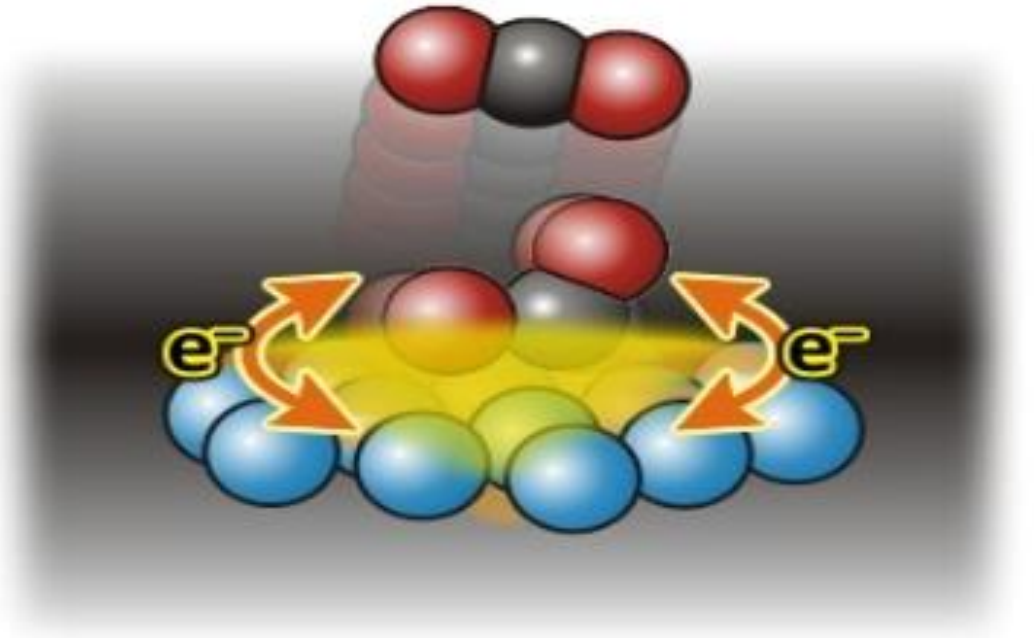
INSTRUMENTAL TECHNIQUE

Atmospheric Pressure Chemical Ionization (APCI)



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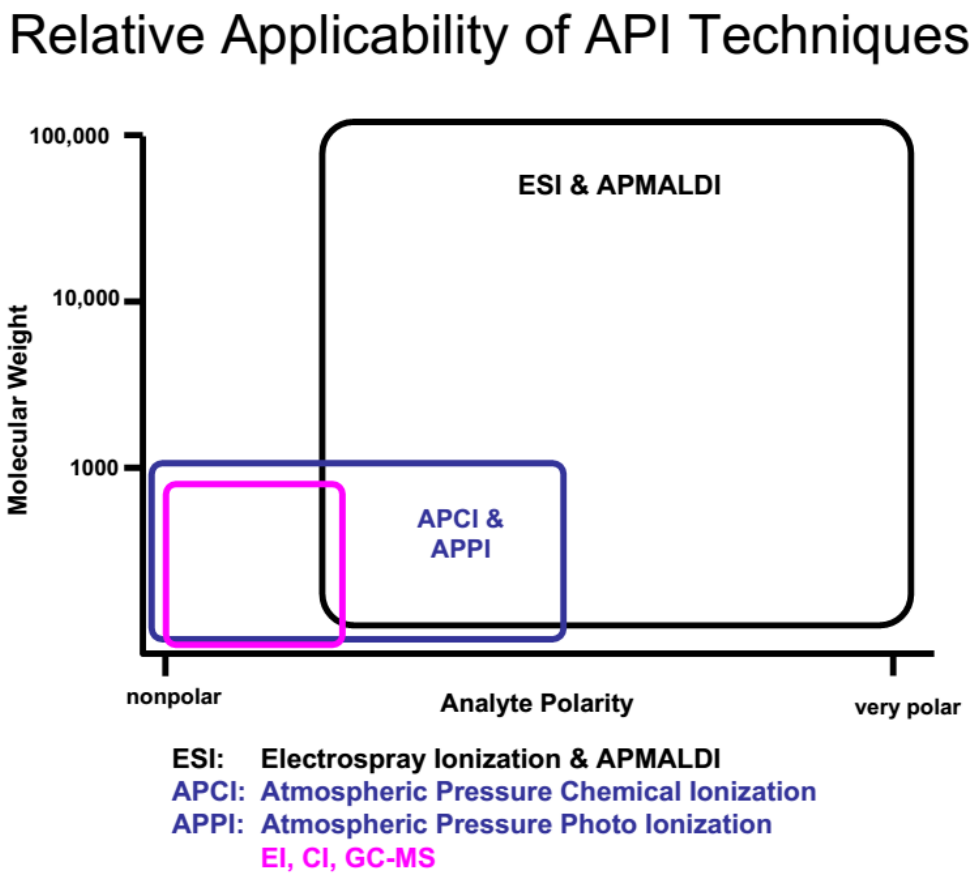
Atmospheric Pressure Ionization (API)

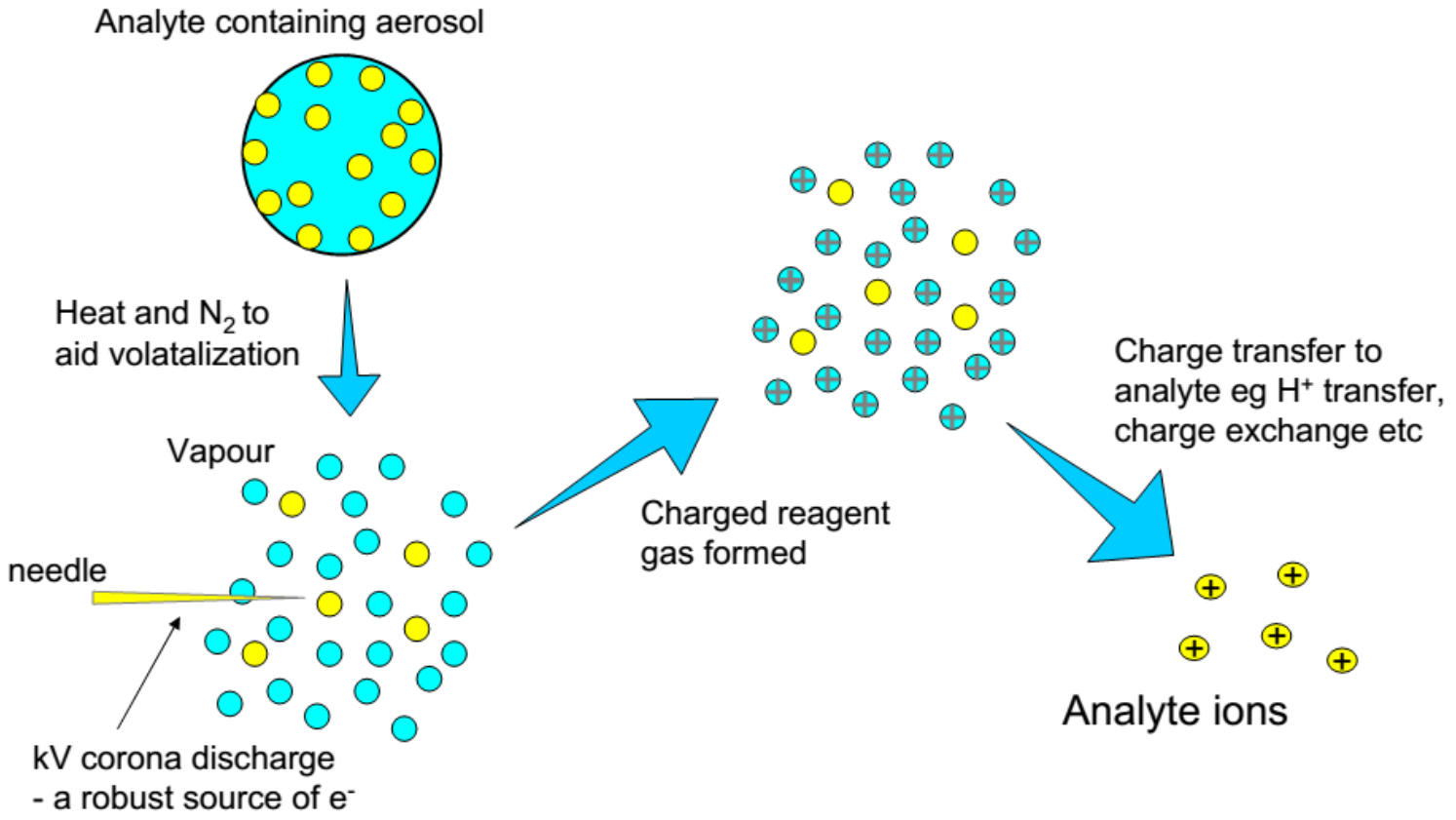
- Conventional ionization methods employ sources that are at high vacuum (EI, CI, FI/FD, FAB/LSIMS, MALDI) and/or temperature (EI, CI, FI/FD).
- The introduction of API sources employing a number of different types of ionization has allowed very robust instruments to be developed for LC/MS.

API Sources

- Electrospray (ESI) Ionization
- Atmospheric Pressure Chemical Ionization (APCI)
- Atmospheric Pressure Photo Ionization (APPI)
- Atmospheric Pressure MALDI

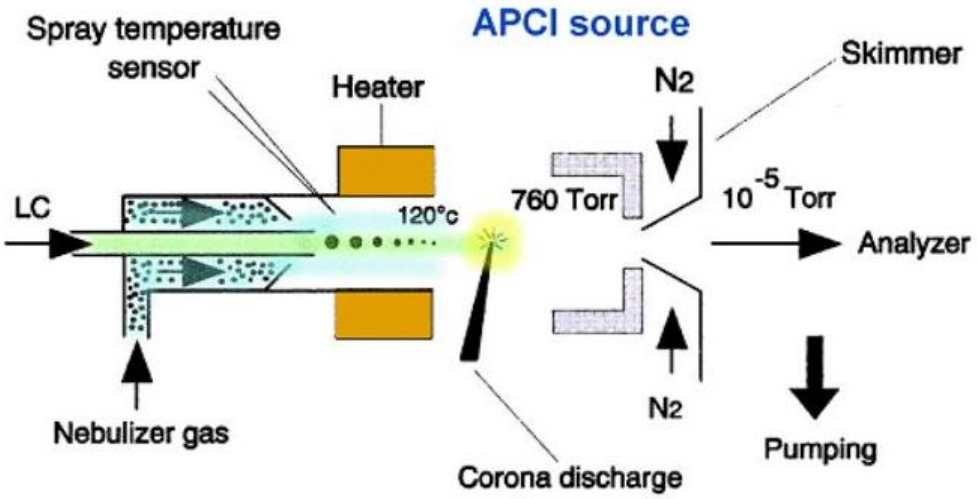


Atmospheric Pressure Chemical Ionization (APCI)



Atmospheric pressure chemical ionization (APCI) is an ionization method used in mass spectrometry which utilizes gas-phase ion-molecule reactions at atmospheric pressure (10^5 Pa), commonly coupled with high-performance liquid chromatography (HPLC). APCI is a soft ionization method similar to chemical ionization where primary ions are produced on a solvent spray. The main usage of APCI is for polar and relatively less polar thermally stable compounds with molecular weight less than 1500 Da. The application of APCI with HPLC has gained a large popularity in trace analysis detection such as steroids, pesticides and also in pharmacology for drug metabolites.

Instrumentation



A typical APCI usually consists of three main parts:

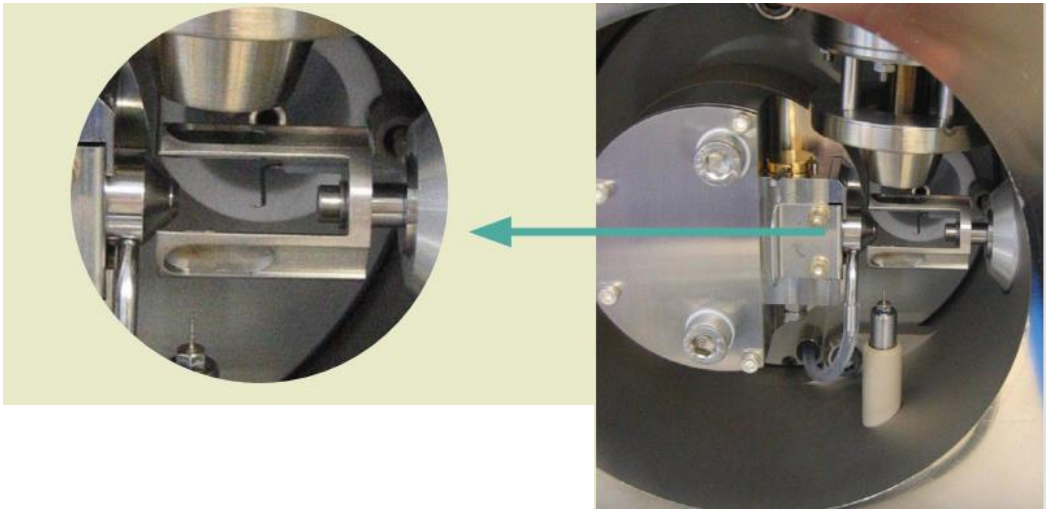
a **nebulizer probe** which can be heated to 350-500^{o}C

an **ionization region** with a corona discharge needle

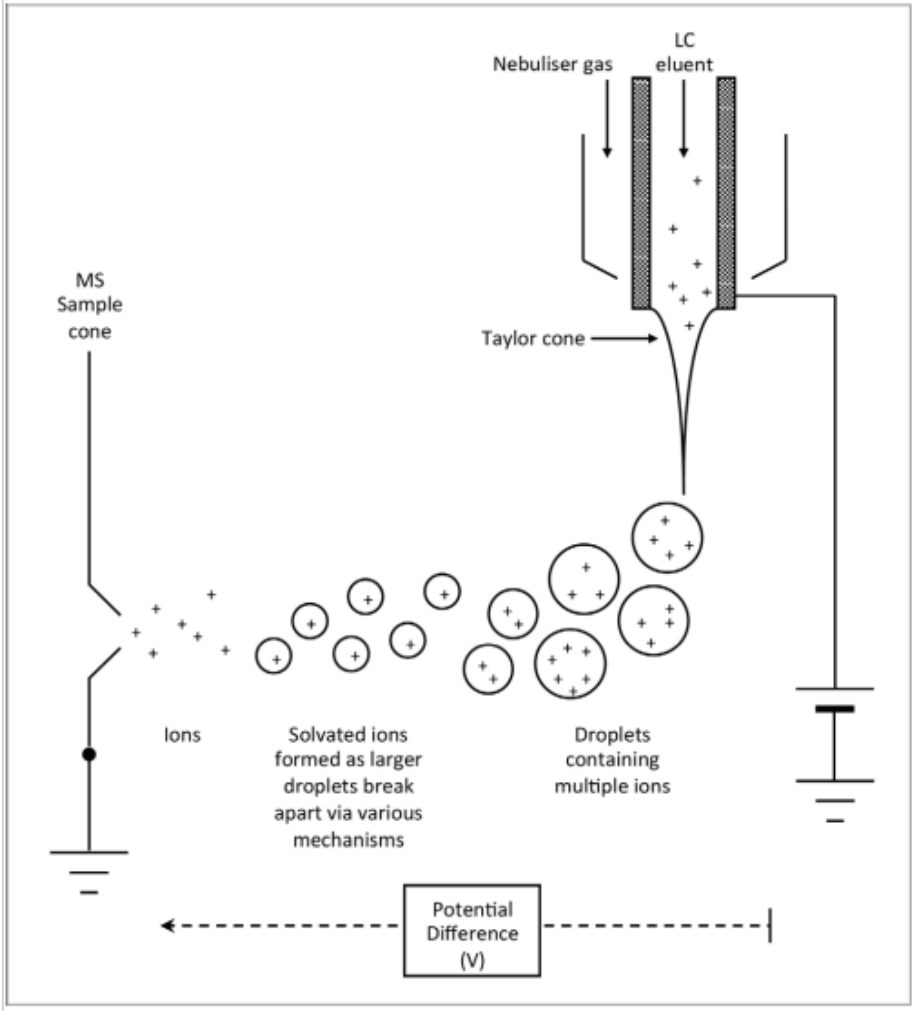
an **ion-transfer region** under intermediate pressure

- By the combination effects of heat and gas flow, the emerged mist is converted into a gas stream.

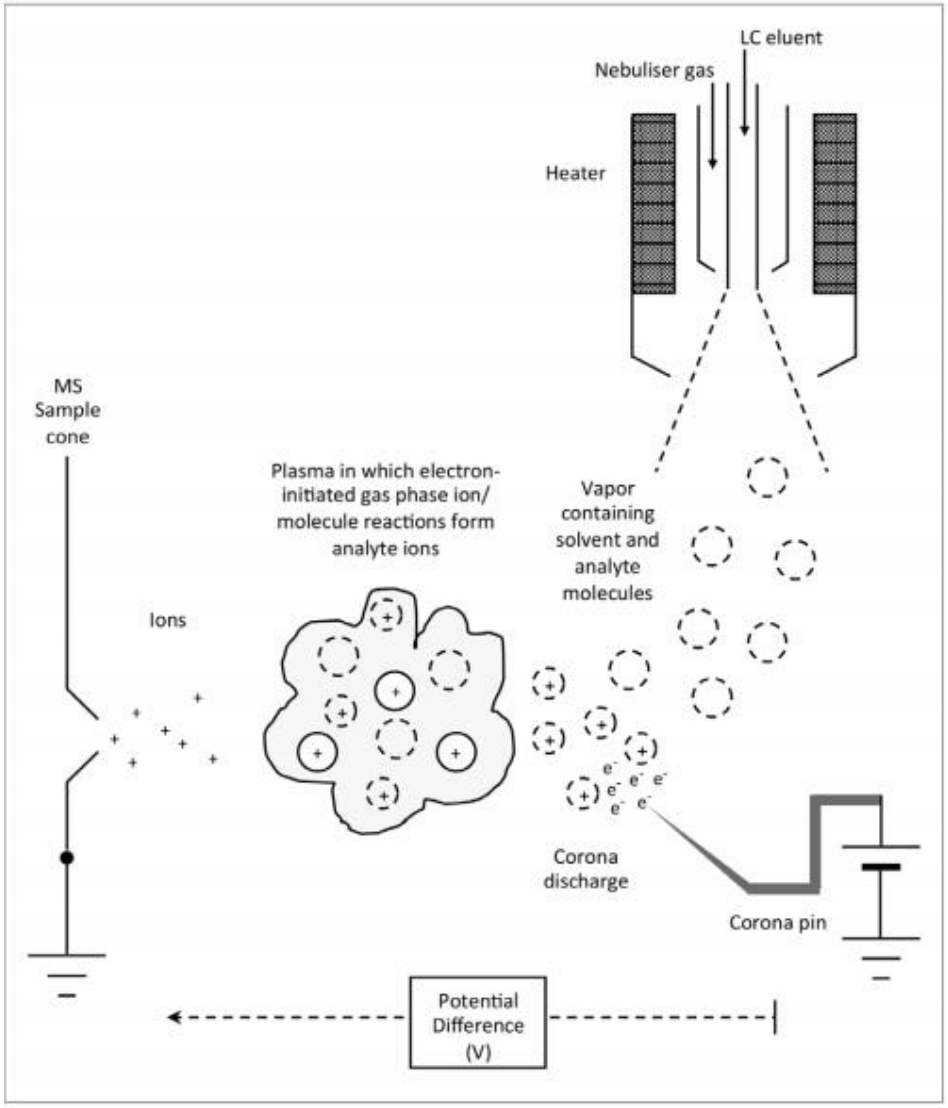
- Once the gas stream arrives in the ionization region under atmospheric pressure, molecules are ionized at corona discharge which is 2 to 3 kV potential different to the exit counter-electrode.



ELECTROSPRAY IONIZATION

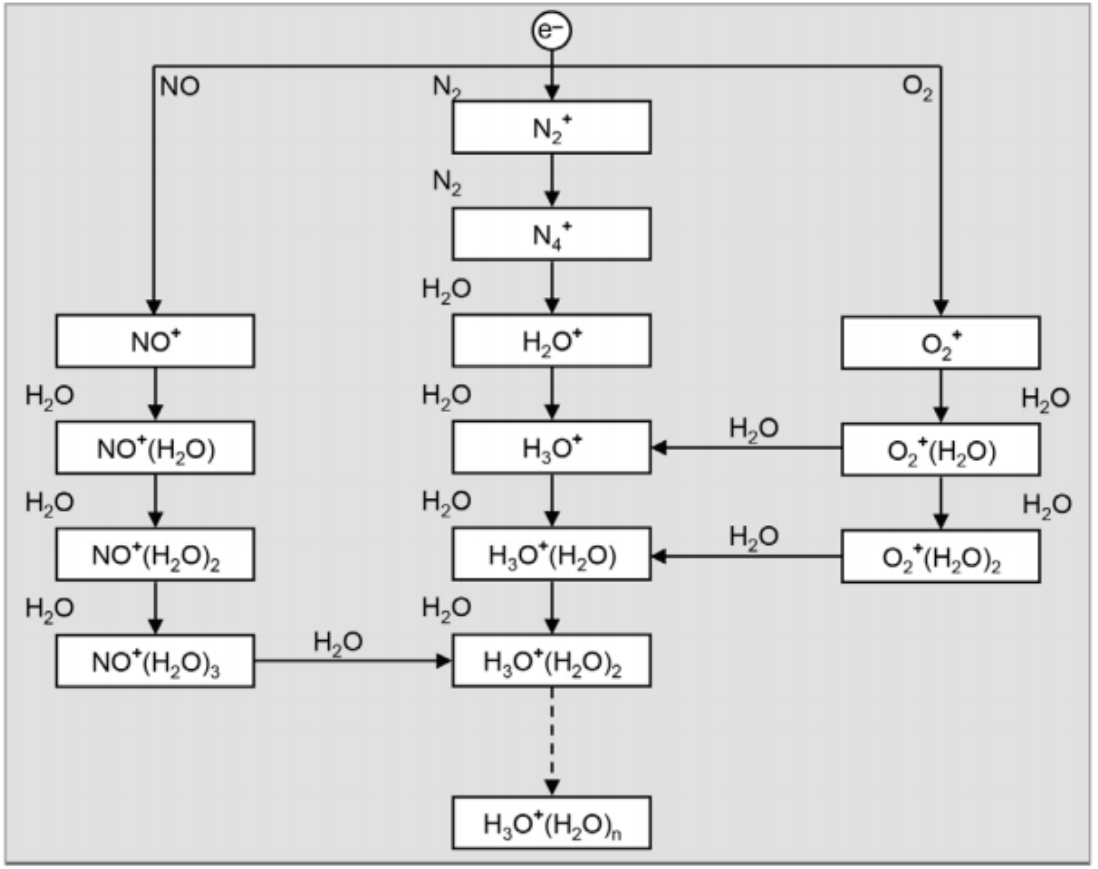


ATMOSPHERIC PRESSURE CHEMICAL IONIZATION



APCI Mechanism

Electrons initially ionize atmospheric species – primarily nitrogen molecules – by electron bombardment.
A sequence of clustering and/or charge transfer reactions take place; finally, the protonated water clusters formed from these reactions can go on to produce positive analyte ions via charge exchange or proton exchange mechanisms.

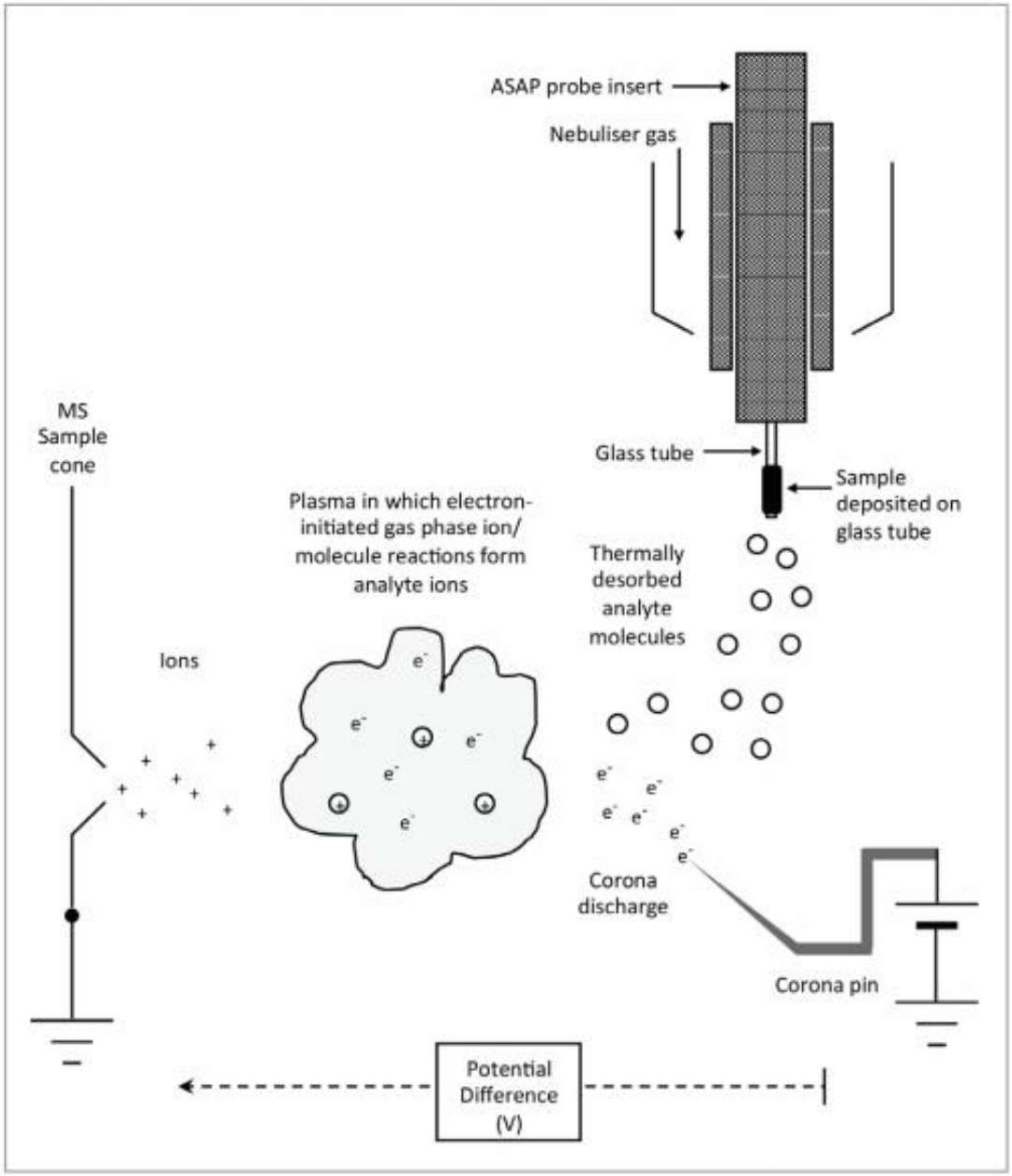


Schematic of reactions involving atmospheric species that can form positive ions in APCI

$$H^+(H_2O)_n + M \rightarrow MH^+(H_2O)_m + (n-m)H_2O$$
$$MH^+(H_2O)_m \rightarrow MH^+ + mH_2O$$

Alternatively electrons can interact with gas phase molecules that can then go to react with the analytes, typically via proton abstraction, resulting in the formation of negative ion species of interest.

Atmospheric Solids Analysis Probe

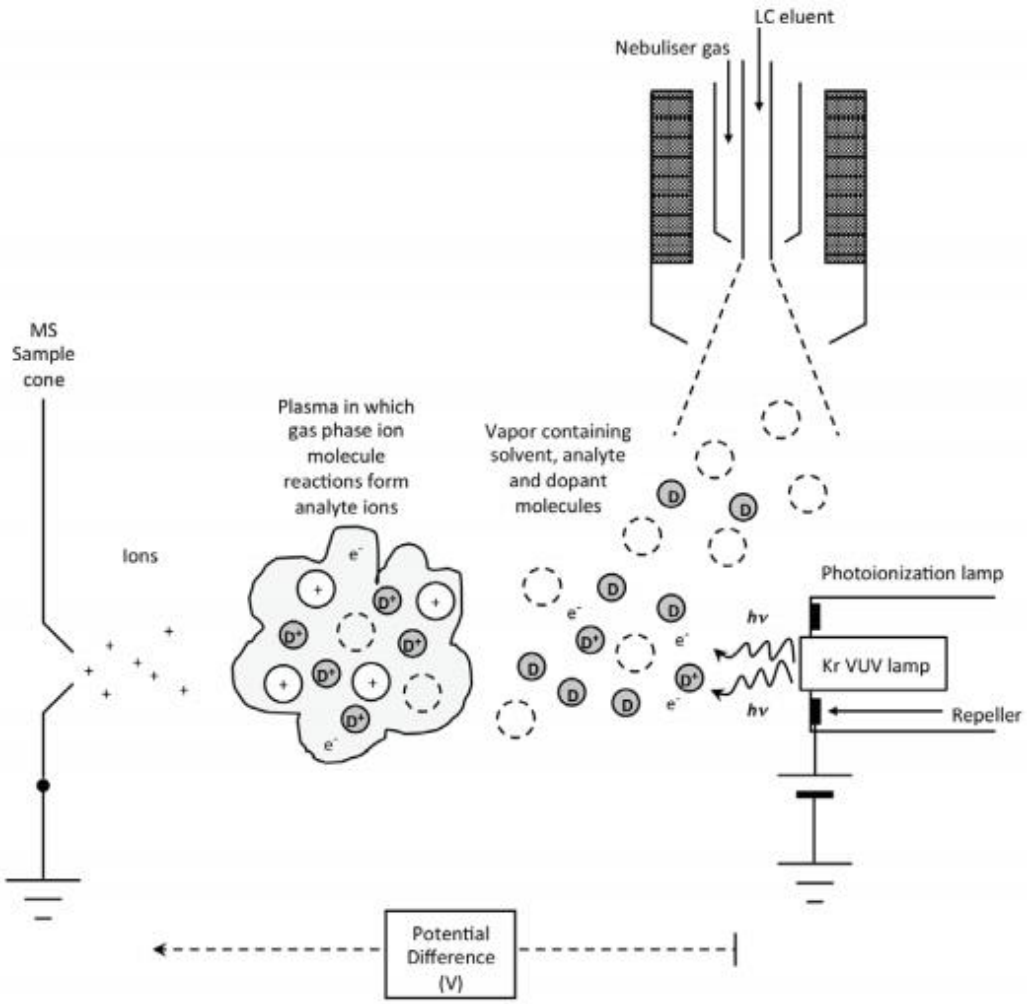


The Atmospheric Solids Analysis Probe (ASAP) is a useful tool for the rapid direct analysis of volatile and semi-volatile, solid and liquid samples using atmospheric pressure ionization.

The ASAP technique utilizes the heated nitrogen desolvation gas to vaporize the sample and a corona discharge for sample ionization.

This allows low polarity compounds not amenable to ESI, APCI and APPI to be ionized with a high degree of sensitivity.

Atmospheric Pressure Photo-ionization (APPI)



Unlike APCI, APPI does not have a corona discharge-instead, photons are emitted by a vaccum ultraviolet (VUV) lamp and photoionize gaseous species forming radical cations and electrons.

The most commonly used VUV lamp is a krypton Lamp, which emits photons with approximately 10 eV energy. If the species has an ionization energy less than 10 eV it can be ionized and form radical cations and electrons.

Dopant	IE (eV)[19]	PA* (kJ.mol^{-1})[19]
Acetone	9.70	812
Tetrahydrofuran (THF)	9.40	822
Benzene	9.24	750
Chlorobenzene	9.07	753
Bromobenzene	9.00	754
Toluene	8.83	784
Anisole	8.20	840

PA: Proton Affinity

History

The first atmospheric pressure ionization source was developed by Horning, Carroll and their co-works in the 1970s at the Baylor College of Medicine (Houston, TX).
Initially, ^{63}Ni foil was used as a source of electrons to perform ionization.
Latterly in 1975, corona discharge electrode was developed, which had a larger dynamic response range.
APCI was applied to GC/MS and LC/MS also by Horning's group in 1975.

Advantages

- Advantage of using APCI over other ionization methods is that it allows for the high flow rates typical of standard bore HPLC (0.2-2.0mL/min) to be used directly, often without diverting the larger fraction of volume to waste.
- Additionally, APCI can often be performed in a modified ESI source. The ionization occurs in the gas phase, unlike ESI, where the ionization occurs in the liquid phase. A potential advantage of APCI is that it is possible to use a nonpolar solvent as a mobile phase solution, instead of a polar solvent, because the solvent and molecules of interest are converted to a gaseous state before reaching the corona discharge needle.
- Because of APCI involves a gas-phase chemistry, there is no need to use special conditions such as solvents, conductivity, pH for LC. APCI appeared to be more versatile LC/MS interface and more compatible with reversed-phase LC than ESI.


THANK
YOU !