Optimization of a Vacuum Ultraviolet Photoionization source for Gas Chromatography used with a High Resolution Time of Flight Mass Spectrometer

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Overview

A soft ion source for GC/MS has been developed and interfaced with a high resolution time-of-flight mass spectrometer. This ion source utilizes a dopant (cyclohexane) to assist the ionization process. However even with a dopant added to the ion source, analyte ions can be generated by several different processes. The goal of this work was to use a tune solution to assist in understanding the effect of source parameters (source temperature, source pressure, and dopant liquid flow rate) on the ionization process. Once the influence of these parameters is understood ion source settings can be tuned for optimal results and/or a specific targeted analysis.

Introduction

Photoionization sources for GC/MS have several ionization mechanisms generating primarily molecular ions (M^+) and protonated molecular ions (MH^+). The type of ion generated for any specific analyte is based on several parameters including ionization energy, proton affinity, and polarity.

This work describes the use of a tune mixture, which can be selectively added to the dopant gas stream prior to the source. A steady state signal is generated allowing optimization of the ion source. The tune mixture is a combination of 100 ng/µl Benzophenone (in Methylene Chloride) and Toluene at a 1:1 ratio. Importantly, this mixture generates both M^+ and MH^+ parent ions which allow the study of ionization via proton transfer and molecular ion formation. In addition, ionization of the dopant in conjunction with the tune mix can also be studied.

Various source parameters were investigated including:

- Ion Source Temperature
- Ion Source Pressure
- Dopant Liquid Flow Rate

The influence of these parameters on sensitivity and degree of fragmentation are presented. In addition, results for a test mixture when run under multiple ion source conditions is included.

Methods

A dual gas flow configuration is used to (a) deliver the dopant (and tune compounds) and to (b) provide a makeup gas to assist in analyte flow. The gas flow, dopant delivery, tune solution reservoir, and valve arrangement is shown in Figure 1.

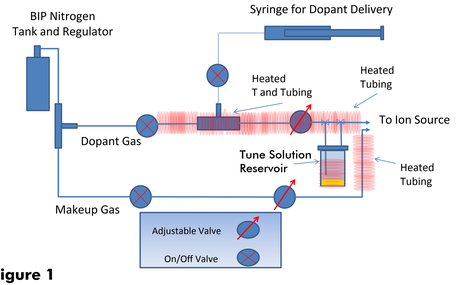


Figure 1

A GC transfer line is sealed to the ion source which is then interfaced to the mass spectrometer. Figure 2 shows an expanded view of the interior of the ion source. Note the flow of the dopant (and tune compounds) and makeup gas around the GC capillary.

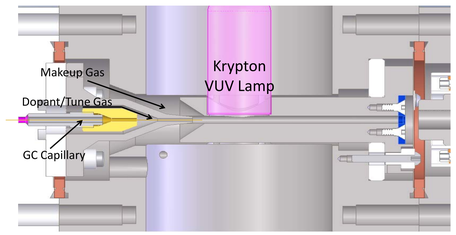


Figure 2

Typical Operating Conditions

- Dopant: Cyclohexane
- Tune Solution: 100 ng/µl Benzophenone in Methylene Chloride, Toluene at a 1:1 ratio
- Tune Vial Temperature: 35° C
- Makeup and Dopant Carrier Gas: BIP grade Nitrogen
- GC Column: 30 m Rxi®-5, 2-3 mm beyond the source cone tip

Results

Ion Source Temperature: Results for ion source temperature testing are shown in Figure 3. Sensitivity decreases with increasing temperature for both M^+ and MH^+ species while fragmentation remains relatively constant across this temperature range.

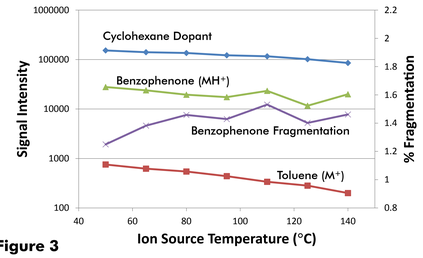


Figure 3

Ion Source Pressure: Source pressure was adjusted using the makeup gas. Opposing trends are observed (Figure 4): low pressure yields high sensitivity for MH^+ ions and high pressure yields high sensitivity for M^+ ions.

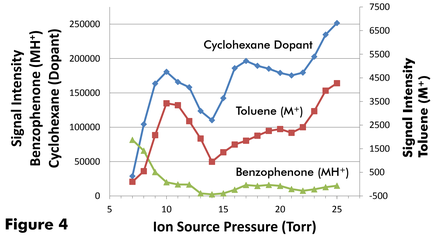


Figure 4

Fragmentation increased slightly at higher source pressure. See Figure 5 below.

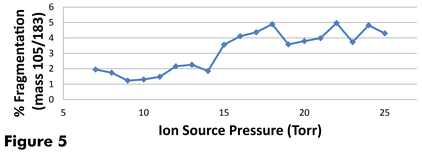


Figure 5

Results

Dopant Liquid Flow Rate: A range of dopant liquid flow rates was tested (Figure 6). Opposing trends are again observed for M^+ and MH^+ species. Note that optimizing for dopant intensity would lead to poor analytical results for M^+ species.

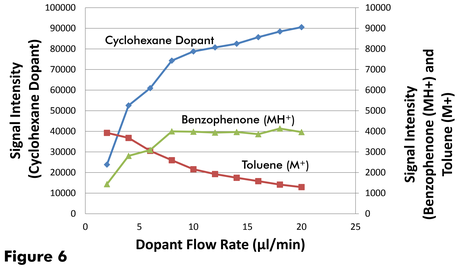


Figure 6

Testing Various Optimized Conditions: Based on the results of source optimization using the tune mix, a set of three source conditions was established for testing on a compound mixture. See source conditions in Table 1 below:

Source Optimized	Source Temp. (°C)	Source Pressure (Torr)	Dopant Flow Rate (µl/min)
M^+	50	25	4
Compromise	50	17	10
MH^+	50	7	16

Table 1

A test mixture (Table 2) was injected into the GC to explore various ion source conditions. Relatively large amount of analyte was injected to ensure that, when possible, both M^+ and MH^+ species would be observed. Note the analyte number listed in Table 2 corresponds to the analyte number shown in Figures 7 and 8.

Analyte Number	Compound	Amount Injected on Column
1	2,6 Dimethylphenol	3.2 ng
2	2-ethylhexanoic acid	3.8 ng
3	2,6 Dimethylaniline	3.2 ng
4	Methyl Caprate	4.2 ng
5	Methyl undecanoate	4.2 ng
6	Dicyclohexylamine	3.1 ng
7	Methyl dodecanoate	4.1 ng

Table 2

Results

Results for the testing of various source conditions are summarized in Figure 7. Each analyte, except 2-ethylhexanoic acid, produces both M^+ and MH^+ species. In each case, sensitivity for the M^+ and MH^+ ions shifts as the source condition are changed to favor a particular optimum condition.

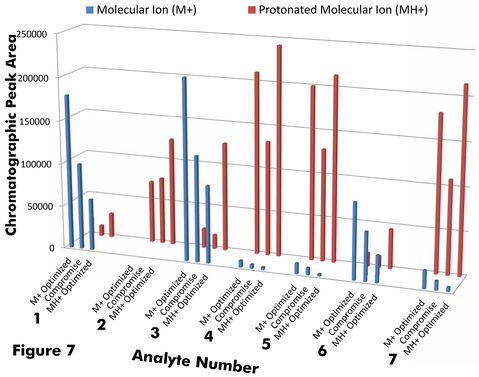


Figure 7

Figure 8 shows the sum of M^+ and MH^+ ions for each optimized condition. Note that in many cases total ionization efficiency remains nearly constant.

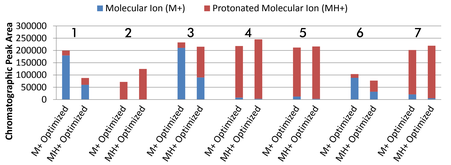


Figure 8

Conclusions

- Tune solution allows optimization of ion source parameters for both proton transfer and direct ionization
- Independent ionization processes exist for M^+ and MH^+
- Optimizing for dopant signal intensity yields inferior results
- Degree of fragmentation remains relatively constant over a range of source conditions