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Investigation of the Dynamics within the Selexion DMS Cell with regard to the influence of Charged Aspirated Droplets /-Fragments

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Introduction	Instrumentation
Electrospray ionization (ESI) is the most important atmospheric pressure ionization (API) method due to its alleged property of soft ionization [1]. Recent experiments have demonstrated that charged droplets from ESI are aspirated into mass spectrometers (MS) and can pass through the vacuum stages of the instruments, causing adverse effects [2,3]. Differential ion mobility spectrometry (DMS) adds an additional separation dimension based on differential ion mobility under high- and low-field conditions. Field-dependent cluster-decluster reactions, induced by gas-phase modifiers, are one mportant mechanism leading to differential mobilities [4]. A DMS stage allows to probe the presence of aspirated droplets and their chemical characteristics atmospheric pressure, upstream to the MS vacuum system.	 1.Analyte Thermometer lons (5 μM) 2. LC-System Agilent 1200 series Isocratic Pump, G1310A 3. Solvents Acetonitrile, ≥ 99.8 % HPLC (Fisher scientific) 2-Propanol, ≥ 99.5% HPLC (Fisher scientific) Formic acid, ≥ 98 % Generation of the utilized Triple Quad 6500 System (Sciex). Using the lonDrive Turbo V ion source with the

Influence of DMS Resolution Enhancement DR



Fig. 2 Total ion intensity signal of CoV scans with vary CE (left: CE 100 V, right: CE 50 V, SV of 4.1 kV, **Droplet-Scan**), showing the effect of increasing the ion residence time in the DMS cell with the addition of a throttle gas flow (DR, open: 0 psi, med: 34 psi, high: 43 psi). From the broad signal without throttle gas (open), two distinct signals emerge with increasing residence time (DR=high), hinting towards the existence of two distinct types of droplets in the DMS cell.

Fig. 3 Mass spectra of the emerged signals at $\frac{2}{3}$ DR = high (43 psi, CE = 100 V, Droplet-Scan). blue: CoV 1-5 V, green: CoV 5-9 V. The light blue shading marks the LMCO. Both spectra show a common general structure but the relative intensities of the droplet



puriss. p.a. (ACS reagent) TurbolonSpray ESI probe and the SelexIon DMS Cell.

Droplet-Scan mode^[2]

Utilized Triple Quad (Fig. 1) operates in high mass mode (m/z = 5 - 2000) Mass selective Quadrupole Q1 is switched to RF-only (high-pass filter) Low mass cut off (LMCO) is approximately at m/z = 1550Only droplets /-fragments with a m/z > LMCO are transmitted to the collision cell Mass analysis is performed with Q3



Fig. 4: Extracted ion signals of CoV scans (lonograms) of thermometer ions (H₂O:ACN:FA; v/v/v; 50+50+0.1) using the **Droplet-** and **Q1-Scan** method (SV = 3.9 kV)

The Q1-scan shows the differential mobility characteristics of the *bare* thermometer ions: the analytes appear at distinct CoV values with similar widths of the individual signals. In contrast, in droplet scan mode all analytes appear at essentially the same CoV values in broad signals with very similar shape.

This strongly suggests, that all analytes can be transported through the DMS cell by the same droplet / cluster system: the large ESI droplets / droplet fragments essentially act as "ferry" for the passage of the analytes through the DMS cell.

Comparison of Q1- and Droplet-Scan

fragment region (m/z > 700) and the bare analyte signals (m/z < 250) differ.

$CoV = 5 V, SV = 4.1 k^{1}$ (., 1.0 (.) 0.8 ntensity 0.4 -0.2 -125 150 CE (V) 1750 500 750 1000 1500 1250 m/zIntensity (a.u.) 2 250 m/z() 1.00 () 1.00 () 0.75 ntensity 0.22 750 1000 250 m/*z*

Collision Energy (CE) Scans

Collision energy (CE) scans in **Droplet-scan** with a SV of 4.1 kV. *left:* CoV 5 V, *right*: CoV 6 V

Upper panels: Total ion intensity and mass spectra of the green shaded sections of the CE scan. The light blue shading in the spectra marks the LMCO.

Lower panel: Extracted analyte signals of the CE scan.

The total ion intensity signals and the mass spectra in dependency of the CE have very different shapes for the two investigated compensation voltages. This indicates that different species of aspirated charged droplets/-fragments pass through the DMS in dependency of the CoV.

The mass spectra clearly show the release of analyte ions from the charged droplets/-fragments and complex signal structures which may stem from large solvent cluster structures.



Impact of Modifier





The extracted ion signals show the release of $\overline{}_{\tau}$ analyte ions at higher CE levels. Remarkably, a very $\overline{\underline{a}}$ different signal structure is observable for the $\frac{1}{2}$ different CoV values, strongly supporting the $\frac{1}{2}$ notion that different droplet/fragment ensembles pass through the DMS cell.

CoV (V)

Fig. 7 Extracted ion signals of a CoV scan using the Q1- and Droplet-Scan with iso-Propanol as gas phase modifier (SV = 4 kV). The Q1-Scan shows a negative CoV shift (cf. Fig. 4) due to molecular cluster formation in *i*-PrOH-modified nitrogen. In contrast, the signals in droplet scan mode are almost not affected by the gas phase modifier.

Conclusion

Comparison of Q1- and droplet-scans reveals that analyte ions embedded into droplets display very different CoV values (Fig. 4) Analyte ions can be transported through the DMS cell within charged droplets

Usage of a Modifier, like *iso*-Propanol, has negligible effect on the > differential mobilities of the charged droplets / droplet fragment system (Fig. 7)

With increased ion residence time in the DMS, a separation of the broad ion signal in two distinct sub-signals is apparent (Fig. 2, 3)

CE scans at different CoVs reveal significantly different characteristics of those sub signals (Fig. 5, 6)

This strongly suggests different types or families of aspirated charged droplets/-fragments pass through the DMS device in dependence of the CoVs

Reference

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