

# Breakthrough in Quantitation and Linearity in Particle Beam LC/MS through Improvements in Aerosol Generation and Particle Transport.

Scott Niemann – CSS Analytical Co Inc. Shawnee, Kansas . Dr. Richard F. Browner - Georgia Institute of Technology Atlanta, Georgia

## INTRODUCTION

Particle Beam LC/MS provides unique capabilities for identification of *unknown compounds* not amenable to other Mass Spectral techniques such as Electrospray LC/MS and GC/MS. Particle Beam remains the only LC-coupled technique which provides the superior identification capability of Electron Impact spectra when used with commercially available reference data bases, such as Wiley, NIST, etc..

Some early commercial PB LC/MS instruments suffered from a lack of linear range as a result of the use of very simple nebulizers, (tube inside of a tube) producing a poorly shaped spray pattern, filled with inappropriately sized aerosol droplets.

This paper will discuss the benefits of the use of a patented device, Oscillating Capillary Nebulizer (OCN), that when combined with a highly efficient momentum separator can give much improved results.

Practical examples and data will be shown using compounds of biomedical, pharmaceutical and environmental significance, covering a wide range of molecular weights and compound types.



Old Style Nebulizer Fig. 1.



OCN Fig. 2.

## INSTRUMENT AND CONDITIONS

The particle beam LCMS system included the following components: Agilent Model 1100 modular HPLC system (Agilent Technologies, Inc.) with quaternary pump, vacuum degasser, 100 vial autosampler and variable wavelength detector. The samples were presented after separation via a typical 2mm ID C18 column. The Genesis II particle beam interface (CSS Analytical Co Inc.) was attached to an Agilent 5973 MSD with turbo molecular pump so that samples can be analyzed by LC/MS, but with electron impact ionization and chemical ionization. The Agilent 5973 is a bench top quadrupole mass spectrometer with mass range of 1.6 to 800 mass units, 10,000 volt HED, and is available with EI or EI/CI capabilities.

The Genesis II is an improved particle beam interface, which delivers a higher amount of analyte to the ion source, when compared to previous commercial interfaces.

## MECHANISMS OF THE AEROSOL SPRAY

On a typical concentric tube gas assisted nebulizer (Figure 1), the initial droplet increases in size on the tip of the inner liquid tube until it wets the entire surface of the tip of the inner liquid tube, and grows until droplet shearing occurs. Droplets are sheared from every side of the inner (liquid) tube, so long as enough of the droplet is presented to the shearing force of the nebulizing gas. Often times the inner tube is pushed over to the side, by the force of the nebulizing gas, rather than remaining centered within the outer tube. This results in the asymmetric shearing of droplets only from a portion of the initial droplet that is closest to the flow of nebulizing gas. This makes the spray shape uneven (arbitrary vector direction) and the size of the droplets of questionable and highly variable size.

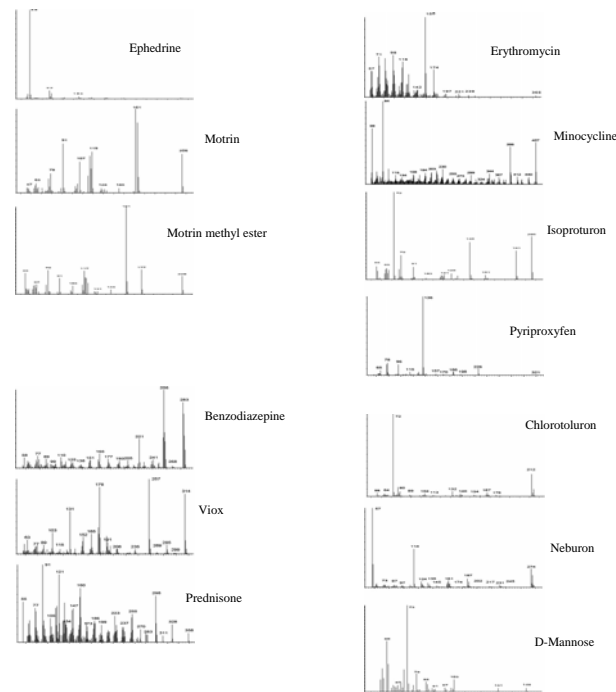
For the Self Oscillating Nebulizer, OCN (Figure 2), the droplet increases in size, but at the same time the inner tube is oscillating at a frequency of as much as 2 Hz. This standing wave, whose height is less than the inner diameter of the outer tube, provides a violent shaking effect on the tip of the inner tube, applying a shearing force perpendicular to the inner tube which then presents a smaller initial droplet to the shearing force of the nebulizing gas. This orthogonal shearing force, in addition to the shearing force supplied by the nebulizing gas will remove much smaller, uniformly sized droplets.

## MECHANISMS OF PARTICLE TRANSPORT

Aerosol from the nebulizer is sprayed into a heated desolvation chamber where there is a slight vacuum. This combination of vacuum and heat causes the mobile phase (m.p.) to be evaporated from the droplets. As the m.p. is evaporated, the sample molecules combine to form a particle. Sample particles and gas (m.p.) molecules are collected by a tapered nozzle and passed into a 2-stage skimmer arrangement forming a momentum separator. Each stage of the separator is variably pumped so that the vapor molecules with little momentum will be evacuated as they diffuse away from the center hole of the skimmers. The larger sample particles have greater momentum and will not diffuse much while passing through the center hole of the skimmers. The momentum separator is attached to the mass spectrometer via a transport tube, where the sample will proceed to the MS ion source.

The CSS Analytical Genesis II Particle Beam Interface uses a revolutionary (and proprietary) design. Chief among its features are two fully adjustable skimmers. Skimmer gap and skimmer diameter can be matched to the compound of interest if desired, in order to maximize particle transport into the Mass Spec Ion Source. Skimmer matching is based on the particle's mass. While molecular weight plays a role, (heavy items have momentum and can "jump" across a skimmer gap, light items may get "sucked" down the hole) it is not the only factor. More importantly, is a molecule's ability to form dry particles – CLUMPS. More work will be done on this interesting theme.

## DATA



## CONCLUSIONS

Included above are examples of interesting and useful compounds from life sciences and from the environmental arena. Spectra from compounds of various molecular weights are pictured, suggesting the usefulness of the particle beam interface with EI spectra via separation by liquid chromatography. The use of the patented OCN as a gas assisted nebulizer provides a greater quantity of droplets of optimum size, versus a wider range of droplet sizes as produced by the typical sprayer. Linearity and sensitivity improvements provided by the OCN are enhanced by the cleverly re-designed momentum separator and associated apparatus. Data which could not be included in this work is available by request. Send your request to Sniemann@cssco.com . Thank you for your kind interest.