# Development of a Soft Ionization Discharge Source for Gas Chromatography Used with a High Resolution Time-of-Flight Mass Spectrometer

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## Overview

A soft ionization source for GC has been developed and used with a **LECO Citius®** high resolution time-of-flight mass spectrometer. Characteristics include:

- Dual mode of operation incorporating either Glow Discharge (GD) or Photoionization (PI)
- Soft ionization generating molecular and quasi-molecular ions for a wide range of analytes
- Operation at elevated pressures vs conventional GCMS ion sources such as EI and CI
- Use with a high resolution MS provides high mass accuracy and can eliminate chemical background

## Introduction

A soft ion source (i.e., ionization which primarily creates molecular or quasi-molecular ions), coupled to GC can be complimentary to conventional EI, particularly when interfaced with an MS system which provides high resolution and high mass accuracy. Advantages include:

- High resolution can effectively eliminate chemical background on analyte signals
- Soft ionization allows for unambiguous, or nearly unambiguous, chemical formula assignment
- Coupling to GC allows separation of isomers and reduction in non-spectroscopic matrix effects

A typical approach to soft ionization for GC is to use Chemical Ionization (CI). These systems use Methane, Ammonia, or Isobutane as reagent gas or gases. Limitations of this technique include:

- Considerable chemical background
- Selective or inefficient ionization
- Adduct species formation from analyte ions

This work describes progress on the development of an alternative system that can use either GD or PI as a soft ion source for GC. The GC transfer line is sealed to the ion source chamber which is then coupled to the interface of the MS creating an ion source which is isolated from atmosphere but is operated at pressures of 80-200 torr.

## Methods

### Glow Discharge

- An electrical circuit (Fig. 1) is used to generate a glow discharge (Fig. 2)

**Fig. 1**

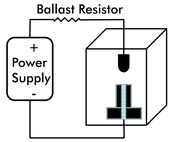
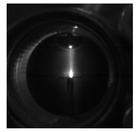
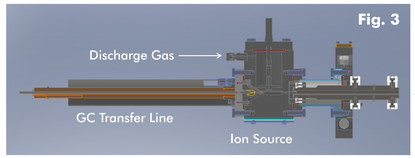



**Fig. 2**



- Discharge gas species are swept into the ionization region where they can react with analytes eluting from the GC, creating analyte ions which are transferred to the MS (Fig. 3)

**Fig. 3**




Typical Operating Conditions

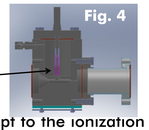
| | |
|---|---|
| Discharge Gas | Argon |
| Ion Source Pressure | 80-200 torr |
| Discharge Voltage | ~3 kV |
| Discharge Current | 1 mA |

- Both $M^+$ and $MH^+$ species can be seen. Protonation is likely the result of residual moisture in the ion source or impurities in the discharge gas

### Photoionization

- PI lamp (Fig. 4) replaces the GD electrodes

**Fig. 4**




- Dopant vapor (typically cyclohexane) is swept to the ionization region
- Two step ionization process
  1) Dopant + hν → Dopant Ions
  2) Dopant Ions + Analyte → Analyte Ions + Dopant

## Results: GD

**Fig. 5**. Typical background spectrum from the GD source. Spectrum contains primarily $Ar^+$ and $Ar_2^+$. The inset is a chromatogram of a 10 pg Benzophenone ($MH^+$) injection.

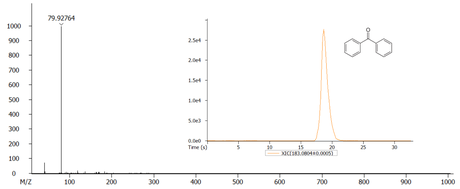



**Fig. 6**. Total Ion Chromatogram of Restek 8270 (76 component MegaMix).

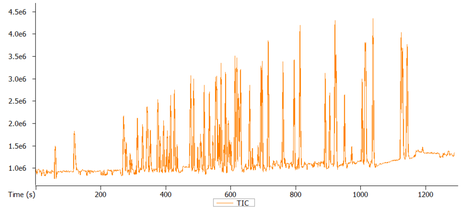
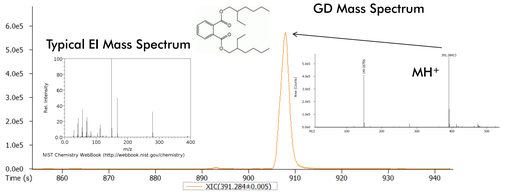



**Fig. 7.** Mass Spectrum of Bis (2-ethylhexyl) phthlate. Notice the large molecular ion ($MH^+$) signal and relatively simple fragmentation pattern compared to a typical EI mass spectrum.




## Results: GD Continued

**Fig. 8.** Dichlorobenzene isomers ($M^+$) in Restek MegaMix. Mass accuracy better than 1 ppm is achieved.

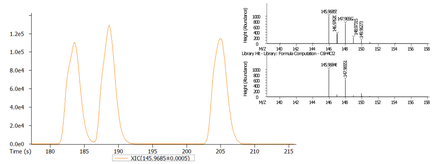



**Fig. 9.** Determination of PAH's in Restek MegaMix. Minimal fragmentation is seen.

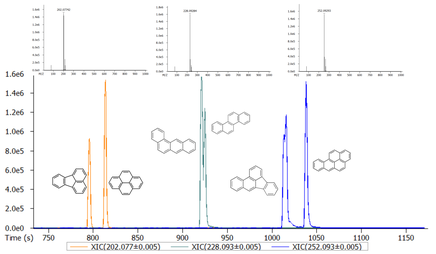
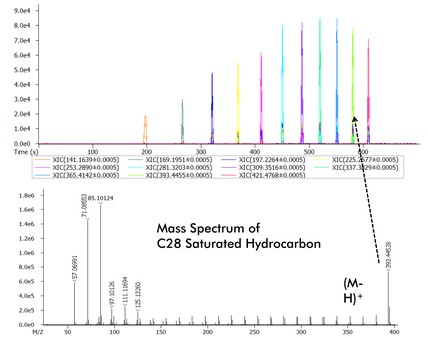



**Fig. 10.** Chromatogram of C10-C30 Saturated hydrocarbon mix. The molecular ion is in the form $(M\text{-}H)^+$.




## Results: PI

**Fig. 11.** Typical background spectrum from PI using cyclohexane as a dopant.

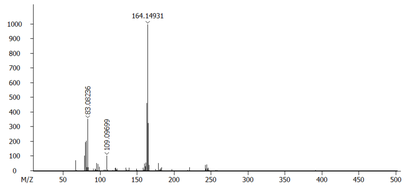
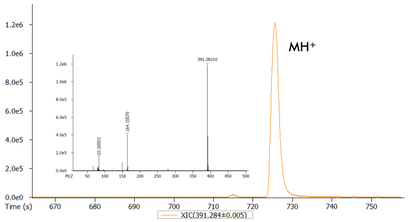



**Fig. 12.** Chromatogram and Mass Spectrum of Bis (2-ethylhexyl) phthlate. Notice the large molecular ion ($MH^+$) signal. Compared to the GD data in Figure 7, ionization favors the precursor ion to an even greater degree.




## Conclusions

Demonstrated progress on the development of a new soft ion source for GC includes:

- Use of GD or PI modes of operation
- Operation at elevated pressures compared to conventional GC ion sources
- Controlled environment relative to atmospheric ionization techniques
- Relatively soft ionization producing strong molecular or quasi-molecular ions
- A powerful tool when combined with high resolution and high mass accuracy