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PREDICTION OF ION SEPARATION FROM LITERATURE DATA FOR THE ION MOBILITY DETECTOR

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SUMMARY

This paper presents a method to predict selectivity of an ion mobility detector for capillary gas chromatography. In the process of describing this method, a term called the "reduced drift constant", t_k, is defined to be

$$t_k = t(E/L)(760/P)(T/273)$$

where t is the drift time of the ion in milliseconds, E is the electric field in volts per centimetre, L is the length of the drift tube in centimetres, P is the pressure of the drift gas in torr and T is the temperature of the drift gas in degrees Kelvin.

Ion mobility separation between two ions can be predicted from literature data when they satisfy the inequality

$$t_{k2} - t_{k1} > t_{k2}/R$$

where t_{k2} is the reduced drift constant of the ion with the lower mobility, t_{k1} is the reduced drift constant of the ion with the higher mobility and R is the resolution of the ion mobility spectrometer. For two ions satisfying this inequality, it can be shown that the chromatographic detector selectivity for one ion over another is greater than 100.

INTRODUCTION

Over the past few years a unidirectional flow design for an ion mobility spectrometer has been demonstrated to be useful as a sensitive and selective detector for capillary gas chromatography (GC)[1–6].

One requirement for selective detection after GC with ion mobility spectrometry (IMS) is that the ion of interest be separated from interfering ions. Currently, in order to determine if one ion can be selectively detected from another, Br^- from I^-, for example, two test compounds, one containing bromine and the other containing iodine, must be evaluated experimentally. While the mobilities of bromide and iodide are known to be different, it is not clear from mobility data alone whether these ions can be separated sufficiently to permit selective detection of iodine compounds in the presence of bromine compounds, or *vice versa*. For many analytical problems it would be convenient if ion mobility separation and selective GC detection could be predicted from literature data without having to resort to experiments for every individual case.

Recently, we have defined the practical resolving power of an ion mobility spectrometer by analogy to the single peak definition often used in mass spectrometry[6]. Defining IMS resolution (R) in terms of mobility drift times rather than masses, the relation is given as

$$R = t/2w \tag{1}$$

where t is the drift time in milliseconds and w is the ion peak duration at half height.

Unfortunately, the standard method of recording ion mobility data, the reduced ion mobility constant (K_0), is not convenient for use with this definition of IMS resolution. Reduced mobility constants are calculated from

$$K_0 = (1000L/tE)(P/760)(273/T) \tag{2}$$

where L is the ion drift length in centimetres, E is the potential gradient in volts per centimetre, t is the drift time in milliseconds, P is the pressure in torr, and T is the absolute temperature of the drift gas. The major advantage of reporting ion mobility data in terms of reduced mobility constants is to permit comparison of results from one laboratory to another. Also mobility constants are convenient because through the Einstein relation ($K_0 = qD/kT$) they become direct measurements of diffusion coefficients[7]. For most analytical purposes, however, this direct correlation with diffusion coefficients is not as important as a convenient term for use with the resolution equation.

This paper defines a term called the reduced drift constant (t_k) which can be used to predict the mobility separation of ions of interest. It also demonstrates this constant's application to halide ion separation, and describes its use for the estimation of response selectivity when ion mobility spectrometry is used as a detection method after chromatography.

DEFINITIONS

In a manner similar to that for the definition of reduced mobility constants (eqn. 2), an ion drift time can be corrected for temperature and pressure to produce a reduced drift time (t_0).

$$t_0 = t(760/P)(T/273) \tag{3}$$

Substitution into eqn. 2 gives

$$t_0 = (1000/K_0)(L/E) \tag{4}$$

Multiplying this reduced drift time by the ratio E/L produces a value which is independent of the electric field and the drift tube length, giving the final relation

$$t_k = 1000/K_0 \tag{5}$$

where t_k is called the reduced drift constant with units of (V) (ms)/(cm^2). For the analytical chemist, this reduced drift constant serves the same important function as the reduced mobility constant of providing a method for intra- and inter-laboratory comparison of data and can also be conveniently used with the resolution equation to predict the separation of one ion species from another. Of course, t_k values can also be calculated directly from drift time data using the following equation.

$$t_k = t(E/L)(760/P)(T/273) \tag{6}$$

EXPERIMENTAL

The ion mobility separations and measurements reported in this paper were accomplished with a Phemto-Chem 100 (PCP, West Palm Beach, FL, U.S.A.) ion mobility spectrometer. The ionization source consisted of a 11 millicurie nickel-63 ionization source, and the data was obtained via a Model 1072 Nicolet Signal Averager. Table I provides a summary of the experimental conditions used in obtaining the spectra reported in this paper.

The IMS resolution of the instrument used in this study was calculated from the major positive reactant ion, $(H_2O)_nH^+$. As an example of how drift constants and IMS resolution can be used to predict ion separation, the separation of chloride, bromide, and iodide ions was investigated. Chloride and bromide ions were produced by the dissociative capture of electrons by chlorobenzene and bromobenzene while the iodide ion was produced by the dissociative capture of electrons by methyl iodide. Introduction of these test compounds was accomplished by the injection of 0.05 μl of liquid using a Microliter Hamilton syringe (Model 7101). Spectra were taken only after each spectrum had stabilized.

RESULTS AND DISCUSSION

With the exception of a direct relation to diffusion coefficients, reduced drift constants (t_k) have all the positive attributes for reporting ion mobility data as re-

TABLE I

EXPERIMENTAL PARAMETERS FOR THE ION MOBILITY SPECTROMETER

Drift tube temperature	150°C
Atmospheric pressure	762.6 Torr
Nitrogen carrier gas flow-rate	250 ml/min
Nitrogen drift gas flow-rate	350 ml/min
Ion-molecule reactor length	6 cm
Ion-drift tube length	8 cm
Electric field	214 V/cm
Injection pulse width	0.1 ms
Repetition period	24 ms
Number of scans	1024

duced ion mobility constants plus several advantages which make them more convenient and practical for the analytical application of ion mobility spectrometry. One practical advantage is that they increase with decreasing mobility of the ion. This relation is more compatible with the concept of retention times in chromatography and thus more familiar to many analytical chemists. More importantly, however, is that t_k values are directly proportional to ion drift times and can be conveniently used in the IMS resolution equation.

In this paper we define separation to occur when the ion peak of interest is contaminated with less than 1% of the adjacent peak. If peaks are gaussian in shape, then this condition of separation is just satisfied for two ions producing the same size peaks when the valley between them is 12.5% of their peak heights. Also, the difference between their drift times will be equal to two times the peak duration at half height or 4.7 sigma. Thus, the requisite for ion mobility separation is

$$t_2 - t_1 > 2w_2 = t_2/R \tag{7}$$

where t_1 and t_2 are the actual drift times in milliseconds of the two ions in question and $t_2 > t_1$, w_2 is the peak duration at half height of the peak with a drift time of t_2 and R is the resolution of the spectrometer.

From eqn. 6 it can easily be shown that for a given drift length, electric field, pressure and temperature the inequality

$$t_{k2} - t_{k1} > t_{k2}/R \tag{8}$$

also predicts separation. Thus, separation can be predicted from reduced mobility constants reported in the literature and the resolution of the spectrometer to be used.

The resolution of our instrument under the conditions cited in Table I was determined to be 23 for the positive reactant ion $(H_2O)_nH^+$. For ion mobility spectrometers using beta ionization, this positive reactant ion peak is always present and resolution of the instrument can be checked regularly without having to run a doping experiment to introduce compounds that will produce Cl^- ions. Thus, this primary reactant ion peak serves as a convenient measurement of resolution and the value obtained provides an estimate of the minimum separation performance that can be expected from the instrument. For more information on the measurement of resolution in IMS, see ref. 6.

As an example of how this approach is executed, reduced mobility constants for chloride, bromide, and iodide ions were found in the literature and are listed in Table II along with their drift constants calculated using eqn. 5. For separation to occur between any two of these three ions, the difference in their reduced drift constants must be greater than t_{k2}/R. Thus, to separate chloride from bromide the difference in their t_k values must be greater than 380/23 or 16.5. Since the difference in t_k values is 38, their separation is easily achieved as shown in Fig. 1a.

A more difficult test is the separation of bromide and iodide ions. The difference between their t_k values is only 15 while the t_{k2}/R ratio is 17.2. Thus, under these conditions, separation would not be expected to occur with less than an 12.5% valley between the two peaks. Fig. 1b shows an ion mobility spectrum of these two ions. In agreement with this prediction, the valley between the peaks occurred at 20% of the average peak height as shown in Fig. 1b.

TABLE II

ION MOBILITY DATA FROM LITERATURE[9]

Ion	*Reduced mobility constant*	*Reduced drift constant*
Chloride	2.92	342
Bromide	2.63	380
Iodide	2.53	395

A major advantage of this approach is for prediction of chromatographic detector selectivity. If an ion mobility spectrometer is operated as a tunable selective detector for GC as described in ref. 8, its response can be tuned to ions with a specific drift time *t*. In practice the spectrometer is adjusted to respond to all ions that travel the length of the drift tube within a certain "window" of time. If this window is *t* ± *w*, then 98.1% of the total current of the ion of interest that has migrated through the drift tube will be collected. Ions drifting at different times will have a lower sensitivity. Thus, detector selectivity can be defined as the ratio of sensitivities of the

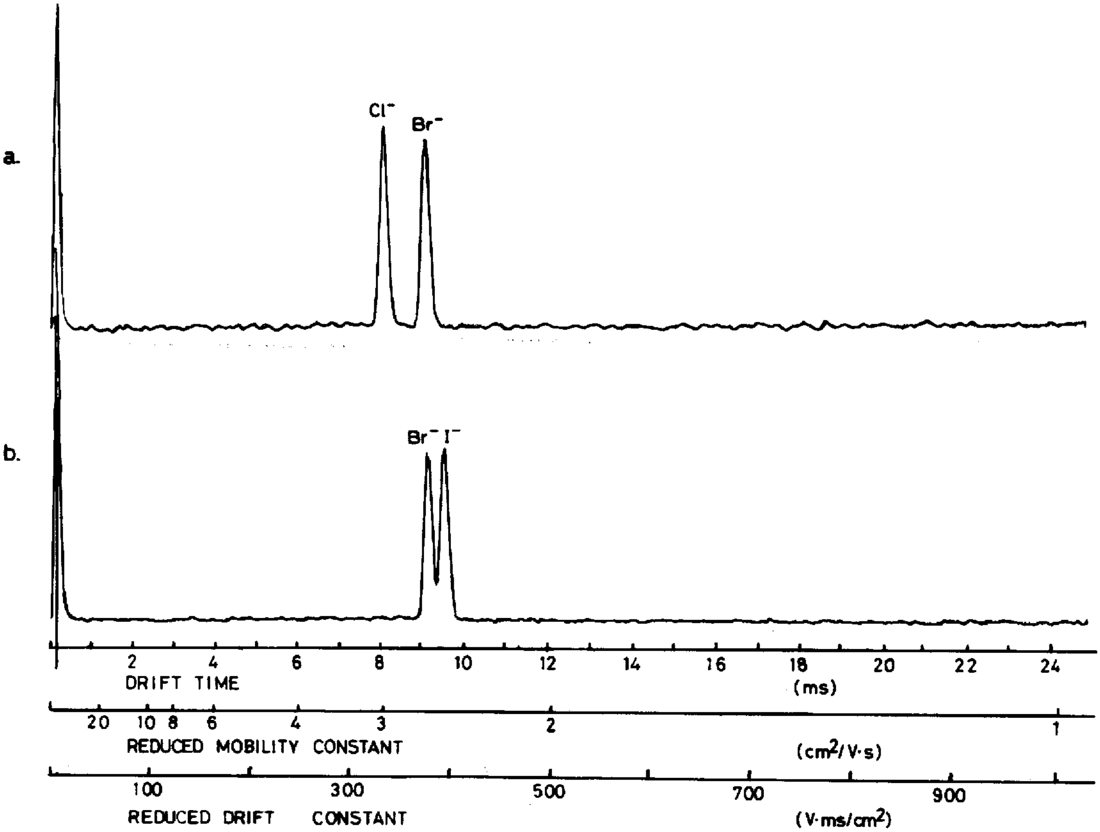

Fig. 1. (a) Mobility separation of chloride and bromide ions; (b) mobility separation of bromide and iodide ions.

ion of interest and an interfering ion. For the selective detection of bromide ions under the conditions presented in this paper, the detection "window" would extend from 8.93 ms to 9.37 ms with a median value of 9.15 ms. If an interfering ion is separated by 4.7 sigma (the conditions used to define separation), then the detector selectivity against the interfering ion will be 98.1%/0.94% or *ca.* 100. For ions that are separated by more than 4.7 sigma selectivity will be greater than 100.

As pointed out in ref. 6, when resolution is not diffusion limited it is not independent of drift time. For example, if instrument resolution had been determined from either the chloride ion, the bromide ion, or the iodide ion, it would have been found to be 18, 20, or 21, respectively, rather than 23 which was the value obtained from the primary positive reactant ion, $(H_2O)_nH^+$. We recommend the use of the hydrated proton reactant ion for the determination of instrument resolution for the convenience that this ion affords the analyst. In a clean ion mobility spectrometer using a ^{63}Ni ion source, the hydrated proton reactant ion is always present in sufficient quantity for easy detection. Thus, resolution measurements can be obtained almost instantaneously after turning on the instrument or changing parameters. In general, this reactant ion drifts with a velocity which is faster than those of most organic ions and similar to those of most inorganic ions. Thus, instrument resolution predicted from this reactant ion will almost always be less than those calculated from organic ions and similar to those calculated from inorganic ions. Some inorganic ions, however, will produce resolutions that are smaller than those calculated from the hydrated proton. Remember that the resolution calculated from the chloride ion was 18 while that calculated from the hydrated proton was 23. But the minimum difference in reduced drift constants required for separation of chloride from another ion is 345/18 or 19 when calculated from actual resolution and 345/23 or 15 when calculated from the resolution which determined from the reactant ion. Thus, it appears that the resolution calculated from the hydrated proton peak provides a good estimate of the separation power of the spectrometer and allows a reasonable prediction of separation between two ions.

There are reasons, however, why one should be cautious when using this reactant ion to predict resolution and separation. Because the actual charge-carrying species are a mixture of H_3O^+, $H_5O_2^+$, $H_7O_3^+$, and $H_9O_3^+$ in equilibrium with each other and with water vapor, the average ion size and mass are depenent on both the drift gas temperature and on the H_2O concentration in the drift gas. Since the resolving power of an instrument is also a function of temperature and must be measured for each operating temperature[7], the effect of temperature is not critical for reproducible predictions of separation. The concentration of H_2O in the drift gas, however, is extremely important. For most ion mobility work, nitrogen is purified by a standard procedure which insures that the H_2O concentration is *ca.* 100 ppm and that it is reasonably constant from one instrument to another. Nevertheless, contamination with excess H_2O could significantly alter the instrument resolution calculated from the reactant ion, but not affect the actual resolving power of the instrument for ions which do not undergo chemical interaction with water. To insure that the ion mobility spectrometer is operating properly prior to measuring resolution, ion mobility measurements for the reactant ion should match those reported in ref. 9. In this work, the reduced drift constant for the hydrated proton was 433, matching that calculated from the reduced mobility data given in ref. 9.

A further complication with this method is the reliability of reduced ion mobility constants reported in the literature and with the uncertainty of their behavior at various temperatures. We have recently completed a tabulation of over 1000 reduced mobility constants reported in the literature. Only a fraction of these were determined with mass identified experiments and even fewer have been corroborated by other laboratories.

For reasons discussed above, the method presented in this paper cannot be considered exact, but it does provide a convenient and practical first approach for the prediction of ion separation and GC detection selectivity. Its use should help to more completely evaluate the role of ion mobility spectrometry as a detection method for chromatography.

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