Database of proteinogenic amino acid reference spectra for Bismuth-cluster ToF-SIMS. II. Positive polarity

Maciej Kawecki^{a)}

Laboratory of Nanoscale Materials Science, Empa, CH-8600 Dübendorf, Switzerland and
 Department of Physics, University of Basel, CH-4056 Basel, Switzerland

Laetitia Bernard

Laboratory of Nanoscale Materials Science, Empa, CH-8600 Dübendorf, Switzerland

(Received 6 February 2018; accepted 1 May 2018; published 10 July 2018)

The number of time-of-flight secondary ion mass spectrometry studies on biological tissues and cells strongly increased since the development of primary ion sources that allow not only elemental but also molecular analysis. Still, substantial fragmentation during ionic bombardment results in a large amount of peaks, rendering data analysis complex. Complete and trustable sets of reference spectra for the main biological building blocks such as proteins, sugars, and lipids are required. Here, the authors provide a database of reference spectra for the 21 proteinogenic amino acids + glycine for bismuth instruments. Paper I of this two-part article series contains the negative polarity spectra and Paper II the positive polarity spectra. These reference spectra were obtained with the primary ion Bi_3^+ , and spectra for the primary ions Bi_1^+ and Bi_3^{++} are contained in the supplementary material as ASCII files. *Published by the AVS.*

<https://doi.org/10.1116/1.5024988>

Keywords: ToF-SIMS, amino acid, mass spectrometry, fragmentation

Accession #: 01453, 01454, 01455, 01456, 01457, 01458, 01459, 01460, 01461, 01462, 01463, 01464, 01465, 01466, 01467, 01468, 01469, 01470, 01471, 01472, 01473, 01474

Technique: SIMS

Host Material: Silicon (100) wafer

Instrument: IONTOF TOF-SIMS.5

Major Species in Spectra: C, H, N, O, S

Minor Species in Spectra: Na, K, Si

Published Spectra: 22

Spectra in Electronic Record: 66

Published Figures: 44

Spectral Category: Reference

INTRODUCTION

Partial amino acid databases for time-of-flight secondary ion mass spectrometry (ToF-SIMS) reference mass spectra have been already conducted based on the now largely replaced monoatomic argon (Ref. 1) and caesium (Ref. 2) primary ion sources. The characteristic molecular fragmentation in ToF-SIMS measurements, however, depends on the primary ion impacting the surface. The current standard primary ion source is the bismuth/manganese liquid metal ion source. For bismuth and bismuth cluster primary ions, only limited lists attributing prominent peaks to specific amino acids can be found in the literature, e.g., Ref. 3. Here, we provide a database of original reference spectra for the 21 proteinogenic amino acids + glycine as well as the complete corresponding peak lists determining the fragmentation products. Fragments which uniquely represent specific amino acids are highlighted in Table 24. This Paper II of the database contains the positive polarity spectra. Negative polarity spectra are contained in Paper I (Ref. 4).

The amino acids were purchased through Sigma Aldrich (Article number: 09416, purity > 99.0%). Each amino acid was dissolved in H_2O (Sigma Aldrich, Article number: 270733) and 0.1 M solutions were so prepared. Host silicon wafers of 1×1 cm size were first washed by submersion in subsequent ultrasound baths of 2×15 min in acetone and 1×15 min in ethanol, and then plasma-treated for a duration of 10 min to render the surface hydrophilic. The 0.1 M amino acid solutions were subsequently drop-deposited inside a laminar flow chamber on separate silicon wafers. It was

made sure that each deposited droplet is spread over the entire wafer surface before leaving the wafers in the laminar flow chamber for drying.

The spectra were obtained on a ToF-SIMS.5 instrument (IONTOF) equipped with a 25 keV bismuth-manganese liquid metal ion gun. The instrument was operated in high current bunched mode. The primary ion dose was kept below the static limit (10^{12} ions/ cm^2) for each spectrum, and a low-energy electron flood gun was used to compensate charging effects. The raster size was $200 \times 200 \mu\text{m}^2$ with a raster resolution of 128×128 , a cycle time of 100 μs and primary ion currents of 1.54 pA for Bi_1^+ , 0.37–0.4 pA for Bi_3^+ , and 0.44 pA for Bi_3^{++} . Fifty scans were acquired per single mass spectrum. All presented spectra are normalized to their respective total ion count. Note that variations in mass resolution among the reference spectra (see Fig. 23) are due to crystallization geometry differences between the amino acids.

Figures and tables presented contain only attributions for the most prominent peaks. Complete peak-lists attributing fragmentation products to 50–100 main peaks for each amino acid are included in the attachment. In the figures, the full molecule is referred to with “M.” Polymerization products are marked with “p.p.”, cationization products with “c.p.” and contaminants with “c.” Major peaks where a unique attribution was not possible, e.g., due to an overlap beyond mass resolution of two potential fragmentation products, are marked with “n.a.” standing for *not (uniquely) attributed*. In the label of the supplementary material files, the *Spectrum ID#* uniquely identifies each amino acid. Mass spectra acquired using Bi_3^+ , Bi_1^+ , and Bi_3^{++} primary ions are further identified by the file-suffix “01,” “02,” and “03,” respectively, and peak lists in ASCII format by the file-suffix “04.”

^{a)}Electronic mail: maciej.kawecki@empa.ch

SPECIMEN DESCRIPTION (ACCESSION # 01453, 01454, 01455, 01456, 01457, 01458, 01459, 01460, 01461, 01462, 01463, 01464, 01465, 01466, 01467, 01468, 01469, 01470, 01471, 01472, 01473, 01474) —————

Host Material: Silicon (100) wafer

CAS Registry #: 7440-21-3

Host Material Characteristics: Homogeneous; solid; single crystal; semiconductor; semiconductor

Chemical Name: L-alanine (01453), L-arginine monohydrochloride (01454), L-asparagine (01455), L-aspartic acid (01456), L-cysteine (01457), L-cystine (01458), L-glutamic acid (01459), L-glutamine (01460), glycine (01461), L-histidine monohydrochloride (01462), L-4-hydroxyproline (01463), L-isoleucine (01464), L-leucine (01465), L-lysine monohydrochloride (01466), L-methionine (01467), L-phenylalanine (01468), L-proline (01469), L-serine (01470), L-threonine (01471), L-tryptophan (01472), L-tyrosine (01473), L-valine (01474)

Source: Sigma Aldrich

Host Composition: Si and SiO₂

Form: Crystalline powder dissolved in DI H₂O and subsequently drop-deposited on the host wafer

Lot Number: L-alanine: BCBS2461V, L-arginine monohydrochloride: 1361811V, L-asparagine: 1371738V, L-aspartic acid: BCBR6815V, L-cysteine: BCBR4500V, L-cystine: BCBS1903V, L-glutamic acid: 1423805V, L-glutamine: BCBR7569V, glycine: 1119375V, L-histidine monohydrochloride: BCBS1876V, L-4-hydroxyproline: BCBL2666V, L-isoleucine: 1423806V, L-leucine: BCBBQ9986V, L-lysine monohydrochloride: BCBN9886V, L-methionine: 1423807V, L-phenylalanine: BCBQ1493V, L-proline: BCBP4505V, L-serine: 1336081V, L-threonine: BCBQ4901V, L-tryptophan: BCBR0168V, L-tyrosine: BCBR7417V, L-valine: BCBM0163V

Structure: L-alanine: C₃H₇NO₂, L-arginine monohydrochloride: C₆H₁₄N₄O₂·HCl, L-asparagine: C₄H₈N₂O₃, L-aspartic acid: C₄H₇NO₄, L-cysteine: C₃H₇NO₂S, L-cystine: C₆H₁₂N₂O₄S₂, L-glutamic acid: C₅H₉NO₄, L-glutamine: C₅H₁₀N₂O₃, glycine: C₂H₅NO₂, L-histidine monohydrochloride: C₆H₉N₃O₂·HCl, L-4-hydroxyproline: C₅H₉NO₃, L-isoleucine: C₆H₁₃NO₂, L-leucine: C₆H₁₃NO₂, L-lysine monohydrochloride: C₆H₁₄N₂O₂·HCl, L-methionine: C₅H₁₁NO₂S, L-phenylalanine: C₉H₁₁NO₂, L-proline: C₅H₉NO₂, L-serine: C₃H₇NO₃, L-threonine: C₄H₉NO₃, L-tryptophan: C₁₁H₁₂N₂O₂, L-tyrosine: C₉H₁₁NO₃, L-valine: C₅H₁₁NO₂

History and Significance: The proteinogenic amino acids are the building blocks of all proteins in the known life forms. Complete spectra databases of organic molecules facilitate the interpretation of ToF-SIMS data from biological specimen. However, it should be kept in mind that in biological specimens amino acids are incorporated into larger molecules (proteins, peptidoglycans, etc.) which affects the fragmentation patterns.

As Received Condition: Samples received in powder form

Analyzed Region: Regions of 200 × 200 μm² on maximally homogeneous specimen sites

Ex Situ Preparation/Mounting: 0.1 M amino acid solutions were prepared in H₂O and drop-deposited on separate 1 × 1 cm large plasma-treated Si-Wafers in a laminar flow chamber.

In Situ Preparation: None

Charge Control: Low energy electrons

Temp. During Analysis: 300 K

Pressure During Analysis: 5.6 × 10⁻⁸ Pa

Prealysis Beam Exposure: None

INSTRUMENT CONFIGURATION —————

Manufacturer and Model: IONTOF TOF-SIMS.5

Analyzer Type: Time-of-flight

Detector Type: Microchannel plate

Experiment Type: Mass spectra

Sample Rotation: None

Oxygen Flood Source: None

Other Flood Source: Low energy electrons

Energy Acceptance Window: 14.3 eV

Postacceleration Voltage: 10 000 eV

Sample Bias: 0 eV

Specimen Normal-to-analyzer (Θ_e): 0°

■ Ion Sources

Ion Source 1 of 1

Purpose of this Ion Source: Analysis beam

Ion Source Manufacturer: IONTOF (Münster, Germany)

Ion Source Model: 25 keV Bi/Mn cluster source

Beam Mass Filter: Electrodynamic mass filter

Beam Species and Charge State: Bi₃⁺

Beam Gating Used: None

Beam Voltage: 25 000 eV

Net Beam Voltage (impact voltage): 25 000 eV

Ion Pulse Width: 29.3 ns

Ion Pulse Rate: 10 kHz

Pulsed Beam Current: 0.00037–0.0004 nA

Current Measurement Method: Faraday cup

Beam Raster Size: 200 × 200 μm²

Beam Incident Angle: 45°

Source-to-Analyzer Angle: 45°

ACKNOWLEDGMENTS —————

The authors are thankful for the funding received from the Swiss National Science Foundation through the Grant No. CR23I2-162828.

REFERENCES —————

1. Preinstalled database on IONTOF GmbH instruments.
2. N. T. Samuel, M. S. Wagner, K. D. Dornfeld, and D. G. Castner, *Surf. Sci. Spectra* **8**, 163 (2001).
3. M. Urbini, V. Piteto, F. de Notaristefani, F. Scaldaferrì, A. Gasbarrini, and L. Tortora, *Anal. Bioanal. Chem.* **409**, 6097 (2017).
4. M. Kawecki and L. Bernard, *Surf. Sci. Spectra* **25**, 015001 (2018).

ALANINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01453	44.0495	$C_2H_6N^+$	Alanine
...	55.0178	$C_3H_3O^+$	...
...	56.0495	$C_3H_6N^+$	...
...	70.0287	$C_3H_4NO^+$	...
...	74.0600	$C_3H_8NO^+$	...
...	90.0550	$C_3H_8NO_2^+$	...

Accession #	01453-01, 01453-02, 01453-03, 01453-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_4N^+ , $C_3H_7NO_2^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

ARGININE (HYDROCHLORIDE)

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01454	60.0556	CH_6N_3^+	Arginine
...	70.0777	$\text{C}_5\text{H}_{10}^+$	...
...	73.0634	$\text{C}_2\text{H}_7\text{N}_3^+$	...
...	87.0791	$\text{C}_3\text{H}_9\text{N}_3^+$	...
...	100.0869	$\text{C}_4\text{H}_{10}\text{N}_3^+$	...
...	112.0869	$\text{C}_5\text{H}_{10}\text{N}_3^+$	...
...	130.1213	$\text{C}_5\text{H}_{14}\text{N}_4^+$	...
...	160.1081	$\text{C}_6\text{H}_{14}\text{N}_3\text{O}_2^+$	...
...	175.1190	$\text{C}_6\text{H}_{15}\text{N}_4\text{O}_2^+$	...

Accession #	01454-01, 01454-02, 01454-03, 01454-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

ASPARAGINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01455	70.0287	$C_3H_4NO^+$	Asparagine
...	74.0237	$C_2H_4NO_2^+$	...
...	87.0553	$C_3H_7N_2O^+$	...
...	89.0709	$C_3H_9N_2O^+$	...
...	116.0342	$C_4H_6NO_3^+$	...
...	133.0608	$C_4H_9N_2O_3^+$	...

Accession #	01455-01, 01455-02, 01455-03, 01455-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , CH_2N^+ , $C_4H_{10}N_2O_3^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

ASPARATIC ACID			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01456	70.0287	$C_3H_4NO^+$	Asparatic acid
...	74.0237	$C_2H_4NO_2^+$	...
...	88.0393	$C_3H_6NO_2^+$	...
...	90.0550	$C_3H_8NO_2^+$	...
...	134.0448	$C_4H_8NO_4^+$	...

Accession #	01456-01, 01456-02, 01456-03, 01456-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , CH_2N^+ , $C_4H_9NO_4^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

CYSTEINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01457	31.9715	S ⁺	Cysteine
...	34.9950	H ₃ S ⁺	...
...	44.9793	CHS ⁺	...
...	46.9950	CH ₃ S ⁺	...
...	58.9950	C ₂ H ₃ S ⁺	...
...	75.0137	C ₂ H ₅ NS ⁺	...
...	76.0215	C ₂ H ₆ NS ⁺	...
...	86.9899	C ₃ H ₃ OS ⁺	...
...	88.0393	C ₃ H ₆ NO ₂ ⁺	...
...	90.0550	C ₃ H ₈ NO ₂ ⁺	...
...	105.0005	C ₃ H ₅ O ₂ S ⁺	...
...	122.0270	C ₃ H ₈ NO ₂ S ⁺	...

Accession #	01457-01, 01457-02, 01457-03, 01457-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH ₃ ⁺ , NH ₃ ⁺ , CH ₂ N ⁺ , C ₃ H ₇ SNO ₂ ⁺
Primary Ion Dose	4.73 × 10 ¹¹ cm ⁻²
Primary Species	Bi ₃ ⁺
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	200 × 200 μm ²

CYSTINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01458	63.9436	S_2^+	Cystine
...	58.9950	$C_2H_3S^+$	...
...	76.0215	$C_2H_6NS^+$	...
...	120.0114	$C_3H_6NO_2S^+$	...
...	122.0270	$C_3H_8NO_2S^+$	...
...	151.9834	$C_3H_6NO_2S_2^+$	...
...	195.0256	$C_5H_{11}N_2O_2S_2^+$	...
...	207.0256	$C_6H_{11}N_2O_2S_2^+$	...
...	241.0311	$C_6H_{13}N_2O_4S_2^+$	...

Accession #	01458-01, 01458-02, 01458-03, 01458-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_6H_{14}N_2O_4S_2^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$
Comment	Region of interest, defined by a minimum threshold of the $C_2H_4NO_2^+$ signal, was applied to eliminate the substrate signal.

GLUTAMIC ACID			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01459	84.0444	$C_4H_6NO^+$	Glutamic acid
...	84.0808	$C_5H_{10}N^+$	...
...	91.0628	$C_3H_9NO_2^+$	...
...	102.0550	$C_4H_8NO_2^+$	...
...	148.0604	$C_5H_{10}NO_4^+$	...

Accession #	01459-01, 01459-02, 01459-03, 01459-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_5H_{10}NO_4^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

GLUTAMINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01460	84.0444	$C_4H_6NO^+$	Glutamine
...	86.0600	$C_4H_8NO^+$	...
...	101.0709	$C_4H_9N_2O^+$	...
...	102.0550	$C_4H_8NO_2^+$	...
...	103.0866	$C_4H_{11}N_2O^+$	...
...	114.0550	$C_5H_8NO_2^+$	...
...	130.0499	$C_5H_8NO_3^+$	...
...	147.0764	$C_5H_{11}N_2O_3^+$	...

Accession #	01460-01, 01460-02, 01460-03, 01460-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , CH_2N^+ , $C_5H_{12}N_2O_3^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

GLYCINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01461	43.0718	$C_2H_3O^+$	Glycine
...	60.0444	$C_2H_6NO^+$	...
...	76.0393	$C_2H_6NO_2^+$	...

Accession #	01461-01, 01461-02, 01461-03, 01461-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_2H_5NO_2^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

HISTIDINE (HYDROCHLORIDE)

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01462	81.0447	$C_4H_5N_2^+$	Histidine
...	82.0526	$C_4H_6N_2^+$	...
...	83.0604	$C_4H_7N_2^+$	...
...	93.0447	$C_5H_5N_2^+$	...
...	94.0526	$C_5H_6N_2^+$	...
...	95.0604	$C_5H_7N_2^+$	...
...	110.0713	$C_5H_8N_3^+$	...
...	156.0768	$C_6H_{10}N_3O_2^+$	...

Accession #	01462-01, 01462-02, 01462-03, 01462-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_6H_9N_3O_2^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

HYDROXYPROLINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01463	68.0621	$C_5H_8^+$	Hydroxyproline
...	74.0237	$C_2H_4NO_2^+$	...
...	84.0444	$C_4H_6NO^+$	...
...	86.0600	$C_4H_8NO^+$	...
...	87.0679	$C_4H_9NO^+$	...
...	88.0757	$C_4H_{10}NO^+$	...
...	114.0550	$C_5H_8NO_2^+$	...
...	116.0706	$C_5H_{10}NO_2^+$	...
...	132.0655	$C_5H_{10}NO_3^+$	...

Accession #	01463-01, 01463-02, 01463-03, 01463-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , $C_5H_9NO_3^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

ISOLEUCINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01464	69.0699	$C_5H_9^+$	Isoleucine
...	70.0651	$C_4H_8N^+$	...
...	75.0315	$C_2H_5NO_2^+$	...
...	84.0808	$C_5H_{10}N^+$	...
...	86.0964	$C_5H_{12}N^+$	...
...	87.1043	$C_5H_{13}N^+$	...
...	132.1019	$C_6H_{14}NO_2^+$	...

Accession #	01464-01, 01464-02, 01464-03, 01464-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , CH_2N^+ , $C_6H_{13}NO_2^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

LEUCINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01465	70.0777	$C_5H_{10}^+$	Leucine
...	74.0237	$C_2H_4NO_2^+$	...
...	84.0808	$C_5H_{10}N^+$	...
...	86.0964	$C_5H_{12}N^+$	...
...	132.1019	$C_6H_{14}NO_2^+$	...

Accession #	01465-01, 01465-02, 01465-03, 01465-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , CH_2N^+ , $C_6H_{13}NO_2^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

LYSINE (HYDROCHLORIDE)			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01466	84.0808	$C_5H_{10}N^+$	Lysine
...	86.0954	$C_5H_{12}N^+$	...
...	91.0628	$C_3H_9NO_2^+$	...
...	96.0808	$C_6H_{10}N^+$	...
...	98.0964	$C_6H_{12}N^+$	...
...	110.0839	$C_6H_{10}N_2^+$	...
...	128.0706	$C_6H_{10}NO_2^+$	...
...	132.1019	$C_6H_{14}NO_2^+$	...
...	147.1128	$C_6H_{15}N_2O_2^+$	...

Accession #	01466-01, 01466-02, 01466-03, 01466-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_6H_{14}N_2O_2^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

METHIONINE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01467	31.9715	S ⁺	Methionine
...	46.9950	CH ₃ S ⁺	...
...	61.0106	C ₂ H ₅ S ⁺	...
...	74.0185	C ₃ H ₆ S ⁺	...
...	75.0315	C ₂ H ₅ NO ₂ ⁺	...
...	88.0215	C ₃ H ₆ NS ⁺	...
...	88.0341	C ₄ H ₈ S ⁺	...
...	102.0550	C ₄ H ₈ NO ₂ ⁺	...
...	104.0528	C ₄ H ₁₀ NS ⁺	...
...	133.0318	C ₅ H ₉ O ₂ S ⁺	...
...	150.0583	C ₅ H ₁₂ NO ₂ S ⁺	...

Accession #

01467-01, 01467-02, 01467-03, 01467-04

■ Host Material
 ■ Technique
 Secondary Source Polarity
 Mass Range Minimum
 Mass Range Maximum
 Species Used for Mass Calibration
 Primary Ion Dose
 Primary Species
 Primary Ion Pulse Width
 Pulsed Beam Current
 Beam Raster Size
 Comment

Silicon wafer

SIMS

Positive

0 Da

250 Da

CH₃⁺, NH₃⁺, NH₄⁺, CH₂N⁺, C₅H₁₃SNO₂⁺

5.11 × 10¹¹ cm⁻²

Bi₃⁺

29.3 ns

0.0004 nA

200 × 200 μm²

The assignments C₂H₅O₂⁺ and C₃H₆O₂⁺ (in brackets) show a substantially lower deviation but are, in the author's judgment, sufficiently inconsistent with the fragmentation patterns observed in other amino acids to warrant the choice of peak attribution made above.

PHENYLALANINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01468	77.0386	$C_6H_5^+$	Phenylalanine
...	91.0628	$C_3H_9NO_2^+$	...
...	103.0542	$C_8H_7^+$	...
...	105.0699	$C_8H_9^+$	...
...	107.0491	$C_7H_7O^+$	...
...	115.0628	$C_5H_9NO_2^+$	...
...	120.0808	$C_8H_{10}N^+$	...
...	121.0886	$C_8H_{11}N^+$	...
...	166.0863	$C_9H_{12}NO_2^+$	...

Accession #	01468-01, 01468-02, 01468-03, 01468-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_9H_{11}NO_2^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

PROLINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01469	68.0621	$C_5H_8^+$	Proline
...	70.0651	$C_4H_8N^+$	...
...	70.0777	$C_5H_{10}^+$	...
...	71.0730	$C_4H_9N^+$	...
...	72.0808	$C_4H_{10}N^+$	...
...	116.0706	$C_5H_{10}NO_2^+$	...

Accession #	01469-01, 01469-02, 01469-03, 01469-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , $C_5H_9NO_2^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

SERINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01470	60.0444	$C_2H_6NO^+$	Serine
...	70.0287	$C_3H_4NO^+$	...
...	73.0284	$C_3H_5O_2^+$	...
...	88.0393	$C_3H_6NO_2^+$	...
...	106.0499	$C_3H_8NO_3^+$	...

Accession #	01470-01, 01470-02, 01470-03, 01470-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_3H_9NO_3^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

THREONINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01471	56.0621	$C_4H_8^+$	Threonine
...	74.0600	$C_3H_8NO^+$	...
...	84.0444	$C_4H_6NO^+$	...
...	102.0550	$C_4H_8NO_2^+$	...
...	120.0655	$C_4H_{10}NO_3^+$	...

Accession #	01471-01, 01471-02, 01471-03, 01471-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_4H_{11}NO_3^+$
Primary Ion Dose	$5.11 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.0004 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

TRYPTOPHAN			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01472	77.0386	$C_6H_5^+$	Tryptophan
...	115.0417	$C_8H_5N^+$	...
...	117.0573	$C_8H_7N^+$	...
...	118.0651	$C_8H_8N^+$	...
...	130.0651	$C_9H_8N^+$	...
...	132.0808	$C_9H_{10}N^+$	...
...	143.0730	$C_{10}H_9N^+$	...
...	144.0682	$C_9H_8N_2^+$	...
...	169.0917	$C_{10}H_{11}N_2^+$	...
...	188.0944	$C_{11}H_{12}N_2O^+$	...
...	205.0972	$C_{11}H_{13}N_2O_2^+$	...

Accession #	01472-01, 01472-02, 01472-03, 01472-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_{11}H_{13}N_2O_2^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

TYROSINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01473	77.0386	$C_6H_5^+$	Tyrosine
...	91.0542	$C_7H_7^+$	...
...	107.0491	$C_7H_7O^+$	...
...	115.0417	$C_8H_5N^+$	...
...	121.0648	$C_8H_9O^+$	...
...	136.0757	$C_8H_{10}NO^+$	...
...	149.0107	$C_7H_3NO_3^+$	...
...	165.0546	$C_9H_9O_3^+$	...
...	182.0812	$C_9H_{12}NO_3^+$	...

Accession #	01473-01, 01473-02, 01473-03, 01473-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_9H_{12}NO_3^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

VALINE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01474	55.0542	$C_4H_7^+$	Valine
...	68.0495	$C_4H_6N^+$	...
...	72.0808	$C_4H_{10}N^+$	...
...	73.0886	$C_4H_{11}N^+$	...
...	75.0315	$C_2H_5NO_2^+$	...
...	118.0862	$C_5H_{12}NO_2^+$	...

Accession #	01474-01, 01474-02, 01474-03, 01474-04
■ Host Material	Silicon wafer
■ Technique	SIMS
Secondary Source Polarity	Positive
Mass Range Minimum	0 Da
Mass Range Maximum	250 Da
Species Used for Mass Calibration	CH_3^+ , NH_3^+ , NH_4^+ , CH_2N^+ , $C_5H_{13}NO_2^+$
Primary Ion Dose	$4.73 \times 10^{11} \text{ cm}^{-2}$
Primary Species	Bi_3^+
Primary Ion Pulse Width	29.3 ns
Pulsed Beam Current	0.00037 nA
Beam Raster Size	$200 \times 200 \mu\text{m}^2$

EXPANDED $[M+H]^+$ PEAKS FOR EACH AMINO ACID SPECTRUM

01453-01, 01454-01, 01455-01, 01456-01, 01457-01, 01458-01, 01459-01,
01460-01, 01461-01, 01462-01, 01463-01, 01464-01, 01465-01, 01465-01,
01467-01, 01468-01, 01469-01, 01470-01, 01471-01, 01472-01,
01473-01, 01474-01

Accession #

SPECTRAL FEATURES TABLE			
Mass (Da)	Peak assignment	Peak present in following amino acids:	Peak most prominent in:
17.0260	NH ₃ ⁺	all amino acids	—
18.0338	NH ₄ ⁺	all amino acids	—
28.0182	CH ₂ N ⁺	all amino acids	—
30.0338	CH ₄ N ⁺	all amino acids	—
31.9715	S ⁺	cysteine, cystine, methionine	cysteine, cystine, methionine
34.9950	SH ₃ ⁺	cysteine, cystine, methionine	cysteine, cystine, methionine
39.0229	C ₃ H ₃ ⁺	all amino acids except for glycine	—
41.0386	C ₃ H ₅ ⁺	all amino acids except for glycine	—
42.0338	C ₂ H ₄ N ⁺	all amino acids	—
43.0417	C ₂ H ₅ N ⁺	all amino acids	—
43.0542	C ₃ H ₇ ⁺	most amino acids	—
43.0718	C ₂ H ₃ O ⁺	all amino acids	—
44.0495	C ₂ H ₆ N ⁺	all amino acids	—
44.9793	CHS ⁺	cysteine, cystine, methionine	cysteine, cystine, methionine
45.0335	C ₂ H ₅ O ⁺	all amino acids	—
45.0573	C ₂ H ₇ N ⁺	all amino acids	—
45.9872	CH ₂ S ⁺	cysteine, cystine, methionine	cysteine, cystine, methionine
46.0651	C ₂ H ₈ N ⁺	all amino acids	—
46.9950	CH ₃ S ⁺	cysteine, cystine, methionine	cysteine, cystine, methionine
47.0491	C ₂ H ₇ O ⁺	all amino acids	—
51.0229	C ₄ H ₃ ⁺	multiple amino acids	—
53.0386	C ₄ H ₅ ⁺	multiple amino acids	—
55.0178	C ₃ H ₃ O ⁺	all amino acids except for glycine	—
55.0542	C ₄ H ₇ ⁺	multiple amino acids	—
56.0495	C ₃ H ₆ N ⁺	all amino acids except for glycine	—
56.0621	C ₄ H ₈ ⁺	multiple amino acids	—
57.0335	C ₃ H ₅ O ⁺	all amino acids except for glycine	—
57.0573	C ₃ H ₇ N ⁺	multiple amino acids	—
58.0287	C ₂ H ₄ NO ⁺	all amino acids	—
58.0651	C ₃ H ₈ N ⁺	all amino acids except for glycine	—
58.0777	C ₄ H ₁₀ ⁺	multiple amino acids	—
58.9950	C ₂ H ₃ S ⁺	cysteine, cystine, methionine	cysteine, cystine, methionine
59.0491	C ₃ H ₇ O ⁺	all amino acids except for glycine	—
60.0444	C ₂ H ₆ NO ⁺	all amino acids	—
60.0556	CH ₆ N ₃ ⁺	arginine	arginine
61.0106	C ₂ H ₅ S ⁺	cysteine, cystine, methionine	cysteine, cystine, methionine
61.0284	C ₂ H ₅ O ₂ ⁺	all amino acids	—
63.9436	S ₂ ⁺	cystine	cystine
67.0542	C ₅ H ₇ ⁺	multiple amino acids	—
68.0495	C ₄ H ₆ N ⁺	multiple amino acids	—
68.0621	C ₅ H ₈ ⁺	multiple amino acids	—
69.0335	C ₄ H ₅ O ⁺	multiple amino acids	—
69.0447	C ₃ H ₅ N ₂ ⁺	arginine, asparagine, histidine	asparagine, histidine
69.0573	C ₄ H ₇ N ⁺	multiple amino acids	—
69.0699	C ₅ H ₉ ⁺	multiple amino acids	—
70.0287	C ₃ H ₄ NO ⁺	all amino acids except for glycine	—

Mass (Da)	Peak assignment	Peak present in following amino acids:	Peak most prominent in:
70.0651	C ₄ H ₈ N ⁺	multiple amino acids	—
70.0777	C ₅ H ₁₀ ⁺	multiple amino acids	—
71.0491	C ₄ H ₇ O ⁺	multiple amino acids	—
71.0730	C ₄ H ₉ N ⁺	multiple amino acids	proline
72.0444	C ₃ H ₆ NO ⁺	all amino acids except for glycine	—
72.0808	C ₄ H ₁₀ N ⁺	multiple amino acids	—
73.0284	C ₃ H ₅ O ₂ ⁺	multiple amino acids	—
73.0634	C ₂ H ₇ N ₃ ⁺	arginine	arginine
73.0648	C ₄ H ₉ O ⁺	multiple amino acids	—
73.0886	C ₄ H ₁₁ N ⁺	valine	valine
74.0237	C ₂ H ₄ NO ₂ ⁺	all amino acids	—
74.0362	C ₃ H ₆ O ₂ ⁺	all amino acids except for glycine	—
74.0600	C ₃ H ₈ NO ⁺	all amino acids except for glycine	—
75.0137	C ₂ H ₅ NS ⁺	cysteine, cystine, methionine	cysteine, cystine
75.0315	C ₂ H ₅ NO ₂ ⁺	all amino acids	—
76.0215	C ₂ H ₆ NS ⁺	cysteine, cystine, methionine	cysteine, cystine
76.0393	C ₂ H ₆ NO ₂ ⁺	all amino acids	—
77.0386	C ₆ H ₅ ⁺	multiple amino acids	—
80.0495	C ₅ H ₆ N ⁺	multiple amino acids	—
80.0621	C ₆ H ₈ ⁺	multiple amino acids	—
81.0447	C ₄ H ₅ N ₂ ⁺	multiple amino acids	histidine
82.0526	C ₄ H ₆ N ₂ ⁺	multiple amino acids	histidine
82.0651	C ₅ H ₈ N ⁺	multiple amino acids	—
82.0777	C ₆ H ₁₀ ⁺	multiple amino acids	—
83.0604	C ₄ H ₇ N ₂ ⁺	multiple amino acids	histidine
84.0444	C ₄ H ₆ NO ⁺	multiple amino acids	—
84.0808	C ₅ H ₁₀ N ⁺	multiple amino acids	—
84.0933	C ₆ H ₁₂ ⁺	multiple amino acids	—
86.0600	C ₄ H ₈ NO ⁺	multiple amino acids	hydroxyproline
86.0964	C ₅ H ₁₂ N ⁺	multiple amino acids	isoleucine, leucine
86.9899	C ₃ H ₃ OS ⁺	cysteine, cystine	cysteine, cystine
87.0553	C ₃ H ₇ N ₂ O ⁺	asparagine	asparagine
87.0679	C ₄ H ₉ NO ⁺	multiple amino acids	hydroxyproline
87.0791	C ₃ H ₉ N ₃ ⁺	arginine	arginine
87.0804	C ₅ H ₁₁ O ⁺	multiple amino acids	—
87.1043	C ₅ H ₁₃ N ⁺	multiple amino acids	isoleucine, leucine
88.0215	C ₃ H ₆ NS ⁺	methionine	methionine
88.0341	C ₄ H ₈ S ⁺	methionine	methionine
88.0393	C ₃ H ₆ NO ₂ ⁺	multiple amino acids	—
88.0757	C ₄ H ₁₀ NO ⁺	multiple amino acids	hydroxyproline
89.0386	C ₇ H ₅ ⁺	phenylalanine, tryptophan, tyrosine	—
89.0709	C ₃ H ₉ N ₂ O ⁺	asparagine	asparagine
90.0550	C ₃ H ₈ NO ₂ ⁺	multiple amino acids	—
91.0542	C ₇ H ₇ ⁺	phenylalanine, tryptophan, tyrosine	—
93.0447	C ₅ H ₅ N ₂ ⁺	arginine, histidine, lysine	histidine
94.0526	C ₅ H ₆ N ₂ ⁺	arginine, histidine, lysine	histidine
95.0604	C ₅ H ₇ N ₂ ⁺	arginine, histidine, lysine	histidine

Mass (Da)	Peak assignment	Peak present in following amino acids:	Peak most prominent in:
96.0808	C ₆ H ₁₀ N ⁺	isoleucine, leucine, lysine	—
98.0964	C ₆ H ₁₂ N ⁺	isoleucine, leucine, lysine	—
100.0393	C ₄ H ₆ NO ₂ ⁺	multiple amino acids	—
100.0869	C ₄ H ₁₀ N ₃ ⁺	arginine	arginine
101.0709	C ₄ H ₉ N ₂ O ⁺	asparagine, glutamine	glutamine
102.0464	C ₈ H ₆ ⁺	phenylalanine, tryptophan, tyrosine	—
102.0550	C ₄ H ₈ NO ₂ ⁺	multiple amino acids	—
103.0542	C ₈ H ₇ ⁺	phenylalanine, tryptophan, tyrosine	phenylalanine
103.0866	C ₄ H ₁₁ N ₂ O ⁺	asparagine, glutamine	glutamine
104.0528	C ₄ H ₁₀ NS ⁺	methionine	methionine
105.0005	C ₃ H ₅ O ₂ S ⁺	cysteine, cystine	cysteine, cystine
105.0699	C ₈ H ₉ ⁺	phenylalanine, tyrosine	phenylalanine
106.0499	C ₃ H ₈ NO ₃ ⁺	serine, threonine	serine
107.0491	C ₇ H ₇ O ⁺	phenylalanine, tyrosine	—
107.0577	C ₃ H ₉ NO ₃ ⁺	hydroxyproline, serine, threonine	serine
110.0713	C ₅ H ₈ N ₃ ⁺	arginine, histidine	histidine
110.0839	C ₆ H ₁₀ N ₂ ⁺	lysine	lysine
112.0869	C ₅ H ₁₀ N ₃ ⁺	arginine	arginine
114.0550	C ₅ H ₈ NO ₂ ⁺	multiple amino acids	—
114.1026	C ₅ H ₁₂ N ₃ ⁺	arginine	arginine
115.0417	C ₈ H ₅ N ⁺	phenylalanine, tryptophan, tyrosine	—
115.0628	C ₅ H ₉ NO ₂ ⁺	multiple amino acids	—
116.0342	C ₄ H ₆ NO ₃ ⁺	asparagine	asparagine
116.0706	C ₅ H ₁₀ NO ₂ ⁺	multiple amino acids	proline
117.0573	C ₈ H ₇ N ⁺	phenylalanine, tryptophan, tyrosine	—
118.0651	C ₈ H ₈ N ⁺	phenylalanine, tryptophan, tyrosine	phenylalanine, tryptophan
118.0862	C ₅ H ₁₂ NO ₂ ⁺	multiple amino acids	aspartic acid, glutamic acid, valine
119.0491	C ₈ H ₇ O ⁺	phenylalanine, tryptophan, tyrosine	—
120.0114	C ₃ H ₆ NO ₂ S ⁺	cysteine, cystine	cysteine, cystine
120.0444	C ₇ H ₆ NO ⁺	tryptophan, tyrosine	tryptophan
120.0655	C ₄ H ₁₀ NO ₃ ⁺	threonine	threonine
120.0808	C ₈ H ₁₀ N ⁺	phenylalanine	phenylalanine
121.0648	C ₈ H ₉ O ⁺	phenylalanine, tryptophan, tyrosine	—
121.0886	C ₈ H ₁₁ N ⁺	phenylalanine	phenylalanine
122.0270	C ₃ H ₈ NO ₂ S ⁺	cysteine, cystine	cysteine, cystine
128.0706	C ₆ H ₁₀ NO ₂ ⁺	isoleucine, leucine, lysine	isoleucine, leucine, lysine
129.0420	C ₅ H ₇ NO ₃ ⁺	glutamic acid, glutamine, hydroxyproline	glutamine
129.1135	C ₅ H ₁₃ N ₄ ⁺	arginine	arginine
130.0499	C ₅ H ₈ NO ₃ ⁺	glutamic acid, glutamine, hydroxyproline	glutamine
130.0651	C ₉ H ₈ N ⁺	phenylalanine, tryptophan, tyrosine	tryptophan
130.1213	C ₅ H ₁₄ N ₄ ⁺	arginine	arginine
131.0730	C ₉ H ₉ N ⁺	phenylalanine, tryptophan, tyrosine	tryptophan
131.1291	C ₅ H ₁₅ N ₄ ⁺	arginine	arginine
132.0655	C ₅ H ₁₀ NO ₃ ⁺	glutamic acid, glutamine, hydroxyproline	hydroxyproline
132.0808	C ₉ H ₁₀ N ⁺	phenylalanine, tryptophan, tyrosine	tryptophan
132.1019	C ₆ H ₁₄ NO ₂ ⁺	isoleucine, leucine, lysine	isoleucine, leucine
133.0318	C ₅ H ₉ O ₂ S ⁺	methionine	methionine

Mass (Da)	Peak assignment	Peak present in following amino acids:	Peak most prominent in:
133.0608	$C_4H_9N_2O_3^+$	asparagine	asparagine
134.0448	$C_4H_8NO_4^+$	asparatic acid	asparatic acid
136.0757	$C_8H_{10}NO^+$	tyrosine	tyrosine
143.0730	$C_{10}H_9N^+$	tryptophan	tryptophan
144.0682	$C_9H_8N_2^+$	tryptophan	tryptophan
147.0764	$C_5H_{11}N_2O_3^+$	glutamine	glutamine
147.1128	$C_6H_{15}N_2O_2^+$	lysine	lysine
148.0604	$C_5H_{10}NO_4^+$	glutamic acid	glutamic acid
149.0107	$C_7H_3NO_3^+$	tyrosine	tyrosine
150.0583	$C_5H_{12}NO_2S^+$	methionine	methionine
151.9834	$C_3H_6NO_2S_2^+$	cystine	cystine
156.0768	$C_6H_{10}N_3O_2^+$	histidine	histidine
157.0760	$C_{10}H_9N_2^+$	tryptophan	tryptophan
158.0839	$C_{10}H_{10}N_2^+$	tryptophan	tryptophan
160.1081	$C_6H_{14}N_3O_2^+$	arginine	arginine
165.0546	$C_9H_9O_3^+$	tyrosine	tyrosine
165.0764	$C_9H_{11}NO_2^+$	tyrosine	tyrosine
166.0863	$C_9H_{12}NO_2^+$	phenylalanine	phenylalanine
169.0917	$C_{10}H_{11}N_2^+$	tryptophan	tryptophan
175.1190	$C_6H_{15}N_4O_2^+$	arginine	arginine
182.0812	$C_9H_{12}NO_3^+$	tyrosine	tyrosine
188.0944	$C_{11}H_{12}N_2O^+$	tryptophan	tryptophan
195.0256	$C_5H_{11}N_2O_2S_2^+$	cystine	cystine
205.0972	$C_{11}H_{13}N_2O_2^+$	tryptophan	tryptophan
207.0256	$C_6H_{11}N_2O_2S_2^+$	cystine	cystine
241.0311	$C_6H_{13}N_2O_4S_2^+$	cystine	cystine