

## Accepted Manuscript

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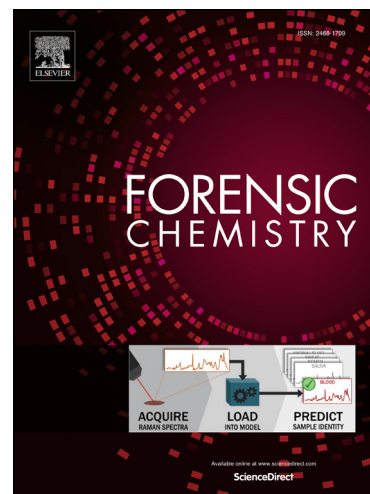
PII: S2468-1709(18)30033-X  
DOI: <https://doi.org/10.1016/j.forc.2018.08.002>  
Reference: FORC 116

To appear in: *Forensic Chemistry*

Received Date: 6 April 2018  
Revised Date: 1 August 2018  
Accepted Date: 13 August 2018

Please cite this article as: B.J. Bills, J. Kinkade, G. Ren, N.E. Manicke, The Impacts of Paper Properties on Matrix Effects During Paper Spray Mass Spectrometry Analysis of Prescription Drugs, Fentanyl and Synthetic Cannabinoids, *Forensic Chemistry* (2018), doi: <https://doi.org/10.1016/j.forc.2018.08.002>

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## The Impacts of Paper Properties on Matrix Effects During Paper Spray Mass Spectrometry Analysis of Prescription Drugs, Fentanyl and Synthetic Cannabinoids

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### Abstract

Designer drugs, drugs synthesized in a lab that mimic other drugs of abuse, have become a major cause of death in the United States. Limitations in either speed, sensitivity or selectivity of current analytical techniques hinders rapid detection of designer drugs. Paper spray mass spectrometry (PS-MS) is a rapid ambient pressure technique capable of detecting analytes in complex matrices. However, due to a lack of sample cleanup and chromatography, matrix effects can have a significant impact on the detection limits. Previous work has shown that the paper spray substrate has an impact on matrix effects, but the current literature lacks a systematic approach to studying different properties of paper with regards to matrix effects. In this work, the effect of pore size, flow rate, and thickness on ionization efficiency and recovery was assessed. Cellulose thin layer chromatography (TLC) plates were made along with a universal spray cartridge to provide a porous spray substrate similar to paper but with easily controllable properties. It was found that substrates with the highest filtration properties (thicker, slower flow rate, or smaller pore sizes) exhibited lower analyte recovery but improved ionization efficiency. This trend was verified with an offline extraction conducted with a 3D printed centrifuge extractor. Paper/solvent combinations were tested with urine samples to determine if selecting a paper and solvent with better ionization efficiency could improve detection limits. While for some drugs minimizing ionization suppression improved detection limits, other drug targets, like those that were charged at physiological pH, were largely unaffected. For analytes that showed improvement, both the paper and the solvent had an impact, although most of the improvement was due to the solvent.

### Introduction

In recent years, designer drugs (drugs produced in a lab to mimic the effects of other drugs of abuse) have become more prevalent<sup>1-3</sup>. Manufacturers take advantage of these drugs' unique structures to try to avoid detection and regulation<sup>1</sup>. Synthetic cannabinoids, for example, are sprayed on dried plant matter and often marketed as herbal incense while being marked as "not for human consumption"<sup>4</sup>. However, the active ingredient may be one or more of any molecule from a library of compounds developed for research purposes<sup>4-5</sup>. This can have disastrous consequences as the dosage is poorly controlled, and the potency of any individual compound can vary wildly<sup>2,5</sup>. As a result, consumers can experience side effects and can end up overdosing<sup>2,4</sup>. Another alarming trend is that fentanyl and its derivatives are being found with increasing regularity as both adulterants in heroin and as drugs of abuse by themselves<sup>2-3</sup>. Coupled with a highly variable range in potency of fentanyl analogues (ranging from less potent

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