

Supporting information

The Determination of Standard Curve

The procedure for determining standard curve of each aldehyde and ketone is as follows. The standard solutions including acetaldehyde 2,4-dinitrophenylhydrazone (AA-DNPH, 200, 160, 100, 50 and 20 mg/L), propionaldehyde 2,4-dinitrophenylhydrazone (PA-DNPH, 100, 80, 50, 20 and 10 mg/L), formaldehyde 2,4-dinitrophenylhydrazone, acetone 2,4-dinitrophenylhydrazone and 2-methyl-2-pentenal 2,4-dinitrophenylhydrazone (FA-DNPH, ACE-DNPH and MP-DNPH, 40, 20, 10, 5 and 4 mg/L, respectively) were prepared and analyzed by HPLC to draw a standard curve.

All compositions in propionic acid were analyzed by GC-MS, and the compounds were identified by comparing mass spectra with NIST 2014 mass spectrum database. The total ion current and mass spectrum of propionic acid are shown in Fig. S1/S2.

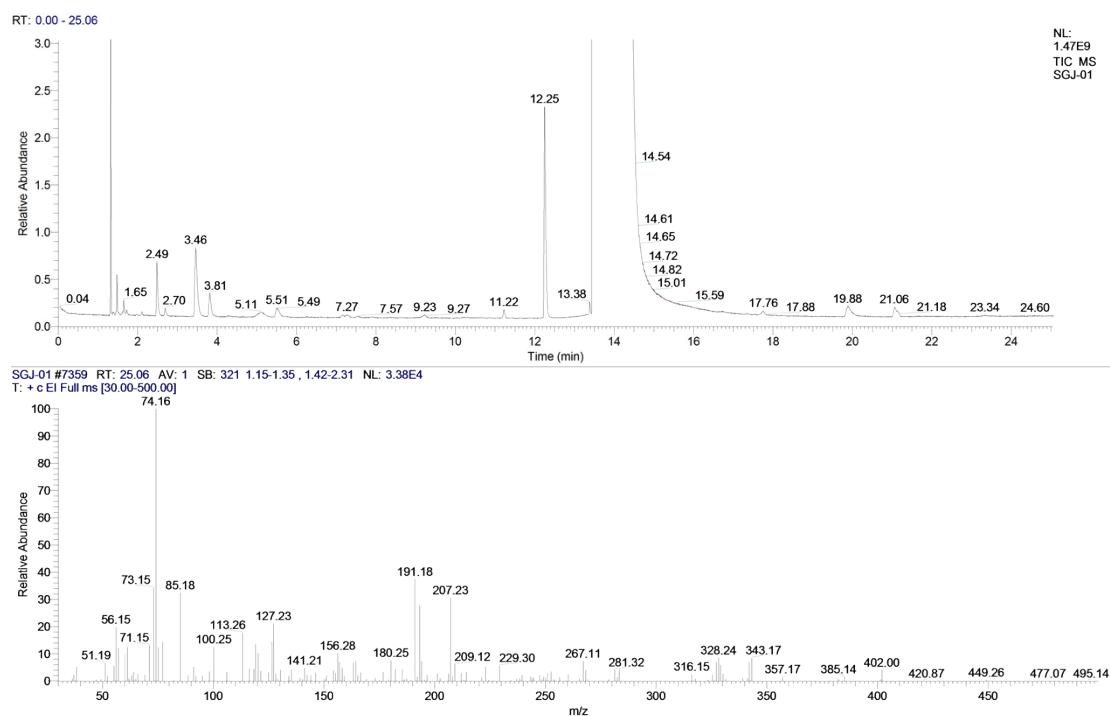
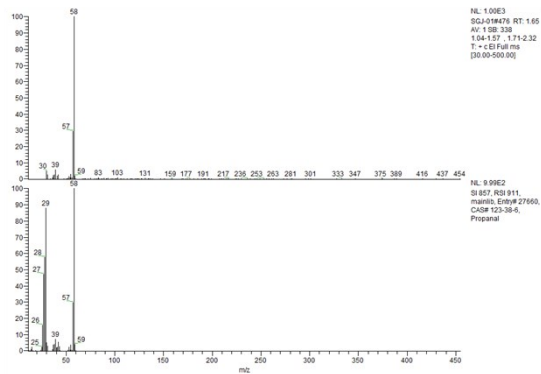
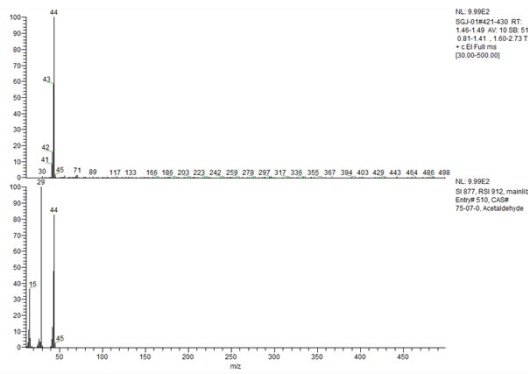
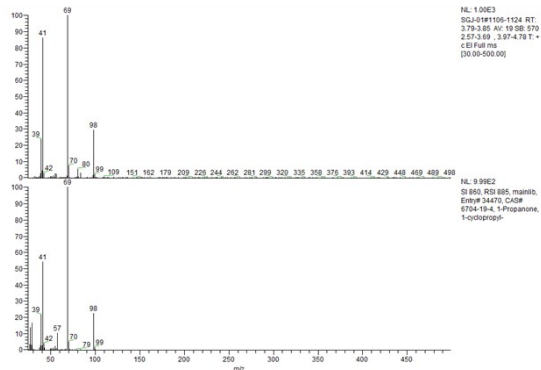
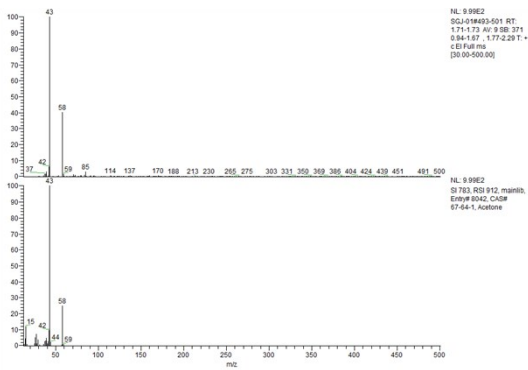


Fig. S1 The total ion current and mass spectrum of propionic acid



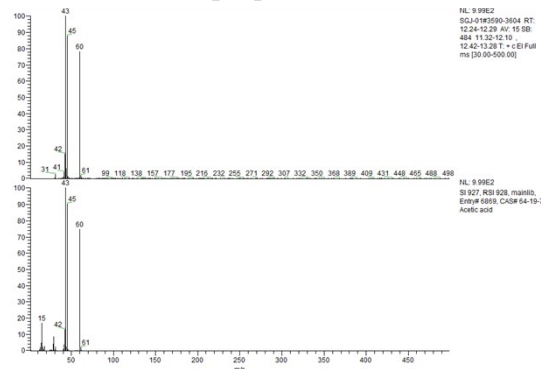
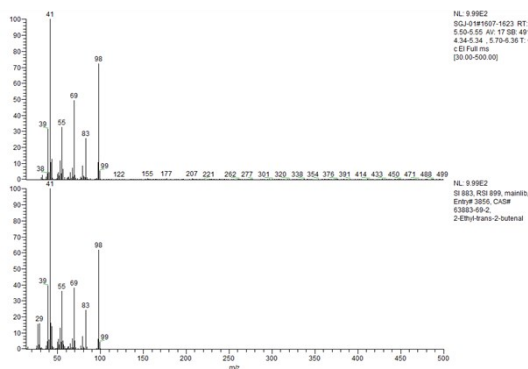
(a) Mass spectrum of acetaldehyde

(b) Mass spectrum of propionaldehyde



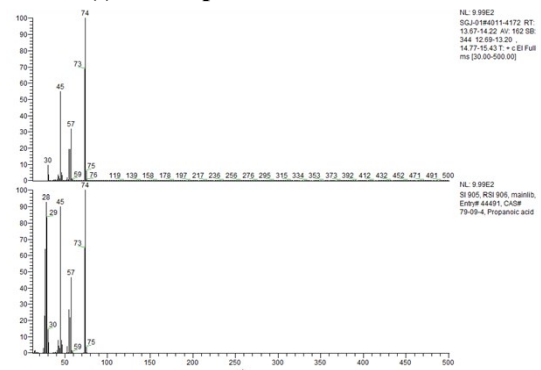
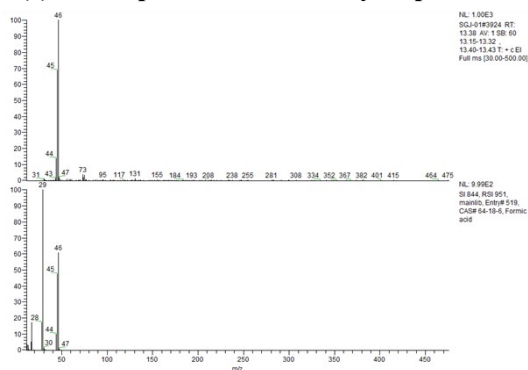
(c) Mass spectrum of acetone

(d) Mass spectrum of 1-cyclopropyl-1-propanone



(e) Mass spectrum of 2-methyl-2-pentenal

(f) Mass spectrum of acetic acid



(g) Mass spectrum of formic acid

(h) Mass spectrum of propionic acid

Fig. S2 Mass spectrums of the main compounds in propionic acid

The relative calibration factors of all compositions in propionic acid are shown in Table S1.

Table S1 Relative calibration factors of all components in propionic acid by GC (n=5)

| Number | Name | Retention time, min | Volume, μ L | Mass, g | Relative calibration factors | | | | | Average |
|--------|-----------------------|---------------------|-----------------|---------|------------------------------|--------|--------|--------|--------|---------|
| | | | | | 1 | 2 | 3 | 4 | 5 | |
| 1 | Formaldehyde | 2.55 | 40.0 | 0.0126 | 1.0499 | 0.7444 | 1.1702 | 0.9172 | 0.9786 | 0.9721 |
| 2 | Acetaldehyde | 2.83 | 90.0 | 0.0698 | 1.0772 | 1.0316 | 1.0465 | 1.0290 | 1.2276 | 1.0824 |
| 3 | Propionaldehyde | 3.09 | 46.4 | 0.0397 | 0.9459 | 0.9316 | 0.9021 | 0.9528 | 1.0180 | 0.9501 |
| 4 | Acetone | 3.20 | 11.6 | 0.0091 | 0.8675 | 0.7047 | 0.8330 | 0.8173 | 0.8456 | 0.8136 |
| 5 | Methyl propionate | 3.74 | 7.2 | 0.0065 | 0.9820 | 0.8871 | 1.0843 | 0.9218 | 0.9855 | 0.9721 |
| 6 | Ethanol | 3.93 | 10.0 | 0.0079 | 0.6830 | 0.7378 | 0.6860 | 0.8983 | 0.8126 | 0.7635 |
| 7 | Ethyl propionate | 4.20 | 110.0 | 0.0978 | 0.7304 | 0.7321 | 0.7346 | 0.7370 | 0.8853 | 0.7639 |
| 8 | 3-Pentanone | 4.48 | 22.4 | 0.0182 | 0.5843 | 0.7332 | 0.5298 | 0.5486 | 0.5710 | 0.5934 |
| 9 | Propyl propionate | 5.35 | 210.0 | 0.1835 | 0.6408 | 0.7696 | 0.6537 | 0.6473 | 0.6528 | 0.6728 |
| 10 | 2-Methyl-2-pentenal | 7.70 | 55.2 | 0.0462 | 0.5505 | 0.5283 | 0.5194 | 0.5947 | 0.5493 | 0.5484 |
| 11 | Acetic acid | 14.68 | 325.6 | 0.3384 | 1.7681 | 1.6496 | 1.8089 | 1.7037 | 1.8256 | 1.7512 |
| 12 | Formic acid | 15.73 | 10.5 | 0.0126 | 2.3826 | 2.3828 | 1.5089 | 2.0476 | 2.2650 | 2.1174 |
| 13 | Propionic acid | 15.81 | -- | -- | 1 | 1 | 1 | 1 | 1 | 1 |
| 14 | 2-Methylbutanoic acid | 19.00 | 14.6 | 0.0135 | 1.2498 | 1.2752 | 1.4891 | 1.5463 | 1.4637 | 1.4048 |
| 15 | 2-Methylvaleric acid | 19.71 | 50.0 | 0.0451 | 2.8725 | 2.0466 | 2.1026 | 2.7234 | 2.0773 | 2.3645 |

The spiked recoveries are shown in Table S2.

Table S2 Spiked recoveries of phenylhydrazone in propionic acid-DNPH solution (n=3)

| Number | Name | C_0 , mg/L | C_1 , mg/L | C_2 , mg/L | Spiked recovery (P), % |
|--------|----------|--------------|--------------|--------------|------------------------|
| 1 | FA-DNPH | 2.450 | 5.114 | 3.874 | 107.52 |
| | | 4.900 | 5.114 | 5.246 | 109.76 |
| | | 9.800 | 5.114 | 7.855 | 108.12 |
| | | 34.094 | 69.420 | 52.086 | 101.93 |
| 2 | AA-DNPH | 68.188 | 69.420 | 68.941 | 100.40 |
| | | 136.377 | 69.420 | 103.110 | 100.31 |
| | | 4.959 | 8.693 | 7.085 | 110.45 |
| 3 | ACE-DNPH | 9.918 | 8.693 | 9.752 | 109.01 |
| | | 19.835 | 8.693 | 15.032 | 107.74 |
| | | 12.901 | 24.335 | 18.953 | 105.20 |
| 4 | PA-DNPH | 25.802 | 24.335 | 25.367 | 102.32 |
| | | 51.604 | 24.335 | 38.045 | 100.29 |
| | | 5.434 | 10.589 | 8.078 | 102.44 |
| 5 | MP-DNPH | 10.867 | 10.589 | 10.812 | 101.54 |
| | | 21.734 | 10.589 | 16.243 | 100.75 |

Note: C_0 , C_1 and C_2 is the content of FA-DNPH/AA-DNPH/ACE-DNPH/PA-DNPH/MP-DNPH in the standard solution, propionic acid derivative solution and the spiked sample, respectively, mg/L

The comparison results of total aldehyde content (as propionaldehyde) in different batches of propionic acid product by GC, HPLC and titration are shown in Table S3.

Table S3 Comparison of analysis results of total aldehyde content (as propionaldehyde) in different production batches of propionic acid by 3 methods

| No. | Batch | Method | Content, mg/L | | | | | | Total aldehyde content (as propionaldehyde) | RSD, % |
|-----|--------|-----------|---------------|--------------|---------|-----------------|---------------------------|---------------------|---|--------|
| | | | Formaldehyde | Acetaldehyde | Acetone | Propionaldehyde | 1-Cyclopropyl-1-propanone | 2-Methyl-2-pentenal | | |
| 1 | 201803 | GC | 0 | 78.303 | 8.803 | 41.887 | 43.407 | 32.124 | 198.693 | 3.54 |
| | | HPLC | 4.350 | 82.093 | 13.006 | 35.482 | 30.621 | 21.740 | 196.170 | 0.87 |
| | | Titration | | | | | | | 577 | 5.38 |
| 2 | 201804 | GC | 6.584 | 132.937 | 11.111 | 65.303 | 68.116 | 55.854 | 337.890 | 7.84 |
| | | HPLC | 8.265 | 138.249 | 16.769 | 61.863 | 59.173 | 40.190 | 335.780 | 0.17 |
| | | Titration | | | | | | | 933 | 4.08 |
| 3 | 201808 | GC | 0 | 125.767 | 10.378 | 63.763 | 47.248 | 34.962 | 288.681 | 3.57 |
| | | HPLC | 6.525 | 130.607 | 16.583 | 59.957 | 33.081 | 26.570 | 296.715 | 2.04 |
| | | Titration | | | | | | | 840 | 1.89 |
| 4 | 201906 | GC | 0 | 69.866 | 8.950 | 42.874 | 50.088 | 33.549 | 193.505 | 2.21 |
| | | HPLC | 1.958 | 83.468 | 12.275 | 35.125 | 36.944 | 28.513 | 200.029 | 1.07 |
| | | Titration | | | | | | | 564 | 6.82 |
| 5 | 202012 | GC | 0 | 62.175 | 5.722 | 27.227 | 35.834 | 20.881 | 148.535 | 5.12 |
| | | HPLC | 2.828 | 74.863 | 8.454 | 23.063 | 23.572 | 13.617 | 157.730 | 3.03 |
| | | Titration | | | | | | | 386 | 8.77 |