59th ASMS Conference on Mass Spectrometry, Denver, CO, June 5-9, 2011

Combined ESI/LIFDI-Ion Source for a FT-ICR Mass Spectrometer

TP 056

Jürgen H. Gross [1], H. Bernhard Linden [2]

[1] Institute of Organic Chemistry, Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.
[2] Linden CMS, Auf dem Berge 25, 28844 Leeste, Germany.

Linden CMS

Concept of the Bruker Dual Source MTP

The Dual Source MTP™ available with Bruker ApexQe FT-ICR mass spectrometers simultaneously handles ions entering via the electrospray interface and ions emerging from the (MA)LDI target. ESI ions are deflected into an ion funnel while those from MALDI are traveling on-axis. Other ionization sources may be attached after removal of the MALDI assembly from the ion source housing.

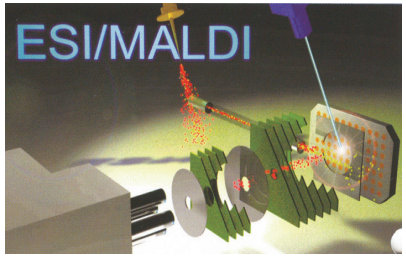
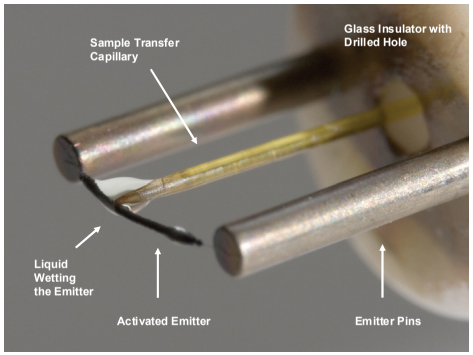


Illustration of the working principle of the Dual Source MTP accepting ions from two different points of origin at the same time. Scheme courtesy of Bruker Daltonik, Bremen.

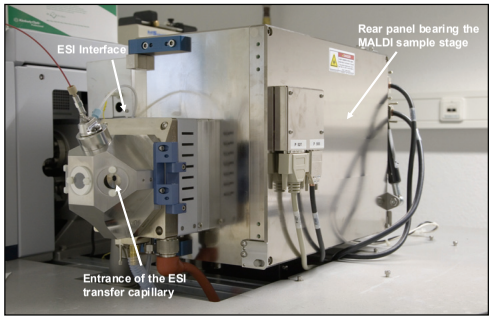
Advantages of LIFDI

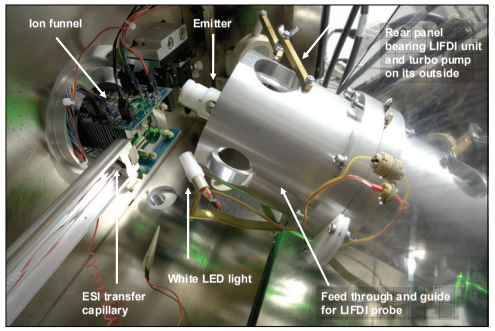


Liquid injection field desorption/ionization (LIFDI) ideally complements ESI to ionize nonpolar analytes. Additionally, LIFDI handles compounds sensitive to oxidation or hydrolysis by providing sample supply under inert conditions [1,2].
As LIFDI has proven capabilities on our sector instrument and on FT-ICR instrumentation elsewhere [3,4], it appeared promising to adapt a LIFDI source to a hybrid quadrupole-FT-ICR instrument such as the Bruker ApexQe.

In LIFDI the sample transfer capillary delivers the analyte in solution directly onto the emitter positioned in the high vacuum of the ion source. The capillary is fed through a drilled hole in the glass insulator bearing the emitter-holding metal pins. The liquid bridges the narrow gap between the end of the capillary and the activated emitter, and thus, prevents it from mechanical damage. The photograph shows solvent wetting the emitter.

Mounting of a LIFDI Unit



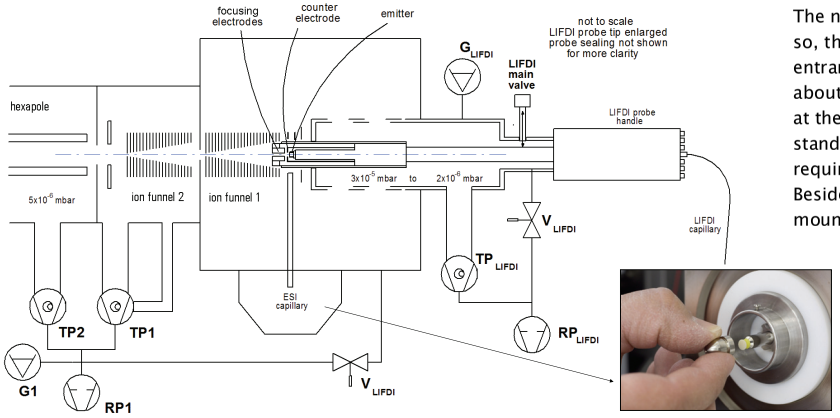


The Dual Source MTP of the Bruker ApexQe FT-ICR mass spectrometer in our lab is capable of simultaneously collecting ions from both ESI interface and MALDI sample plate. This is achieved by an ion funnel operated under rough vacuum of 1.8 mbar. After removal of the housing's rear panel this position is open to accept any other ion source. The prototype LIFDI unit attached to the ApexQe replaces the rear panel of the the ion source housing. The LIFDI probe is aligned as to position the emitter axially into the ion funnel entrance.
After closing the entrance of the ESI transfer capillary with a septum the pressure inside the ion source housing drops to about 8 x10^{-3} mbar by the action of the rotary pump alone. Adding a turbomolecular pump (260 l s^{-1}) to the housing delivers high vacuum of 3 x 10^{-5} mbar.

Upper photograph: Standard configuration of the Dual Source MTP. The rear panel with the entire MALDI unit is replaced by the LIFDI unit. Both cable connections are extended to avoid errors of the data system.

Lower photograph: Open source housing with the LIFDI unit attached. After closing the rear panel the LIFDI probe can further be inserted until the tip is located between the first electrodes of the ion funnel. The emitter is illuminated by a white LED light to enable observation of sample transfer by a video camera.

Construction and Operation of the ESI/LIFDI Combination Source



The new ESI/LIFDI combination ion source can readily be switched to ESI operation. To do so, the turbomolecular pump is switched off, the LIFDI probe is retracted by 1 cm and the entrance of the ESI transfer capillary is opened. ESI spectra may then be acquired after about 2 min vacuum adjustment time. The electrostatic charging of the focusing electrodes at the LIFDI probe's tip serves to deflect ions into the ion funnel and thereby replaces the standard deflection electrode. Switching between positive-ion and negative-ion mode requires about 15 s due to the time required for proper charging of these electrodes. Besides that, there is no noteworthy difference between ESI operation with the LIFDI unit mounted and ESI with the standard configuration of the Dual Source MTP.

Schematic of the LIFDI unit mounted to the ion source housing of the ApexQe instrument. The emitter is positioned in the high vacuum of the ion source housing between the first electrodes of the ion funnel. The additional turbomolecular pump is mounted to the rear panel and evacuates the ion source housing.

Sealing of the ESI transfer capillary is achieved by a septum on its entrance (inserted photograph).

This is the first ESI/LIFDI combination ion source: a prototype developed for a Bruker ApexQe instruments featuring an ion funnel.

Acknowledgment

The Deutsche Forschungsgemeinschaft (DFG) and SFB 623 are acknowledged for funding the FT-ICR instrument and Deutscher Akademischer Austausch-dienst (DAAD) for a travel grant to J. H. G.
We are indebted to Prof. W. Krätschmer for a sample of C_{60}, to Prof. U. Bunz for 3,4,5-tridodecyloxy-benzaldehyde, to Dr. S. Weidner for polystyrenes, and to N. Nieth for measuring reference spectra on our JMS 700 sector instrument.
We thank Bruker Daltonik, Bremen, for assistance with parts of the ion source housing and helpful discussions.

Handouts for Download

Handouts of this poster in PDF format can be downloaded after this ASMS conference at
http://www.linden-cms.de and at
http://www.rzuser.uni-heidelberg.de/~bl5

Experimental

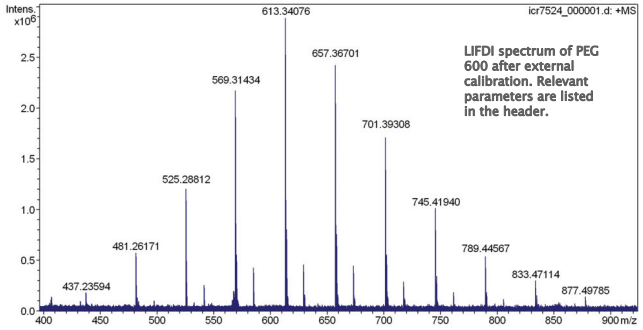
Experiments are performed on a 9.4 T Bruker ApexQe FT-ICR (Qh-ICR hybrid) instrument with Dual Source MTP (ESI-to-MALDI switchable). The standard MALDI sample stage and the deflection electrode at the entrance of the ion funnel are replaced by the LIFDI unit comprising vacuum lock, probe, turbomolecular pump, observation optics, and vacuum gauge. For ESI operation, the LIFDI probe is retracted and its focusing electrodes are used to deflect ions into the funnel. In LIFDI mode, the ESI transfer capillary is sealed by a septum to achieve $< 4 \times 10^{-5}$ mbar. LIFDI spectra are acquired at emission-controlled ion currents of 4×10^{-8} mA.

Typically, ions are accumulated for 1-5 s per transient and then transferred into the ICR cell. 16-64 transients with 1 M data points are acquired in positive-ion broadband mode. The time-domain data are zero-filled and apodized by a sine-bell function prior to Fourier transformation to deliver a magnitude spectrum.

Acquisition is controlled by Bruker ApexControl 3.0.0 software, data analysis is performed using the Bruker DataAnalysis 4.0 software.

Tuning of the LIFDI source is achieved using the persistent cation signal of trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl)-trifluorophosphate, an ionic liquid [5]. Thus, the potentials for ion transfer from the field emitter through the ion funnel into the hQh-interface are adjusted. Polyethylene glycol 600 (below) and PEG1500 are used for external mass calibration to assure mass accuracies of 1 ppm in ESI and LIFDI modes of operation.

Comment PEG 600 1mg/ml in MeOH 1x3s, funnel 15V, skimmer 14V QhTrap, TICmax 4x10-8 LIFDI, TMP260 <3x10-5 mbar, 25 V Emitter HVmax, -5.5 Ablenk, 26mm, 3s Akkum., HexRF 250, FuRF 200 V, Qh optimiert 12,12,12 und Gas 0.90 l



Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
481.26171	C 20 H 42 Na O 11	481.26193	0.2	0.5	23.8	-0.5	ok	even
525.28812	C 22 H 46 Na O 12	525.28815	0.0	0.1	27.4	-0.5	ok	even
569.31434	C 24 H 50 Na O 13	569.31436	0.0	0.0	11.2	-0.5	ok	even
613.34076	C 26 H 54 Na O 14	613.34058	-0.2	-0.3	11.7	-0.5	ok	even
657.36701	C 28 H 58 Na O 15	657.36679	-0.2	-0.3	10.4	-0.5	ok	even
701.39308	C 30 H 62 Na O 16	701.39301	-0.1	-0.1	11.2	-0.5	ok	even
745.41940	C 32 H 66 Na O 17	745.41922	-0.2	-0.2	14.7	-0.5	ok	even
789.44567	C 34 H 70 Na O 18	789.44544	-0.2	-0.3	58.4	-0.5	ok	even
	C 61 H 57	789.44548	-0.2	-0.2	175.2	33.5	ok	even

References

[1] Linden, H.B. Liquid Injection Field Desorption Ionization: a New Tool for Soft Ionization of Samples Including Air-Sensitive Catalysts and Non-Polar Hydrocarbons. *Eur. J. Mass Spectrom.* 2004, *10*, 459-468.

[2] Gross, J.H.; Nieth, N.; Linden, H.B.; Blumbach, U.; Richter, F.J.; Tauchert, M.E.; Tompers, R.; Hofmann, P. Liquid Injection Field Desorption/Ionization of Reactive Transition Metal Complexes. *Anal. Bioanal. Chem.* 2006, *386*, 52-58.

[3] Schaub, T.M.; Rodgers, R.P.; Marshall, A.G.; Qian, K.; Green, L.A.; Olmstead, W.N. Speciation of Aromatics in Petroleum Refinery Streams by Continuous Flow FD-FT-ICR Mass Spectrometry. *Energy & Fuels* 2005, *19*, 1566-1573.

[4] Schaub, T.M.; Hendrickson, C.L.; Quinn, J.P.; Rodgers, R.P.; Marshall, A.G. Instrumentation and Method for Ultrahigh Resolution FD-FT-ICR-MS of Nonpolar Species. *Anal. Chem.* 2005, *77*, 1317-1324.

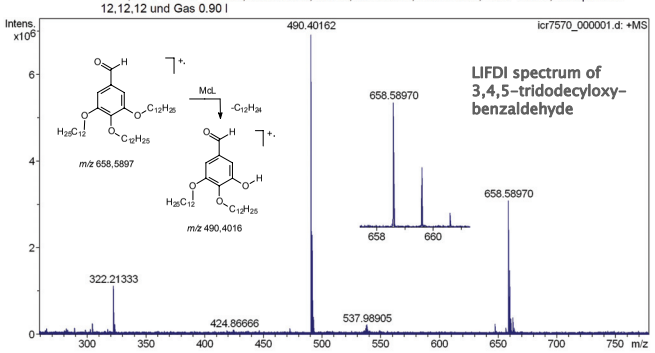
[5] Gross, J.H. Liquid Injection Field Desorption/Ionization Mass Spectrometry of Ionic Liquids. *J. Am. Chem. Soc. Mass Spectrom.* 2007, *18*, 2254-2262.

Applications of the New ESI/LIFDI Combination Source

LIFDI spectra of different compounds are obtained exhibiting good intensity when closed-shell ions such as $[cation]^+$, $[M+H]^+$ or $[M+Na]^+$ are formed. As usual in FD-MS, nonpolar analytes preferably deliver open-shell molecular ions, $M^{+\bullet}$, more readily undergoing radical-induced dissociations. Therefore, spectra of nonpolar compounds are still somewhat unsatisfactory due to reduced ion abundance and increased fragmentation. Presumably, the peculiarities of the ion optics and its specific pressure regimes are causing these molecular ion losses. While the overall transmission increases at higher pressure, collision-induced fragmentation in the ion funnel region and in the hexapole accumulation ion trap cause losses by dissociation (cf. [4, p. 1321]). Techniques and parameters for improvement are being explored.

Analysis Name M:\Data\LIFDI\icr7570_000001.d

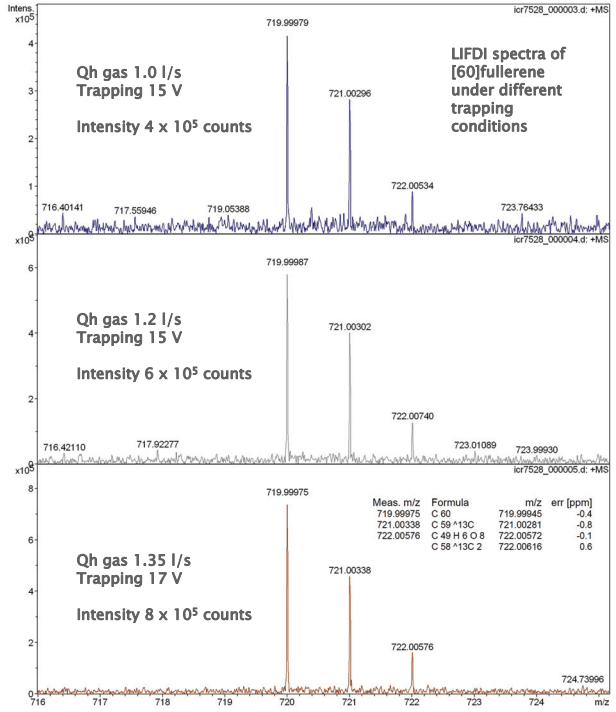
Comment Bunz 1 1mg/ml in THF 2x3s, funnel 15V, skimmer 14V QhTrap, TICmax 4x10-8 LIFDI, TMP260 <3x10-5 mbar, 25 V Emitter HVmax, -5.5 Ablenk, 26mm, 3s Akkum., HexRF 250, FuRF 200 V, Qh optimiert 12,12,12 und Gas 0.90 l



Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
322.21333	C 19 H 30 O 4	322.21386	0.5	1.7	17.9	5.0	ok	odd
490.40162	C 31 H 54 O 4	490.40166	0.0	0.1	6.1	5.0	ok	odd
658.58970	C 43 H 78 O 4	658.58946	-0.2	-0.4	10.4	5.0	ok	odd
	C 44 H 74 N 4	658.59080	1.1	1.7	15.7	10.0	ok	odd

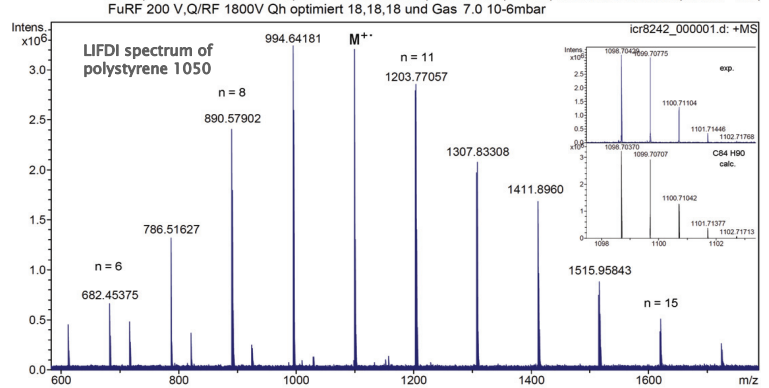
File Name M:\Data\LIFDI\icr7528_000003.d Instrument ICR Apex-Qe

Comment C60 <0.05mg/ml in Toluol 6x3s, funnel 15V, skimmer 14V QhTrap, TICmax 4x10-8 LIFDI, TMP260 <3x10-5 mbar. 25 V Emitter HVmax, -5.5 Ablenk, 26mm, 3s Akkum., HexRF 250, FuRF 200 V, Qh optimiert 15,15,15 und Gas1.0 l



Analysis Name M:\Data\LIFDI\icr8242_000001.d Acquisition Date 12.05.2011 09:56:04

Comment PS1050 aus Toluol, 0.2 mg/ml 2x4s mit 75umKap., funnel 15V, skimmer 14V QhTrap, TICmax 4x10-8 LIFDI, TMP260 <5x10-5 mbar, 25 V Emitter HVmax, -5.5 Ablenk, 26mm, 0.01 und 5s Akkum., HexRF 500, FuRF 200 V,Q/RF 1800V Qh optimiert 18,18,18 und Gas 7.0 10-6mbar



Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
612.37531	C 47 H 48	612.37505	-0.3	-0.4	39.2	24.0	ok	odd
682.45375	C 52 H 58	682.45330	-0.4	-0.7	27.8	24.0	ok	odd
716.43799	C 55 H 56	716.43765	-0.3	-0.5	18.5	28.0	ok	odd
786.51627	C 60 H 66	786.51590	-0.4	-0.5	3.7	28.0	ok	odd
820.50068	C 63 H 64	820.50025	-0.4	-0.5	33.1	32.0	ok	odd
890.57902	C 68 H 74	890.57850	-0.5	-0.6	12.5	32.0	ok	odd
924.56351	C 71 H 72	924.56285	-0.7	-0.7	55.9	36.0	ok	odd
994.64181	C 76 H 82	994.64110	-0.7	-0.7	13.9	36.0	ok	odd
1098.70429	C 84 H 90	1098.70370	-0.6	-0.5	18.1	40.0	ok	odd

Final Statements

- LIFDI spectra of polar and ionic compounds are readily obtained.
- LIFDI spectra of nonpolar aromatic hydrocarbons exhibit intense molecular ions.
- Mass accuracy is equal to ESI mode.
- Source can easily be switched back and forth between ESI and LIFDI operation.
- The first ESI-to-LIFDI switchable combination ion source is presented as a working prototype.
- Collisions during thermalization and trapping probably prevent labile molecular ions from surviving.
- The transmission of the ion funnel can be reduced upon evacuation from 1.8 mbar standard pressure to less than 10^{-4} mbar.
- Molecular ions of aliphatic hydrocarbons have not yet been observed.