

Design and Performance of a New Combination Electro spray and Atmospheric Pressure Chemical Ionization Source

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Overview

An efficient "Field-Free" corona discharge Reagent Ion Gun is demonstrated. It is successfully used as a high-performance APCI source, as a part of ESI/APCI combination source and in Field-Free Desorption APCI experiments.

Introduction

Both Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) are commonly used in mass spectrometry analysis of complex mixtures. ESI is more suitable for the analysis of more polar small molecules and large molecules like peptides, proteins etc. APCI may be employed for smaller volatile compounds like drugs, metabolites, environmental contaminants. Combining ESI and APCI ionization in an atmospheric pressure ion source increases the Mass Spectrometer analytical range and provides the convenience of ionizing a sample with two powerful techniques individually or combined. The new combination ESI and APCI source design incorporates a reagent ion gun to supply APCI reagent ion species. Vaporized sample is ionized through collisions with the reagent ions without passing through a corona discharge.

The development of efficient "field-free" APCI reagent ion gun

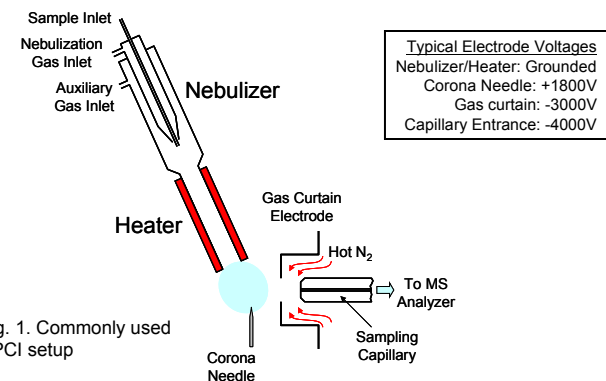


Fig. 1. Commonly used APCI setup

- The flow of analyte vapor quickly expands after the exit from the heated nebulizer assembly, decreasing the analyte concentration around corona needle;
- The optimal, from the point of view of the highest reagent ion production corona needle potential and position, generally does not provide the best transport conditions for analyte ions toward the sampling orifice of mass spectrometer.

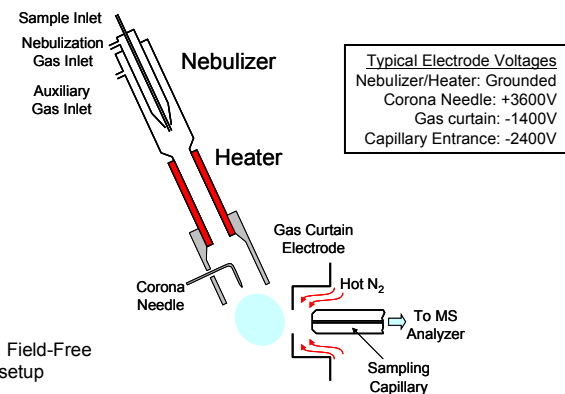


Fig. 2. Field-Free APCI setup

The performance of the new Field-Free (FF) APCI vs. a Standard APCI sources

Flow, $\mu\text{L}/\text{min}$	(A): Positive Ion Mode					(B): Negative Ion Mode		
	Reserpine 2 fM/ μL	Indole 1 pM/ μL	Indole 10 pM/ μL	Progesterone 10 pM/ μL	Cortisone 10 pM/ μL	Flow, $\mu\text{L}/\text{min}$	Reserpine 2 fM/ μL	Cortisone 10 pM/ μL
5	40:508	noise:5K	8.6K:36K	9.7K:49K	6.4K:39K	5	46:256	304:5.5K
10	80:987	noise:10K	15K:71K	18.2K:94K	12.7K:74K	10	92:517	435:14K
20	149:1.8K	noise:14.8K	26K:125K	32K:150K	25.2K:75K	20	137:927	1.3K:27K
40	318:3.8K	noise:24K	46K:191K	58K:267K	45K:214K	40	173:893	3.8K:58K
80	632:6.8K	8.4K:22.6K	65K:200K	83K:390K	59K:301K	80	138:713	8.8K:120K
120	661:10K	7.5K:12K	58K:140K	70K:402K	46K:296K	120	noise:239	6.6K:161K
200	680:9.1K	6.5K:13K	49K:141K	58K:467K	36K:276K	200	noise:193	4.8K:142K

Table 1. Comparison of the peak heights measured with Standard APCI source (blue) vs. FF APCI (red). Direct infusion experiment.

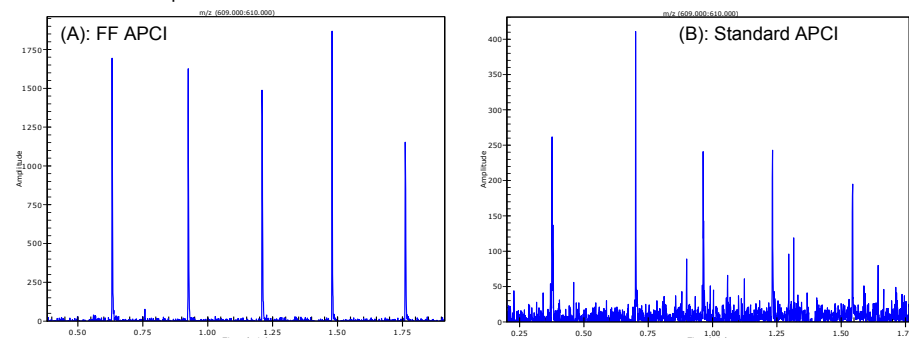


Fig. 3. Base Ion Chromatogram of Reserpine for FF APCI (A) and Standard APCI (B) sources. Flow rate: 1 mL/min; five $1\mu\text{L}$ -injections of 1 pg of Reserpine in Water/Methanol 1/1, 0.1% of Acetic acid. Data recording rate: 20 spectra per second.

Combination APCI/ESI source

ESI/APCI Mode Voltages			
Corona Needle:	+3600V	Gas curtain:	-3400V
Capillary Entrance:	-4400V		

ESI-only Mode Voltages			
Corona Needle:	0V	Gas curtain:	-3400V
Capillary Entrance:	-4400V		

APCI-only Mode Voltages			
Corona Needle:	+3600V	Gas curtain:	-200V
Capillary Entrance:	-1200V		

Electrospray and Reagent Ion Gun are Grounded all the time

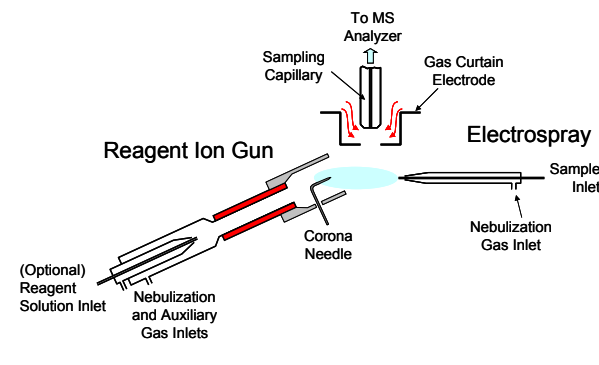


Fig. 4. Combination APCI/ESI source setup

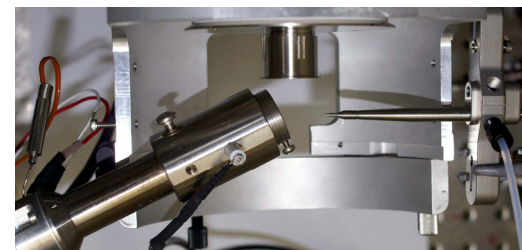


Fig. 4. APCI/ESI combination source interfaced to Analytica of Branford Corsair™ API-TOF mass spectrometer.

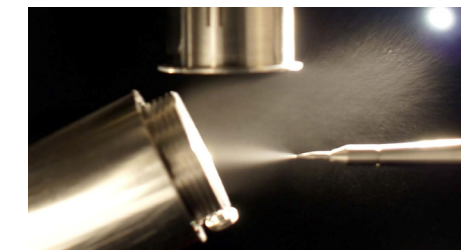


Fig. 5. The plume of droplets created by ESI nebulizer enters the Reaction Ion Gun and is diverted toward TOF entrance.

The performance of the Combination APCI/ESI source vs. Standard APCI and ESI sources

Table 2. Peak Heights for Reserpine (1pg/ μL) and Indole (10pM/ μL) mixture, 50:50 Water/Methanol, 0.1% Acetic acid.

Flow, $\mu\text{L}/\text{min}$	Combination Source						Standard Sources			
	APCI+ESI		ESI		APCI		ESI		APCI	
	Indole	Reserpine	Indole	Reserpine	Indole	Reserpine	Indole	Reserpine	Indole	Reserpine
10	5000	870	1483	869	6781	53	3.9K	10.5K	8.5K	277
20	7586	1871	2611	3117	12.7K	78	16.1K	3.8K	15.9K	511
100	5914	3497	5627	3629	18K	320	12K	3.8K	43K	1050
200	4039	2941	4127	2936	7.1K	385	8.5K	3.5K	50K	1337

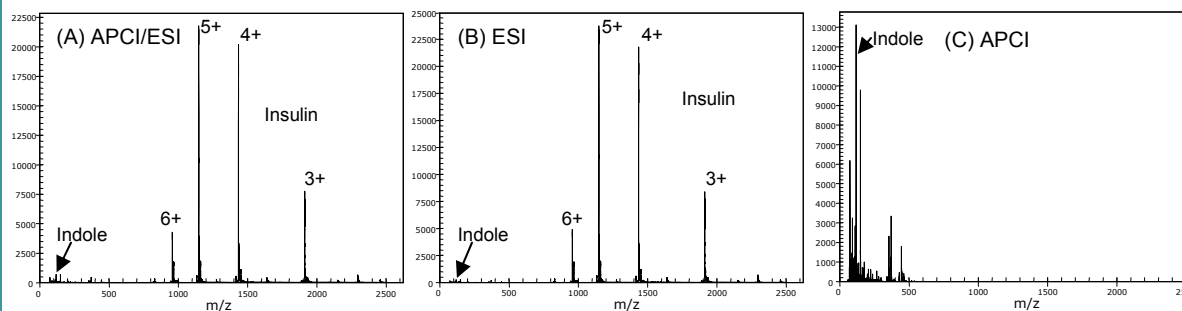


Fig. 6. (A) APCI/ESI, (B) ESI and (C) APCI spectra of Indole and Bovine Insulin mixture (20 and 100 pM/ μL , respectively), in 1:1 Water/Methanol solution, 0.1% Formic Acid.

Field-Free Desorption APCI

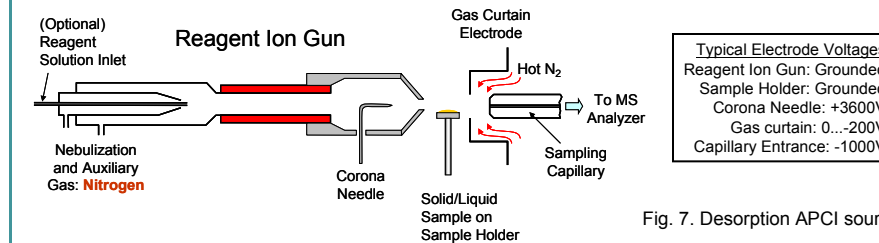


Fig. 7. Desorption APCI source Setup

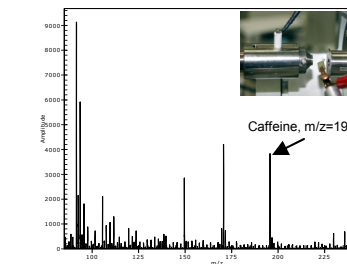


Fig. 8. FF DAPCI of 20pM of Caffeine deposited on stainless steel plate

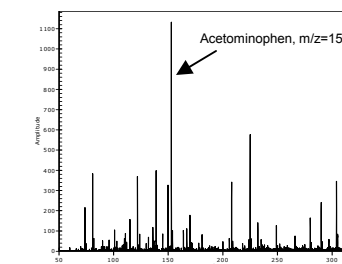


Fig. 9. FF DAPCI of Tylenol pill.

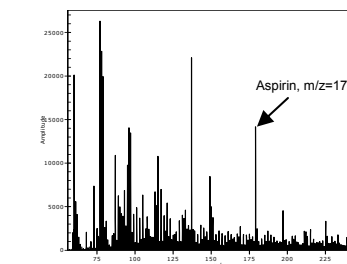


Fig. 10. FF DAPCI of Aspirin pill, Negative ion mode

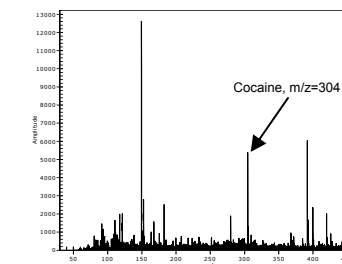


Fig. 10. FF DAPCI of \$20 banknote.

Conclusions

- Efficient Field-Free corona discharge Reagent ion gun confines high electric field of corona needle inside its stainless steel housing.
- Field-free Reagent Ion Gun, used as APCI ion source, demonstrates 3-10 times higher analyte peak heights and signal-to-noise ratio compared to APCI source of commercial design for broad range of analytes, flow rates, in positive and negative ion mode.
- Combination APCI/ESI ion source built on the basis of FF Reagent Ion Gun, provides the possibility of switching between APCI+ESI, ESI-only and APCI-only operation modes by altering of electrical potentials applied to the source electrodes.
- Combination APCI/ESI source demonstrates the performance, comparable to dedicated APCI and ESI sources.
- FF Reagent Ion Gun can be easily adopted for Field-free Desorption APCI experiments. Unprepared samples like commercial drug pills and contaminated surfaces can be quickly analyzed by FF DAPCI.