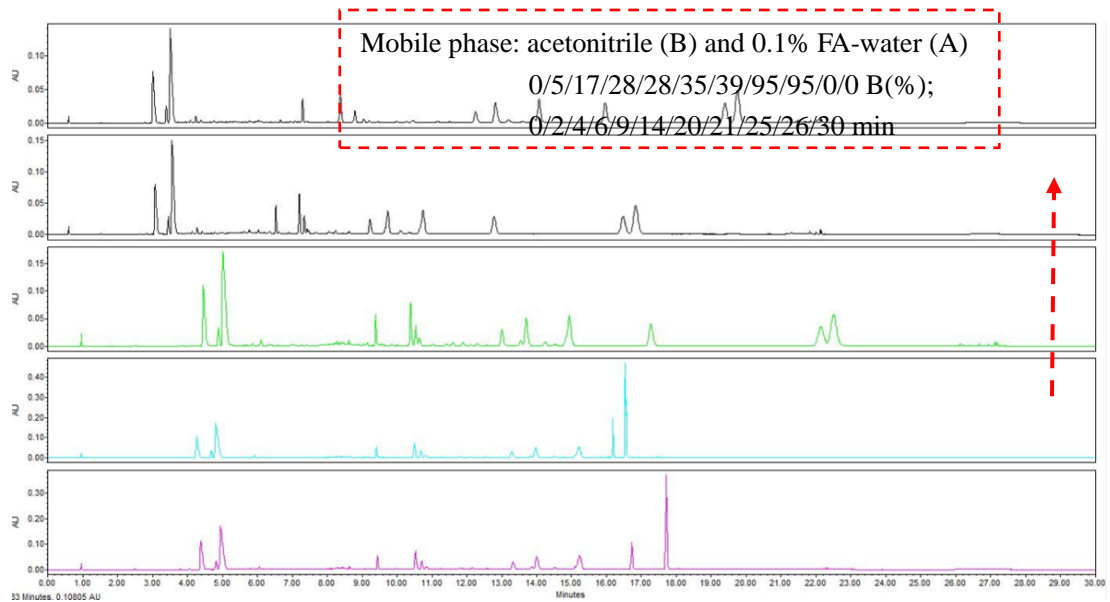
The MSFs obatanind on Q-TOF-MS and QQQ-MS were used to compare the consistency of MSF obtained on ACQUITY QDa detector. The same chromatographic condition as that used in UPLC-PDA-QDa was applied. Positive mode in mass range of  $m/z$  150–800 was adopted at both the two MS instruments. For Waters Xevo G2-S Q-TOF mass spectrometer (Waters Corporation, Milford, MA, USA), capillary voltages of 2 kV, cone voltage of 40 V, cone gas flow of 30 L/h, source temperature of 140 °C, and desolvation gas flow of 700 L/h at 500 °C were utilized. A solution of leucine-enkephalin (1 µg/mL) was used as lock mass for data calibration. For Xevo QQQ micro mass spectrometer (Waters Corporation, Milford, MA, USA), capillary voltages of 3 kV and cone voltage of 30 V was set. Source temperature was 148 °C, and desolvation temperature was 597 °C. Cone gas flow was 50 L/h, and desolvation gas flow was 947 L/h. Data acquisition and processing were performed using MassLynx V4.1 software (Waters Corporation, Milford, MA, USA).



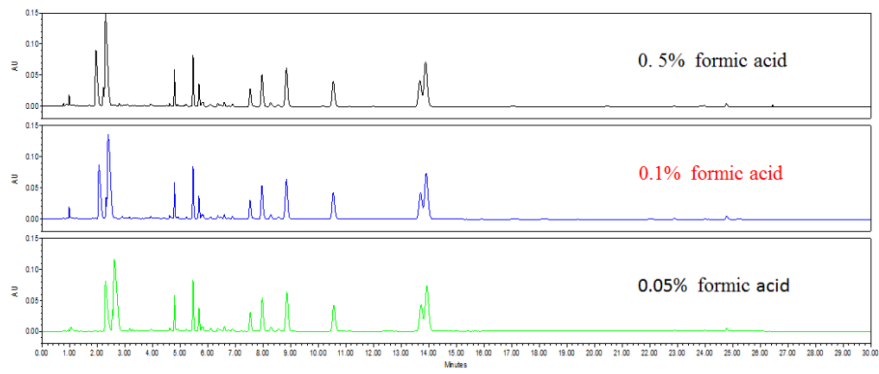
**Figure S1.** Optimization of columns of C18 mechanism.



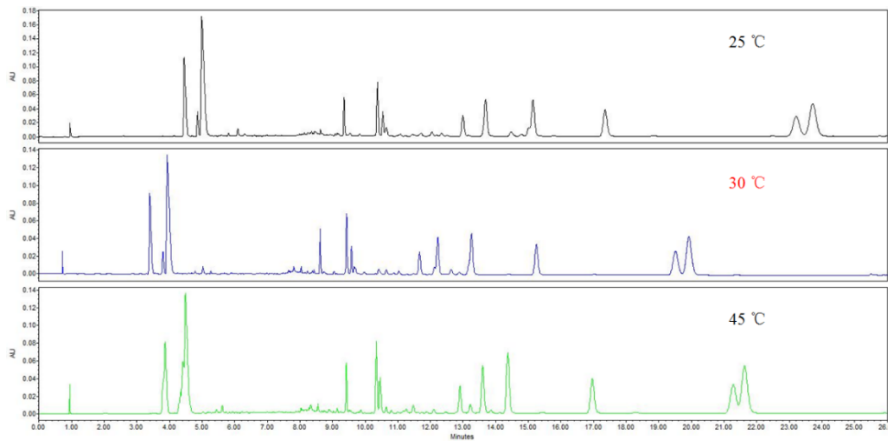
**Figure S2.** Optimization of columns of HILIC mechanism.



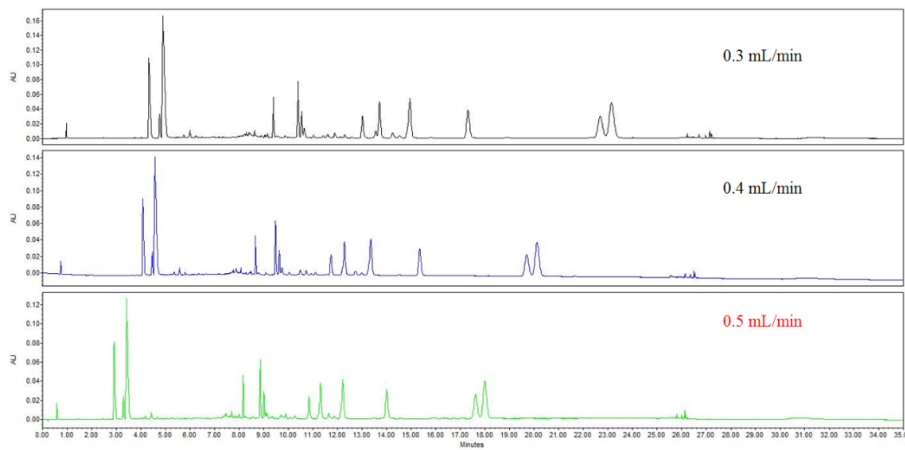
**Figure S3.** Optimization of gradient elution.



**Figure S4.** Optimization of concentration of formic acid.



**Figure S5.** Optimization of gradient elution.



**Figure S6.** Optimization of gradient elution.

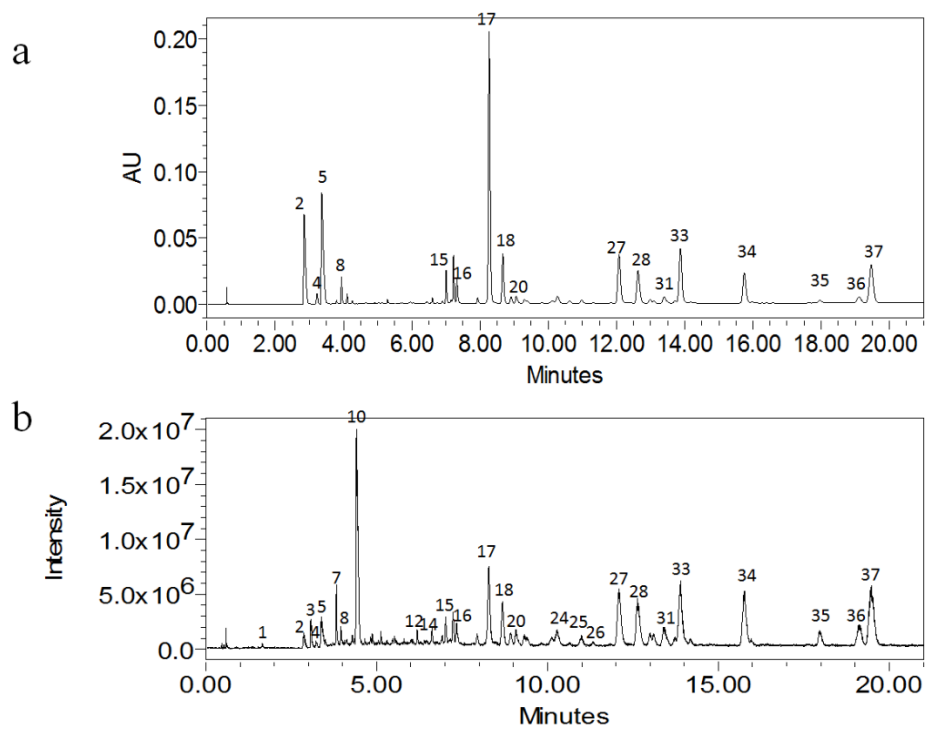


Figure S7. Chromatogram of a representative sample by UPLC-PDA (a)-QDa (b).

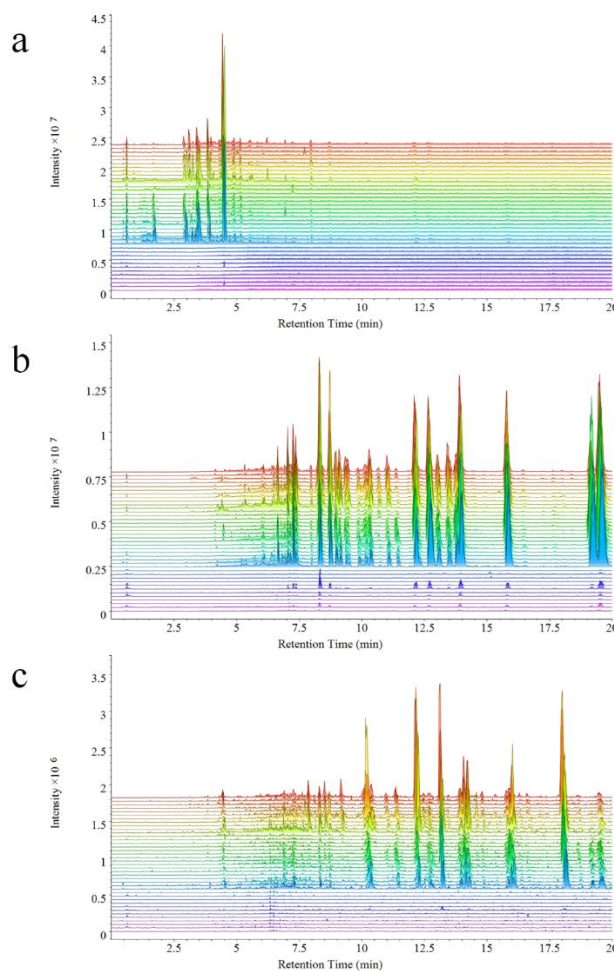
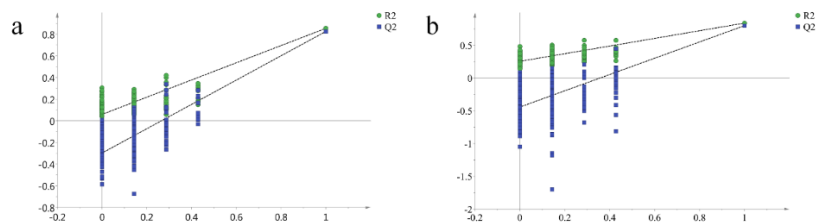
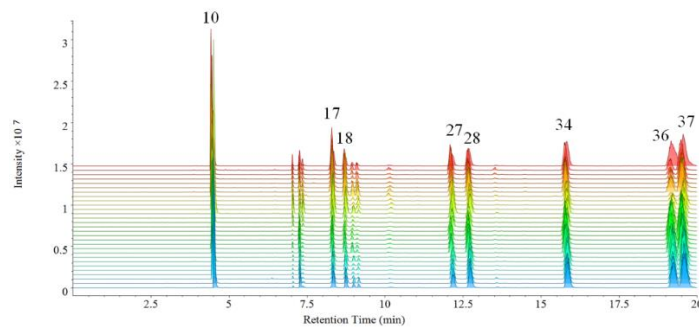


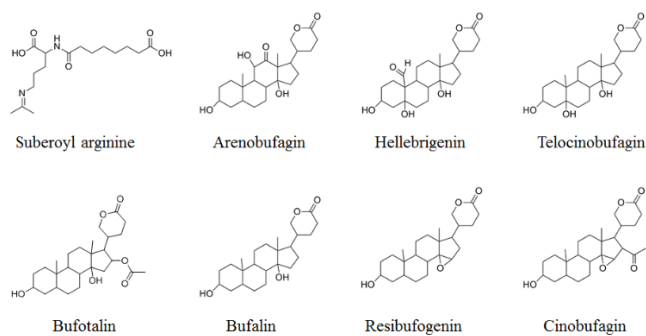
Figure S8. Extraction of different mass ranges (a: 150-380 Da, b: 380-650 Da, c: 650-800 Da)



**Figure S9.** permutation test of OPLS-DA of PDA (a) and QDA (b).



**Figure S10.** Extraction of eight characteristic peaks.



**Figure S11.** The chemical structures of seven characteristic constituents.

**Table S1.** Comparison of different analytical tools.

	<b>Advantages</b>	<b>Drawbacks</b>
<b>Separation</b>		
TLC	High flexibility Easy to use Low cost and high speed	Low reproducibility and resolution Low sensitivity Low efficiency in separation Low accuracy in quantification
HPLC	Automatable operating High resolution, sensitivity and accuracy	Extended analytical time Requirement for large volume of solvent
UHPLC	High resolution separation Reduced analytical time Reduced solvent consumption	Sample preparation have high requirement
HILIC	Suitable for polar compounds Environmentally friendly mobile phase	Narrow range of application
GC	High sensitivity High resolution	Limited to volatile compounds Thermal instability
<b>Detection</b>		
MS	High sensitivity Powerful component characterization	Not easy operation Low precision
UV	Simple operation Wide linear range High precision	Low component characterization Low sensitivity

**Table S2. The information of the 40 batches of VB samples.**

<b>No.</b>	<b>Provider</b>	<b>Production Region</b>	<b>Description</b>	<b>Collection Time</b>
S15	Yongfa Chanchu breeding bases, Changyi district, Jilin	Jilin	Slice	04/2014
S1	Bozhou medicine market	Unknown	Slice	04/2014
S2	Bozhou medicine market	Unknown	Slice	04/2014
S3	Bozhou medicine market	Shandong	Slice	05/2014
S4	Bozhou medicine market	Shandong	Slice	06/2014
S5	Web of Chinese herbal medicins	Unknown	Slice	04/2014
S6	XingWang Chanchu breeding bases	Unknown	Slice	04/2014
S7	Anguo of Hebei	Bozhou	Nubble	09/2014
S8	Anguo of Hebei	Bozhou	Nubble	09/2014
S9	Anguo of Hebei	Bozhou	Nubble	09/2014
S10	Yinfa, Linyi	Sichuan	Nubble	09/2014
S11	Yinfa, Linyi	Jilin	Nubble	09/2014
S12	Yinfa, Linyi	Shandong	Nubble	09/2014
S13	Songjialiang, Linyi	Shandong	Nubble	09/2014
S14	Anguo of Hebei	Bozhou	Nubble	09/2014
S15	Bozhou medicine market	Shandong	Slice	04/2014
S16	Guangming pharmacy, Anguo of Hebei	Jilin	Slice	04/2014
S17	Bozhou medicine market	Henan	Slice	04/2014
S18	Shaanxi medicine market	Sichuan	Nubble	08/2014
S19	Songjialiang, Linyi	Shaanxi	Nubble	09/2014
S20	Guangming pharmacy, Anguo of Hebei	Jilin	Nubble	04/2014
S21	Guangming pharmacy, Anguo of Hebei	Jilin	Slice	04/2014
S22	Bozhou medicine market	Shandong	Slice	04/2014
S23	Bozhou medicine market	Unknown	Slice	04/2014
S24	Shaanxi medicine market	South America	Nubble	08/2014
S25	Yulin medicine market	Bozhou	Slice	08/2014
S26	Yinfa, Linyi	Anhui	Nubble	09/2014
S27	Yinfa, Linyi	Shandong	Nubble	09/2014
S28	Songjialiang, Linyi	Sichuan	Nubble	09/2014