Minimization of Atmospheric Background Contaminants in Nanoelectrospray: Identification & Optimization

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Introduction
The high-surface area of the submicrometer droplets generated by low-flow nanoelectrospray ionization results in the potential ionization of contaminants present in laboratory air: “basics” and coworkers recently reported on a “bath gas” system designed to reduce the background levels using laboratory air (proceedings of the 56th ASMS Conference, June 1-5, 2008, Denver, Colorado). Here we report on the evaluation of two similar systems used in combination with ion-line-LC/MS.

Methods
- Mass Spectrometer (LCQ Deca™; Thermo Fisher Scientific)
- HPLC Pump: Huctor nano-LC
- Spray Pump: Harwood-Apparatus pump with flow sensor

The bath gas system was implemented on a customized digitally-controlled nanospray source (Digital PicoTip™ DPN-150; New Objective, Inc.) mounted to a conventional 3-D ion trap (LCQ Deca™, Thermo Scientific Inc.) with two different air filtration systems. The second system utilized a high-quality, dry-air-compressor (Jan-Air) that was connected to a flow control system (0-12 L/min) with an in-line carbon-based organic vapor filter (Supelco) intended for gas chromatography. The flow rate and volume of air delivered at the bath gas port was measured with a velocity sensing air-flow meter (Testo Inc.). The air flow at the outlet of the delivery system could be adjusted from laminar, to sub-turbulent, to turbulent conditions.

Mobile phase/note: acetonitrile, 0.1% formic acid. Sigma-Aldrich was delivered by a gradient nanoflow LC pump (HiPette) or by continuous infusion from a syringe pump (250 µL syringe; Hamilton). Flow rate was measured to within ±20 µL/min using an in-line flow sensor (Upchurch Scientific™). The typical flow rate for continuous infusion was 400 µL/min. A 110 L ID trimer- tip emitter (FT160-150-DN; New Objective, Inc.) was mounted on the source. High-voltage was applied directly to the mobile phase through a low-impedance Picoseq™ Conductive Liner (PCL-360; New Objective, Inc.). An in-line PEEK™ filter (Upchurch Scientific, P-770) was used to reduce particulate contamination of the emitters.

A three-peptide standard (human angiotensin I, MRFA, bradykinin; Sigma-Aldrich) was prepared at a concentration of 1 pmol/µL (5 to 50% acetonitrile). All samples contained 0.3% formic acid. Standards of the proposed polysiloxane contaminants (dicyclosiloxanes and didecyldimethylcyclosiloxanes) were obtained from Gelbad, Inc. A 110 L ID trimer-tip emitter was deposited onto the interior of a 5 ml glass vial that had been packed with a small “Kemper” tissue. Each vial was positioned in front of the bath gas outlet in order to introduce the volatile component to the nanospray field.

Results
The commonly observed background ions at m/z 371 and 445 were positively identified as cyclosiloxane compounds through the use of reference standards. A systematic study of operational parameters (filter type, gas flow rate, compensation, etc.) was conducted to minimize background ion current without compromising analyte signal. Reduction of the background current from cyclosiloxanes was reduced by 110-fold when using either filtration system. Reduction of these compounds did not alter the high-performance cyclosiloxane compounds. It is not currently possible to completely eliminate the background ion currents without compromising the appearance of the data and may simplify visual interpretation. The considerable impact on the functional or quantitative interpretation has yet to be determined. Air was found to be superior to nitrogen (first element for use with gradient elution LC) as it exhibits a higher breakdown voltage and therefore reduces the chance of corona discharge at the nanospray emitter.

Conclusions
- The background ions at m/z 371 and 445 are confirmed by MS/MS to be cyclosiloxane compounds.
- Minimization of these cyclosiloxane compounds in the atmosphere surrounding the inlet of the mass spectrometer can be achieved with a low-flow bath gas.
- Either low- or high-permeability carbon filters may be used to remove cyclosiloxane compounds from laboratory air.
- Compressed air from a conventional laboratory air compressor can be satisfactorily "washed" for use as a bath gas by a packed bed carbon filter.
- Background levels are typically reduced by 110-fold (i.e. to baseline-spectrometer noise levels).
- Bath gas flow rates that are too high (i.e. turbulent) may result in the destruction of an analyte.

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