water

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Supplementary Information

# Assessment of Glucocorticoid Removal by UVA/Chlorination and Ozonation: Performance Comparison in Kinetics, Degradation Pathway, and Toxicity

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**Table S1.** Available data on measured concentrations of FA, TA, and CP in various environmental samples.

| Glucocorticoid | Type of samples | Country | Concentration (ng/L) | Ref. |
|---|---|---|---|---|
| Triamcinolone acetonide | Hospital wastewater | Netherlands | 14–41 | [4] |
| Fluocinolone acetonide | Surface water | USA | 0.19 ± 0.15 | [19] |
| Triamcinolone acetonide | Surface water | USA | 9.00±0.18 | [19] |
| Clobetasol propionate | Surface water | USA | 0.64 ± 0.16 | [19] |
| Fluocinolone acetonide | Surface water | Germany | <0.05–1.0 | [20] |
| Triamcinolone acetonide | Surface water | Germany | 0.05–12 | [20] |
| Clobetasol propionate | Surface water | Germany | <0.02–3.4 | [20] |
| Fluocinolone acetonide acetate | Surface water | Italian | 0.3–1.2 | [21] |
| Fluocinolone acetonide acetate | Urban wastewater | Italian | 2.3 | [21] |
| Triamcinolone acetonide | Surface water | Italian | 0.9–2.6 | [21] |
| Triamcinolone acetonide | Urban wastewater | Italian | 6.4 | [21] |
| Triamcinolone acetonide | Hospital wastewater | Switzerland | 14 | [22] |
| Triamcinolone acetonide | Surface water | Switzerland | <1 | [22] |
| Clobetasol propionate | Hospital wastewater | Switzerland | 7 | [22] |
| Clobetasol propionate | Surface water | Switzerland | <1 | [22] |
| Triamcinolone acetonide | Surface water | Hungary | <0.63 | [23] |

**Table S2-1.** Pseudo-first-order kinetic models and corresponding $R^2$ of GCs under different light intensities during UVA/chlorination.

| parameter | | Rate constants (k; $h^{-1}$) | coefficients of determination ($R^2$) |
|---|---|---|---|
| FA | 180 mW/cm$^2$ | 0.16096 | 0.99763 |
| | 220 mW/cm$^2$ | 0.18302 | 0.99558 |
| | 250 mW/cm$^2$ | 0.21747 | 0.99306 |
| | 280 mW/cm$^2$ | 0.31851 | 0.98601 |
| TA | 180 mW/cm$^2$ | 0.16852 | 0.99467 |
| | 220 mW/cm$^2$ | 0.18961 | 0.99775 |

| | | | |
|---|---|---|---|
| | 250 mW/cm$^2$ | 0.25434 | 0.99441 |
| | 280 mW/cm$^2$ | 0.33204 | 0.99085 |
| | 180 mW/cm$^2$ | 0.16623 | 0.98153 |
| CP | 220 mW/cm$^2$ | 0.22465 | 0.87598 |
| | 250 mW/cm$^2$ | 0.20964 | 0.88711 |
| | 280 mW/cm$^2$ | 0.23123 | 0.88929 |

**Table S2-2.** Pseudo-first-order kinetic models and corresponding $R^2$ of GCs under different chlorine dosages during UVA/chlorination.

| **parameter** | | **Rate constants (k; h$^{-1}$)** | **coefficients of determination ($R^2$)** |
|---|---|---|---|
| | 0 mg/L | 0.16096 | 0.99763 |
| | 2.5 mg/L | 0.15703 | 0.99426 |
| FA | 5 mg/L | 0.18197 | 0.99827 |
| | 10 mg/L | 0.16191 | 0.99824 |
| | 20 mg/L | 0.15237 | 0.99747 |
| | 0 mg/L | 0.16779 | 0.96715 |
| | 2.5 mg/L | 0.19296 | 0.98740 |
| TA | 5 mg/L | 0.22276 | 0.98554 |
| | 10 mg/L | 0.21048 | 0.89792 |
| | 20 mg/L | 0.19172 | 0.98884 |
| | 0 mg/L | 0.16852 | 0.99467 |
| | 2.5 mg/L | 0.17728 | 0.99584 |
| CP | 5 mg/L | 0.19545 | 0.99516 |
| | 10 mg/L | 0.18491 | 0.99913 |
| | 20 mg/L | 0.16903 | 0.99629 |

**Table S3-1.** Pseudo-first-order kinetic models and corresponding $R^2$ of GCs under different $O_3$ dosages during ozonation.

| **parameter** | | **Rate constants (k; min$^{-1}$)** | **coefficients of determination ($R^2$)** |
|---|---|---|---|
| | 19 mg/L | 0.05140 | 0.99703 |
| FA | 31 mg/L | 0.02348 | 0.99142 |
| | 38 mg/L | 0.02774 | 0.92409 |
| | 59 mg/L | 0.03527 | 0.94070 |
| | 67 mg/L | 0.03170 | 0.85893 |
| | 19 mg/L | 0.11706 | 0.99206 |
| TA | 31 mg/L | 0.03904 | 0.97076 |
| | 38 mg/L | 0.03421 | 0.89608 |
| | 59 mg/L | 0.04009 | 0.87522 |
| | 67 mg/L | 0.04225 | 0.80473 |
| | 19 mg/L | 0.13286 | 0.98912 |
| CP | 31 mg/L | 0.03213 | 0.98839 |
| | 38 mg/L | 0.03011 | 0.92646 |
| | 59 mg/L | 0.03843 | 0.89267 |
| | 67 mg/L | 0.04687 | 0.81886 |

**Table S3-2.** Pseudo-first-order kinetic models and corresponding $R^2$ of GCs under different initial pH values during ozonation.

| parameter | | Rate constants (k; $min^{-1}$) | coefficients of determination ($R^2$) |
|---|---|---|---|
| FA | 4 | 0.11914 | 0.98616 |
| | 5 | 0.01835 | 0.86718 |
| | 6.2 | 0.00913 | 0.88802 |
| | 7.7 | 0.01240 | 0.97747 |
| TA | 4 | 0.21968 | 0.89827 |
| | 5 | 0.02187 | 0.96061 |
| | 6.2 | 0.01416 | 0.88335 |
| | 7.7 | 0.01571 | 0.97318 |
| CP | 4 | 0.27527 | 0.94872 |
| | 5 | 0.02909 | 0.93142 |
| | 6.2 | 0.01489 | 0.89591 |
| | 7.7 | 0.02321 | 0.97886 |

**Table S4-1.** General information of identified transformation products of FA during UVA/chlorination.

| Product | Species | m/z | Molecular formula | Relative molecular weight | Diff (ppm) |
|---|---|---|---|---|---|
| FA-$P_{394}$ | (M-H)- | 393.1507 | $C_{21}H_{27}FO_6$ | 394.1592 | 1.62 |
| FA-$P_{432a}$ | (M-H)- | 431.1866 | $C_{21}H_{30}F_2O_7$ | 432.196 | 2.58 |
| FA-$P_{432b}$ | (M-H)- | 431.1869 | $C_{24}H_{29}FO_6$ | 432.1948 | 1.85 |
| FA-$P_{448a}$ | (M-H)- | 447.2019 | $C_{21}H_{33}FO_9$ | 448.2097 | 2.83 |
| FA-$P_{448b}$ | (M-H)- | 447.2019 | $C_{24}H_{32}O_8$ | 448.2097 | 1.28 |
| FA-$P_{450a}$ | (M-H)- | 449.1974 | $C_{21}H_{32}F_2O_8$ | 450.2065 | 2.99 |
| FA-$P_{450b}$ | (M-H)- | 449.1985 | $C_{24}H_{31}FO_7$ | 450.2054 | −0.57 |
| FA-$P_{470}$ | (M-H)- | 469.2034 | $C_{24}H_{32}F_2O_7$ | 470.2116 | 2.26 |
| FA-$P_{486}$ | (M-H)- | 485.1763 | $C_{24}H_{32}ClFO_7$ | 486.1821 | 1.9 |
| FA-$P_{502}$ | (M-H)- | 501.1697 | $C_{24}H_{32}ClFO_8$ | 502.177 | −0.09 |
| FA-$P_{504}$ | (M-H)- | 503.1854 | $C_{24}H_{34}ClFO_8$ | 504.1926 | 0.82 |

**Table S4-2.** General information of identified transformation products of TA during UVA/chlorination.

| Product | Species | m/z | Molecular formula | Relative molecular weight | Diff (ppm) |
|---|---|---|---|---|---|
| TA-$P_{358}$ | (M-H)- | 357.1499 | $C_{21}H_{23}FO_4$ | 358.158 | 1.97 |
| TA-$P_{365}$ | (M-H)- | 355.1551 | $C_{21}H_{24}O_5$ | 365.1624 | 0.04 |
| TA-$P_{465}$ | (M-H)- | 455.2026 | $C_{23}H_{33}FO_8$ | 465.2159 | 2.95 |
| TA-$P_{476}$ | (M-H)- | 475.2014 | $C_{23}H_{37}ClO_8$ | 476.2177 | 0 |
| TA-$P_{506}$ | (M-H)- | 505.1848 | $C_{23}H_{35}ClO_{10}$ | 506.1919 | −0.36 |

**Table S4-3.** General information of identified transformation products of CP during UVA/ chlorination.

| Product | Species | m/z | Molecular formula | Relative molecular weight | Diff (ppm) |
|---|---|---|---|---|---|
| CP-$P_{464}$ | (M-H)- | 463.1881 | $C_{22}H_{34}ClFO_7$ | 464.1977 | 2.37 |
| CP-$P_{468}$ | (M-H)- | 467.1981 | $C_{25}H_{34}ClFO_5$ | 468.2079 | 2.8 |
| CP-$P_{470}$ | (M-H)- | 469.2243 | $C_{24}H_{35}FO_8$ | 470.2316 | −0.06 |
| CP-$P_{482a}$ | (M-H)- | 481.1772 | $C_{22}H_{36}Cl_2O_7$ | 482.1838 | −2.84 |
| CP-$P_{482b}$ | (M-H)- | 481.1781 | $C_{25}H_{32}ClFO_6$ | 482.1871 | 1.65 |
| CP-$P_{484}$ | (M-H)- | 484.1948 | $C_{25}H_{34}ClFO_6$ | 484.2028 | 2.98 |
| CP-$P_{502}$ | (M-H)- | 501.1429 | $C_{24}H_{32}Cl_2O_7$ | 502.1525 | 2.29 |
| CP-$P_{510}$ | (M-H)- | 509.1740 | $C_{23}H_{36}Cl_2O_8$ | 510.1787 | −2.93 |
| CP-$P_{512}$ | (M-H)- | 511.1893 | $C_{23}H_{38}Cl_2O_8$ | 512.1944 | −2.76 |

**Table S5-1.** General information of identified transformation products of FA during ozonation.

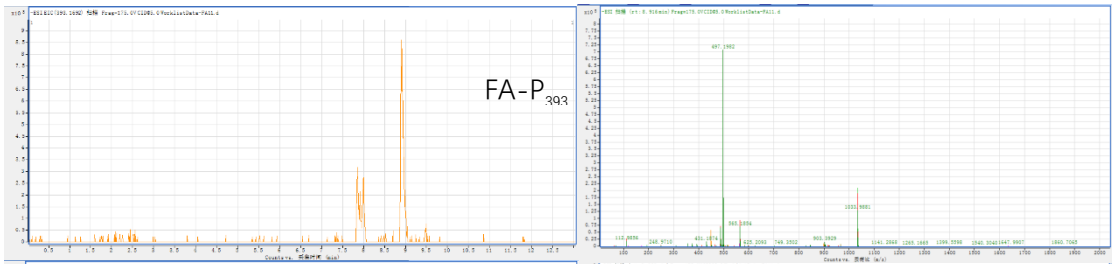
| Product | Species | m/z | Molecular formula | Relative molecular weight | Diff (ppm) |
|---|---|---|---|---|---|
| FA-$P_{382a}$ | (M-H)- | 381.1709 | $C_{20}H_{27}FO_6$ | 382.1792 | 2.11 |
| FA-$P_{382b}$ | (M-H)- | 381.1707 | $C_{23}H_{26}O_5$ | 382.178 | 0.42 |
| FA-$P_{400}$ | (M-H)- | 399.1819 | $C_{20}H_{29}FO_7$ | 400.1897 | 1.14 |
| FA-$P_{406}$ | (M-H)- | 405.1709 | $C_{22}H_{27}FO_6$ | 406.1792 | 1.39 |
| FA-$P_{410}$ | (M-H)- | 409.1667 | $C_{21}H_{27}FO_7$ | 410.1741 | 0.58 |
| FA-$P_{432}$ | (M-H)- | 431.1867 | $C_{21}H_{30}F_2O_7$ | 432.196 | 2.45 |
| FA-$P_{442}$ | (M-H)- | 441.1737 | $C_{22}H_{28}F_2O_7$ | 442.1803 | −1.5 |
| FA-$P_{464}$ | (M-H)- | 463.1778 | $C_{21}H_{30}F_2O_9$ | 464.1858 | 1.12 |
| FA-$P_{414}$ | (M-H)- | 413.1602 | $C_{23}H_{26}O_7$ | 414.1679 | 1.71 |
| FA-$P_{416}$ | (M-H)- | 415.1757 | $C23H28O_7$ | 416.1835 | 1.36 |
| FA-$P_{424}$ | (M-H)- | 423.1816 | $C_{22}H_{29}FO_7$ | 424.1897 | 2.28 |
| FA-$P_{434}$ | (M-H)- | 433.1671 | $C_{20}H_{28}F_2O_8$ | 434.1752 | 2.17 |
| FA-$P_{436}$ | (M-H)- | 435.1757 | $C_{23}H_{29}FO_7$ | 436.1898 | 0.62 |
| FA-$P_{438}$ | (M-H)- | 437.1766 | $C23H28F_2O_6$ | 438.1854 | 2.9 |
| FA-$P_{472}$ | (M-H)- | 471.1836 | $C_{23}H_{30}F_2O_8$ | 472.1909 | 0.07 |

**Table S5-2.** General information of identified transformation products of TA during ozonation.

| Product | Species | m/z | Molecular formula | Relative molecular weight | Diff (ppm) |
|---|---|---|---|---|---|
| TA-$P_{396}$ | (M-H)- | 395.1508 | $C_{20}H_{25}FO_7$ | 396.1584 | 0.88 |
| TA-$P_{422}$ | (M-H)- | 421.1865 | $C_{22}H_{30}O_8$ | 422.1941 | 0.58 |
| TA-$P_{424}$ | (M-H)- | 423.2015 | $C_{22}H_{32}O_8$ | 424.2097 | 1.9 |
| TA-$P_{430}$ | (M-H)- | 429.1901 | $C_{24}H_{30}O_7$ | 430.1992 | 2.45 |
| TA-$P_{432a}$ | (M-H)- | 431.2074 | $C_{21}H_{33}FO_8$ | 432.2159 | 2.73 |
| TA-$P_{432b}$ | (M-H)- | 431.2087 | $C_{24}H_{32}O_7$ | 432.2148 | −1.54 |
| TA-$P_{442}$ | (M-H)- | 441.1930 | $C_{22}H_{31}FO_8$ | 442.2003 | 0.09 |
| TA-$P_{448a}$ | (M-H)- | 447.2020 | $C_{21}H_{33}FO_9$ | 448.2109 | 2.89 |
| TA-$P_{448b}$ | (M-H)- | 447.2022 | $C_{24}H_{32}O_8$ | 448.2097 | 0.54 |
| TA-$P_{458}$ | (M-H)- | 457.1865 | $C_{22}H_{31}FO_9$ | 458.1952 | 2.99 |
| TA-$P_{476}$ | (M-H)- | 475.1971 | $C_{22}H_{33}FO_{10}$ | 476.2058 | 1.45 |
| TA-$P_{460}$ | (M-H)- | 459.2020 | $C_{22}H_{33}FO_9$ | 460.2190 | 2.82 |
| TA-$P_{484}$ | (M-H)- | 483.2032 | $C_{24}H_{33}FO_9$ | 484.2109 | 0.38 |
| TA-$P_{488}$ | (M-H)- | 487.1982 | $C_{23}H_{33}FO_{10}$ | 488.2058 | 0.9 |

**Table S5-3.** General information of identified transformation products of CP during ozonation.

| Product | Species | m/z | Molecular formula | Relative molecular weight | Diff (ppm) |
|---|---|---|---|---|---|
| CP-$P_{412}$ | (M-H)- | 411.1576 | $C_{21}H_{29}ClO_6$ | 412.1653 | 1.54 |
| CP-$P_{424}$ | (M-H)- | 423.1570 | $C_{22}H_{29}ClO_6$ | 424.1653 | 0.67 |
| CP-$P_{428}$ | (M-H)- | 427.1531 | $C_{21}H_{29}ClO_7$ | 428.1602 | 0.64 |
| CP-$P_{432}$ | (M-H)- | 431.1623 | $C_{24}H_{29}ClO_5$ | 432.1704 | −0.25 |
| CP-$P_{440}$ | (M-H)- | 439.1519 | $C_{22}H_{29}ClO_7$ | 440.1602 | 4.46 |
| CP-$P_{444}$ | (M-H)- | 443.1621 | $C_{22}H_{30}ClFO_6$ | 444.1715 | 2.73 |
| CP-$P_{466}$ | (M-H)- | 465.1675 | $C_{24}H_{31}ClO_7$ | 466.1758 | 3.62 |
| CP-$P_{486}$ | (M-H)- | 485.1743 | $C_{24}H_{32}ClFO_7$ | 486.1821 | 1.32 |
| CP-$P_{490}$ | (M-H)- | 489.1684 | $C_{23}H_{32}ClFO_8$ | 490.177 | 3.05 |
| CP-$P_{515}$ | (M-H)- | 514.1534 | $C_{25}H_{32}ClFO_8$ | 515.1832 | 3.46 |
| CP-$P_{498}$ | (M-H)- | 497.1742 | $C_{25}H_{32}ClFO_7$ | 498.1821 | 0.96 |
| CP-$P_{502}$ | (M-H)- | 501.1691 | $C_{24}H_{32}ClFO_8$ | 502.177 | 2.44 |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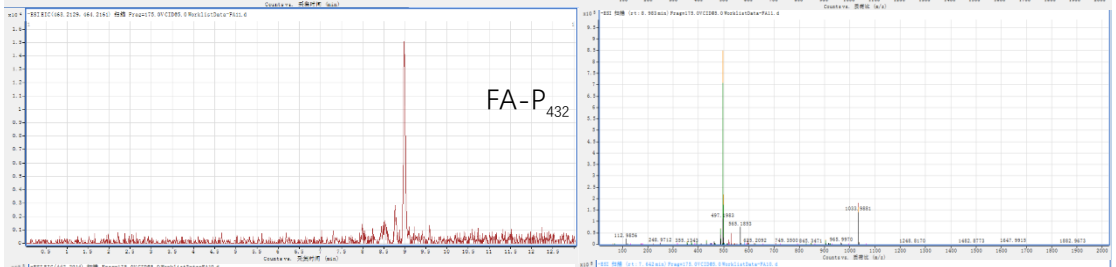
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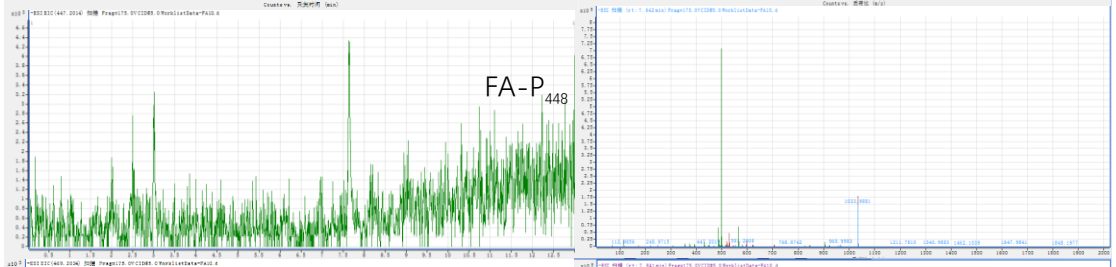
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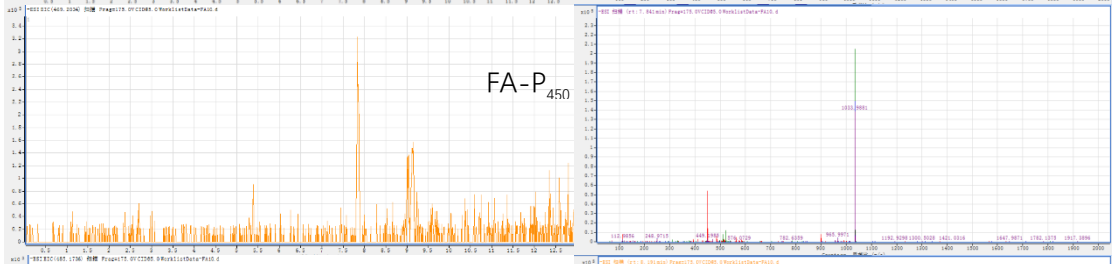
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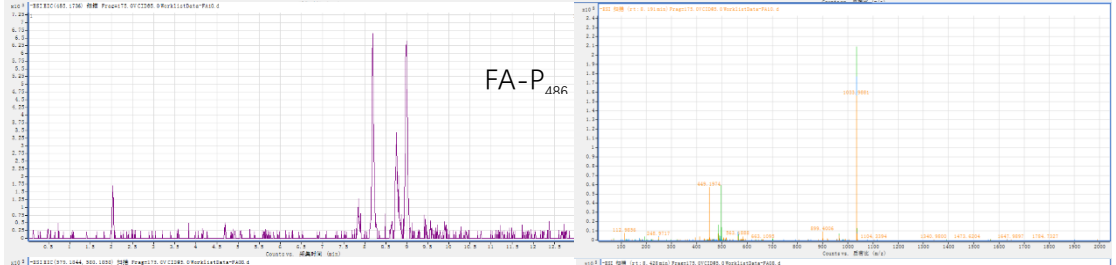
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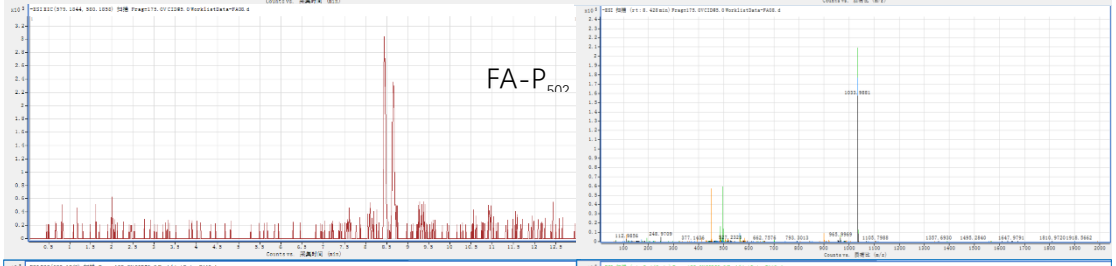
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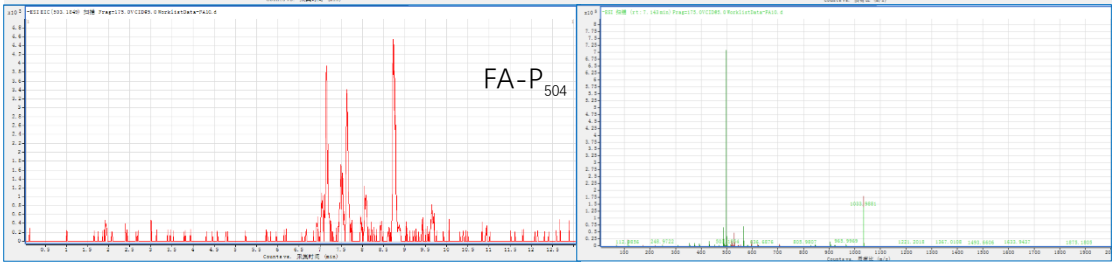
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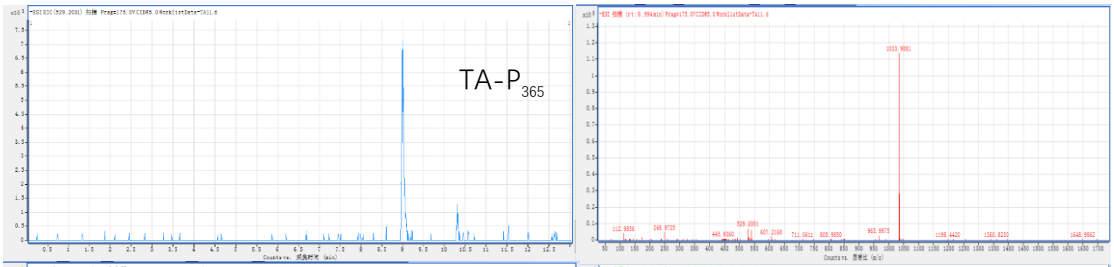
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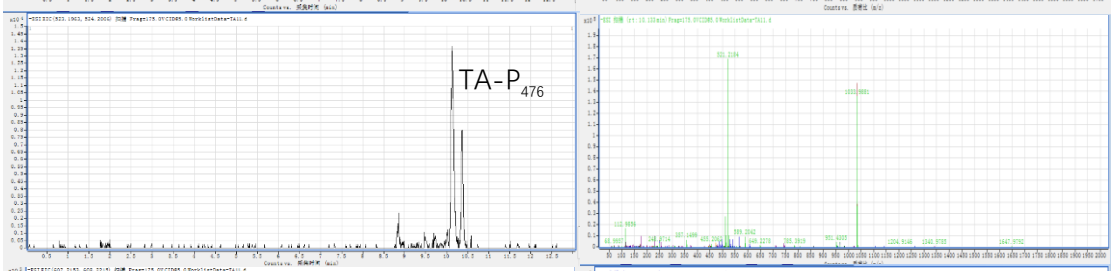
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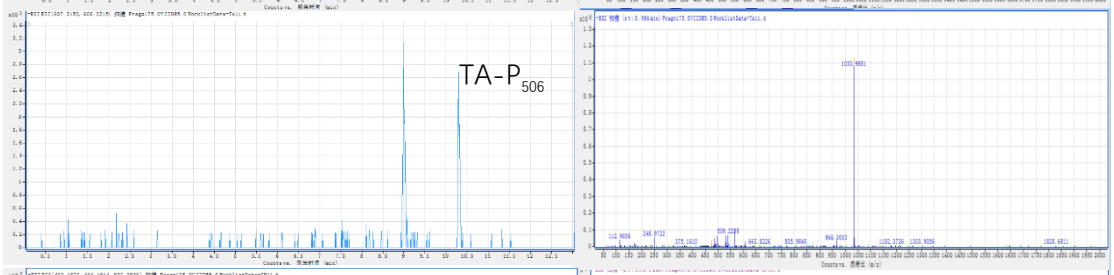
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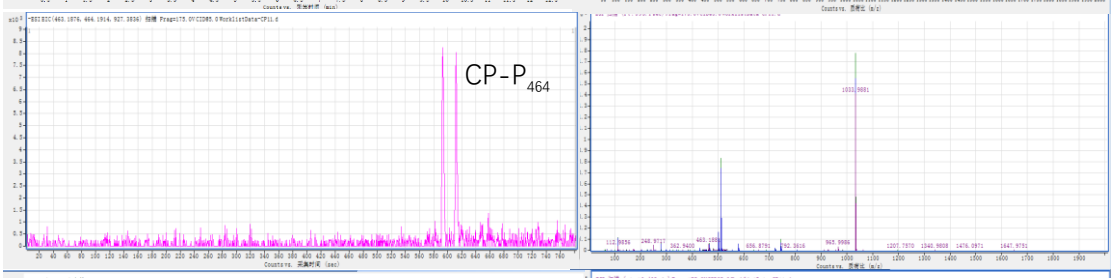
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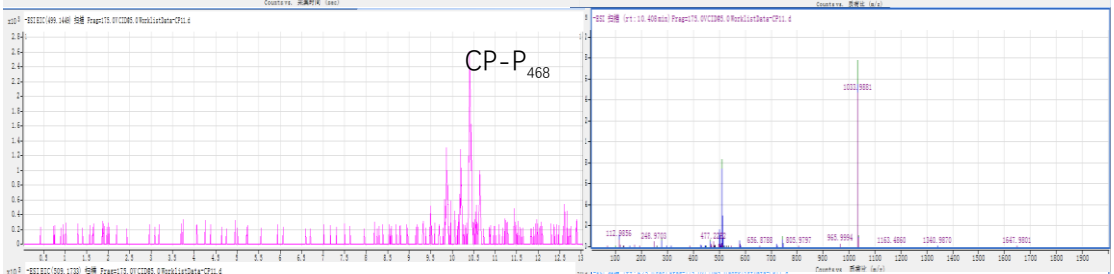
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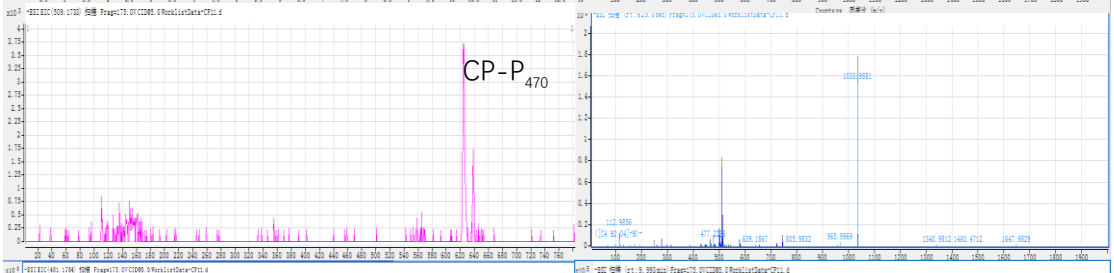
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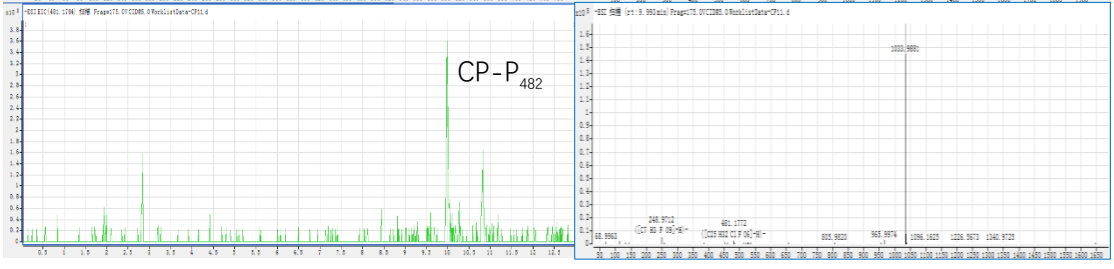
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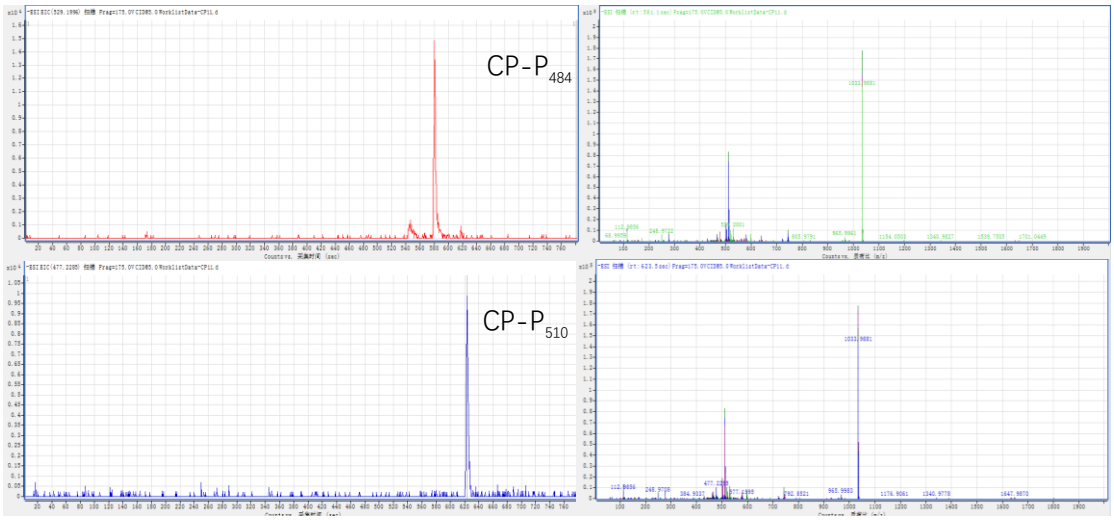
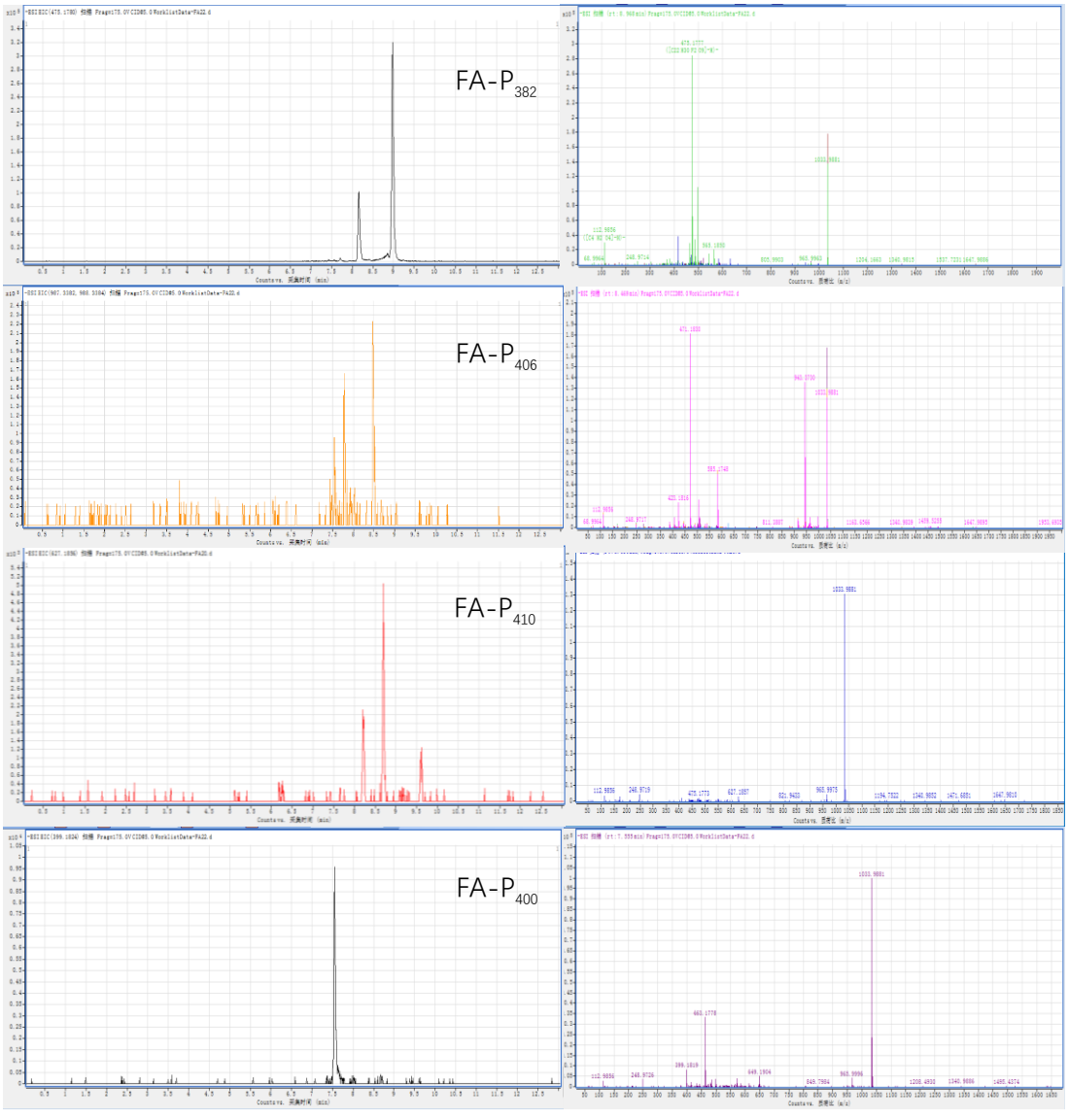
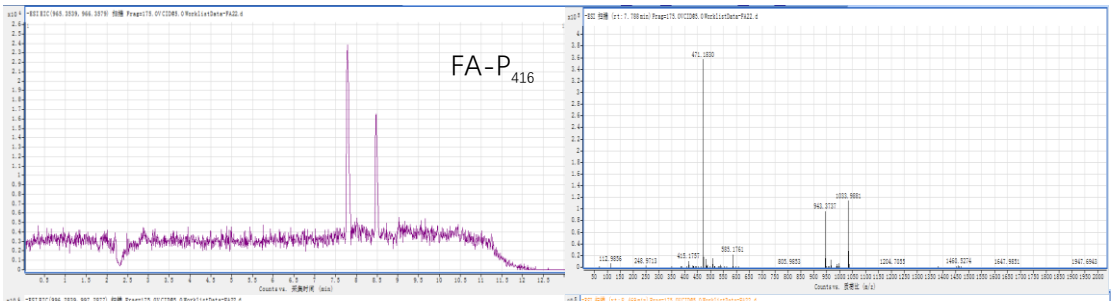



**Figure S1-1.** Extracted ion chromatographs and mass spectrometry fragments for intermediates of GCs during UVA/chlorination.

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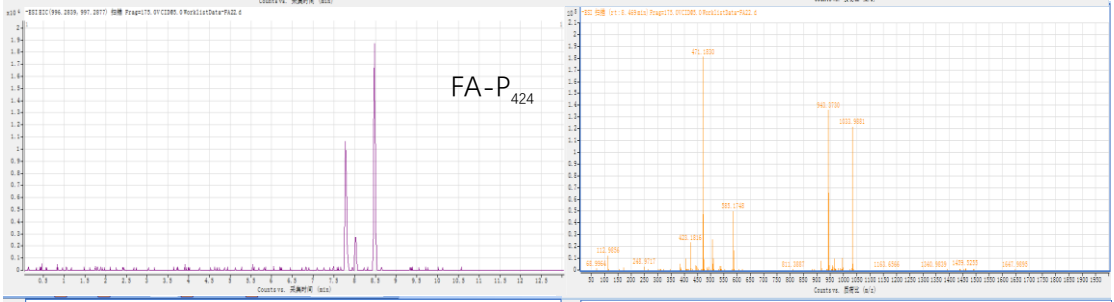
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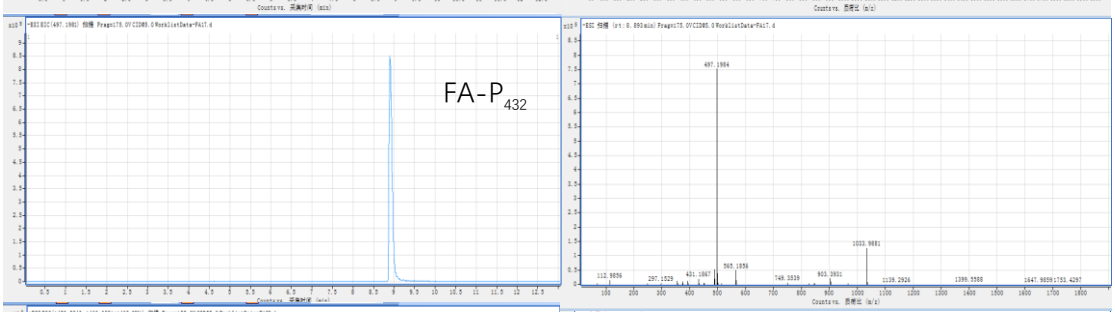
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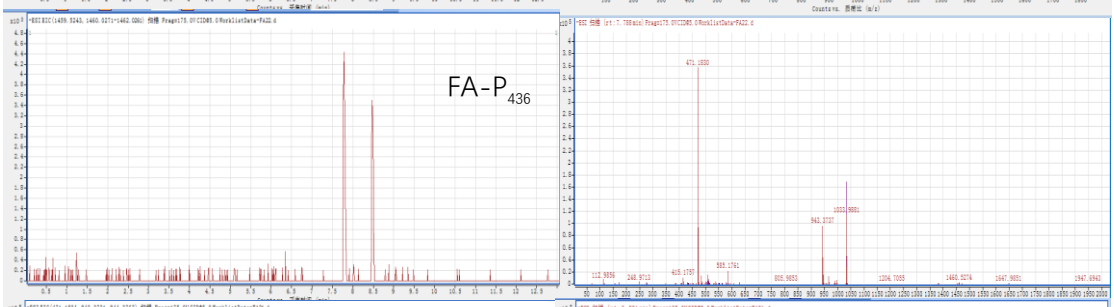
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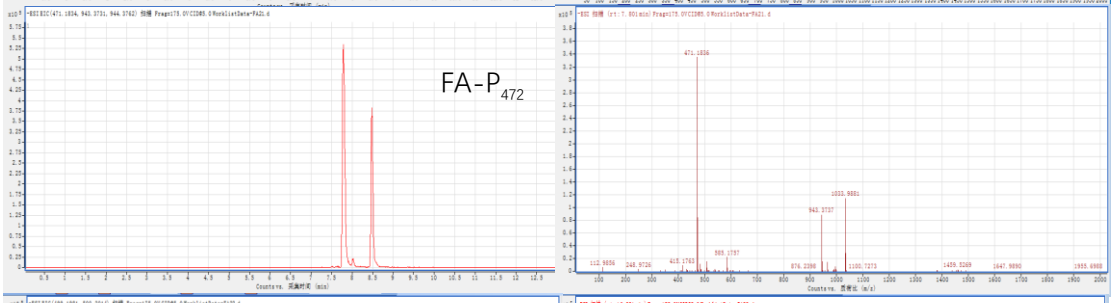
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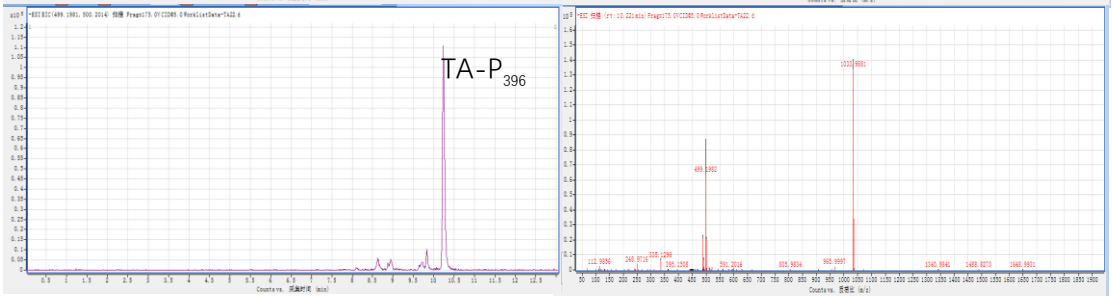
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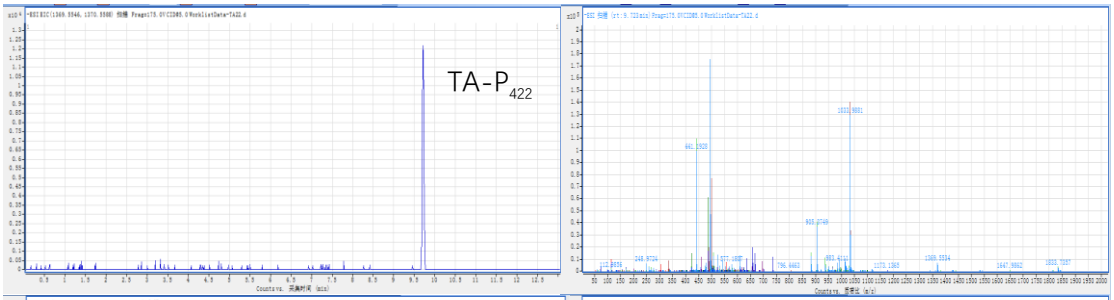
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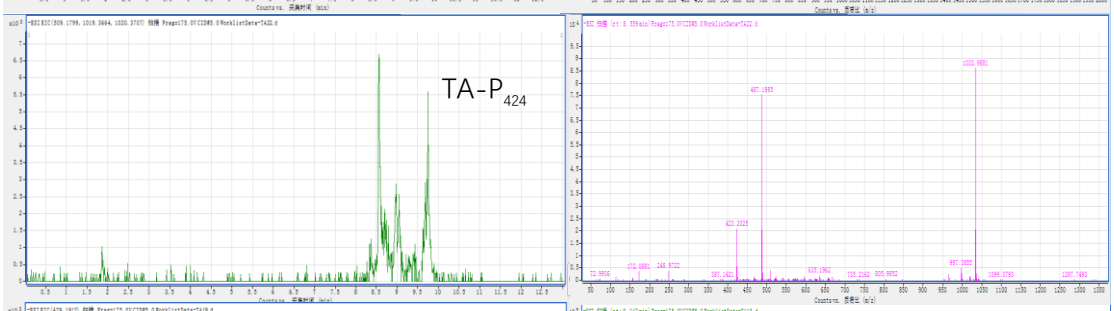
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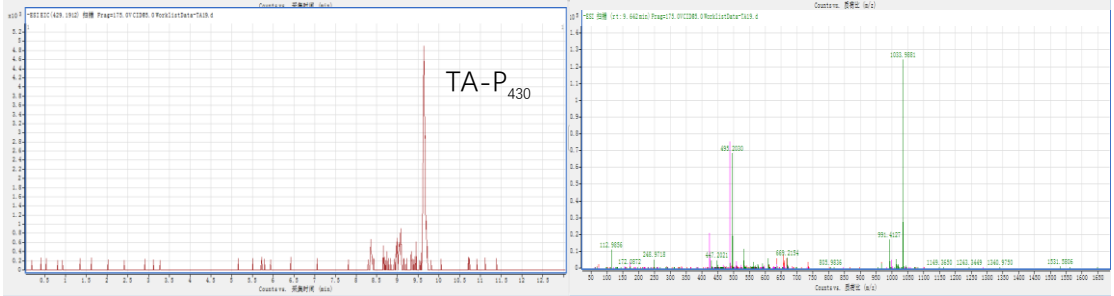
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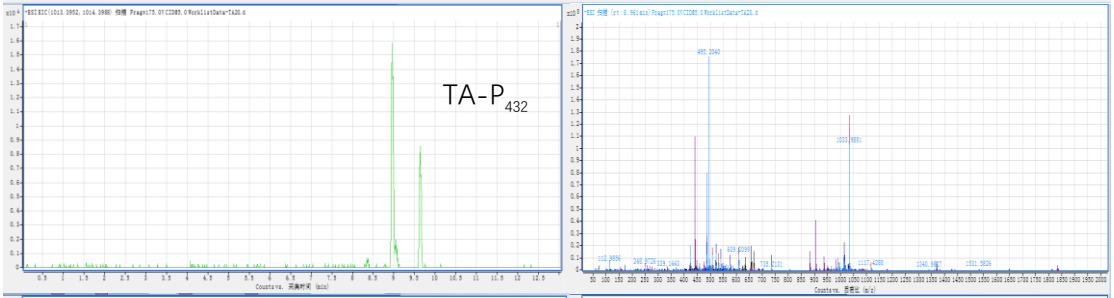
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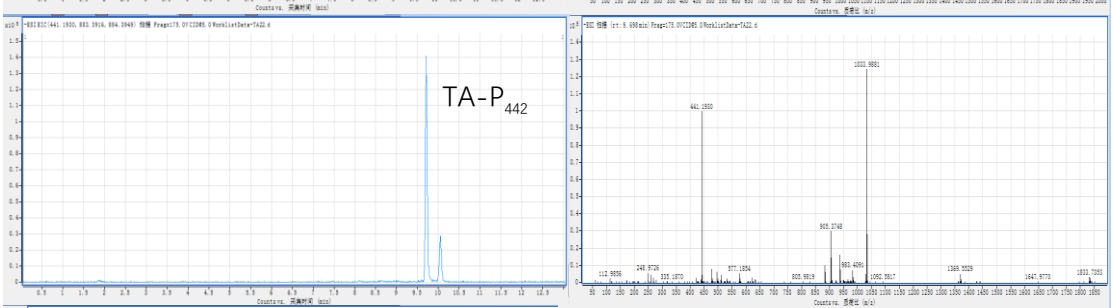
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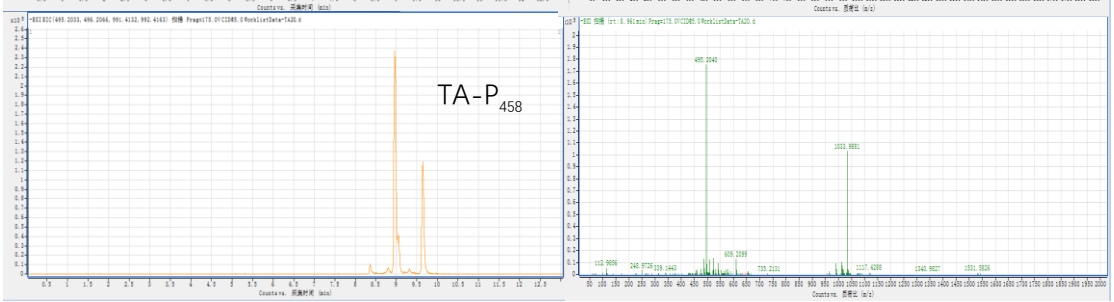
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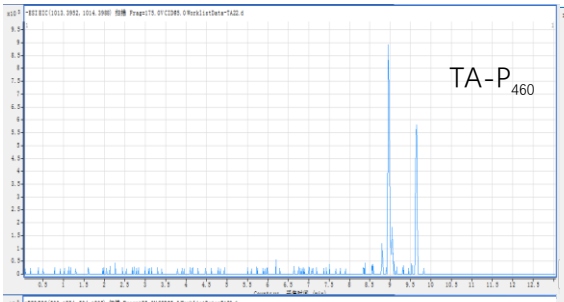
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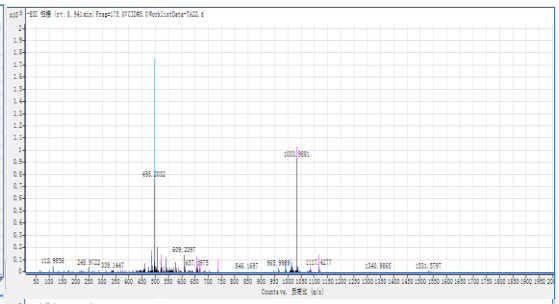

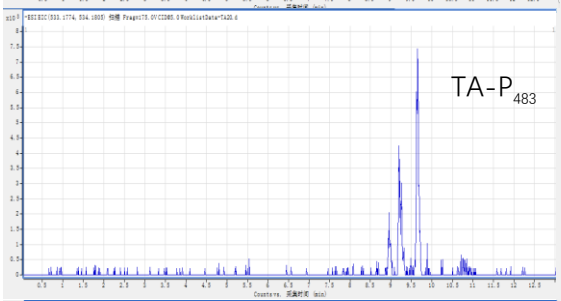
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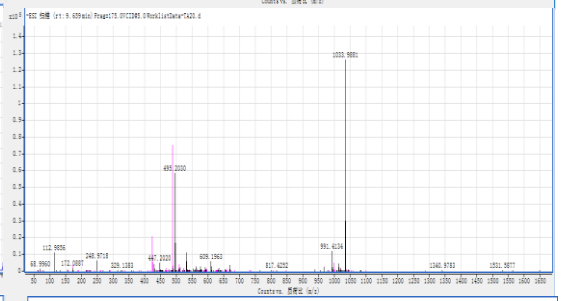

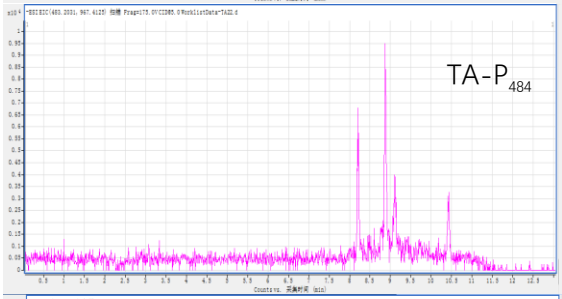
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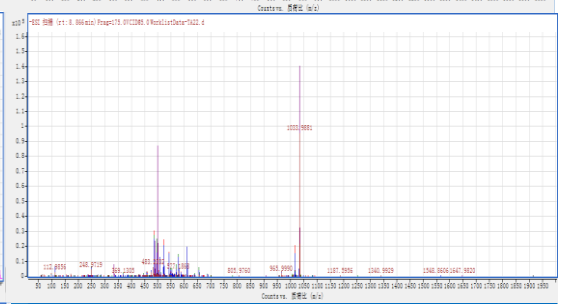

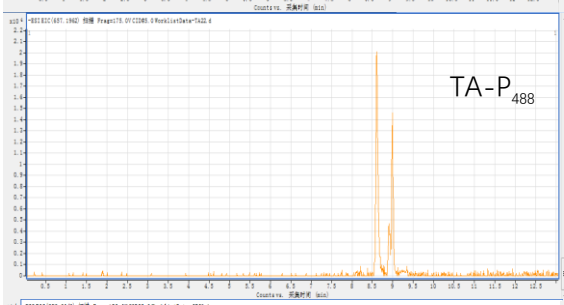
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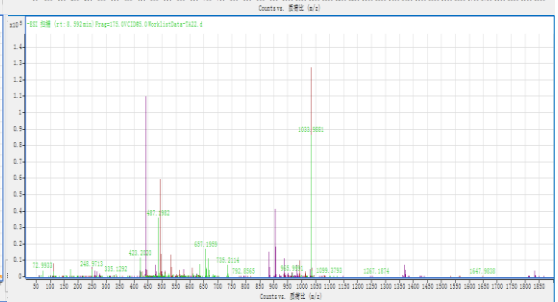

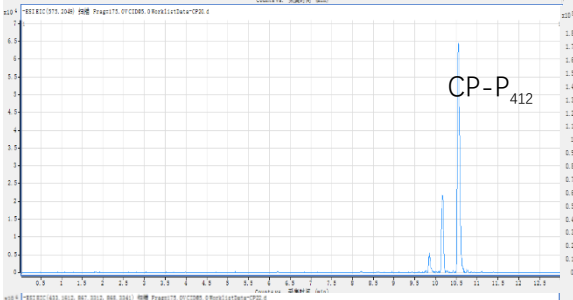
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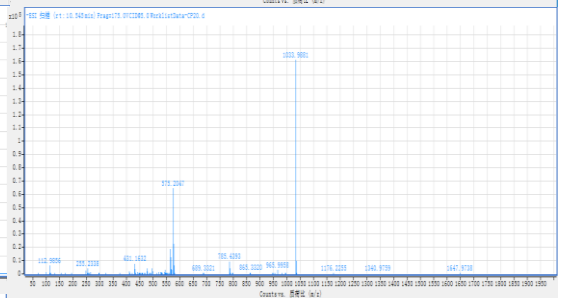

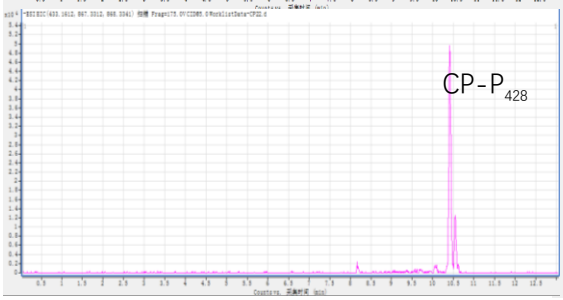
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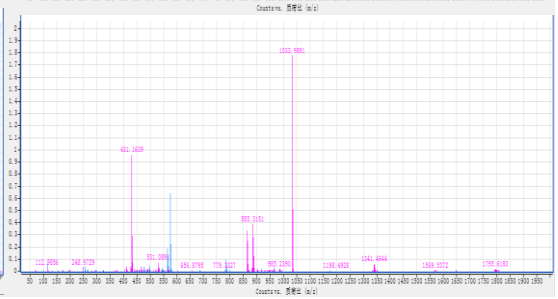

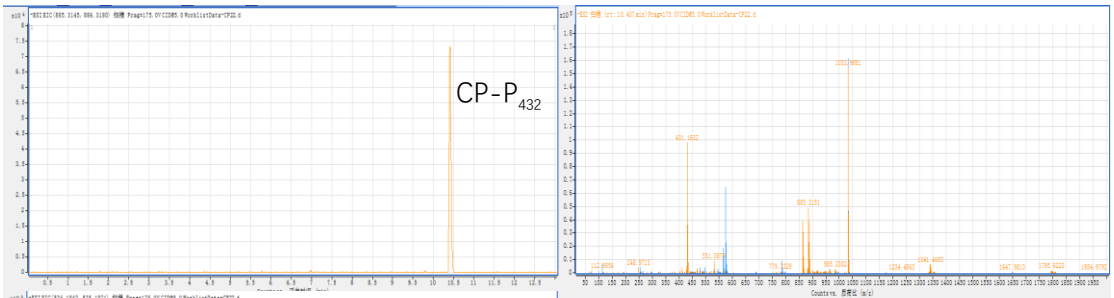
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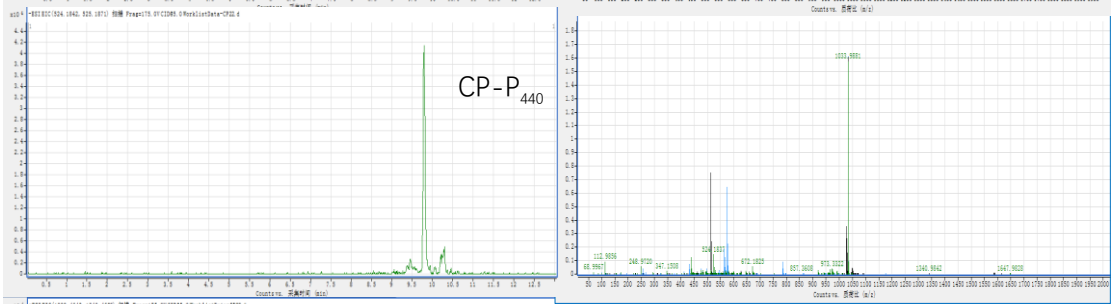
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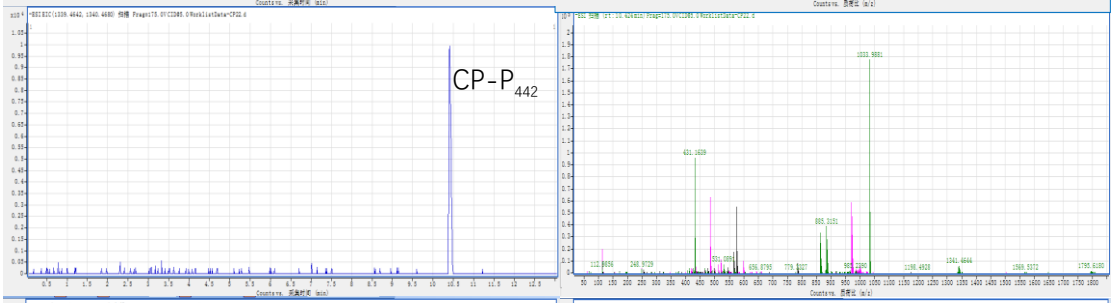
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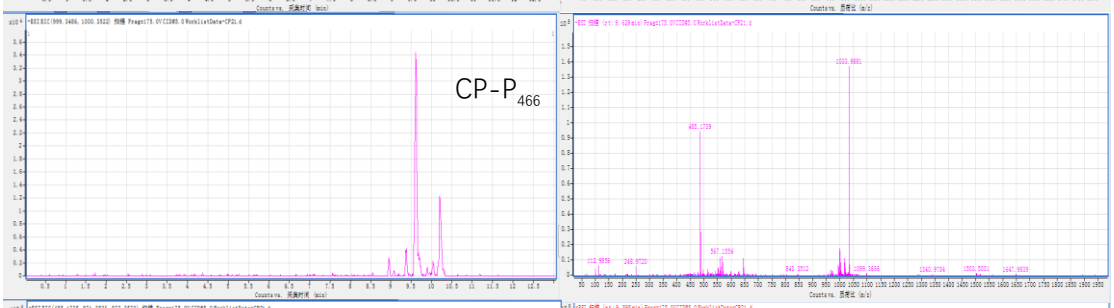
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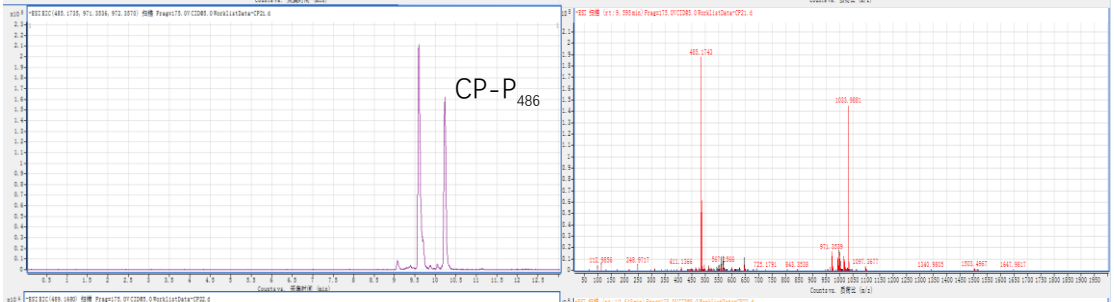
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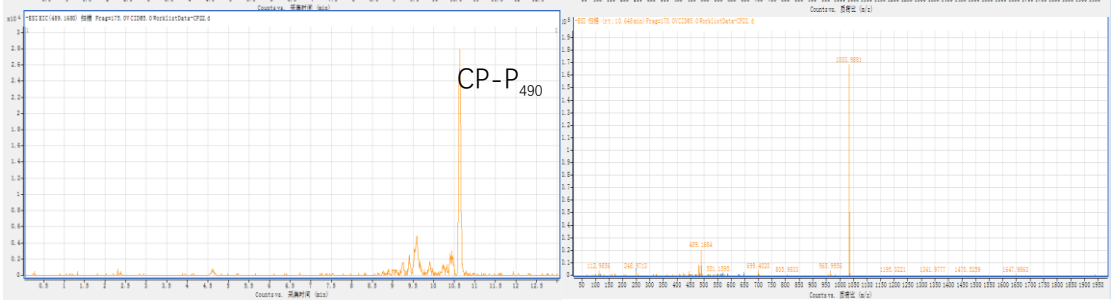
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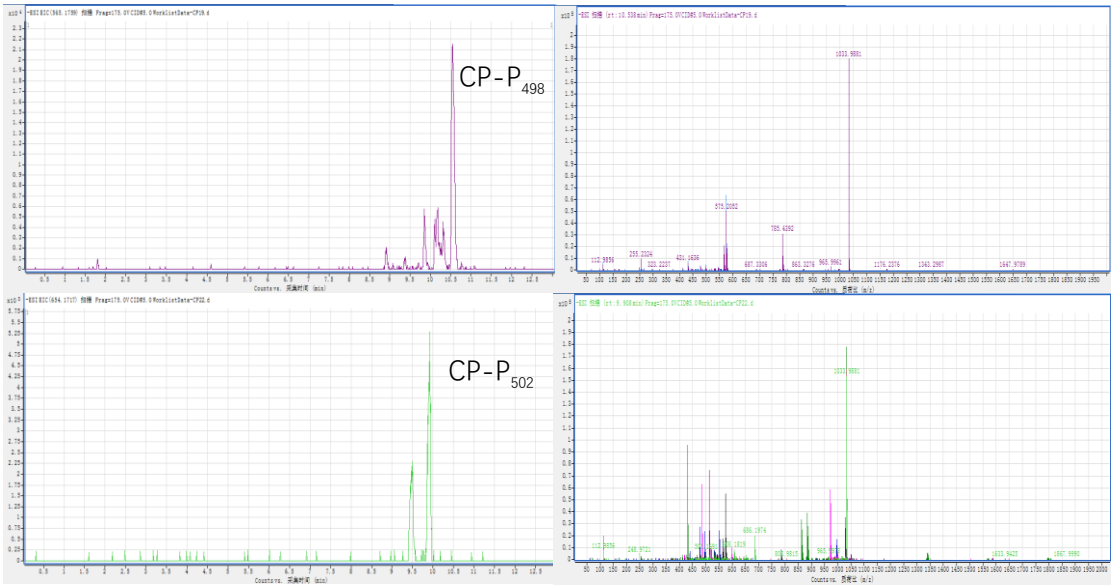


**Figure S1.-2** Extracted ion chromatographs and mass spectrometry fragments for intermediates of GCs during ozonation.

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