# Supporting Information

## Comparative study on a kilowatt-MPT-MS-based method with two ion polarity modes for inert metal palladium

Tao Jiang[1,4], Feng Jiang[3], Zemin Zhuo[1], Huaxin Liu[2], Bin Hu[1], Mei Li[1,4], Lei Li[1,4], Zhengxu Huang[1,4*], Zhen Zhou[1], Zhiqiang Zhu[2*]

[1] Institute of Mass Spectrometry and Atmospheric Environment, Guangdong Provincial Engineering Research Center for On-line Source Apportionment System of Air Pollution, Jinan University, Guangzhou, Guangdong 510632, China ;

[2] Quantum Information Research Center, Shangrao Normal University, Jiangxi 334001, China;

[3] Key Laboratory of Environment and Resource Utilization of Poyang Lake, Ministry of Education, School of Environment and Chemical Engineering, Nanchang University, Nanchang 330031, China;

[4] Guangzhou Hexin Instrument Co., Ltd, Guangzhou 510530, China;

**Corresponding Authors:**

***Zhiqiang Zhu***

***E-mail:***zhiqiangz@iccas.ac.cn*. **Tel: +86-793-8150637;**

***Zhengxu Huang***

***E-mail:** *jtostrich@163.com*. **Tel: +86-020-85225991;**

**Figure and table of content**

**Table S6. the ionization energy, proton affinity energy, and electron affinity energy of various main substances.**

**Table S7. A list of reactions and the rate constants.**

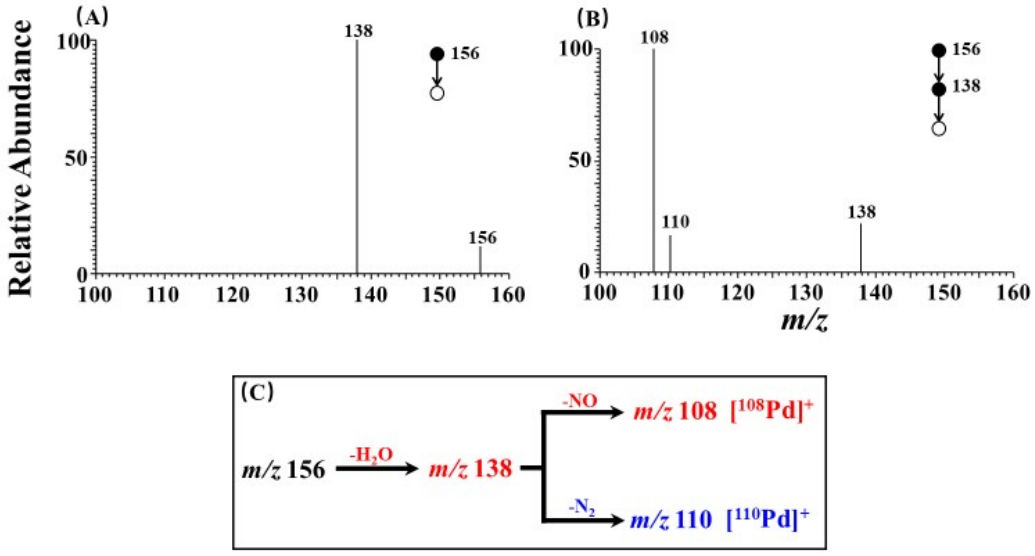


**Figure S1. Multi-stage MS spectra of palladium adduct ion (*m/z* 157) and proposed fragmentation pathway (C) obtained by LTQ Mass Spectrometry in positive ion mode.**

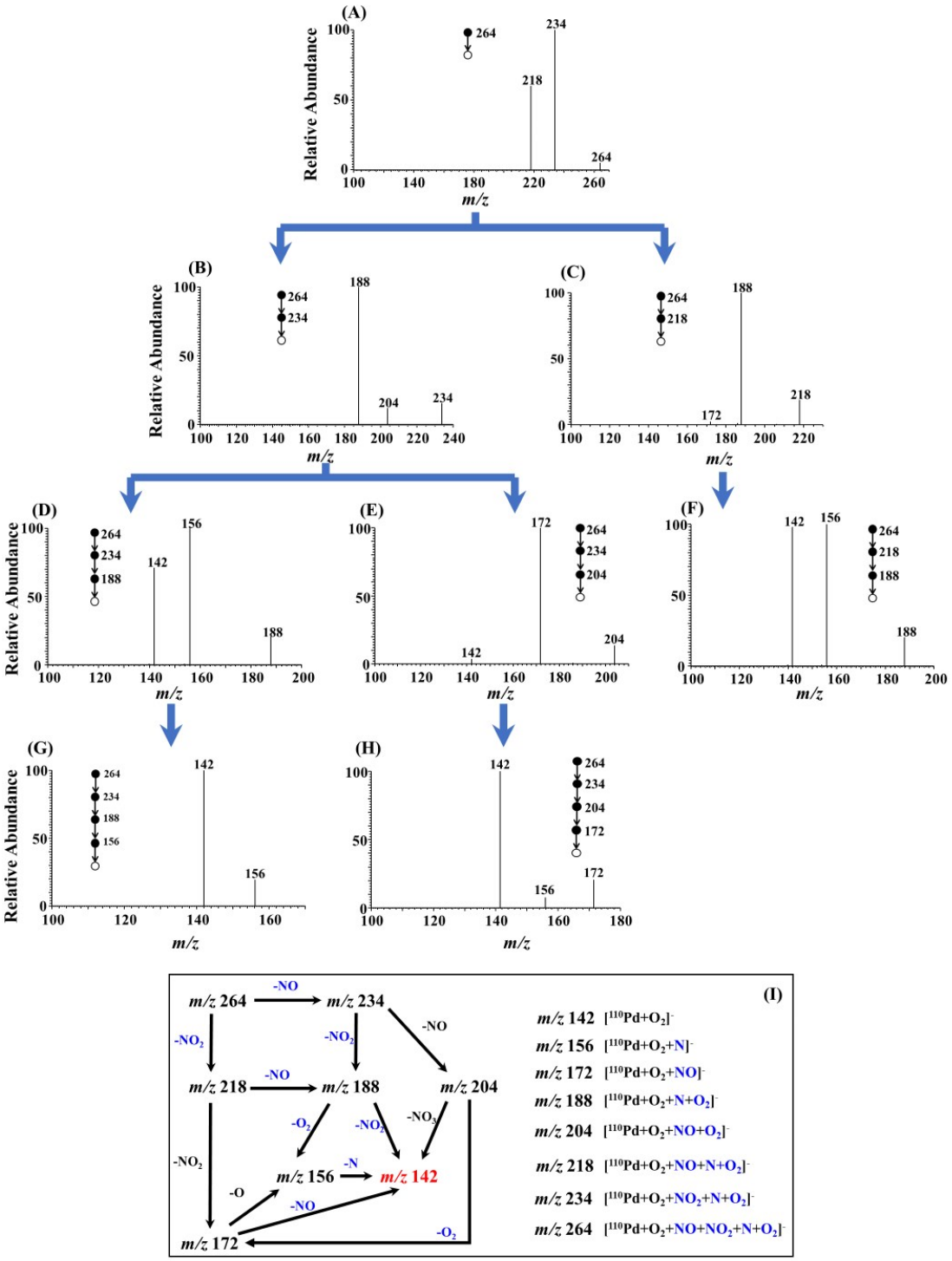


**Figure S2. Multi-stage MS spectra of palladium adduct ion (*m/z* 264) (A-H) and proposed fragmentation pathway (I) obtained by LTQ Mass Spectrometry with negative ion mode.**

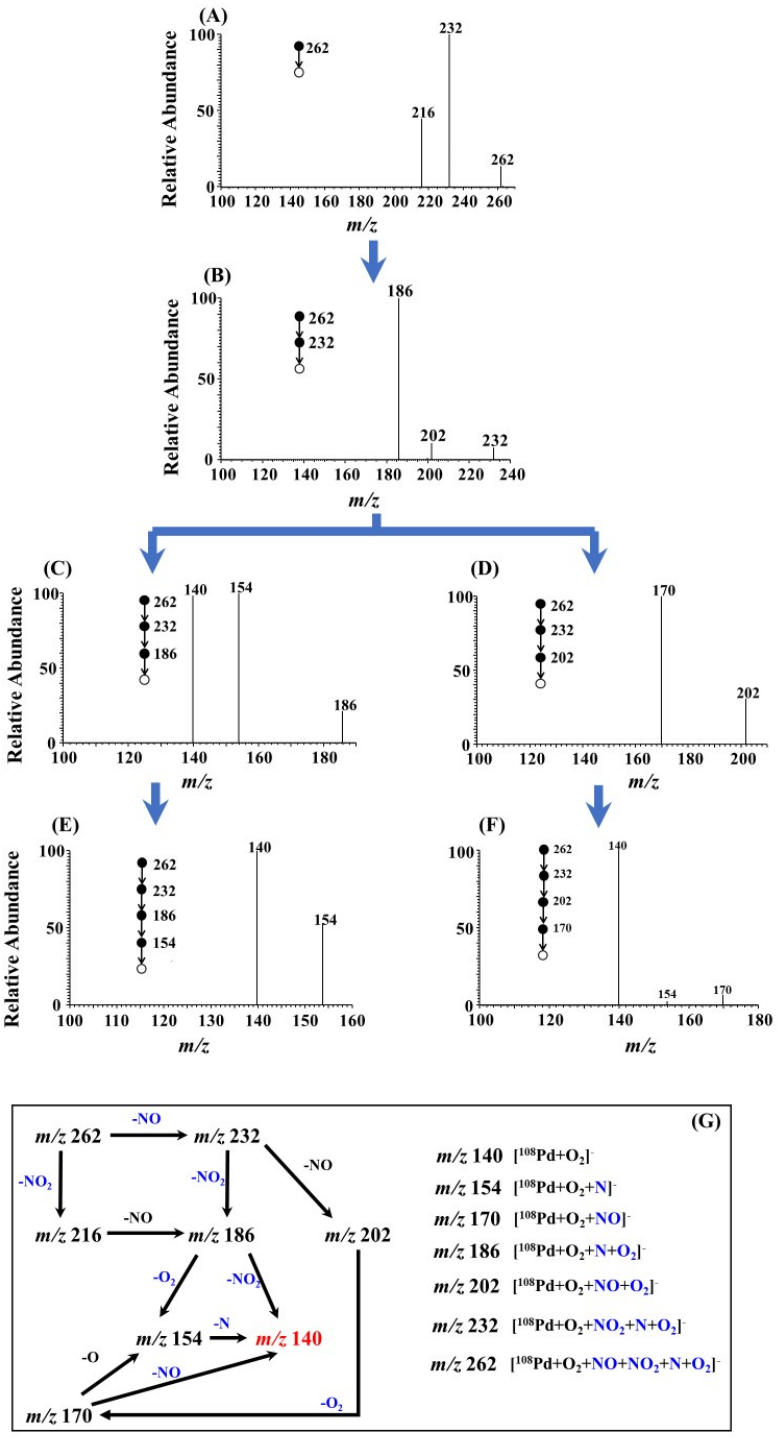


**Figure S3. Multi-stage MS spectra of palladium adduct ion (*m/z* 262) (A-F) and proposed fragmentation pathway (G) obtained by LTQ Mass Spectrometry with negative ion mode.**

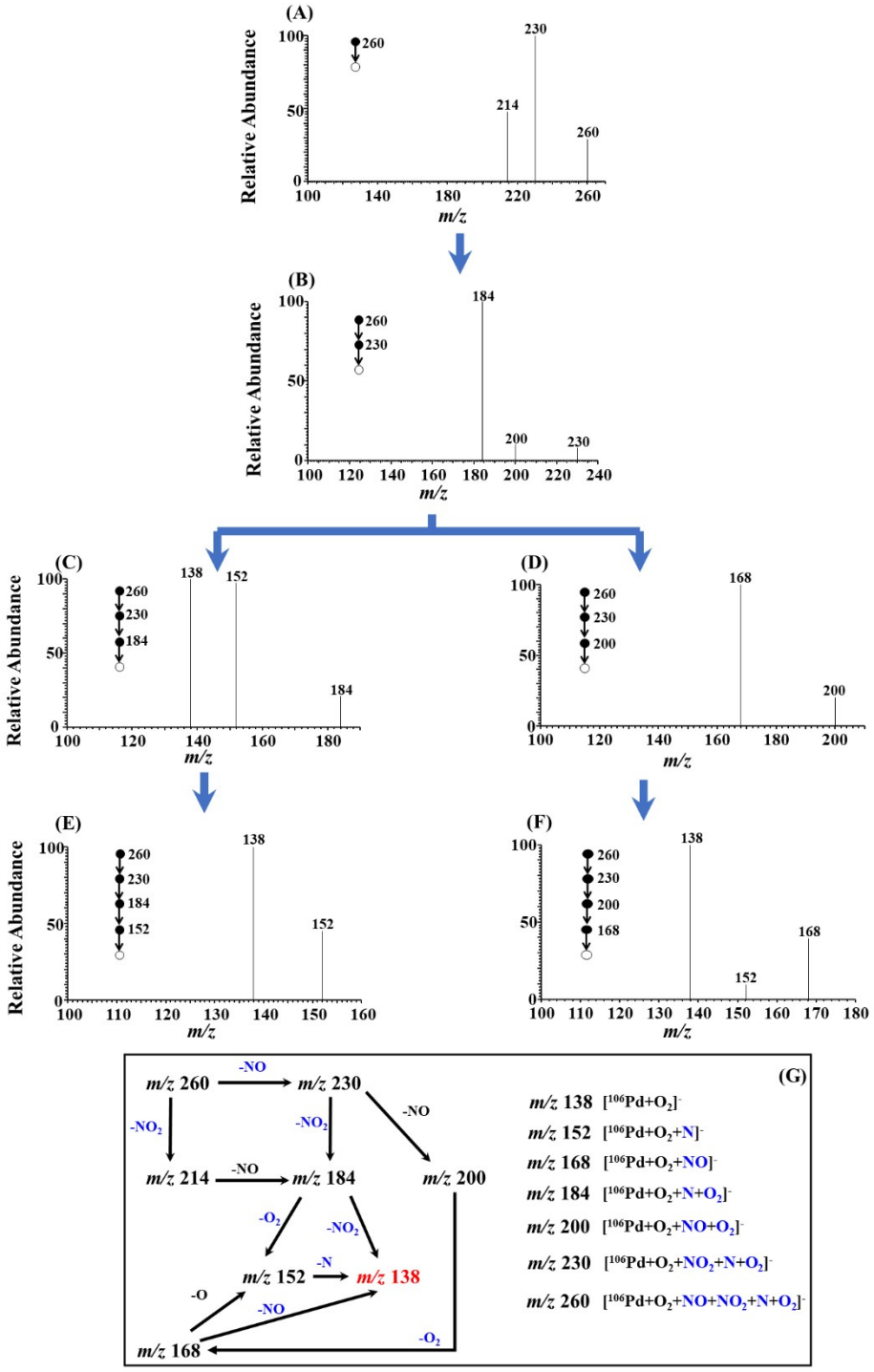


**Figure S4. Multi-stage MS spectra of palladium adduct ion (*m/z* 260) (A-F) and proposed fragmentation pathway (G) obtained by LTQ Mass Spectrometry with negative ion mode.**

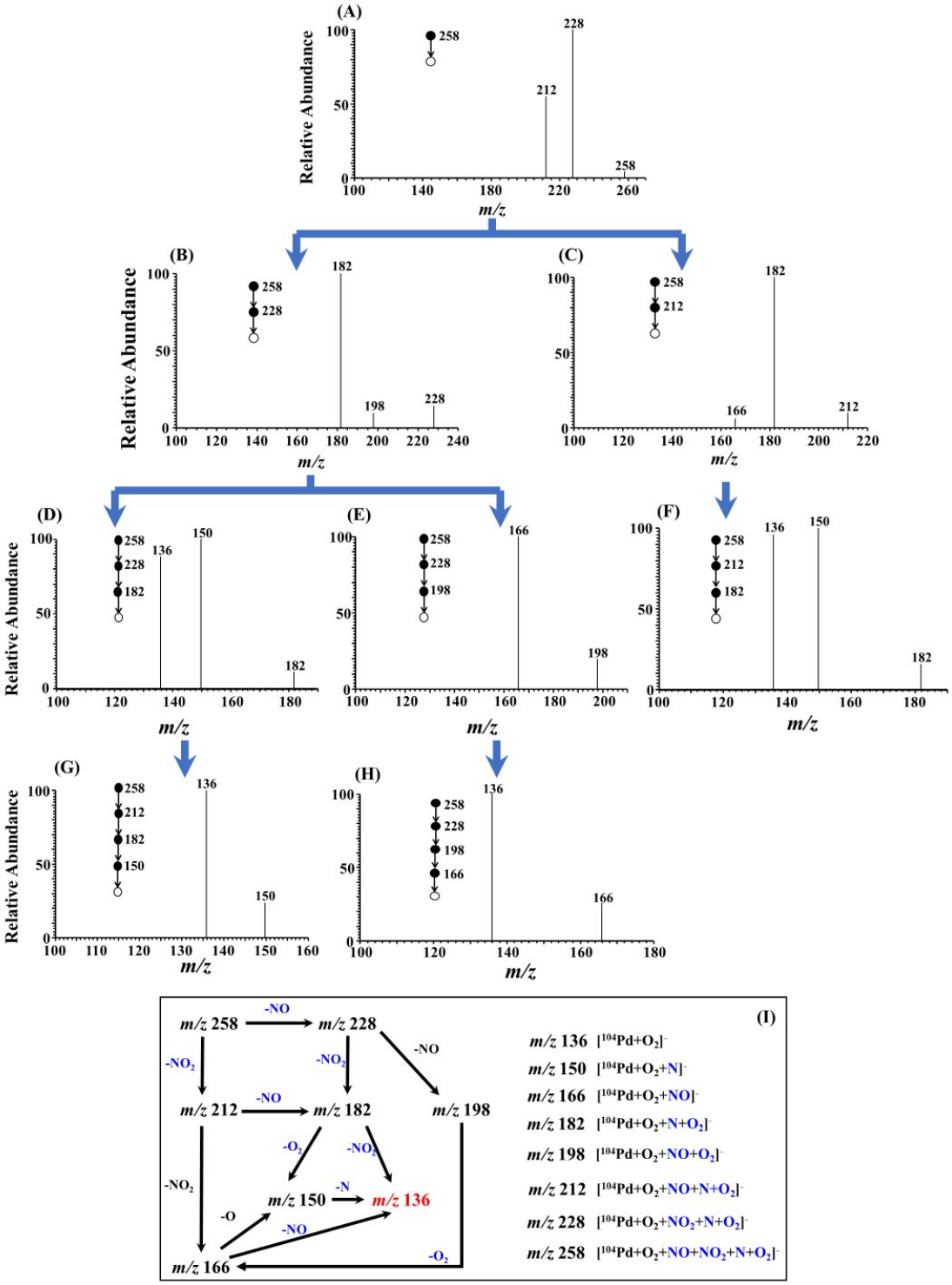


**Figure S5. Multi-stage MS spectra of palladium adduct ion (*m/z* 258) (A-H) and proposed fragmentation pathway (I) obtained by LTQ Mass Spectrometry with negative ion mode.**

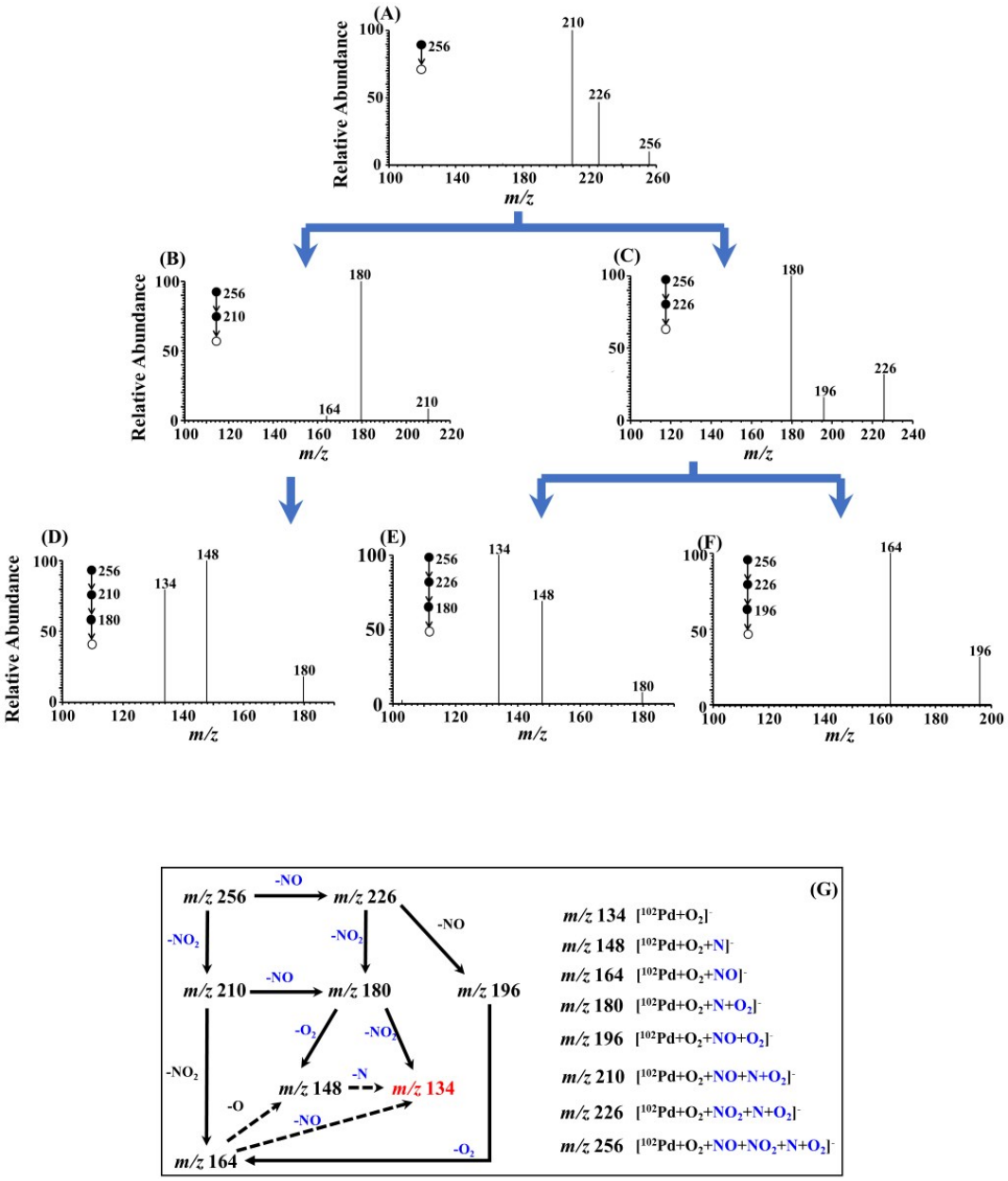


**Figure S6. Multi-stage MS spectra of palladium adduct ion (m/z 256) (A-E) and proposed fragmentation pathway (G) obtained by LTQ Mass Spectrometry with negative ion mode.**

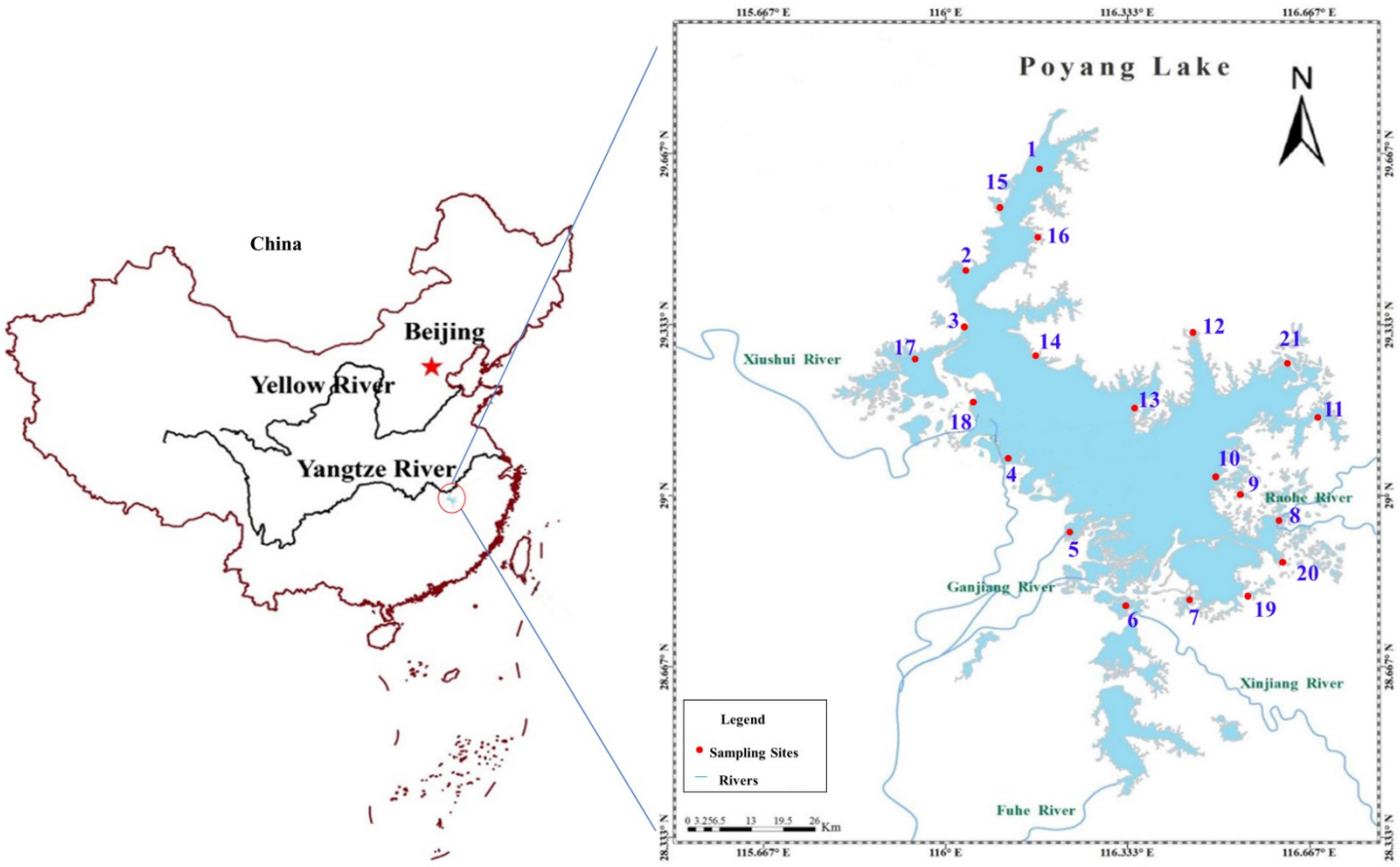


**Figure S7. Sampling sites of water samples in Poyang Lake.**

*1-Hu Kou, 2-Xing Zi, 3-Gang Kou, 4-Xiao Tan Lake, 5-Chang Lake, 6-Zhong Zhou, 7-Da Lake, 8-The Entrance of Rao River, 9-Lian Lake, 10-Long Kou, 11-Hu Shan, 12-Mao Shan Lake, 13-Lun Lake, 14-Du Chang, 15-Xia Qing Shan, 16-Xie Jia Lake, 17-Bang Lake, 18-Dong Jia Lake, 19-Du Shan, 20-Da Lian Zi Lake, 21-Tai Yang Lake.

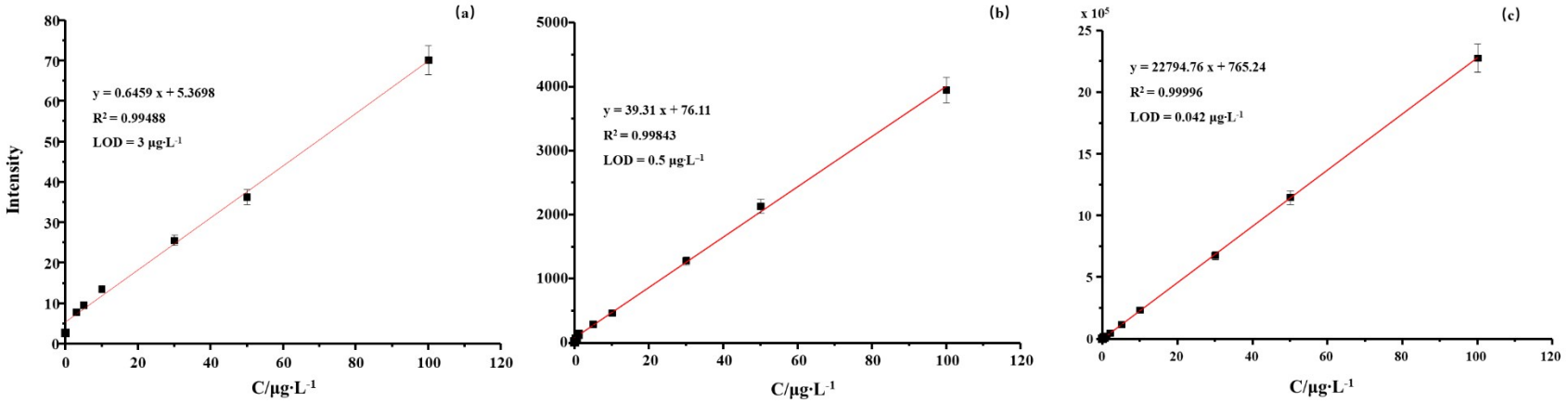


**Figure S8. Calibration curves of *m/z* 106 in positive mode (a) and *m/z* 229 in negative mode (b) by MPT-MS; Calibration curves of *m/z* 105 in positive mode (c) by ICP-MS ;**

**Table S1 Comparison of natural isotopic abundance and experimental value of palladium**

| Natural isotopic | Positive mode | | | Negative mode | | | Natural isotopic abundance[1] |
|---|---|---|---|---|---|---|---|
| | *m/z* | Intensity | Experimental value | *m/z* | Intensity | Experimental value | |
| $^{102}$Pd | 150 | 52036.8 | 1.24% | 256 | 860 | 1.02% | 1.02% |
| $^{104}$Pd | 152 | 548022.9 | 13.10% | 258 | 9500 | 11.22% | 11.14% |
| $^{105}$Pd | 153 | 1079507.6 | 25.81% | 259 | 18900 | 22.32% | 22.33% |
| $^{106}$Pd | 154 | 1023983.4 | 24.48% | 260 | 23000 | 27.16% | 27.33% |
| $^{108}$Pd | 156 | 999990.3 | 23.91% | 262 | 22400 | 26.45% | 26.46% |
| $^{110}$Pd | 158 | 479324.3 | 11.46% | 264 | 10020 | 11.83% | 11.72% |

**Table S2 Analytical results for different concentrations of palladium (*m/z* 106) by MPT-MS$^3$ with positive mode**

| C/(μg•L$^{-1}$) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | AVERAGE | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 2.59 | 2.83 | 2.1 | 2.02 | 2.42 | 2.05 | 3.85 | 2.9 | 2.41 | 2.91 | 2.57 | 2.60 | 0.53 | 20.17% |
| 3 | 7.84 | 7.12 | 8.48 | 7.83 | 7.56 | 8.49 | 7.87 | 7.59 | 6.48 | 8.87 | 7.54 | 7.79 | 0.67 | 8.58% |
| 5 | 9.91 | 8.96 | 9.77 | 9.33 | 9.98 | 9.79 | 9.37 | 9.19 | 9.73 | 9.36 | 9.18 | 9.51 | 0.34 | 3.59% |
| 10 | 13.22 | 14.81 | 13.26 | 14 | 13.19 | 14.22 | 12.81 | 14.22 | 13.23 | 12.86 | 13.23 | 13.55 | 0.65 | 4.80% |
| 30 | 25.23 | 25.93 | 25.19 | 25.83 | 25.45 | 25.91 | 25.16 | 25.97 | 25.13 | 25.86 | 25.44 | 25.55 | 0.35 | 1.36% |
| 50 | 36.92 | 37.33 | 36.54 | 37.34 | 35.63 | 36.67 | 35.33 | 35.76 | 36.49 | 35.56 | 35.86 | 36.31 | 0.72 | 1.98% |
| 100 | 68.63 | 69.43 | 69.73 | 69.8 | 70.15 | 72.41 | 70.72 | 69.87 | 69.49 | 71.73 | 69.84 | 70.16 | 1.08 | 1.54% |

**Table S3 Analytical results for different concentrations of palladium (*m/z* 229) by MPT-MS$^2$ with negative mode**

| C/(μg•L$^{-1}$) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | AVERAGE | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 12.4 | 14.4 | 12.1 | 13.6 | 12.6 | 12.0 | 16.3 | 14.6 | 10.5 | 14.2 | 14.1 | 13.35 | 1.6 | 12.01% |
| 0.5 | 56.6 | 66 | 59 | 62 | 57 | 60 | 59 | 58.8 | 58.6 | 58.4 | 58.2 | 59.42 | 2.61 | 4.39% |
| 1 | 127 | 139 | 124 | 133 | 136 | 134 | 132 | 139 | 129 | 121 | 123 | 130.64 | 6.31 | 4.83% |
| 5 | 316 | 309 | 261 | 279 | 275 | 302 | 287 | 278 | 300 | 310 | 300 | 292.45 | 17.48 | 5.98% |
| 10 | 468 | 493 | 477 | 459 | 471 | 479 | 440 | 442 | 457 | 480 | 488 | 468.55 | 17.43 | 3.72% |
| 30 | 1267 | 1280 | 1267 | 1270 | 1280 | 1289 | 1270 | 1304 | 1288 | 1311 | 1298 | 1284.00 | 15.39 | 1.2% |
| 50 | 2120 | 2150 | 2110 | 2140 | 2230 | 2127 | 2134 | 2148 | 2134 | 2088 | 2089 | 2133.64 | 38.29 | 1.79% |
| 100 | 3940 | 4030 | 3980 | 3960 | 3850 | 4032 | 3902 | 3976 | 4083 | 3782 | 3941 | 3952.36 | 85.52 | 2.16% |

**Table S4 Analytical results for different concentrations of palladium (*m/z* 105) by ICP-MS with positive mode**

| C/(μg•L$^{-1}$) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | AVERAGE | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 600 | 500 | 601 | 553 | 610 | 574 | 600 | 583 | 583 | 594 | 587 | 580.45 | 30.93 | 5.33% |
| 0.5 | 1020 | 9754 | 9782 | 10143 | 10505 | 1086 | 10028 | 9989 | 9951 | 10013 | 10014 | 8389.55 | 3632.60 | 43.30% |
| 1 | 23222 | 22871 | 22761 | 22518 | 22297 | 22077 | 21857 | 21637 | 21816 | 21996 | 22076 | 22284.36 | 499.59 | 2.24% |
| 2 | 48193 | 44379 | 47941 | 46323 | 46167 | 45962 | 46756 | 45550 | 45345 | 45139 | 45933 | 46153.45 | 1141.40 | 2.47% |
| 5 | 116000 | 119872 | 114771 | 116173 | 117264 | 116167 | 115070 | 113973 | 112876 | 111778 | 119681 | 115784.09 | 2524.95 | 2.18% |
| 10 | 233307 | 230255 | 231782 | 226314 | 228551 | 245405 | 248260 | 231114 | 233969 | 2468234 | 239678 | 437897.18 | 673421.79 | 153.79% |
| 30 | 669723 | 689410 | 677831 | 687029 | 671058 | 685087 | 669116 | 673145 | 667174 | 661203 | 675232 | 675091.64 | 8916.95 | 1.32% |
| 50 | 1162846 | 1126319 | 1131712 | 1137251 | 1154718 | 1132186 | 1169654 | 1167121 | 1154589 | 1142057 | 1129525 | 1146179.82 | 16076.84 | 1.40% |
| 100 | 2271870 | 2285717 | 2277452 | 2283928 | 2286718 | 2289509 | 2262300 | 2275090 | 2267881 | 2290672 | 2283462 | 2279509.00 | 9293.81 | 0.41% |

**Table S5 Comparison of the levels of palladium in the environmental sample in this study with those in selected sites from the literature**

| Sample | Location | Other parameters | Concentration | Ref. |
|---|---|---|---|---|
| Fresh water | Poyang Lake, China | 2020 | 0.65-1.86 $\mu g \cdot L^{-1}$ | This method |
| Seawater | Pacific Ocean | / | 40 $pg \cdot L^{-1}$ | [2] |
| River water | Rhein, Schwarzbach, Germany | / | 0.0004 $\mu g \cdot L^{-1}$ | [3] |
| Manganese nodules | deep-sea | / | 3.7-11.4 $\mu g \cdot kg^{-1}$ | [4] |
| Sediment | Molndal river, Goteborg | 1998 | 13.9 $\mu g \cdot kg^{-1}$ | [5] |
| Surface sediments | Boston Harbor | 1987, 1993, 1996 | 19.93; 3.24; 4.22 $\mu g \cdot kg^{-1}$ | [6] |
| River sediment | Molndal river, Sweden | 1999 | 38.7 $\mu g \cdot kg^{-1}$ | [7] |
| Snow | Greenland, the Alps | remote areas | 0.01-16.9 $ng \cdot kg^{-1}$ | [8, 9] |
| Ice, Snow | Mont Blanc | remote areas | 0.0005-0.01 $\mu g \cdot kg^{-1}$ | [10] |
| Urban river | Goteborg, Sweden | near a heavy traffic car park | 0.0102 $\mu g \cdot kg^{-1}$ | [11] |

*1 ppb = 1 $\mu g \cdot L^{-1}$ = 1 $\mu g \cdot kg^{-1}$

**Table S6. the ionization energy, proton affinity energy, and electron affinity energy of various main substances[12].**

| Formula | Ionization Energy (IE)/eV | Proton Affinity (PA)/kJ•mol$^{-1}$ | Electron Affinity (EA)/eV |
|---|---|---|---|
| O | 13.62 | 485.20 | 1.439157 ± 0.000004 |
| $O_2$ | 12.07 | 421.00 | 0.4480 ± 0.0060 |
| $O_3$ | 12.53 | 625.50 | 2.1030 ± 0.0040 |
| OH | / | 593.20 | 1.82767 |
| $H_2O$ | 12.62 | 691.00 | / |
| N | 14.53 | 342.20 | / |
| $N_2$ | 15.58 | 493.80 | / |
| NO | 9.26 | 531.80 | 9.26438 ± 0.00005 |
| $NO_2$ | 9.59 | 591.00 | 2.2730 ± 0.0050 |
| Ar | 15.78 | 369.20 | / |

Note: Energy(Ar*)= E(Ar*)=11.55-14.58eV[13],E($Ar^+$)=15.78eV[14],E($Ar_2^+$)= 14 eV[14].

**Table S7. A list of reactions and the rate constants.**

| Index | Reaction | Rate constant[a] | Ref. | Note |
|---|---|---|---|---|
| (R1) | $e_{(h)} + Ar \rightarrow Ar^+ + 2e_{(l)}$ | $2.3\times10^{-14}(T_e[eV])^{-4.5}\exp(-15.76/(T_e[eV]))$ | 15, 16 | / |
| (R2) | $2e_{(h)} + Ar^+ \rightarrow Ar^* + e$ | $8.75\times10^{-39}(T_e[eV])^{-4.5}$ | 16 | / |
| (R3) | $Ar^* + O_2 \rightarrow Ar^* + 2O$ | (*E/N*) | 17 | $E(Ar^*)>IE(O_2)$ |
| (R4) | $e_{(h)} + N_2 \rightarrow e_{(l)} + 2N$ | $2.0\times10^{-11}$ | 18 | $E(e_{(h)})>IE(N_2)$ =15.58 eV |
| (R5) | $e_{(h)} + O_2 \rightarrow O + O(^1D) + e_{(l)}$ | $1.82\times10^{-14}\varepsilon^{-0.13}\exp(-10.7/\varepsilon)$ | b | $IE(e_{(h)})>IE(O_2)$ |
| (R6) | $N + O_2 + M \rightarrow NO + O + M$ | (*E/N*) | 19 | / |
| (R7) | $NO + O + O_2 \rightarrow NO_2 + O_2$ | $8.6\times10^{-32}$ | 18 | / |
| (R8) | $e_{(l)} + NO_2 + M \rightarrow NO_2^- + M$ | $1.5\times10^{-42}$ | 18 | / |
| (R9) | $O + 2O_2 \rightarrow O_3 + O_2$ | $6.9\times10^{-34}$ | 18 | / |
| (R10) | $e_{(l)} + O + O_2 \rightarrow O^- + O_2$ | $1.0\times10^{-43}$ | 20 | $EA(O)> EA(O_2)$ =0.43eV |
| (R11) | $e_{(l)} + O_2 \rightarrow O_2^-$ | $9.72\times10^{-15}\varepsilon^{-1.62}\ 10^{(-14.2/\varepsilon)}$ for $\varepsilon>1.1$; $2.78\times10^{-20}$ for $\varepsilon<1.1$ | b | / |
| (R12) | $O_3 + e_{(l)} + M \rightarrow O_3^- + M$ | $1\times10^{-43}$ | 20 | / |
| (R13) | $O^-(O_2^-, O_3^-) + NO_2 \rightarrow O\ (O_2, O_3) +$ | / | 21 | $EA(NO_2)>$ EA(O), $EA(O_2)$, and $EA(O_3)$ |

| | | | | |
|---|---|---|---|---|
| | $NO_2^-$ | | | |
| (R14) | $NO_2^- + O_3 \rightarrow NO_3^- + O_2$ | $1.2\times10^{-10}$ | 22 | / |
| (R15) | $e_{(h)} + N_2 \rightarrow 2e_{(l)} + N_2^+$ | $1\times10^{-16}\varepsilon^{1.90}\exp(-14.6/\varepsilon)$ | 20 | $E(e_{(h)})>IE(N_2)>E(Ar^*)$ |
| (R16) | $N_2^+ + H_2O \rightarrow N_2 + H_2O^+$ | $1.8\times10^{-9}$ | 23 | / |
| (R17) | $N_2^+ + NO \rightarrow NO^+ + N_2$ | $3.9\times10^{-10}$ | 23 | / |
| (R18) | $H_2O^+ + nH_2O \rightarrow [H_2O+nH_2O]^+$ | / | 24 | / |
| (R19) | $[H_2O+H_2O]^+ + hv \rightarrow H_3O^+ + OH + e_{(l)}$ | / | 24 | / |
| (R20) | $H_3O^+ + H_2O \rightarrow H_3O^+(H_2O)$ | $3.2\times10^{-27}$ | 23 | / |
| (R21) | $H_3O^+(H_2O)+ H_2O \rightarrow H_3O^+(H_2O)_2$ | $7.4\times10^{-27}$ | 23 | / |
| (R22) | $H_3O^+(H_2O)_2 + H_2O \rightarrow H_3O^+(H_2O)_3$ | $2.5\times10^{-27}$ | 23 | / |

[a] $\varepsilon$ is means electron energy in (eV). Te(=$2e\varepsilon/3k_b$, where $e$ is electron charge and $k_b$ is Boltzmann constant). The unit of reaction rate constant is ($s^{-1}$), ($m^3\ s^{-1}$), or ($m^6\ s^{-1}$).

[b] Rate constant is calculated by solving electron Boltzmann equation[25] in humid air (79% $N_2$, 20% $O_2$, and 1% $H_2O$) at 300 K, M being a third body (Ar, $N_2$, $O_2$ or $H_2O$).

$e_{(h)}$: high-energy electrons, $e_{(l)}$: low-energy electrons, IE: Ionization Energy, EA: electron affinity.

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