Design and Construction of a Benchtop High Resolution Atmospheric Pressure Resistive Glass Drift Tube Ion Mobility Spectrometer

Paula Holmes, Ph.D.[1], Facundo Fernandez, Ph.D.[2], Prabha Dwivedi, Ph.D.[2], Joel Keelor[2] and Bruce Laprade[1]
[1]PHOTONIS USA, Sturbridge, MA; [2]Georgia Institute of Technology, Atlanta GA

PHOTONIS | INDUSTRY | SCIENCE | MEDICAL

Introduction:

Ion mobility spectrometry (IMS) has become widely accepted for the detection of chemical warfare agents, explosives and narcotics as well as for pharmaceutical quality control and pesticide screening of food. Currently available commercial IMS instruments have resolving power between 10-60. In order to minimize the frequency of false positive and false negative results, it is necessary to design and construct an ion mobility spectrometer with high separation power without compromising instrument simplicity, serviceability, and cost.

Resistive Glass drift tubes provide key benefits such as uniform electric fields with minimal radial inhomogeneities and ease of construction. In addition, the single-piece construction allows uniform counter flow of drift gas without the need for additional containment. The photo below in Figure 1 shows the benchtop prototype ion mobility instrument constructed with Resistive Glass reaction and drift tubes. All associated electronics are contained in the enclosure beneath the IMS.

Figure 2 is a horizontal cross-section of the prototype instrument showing the reaction and drift tubes along with the Bradbury-Nielsen style ion gate and Faraday plate anode.

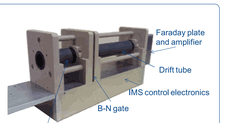


Figure 1: Photo of Resistive Glass tube IMS prototype.

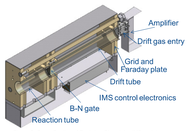


Figure 2: Cross-Section of Resistive Glass tube IMS prototype

Background:

PHOTONIS Resistive Glass tubes are designed to guide ions by generating a uniform electric field. Resistive Glass tubes are composed of a proprietary lead silicate glass that has been hydrogen fired to create an integral semi-conductive layer, not simply a coating. This robust resistive layer is typically several hundred angstroms thick. The resistivity can be varied over several orders of magnitude from 10^6 to 10^{11} ohms/square to suit the specific application such as drift tubes, capillary inlet tubes and reflectron lenses shown in Figure 4.

Resistive Glass products are highly uniform in resistivity. 4-point probe data indicates an overall variation in resistance of +/- 1.5% across a 75 mm plate. Kelvin probe data indicates that the uniform resistance results in a uniform electric field. The Resistive Glass provides a uniform gradient with no significant anomalies. The smooth gradient indicates extremely uniform resistivity in the surface of the glass.

Figure 4. Examples of products made with Resistive Glass.

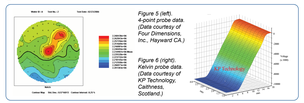


Figure 5 (left). 4-point probe data. (Data courtesy of Four Dimensions, Inc., Hayward CA.)

Figure 6 (right). Kelvin probe data. (Data courtesy of KP Technology, Caithness, Scotland.)

Methods:

Reaction and drift regions of the ion mobility spectrometer were fabricated using Resistive Glass technology. The dimensions of the tubes were 40 mm OD and 30 mm ID. The length of the reaction and drift tubes were 90 mm and 250 mm, respectively. Ionization was achieved by either a corona discharge or a Direct Analysis in Real Time, DART SVP source manufactured by IonSense, Inc. The voltage applied to the entrance of the Resistive Glass reaction tube was 12 kV (field strength of approximately 400 V/cm) while the corona voltage was set to 14.8 kV. For the DART SVP trials, the source operated at ground. Dry nitrogen drift gas flowed at a rate of 1 l/min. Dry nitrogen was also used as the DART gas with a flow rate of 2 l/min. The IMS was operated at room temperature for all experiments, although the instrument incorporated integral heaters and can be operated at 150°C.

Ion gating was accomplished with a Bradbury-Nielsen type electronic gate. The pulse width was set to 200 µs using a Stanford Research Systems Model DG535 pulse generator. The 30 mm diameter Faraday plate detector was located 0.7 mm from the back end of the drift tube. A Tektronix Model TDS 2002B digital storage oscilloscope captured 128 sweeps for each mobility spectrum with a 100 ms total scan time. All spectra are presented in raw form without background subtraction. Custom gate driver and amplifier circuits were designed and built to enhance the spectrometer's operation.

Resolving power was measured to demonstrate the capability of the Resistive Glass tube IMS using the ratio of the measured drift time to peak width (FWHM), $R_D = t_d/w_{0.5}$. Analytical performance was evaluated for a well known calibrant and a chemical warfare agent simulant. Reduced mobility K_o values were calculated in order to confirm the identification of the observed signals using the formula, $K_o = K * P/P_o * T_o/T$. Experimentally determined values were then compared to those published in the literature.

The Bradbury-Nielsen type ion gate was built using photo-etching technology. The unique design and approach taken in building the ion gate resulted in a device that is robust, high-performance, low cost, and simple to assemble when compared to the conventional winding technique. The ability to handle entire grid sets rather than individual wires to insure precise positioning of all wires provides a distinct advantage to traditional approaches.

Grids were fabricated from titanium foil resulting in sets of 75 µm diameter wires connected by end tabs. The grids were bonded to alumina frames in an assembly fixture which also permitted uniform wire tensioning. The resulting gate halves were then assembled into a final gate with 635 µm spacing between adjacent wires. Figures 7 and 8 (below) illustrate the gate assembly process.

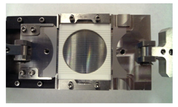
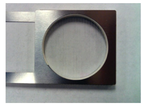


Figure 7 (left): Ion gate partially installed in assembly fixture.

Figure 8 (right) shows a fully assembled gate with 635 µm spacing.



Results:

Ion mobility spectra were acquired for a well-known calibration compound, di-tert-butylpyridine (2,6 DtBP) and Sarin simulant, dimethyl methylphosphonate (DMMP).

Corona Discharge:

Figure 9 (right) shows the prototype instrument with a corona discharge assembly for sample ionization.

The mobility spectrum shown in Figure 10 was generated from four micrograms of the calibrant di-tert-butylpyridine (2,6 DtBP) in methanol. The peak at 39.7 ms is attributed to the DtBP while the peaks at shorter drift times are attributed to background ions. A resolving power of 82 was calculated for the background ion at a drift time of 29.4 ms.

Twenty-four micrograms of di-methyl-methylphosphonate (DMMP) in methanol was also analyzed. Figure 11 shows the mobility spectrum for the DMMP sample. The peak at 45 ms is attributed to the DMMP proton bound dimer while the remaining peaks are unidentified DMMP response peaks, likely due to clustering. The resolving power for the dimer was found to be 64.

DART SVP:

Figure 12 (below) shows the IMS prototype with the DART SVP ionization source along with a sample holder and screen mounted to the front of the Resistive Glass reaction tube.[1,2] The DART capillary tube was positioned about 1 mm from the screen after sample spotting.

Four micrograms of DtBP in methanol was spotted onto the screen mounted to the IMS sample holder. The DART source was kept at room temperature. The mobility spectrum in Figure 13 shows the expected DtBP peak at a drift time of about 40 ms. A small background ion peak was also observed. The measured resolving power for the DtBP peak is 83.

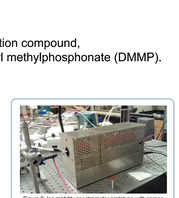


Figure 9: Ion mobility spectrometer prototype with corona discharge source.

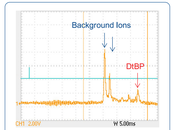


Figure 10: Ion mobility spectrum of DtBP with corona discharge source.

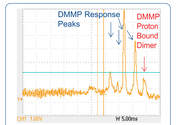


Figure 11: Ion mobility spectrum of DMMP with corona discharge source.

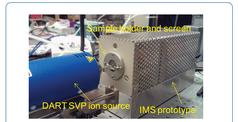


Figure 12 Ion mobility spectrometer prototype with the IonSense DART SVP source.

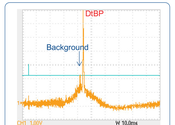


Figure 13: Ion mobility spectrum of DtBP with DART source at room temperature.

1. *Analytical Chemistry*, 2011, 83, p.1908-1915
2. US Patent Application 20120068063: *Direct Atmospheric Pressure Sample Analyzing System*, Filed 28 May, 2012; Published 22 March, 2012.

Results (continued):

Twenty four micrograms of DMMP in methanol was also spotted on the sample screen. Again, the temperature of the DART source was kept at ambient. The mobility spectrum in Figure 14 (right) shows the expected DMMP peaks along with the background ion peaks.

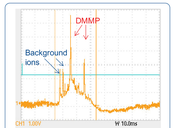


Figure 14: Ion mobility spectrum of DMMP with DART source at room temperature.

The DMMP monomer appears at a drift time of 34.8 ms with a resolving power of 87.5 and the DMMP proton bound dimer appears at 44.8 ms with a resolving power of 112.

The temperature of the DART source was then increased to 300°C which is the typical operating temperature for most samples. The DMMP analyte was spotted and a mobility spectrum was acquired. The sharpness of the peaks remained high and a resolving power of 150 was measured for the DMMP proton bound dimer (Figure 15), which approaches the theoretical limit. The results of increasing the DART temperature support the assumption that the gas is aiding de-clustering and drying of the ions, thus increasing the resolving power.

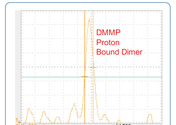


Figure 15. Ion mobility spectrum of DMMP Proton Bound Dimer with DART source at 300°C.

The measured drift time for the DtBP and DMMP along with the precise room temperature and pressure were used to calculate the reduced mobility, K_o in $cm^2/V\text{-}s$. The K_o values determined from these experiments are generally in good agreement with those published in the literature (Table 1).

The K_o value for the DMMP monomer from the corona trial is noticeably less than the reported value and the value obtained from the DART experiment. This is consistent with the longer drift time observed for the DMMP monomer when the corona source was used and supports the idea that the DART gas may be aiding declustering and drying of the ions in the reaction region.

Table 1: Reduced mobility values for DtBP and DMMP with corona discharge and DART sources.

	Experimental K_o ($cm^2/V\text{-}s$)		Published K_o ($cm^2/V\text{-}s$)
	Corona Discharge	DART SVP	
DtBP	1.42	1.41	1.42-1.46*
DMMP Monomer	1.37, 1.52, 1.66, 1.77 (cluster)	1.62	1.58**
DMMP Proton Bound Dimer	1.25	1.26	1.25**

* G. A. Eiceman, E. G. Nazarov, J. A. Stone, *Analytica Chimica Acta* 2003, 493, 185-194.
** *Ion Mobility and Mass Spectrometric Investigations of Organophosphates Related to Chemical Warfare Agents and Pesticides* (p.55). Price, Sarah Ellen (2010) Ph.D. thesis, University of Birmingham.

Conclusions:

- A benchtop ion mobility spectrometer with ultra high resolving power was designed and constructed with Resistive Glass tubes and a photo-etched Bradbury-Nielsen type ion gate.
- Resolving power of 64-150 was achieved for background ions, a calibrant and a chemical warfare simulant.
- Greater resolving power was achieved with the DART SVP ion source compared to the corona discharge source.
- Good agreement was found between the measured reduced mobility values of DtBP and DMMP and those published in the literature.
- Four micrograms of DtBP and twenty four micrograms of DMMP were detected with ease and with signal to noise ratios greater than 10.