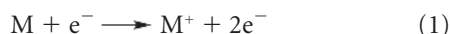


# Improving Ionization in Mass Spectrometry

Ronald Starcher

**B**ecause of its many unique characteristics, mass spectrometry (MS) has been elevated to an unequaled position among analytical methods. MS provides outstanding sensitivity and detection limits and unparalleled diversity in applications. To produce a mass spectrum, the first step in the analysis of compounds is the production of gas-phase ions of the compound. Numerous methods are used for accomplishing this task, and the most common require the generation of electrons as an essential part of the process.

Electron ionization (EI) uses a stream of electrons that are accelerated across an ionization chamber, where they interact with the injected sample gaseous molecules. The interaction produces molecular ions and ionic fragments of molecules that are injected into the mass filter:



Some substances fragment so readily under EI conditions that either no molecular ions survive, or so few survive that it is difficult to be sure whether or not the ones observed represent some impurity.

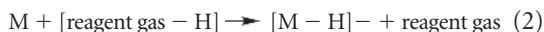
Consequently, chemical ionization (CI) techniques have been developed to extract molecular mass information. In CI, sample ions are produced by ion-molecule reactions rather than electron interaction.

A reagent gas is ionized (usually using EI) and allowed to react with the sample. The reaction noted below produces a quasimolecular ion of the sample.

Positive ion mode:



Negative ion mode:



The method most commonly used to produce the electrons necessary to generate ions for the mass filter in EI, and to ionize the reagent gas in CI, involves the use of a heated filament emitting electrons to bombard either the sample or an intermediate gas. Heretofore, the filament source was the most cost-effective means for generating the large quantities of electrons necessary to produce ions. However, filaments have a number of inherent deficiencies:

- Electron emission current changes as a function of temperature. As a consequence, a stabilization period is required while the filament heats up to its operating temperature. It is not unusual for there to be a 10-to-1 change in resistance from hot to cold. This results in changes in the electron stream and consequent changes in the amount and type of ions produced and sent to the analyzer.
- Filaments require large amounts of power. Typically the power required is almost always 5 to 10 W, regardless of design or manufacturer.
- Filaments have a limited lifetime. Heating of the filament causes material to evaporate from the outer surface of the center of the filament. As the filament gradually grows thinner, it is much more prone to breakage.
- Filaments generally require the use of an emission regulator to compensate for changes in filament output. The output changes occur as a result of variations in filament resistance, changes in heat loss, and changes in pressure.
- Filament output is not uniform. Electron emission is essentially a point source. Consequently, electron flux density along any axis varies inversely as a function of the square of the distance from the filament.

BURLE Electro-Optics (Sturbridge, MA) has designed a patented alternative to filament sources that alleviates most of these problems. The Electron Generator Array (EGA) consists of millions of precision glass tubes (pores) fused to-

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gether to produce a uniform and mechanically rigid structure. They are processed so that when a voltage is applied across the thickness, each pore produces a beam of electrons. With each of the millions of pores producing electrons, the resultant electron flux is extremely uniform and dense.

### Theory of Operation

For normal operation, a bias of as much as 1200 V is applied across the EGA (output positive with respect to input). The bias current flowing through the semiconductive layer on the inner surface of each channel supplies the electrons necessary to continue the avalanche multiplication process.

This process, as it would occur in a single channel of a standard EGA, is illustrated in Figure 1b. The reduced lead

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silicate material is processed to produce a low work function surface on the interior walls of the channels. When a voltage is applied, electrons are spontaneously generated along the length of the channel. These electrons are accelerated down the channel toward the output end. When these electrons strike the channel wall, additional secondary electrons are generated. This process is continuously repeated, yielding typically  $10^4$  electrons at the output of each channel.

Higher output currents can be achieved by operating two or more microchannel plates (MCPs) in a stack. If two or more MCPs are stacked in series,

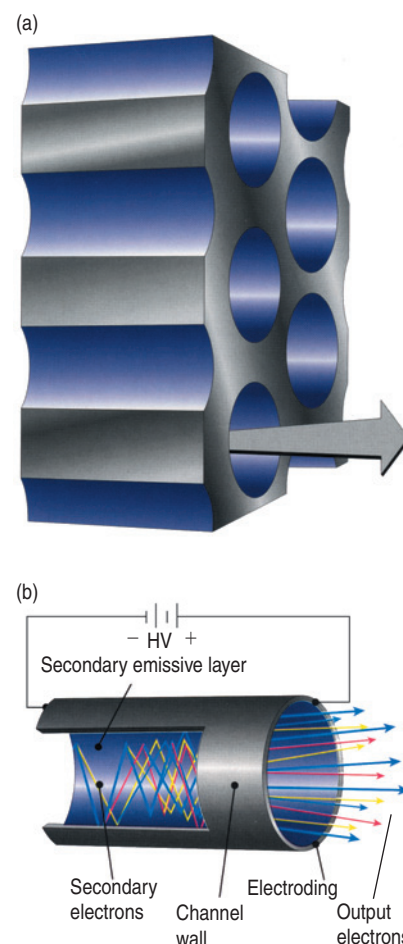
a channel will generate a pulse of  $10^6$  or more electrons. Output currents in excess of  $10^8$  electrons per channel can be achieved with a z-stack configuration.

### Advantages

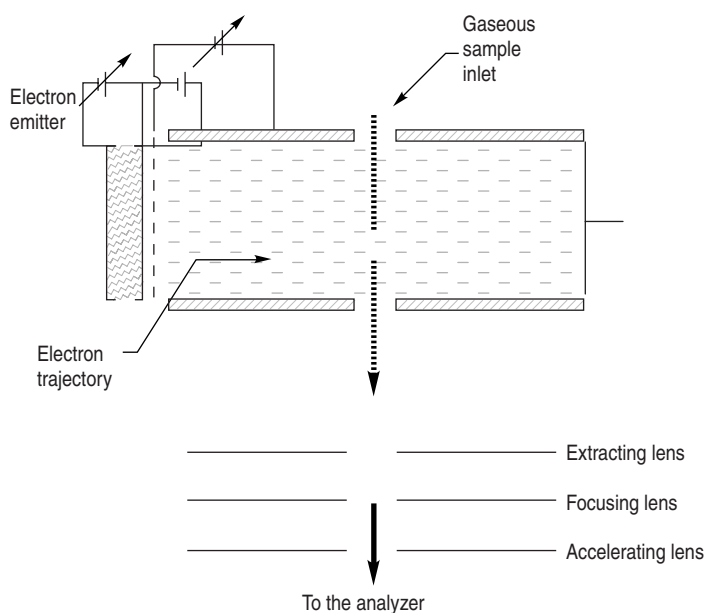
An EGA doesn't require any warm-up time, and won't burn out. No heat-up and stabilization period is required. Once the operating voltage is applied, the EGA will instantaneously provide a uniform, tunable electron flux proportional to the voltage. EGAs require much less maintenance than filament sources (no cleaning or replacement required) while providing much higher current densities. EGAs are available with emission areas in a variety of shapes and sizes as large as 150 mm in diameter.

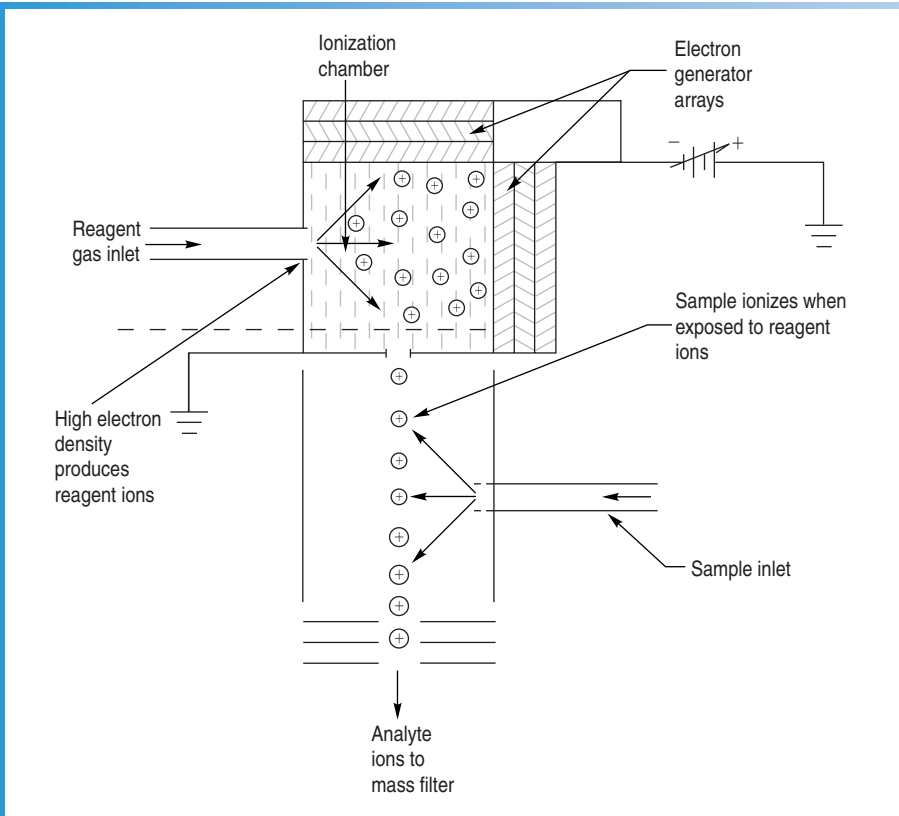
In MS applications, EGAs can be used as the electron source in EI and CI processes. This technology will perform as a cold ionization source. In conventional sources, the heat from the filament often causes pyrolysis effects,

**Figure 1 (right).** Schematics showing (a) an EGA cross section and (b) the operation of a single channel.



**Figure 2 (below).** Use of an EGA as an EI source.





**Figure 3.** Use of an EGA as a CI source.

which occur when the heat from the filament chemically changes the unknown substances to be identified. Once ionized, this altered substance does not produce an ion that represents the original substance. The use of a cold electron source effectively eliminates this concern. The EGA does not produce

## Unlike filament sources, no warm-up period is required.

any heat or light in operation. Consequently, many fewer unwanted ions are produced, significantly reducing the noise of the system. Figure 2 illustrates the configuration of an EGA as an ionization source in an EI source.

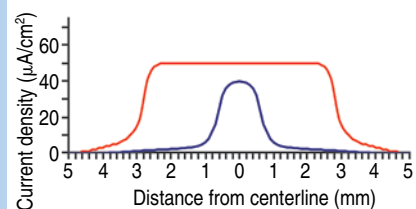
In addition, the ionization space is significantly larger. The EGA can be configured to maximize the amount of ions that are produced. This increases

the number of ions that get to the mass filter and subsequently to the detector. With more sample ions reaching the detector, the instrument sensitivity increases.

The EGA can also provide benefits when incorporated into a CI source. Figure 3 depicts a possible configuration of EGAs in that application.

### Flux Density

Typically, a single EGA will produce an electron flux density of  $1.0 \times 10^{-10}$  A/cm<sup>2</sup>. By using a chevron or Z-stack configuration, current densities as high as  $2.0 \times 10^{-5}$  A/cm<sup>2</sup> can be obtained. The flux density is uniform to within 10% across the entire emission area. Figure 4 compares the cross-sectional flux density of a typical EGA versus a filament source. The measurement was made along an axis parallel to the EGA at a distance of 100 mm from the EGA. Note that the EGA flux density is very uniform across the entire cross section of the active area. The filament's flux density, however, drops off exponentially from its maximum as you move



**Figure 4.** Cross-sectional electron flux density.

along any straight line transecting the electron flux.

For spectroscopic applications, the EGA will provide a uniform electron flux over a larger area in the ionization space than is possible with conventional filament sources. Consequently, more ions are likely to be produced, resulting in larger signals at the detector, effectively increasing the sensitivity of the entire instrument. In addition, the electron flux density is tunable. Varying the bias voltage across the EGAs will change the electron output proportionally. Again, the EGA provides versatility by allowing the electron source to be adjusted to the optimum output that maximizes instrument performance without the extensive stabilization times required for filament sources.

It should also be noted that the EGA provides fine emission level control. The electron flux is a function of the applied voltage. This provides the ability to rapidly change the flux density by merely adjusting the EGA bias voltage. Unlike filament sources that must reach thermal stability before the output has stabilized at the new setting, the EGA reacts instantly to a change in bias voltage settings.

### Stability

Once properly degassed, the EGA will provide stability during its lifetime. On application of the bias voltage, the EGA will provide virtually instantaneous, solid electron flux.

The output will vary less than 1% in 24 h and will drift less than 10% after 40 coulombs/cm<sup>2</sup> of extracted charge. The EGA was operated as a chevron at 2400 V ( $1 \times 10^{-5}$  A/cm<sup>2</sup>) in excess of 430 h continuously.

In addition to long-term stability, the EGA provides short-term benefits. Once power is applied, the EGA provides virtually instantaneous, highly stable electron flux. Unlike filament sources, no warm-up period is required.

The EGA achieves a solid, stable output less than a second after being turned on, while the filament can take as long as 5 min to stabilize enough to be useful.

### Power Requirements

A filament ionization source typically consumes 5 to 10 W of power. The vast majority of this power is used to heat the filament, which in turn boils off electrons. The actual electron current is only a small portion of the total current

## The output electron flux is remarkably parallel.

drawn by the filament. The typical filament might consume 5 to 10 W of power to produce an emission current of 10  $\mu\text{A}$ . By comparison, an EGA producing a 50- $\mu\text{A}$  flux, evenly distributed over a 50-mm  $\times$  8-mm area, will have a total power consumption of less than half of a watt. Virtually all of the current is used to produce the electron flux. There is no heating of the EGA. Consequently, there are no measurement inaccuracies due to pyrolysis effects and no problems with condensation of evaporated material.

### Beam Shape

The output electron flux from an EGA is remarkably parallel. The electron beam is essentially the same shape as the EGA. Note in Figure 4 the sharp edges of the flux. They closely match the shape of the EGA itself. The beam shape is also independent of the output field strength. This field strength can be varied over a wide range without disturbing the flux shape. Again, this contrasts sharply with the output of fila-

ment sources that have beam shapes that are highly dependent on field strength.

Because the EGA can be manufactured in virtually any shape, an electron beam can be produced in a wide variety of shapes to a variety of needs.

### Noise

Filaments generate large quantities of heat and light, in addition to electrons. These additional emissions can cause uncontrolled and unwanted ionization and fragmentation in MS applications. The EGA produces only electrons. There is no heating or emitted photons to generate noise in the ionization space. Pyrolytic effects are virtually eliminated from the system.

### Conclusion

The EGA helps solve many problems associated with filament sources. The EGA exhibits long life, stability, and higher current densities. It provides virtually instantaneous turn-on and does not heat up, eliminating the problems associated therewith. The EGA can be configured to provide tunable electron energies and flux densities, and it provides the flexibility to produce a very uniform electron flux over a large area. This can generate more sample ions, which can significantly increase instrument sensitivity.

### Acknowledgments

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