Abstract (EN)

The first part of the thesis describes the ionization reactions in the APCI source in the presence (enclosed configuration) and absence (open configuration) of the ion source housing. Commercial APCI source was modified and used in enclosed, as well as open configuration. All other parameters were kept the same (including the source geometry). In the positive mode, the biggest differences were observed for non-polar analytes dissolved in aprotic solvents like toluene, chloroform and carbon disulfide. Protonated species were dominant in the open configuration, while radical cations were mostly present in the enclosed configuration. The excessive protonation in open ion source was caused by the diffusion of water vapor molecules into the ionization region from the atmosphere. Water vapor molecules were also responsible for the formation of an ion $[M + 19]^+$ from alkynes in the open configuration. The fragmentation study confirmed that the ion $[M + 19]^+$ was a 2-methylketone formed by the addition reaction. The formation of such artifacts can pose problems in qualitative analysis. On the other hand, the ion $[M + 55]^{+\bullet}$ was observed in the enclosed ion source as a reaction product of unsaturated compounds with acetonitrile solvent molecules. Its fragmentation can be used for the double bond determination of the original unsaturated compound. However, the formation of the ion $[M + 55]^{+\bullet}$ was suppressed in the open configuration by atmospheric oxygen. Atmospheric oxygen also suppressed charge transfer reactions in the negative mode in open configuration due to its positive electron affinity. In conclusion, an enclosed configuration was demonstrated to be a better alternative, since the ionization in the enclosed APCI source can be controlled by adding additives into the mobile phase or the nebulizing gas.

The second part of the thesis describes three low-flow APCI sources (for approximately 0.05 – 10.0 μl/min liquid flow rates), namely microchip APCI source, APCI with an open tubular nebulizer, and GDVN-APCI source. The latter two were developed in our laboratories. All three sources were producing a stable signal and were demonstrated to be suitable for direct infusion analysis. Besides, limits of detection of all tested compounds were lower in low-flow APCI sources than in commercial high-flow APCI source. APCI with open tubular nebulizer had the simplest and cheapest construction among all ion sources; however, observed peak tailing and memory effects prevent its use in LC/MS system. On the other hand, microchip APCI source (as demonstrated also in other works) and GDVN-APCI source were suitable for the hyphenation of HPLC with MS.

APCI source with the open tubular nebulizer and microchip APCI source used high temperatures for the nebulization of liquid samples. The heater had to be situated very near to the sample delivery capillary for the proper nebulization. Therefore, both ion sources were prone to clogging of the sample delivery capillary. On the other hand, GDVN-APCI source generated a narrow spray of droplets to 10 cm distance, so the heating could be placed few milliliters behind the orifice of the sample delivery capillary. As a result, no clogging of the sample delivery capillary was observed. At this moment, GDVN-APCI source has great potential to be commercialized.

Key words: atmospheric pressure chemical ionization, corona discharge, gas dynamic virtual nozzle, gas-phase reactions, ion source housing, mass spectrometry, microchip, miniaturization, nebulizer, open tubular nebulizer