Supplementary Information

Intact living-cell electrolaunching ionization mass spectrometry for single-cell metabolomics

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1. Experimental Section

**Cell lines, reagents and materials.** A549, HEK-293, KB, B104, and CPXTNA-2 cells were obtained from the Cell Resource Center of the Institute of Basic Medical Sciences, Chinese Academy of Medical Sciences. Dulbecco’s modified Eagle medium (DMEM), trypsin-ethylenediaminetetraacetic acid (0.25%, trypsin-EDTA), penicillin-streptomycin (100 U·mL$^{-1}$), dimethyl sulfoxide (99.5%, DMSO), fetal bovine serum (FBS), and phosphate-buffered saline (PBS) were purchased from Thermo Fisher Gibco. DNase I and collagenase D were purchased from R&D Novus Tocris MerckMillipore Inc. ACK lysis buffer was purchased from Gen-View Scientific Inc. DiO [DiOC18(3), a green fluorescent probe for the cell membrane] was purchased from Shanghai Yesen Biotechnology Co. Ltd. Liposomes were donated by FluidicLab (https://www.fluidiclab.com/). All other reagents were purchased from Thermo Fisher Scientific. Fused silica capillaries were purchased from Yongnian Ruifeng Chromatographic Device Co. The Minute$^TM$ plasma membrane protein isolation kit SM-005 was acquired from Invent Biotechnologies, Inc. The long-distance microscope objective lens (50×, 0.42 NA) was manufactured by Mitutoyo. The high-performance, high-speed camera (MEMRECAM ACS-3) was manufactured by NAC Image Technology Inc.

**Fabrication of narrow-bore capillaries.** A 30-cm-long capillary was cut, and one end was etched using the wet etching protocols established previously by our research group to obtain a tip$^{[1,2]}$. Then, the capillary tip was stored in an airtight, dust-free environment for future use.

**Preparation of cell suspensions.** Cells were trypsinized using trypsin-EDTA (0.25%) when grown to a coverage of 80–90%. The trypsinization process was terminated using a fresh culture medium. Then, the trypsin-EDTA-containing residual culture medium was removed by centrifugation (1200 rpm, 3 min), and the obtained cells were resuspended in a DMEM culture medium. Appropriate volumes of cell suspensions were centrifuged at 1200 rpm for 3 min to remove the culture medium and cleaned with 150 mmol/L ammonium formate (pH = 7.4). Finally, the cells were resuspended in 40 mmol/L ammonium formate aqueous solution.

**Build an online ILCEI-MS visualization platform.** The platform comprised a self-designed and self-manufactured MS ion source and a microscopic high-speed camera system composed of a long-distance microscope objective lens (50×, 0.42 NA) X and a high-performance, high-speed camera (MEMRECAM ACS-3). The operation of the ILCEI-MS system was visually recorded using this platform.

**Numerical simulation of hydrodynamics in cell motion process at the exit of the narrow capillary emitter with a constant-inner-diameter**

**Model settings.** To simulate the flow of particles in a multiphase system flow, the Eulerian model was used along with the dynamic mesh method for the dynamic simulation of particle motion. A velocity distribution diagram of the particle at the exit of the emitter was obtained. The Dynamic Mesh Zones software was used for the calculation.
(2) **Border conditions.** The liquid phase system is comprised of water. The flow rate was 1 μL/min, and the I.D.s of the emitters were 16, 50, and 100 μm. At the pressure exit, a 15-μm-diameter rigid particle with a density of 1552 kg/m³, the same as the cell density, was present. No voltage was applied to the simulation system. Opening the gravity tab and a comprehensive motion trajectory was obtained. The changes in the cell’s exit velocity and shear stress received on the cell surface were simulated by computer with increasing capillary diameter.

**Verification of cell integrity using DiO.** A549 cells in the logarithmic growth phase were collected, the medium was removed, and the cells were rinsed with PBS 3 times. A total of 5 mL of 10 μmol/L DiO working solution (dissolved in DMEM supplemented with 10% FBS) was added to the culture flask, which was then incubated at 37°C for 15 min, rinsed with PBS 3 times, and trypsinized to prepare a cell suspension. These cells were injected using ILCEI-MS and collected at the ion inlet of the mass spectrometer. Then, their morphology was characterized by a microscopic imaging method.

**Verification of cell viability using CCK8.** A549 cells were selected after subculture for 2 days for the experiment. A549 cells that passed the ILCEI-MS sampling device in front of the ion inlet of the mass spectrometer were selected as the experimental group (using a centrifuge tube containing culture medium to receive the cells). The cells that had undergone the ILCEI-MS sample preparation process were collected as the control group (the cells were immediately centrifuged and resuspended in the medium after the sample preparation process was completed), and the cells without any treatment were used as the blank group. Next, 5000 cells/well were inoculated on a 96-well culture plate. Each sample was prepared with triplicate wells, to which 10 μL of the CCK8 reaction solution was directly added after inoculation, and the cells were incubated for 30 min at 37 °C in the dark. A microplate reader (SpectraMax M4, AD, USA) was used to measure the absorbance at a wavelength of 450 nm.

**Preparation of cell lysis solution.** The cell suspension (1 mL) with a density of 1×10⁷ cells/mL was centrifuged at 1000 rpm for 5 min at room temperature. After the supernatant was removed, the cells were resuspended in 200 μL of 80% (v/v) methanol aqueous solution at -80°C and sonicated in an ice bath for 5 min. After incubating at -20°C for 30 min, the solution was sonicated in an ice bath for 5 min, followed by centrifugation for 20 min (4°C, 17,000 g). Finally, the supernatant was taken for MS detection.

**Establishment of mouse tumor-bearing models of metastatic lung cancer.** A single-cell suspension with a density of 1×10⁷ cells/mL was prepared after the A549 cell culture. Nine C57/BL6 male mice aged 6–8 weeks were randomly divided into an experimental group (five mice) and a control group (four mice). The mice were fixed in a mouse fixator, and the tails were wiped with a 75% alcohol cotton ball to disinfect and dilate the blood vessels; the experimental group and the control group were injected with 0.10 mL cell suspension and physiological saline, respectively. The flow rate was controlled during cell injection to prevent embolism. Mouse rearing and experiments were carried out in an SPF laboratory animal room for 20 days.

**Preparation of single-cell suspension of mouse tissues.** Preparation of Liberase/DNase digestive
solution: The required amount of digestive solution was prepared according to the ratio of 965 μL of 1640 basal medium, 25 μL of 40× collagenase D and 10 μL of 100× DNase I per mL. Mice were killed by cervical dislocation, and their lung, liver and heart organs were harvested. Digestive juice was injected into the tissues by the perfusion method. The tissues were then completely immersed in digestive juice and incubated at 37°C for 30–45 min. The tissue was placed on a 40 μm filter and gently ground to isolate as many tissue cells as possible. The cells were rinsed several times with PBS/EDTA solution until all isolated cells were collected. After centrifugation at 1000 rpm for 5 min, the supernatant was discarded. ACK lysis buffer was added to the cell precipitate at a volume 3-5 times that of the cells, and the cells were gently resuspended. The red blood cells were lysed at room temperature for 2–3 min and centrifuged at 1000 rpm for 5 min, and the supernatant was removed. The appropriate amount of PBS was used to wash the cells twice, and the cells were detected using ILCEI-MS.

It should be noted that to prevent residual cell clumps in the cell suspension from affecting the detection; the cells were filtered again with a 40 μm filter before mass spectrometric detection.

We complied with all relevant ethical regulations, and the animal experiment was approved by the Ethics Committee of Beijing University of Technology, China. The approval number is HS202103001.

Quality control during single-cell detection. (1) We tested a blank sample (cell-free mobile phase) under the same experimental conditions before each cell sample test. Quality control of the detection system was achieved by controlling the intensity and stability of the ion signal in the blank sample, which was seen as the background and was subtracted from the cell detection data during subsequent data processing. (2) We decrease the cell density in the injection capillary by reducing the cell density in the cell suspension; In addition, we use the narrow capillary (the I.D. was slightly smaller than the cell’s diameter) for single-cell separation and injection. Due to the confinement effect of narrow inner diameter capillaries, single-cells were adequately isolated with the expanded distance between single-cells in the injection capillary. Finally, we achieved suitable injection flow rates by controlling the injection pressure. Through the above three points, the time interval between single-cells involved in ionization was optimized, which ensured that multiple cell ionization does not occur within one scan time of the mass spectrometer. In order to further improve the controllability of the experiments, we constructed the ILCEI-MS on-line visualization platform, via a large number of on-line visualization characterization data to prove that the electro-launching images of multiple single-cells match the detection signals of mass spectrometry. Based on the above efforts, it is basically guaranteed that each signal peak in total ion chromatogram (TIC) from the ILCEI-MS system corresponds to a single-cell; they are not produced by the superposition of signals from multiple cells.

Single-cell mass spectrometry. All mass spectral data were acquired on an LTQ Orbitrap XL mass spectrometer (Thermo Scientific, San Jose, CA, USA). The MS parameters were set as follows: The voltage was controlled at ~1.4 kV, and the spray current was controlled at 0.2–0.7 μA, although slight differences were observed according to specific experimental conditions. The following conditions were used: inlet temperature, 350 °C; resolution, 30000; maximum injection time, 50 ms; AGC target, $1 \times 10^5$; and scanning range, $m/z$ 100–1000 or 300–1000. The MS-ddMS$^2$ parameters were set as follows: voltage, 2.3 kV; ion inlet temperature, 350°C; resolution, 30000;
maximum injection time, 500 ms; AGC target, $2 \times 10^5$; and scanning range, $m/z$ 100–1000. In vitro cultured cells were analyzed using 15 μm inner diameter (I.D.) capillaries. The single-cells obtained from the liver and heart were larger in volume through microscopic observation, therefore, in this part of the experiment, a 25 μm I.D. capillary was used to complete the separation, transport and electroemission ionization mass spectrometry detection of the single-cells.

**Data analysis and metabolite identification.** A single-cell signal peak must be selected with an intensity greater than 10% of the median intensity of the top 30 peaks in the TIC. Raw data processing was performed on a metabolite data analysis platform developed by our group [3]. The source code of the MATLAB software used is https://github.com/HansenZhao/PeakPicker. The S/N ratio calculation method of single-cell peaks in TIC of ILCEI-MS that refers to the Wei's work [4]. The S/N ratio of single-cell peaks to evaluate the detection sensitivity of ILCEI-MS. Ions of mass spectra with an S/N ratio of >5 and an occurrence frequency of >10% in all cell events were considered as detected signals. Lipid metabolites are the major constituents of cell membranes, and hence, they could be used as a reliable reference for the differentiation of cell profiles and the electrolaunching ionization of sensitive substances. Nonlinear reduction of complex metabolic data sets using a machine learning method is based on t-SNE, which can qualitatively discriminate subtle groups and visualize the difference in the two-dimensional plane. A scatter plot displays the statistics of the difference in the content of a certain metabolite in all the single-cells among each group of samples.

Single-cell metabolites were identified by matching ddMS$^2$ spectra obtained from population cells with the standard spectra using mzCloud (https://www.mzcloud.org/), Human Metabolome Database 5.0 (HMDB) (http://www.hmdb.ca/) and MassBank Database 2.1.8 (http://www.massbank.jp/Index). More information about single-cell metabolite matching could be obtained by referring to various databases available online, including the Kyoto Encyclopedia of Genes and Genomes (KEGG) (https://www.genome.jp/kegg/). Metabolic pathway analysis was performed on MetaboAnalyst 5.0 (http://www.metaboanalyst.ca/).
2. Supplementary Figures

Figure S1. Comparison of single-cell separation effects with different I.D. (a) 16 μm I.D. capillary, (b) 50 μm I.D. capillary.

Observations on the transport of cell suspensions (A549 cells, diameter ~20 μm) in capillaries with different I.D.s show that single intact cells exist independently and are separated completely in a 16 μm I.D. capillary, whereas obvious cell stacking occurs in a 50 μm I.D. capillary, leading to poor separation. This is due to the more obvious spatial confinement of the narrow-bore capillary. These results suggest that a narrow capillary with an I.D. close to the diameter of a cell is a prerequisite for the separation of single-cells.
Figure S2. Effect of the presence or absence of a tip on the detection of KB cells by mass spectrometry. (a) The photo of two kinds of emitters; (b) Total ion chromatogram (TIC) of MS by capillary emitter I with a tip (the end outer diameter (O.D.) of 20 μm); (c) TIC of MS by capillary emitter II without a tip (the end O.D. of 340 μm).

The results show that a single-cell MS signal cannot be generated by a capillary without a tip, whereas an intense signal can be generated using a capillary with a tip. This result confirms that a capillary wall thinned by etching is necessary to generate a single-cell MS detection signal.
Figure S3. Comparison of the durability of the pulled and the etched tips. (a) Microscopic image of the emitters before infusion of cell suspension; (b) Microscopic image of the emitters after continuous infusion of cell suspension for 3 minutes.

The pulled tip (I) was prepared by a puller and broken under a microscope to obtain an open I.D. of ~16 μm. The constant-I.D. tip (II) was fabricated by the method developed by our group1-2; the I.D. of the tip was 16 μm. A549 cell suspension (the cell density is $5 \times 10^5$ mL) was used for the experiment, and the flow rate was 1 μL/min. After running for 3 minutes, emitter I became plugged (see the red circle), whereas emitter II remained unobstructed. This experimental result confirmed that the tip with a constant-I.D. has a low risk of fluidic clogging, enabling a stable flow rate and long operating life, which are important for high-throughput detection of complex biological samples.
Figure S4. The photo of the ILCEI-MS on-line visualization platform. The platform comprised a self-designed and self-built ILCEI-MS ion source and a microscopic high-speed camera system composed of a long-distance microscope objective lens (50×, 0.42 NA, Mitutoyo, Japan) and a high-performance, high-speed camera (MEMRECAM ACS-3, NAC, Japan). The electrolaunching process of the tip during single-cell detection was visually recorded using this platform.

Figure S5. Single-cell participated in the electrolaunching process and the data collected synchronously by mass spectrometry.
Figure S6. Mass spectrometry of cell membrane debris sample and intact living cell sample.  
(a) Comparison of TIC between the cell membrane debris sample (black line) and the intact living cell sample (red line); (b) Comparison of the mass spectra between the cell membrane debris sample (top) and the intact living cell sample (bottom). We used a Minute™ plasma membrane protein isolation kit to extract cell membranes in the bulk solution and mixed them with 40 mmol/L ammonium formate aqueous solution to prepare a sample of cell membrane debris. Mass spectrometry detection was performed under the same conditions for the cell suspension, and the difference of the mass spectrometric signals of the two samples was compared. It can be seen from a that there is no obvious spike in the TIC of the cell membrane debris sample, demonstrating that the ionization of cell membrane debris cannot cause the violent fluctuations of mass spectrometry signals like intact cells. As shown in b, the peak shape and ion intensity of the mass spectrum of the cell membrane debris sample are very different from the mass spectrometry signal of intact living single-cells. The ion intensity of the cell membrane debris sample is one order of magnitude lower than that of intact living single-cells. Even if large cell debris occasionally causes a signal peak similar to the signal peak appearing at 0.09 min in the TIC of the cell membrane debris sample. We set a threshold for single-cell data extraction, that is, only extracting peaks with a signal-to-noise ratio of more than 3.0 in the MS TIC. The extraction will further remove the influence of cell debris on the analysis results, ensuring that our subsequent analysis data come from intact single-cells.
Figure S7. MS’s TIC of the perfusion injection of three kinds of samples. From top to bottom are 40 mmol/L ammonium formate aqueous solution (black line), the cell lysate of lung cancer cells (red line, the collected supernatant after the centrifugation at 17,000 g), the liposome suspension with an average diameter of 200 nm (green line). There is no obvious spike in TICs of the three kinds of samples.

Figure S8. The relative standard deviation (RSD) of 1000 scans of the mass spectrum signal. (a) 40 mmol/L ammonium formate aqueous solution; (b) Signal of the cell lysate of lung cancer cells; (c) Signal of the liposome suspension with an average diameter of 200 nm. The red dotted line represents the average RSD. The RSD data come from the built-in function of the LTQ-Orbitrap XL mass spectrometer, which is used to evaluate the stability of the ion source before the instrument is calibrated. Technical specifications require that the average RSD value of 100 scans is less than 15% for mass spectrometer calibration. We collected 1000 scans, and the average RSD value is less than 7%, reaching the signal stability level that can be used for mass spectrometer calibration, which proves that the system stability of this method is reliable.
Figure S9. Comparison of cells status before and after electrolaunching. (a) Cells suspended in 40 mmol/L ammonium formate aqueous solution before electrolaunching; (b) Cells collected at the inlet of the mass spectrometer (bright-field imaging); (c) Cells collected at the inlet of the mass spectrometer (fluorescence imaging, by DiO cell membrane green fluorescent probe stained). It can be seen that all the fluorescence signals come from the intact cells, and no luminous cell debris is seen. It means that most of the cells still maintained a complete structure.

Figure S10. Cell viability verification by CCK8. CG (control group): The cells that underwent the sample preparation process from ILCEI-MS. EG (experimental group): The cells collected near the mass spectrometry ion entrance. Cells without any treatment were used as the blank group, of which cell viability is considered to be 100%. The data show that most cells still maintained an alive status.
Figure S11. Comparison of the mass spectrometry injection status of different solutions under the same conditions. (a1, b1, and c1) High-speed camera screenshots of the liquid cones. (a2, b2, and c2) High-speed screenshots of the plume morphology. (a1, a2) The electrospray status with a methanol aqueous solution (70% v/v); (b1, b2) The electrospray status with an aqueous solution; (c1, c2) The electrolaunching status with a suspension of A549 cells suspension. A constant-I.D. emitter of 16/20 μm (I.D./O.D.) with a thin-wall tip was used; the injection current was approximately 0.3 μA to ensure that the initial droplets carried an equal amount of charge per unit time, and the distance between the emitter and ion inlet was 3 mm.

To further investigate the ionization characteristic of ILCEI, we observed the plume morphology. The three liquids produced hydraulic cones of different shapes at the same launching/spray current (approximately 30 μA to ensure that the initial droplets carried an equal amount of charge per unit time); this phenomenon intuitively proves that the plume morphology of the three liquids is different. But the more important difference was that the initial droplets of the three liquids produced diverse fragmentation in the air flight zone (a2, b2 and c2). According to the Rayleigh limit theory [5], the net charge $Q_R$ of a charged droplet should satisfy the equation:

$$Q_R = 8\pi(\varepsilon_0\gamma r_0^3)^{1/2}$$

where $\varepsilon_0$ is the vacuum permittivity, $\gamma$ is the surface tension, and $r_0$ is the radius of the droplet. With the same net charge, droplets formed with a high proportion of methanol solution had a low surface
tension and were more likely to reach the Rayleigh limit and split. Therefore, a_2 spray plume was larger than b_2. The results shown in b_2 and c_2 were obtained under the same liquid mobile phase conditions and should, in theory, have roughly the same liquid surface tension. However, the A549 cell suspension exhibited less droplet splitting (c_2) because of the presence of whole cells in the initial droplets of the cell suspension for electrolaunching, which hindered droplet shrinkage. The maintained large surface area avoided reaching the Rayleigh limit and thus prevented the droplets from splitting. Because droplet splitting was accompanied by a random distribution of net charge, decreased droplet splitting would result in more charge remaining on the surface of the mother droplet. In addition, very few mobile phases mean very few impurity molecules in the mother liquid droplets. Thus, cell components retained in the mother droplet will have a greater chance of gaining charge and thus achieve more adequate ionization. All cell components enter the entrance of the mass spectrometer, thus avoiding the loss of the sample in the atmospheric path and improving the sample collection rate. For a homogeneous solution, the sample molecules are always accompanied by a large number of solvent molecules during the multiple splitting process of charged droplets, so there is fierce competition for charges between a large number of impurities and a small number of samples. Coupled with the dilution and annihilation of sample ions in the atmosphere, and the very low ion acquisition ratio at the MS inlet, these have led to a serious decrease in the detection sensitivity of the sample.

**Figure S12. Violin plots of ions per cell in ILCEI-MS dataset of living A549 cells.** Each dot represents a single-cell. (a) 306 living A549 cells were detected in positive ion mode, and the average detected coverage is about 800 ions/cell; (b) 376 living A549 cells were detected in negative ion mode, and the average detected coverage is about 745 ions/cell.
Figure S13. Single-cell mass spectra of five different types of cells (A549, KB, HEK-293, B104, and CTXTNA-2).
Figure S14. Photographs of the liver, heart, and lung (from left to right) of the dissected mice. (a) Healthy mouse; (b) Lung cancer mouse. The lung masses (the white dotted circle indicated by the arrow) of the lung cancer mouse were obvious, and the liver was enlarged and hard, indicating that the mouse had shown obvious symptoms.

Figure S15. The cell suspensions of visceral digestion from a healthy mouse. Suspensions of heart, liver, and lung cells are shown from left to right successively.

Figure S16. The cell suspensions of visceral digestion from a lung cancer mouse. Suspensions of heart, liver, and lung cells are shown from left to right successively.

It was found that the single-cells obtained from the heart and liver were larger in volume through microscopic observation; therefore, in this part of the experiment, a 25 μm I.D. capillary was used to complete the separation, transport, and electron-emission ionization mass spectrometry detection of the single-cells.
Figure S17. ILCEI-MS data of cell suspension digested from the heart of a healthy mouse. From top to bottom are TIC and EIC, respectively. EIC extracted based on m/z 806.40–806.60, which acts as the reference of single-cell data.

Figure S18. ILCEI-MS data of cell suspension digested from the liver of a healthy mouse. From top to bottom are TIC and EIC, respectively. EIC extracted based on m/z 874.60–874.90, which acts as the reference of single-cell data.
Figure S19. ILCEI-MS data of cell suspension digested from the lung of a healthy mouse. From top to bottom are TIC and EIC, respectively. EIC extracted based on $m/z$ 760.40–760.70, which acts as the reference of single-cell data.

Figure S20. ILCEI-MS data of cell suspension digested from the heart of a lung cancer mouse. From top to bottom are TIC and EIC, respectively. EIC extracted based on $m/z$ 806.40–806.60, which acts as the reference of single-cell data.
Figure S21. ILCEI-MS data of cell suspension digested from the liver of a lung cancer mouse. From top to bottom are TIC and EIC, respectively. EIC extracted based on m/z 874.60–874.90, which acts as the reference of single-cell data.

Figure S22. ILCEI-MS data of cell suspension digested from the lung of a lung cancer mouse. From top to bottom are TIC and EIC, respectively. EIC extracted based on m/z 760.40–760.70, which acts as the reference of single-cell data.
Figure S23. Violin plots of ions per cell in ILCEI-MS dataset of lung tissue cells of lung cancer model mice and healthy mice. Each dot represents a single-cell. (a) 1438 cells were detected from the lung tissue of lung cancer model mice, and the average detected coverage is about 773 ions/cell; (b) 930 cells were detected from the lung tissue of healthy mice, and the average detected coverage is about 787 ions/cell.
3. Supplementary Videos

Video S1. At a shooting speed of 10000 frames/s and a magnification of 500x, the motion of an A549 cell in a 16 μm I.D. capillary.

Individual A549 cells can be seen in the narrow capillary being squeezed into an oval shape and moving towards the capillary outlet. This vivid scene strongly proves the excellent single-cell separation and transportation capacity of the narrow-bore capillary.

Video S2. At a shooting speed of 10000 frames/s and a magnification of 200x, the motion of multiple A549 single-cells moves independently and orderly in a 16 μm I.D. capillary.

It further fully demonstrates the excellent single-cell separation and transportation capability of the narrow-bore capillary. The scale bar in the video is 100 μm.

Video S3. At a shooting speed of 50000 frames/s and a magnification of 500x, the whole A549 single-cell droplets producing process by narrow capillary emitter with constant-I.D. throughout the column.

In negative ion mode, the electrolaunching voltage is 1.36 kV, the I.D./O.D. of the emitter is 16/20 μm, the liquid phase is 40 mmol/L ammonium formate aqueous solution, and the flow rate is 1 μL/min. The video material clearly shows the formation of single-cell droplets. We can clearly see that most of the volume of the droplets is occupied by an integrate single A549 cell, and only an ultra-thin layer liquid film on the periphery is composed of the liquid phase. This fully proves the conclusion that the single-cell droplet hardly introduces the sample dilution.

Video S4. Video recording of the working scene of ILCEI-MS characterized by high-speed camera online visualization.

It can be seen that the high-speed camera and mass spectrometry data acquisition are synchronized according to the video.

Video S5. The integrated video of high-speed camera acquired in supplementary video S4 and synchronous acquired mass spectrometry data.

It can be found that the interval generated by three successive single-cell droplets and the interval of retention time of three independent signal peaks collected by the mass spectrum are perfectly matched. Those prove that each signal peak in the total ion chromatograms obtained by ILCEI-MS is from one single-cell.

Video S6. At a shooting speed of 50000 frames/s and a magnification of 200x, the integrated video of three videos of single-cell droplets generating, flying in the atmosphere, and entering into the MS inlet.

From the video, we can clearly see that pulsed droplets with uniform diameter are produced by the novel single-cell droplet electrolaunching mode and these droplets do not split obviously during the flight in the atmosphere and enter into the MS inlet in the form of an intact structure, which vividly demonstrates features of the new electrolaunching technology proposed in this work. It also strongly proves our conclusion that an in-source ionization occurs by single-cell droplets. The scale
Video S7. Comparison of electrolaunching / spray images of cell suspensions by using constant-I.D. narrow capillary emitters with different outer diameters under the same voltage parameter.

By comparison of emitters with 16 μm I.D. and different outer diameters, we find that the emitter with 20 μm O.D. can produce single-cell droplets with almost zero dilution, while the cells are stuck in the emitter cone of the 80 μm O.D. emitter stays and are difficult to eject. This data illustrates that the single-cell electrolaunching mode proposed in this work needs to be based on thin-wall emitters. The scale bar in the video is 100 μm.

Video S8. The difference between the ionization states of ILCEI and ESI.

The video file includes three columns. From left to right are event A of 40 mmol/L ammonium formate in methanol (v/v: 70/30) solution, event B of 40 mmol/L ammonium formate solution, and event C of A549 cells suspended in 40 mmol/L ammonium formate aqueous solution. Each event contains two kinds of characterization results of the same scene captured by a high-speed microscope camera (top) and a commercial Nano-ESI camera under laser irradiation (bottom). From the video, it can be seen that cell suspension C has the shortest electrolaunching cone length; the formed droplets fly through the atmosphere into the ion transfer tube along a very thin straight line. The difference between B and C illustrates the difference between single-cell droplets and ordinary charged droplets in the ionization process. That is, single-cell droplets do not undergo a droplet splitting in the atmosphere (charged droplet splitting is a prerequisite for ionization in ESI theory). This set of data intuitively shows that the ILCEI is indeed a new mode different from the ESI, and also supports the inference that single-cell droplets are ionized within the inlet of the mass spectrometer.
4. Supplementary Table.

**Table S1.** The velocity of the single-cell and average shear stress of wall surface on the single-cell at the outlet of capillary emitters with different I.D..

| Emitter I.D. (μm) | Exit velocity (m/s) | Average shear stress (Pa) |
|-------------------|---------------------|--------------------------|
| 16                | 0.083               | 0.04                     |
| 50                | 0.0085              | 0.0006                   |
| 100               | 0.00212             | 0.00016                  |
Table S2. 368 cellular metabolites were identified for A549 cells, 249 and 119 in positive and negative ion modes, respectively (scan range m/z 100–1000). For the detection of metabolite extract from population cells, ddMS\(^2\) mode with higher energy collisional dissociation (HCD) was used. The metabolites extracted from population cells were initially identified by searching mzCloud Advanced Mass Spectral Database (https://www.mzcloud.org/) with MS/MS fragments. Selected top five candidates were further verified through matching the Human Metabolome Database 5.0 (HMDB) (http://www.hmdb.ca/) and MassBank Database 2.1.8 (http://www.massbank.jp/Index). The metabolites with the same molecular weight could not be separated by existing methods. Therefore, the metabolite would remain if characteristic product ions were contained in the MS/MS fragments. If the intensities of all characteristic product ions of the metabolite were less than 10%, the metabolite would be ignored. Non-endogenous components are not excluded from the list.

| NO. | Metabolites               | Formula | m/z     | Mass   | Ions        | CAS_ID     | HMDB_ID       | KEGG_ID | MS/MS fragments |
|-----|---------------------------|---------|---------|--------|-------------|------------|---------------|---------|-----------------|
| 1   | 2-Piperidinone            | C\(_5\)H\(_9\)NO | 100.0750 | 99.1311 | M+H         | 675-20-7   | HMDB0011749  | —       | 81.68;71.80     |
| 2   | 2,3-Dihydrobenzofuran     | C\(_8\)H\(_8\)O | 103.0500 | 120.0575 | M+H-H\(_2\)O | 496-16-2   | HMDB0013815  | —       | 77.0382;53.0382;51.801 |
| 3   | Pentanoic acid            | C\(_5\)H\(_10\)O\(_2\) | 103.0750 | 102.0681 | M+H         | 109-52-4   | HMDB0000892  | C00803  | 50.666;70.9794;54.6772 |
| 4   | N-Methylalanine           | C\(_4\)H\(_9\)NO | 104.0700 | 103.0633 | M+H         | 3913-67-5  | HMDB0094692  | —       | 72.3887         |
| 5   | Gamma-Butyrolactone       | C\(_4\)H\(_6\)O\(_2\) | 104.0700 | 86.0368  | M+NH\(_4\)  | 96-48-0    | HMDB0000549 | C01770  | 66.0566;86.096   |
| 6   | 4-Aminobutanoic acid      | C\(_4\)H\(_9\)NO\(_2\) | 104.0700 | 103.0633 | M+H         | —          | HMDB0000112  | C00334  | 84.0792;86.0961  |
| 7   | Choline                   | C\(_3\)H\(_14\)NO | 104.1071 | 104.1075 | M+         | 62-49-7    | HMDB00097    | C00114  | 60.1            |
| 8   | 2-Phenylethanol           | C\(_8\)H\(_10\)O | 105.0540 | 122.0732 | M+H-H\(_2\)O | 1960/12/8  | HMDB0033944  | C05853  | 79.0538;77.0382;66.0567 |
| 9   | Ethylbenzene              | C\(_8\)H\(_10\) | 107.0856 | 106.0777 | M+H         | 100-41-4   | HMDB59905    | C07111  | 75.0229;91.0542  |
| 10  | O-Toluidine               | C\(_6\)H\(_8\)N | 108.0441 | 107.1531 | M+H         | 95-53-4    | HMDB0041965  | C14403  | 107.83;92.76;91.03 |
| 11  | 2,5-Dimethylpyrazine      | C\(_6\)H\(_12\)N\(_2\) | 109.0764 | 108.1411 | M+H         | 123-32-0   | HMDB0035289  | —       | 80.89;66.81      |
| 12  | Glycerol                  | C\(_3\)H\(_8\)O\(_3\) | 110.0816 | 92.0473  | M+NH\(_4\)  | 56-81-5    | HMDB00131    | C00116  | 75.0441         |
|    | Name                                      | Chemical Formula | m/z Values | Charge | HMDB ID | Purity Values |
|----|-------------------------------------------|------------------|------------|--------|----------|---------------|
| 13 | 5-Methyl-2-furancarboxaldehyde            | C₆H₆O₂           | 110.0441   | M+H   | 620-02-0 | 83.0491;93.0335 |
| 14 | L-(Aminomethyl)phosphonic acid           | CH₆NO₃P         | 112.0010   | M+H   | 1066-51-9 | 78.4077       |
| 15 | Dimethyl sulfone                          | C₃H₆O₂S         | 112.0420   | M+NH₄ | 97-71-0  | 64.0805;78.4075;70.0649 |
| 16 | Cytosine                                  | C₄H₅NO₃         | 111.0427   | M+H   | 71-30-7  | 69.0453;95.0245 |
| 17 | Methyl-L-proline                          | C₆H₁₁NO₂        | 112.0750   | M+H-H₂O | 6078-09-1 | 84.0805;70.0649 |
| 18 | Pipelic acid                              | C₄H₇NO₂         | 130.0483   | M+H   | 129.1570 | 69.0335       |
| 19 | Epsilon-caprolactam                      | C₆H₁₁NO         | 114.0901   | M+H   | 105-60-2 | 86.0598       |
| 20 | Methylsuccinic acid                       | C₅H₈O₄          | 115.0360   | M+H-H₂O | 498-21-5  | 66.0568       |
| 21 | Cis-Acetylacrylate                        | C₅H₈O₃          | 115.0392   | M+H   | —        | 60.0335       |
| 22 | Proline                                   | C₅H₉NO₂         | 116.0700   | M+H   | 147-85-3 | 70.0647       |
| 23 | 3-Phenylpropanal                          | C₅H₁₀O           | 117.0540   | M+H-H₂O | 104-53-0  | 71.0681;91.0539;66.0568 |
| 24 | Dihydrocarvone                            | C₁₀H₁₆O         | 117.1020   | M+H+2H₂O | 5524-05-0 | 91.0539;66.0568 |
| 25 | Betaine                                   | C₅H₁₃NO₂        | 118.0860   | M+H   | 107-43-7 | 72.0804;92.0572 |
| 26 | Pyrrolidine                               | C₅H₉N           | 118.0860   | M+H   | 71-0735  | 72.0805       |
| 27 | 4-Propylphenol                            | C₅H₁₂O          | 119.0700   | M+H   | 123-75-1 | 91.0539;104.0617 |
| 28 | 3-Hydroxy-3-methylbutanoic acid          | C₂₅H₃₆O₉        | 119.0706   | M+H-H₂O | 645-56-7  | 91.0542       |
| 29 | Pralidoxime                               | C₅H₉N₂O        | 120.0650   | M+H-H₂O | 154-97-2  | 103.0539;91.0539;77.0383 |
| 30 | Homoserine                                | C₄H₉NO₃        | 120.0658   | M+H   | 572-15-1 | 102.091       |
|    |                                           | C₂H₆NO₃        | 256.1390   | 2M+NH₄ | —        | 102.091;88.0754;70.0648 |
| No. | Name                                      | Molecular Formula | m/z Data               | HMDB ID             | Common Name                  | Other Data                   |
|-----|-------------------------------------------|-------------------|------------------------|---------------------|-----------------------------|-----------------------------|
| 31  | 2-Hydroxyphenethylamine                    | C₈H₁₁NO           | 120.0805               | 137.0841            | M+H-H₂O 7568-93-6           | C02735 103.0539;91.0539;77.0382 |
| 32  | Tyramine                                   | C₈H₁₁NO           | 120.0808               | 137.0841            | M+H-H₂O 51-67-2             | C00483 105.0444;91.0539;77.0382 |
| 33  | 2-Hydroxynicotinic acid                    | C₆H₅NO₂           | 122.0270               | 139.0269            | M+H-H₂O 609-71-2            | — 66.0566;92.0571            |
| 34  | Ethylaniline                               | C₈H₁₁N            | 122.0960               | 121.0891            | M+H 103-69-5                | C14455 81.0444;66.0565;72.3884 |
| 35  | Hydroxyurea                                | CH₂N₂O₂           | 123.0300               | 76.0273             | M+HCOO+2H 127-07-1          | C07044 77.0382               |
| 36  | Nicotinamide (Vitamin B3)                 | C₆H₆N₂O           | 123.0440               | 122.0732            | M+H 589-18-4                | C00153 80.0491;105.0444;77.0383 |
| 37  | 4-Methylbenzenemethanol                    | C₈H₁₀O            | 123.0800               | 122.0732            | M+H 589-18-4                | C06757 80.0491;105.0444;77.0383 |
| 38  | Tyrosine                                  | C₄H₆O             | 124.9995               | 86.0368             | M+K 503-64-0                | — 69.0335                   |
| 39  | Pimelic acid                              | C₅H₈N₂O₂          | 125.0590               | 160.0736            | M+H-2H₂O 111-16-0           | C02656 98.9839;80.9733       |
| 40  | 2-Aminoethylphosphonate                   | C₇H₁₂NO₃P         | 126.0160               | 125.0242            | M+H 2041-14-7               | C03557 98.9839;92.9697       |
| 41  | Taurine                                   | C₇H₁₂NO₃S         | 126.0233               | 125.0147            | M+H 107-35-7                | C00047 107.92               |
| 42  | Pyruvate                                  | C₇H₁₅N₂O₂         | 127.0503               | 126.0424            | M+H 65-71-4                 | C00178 109.0402             |
| 43  | 5-Hydroxymethyl-2-furancarboxaldehyde     | C₅H₄O₃            | 127.0520               | 126.1100            | M+H 67-47-0                 | — 109.02;81.01              |
| 44  | Dihydrothymine                            | C₅H₄N₂O₂          | 129.0540               | 128.0586            | M+H 696-04-8                | C00906 112.1117;84.0805     |
| 45  | Lysine                                    | C₆H₁₄N₂O₂         | 129.0910               | 146.1055            | M+H-H₂O 56-87-1             | C00047 84.0805;70.0648      |
| 46  | 5-Oxoproline                              | C₅H₇NO₃           | 130.0490               | 129.0426            | M+H —                      | — 101879 84.0441;113.1151  |
| 47  | Indole-3-carbinol                         | C₅H₆NO            | 130.0490               | 147.0684            | M+H-H₂O 700-06-1            | — 103.0538                 |
| 48  | L-aminocyclopentanecarboxylic acid        | C₆H₁₁NO₂          | 130.0860               | 129.0790            | M+H 52-52-8                 | C03969 85.0837;113.115     |
| 49  | Hydroxyproline                            | C₃H₆NO₃           | 132.0650               | 131.0582            | M+H 13504-85-3              | C01157 86.0961             |
|   | Name                                | Formula       | M+H     | M+HCOO+2H | HMDB ID          | C00 No | M+HCOO+2H 1-6     |
|---|-------------------------------------|---------------|---------|-----------|------------------|--------|------------------|
|50 | Beta-Guanidinopropionic acid        | C₆H₇N₃O₂     | 132.0650| 131.0695  | HMDB0013222      | C03065 | 86.0961;115.054  |
|51 | Acetyl-L-alanine                    | C₅H₉NO₃     | 132.0650| 131.0582  | HMDB0000766      |        | 86.0961;90.0462  |
|52 | 5-Aminolevulinic acid               | C₄H₉N₃O₂     | 149.0930| 131.0582  | HMDB0001149      | C00430 | 86.0961;115.0539;90.0462 |
|53 | Creatine                            | C₄H₇N₃O₂     | 132.0650| 131.0695  | HMDB0000064      | C00500 | 86.0961;115.054;90.0461 |
|54 | 2-Pyrrolidinone                     | C₅H₉NO      | 132.0650| 85.0528   | HMDB0002039      | C11118 | 86.0961          |
|55 | Isoleucine                          | C₆H₁₃NO₂     | 132.1010| 131.0946  |                  |        |                  |
|56 | Piperidine                          | C₅H₁₅N       | 132.1010| 85.0891   | HMDB003401       | C01746 | 86.0961;66.0566  |
|57 | Gamma-Caprolactone                  | C₄H₁₀O₂      | 132.1010| 114.0681  | HMDB0003843      |        | 86.0961;66.0565;115.0539 |
|58 | Delta-Hexalactone                   | C₆H₁₀O₂      | 132.1010| 114.0681  | HMDB0000453      |        | 86.0961;66.0565;115.0539 |
|59 | Leucine                             | C₆H₁₃NO₂     | 132.1017| 131.0941  | HMDB000687       | C00123 | 86.0961;66.0566;115.054 |
|60 | 4-Vinylguaiacol                     | C₈H₁₀O₂      | 133.0490| 150.0681  | HMDB0013744      | C17883 | 91.0539;105.0444 |
|61 | Cinnamaldehyde                      | C₉H₁₂O       | 133.0634| 132.1592  | HMDB0003441      | C00500 | 132.83;114.91;104.80;90.85 |
|62 | Ornithine                           | C₅H₁₂N₂O₂    | 133.0976| 132.0894  | HMDB000214       | C00077 | 115.0534         |
|63 | Ortho-Hydroxyphenylacetic acid      | C₈H₈O₃       | 135.0440| 152.0473  | HMDB000669       | C05852 | 105.0444;77.0382 |
|64 | 4-Hydroxy-3-methylbenzoic acid      | C₆H₈O₃       | 135.0440| 152.0473  | HMDB0004815      | C14103 | 107.0852;91.0539 |
|65 | Cinnamyl alcohol                    | C₉H₁₀O       | 135.0650| 134.0732  | HMDB0029698      | C02394 | 91.0539;105.0695;119.06 |
|66 | 2-Methylacetophenone                | C₆H₁₀O       | 135.0807| 134.0726  | HMDB32386        |        | 93.0699;117.0699 |
|67 | 2,4-Dimethylbenzaldehyde           | C₈H₁₀O       | 135.0825| 134.1751  | HMDB0032142      |        | 107.0855         |
|68 | Piperitone                          | C₁₀H₁₀O      | 135.1010| 152.1201  | HMDB0034975      |        | 109.0102         |
|   | Name                                       | Molecular Formula | M+H or M+H2O     | HMDB ID         | C0000  | Mass Difference |
|---|--------------------------------------------|-------------------|-------------------|-----------------|--------|-----------------|
|69 | Pulegone                                   | C10H10O           | 135.1010          | 89-2-7          | HMDB0035604 | 105.0444, 92.0254, 109.0104 |
|70 | Benzothiazole                              | C6H5NS            | 136.0219          | 95-16-9         | HMDB0032930 | 135.92, 107.87 |
|71 | Acetylarylamine                            | C8H10NO           | 136.0610          | 103-84-4        | HMDB0001250 | 91.0539, 107.0488, 109.0103 |
|72 | Erythro-1,4-lactone                        | C4H4O4            | 136.0610          | 15667-21-7      | HMDB0000349 | 119.0349, 91.0539 |
|73 | Tetrahydro-2-methylthiophen-3-ol           | C4H10OS           | 136.0610          | 149834-43-5     | HMDB0035244 | 119.0349, 91.0539 |
|74 | 2-Phenylacetamide                          | C8H9NO            | 136.0610          | 103-81-1        | HMDB0010715 | 91.0539 |
|75 | Ethyl carbamate                            | C3H7NO2           | 136.0610          | 51-79-6         | HMDB0031219 | 119.0349, 91.0539 |
|76 | 4,6-Diamino-5-formamidopyrimidine          | C6H2N2O           | 136.0750          | 1758-80-1       | HMDB0004816 | 119.0349, 92.024, 109.0104 |
|77 | 2,4-diaminobutyric acid                    | C6H10N2O2         | 136.0960          | 1758-80-1       | HMDB0006284 | 119.0349, 92.024 |
|78 | Amphetamine                                | C9H13N            | 136.0960          | 6960-22-9       | HMDB0014328 | 119.0348, 91.0539 |
|79 | 3-Phenylpropylamine                        | C9H13N            | 136.0960          | 682-22-9        | HMDB0245973 | 119.0349, 91.0539, 107.0488 |
|80 | 4-Fluoroamphetamine                       | C6H2FN            | 136.0960          | 1626-71-7       | HMDB0246424 | 91.0539, 109.0103 |
|81 | 5-Methylnicotinamide                       | C7H8N2O           | 137.0590          | 6960-22-1       | HMDB0013704 | 92.0492, 78.0335, 96.0441 |
|82 | Benzamideoxide                             | C7H8N2O           | 137.0707          | 613-92-3        | HMDB0248971 | 78.0335 |
|83 | 2-Methoxybenzaldehyde                      | C8H8O2            | 137.0707          | 135-02-4        | HMDB0033766 | 94.0648, 92.0492, 78.0335 |
|84 | Phenyl isocyanate                          | C6H6NO            | 137.0707          | 103-71-9        | HMDB0062270 | 94.0648, 92.0492 |
|85 | 2,3-Butanediol                             | C5H10O2           | 137.0708          | 513-85-9        | HMDB0003156 | 92.0491 |
|86 | 2-Aminobenzamide                           | C7H8N2O           | 137.0708          | 88-68-6         | HMDB0033947 | 94.0648, 119.0349 |
|87 | 3-Aminobenzamide                           | C7H8N2O           | 137.0710          | 3544-24-9       | HMDB0245814 | 94.0648, 92.0492, 78.0335 |
|   | Name                          | Chemical Formula | Molecular Mass | Adducts           | Database ID  | Concentration     |
|---|-------------------------------|------------------|----------------|-------------------|--------------|-------------------|
| 88 | Geraniol                      | C₁₀H₁₉O          | 137.1320       | M+H₂O             | HMDB0035155  | C01500           |
| 89 | Aniline                       | C₆H₁₃N           | 138.0310       | M+H+2Na           | C00292       | 95.0682;93.0525;66.0565 |
| 90 | Trigonelline                  | C₃H₇NO₂          | 138.0520       | M+H               | HMDB0000875  | C01004           |
| 91 | 2-Hydroxypropyridine          | C₄H₇NO           | 142.0470       | M+HCO₂+2H         | HMDB0013751  | C02502           |
| 92 | Clomethiazole                 | C₆H₈ClNS         | 144.0050       | M+H-H₂O           | —            | 66.0565;96.0442  |
| 93 | Stachydrine                   | C₇H₁₃NO₂         | 144.1010       | M+H               | HMDB004827   | C10172           |
| 94 | Methyl aminolevulinate        | C₆H₁₁NO₃        | 144.0810       | M+H               | HMDB0015127  | D08204           |
| 95 | Spermidine                    | C₆H₁₉N₃          | 146.1650       | M+H               | —            | 117.057;72.0805;84.0805 |
| 96 | Vigabatrin                    | C₄H₁₁NO₂         | 147.1010       | M+NH₄             | HMDB0015212  | C07500           |
| 97 | Cis-Jasmone                   | C₁₁H₁₉O          | 147.1010       | M+H₂O             | HMDB0035601  | C08490           |
| 98 | Ethylglycine                  | C₆H₁₀NO₂         | 148.0790       | M+H+2Na           | HMDB0041945  | —                |
| 99 | N,N-Dimethylhistidine         | C₈H₁₃N₂O₂        | 148.0960       | M+H₂H₂O           | —            | 121.0393;66.0564 |
| 100| 3,4-Dihydroxymandelic acid    | C₆H₆O₃           | 149.0230       | M+H+2H₂O          | HMDB0001866  | C05580           |
| 101| Ethylparaben                  | C₆H₁₀O₃          | 149.0440       | M+H₂O             | HMDB0032573  | D01647           |
| 102| Dihydrojasmine                | C₁₁H₁₉O          | 149.1320       | M+H₂O             | HMDB0031565  | —                |
| 103| Methionine                    | C₅H₁₁NO₂S        | 150.0589       | M+H               | HMDB0000696  | C00073           |
| 104| (−)-Carvone                   | C₁₀H₁₆O          | 151.0960       | M+H               | HMDB0035089  | C01767           |
| 105| 10-Hydroxy-2-decenolic acid   | C₁₀H₁₈O₅         | 151.0960       | M+H₂H₂O           | HMDB00244269 | —                |
| 106| 2-Furoylglycine               | C₅H₇NO₄          | 152.0230       | M+H₂O             | HMDB0000439  | —                |
| 107| Guanine                       | C₅H₉O₃           | 152.0568       | M+H               | HMDB0000132  | C00242           |
|   | Name                          | Formula  | M+H   | Comments     | HMDB ID     | C0506   |
|---|-------------------------------|----------|-------|--------------|-------------|---------|
| 108 | 2-(Methylamino)benzoic acid   | C_8H_9NO_2 | 152.0700 | M+H | 119-68-6     | HMDB0032609 | C03005  |
| 109 | Diethyl phosphate             | C_4H_10O_2P | 155.1060 | M+H | 598-02-7     | HMDB0012209 | C06608  |
| 110 | Histidine                     | C_6H_9N_2O_2 | 156.0760 | M+H | 71-00-1      | HMDB0000177 | C00135  |
| 111 | 4,6-Dioxoheptanoic acid       | C_7H_10O_4 | 159.0650 | M+H | 51568-18-4   | HMDB0000635 | —     |
| 112 | 2-Phenyl-4-pentenal           | C_7H_10O   | 161.0964 | M+H | 24401-36-3   | HMDB0035207 | —     |
| 113 | Bethanechol                   | C_6H_10N_2O_2 | 161.1170 | M+H | 574-38-4     | HMDB0015154 | C06850  |
| 114 | 2-Amino-2-deoxymannose        | C_9H_13NO_5 | 162.0760 | M+H-H_2O | 14307-02-9 | C03570  | 103.0386;85.0281;66.0561 |
| 115 | Carnitine                     | C_8H_16NO_3 | 162.1121 | M+H       | 541-15-1     | HMDB000062 | C00318  |
| 116 | Cassiastearoptene             | C_10H_16O_2 | 163.0750 | M+H | 1504-74-1    | HMDB0033830 | —     |
| 117 | N,N-Dimethylaniline           | C_8H_11N    | 163.1070 | M+CH_CN+H | 121-69-7    | HMDB0001020 | C02846  | 105.0443;77.0382;92.0253 |
| 118 | 4-Guanidinobutyric acid       | C_10H_16N_2O_2 | 163.1320 | M+NH_4 | 13890-14-7  | HMDB0003464 | C01035  | 70.0649;62.9288;80.0492 |
| 119 | Benzeneebutanoic acid         | C_10H_14O_2 | 165.0903 | M+H | 1821-12-1    | HMDB0000543 | —     | 146.93;136.92;122.88 |
| 120 | Ethenzamide                   | C_9H_11NO_2 | 166.0710 | M+H | 938-73-8     | D01466   | 120.0804;103.0539;107.0488 |
| 121 | Pholedrine                    | C_10H_12NO  | 166.1230 | M+H | 370-14-9     | D08370   | 120.0804;107.0488;93.0695 |
| 122 | Hordenine                     | C_10H_12NO | 166.1230 | M+H | 539-15-1     | HMDB0004366 | C06199  | 103.0539;93.0696;91.0539 |
| 123 | Erythrose                     | C_4H_8O_4   | 167.0550 | M+HCOO+2H | 1758-51-6   | HMDB0250746 | —     | 121.0281 |
| 124 | 3-Methylxanthine              | C_9H_14N_2O_2 | 167.0550 | M+H | 1076-22-8    | HMDB001886 | C16357  | 121.0394;148.9594 |
| 125 | 4-Hydroxymandelonitrile       | C_8H_14NO_2 | 167.0890 | M+NH_4 | —     | C00650   | 104.0572;64.9269;121.0394 |
| 126 | Phthalic acid                 | C_8H_4O_4   | 167.1430 | M+H | 88-99-3      | HMDB0002107 | C01606  | 121.0394 |

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**Notes:**
- **HMDB ID**: HMDB (Human Metabolome Database) identifier.
- **C0506**: Compound ID in the NIST Mass Spectral Database.
| ID  | Chemical Name                | Molecular Formula | m/z  | Adduct   | PubChem CID | HMDB CID     | Accuracy     |
|-----|------------------------------|-------------------|------|----------|-------------|--------------|--------------|
| 127 | Norepinephrine               | C10H11NO3         | 170.0810 | M+H      | 51-41-2     | HMDB0037685  | C00547       | 64.9269;134.0597;72.3879 |
| 128 | Camphor                      | C10H16O           | 170.1540 | M+NH4    | 76-22-2     | HMDB0059838  | C18369       | 66.0553 |
| 129 | Juglone                      | C10H12O3          | 175.0360 | M+H      | 481-39-0    | HMDB0030773  | C03840       | 91.0539;66.0561;105.0696 |
| 130 | Arginine                     | C4H14N4O2         | 175.1193 | M+H      | 74-79-3     | HMDB0000517  | C00062       | 70.0664;116.0718;130.0991 |
| 131 | Acetyl-L-aspartic acid        | C4H9NO5           | 176.0550 | M+H      | 997-55-7    | HMDB000812   | C01042       | 70.0648;133.0646 |
| 132 | High Proline                 | C4H11NO3          | 176.0910 | M+HCOO2H | 56879-46-0  | HMDB29444    | —            | 66.0561;70.0648 |
| 133 | 4,6,8-Megastigmatriene       | C13H20            | 177.1642 | M+H      | 51468-86-1  | HMDB0035180  | —            | 81.0699;93.0699;107.0855 |
| 134 | Norleucine                   | C4H13NO2          | 178.1070 | M+HCOO2H | 139-82-0    | HMDB01645    | C01933       | 120.9818;109.9658;86.0961 |
| 135 | 6-Deoxyfagomine              | C4H13NO2          | 178.1070 | M+HCOO2H | 197449-09-5 | HMDB0036382  | —            | 86.0961 |
| 136 | Alpha-Terpineol acetate      | C12H20O2          | 179.1430 | M+H-H2O  | 80-26-2     | HMDB0032051  | C12300       | 66.0564 |
| 137 | Beta-D-Glucosamine           | C4H13NO3          | 180.0860 | M+H      | 14257-69-3  | HMDB0030091  | C08349       | 107.0726;120.0805 |
| 138 | Mexiletine                   | C11H17NO          | 180.1380 | M+H      | 180966-61-4 | HMDB0014523  | C07220       | 120.0806;107.0727 |
| 139 | Methylephedrine              | C11H15NO          | 180.1380 | M+H      | 552-79-4    | HMDB0041932  | —            | 107.0726 |
| 140 | Picolinoylglycine             | C4H9N2O3          | 181.0620 | M+H      | 516-29-5    | HMDB0059766  | —            | 153.0694;66.0564;107.06 |
| 141 | P-Mentha-1,3,8-triene         | C10H14            | 181.1220 | M+HCOO2H | 18368-95-1  | HMDB0037013  | —            | 66.0564;135.0549;107.06 |
| 142 | 5-Hydroxymethyluracil        | C4H8N2O3          | 184.0730 | M+H-2H2O+2H | 4433-40-3 | HMDB0000469  | C03088       | 124.9995;98.9839 |
| 143 | 5-Methylmercaptopurine        | C4H9NS            | 184.0730 | M+NH4    | 133762-85-3 | HMDB0060412  | C16614       | 124.9995;71.0726;98.9839 |
| 144 | Phosphorylcholine             | C9H2NO5P          | 184.0736 | M+H      | 3616-04-4   | HMDB0001565  | C00588       | 60.0808;86.0972;98.9791 |
| 145 | Methyprylon                   | C10H17NO2         | 184.1330 | M+H      | 125-64-4    | HMDB0015239  | D01150       | 124.9995;86.0962;98.9839 |
| 146 | Val-Cys                       | C4H9N2O3S         | 185.0940 | M+H-H2O  | —          | HMDB0029124  | —            | 105.1099 |
| No. | Chemical Name                          | Formula       | MW (g/mol) | Exact MW  | Charge    | HMDB ID   | CAS No.       | HMDB ID   |
|-----|---------------------------------------|---------------|------------|------------|-----------|-----------|---------------|------------|
| 147 | Triethylenetetramine                  | C₆H₁₄N₄      | 185.1170   | 146.1531   | M+K 112-24-3 | C07166    | 87.0994;98.9838 |
| 148 | Acetylcysteine                        | C₇H₁₇NO₃S    | 186.0800   | 163.0303   | M+Na 616-91-1 | C06809    | 140.0015;86.0961;66.0564 |
| 149 | 5-Hydroxycytosine                     | C₆H₁₄N₃O    | 186.0160   | 139.0269   | M⁺HCOO⁺2H 15864-85-4 | HMDB002658 | C01020 | 140.0015;86.0961;66.0565 |
| 150 | 4-Hydroxycyclohexylcarboxylic acid    | C₅H₁₃O₃      | 186.1120   | 144.0786   | M+CH₃CN+H 3685-26-5 | HMDB001988 | —    | 127.0037;66.0564;144.3115 |
| 151 | 5-(2-Hydroxyethyl)-4-methylthiazole   | C₆H₁₅N₃S    | 188.0140   | 143.0405   | M⁻H+2Na 137-00-8 | HMDB002985 | C04294 | 144.0804 |
| 152 | 5-Methoxyindole-3-acetic acid         | C₁₁H₁₄NO₃    | 188.0680   | 205.0739   | M⁻H⁺H₂O 3471-31-6 | HMDB0004096 | C05660 | 118.0648;146.0597;144.0804 |
| 153 | NS-Acetylsermidine                    | C₉H₁₆N₄O     | 188.1640   | 189.1841   | M+H 34450-15-2 | HMDB002189 | C01029 | 146.0596;144.0804 |
| 154 | Diaminopimelic acid                   | C₅H₁₄N₂O₄    | 191.1040   | 190.0954   | M⁺H 583-93-7 | HMDB0001370 | —    | 116.9507 |
| 155 | Megastigmatrienone                    | C₁₃H₁₈O₅      | 191.1270   | 190.1358   | M⁺H — | HMDB0059906 | —    | 160.018;149.0132;109.966 |
| 156 | Spermine                              | C₁₀H₂₀N₄     | 203.2230   | 202.2157   | M⁺H 71-44-3 | HMDB0001256 | C00750 | 84.0805;112.1119 |
| 157 | Acetylcarnitine                       | C₉H₁₈N₄O     | 204.1239   | 203.1158   | M⁺H 3040-38-8 | HMDB000201 | C00750 | 84.0805;112.1119 |
| 158 | Tetrahydro-L-biopterin                | C₁₃H₁₈N₄O₃    | 206.1000   | 241.1175   | M⁺H⁻₂H₂O 69056-38-8 | HMDB000027 | C00272 | 96.0805;62.9288;109.9659 |
| 159 | Betamicine                            | C₉H₁₃N₃O     | 206.1000   | 159.0895   | M⁺HCOO⁺2H 515-25-3 | HMDB0029412 | C08269 | 96.0805;83.0601;91.9554 |
| 160 | Pregabalin                            | C₈H₁₆N₂O₂     | 206.1380   | 159.1259   | M⁺HCOO⁺2H 14855-50-8 | HMDB0014375 | D02716 | 96.0805;83.0601 |
| 161 | 1-Methylguanine                       | C₄H₉N₂O₂     | 207.0980   | 165.0651   | M⁺HCH₃CN+H 938-85-2 | HMDB0003282 | C04152 | 137.0081 |
| 162 | 3-Amino-2-methylpropanoic acid        | C₄H₉N₂O₂     | 207.1350   | 103.0633   | 2M⁺H 144-90-1 | HMDB0003911 | C05145 | 75.0258 |
| 163 | Phosphoserine                         | C₆H₁₈O₅P     | 207.9980   | 185.0089   | M⁺Na 1446756-47-3 | HMDB0000272 | C01005 | 64.927;109.966;96.0806 |
| 164 | Aminocaproic acid                     | C₆H₁₃NO₂      | 207.9980   | 131.0946   | M⁺H⁻₂K 60-32-2 | HMDB0001901 | C02378 | 64.927;96.0806;70.0649 |
| 165 | Genipin                               | C₁₁H₁₄O₅      | 209.0770   | 226.0841   | M⁺H⁻₂H₂O 6902-77-8 | HMDB0035830 | C09780 | 64.9269;97.0837;138.9873 |
|   | Name                  | Molecular Formula | MW | Exact Mass (ppm) | Monoisotopic Mass (ppm) | HMDB ID          | PubChem ID | Exact Mass (ppm)  |
|---|----------------------|-------------------|----|------------------|-------------------------|----------------|------------|------------------|
|166| Kynurenine           | C_{10}H_{7}N_{2}O_{3} | 209.0770 | 208.0848 | M+H | 2922-83-0 | HMDB0000684 | C00328 | 64.927;135.9815;165.0698 |
|167| Jasmonic acid        | C_{14}H_{10}O_{3}  | 211.1330 | 210.1256 | M+H | 6894-38-8 | HMDB0032797 | C08491 | 192.9801;152.0129 |
|168| Isoprenaline         | C_{11}H_{14}NO_{2} | 212.1280 | 211.1208 | M+H | 7683-59-2 | HMDB0015197 | C07056 | 165.9746;137.98;135.9817 |
|169| Gabapentin           | C_{4}H_{12}NO_{2}  | 218.1380 | 171.1259 | M+HCOO+2H | 360-70-3 | HMDB0005015 | C07018 | 171.9928 |
|170| Allocystathionine    | C_{6}H_{13}NO_{2}S| 223.0630 | 222.0674 | M+H | 535-34-2 | HMDB0000455 | C00328 | 64.927;135.9815;165.0698 |
|171| Gly-Phe              | C_{11}H_{14}NO_{2} | 223.0960 | 222.1004 | M+H | 3321/3/7 | HMDB0028848 | —      | 207.0321;178.0304 |
|172| Canavanine           | C_{6}H_{12}N_{2}O_{3} | 223.0630 | 176.0909 | M+HCOO+2H | 543-38-4 | HMDB0000455 | C00328 | 178.0307 |
|173| Acetyl-L-tyrosine    | C_{11}H_{13}NO_{2} | 224.0919 | 223.0845 | M+H | 537-55-3 | HMDB0000866 | C01657 | 165.0552;206.0817 |
|174| 2-Amino-2-methyl-1,3-propanediol | C_{4}H_{13}NO_{2} | 228.1950 | 105.0790 | 2M+NH_{4} | 115-69-5 | —      | C11260 | 88.0754 |
|175| Ergothioneine        | C_{6}H_{13}NO_{2}S| 230.1030 | 229.0885 | M+H | 497-30-3 | HMDB0003045 | C00542 | 85.1009;66.0549 |
|176| Benzaldehyde         | C_{6}H_{14}O      | 230.1030 | 106.0419 | 2M+NH_{4} | 100-52-7 | HMDB0006115 | C00193 | 66.0549 |
|177| Pyridoxal phosphate  | C_{6}H_{13}NO_{5}P| 230.1380 | 247.0246 | M+H+H_{2}O | 54-47-7 | HMDB001491 | C00018 | 66.0549 |
|178| Diethyl phthalic acid| C_{12}H_{14}O_{4} | 245.0760 | 222.0892 | M+Na | 88988-18-1 | HMDB0094660 | C14175 | 151.0114;163.0288 |
|179| Carnitine 2-methyl-C4 | C_{12}H_{25}NO_{4} | 246.1690 | 245.1627 | M+H | 31023-25-3 | HMDB000378 | —      | 85.0281 |
|180| Myristic acid        | C_{14}H_{26}O_{2} | 246.2430 | 228.2089 | M+NH_{4} | 544-63-8 | HMDB0000806 | C06424 | 229.2168 |
|181| Ser-Lys              | C_{13}H_{19}N_{3}O_{4} | 256.1210 | 233.1376 | M+Na | 22677-61-8 | HMDB0029044 | —      | 102.091;88.0754;70.0648 |
|182| Hexadecanamide/Palmitic amide | C_{16}H_{33}NO_{2} | 256.2609 | 255.4393 | M+H | 629-54-9 | HMDB0012273 | —      | 101.92;87.89 |
|183| Glu-Gln              | C_{6}H_{13}NO_{3} | 258.1000 | 275.1117 | M+H+H_{2}O | —      | HMDB0011738 | C05283 | 102.0911;184.0731 |
|184| Benzamidine          | C_{7}H_{25}N_{2} | 258.1690 | 120.0687 | 2M+NH_{4} | 618-39-3 | HMDB024970 | C01784 | 104.1067 |
|185| Pantothenate         | C_{6}H_{17}NO_{5} | 264.0790 | 219.1107 | M+H+2Na | 79-83-4 | HMDB0000210 | C00864 | 66.0541;189.0447;92.9736 |
| No. | Compound                         | Formula       | MW (calc) | MW (exp) | Tolerance (ppm) | HMDB ID            | CID      | Exact Mass (ppm) |
|-----|----------------------------------|---------------|-----------|----------|-----------------|---------------------|----------|-----------------|
| 186 | Thiamine                         | C_{12}H_{17}N_{4}O_{5}S | 265.1109  | 265.1123 | 70-16-6          | HMDB0000235         | C00378  | 144.0483        |
| 187 | Acetyl-N-formyl-5-methoxykynurenamin | C_{14}H_{15}N_{2}O_{4} | 265.1110  | 264.1110 | M+H 52450-38-1   | HMDB0004259         | C05642  | 232.0867;189.0446 |
| 188 | Glycerophosphocholine             | C_{14}H_{36}N_{4}O_{3} | 280.0910  | 257.1028 | M+Na —           | HMDB0000086         | —       | 104.1068;86.0962 |
| 189 | Alloisoleucine                    | C_{16}H_{13}NO_{2} | 280.2270  | 131.0946 | 2M+NH_{4} 1509-34-8 | HMDB0000557         | C21096  | 104.1068;73.0466 |
| 190 | Oleamide                          | C_{16}H_{19}NO | 282.2796  | 281.2719 | M+H 301-02-0     | HMDB02117           | C19670  | 83.0855;97.1012  |
| 191 | Alanyllysine                      | C_{18}H_{19}N_{2}O_{3} | 284.0980  | 217.1426 | M-2H+3Na 6366-77-4 | HMDB0028692         | —       | 102.0912;88.0755 |
| 192 | Prolyl-Tryptophan                 | C_{16}H_{14}N_{3}O_{3} | 284.1330  | 301.1426 | M+H-H 2457-80-9  | HMDB0029028         | —       | 102.0911;66.0538;70.0648 |
| 193 | Vitamin A                         | C_{20}H_{16}O | 287.2375  | 286.2297 | M+H 68-26-8      | HMDB0000305         | D0069  | 269.2264        |
| 194 | Muramic acid                      | C_{16}H_{17}NO_{7} | 296.0665  | 251.1005 | M-H+2Na 1114-41-6 | HMDB0028692         | —       | 105.1101;       |
| 195 | 5'-Methylthioadenosine           | C_{11}H_{12}N_{2}O_{5}S | 298.0965  | 297.0896 | M+H 2457-80-9    | HMDB0001173         | C00170  | 136.0616;104.1068;75.0261 |
| 196 | Methyylimidazoleacetic acid       | C_{16}H_{12}N_{2}O_{2} | 298.1490  | 140.0586 | 2M+NH_{4} 2625-49-2 | HMDB0002820         | C05828  | 75.0261;97.0282 |
| 197 | Sphingosine                       | C_{18}H_{14}NO_{3} | 300.2885  | 299.4919 | M+H 123-78-4     | HMDB0000252         | C00319  | 282.22;256.21;238.27;212.21 |
| 198 | Palmitoyl ethanolamide           | C_{18}H_{34}NO_{2} | 300.2901  | 299.2824 | M+H 544-31-0     | HMDB0002100         | C16512  | 239.2369;282.2791 |
| 199 | Sphinganine                       | C_{18}H_{16}N_{2}O_{2} | 302.3059  | 301.2981 | M+H 764-22-7     | HMDB000269           | C00836  | 284.2973        |
| 200 | 11,12-EET                        | C_{20}H_{34}O_{2} | 303.2306  | 320.4730 | M+H-H_{2}O —    | HMDB0244445         | C14770  | 166.84;149.00   |
| 201 | Oleoyl ethanolamide              | C_{20}H_{34}NO_{2} | 308.2957  | 325.2981 | M+H-H_{2}O 111-58-0 | HMDB0002088         | C20792  | 265.2526        |
| 202 | MG(16:0)                          | C_{16}H_{36}O_{4} | 313.2743  | 330.2770 | M+H-H_{2}O —    | HMDB0011564         | —       | 81.0522         |
| 203 | Phytosphingosine                 | C_{18}H_{34}NO_{3} | 318.3007  | 317.2930 | M+H 554-62-1     | HMDB0004610         | C12144  | 282.2797;300.2903 |
| 204 | Guanosine                         | C_{10}H_{13}N_{5}O_{5} | 322.0551  | 283.0917 | M+K 118-00-3     | HMDB0000133         | —       | 151.0489        |
| ID  | Name                                               | Formula          | MRM                | MRM                | MRM                | MRM                | MRM                |
|-----|----------------------------------------------------|------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 205 | MG(0:0/15:0/0:0)                                    | C_{11}H_{20}O_{4} | 334.2957           | 316.2614           | M+NH_{4}           | --                 | --                 |
| 206 | 3-Methyl-5-pentyl-2-furanundecanoate                | C_{21}H_{40}O_{4} | 337.2737           | 336.2664           | M+H               | 5781-37-8          | --                 |
| 207 | Adenosine 2'-phosphate                              | C_{10}H_{14}N_{5}O_{7}P | 348.0712       | 347.0631           | M+H               | 130-49-4           | HMDB0011617        |
| 208 | MG(0:0/i-17:0/0:0)                                  | C_{20}H_{40}O_{4} | 362.3271           | 344.2927           | M+NH_{4}           | --                 | --                 |
| 209 | Lithocholic acid                                    | C_{24}H_{40}O_{3} | 415.2602           | 376.2977           | M+K               | 434-13-9           | HMDB0000761        |
| 210 | Lysope 16:0                                         | C_{24}H_{50}NO_{7}P | 496.3390       | 495.3325           | M+H               | 17364-16-8         | HMDB0010382        |
| 211 | LPC(16:0)                                           | C_{24}H_{50}NO_{7}P | 496.3401       | 495.3325           | M+H               | --                 | --                 |
| 212 | LPC(18:1)                                           | C_{26}H_{52}NO_{7}P | 522.3555       | 521.3481           | M+H               | --                 | --                 |
| 213 | LPC(18:0)                                           | C_{26}H_{52}NO_{7}P | 524.3720       | 523.3638           | M+H               | --                 | --                 |
| 214 | DG(32:1)                                            | C_{35}H_{66}O_{5} | 549.4890           | 566.4910           | M+H-H_{2}O         | --                 | HMDB0007211        |
| 215 | Ceramide                                            | C_{42}H_{81}NO_{3}P | 648.6310       | 647.6216           | M+H               | --                 | HMDB0004953        |
| 216 | PC(28:0)                                            | C_{36}H_{72}NO_{8}P | 678.5078       | 677.4996           | M+H               | --                 | HMDB0007866        |
| 217 | PC(29:1)                                            | C_{37}H_{74}NO_{8}P | 690.5071       | 689.4996           | M+H               | --                 | --                 |
| 218 | PC(29:0)                                            | C_{36}H_{72}NO_{8}P | 692.5236       | 691.5152           | M+H               | --                 | --                 |
| 219 | PC(30:1)                                            | C_{37}H_{74}NO_{8}P | 704.5239       | 703.5152           | M+H               | --                 | --                 |
| 220 | PC(30:0)                                            | C_{37}H_{74}NO_{8}P | 706.5397       | 705.5309           | M+H               | --                 | --                 |
| 221 | PC(31:1)                                            | C_{38}H_{76}NO_{8}P | 718.5396       | 717.5309           | M+H               | --                 | --                 |
| 222 | DG(44:9)                                            | C_{44}H_{82}O_{7} | 718.5758           | 718.5536           | M+NH_{3}H_{2}O     | --                 | --                 |
| 223 | PC(31:0)                                            | C_{39}H_{78}NO_{8}P | 720.5561       | 719.5465           | M+H               | --                 | --                 |
| 224 | PC(32:1)                                            | C_{40}H_{80}NO_{8}P | 732.5553       | 731.5465           | M+H               | --                 | --                 |

| 37 |
|    |                                 | C_{a}H_{b}NO_{c}P |   |   |   |   |   |   |   |
|----|----------------------------------|-------------------|---|---|---|---|---|---|---|
| 225 | PC(32:0)                          |                   | 734.5710 | 733.5621 | M+H     |   |   |   | 184.0728 |
| 226 | PC(33:3)                          |                   | 742.5402 | 741.5308 | M+H     |   |   |   | 184.0731 |
| 227 | PC(33:2)                          |                   | 744.5554 | 743.5465 | M+H     |   |   |   | 184.0728 |
| 228 | PC(34:0)                          |                   | 744.5920 | 761.5934 | M+H-H_{2}O |   |   |   | 184.0728 |
| 229 | PC(33:1)                          |                   | 746.5713 | 745.5622 | M+H     |   |   |   | 184.0729 |
| 230 | PC(34:1)                          |                   | 760.5862 | 759.5778 | M+H     |   |   |   | 184.0729 |
| 231 | PC(35:5)                          |                   | 766.5391 | 765.5309 | M+H     |   |   |   | 184.0728 |
| 232 | PC(36:4)                          |                   | 768.5908 | 767.5465 | M+H     |   |   |   | 184.0729 |
| 233 | PC(35:3)                          |                   | 770.5714 | 769.5621 | M+H     |   |   |   | 184.0731 |
| 234 | PC(35:2)                          |                   | 772.5867 | 771.5778 | M+H     |   |   |   | 184.0729 |
| 235 | PC(35:1)                          |                   | 774.6024 | 773.5935 | M+H     |   |   |   | 184.0728 |
| 236 | PC(36:5)                          |                   | 780.5547 | 779.5465 | M+H     |   |   |   | 184.0731 |
| 237 | PC(36:3)                          |                   | 784.5870 | 783.5778 | M+H     |   |   |   | 184.0727 |
| 238 | PC(36:2)                          |                   | 786.6021 | 785.5935 | M+H     |   |   |   | 184.0730 |
| 239 | PC(34:2)                          |                   | 796.5260 | 795.5622 | M+K     |   |   |   | 184.0733 |
| 240 | PC(37:2)                          |                   | 800.6172 | 799.6091 | M+H     |   |   |   | 184.0729 |
| 241 | PC(38:7)                          |                   | 804.5530 | 803.5465 | M+H     |   |   |   | 184.0729 |
| 242 | PC(38:6)                          |                   | 806.5719 | 805.5622 | M+H     |   |   |   | 184.0728 |
| 243 | PC(38:5)                          |                   | 808.5868 | 807.5778 | M+H     |   |   |   | 184.0729 |
| 244 | PC(36:1)                          |                   | 810.6027 | 787.6091 | M+Na    |   |   |   | 627.5323;751.5248 |
| NO. | Metabolites          | Formula (CAS_ID) | Precursor (M+H) | Mass (Observed) | Ions | CAS_ID       | HMDB_ID       | KEGG_ID | MS/MS fragments |
|-----|----------------------|------------------|-----------------|----------------|------|--------------|---------------|---------|-----------------|
| 245 | PC(38:3)             | C_{27}H_{44}O_{3} | 812.6190        | 811.6091       | M+H  | —            | —             | —       | —               |
| 246 | PC(38:2)             | C_{26}H_{40}NO_{2}P | 814.6330       | 813.6248       | M+H  | —            | —             | —       | —               |
| 247 | PC(40:7)             | C_{26}H_{40}NO_{3}P | 832.5866       | 831.5778       | M+H  | —            | —             | —       | —               |
| 248 | PC(40:6)             | C_{26}H_{40}NO_{3}P | 834.6016       | 833.5935       | M+H  | —            | —             | —       | —               |
| 249 | PC(40:5)             | C_{26}H_{40}NO_{3}P | 836.6206       | 835.6091       | M+H  | —            | —             | —       | —               |
|     | **Negative ion mode**|                  |                 |                |      |              |               |         |                 |
| 250 | 2-Oxobutanoic acid   | C_{4}H_{6}O_{3}   | 101.0245        | 102.0317       | M-H  | 600-18-0     | HMDB0000005  | C00109  | 83.0139         |
| 251 | Serine               | C_{3}H_{7}NO_{3}   | 104.0360        | 105.0426       | M-H  | 302-84-1     | HMDB0000187  | C00065  | 74.0248;58.8439 |
| 252 | P-Cresol             | C_{7}H_{8}O       | 107.0500        | 108.0575       | M-H  | 106-44-5     | HMDB0001858  | C01468  | 79.9574;66.0735;92.9932 |
| 253 | Butyric acid         | C_{4}H_{8}O_{2}   | 109.0300        | 88.0524       | M+Na-2H | 107-92-6 | HMDB0000039  | C00246  | 60.9470;81.9534;53.9918 |
| 254 | Pyrrole-2-carboxylic acid | C_{5}H_{8}NO_{2} | 110.0250        | 111.0320       | M-H  | 634-97-9     | HMDB0004230  | C05942  | 66.0734;80.0381 |
| 255 | 3-Furancarboxylic acid | C_{5}H_{8}O_{2}  | 111.0090        | 112.0160       | M-H  | 488-93-7     | HMDB0004444  | C00106  | 78.9592;66.0734;72.4084 |
| 256 | 2,4-Hexadienoic acid | C_{5}H_{8}O_{2}  | 111.0450        | 112.0524       | M-H  | 110-44-1     | HMDB0029581  | D05892  | 66.0734;94.6238 |
| 257 | Creatinine           | C_{4}H_{5}N_{2}O  | 112.0410        | 113.0589       | M-H  | 60-27-5      | HMDB0000562  | C00791  | 68.1633         |
| 258 | Glutaric acid        | C_{5}H_{9}O_{4}   | 113.0250        | 132.0423       | M-H_{2}O-H | 110-94-1 | HMDB0000661  | C00849  | 68.9959;79.9563 |
| 259 | 2-Methyl-3-pentenoic acid | C_{6}H_{10}O_{2} | 113.0610        | 114.0681       | M-H  | 1879-03-4    | —             | —       | 68.9959;66.0734; |
| 260 | Iminodiacetic acid   | C_{4}H_{7}NO_{4}  | 114.0200        | 133.0375       | M-H_{2}O-H | 142-73-4 | HMDB0011753  | C19911  | 68.7729;71.7443;58.8481 |
| 261 | Malic acid           | C_{4}H_{6}O_{3}   | 115.0040        | 134.0215       | M-H_{2}O-H | 6915-15-7 | HMDB0000744  | C00711  | 72.4083         |
|   | Name                  | Molecular Formula | Mass (m/z)   | Formula | Database Code | Accession | Molar Mass |
|---|-----------------------|-------------------|--------------|---------|---------------|-----------|------------|
| 262 | 2,3-Dihydroxy-isovalerate | C₅H₁₀O₄ | 115.0400 | M-H₂O-H | HMDB0012141 | C04039 | 194.51-56.0 |
| 263 | Hexanoic acid         | C₆H₁₂O₂ | 115.0770 | M-H     |               | C01585 | 116.0837   |
| 264 | Methylmalonic acid    | C₅H₉NO₂ | 117.0200 | M-H     | HMDB000202    | C02170 | 156.05-2   |
| 265 | Salicylamide          | C₇H₇NO₂ | 118.0300 | M-H₂O-H | HMDB0015687   | D01811 | 65.075-90.0350.0 |
| 266 | Allo-threonine        | C₄H₉NO₃ | 118.0510 | M-H     |               | C05519 | 119.0582   |
| 267 | Trehonine             | C₄H₉NO₃ | 118.0510 | M-H     | HMDB0000167   | C00188 | 130.955-55.1 |
| 268 | 4-Methylbenzaldehyde  | C₆H₇O    | 119.0500 | M-H     | HMDB0029638   | C06758 | 104.087-0  |
| 269 | 4-hydroxystyrene      | C₆H₇O    | 119.0500 | M-H     | HMDB0004072   | C05627 | 262.8-17-3 |
| 270 | Benzoic acid          | C₇H₆O₂   | 121.0300 | M-H     | HMDB0001870   | C00180 | 122.0368   |
| 271 | 3-Hydroxybenzaldehyde | C₇H₆O₂   | 121.0300 | M-H     | HMDB0000167   | C00188 | 122.0368   |
| 272 | Maltol                | C₆H₉O₂   | 125.0250 | M-H     | HMDB0030776   | C11918 | 118.071-8  |
| 273 | 1H-Imidazol-1-ylacetic acid | C₅H₇N₂O₂ | 125.0250 | M-H     | HMDB0029736   | C06758 | 228.8-40.10-2 |
| 274 | 1,2,3-Trihydroxybenzene | C₅H₇O₃   | 125.0250 | M-H     | HMDB0013674   | C01108 | 87.066-1   |
| 275 | 2-methyl-1,3-Cyclohexanedione | C₇H₁₀O₂ | 125.0610 | M-H     | HMDB0034080   | C06104 | 119.055-1  |
| 276 | Adipic acid           | C₄H₁₀O₄  | 127.0400 | M-H₂O-H | HMDB0000448   | C06104 | 146.0579   |
| 277 | Cyclohexanecarboxylic acid | C₆H₁₂O₂  | 127.0770 | M-H     | HMDB0031342   | C09822 | 128.0837   |
| 278 | Pyroglutamic acid     | C₄H₇NO₃ | 128.0354 | M-H     | HMDB000805    | C01585 | 129.0426   |
| 279 | Hydroxyisocaproic acid | C₄H₁₂O₃  | 131.0720 | M-H     | HMDB0000746   | C02170 | 132.0786   |
| 280 | 2-Ethyl-2-Hydroxybutyric acid | C₄H₁₂O₃ | 131.0720 | M-H     | HMDB0001975   | C02170 | 132.0786   |
| 281 | Maleic acid           | C₄H₆O₄   | 132.0300 | M-H₂O⁻₂H | HMDB000176    | C01384 | 116.0110   |
| Line | Compound                     | Chemical formula | Unimolecular mass (m/z) | M+H (Da) | HMDB ID     | Compound mass (m/z) | HMDB ID     | Compound mass (m/z) | HMDB ID     | Compound mass (m/z) | HMDB ID     |
|------|-----------------------------|------------------|-------------------------|----------|-------------|---------------------|-------------|---------------------|-------------|---------------------|-------------|
| 282  | Adenine                     | C$_5$H$_5$N$_3$  | 134.0470                | 135.0545 | 134434-49-4 | C00147              | 107.0363    | 92.0254             |             |                     |             |
| 283  | 4-Oxopentanoate             | C$_5$H$_6$O$_3$  | 135.0450                | 116.0473 | 123-76-2    | HMDB0000720         | 75.0088    | 72.4078;60.9468     |             |                     |             |
| 284  | 4-Hydroxybenzoic acid       | C$_5$H$_6$O$_3$  | 137.0240                | 138.0317 | 99-96-7     | HMDB000500          | 93.0458    | 78.9590             |             |                     |             |
| 285  | 2,5-Dihydroxybenzaldehyde  | C$_5$H$_6$O$_3$  | 137.0240                | 138.0317 | 1194-98-5   | HMDB0004062         | 66.0733    | 78.9591;96.8327     |             |                     |             |
| 286  | 2-(4-Hydroxyphenyl)ethanol  | C$_5$H$_9$O$_2$  | 137.0610                | 138.0681 | 2380-91-8   | C13638              | 66.0732    | 93.0346             |             |                     |             |
| 287  | 4-Nitrophenol               | C$_6$H$_5$NO$_3$ | 138.0200                | 139.0269 | 100-02-7    | HMDB001232          | 108.0455   | 66.0732;94.0299     |             |                     |             |
| 288  | 2-Aminoethyl dihydrogen phosphate | C$_5$H$_9$NO$_3$P | 140.0120               | 141.0191 | 1071-23-4   | HMDB000224          | C00346     | 78.9591             |             |                     |             |
| 289  | Daminozide                  | C$_6$H$_12$N$_2$O$_3$ | 141.0560              | 160.0848 | 1596-84-5   | C10996              | 58.7564    | 100.8584;108.0046   |             |                     |             |
| 290  | Ectoine                     | C$_6$H$_9$O$_2$  | 141.0560                | 142.0742 | 96702-03-3  | C06231              | 84.1901    | 75.3660;102.1730    |             |                     |             |
| 291  | 4-Hydroxyvalproic acid      | C$_6$H$_9$O$_3$  | 141.0920                | 160.1099 | 60113-82-8  | HMDB0013900         | C16649     | 66.0732;114.5427    |             |                     |             |
| 292  | Trimethadione               | C$_6$H$_7$N$_2$O | 142.0510                | 143.0582 | M-H         | HMDB001491         | D00392     | 60.9468             |             |                     |             |
| 293  | Indole-3-carboxaldehyde     | C$_6$H$_7$NO     | 144.0460                | 145.0528 | 487-89-8    | HMDB0029737         | C08493     | 66.0732;51.0292;60.9468 |             |                     |             |
| 294  | 4-Hydroxyquinoline          | C$_6$H$_7$NO     | 144.0460                | 145.0528 | 611-36-9    | C06343              | 66.0732    | 72.4076;95.3761     |             |                     |             |
| 295  | Glutamine                   | C$_6$H$_10$N$_2$O$_3$ | 145.0510              | 146.0691 | 56-85-9     | HMDB000641         | C00064     | 66.0733;84.0454;127.0511 |             |                     |             |
| 296  | 2-Methylglutaric acid       | C$_6$H$_7$O$_4$  | 145.0510                | 146.0579 | 617-62-9    | HMDB000422         | 84.0454    | 74.0248             |             |                     |             |
| 297  | Isatin                      | C$_6$H$_7$NO$_2$ | 146.0250                | 147.0320 | 91-56-5     | HMDB0061933         | C11129     | 66.0732;92.9935;69.6941 |             |                     |             |
| 298  | Glutamic acid               | C$_6$H$_7$NO$_4$ | 146.0460                | 147.0532 | M-H         | HMDB0000148        | C00025     | 119.0502;101.0244;85.0295 |             |                     |             |
| 299  | Tartaric acid               | C$_6$H$_7$O$_8$  | 149.0100                | 150.0164 | M-H         | HMDB0029878         | C02107     | 72.4077             |             |                     |             |
| S. No. | Name                                      | Chemical Formula | M.Wt | M-H M.Wt | HMDB No.       | CID No. | Other M.Wt |
|--------|-------------------------------------------|------------------|------|----------|----------------|---------|------------|
| 300    | 4-Coumaryl alcohol                        | C₉H₁₀O₂          | 149.0610 | 150.0681 | 3690/5/9       | HMDB03654 | 102.7635;51.3836 |
| 301    | 3-Hydroxyanthranilic acid                 | C₇H₆NO₃         | 152.0350 | 153.0426 | 548-93-6       | HMDB0001476 | C00632 108.0454   |
| 302    | 3-Amino-4-Hydroxybenzoic acid             | C₇H₆NO₃         | 152.0350 | 153.0426 | 570-23-0       | HMDB0001972 | — 66.0732;79.9575 |
| 303    | Linalool                                  | C₁₀H₁₄O          | 153.1290 | 154.1358 | 126-90-9       | HMDB0036101 | C11389 66.0732;97.0407;81.0459 |
| 304    | 2-Deoxy-D-ribose                         | C₅H₁₀O₄         | 155.0350 | 134.0579 | 333-67-5       | HMDB0245099 | — 94.0492 |
| 305    | Shiikimic acid                            | C₇H₆O₃          | 157.0250 | 158.0328 | 5988-19-2      | HMDB0003349 | 114.9887 |
| 306    | Dihydroorotic acid                        | C₅H₆N₂O₄       | 157.0250 | 340.0577 | 13184-27-5    | HMDB0000828 | 89.0245;114.9887 |
| 307    | Salicylic acid                            | C₇H₆O₃          | 157.0250 | 138.0317 | 69-72-7        | HMDB0001895 | C00805 113.0094 |
| 308    | Ureidosuccinic acid                       | C₁₀H₉N₂O₄S      | 157.0250 | 340.0577 | 13184-27-5    | HMDB0000828 | 89.0245;114.9887 |
| 309    | 3,3-Dimethylglutaric acid                 | C₇H₁₂O₄         | 159.0660 | 160.0736 | 4839-46-7      | HMDB0002441 | — 114.9887;78.9592;66.0733 |
| 310    | 5-Hydroxyvalproic acid                    | C₉H₁₀O₃          | 159.1030 | 160.1099 | 53660-23-4     | HMDB0013898 | C16650 130.9836;114.9887 |
| 311    | Carboxymethyl-L-cysteine                  | C₅H₉NO₄S       | 160.0700 | 179.0252 | 638-23-3       | HMDB0029415 | D06393 86.9911;74.0249;116.0175 |
| 312    | 3-Hydroxy-3-methylglutaric acid           | C₉H₁₀O₃          | 161.0460 | 162.0528 | 503-49-1       | HMDB0000355 | C03761 144.3546;129.0362;75.3499 |
| 313    | Phenylalanine                             | C₉H₁₁NO₂        | 164.0715 | 165.0790 | 149597-92-2    | HMDB0000159 | C0079 147.0449;103.0553;72.0092 |
| 314    | Homogentisic acid                          | C₈H₈O₄          | 167.0350 | 168.0423 | 451-13-8       | HMDB0000130 | C00544 123.0564;109.0490;66.0733 |
| 315    | 4-Ipomeanol                               | C₉H₁₂O₅          | 171.0710 | 168.0786 | 55659-41-1     | HMDB0030472 | — 66.0733 |
| 316    | Glycerophosphoric acid                    | C₈H₁₂O₅P        | 171.0600 | 172.0137 | 17181-54-3     | HMDB0002520 | C02979 78.9591;96.9695 |
| 317    | Carglumic acid                            | C₆H₁₀N₂O₃       | 171.0410 | 190.0590 | 1188-38-1      | HMDB0015673 | C05829 128.0352;142.9662 |
| 318    | Phenoxyacetic acid                        | C₃H₄O₃          | 171.0410 | 152.0473 | 122-59-8       | HMDB0031609 | C02181 78.9591;66.0733 |
| 319    | Decanoic acid                             | C₁₀H₂₀O₂        | 171.1390 | 172.1463 | 334-48-5       | HMDB0000511 | C01571 78.9591;66.0733;96.9697 |
| No. | Name                                | Chemical Formula   | M/Charge       | MZ          | HMDB ID      | C08278   | C01419   | C00082   | C00392   | C01507   | C00279   | C10906   | C07207   | C06890   | C01546   |
|-----|-------------------------------------|--------------------|---------------|-------------|--------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 320 | Suberic acid                        | C₈H₁₄O₄            | 173.0820      | 174.0892    | M-H         | 505-48-6 | 131.0825 | 93.0346  | 66.0733  |          |          |          |          |          |          |
| 321 | Cysteinylglycine                    | C₇H₁₆N₂O₅S        | 177.0340      | 178.0412    | M-H         | 19246-18-5 | 74.0248 | 131.0463 | 99.0564  |          |          |          |          |          |          |
| 322 | Acetylthreonine                     | C₅H₁₁NO₄           | 177.0920      | 161.0688    | M+NH₄-2H    | 17093-74-2 |        | 74.0248 | 99.0563  |          |          |          |          |          |          |
| 323 | Nicotinuric acid                    | C₃H₂NO₃            | 179.0460      | 180.0535    | M-H         | 583-08-4   | 109.0407 | 135.0562 |          |          |          |          |          |          |          |
| 324 | 1,7-Dimethylxanthine                | C₂H₆N₂O₂           | 179.0710      | 180.0647    | M-H         | 611-59-6   |        |          |          |          |          |          |          |          |          |
| 325 | 3-Hydroxycaprylic acid              | C₉H₁₆O₃            | 180.0660      | 181.0739    | M-H         | 55520-40-6 | 109.0407 | 135.0563 |          |          |          |          |          |          |          |
| 326 | Tyrosine                            | C₉H₁₀O₃            | 181.0715      | 182.0790    | M-H         | 69-65-8    |        |          |          |          |          |          |          |          |          |
| 327 | D-P-Coumaric acid                   | C₇H₈O₃             | 180.0660      | 164.0473    | M+NH₄-2H    | 501-98-4   | 119.0501 | 163.0397 | 93.0346  |          |          |          |          |          |          |
| 328 | 2-Hydroxycinnamic acid              | C₈H₆O₃             | 180.0660      | 164.0473    | M+NH₄-2H    | 614-60-8   | 119.0502 | 93.0347  | 66.0734  |          |          |          |          |          |          |
| 329 | Mannitol                            | C₆H₁₄O₆            | 181.0715      | 182.0790    | M-H         | 69-65-8    | 101.0244 | 71.0140  | 89.0244  |          |          |          |          |          |          |
| 330 | Iditol                              | C₆H₁₄O₆            | 181.0715      | 182.0790    | M-H         | 488-45-9   | 101.0244 | 71.0140  | 89.0245  |          |          |          |          |          |          |
| 331 | Asp-Ala                             | C₆H₁₂N₂O₅          | 185.0570      | 204.0746    | M-H₂O-H     | 13433-02-8 |          |          |          |          |          |          |          |          |          |
| 332 | 1-Hydroxy-2-Naphthoate              | C₁₁H₈O₃            | 187.0418      | 188.0473    | M-H         | 86-48-6    |          | 115.0208 | 157.0312 | 66.0733  |          |          |          |          |          |
| 333 | 2-Amino-3-methylimidazo[4,5-f]quinoline | C₁₁H₁₀N₄       | 197.0820      | 198.0905    | M-H         | 76180-96-6 |          | 169.0159 | 66.0734  |          |          |          |          |          |          |
| 334 | Erythrose-4-phosphate               | C₄H₆O₃P            | 198.9970      | 200.0086    | M-H         | 585-18-2   |          |          |          |          |          |          |          |          |          |
| 335 | Fructose                            | C₆H₁₂O₆            | 201.0377      | 180.0634    | M+Na-2H     | 57-48-7    |          |          |          |          |          |          |          |          |          |
| 336 | Zalcitabine                         | C₃H₁₃N₂O₃          | 210.0880      | 211.0957    | M-H         | 7481-89-2  |          |          |          |          |          |          |          |          |          |
| 337 | 4-Aminohippuric acid                | C₄H₁₀N₂O₃          | 210.0890      | 194.0691    | M+NH₄-2H    | 61-78-9    |          |          |          |          |          |          |          |          |          |
| 338 | 2-Furanoic acid                     | C₃H₆O₃             | 223.0280      | 112.0160    | 2M-H        | 88-14-2    |          |          |          |          |          |          |          |          |          |
|   | Name                                      | Chemical Formula | Mass Accuracy  | Charge | HMDB ID         | MHDB ID  |
|---|-------------------------------------------|------------------|----------------|--------|-----------------|----------|
|339| Thymidine                                 | C10H14N3O5       | 223.0760       | M-H2O-H | 50-89-5         | C00214   |
|340| Umbelliferone                             | C9H14O3          | 213.1540       | M-H     | 93-35-6         | C09315   |
|341| Glycyltyrosine                            | C15H16N2O4       | 237.0910       | M-H     | 658-79-7        | —        |
|342| Tyr-Gly                                   | C15H16N2O4       | 237.0911       | M-H     | 673-08-5        | —        |
|343| 5(R)-hydroperoxy-EPE                      | C18H20N2O3S      | 237.0915       | M-H     | 7365-45-9       | —        |
|344| Uridine                                   | C9H14N3O6        | 243.0620       | M-H     | 58-96-8         | C00299   |
|345| 2-cis-Hexadecenoic acid                   | C16H30O2         | 253.2170       | M-H     | 2825-68-5       | —        |
|346| Gamma-Glutamylglutamic acid               | C10H20N3O7       | 257.0751       | M-H2O-H | 1116-22-9       | C05282   |
|347| Myo-Inositol 6-phosphate                  | C4H15O3P         | 259.0220       | M-H     | 15421-51-9      | C01177   |
|348| 14-Methylhexadecanoic acid                | C17H34O2         | 269.2480       | M-H     | 5918-29-6       | C0031067 |
|349| Zidovudine                                | C10H13N5O4       | 288.0660       | M+Na2H  | 30516-87-1      | C07210   |
|350| Embelin                                   | C17H20O4         | 293.1760       | M-H     | 550-24-3        | C10342   |
|351| Acetylgalactosamine 1-Phosphate           | C10H16N2O5P      | 300.0480       | M-H     | 6866-69-9       | C04256   |
|352| Glutathione                               | C10H17N3O8S      | 306.0737       | M-H     | 70-18-8         | C00051   |
|353| 13-HpODE                                  | C11H13O4         | 311.2220       | M-H     | 23017-93-8      | —        |
|354| Ethyl stearate                            | C20H40O2         | 311.2950       | M-H     | 111-61-5        | C0034156 |
|355| Acetylcytosine                            | C11H16N3O4       | 320.0880       | M+NH4-2H | 3106-85-2      | C12270   |
|356| Cytidine monophosphate                    | C9H14N3O6P       | 322.0409       | M-H     | 63-37-6         | C00055   |
|357| Uridine 5-Monophosphate                   | C11H16N3O6P      | 323.0290       | M-H     | 58-97-9         | C00105   |
|358| Docosahexaenoic acid                      | C22H32O2         | 327.2170       | M-H     | 25377-50-8      | C06429   |
|     | Name                                   | Formula       | MW1 | MW2  | Charge | HMDB  | CID   | Purity  |
|-----|----------------------------------------|---------------|-----|------|--------|-------|-------|---------|
| 359 | Fructose-2,6-diphosphate               | C9H14O12P2    | 338.9890 | 339.9961 | M-H   | HMDB0001047 | C00665 | 96.96   |
| 360 | Quercetin                              | C15H10O7      | 338.9890 | 302.0427 | M+K-2H | HMDB0005794 | C00389 | 283.8553;302.7115 |
| 361 | Heneicosaonic acid                     | C21H42O2      | 339.3260 | 326.3185 | M-H   | HMDB0002345 | —      | 283.8548 |
| 362 | Penicillin v                           | C16H18N2O5S  | 371.0650 | 350.0936 | M+Na-2H | HMDB014561 | C08126 | 93.0344 |
| 363 | Cysteine-glutathione disulfide         | C11H22N4O8S2  | 442.1120 | 426.0879 | M+NHa-2H | 13081-14-6 | —      | 381.4482;158.9249 |
| 364 | 5'-DGTP                                | C10H18N3O8P3  | 505.9880 | 506.9957 | M-H   | HMDB0001440 | C00286 | 158.9254 |
| 365 | UDP-D-galactose                        | C12H22N2O13P2 | 565.0470 | 566.0550 | M-H   | HMDB0000302 | C00052 | 323.0275;384.9829;241.0111 |
| 366 | UDP-glucose                            | C12H22N2O13P2 | 565.0470 | 566.0550 | M-H   | HMDB0000935 | C00167 | 402.9937 |
| 367 | Uridine diphosphate glucuronic acid    | C12H22N2O13P2 | 579.0270 | 580.0343 | M-H   | HMDB0000290 | C00043 | 158.9251;272.9564;282.0376 |
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