

Electronic Supplementary Information

A nickel(II) complex under water-oxidation reaction: What is the true catalyst?

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Experimental Section

Materials

All reagents and solvents were obtained from commercial sources and used without further purification. Nickel(II) phthalocyanine-tetrasulfonate tetrasodium salt (**1**) and fluorine tin oxide coated glass (FTO) were purchased from Sigma-Aldrich.

Characterization

SEM was carried out with an LEO 1430VP. The X-ray powder patterns were recorded with a Bruker D8 ADVANCE diffractometer (CuK_α radiation). Visible spectra were recorded by a mini spectrophotometer (Pooyesh Tadbir Karaneh (Phystec), Iran). AFM was measured by Dualscope/ Rasterscope C26, DME, Denmark. Ni L-edge NEXAFS was measured at 10D XAS KIST beamline Pohang Light source. Magnetization was measured between 2 K and 300 K in a constant magnetic field of 10 mT, and as a function of magnetic field at 300 K and 2 K using a Quantum Design MPMS-XI-5 SQUID magnetometer.

Experimental Details for X-ray absorptions

The extended edge X-ray absorption fine structure (EXAFS) measurements on HF-Ni and reference materials (NiO and Ni) were performed at the hard X-ray 1D XAS KIST-PAL beamline, Pohang accelerator laboratory, operating at 3.0 GeV with a maximum storage current of 320 mA. 1D XAS KIST-PAL beamline is a bending magnet X-ray Scattering (XRS)

beamline which uses Si(111) double crystal monochromator to give a wide range of monochromatic energies (4-16 keV). To measure EXAFS spectra of these materials, higher harmonics were removed by detuning incident beam intensity to 60% of maximum intensity. The ionization chamber filled with He was used to record the intensity of the incident X-rays. The fluorescence EXAFS signal was measured by a passivated implanted planar silicon (PIPS) detector. Before the measurement, reference foil (Ni) is used for energy calibration. Under stationary conditions, extended X-ray absorption fine-structure (EXAFS) measurements were performed at the Ni *K*- edge in the step scanning mode.

The program Athena was used to identifying the beginning of the absorption edge (E_0), fit pre- and post-edge backgrounds, and hence to obtain the normalized absorbance χ as a function of the modulus of the photoelectron wave vector k . The fitting was carried out using ARTEMIS in the k range 3–10.5 Å. The EXAFS data is Fourier transformed to R-space to investigate the atomic structure and relative bond-lengths with respect to absorbing atoms. The theoretical structure for reference oxides was generated using the ATOM. In the fitting, values of coordination number (N), bond length (R_i) and Debye-Waller (σ^2) factors are kept free. The parameter ϵ_0 , which is a correction to edge energy, was free to vary in all fitting. The errors in the fit parameters of R_i and σ^2 were obtained from 90% of happiness factor as calculated in IFEFFIT.

Electrochemistry

Electrochemical experiments were performed using an EmStat³⁺ from PalmSens (Netherlands). Cyclic voltammetry studies were carried out with a conventional three-electrode setup, in which FTO, or Hg|HgO, and a platinum foil served as working, the reference and the auxiliary electrodes, respectively. All potentials in this project were reported vs. Ag|AgCl|KCl_{sat}. The distance between two opposite sides of the FTO electrode was measured by a digital caliper MarCal 16ER model (Mahr, Germany). The temperature was measured by Laserliner 082 (Germany).

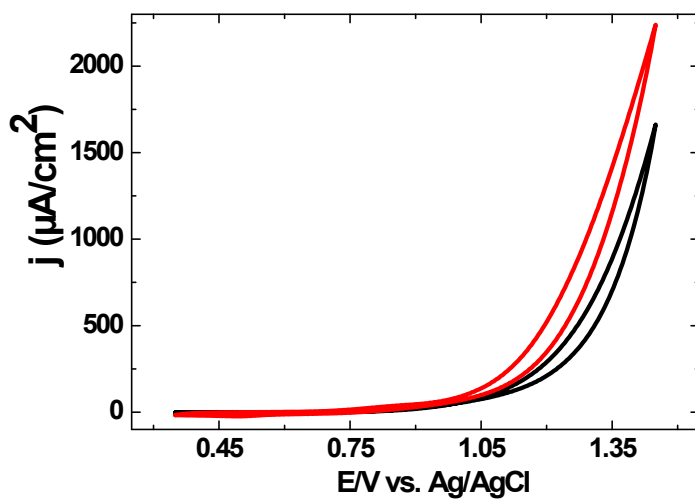


Figure S1 | CV for the FTO after 250 continuous CVs in the presence (red) and in the absence (black) of **1** (0.51 mM) in phosphate buffer (20.0 mL; 0.25 M) at pH = 11.0 and with scan rate 50 mV/s. These CVs were obtained in phosphate buffer (20.0 mL; 0.25 M) at pH = 11.0 and with scan rate 50 mV/s.

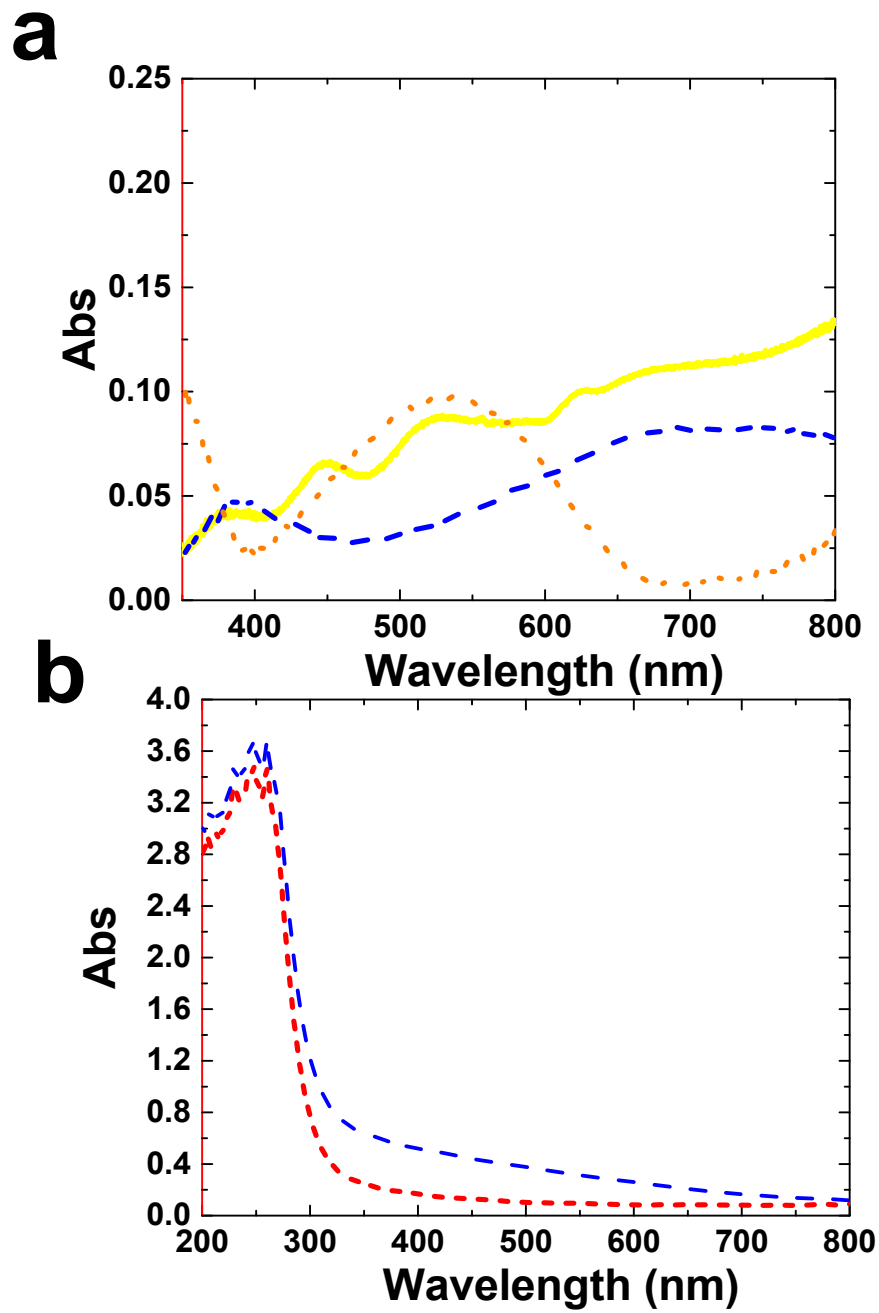


Figure S2 | UV-visible spectra. UV-visible spectra for NiOOH (blue), NiO (orange) and NiOOH (yellow) after a few hours (a). UV-visible spectra for FTO (red) and FTO-1 (blue) (b).

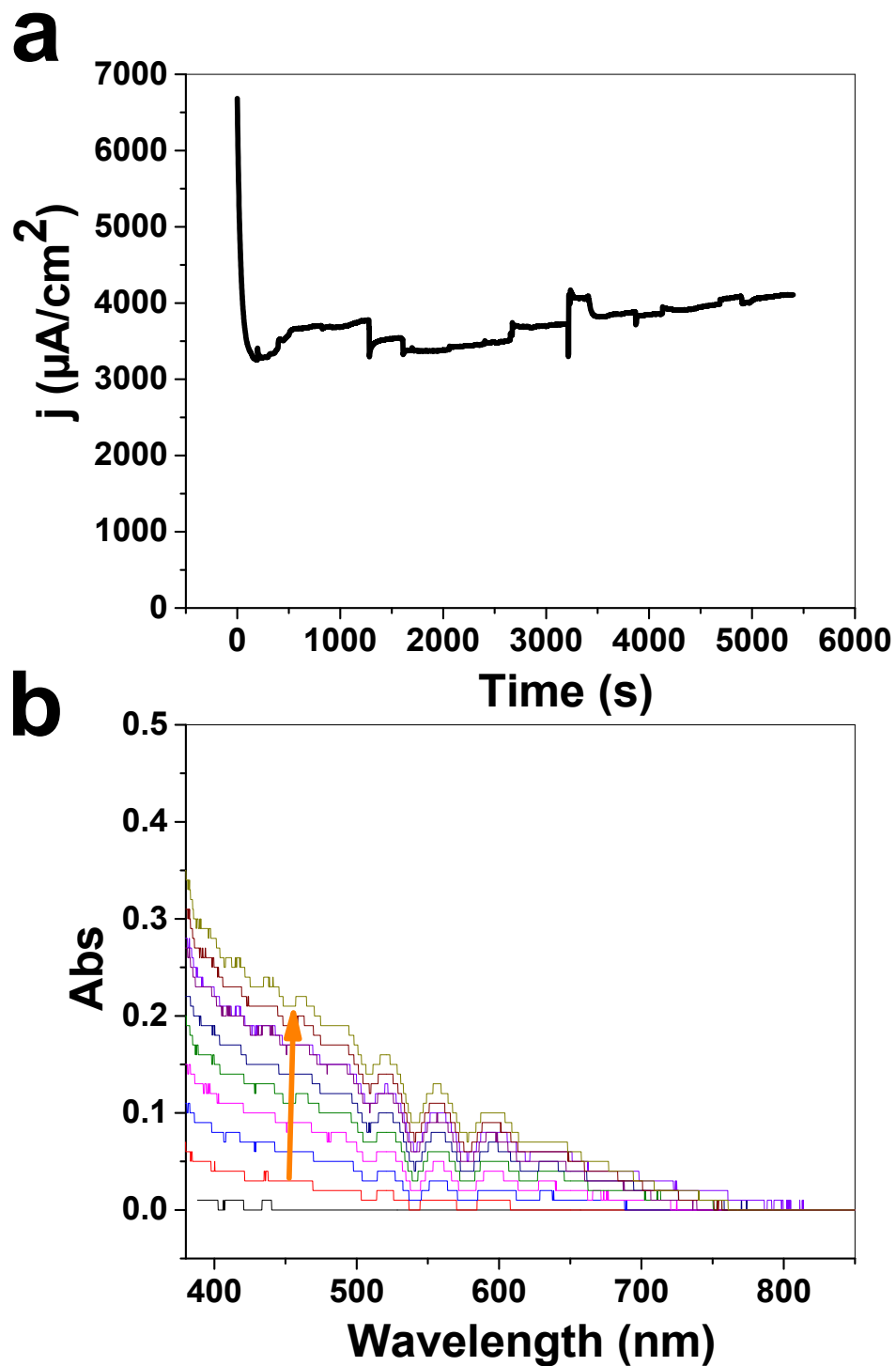


Figure S3 | spectroelectrochemistry. Spectroelectrochemistry in the presence of $\text{Ni}(\text{ClO}_4)_2$ (saturated) in phosphate buffer (5.0 mL; 0.25 M) at pH = 11 (amperometric condition: 1.6 V) after 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 113 minutes.

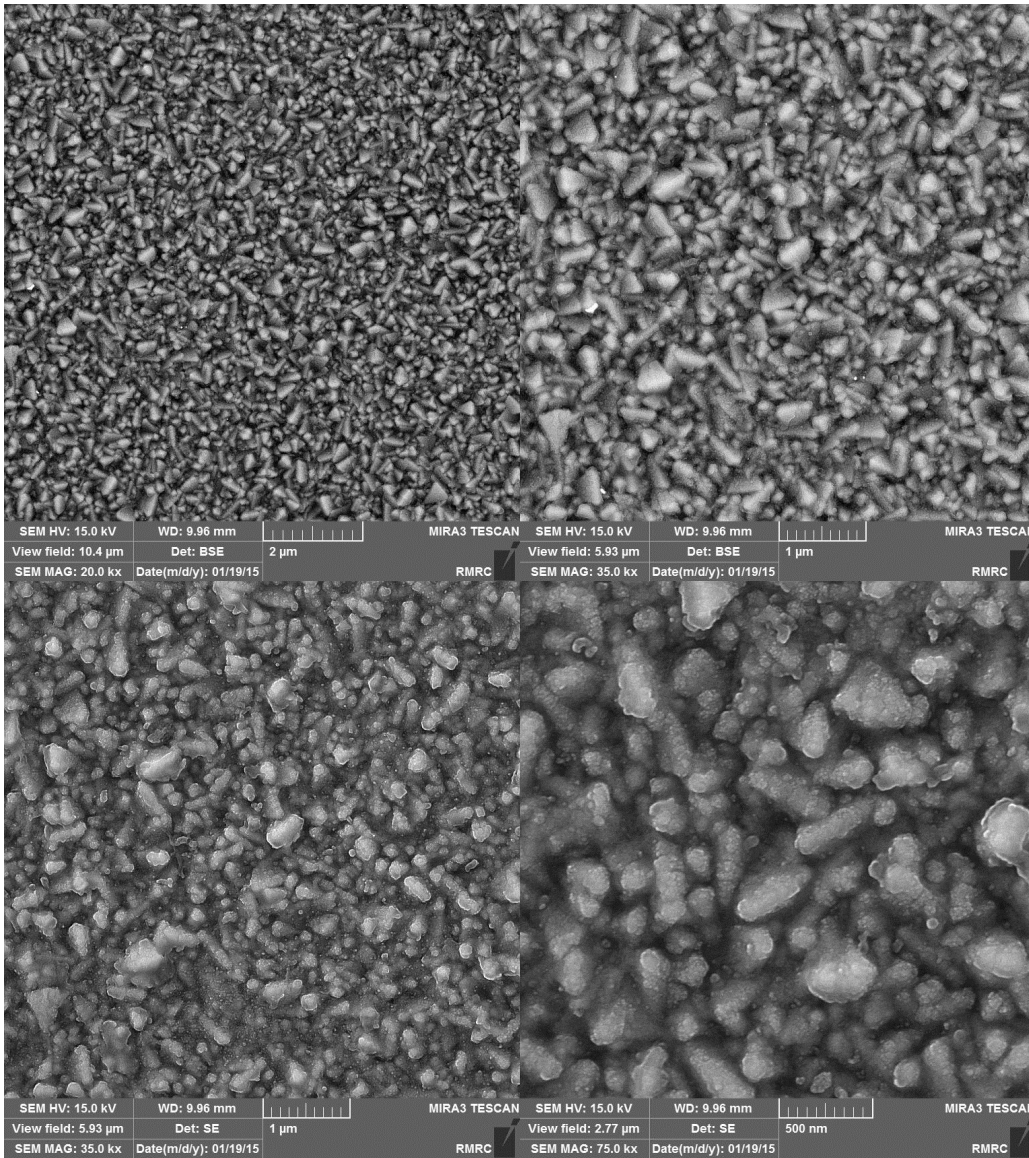


Figure S4 | The SEM images. SEM images of fresh FTO.

Liquid chromatography-electrospray ionization- mass (LC-ESI)

LC condition :

Column: Eclipse XDB-C18(4.6 x150 mm , 5µm)

Column temperature : 25°C

Mobile phase : A= Water +0.1% acetic acid

B= methanol

Gradient

Time(min e)	B%	Flo w
0	5	0.3
25	60	0.3
40	10	0.3
	0	

Flow rate: 0.3 ml/min

Injection volumes: 10µL

MS condition :

Mode : positive ESI using the Agilent G6410 Triple Quadrapole Mass spectrometer

Nebulizer : 15 psi

Drying gas flow : 6 ml/min

V capillary : 4500V

Drying gas temperature: 300°C

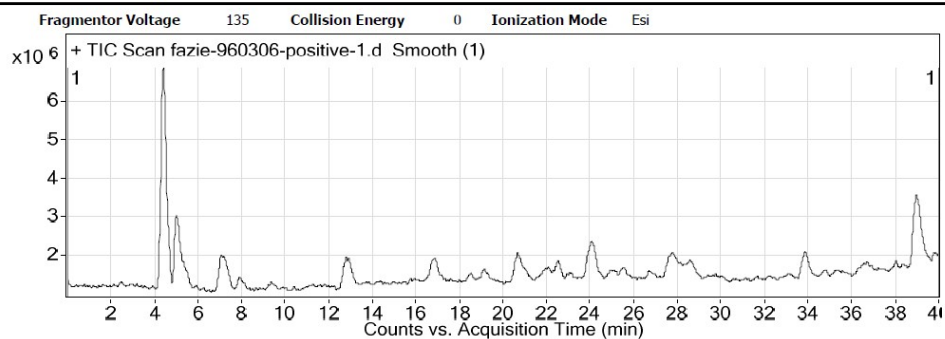
Dwell time: 500msec

Fragmentor : 135 v

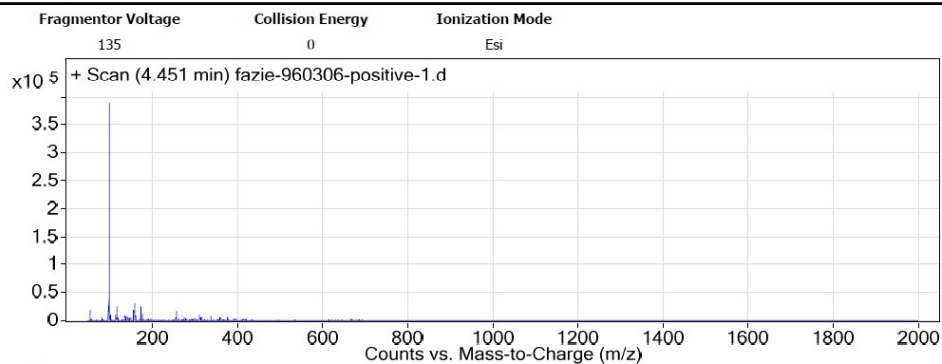
Qualitative Analysis Report

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Sample Type	Sample	Position	Vial 1
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	Success
DA Method	Default.m	Comment	

User Chromatograms



User Spectra

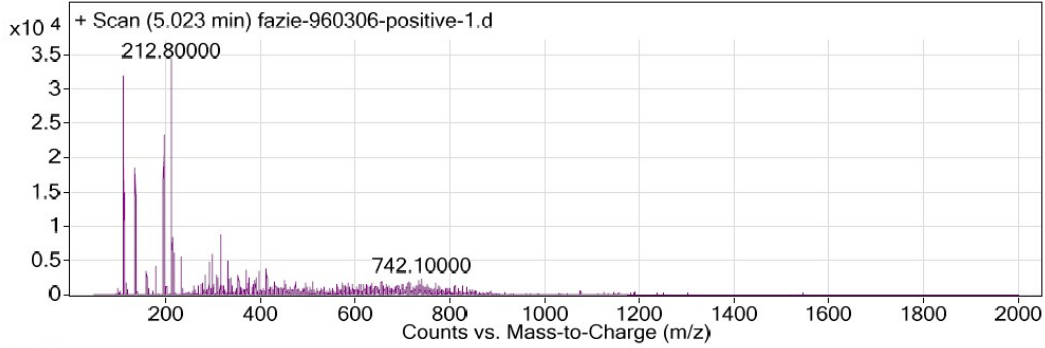


Peak List

m/z	Abund.
54.9	19567
98.9	388070
117	24638
159	31137
175	26207

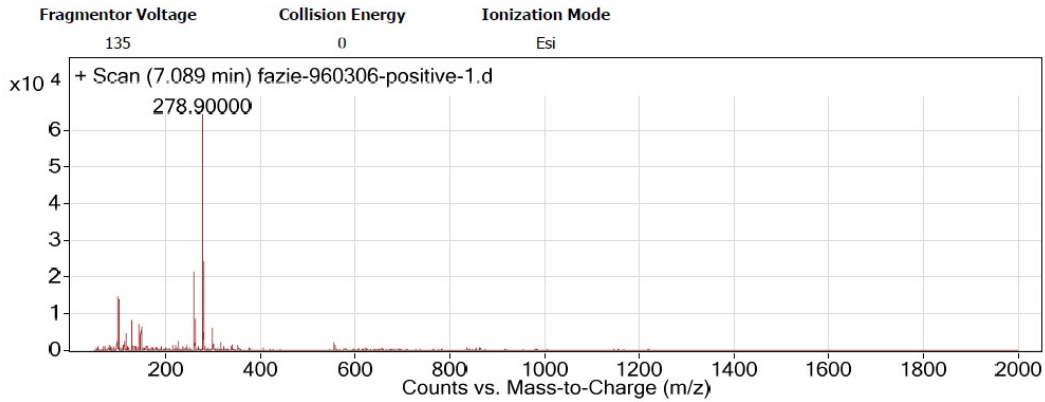
Fragmentor Voltage 135 Collision Energy 0 Ionization Mode Esi

Qualitative Analysis Report



Peak List

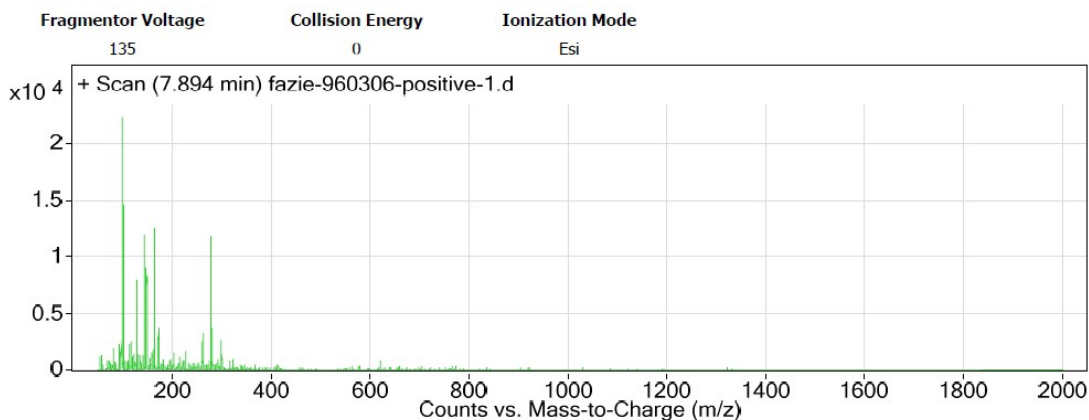
m/z	Abund.
112.9	31964
114.9	15020
136.9	18490
196.9	23428
212.8	35361
214.8	8490
218.9	6176
234.8	5618
300.9	5883
316.8	8884



Peak List

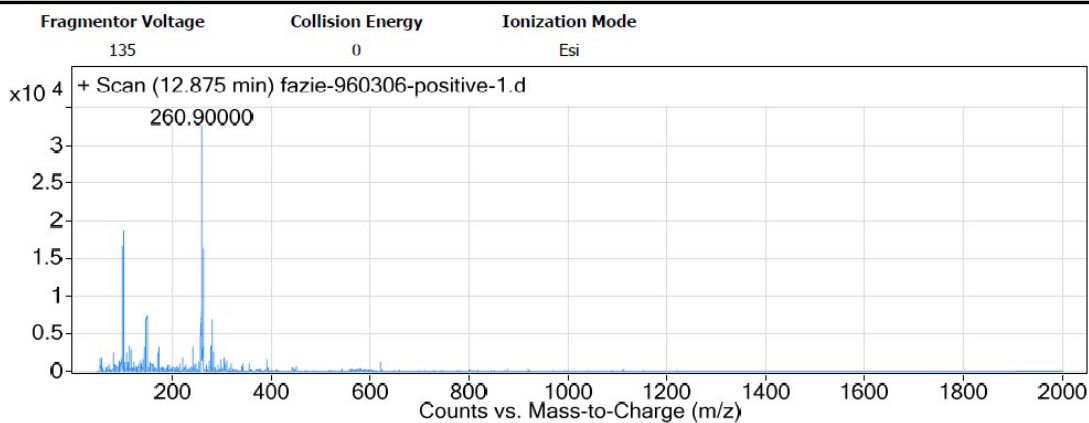
m/z	z	Abund.
98.9		14645
102.1		14137
130.2		8272
145		7150
149.1		6433
260.9	1	21560
262.9	1	8630
278.9	1	66152
279.9	1	7495
280.9	1	24498

Qualitative Analysis Report



Peak List

m/z	z	Abund.
99		22279
102.1	1	14539
130	1	7932
145		11981
147		8996
148		7910
149		8327
165.1		12549
279		11875
280.8		3773

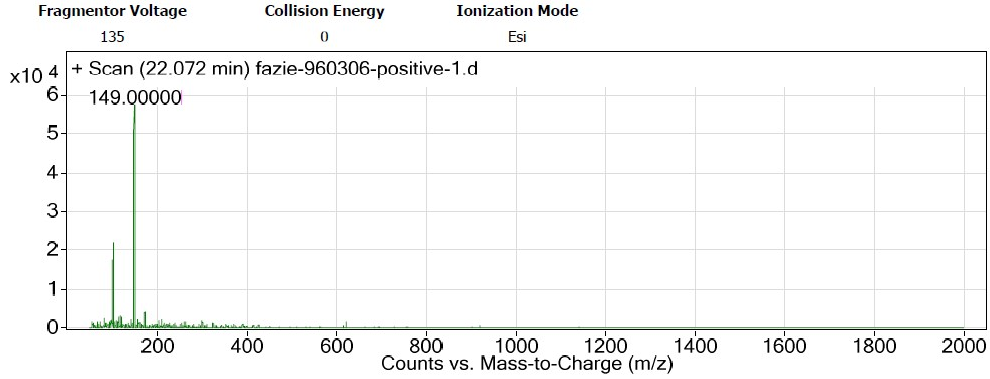


Peak List

m/z	z	Abund.
99	1	16694
102.1		18767
114.9		3399
149		7434
259.9		28123
260.9		33521
261.9		18676
263		16393
277.8		3367

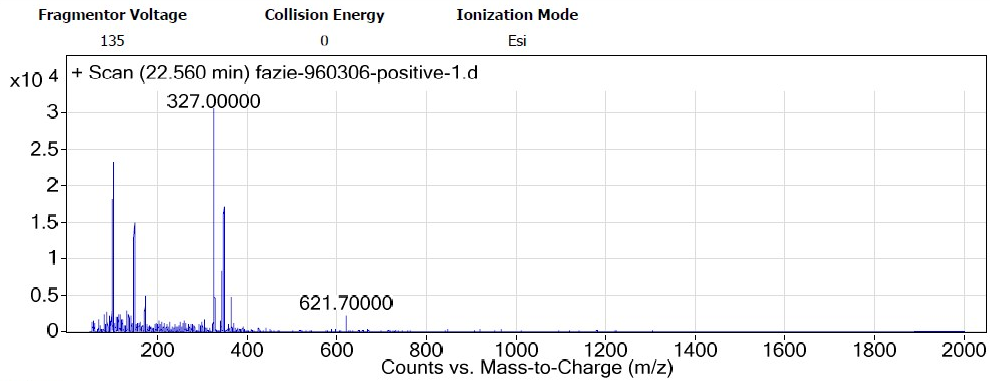
Qualitative Analysis Report

m/z	Abund.
278	15564
283	34278
284.2	5415
284.9	5469
305	17653



Peak List

m/z	Abund.
99	17639
102.1	22062
118	3260
149	59026
150.1	6592
172.9	4082

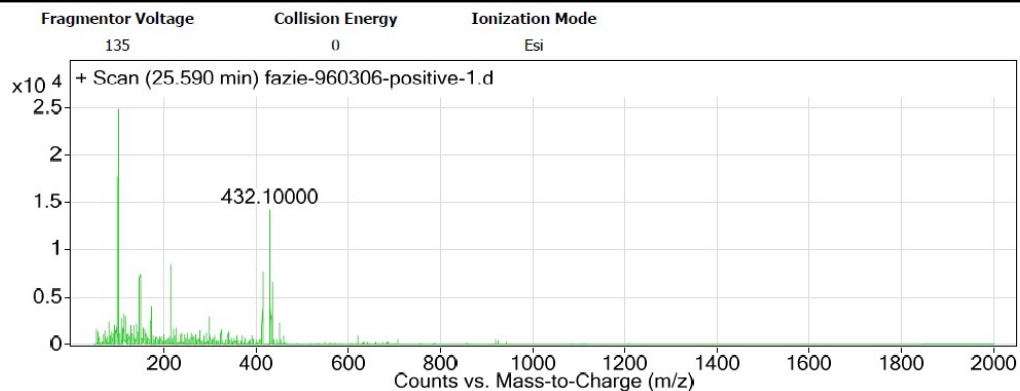


Peak List

m/z	z	Abund.
99		18182
102.1		23201
102.9		3303
149	1	14897
173.1		4874
327	1	31320
328	1	4697

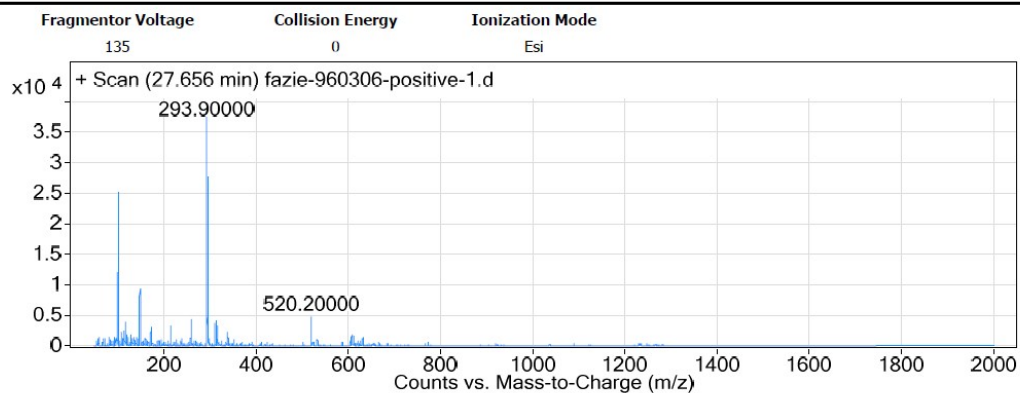
Qualitative Analysis Report

<i>m/z</i>	<i>z</i>	Abund.
173		4893
215		2937
217.2		13981
262.1		3216
340.1	1	8038



Peak List

<i>m/z</i>	<i>z</i>	Abund.
98.9	1	17666
102.1		24780
114.1		3188
149		7338
173.1		3970
217.1		8477
415		7592
432.1		14170
432.9		3140
437.1	1	6532

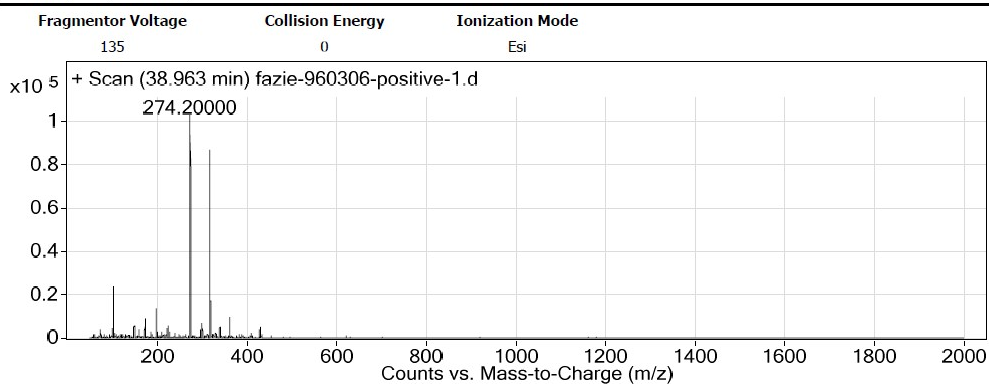


Peak List

<i>m/z</i>	Abund.
98.9	12000
102.1	25130
149	9331

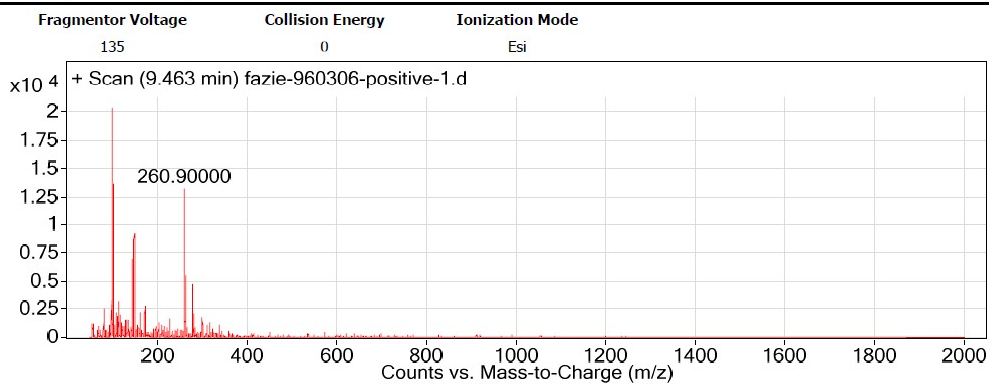
Qualitative Analysis Report

<i>m/z</i>	<i>z</i>	Abund.
98.9		13140
102.1		28043
149		8531
171.1	1	72357
172.1	1	9221
173.1	1	6262
193.1		11686
219.1		5168
264.2		4266



Peak List

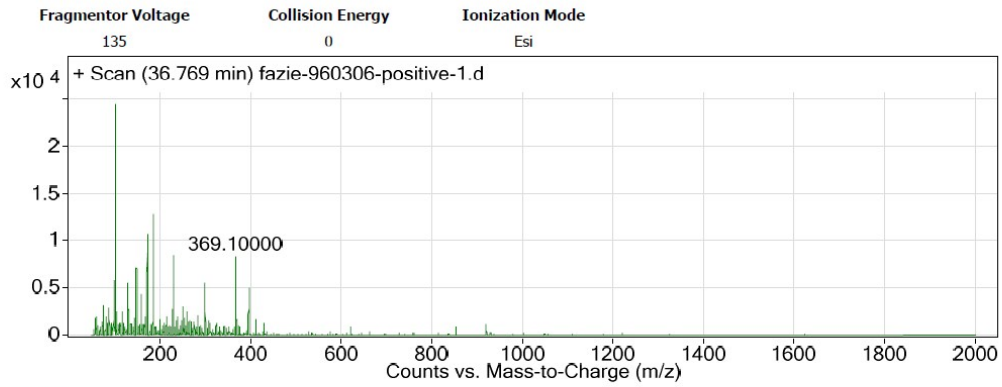
<i>m/z</i>	<i>z</i>	Abund.
102.1		24209
173.1		9372
199.1		13787
225		5963
274.2		105503
275.1		18461
301.1		6589
318.2	1	86649
319.2	1	17388
362.1		9625



Qualitative Analysis Report

Peak List

<i>m/z</i>	<i>z</i>	Abund.
99		20350
102	1	13631
115		3218
145		6994
149		9253
173		2785
260.9		13222
262.1		2698
262.9		5485
278.9		4726



Peak List

<i>m/z</i>	<i>z</i>	Abund.
98.9		5809
102.1		24434
129.1		5492
148.9		7119
173		10675
187.1		12818
231.1	1	8517
300.9		5502
369.1		8281
397.1		4987

--- End Of Report ---

LC condition :

Column: Eclipse XDB-C18(4.6 x150 mm , 5µm)
Column temperature : 25°C
Mobile phase : A= Water +0.1% acetic acid
B= methanol
Gradient

Time(min e)	B%	Flow
0	20	0.3
20	60	0.3
35	10	0.3
25	10	0.3

Flow rate: 0.3 ml/min
Injection volumes: 10µL

MS condition :

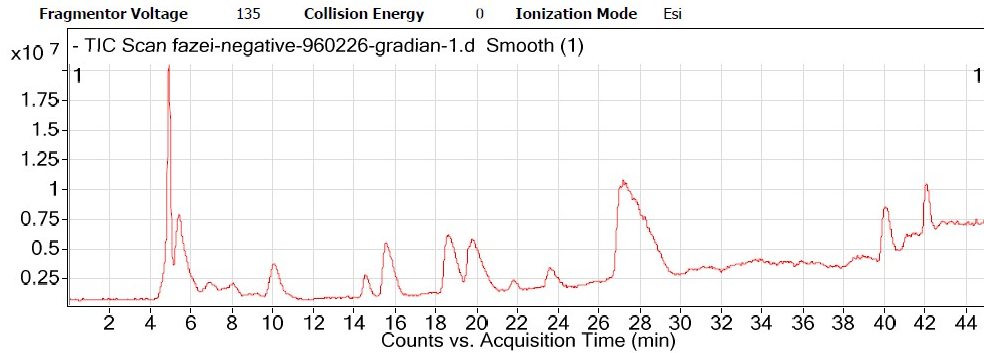
Mode : negative ESI using the Agilent G6410 Triple Quadrapole Mass spectrometer

Nebulizer : 15 psi
Drying gas flow : 6 ml/min
V capillary : 4500V
Drying gas temperature: 300°C
Dwell time: 500msec
Fragmentor : 135 v

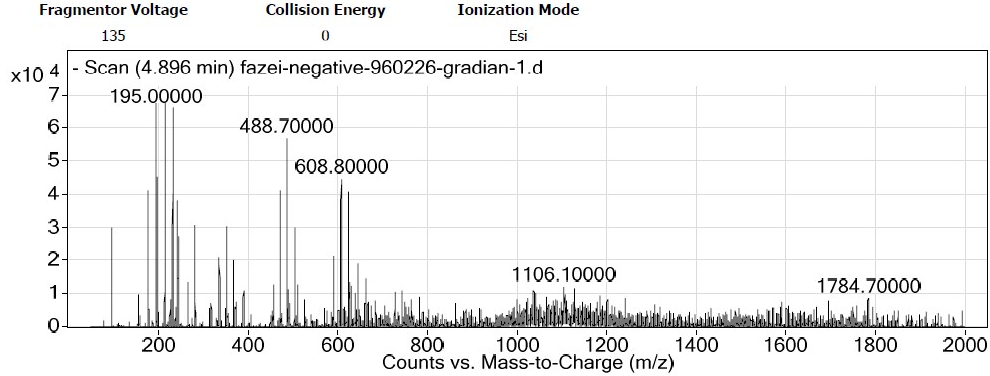
Qualitative Analysis Report

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Sample Type	Sample	Position	Vial 1
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	Success
DA Method	Default.m	Comment	

User Chromatograms



User Spectra

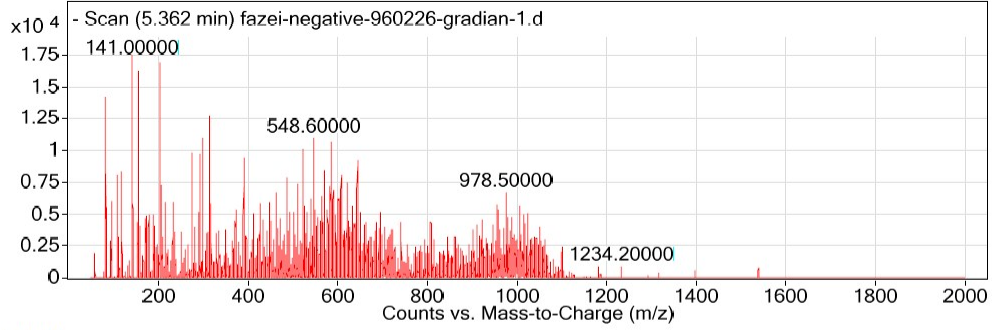


Peak List

m/z	Abund.
177	41269
195	69024
199	45363
216.9	68550
233	66279
244	38171
472.8	41057
488.7	56869
608.8	44566
624.7	40556

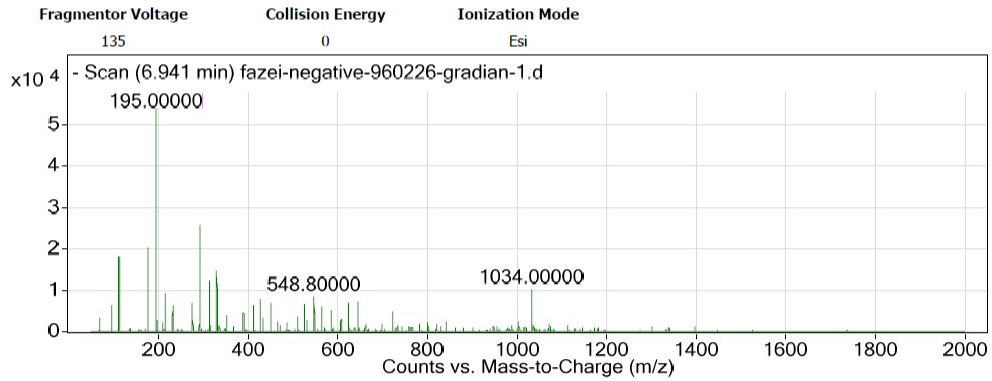
Fragmentor Voltage: 135 Collision Energy: 0 Ionization Mode: Esi

Qualitative Analysis Report



Peak List

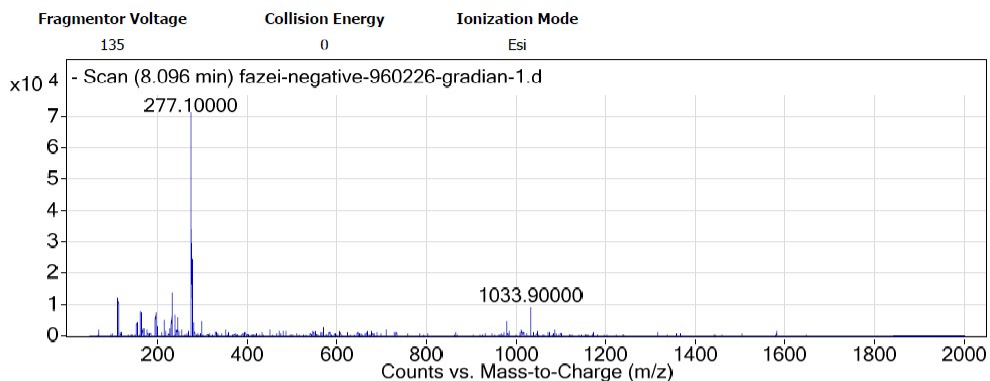
m/z	Abund.
82.9	14169
141	17945
157	16248
205	16916
276.8	9832
299	10952
314.9	12726
524.7	10088
548.6	10977
586.7	10717



Peak List

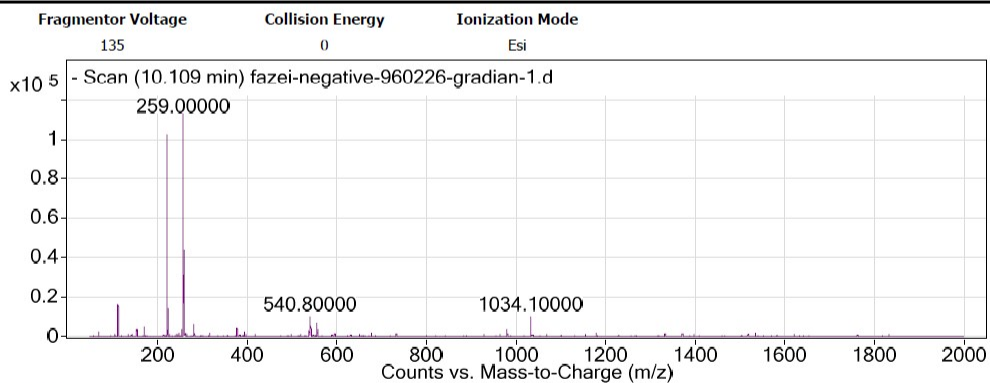
m/z	Abund.
113.1	17968
177	20356
195	55291
216.9	9129
292.8	25744
314.9	12153
330.9	14564
428.8	7771
548.8	8435
1034	10038

Qualitative Analysis Report



Peak List

m/z	z	Abund.
112.9		12107
162.8		7694
165		7589
196.9		7359
233		13691
241		6773
277.1	1	72870
278.1	1	6891
279		24530
1033.9		9135

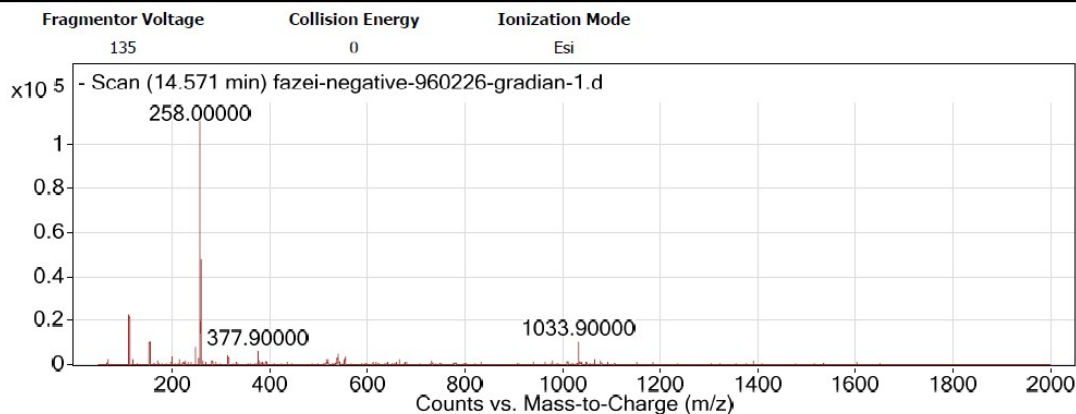


Peak List

m/z	z	Abund.
113.1		16045
223		102225
223.9		14320
224.9		9045
258		65256
259	1	115924
260	1	43745
261.1		43957
540.8		10154

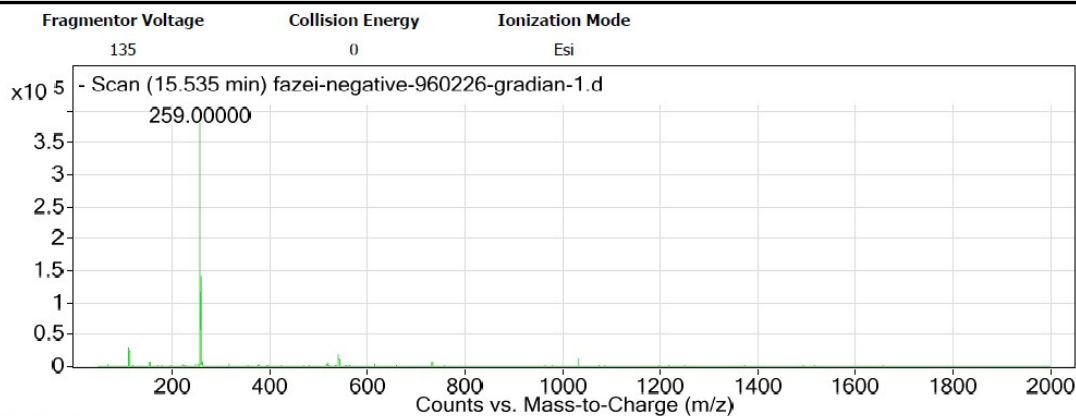
Qualitative Analysis Report

m/z	z	Abund.
1034.1		9757



Peak List

m/z	Abund.
113.1	22669
155	10174
248.7	8110
258	113093
259.1	56953
260	47545
261.1	19556
377.9	6060
1033.9	10659

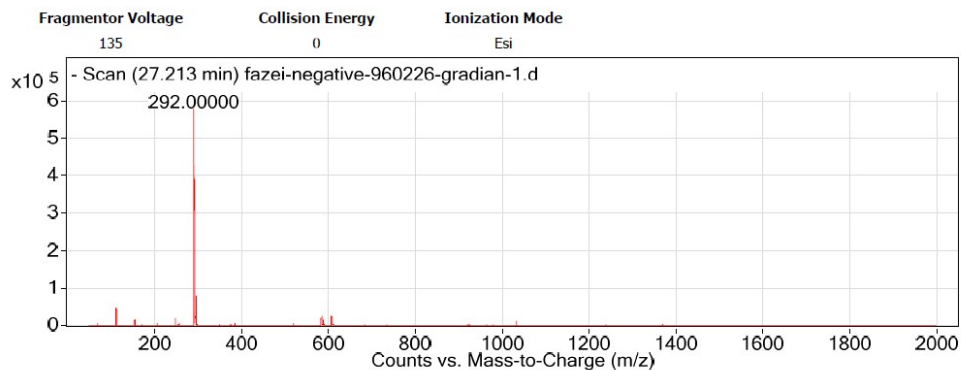


Peak List

m/z	Abund.
112.9	29520
259	390402
259.9	38588
261	142334

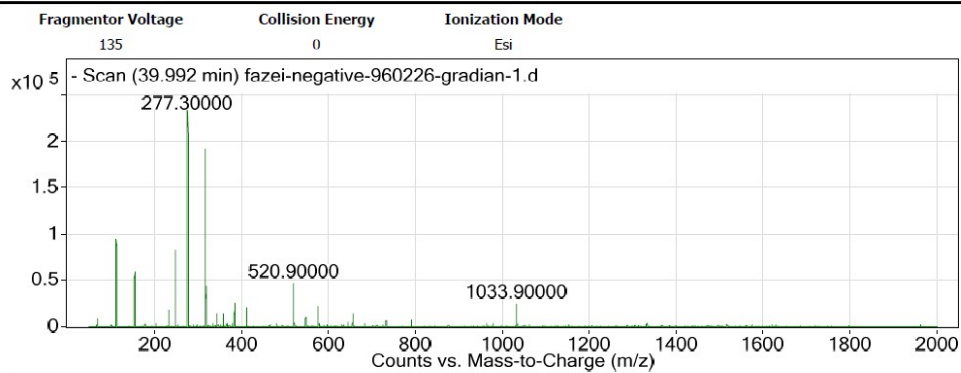
Fragmentor Voltage: 135 Collision Energy: 0 Ionization Mode: Esi

Qualitative Analysis Report



Peak List

m/z	Abund.
113	48113
292	592630
293.1	58964
294	391822
294.9	41253
295.9	78613

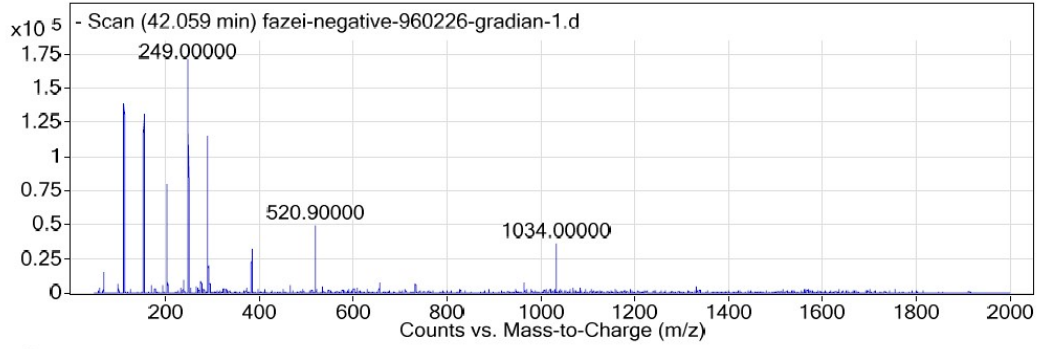


Peak List

m/z	Abund.
113.1	94449
155.1	59152
248.9	83113
277.3	239451
278.2	44844
318.3	192262
319.4	43788
385	25701
520.9	46814
1033.9	24355

Fragmentor Voltage: 135 Collision Energy: 0 Ionization Mode: Esi

Qualitative Analysis Report



Peak List

m/z	Abund.
111.1	26985
113.1	138456
155.1	130856
205.2	79390
249	175415
250.2	160614
291.2	114963
385.1	32258
520.9	49429
1034	36334

--- End Of Report ---