Supplementary information 1

1. Firstly, the UPLC-MS data was converted to NetCDF or ASCII format using databridge, then, the files with Matlab format were obtained using our software, in which different ion curves could be observed, similarly to GC-MS data. Certainly, other methods were also feasible.

Fig 1-a: positive modes

Fig 1-b: negative modes

Fig 1-c: PDA

2. Secondly, the background was deducted and smoothing was conducted using the ordinary linear deduction. Certainly, other software could be used, including MZ mine 2 (free).

The figure (left) before treatment and the figure (right) after treatment can be seen below.

Fig 2a
3. Now, an example is shown, which is the segment in the range of 5.16-5.62 min taken from the negative ion mode. The rankmap on the basis of the eigenstructure tracking analysis, which can be seen below, and the selective regions (pure component) marked with 1, 2 and 3 could be clearly observed. The zero component region of each component was also determined, being the detailed steps described in the references.\textsuperscript{11,12}

4. Maybe the program about the rankmap can’t be written, a simple method can be introduced. As
a precondition, the visualization of all ions should be conducted in Matlab or other suitable software. The “pure” zone can be observed in figure below, and the corresponding mass spectrum can be obtained, that is vertical column in the matrix. For some zones with interferences (grey), the ion ascription can be evaluated according to the simple inference, such as “deduce” zone (5.31 min), interfered by two grey peaks.

Fig 4-a negative ion mode

Fig 4-b positive ion mode

5. Finally, pure mass spectrum could be obtained in the corresponding selective regions of the positive and negative mode, which are shown below. Nevertheless, pure mass spectrum is the guarantees and premise before qualitative analysis.

Fig 5a (black peak, 5.31 min)

Fig 5b (blue peak, 5.45 min)

Fig 5b (red peak, 5.45 min)
6. The corresponding UV spectrum (liquiritin, 5.45 min) could also be obtained. For some complicated data, we should use HELP, AMWFA, EFA and other classic chemometrics methods.

7. Pure spectrum is the guarantees and premise before qualitative analysis. Moreover, we should mine some useful information from pure spectrum. For example, some programs based on isotope program, such as Massworks, MZmine 2, have been widely used to improve low-resolution data under "Continum" or "Profile" mode, followed by determination of molecular formulas. Additionally, there are simple methods to process the GC-MS data using Origin software. Based on the reliable mass information, the main components could be identified by comparison with an in-house database.

For isotopic profile improvement of the data came from licorice (Fig 7-a), which analyzed by AB MS. We can use Gaussian fitting and simple external calibration methods to obtain accurate mass. More details regarding the calibration process using Origin 8.6 can be found in the study by He et al. That is to say, a mixture of several external calibration standards (or the known compounds in Licorice) were measured, their molecular ions were extracted and isotopic profiles were fitted. The errors were calculated by subtracting the measured value (accurate mass) from the true value (exact mass). The obtained statistical standard calibration curve of the known masses against the calculated errors was linearly fitted, and the parameters were used for the calibration step of unknown compounds. And the results were precise.
Here, we have gotten some vague profiles, such as m/z 419 from Liquiritin (5.45 min) in licorice (Fig 7-b). The corrected data (Fig 7-c) could not provide enough precision when compared with high resolution MS, on the other hand it provides a reference for the qualitative analysis to a certain extent.

Fig 7-b

As result, the precursor ions of different compounds also produce their characteristic fragment ions, for instance, the different cleavage rules occurred among flavonoid glycoside, chalcone, flavanones, triterpenoid saponins and coumarins. Although MS\textsuperscript{n} fragment ions of these compounds are very complex, the structures and compound name could be readily inferred according to the existing references, such as liquiritin in licorice (5.45 min), the cleavage rule was shown in Fig 8, and that of liquiritin apioside (5.31 min) is similar.

Fig 7-c
For some isomers, the qualitative analysis should be accomplished in accordance to the retention time provided by the known reference, or references substances.