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Technical note

Parallel path nebulizer: Critical parameters for use with microseparation techniques combined with inductively coupled plasma mass spectrometry

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Abstract

Four different, low flow parallel path Mira Mist CE nebulizers were evaluated and compared in support of an ongoing project related to the use of microseparation techniques interfaced to inductively coupled plasma mass spectrometry for the quantification of cobalamin species (Vitamin B12). For the characterization of the different Mira Mist CE nebulizers, the nebulizer orientation as well as the effect of methanol on analytical response was the focus of the study. The position of the gas outlet on the nebulizer which consistently provided the maximum signal was when it was rotated to the 11 o'clock position when the nebulizer is viewed end-on. With this orientation the increased signal may be explained by the fact that the cone angle of the aerosol is such that the largest percentage of the aerosol is directed to the center of the spray chamber and consequently into the plasma. To characterize the nebulizer's performance, the signal response of a multielement solution containing elements with a variety of ionization potentials was used. The selection of elements with varying ionization energies and degrees of ionization was essential for a better understanding of observed increases in signal enhancement when methanol was used. Two different phenomena contribute to signal enhancement when using methanol: the first is improved transport efficiency and the second is the "carbon enhancement effect". The net result was that as much as a 30-fold increase in signal was observed for As and Mg when using a make-up solution of 20% methanol at a 15 μL/min flow rate which is equivalent to a net volume of 3 μL/min of pure methanol.

Keywords: Parallel path nebulizer; CE; Speciation; ICP-MS; Mira Mist CE; Transport efficiency; Carbon enhancement; Aerosol

1. Introduction

Sample introduction is considered by many to be the "Achilles' heel" of atomic spectroscopic techniques. Many of the currently available commercial sample introduction devices consisting of both nebulizers and spray chambers continue to possess limitations including poor transport efficiency, large sample consumption, nebulizer clogging and memory effect problems [1–3]. As such, several research groups have focused on improved nebulizer designs [2,4]. More recently, the focus has been on the development and characterization of a variety of low flow nebulizers (e.g. direct injection nebulizer, DIN; high efficiency nebulizer, HEN; microconcentric nebulizer, MCN; microultrasonic nebulizer, μUSN [4–7]. The reason for this is that low sample uptake rates (typically less than 30 μL/min) combined with high nebulizer gas flow rates lead to more efficient nebulization and 100% transport efficiency may even be achieved [8,9]. Using the aforementioned high efficiency low flow nebulizers, finer aerosols are produced and transported very efficiently into the plasma. The transport efficiency can be further improved by the use of organic solvents such as methanol which produces an even finer aerosol as compared to water. This phenomenon was reported by Browner et al. more than two decades ago [10,11].

Low flow nebulizers are of particular interest when interfacing capillary-based microseparation techniques to detection systems such as inductively coupled plasma mass

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spectrometry (ICP-MS). Their crucial role is to provide efficient transport of the effluents coming from the separation capillary column into the plasma. In recent studies, a low flow Mira Mist CE nebulizer was characterized and optimized for use with both capillary electrophoresis ICP-MS (CE-ICP-MS) and micro high performance liquid chromatography ICP-MS (μHPLC-ICP-MS) [7,12]. This parallel path nebulizer allows uptake rates in the range of 1 μL to 2.4 mL depending on the sample solution composition. In addition, it may be used over a wide range of nebulizer gas flow rates and nebulizer clogging is not an issue due to its unique design.

The use of organic solvents in atomic spectrometry has been shown to either suppress or enhance analyte signals [10,13]. Poor measurement precision and accuracy have been reported when using organic solvents due to physical changes in the inductively coupled plasma, an increase in the number of carbon containing polyatomic ions and deposition of carbon on the sampling orifice [10,11,14–18]. However, under restricted or controlled conditions (e.g. low flow nebulizers, addition of oxygen, cooled spray chambers) the presence of organic solvents may be very beneficial in enhancing analyte signal response. Two of the most commonly cited mechanisms for this phenomenon are: (1) improvement in mass transport efficiencies and (2) increased ionization efficiency due to the so-called "carbon enhancement effect". Increased transport efficiency has been attributed particularly to the changes in the physical properties of the sample solutions while the carbon enhancement effect has been attributed to charge transfer reactions generated by ionized carbon species or carbon containing polyatomic species. [11,19–28].

In this study, the performance of four Mira Mist CE parallel path nebulizers have been compared under optimized conditions. The orientation of the gas outlet with respect to the sample outlet was investigated. For this study, a make-up solution consisting of 20% methanol delivered at a flow rate of 15 μL/min simultaneously with multielement analyte solutions was used. Finally, studies were conducted to try to establish if analyte signal enhancement in the presence of methanol was due primarily to improved transport efficiency or the "carbon enhancement effect".

2. Experimental

2.1. ICP-MS instrumentation

All experiments were performed using a Perkin-Elmer Sciex Elan 6000 (Thornhill, Ontario, Canada) inductively coupled plasma mass spectrometer. The spectrometer was operated at 1 kW forward power with a coolant gas flow rate of 15 L/min and an intermediate gas flow rate of 0.86 L/min. The dwell time was 1 s. The isotopes monitored were: ^{75}As, ^{59}Co, ^{24}Mg, ^{208}Pb, ^{103}Rh, ^{82}Se and ^{89}Y. When changing conditions during the nebulizer characterization studies, a 10-min equilibration period was used to ensure stable operating conditions.

A routine daily performance test recommended by the manufacturer was done for the ICP-MS as a part of the optimization. Tuning procedures included continuous nebulization of two multielement solutions containing 10 ppb Mg, Cu, Rh, Cd, In, Ba, Ce, Pb and U; and 10 ppb Co, Be, In and U. For daily optimization, a syringe pump (KD Scientific Inc., New Hope, PA, USA) was operated at 30 μL/min to introduce standard solutions through Teflon tubing attached to the nebulizer.

2.2. Sample introduction systems

Four Mira Mist CE parallel path nebulizers (Burgener Research Inc., Mississauga, Ontario, Canada) coupled with a cyclonic spray chamber were evaluated. For this publication, the letters A–D have been assigned to the different nebulizers. The Mira Mist CE nebulizers were operated using a 1 L/min argon nebulizer gas (controlled by the Elan's mass flow controller) at 85 psi.

To simulate microflows associated with CE, a fused silica 50 μm i.d. capillary column (Polymicro Technologies, Inc., Phoenix, AZ) was used with a sample pumping rate of 340 nL/min and a make-up solution flow rate of 15 μL/min. Two identical syringe pumps (KD Scientific Inc., New Hope, PA, USA) were used to control these flows. The nebulizers may be interfaced with capillary-based microseparation systems using either a tee or a four-way cross (both provide essentially the same dead volume and identical performance). In this work, a four-way cross was used. The cross provides a connection to hold the capillary column which is inserted from one side of the cross and extends all the way to the tip of nebulizer at the opposite side of the cross. The tip of the capillary column is recessed 1 mm from the tip of the nebulizer. The cross provides another port for a make-up solution which is necessary to keep the capillary column wet and it provides a fourth port to maintain the electrical connection using a platinum wire electrode for use with CE.

A 50 mL water cooled, jacketed Glass Expansion cyclonic spray chamber (Glass Expansion Pty. Ltd., Camberwell, Australia) was used to provide constant temperature. The cooled spray chamber minimizes solvent loading and provides improved precision and sensitivity. The recirculating water temperature was set to 5 °C and maintained using a Model 911 recirculating chiller from PolyScience (Niles, IL, USA). A Miniplus peristaltic pump (Gilson, France) was used to drain the waste.

2.3. Reagents and standards

Methanol was obtained from Fisher Scientific (Fair Lawn, NJ, USA). Stock standard solutions (High Purity Standards, Charleston, SC) were diluted with 18 MΩ deionized, distilled water to prepare two different 1 ppm