THE EFFECT OF SAMPLE HOLDER MATERIAL ON ION MOBILITY SPECTROMETRY REPRODUCIBILITY

J. Richard Jadamec and Chih-Wu Su
U.S. Coast Guard Research and Development Center
1082 Shennecossett Road
Groton, CT 06340

Stephen Rigdon
Analysis & Technology, Inc.
258 Bank Street
New London, CT 06320

LaVan Norwood
Tectonic Technologies, Inc.
468 Wells Road
Wethersfield, CT 06109

ABSTRACT

When a positive detection of a narcotic occurs during the search of a vessel, a decision has to be made whether further intensive search is warranted. This decision is based in part on the results of a second sample collected from the same area. Therefore, the reproducibility of both sampling and instrumental analysis is critical in terms of justifying an in depth search. As reported at the 2nd Annual IMS Conference in Quebec City, the U.S. Coast Guard has determined that when paper is utilized as the sample desorption medium for the Barringer IONSCAN, the analytical results using standard reference samples are reproducible. A study was conducted utilizing papers of varying pore sizes and comparing their performance as a desorption material relative to the standard Barringer 50 micron Teflon. Nominal pore sizes ranged from 30 microns down to 2 microns. Results indicate that there is some peak instability in the first two to three windows during the analysis. The severity of the instability was observed to increase as the pore size of the paper is decreased. However, the observed peak instability does not create a situation that results in a decreased reliability or reproducibility in the analytical result.

BACKGROUND

Vessel search for the presence of contraband is one aspect of the US Coast Guard's Law Enforcement mission. Rapid detection of the presence of a narcotic is one of the primary requirements of Law Enforcement Agents engaged in field operations, especially in the maritime environment.

Since 1991, the USCG R&D Center has been actively conducting studies on non-canine contraband detection technologies for illicit drug detection. Two technologies have been

extensively tested and evaluated side by side during the past three years. Both systems analyze collected samples without any sample pretreatment which is an important criterion for field systems. IONSCAN, an Ion Mobility Spectrometer manufactured by Barringer Instruments, is one of these two systems. A sample, collected on a sampling medium, is placed into the IONSCAN sample entrance slot and is then subsequently heated, vaporized and passed into the analytical train in a heated air stream. Any material which is porous, gas permeable, and capable of withstanding the heat generated during the vaporization step can be used as the medium to transfer a collected sample into the IONSCAN for analysis. Filter paper and porous Teflon sheet are two common materials used by the U.S. Coast Guard for transferring the collected sample into the IONSCAN.

When a positive detection of a narcotic occurs during the preliminary search in any situation, a decision has to be made concerning whether a further intensive search is warranted. The impact of an intensive search will be substantially different dependent on the situation. If the positive detection is from a passenger at a port of entrance the delay at a check point and the search of his/her private belongings result in minimal delays and inconvenience. If the suspicious object is cargo, a vehicle, or a vessel, the potential of a destructive and time consuming search could occur. Detaining a vessel for one or more days in not unheard of. Resampling the suspicious area before a further intensive search is undertaken is the normal procedure employed to justify the need to conduct further detailed searching. The same procedure is employed if two canines are available in that verification of an alert is obtained using a second canine. Therefore, reproducibility of sampling and instrumental analysis is critical in justifying an in depth search based upon the analytical data. This is especially true in searches of maritime vessels because of the vessel size, the difficulty of sampling introduced by the multitude of objects and areas, and the limited time available during at-sea boardings.

INTRODUCTION

As reported at the 2nd Annual IMS Conference in Quebec City, it has been determined that when paper is utilized both as the sample collection and transfer material, the Ionscan analytical results for the determination of cocaine are reproducible. Field results from the last twelve months have supported this conclusion.

The logical extension of this research was to determine what effect, if any, different types of paper with different median porosities have on the Ionscan analysis for cocaine. There are two different directions this research could follow. The first is the investigation of several types of paper with varying physical properties and chemical compositions. The second is the investigation of one type of paper composition with varying physical characteristics (i.e. effective pore size, strength, wetability, etc.). For the purpose of this study, we chose to investigate the second condition. This decision was based on the fact that this particular type of paper has been proven effective in the field while introducing no known interferents in the Ionscan analysis for cocaine.

This paper presents the results of our study on the effects of a constant paper formulation with varying pore sizes on the Ionscan analysis for cocaine. Effects on the linear dynamic range of the calibration curve and cocaine peak drift time stability are presented. Teflon membrane, purchased from Barringer Instruments, was used as a sample holder material for comparison purposes.

EXPERIMENTAL METHODS

For the purpose of this study, three papers having similar compositions but of varying pore sizes in addition to Teflon were examined. Material specifications are as follows:

Sample Transfer Material	Nominal Pore Size
- Paper Sheet, Grade 404, purchased from Schleicher and Schuell, Inc.	20-30 micron
- Paper Sheet, Grade 497 purchased from Schleicher and Schuell, Inc.	8-12 micron
- Paper Sheet, Grade 402 purchased from Schleicher and Schuell, Inc.	2-5 micron
- Teflon Sheet Purchased from Barringer Instruments	50 micron

Aside from the different effective pore sizes, the three filter papers purchased from Schleicher and Schuell, Inc. are composed of the same material, 100 percent cotton linters. They are all hardened qualitative low-ash filter papers used primarily for the filtration of precipitates ranging in size from very fine (grade 402) to coarse (grade 404). Grades 404 and 402 contain an additive to increase the wet strength of the material. This additive (not identified by the manufacturer) has been observed not to introduce any interferent peak(s) to the Ionscan analysis. At present, the U.S. Coast Guard uses grade 404 paper in the field.

Calibration curves for each of these sample collection and transfer materials were run on the Ionscan. Standards of cocaine in methanol were used to spot the test materials. The test materials were loaded with concentrations of cocaine ranging from 5ng through 80ng, with five trials being accomplished at each concentration level.

RESULTS

Figure 1 details the calibration curves of the four materials tested. The amplitude of the cocaine peak is somewhat reduced when paper is used as the sample transfer medium relative to Teflon. However, there does seem to be an increase in the linear dynamic range for cocaine when paper is used relative to Teflon. When Teflon is used, it is generally accepted that the linear dynamic range for cocaine extends from the sub-nanogram range to approximately 10 nanograms, as shown in Figure 1. When using paper, this linear dynamic range is extended out to approximately 20 nanograms. The pore size of the paper does not affect the linear dynamic range.

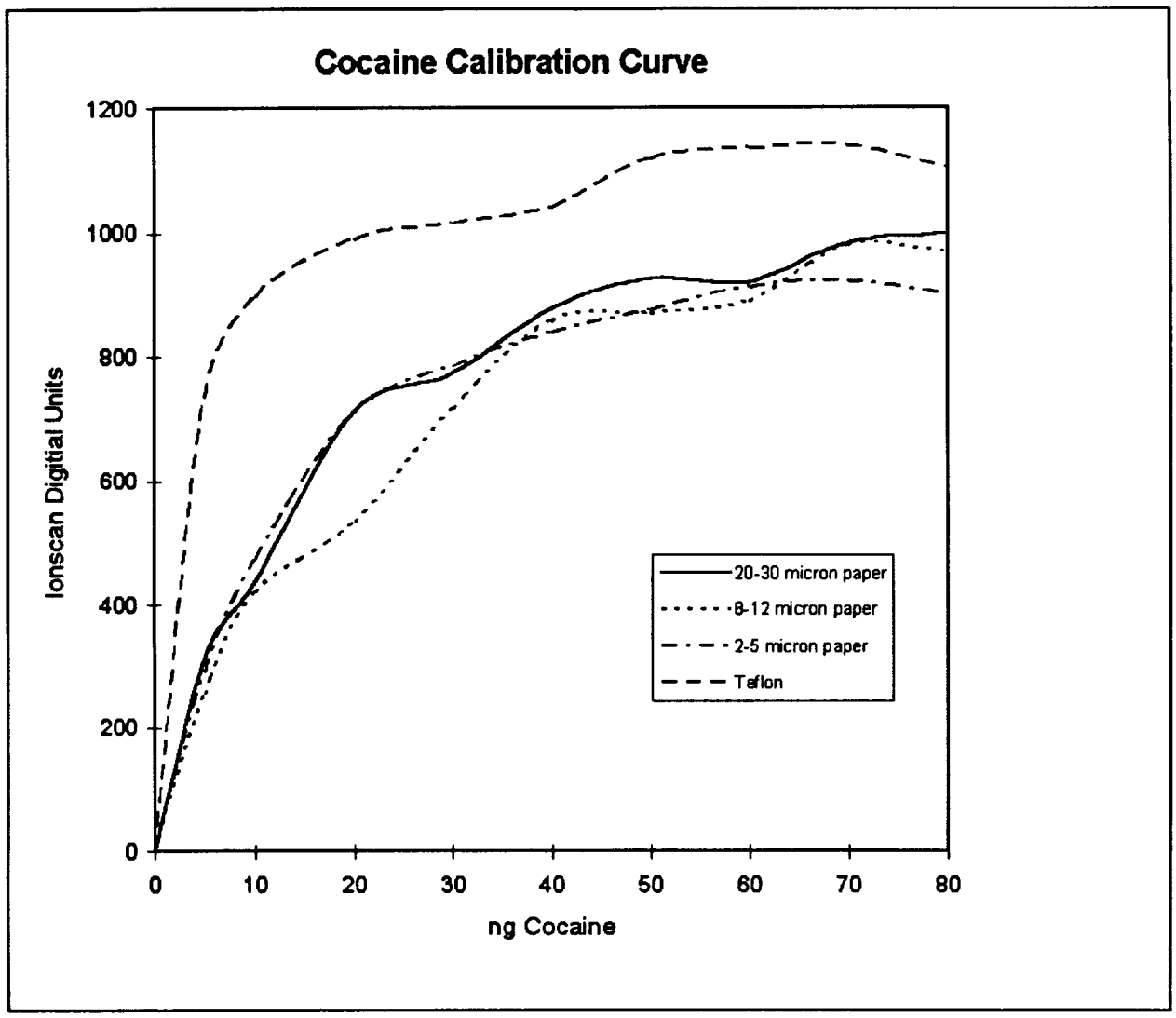

Figure 1
Cocaine Calibration Curves

Figure 2 depicts the calibration curves of the four materials tested as they relate to the number of Ionscan "windows" in which cocaine has been detected. These windows refer to the number of scans (out of a maximum possible 14 based on current instrumental setup parameters) that the Ionscan recognized the peak in question as a valid cocaine peak (i.e., a "hit"). As shown in Figure 2, at lower concentrations the number of windows in which a "hit" was recorded was, at times, reduced when using paper relative to Teflon. Although there is not a discernable difference between different types of paper used in this study, the general trend is that until the concentration level reaches approximately 25 nanograms a decrease in the number of windows in which cocaine is detected is exhibited.

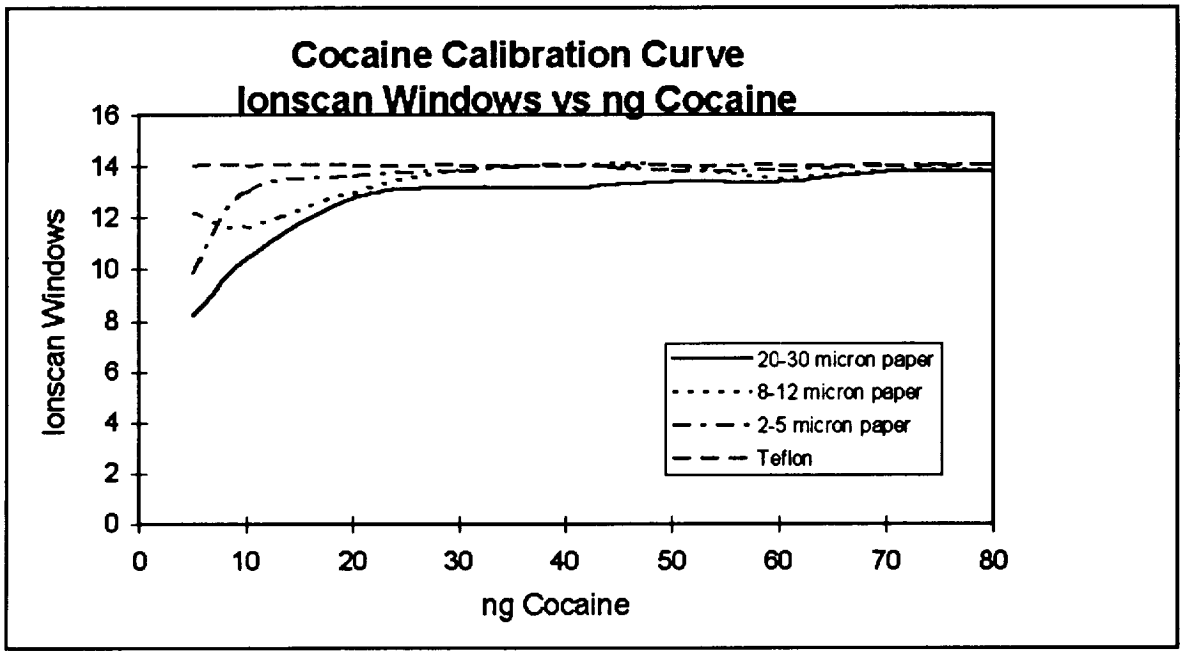

Figure 2
Cocaine Calibration Curve - Ionscan Windows vs. ng Cocaine

When using paper as a desorption media, the greatest concern is whether or not cocaine peak instability is introduced rendering accurate identification of cocaine questionable. The cause for this concern is due to the possibility that the paper impacts on the balanced heated air stream used for sample desorption and within the drift tube. Since the Ionscan is dependent on balanced desorb and drift gas flows, the possibility exists that a partial vacuum may be created in the drift tube if the desorb gas flow is partly blocked. As the mass flow controller struggles to balance the two flows, this partial vacuum will fluctuate as a balanced condition is being achieved. The magnitude of the fluctuation will decrease as a steady state condition is achieved. The net result could be that the cocaine ion is changing drift rates as the analysis progresses with the end result being a cocaine peak with shifting drift times between the early scans and the late scans. This would be detrimental if the cocaine peak "drifted" out of the target window. Figure 3 details the drift of the cocaine peak about the average drift time for the entire analysis. Since any peak instability is already included in the Ionscan algorithm for the average drift time, this is not a perfect analysis. It does, however, give a good representation of the amount of instability that is introduced.

As shown in Figure 3, a certain degree of peak instability is introduced when paper is used as the desorption media. There appears to be an inverse correlation between the pore size and the severity of the peak instability with the smaller pore size paper producing the greatest peak drift. A plot of the peak drift as a function of windows number exhibits a sinusoidal type curve about the average drift time. This may be due to the mass flow controller struggling to balance the flow by constantly adjusting the flow up and down as flow fluctuations are sensed.

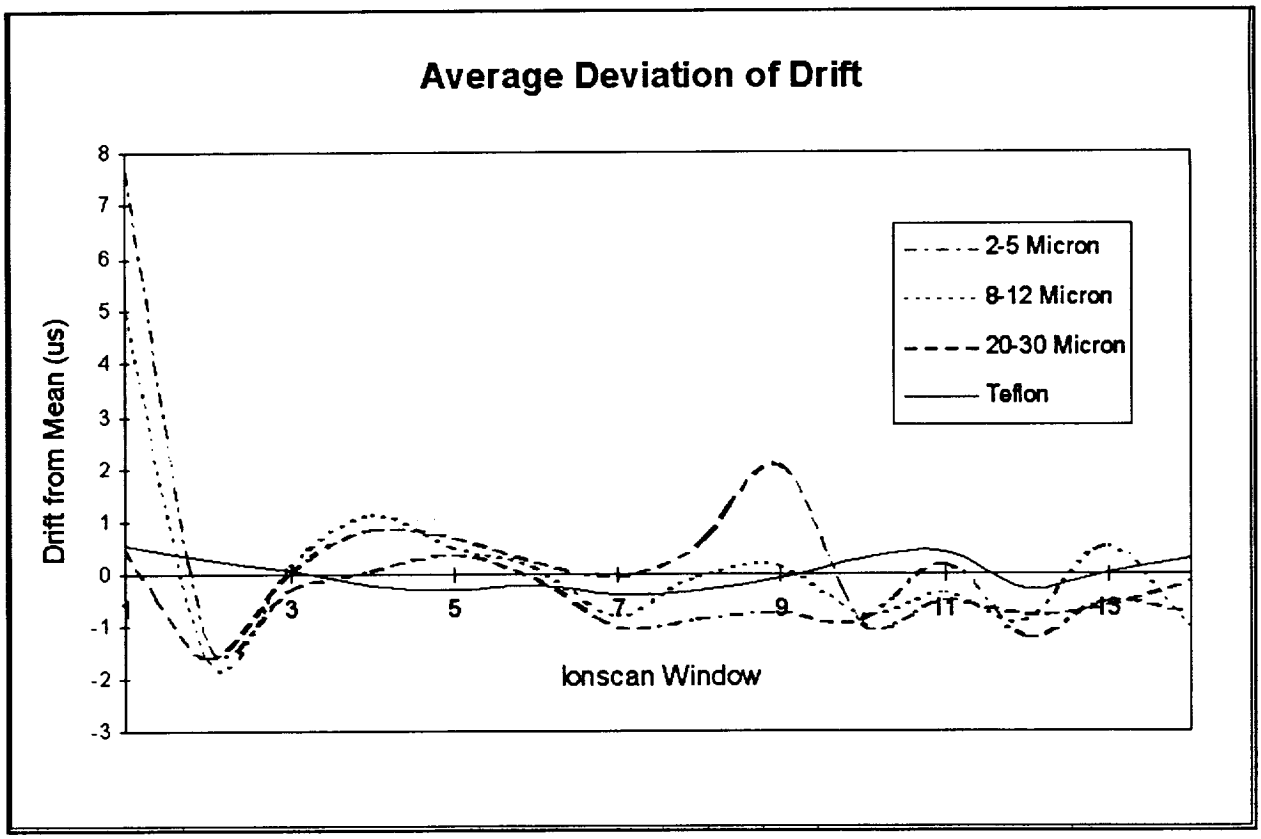

Figure 3
Average Deviation of Drift of Cocaine Peak

DISCUSSION

As evidenced by the results of this study, there is an effect on the Ionscan analysis when paper is utilized as the sample holder material for cocaine. The question that remains is whether this effect is great enough to preclude one from using paper as a sample holder material.

Due to the inherent design characteristics of the Ionscan, and in general IMS technology, quantitation of results has proven to be, at best, questionable over a wide linear dynamic range. IMS technology for cocaine analysis is also affected by sample matrix phenomenon [1]. While quantitation of results is not paramount, there seems to be an aspect of the human nature that always wants to know, "How much was analyzed?" When utilizing paper as a desorption medium, the concentration range in which quantification is possible is increased relative to Teflon. When using Teflon, one has only the amplitude of the response as information to use for quantification purposes since the number of windows is more likely to be at the maximum of fourteen. When using paper, however, the increased linear dynamic range of the amplitude of response coupled with the affected growth curve pattern in this

same range give two pieces of information to use for identification purposes. The results have shown that the windows that are not analyzed as a "hit" are usually the early windows of the analysis. This may be related to the capillary action of the paper which disperses the standard solution within the matrix of the paper as opposed to Teflon. While the total number of windows may be used for identification purposes, examination of the growth pattern of the earlier windows may lend some help in quantifying the result. The overriding fact that must be kept in mind, however, is that quantification with IMS can only be achieved when known, laboratory type samples are being analyzed on known background matrices. When analyzing a field sample, there is an unknown multitude of compounds present. Each one of these unknown compounds, with its corresponding proton affinity, could affect the amplitude of the compound of interest through competition in the ionization "reaction zone". Quantitation in the field is, basically, impossible and may be best performed by the classical standard addition method. However, this classical standard addition method is limited as due to the limited linear dynamic range of the system.

When using paper as a sample transfer material, a gas flow imbalance may be established. The design of the Ionscan calls for a heated air stream to be pushed through the sample transfer material at a rate of approximately 300cc/min. In addition, a heated anvil makes contact with the sample transfer medium during desorption. In combination, the anvil and the heated air stream desorb the compounds on the sample transfer material and transport them into the reaction chamber and eventually into the drift tube. When utilizing paper as the sample transfer material, a certain portion of the desorb air flow may not be allowed to pass through the paper. The effective flow through the paper would therefore be diminished. The mass flow controller within the Ionscan, however, would try to maintain the desorb flow into the Ionscan at the preset level. For this reason, room air would most likely be pulled through the side of the sample holder and sucked into the Ionscan. At the same time, cocaine molecules on the surface of the sample holder material would be vaporized by the heat of desorption and carried into the Ionscan by the rushing room air. This "flow balance" would not be achieved instantaneously, as a perfectly sealed and unhindered desorb air flow region would be. This may explain the increased peak instability observed in the earlier windows as evidenced in Figure 3. The time required for this equilibrium to be established may, in fact, cause a peak not to be recognized or not be present at all in the earlier windows. This is evidenced in Figure 2, with the greatest effect occurring at lower concentration ranges when the population of cocaine ions is reduced. This "blocked flow" condition may also occur when samples are collected with a vacuum device using Teflon as the sample collector. The massive air flow and increased number of particulates may result in passageways of the Teflon filter membrane becoming clogged and effectively "blocked". This same condition may also occur when wipe sampling any material that is greasy, dirty, etc. if the material in question becomes imbedded in the matrix of the sampling material.

Over the last eighteen months, it has been shown that surface wipe sampling is the most effective means of collecting samples in the maritime environment. Vacuum sampling has been judged to be too cumbersome. In addition to the logistical and safety concerns of carrying a vacuum apparatus around a ship, a hand held sampling system of some sort can reach many places that a vacuum cannot. When collecting samples by wiping, Teflon has proven to be not rugged enough. The Teflon filter breaks apart in most instances. Paper, however, has been shown to withstand the rigors of wiping in every conceivable type of maritime environment. The only other material that equals paper in this aspect is cotton gloves. Since the cotton glove itself cannot be analyzed by the Ionscan, some type of transfer to a sample holder material must be accomplished. The transfer efficiency in this

method (estimated to be 10-15%) will reduce the overall detection level capability. Research on new materials that are rugged enough to withstand the rigors of shipboard sampling and can also be used as a sample transfer material are presently being investigated by other law enforcement agencies. An example is the Canadian Customs "Gerry Bag". Until these materials are fully tested in the maritime environment, paper will remain the best option.

The overall conclusion remains that paper is the sample holder material that is best suited for use in the maritime environment. While its analytical properties are not as ideal as Teflon, its field adaptability is far superior. If cost is factored in, it becomes even more superior.

This study was conducted utilizing cocaine as the compound of interest. Therefore, the conclusions drawn herein pertain only to compounds whose drift times approximate cocaine. Further studies should be conducted on other narcotics having shorter drift times. One suggestion would be the study of the behavior of methamphetamine when subjected to the same experimental conditions.

REFERENCES

[1] Fytche, L.M., Hupe, M., Kovar, J.B., and Pilon, P., "Ion Mobility Spectrometry of Drugs of Abuse in Customs Scenarios: Concentration and Temperature Study," Journal of Forensic Sciences, JFSCA, Vol. 37, No. 6, November 1992, pp.1550-1566.