BLANC'S LAW FOR THE ESI ERA: PREDICTING ION MOBILITY IN MIXED DRIFT GASES

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INTRODUCTION

- The majority of drift tube ion mobility spectrometry (DTIMS) measurements are conducted in neat drift gases (N_2, He, Ar, CO_2, etc.) or predefined mixtures (air).[1]
- Blanc's Law provides a means to predict ion mobilities in mixed drift gases, but remains largely unexplored for polyatomic systems
- Blanc's Law is defined as:[2]

$$\frac{1}{K_{0\,mix}} = \sum \frac{X_i}{K_{0\,i}}$$

Equation 1. *Blanc's Law where K_{0mix} is the resulting mobility of the ions in a mixture of drift gases where X_i is the mole fraction of gas i and $K_{0\,i}$ is the mobility of an ion in gas i*

- Mobility separations of ions within a trapped ion mobility spectrometry (TIMS) device are driven by drift gas colliding with the ions trapped in a potential well, and external calibration of the TIMS is required.[3]

AIMS

- **Characterize Blanc's Law for predicting mobilities of large, polyatomic ions generated from ESI**
- **Measure mobilities in mixed drift gases on DTIMS for use in TIMS calibration**
- **Characterize mixed gases within the TIMS**
- **Use Banc's Law as a means for TIMS (re)calibration**

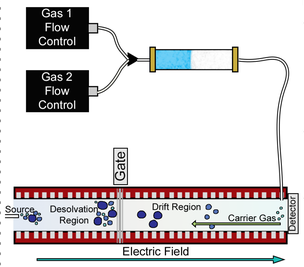
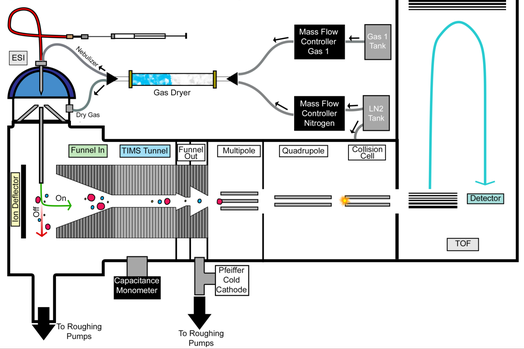


Figure 1A. *Two different gases are mixed depending on the flow rates specified by two mass flow controllers and introduced into the back of the drift region of the drift tube.*

Figure 1B. *The TIMS was modified to by-pass the default flow controller and introduce a two-gas mixture using the same flow controllers for the DTIMS system*



METHODS

- Standard solutions (25 μM) of tetraalkylammonium salts (TXA) and (160 μM) tri-L-alanine (AAA) were electrosprayed into the DTIMS.
- Gases were mixed and added to the back of the drift-tube (Figure 1A)
- Standard solutions of TXA salts, alkyl-trimethylammonium salts (XTMA), and tune mix (TM) were sprayed into the TIMS for calibration.[4] Tri-L-alanine was analyzed using the same TIMS settings. Mixed gases were introduced into the TIMS as in Figure 1B.

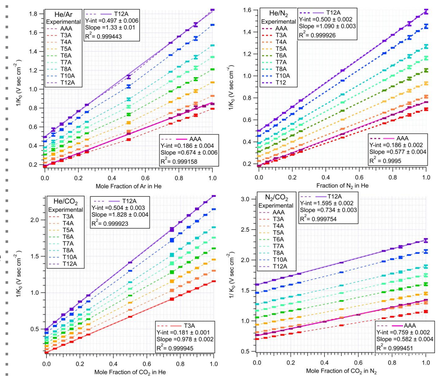


Figure 2. *The mobilities of the TXA salts and AAA were measured in defined binary mixtures in the DTIMS (Figure 1A).*

DTIMS-RESULTS

The inverse mobilities of TXA salts and AAA are predicted by Blanc's Law within error for the DTIMS system (Figure 2). If graphed as a function of gas mole fraction, the relationship of the inverse mobilities is highly linear (R^2>0.999) in most cases. This indicates that Blanc's Law can be used to provide mobilities of gas mixtures for use of TIMS calibration.

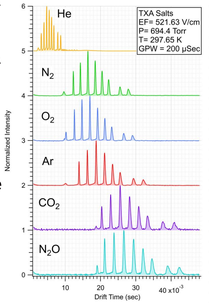


Figure 3. *In the neat drift gases using the same settings taken on the same day, the DTIMS spectra of the TXA salts are shown.*

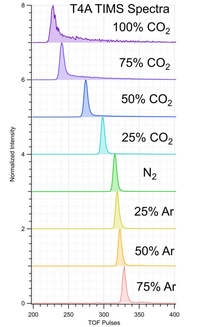


Figure 4. *The TIMS spectra for T4A using the same TIMS voltage and mass spectrometer settings, but using different gas mixtures in the TIMS region.*

TIMS-RESULTS

When binary gas mixtures were added to the TIMS, the measured mobilities (i.e. elution voltages) show deviations from Blanc's Law when adapted to the TIMS (Figure 5). However, any observed deviations were corrected when the calibration procedure converts the elution voltages into the mobility domain (Figure 6).

$$V_{elute\ mix} = \sum X_i V_{elute\ i}$$

Equation 2. *Blanc's Law adjusted to TIMS elution voltages.*

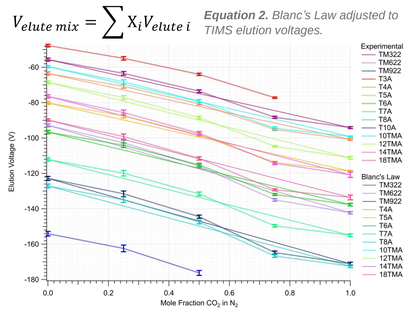


Figure 5. *The TIMS was filled with defined mixtures of N_2 and CO_2 and the elution voltage is monitored as the ratio changed for tune mix, the TXA salts, and the XTMA salts.*

$$V_{elute} = \frac{A}{K_0} + V_{out}$$

Equation 3. *TIMS calibration equation,[5] V_{elute} is elution voltage, K_0 is reference mobility, A and V_{out} were found through linear regression*

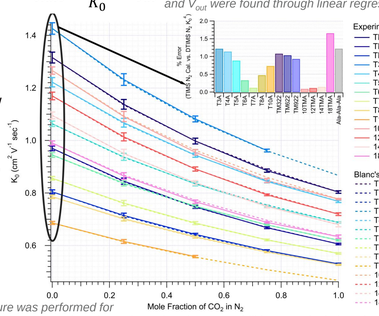


Figure 6. *Once the calibration procedure was performed for each gas mixture using the experimental TXA K_0 values from Figure 2 as known mobilities, any deviations from Blanc's Law in the elution voltage domain (Figure 5) were corrected in the mobility domain (above). The TIMS calibration for this data set gives an error of <2% for all calibrants when compared with previous K_0 values.[4]*

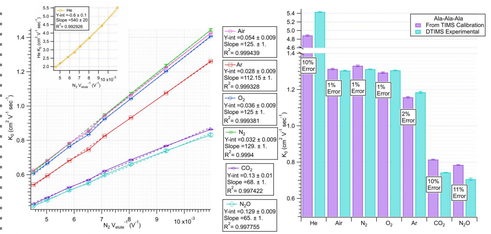


Figure 7. *Mobilities of the TXA salts were measured in N_2 in the TIMS, which was then calibrated with the mobilities measured from the DTIMS in different drift gases. The consequent calibration curves were then used to find the predicted mobility of AAA using the elution voltage in N_2 in the TIMS. The error in mobility from the calibration increases as the gases change from the gas in the TIMS (N_2).*

CONCLUSIONS

- Mobility data of several classes of polyatomic ions are presented in 6 distinct drift gases and in defined mixtures for both the TIMS and DTIMS systems
- Blanc's Law holds for polyatomic systems measured using DTIMS and serves as a way to obtain reference mobilities for mixed drift gases in a TIMS.

BIBLIOGRAPHY

1. May, J. C.; Morris, C. B.; McLean, J. A. Ion Mobility Collision Cross Section Compendium. Anal. Chem. **2017**, 89 (2), 1032–1044.
2. Blanc, A. Recherches sur les mobilités des ions dans les gaz. Journal de Physique Théorique et Appliquée **1908**, 7 (1), 825–839.
3. Michelmann, K.; Silveira, J. A.; Ridgeway, M. E.; Park, M. A. Fundamentals of Trapped Ion Mobility Spectrometry. J. Am. Soc. Mass Spectrom. **2014**, 26 (1), 14–24.
4. Naylor, C. N.; Reinecke, T.; Ridgeway, M. E.; Park, M. A.; Clowers, B. H. Validation of Calibration Parameters for Trapped Ion Mobility Spectrometry. J. Am. Soc. Mass Spectrom. **2019** *Under Review.*
5. Hernandez, D. R.; DeBord, J. D.; Ridgeway, M. E.; Kaplan, D. A.; Park, M. A.; Fernandez-Lima, F. Ion Dynamics in a Trapped Ion Mobility Spectrometer. Analyst **2014**, 139 (8), 1913–1921.

ACKNOWLEDGEMENTS

The authors would like to thank the Department of Chemistry at Washington State University for support and Bruker Daltonics for their instrument and guidance. TR would like to acknowledge support from the NSF under award CHE-1506672 and support for CNN was provided by DTRA Basic Research Program (Grant No. HDTRA1-14-1-0023).

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