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ION MOBILITY SPECTROMETRY - THEORY AND INSTRUMENTATION

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ABSTRACT. The main aspects concerning a new, powerful and very promising trace analysis technique - Ion Mobility Spectrometry (IMS) - are reviewed. Ion Mobility Spectrometry is based upon the separation of ions, which occurs because of their mobility differences in a relatively low intensity electrical field. Ions are obtained by the ionization of the neutral chemical species in the gaseous phase, at atmospheric pressure, by very fast and complex collisional charge exchanges and ion-molecule reactions. Included are sections which deal with the IMS principle, its theoretical basis, atmospheric pressure ionization processes, response characteristics and the corresponding instrumentation. Ion Mobility Spectrometry is definitely a technology with a very promising future, in spite of the current lack of information.

1. Introduction

Ion Mobility Spectrometry (*IMS*) is a modern analytical technique used especially to detect ultra-traces of chemical compounds in the air and so far less known worldwide. This technology emerged in 1970 *[1,2]* and rapidly developed, especially in the last decade. IMS succeeded very soon to pass from the laboratory toward field applications (in industry processes control and environmental pollution control, for instance).

The resurrection of IMS -after a period of slight stagnation in the 1980s- is due mainly to the real-time response, to its amazing detection limits and also to several practical considerations concerning the instrumentation (great simplicity compared with the complex instruments used in mass spectrometry, reliability, ruggedness and miniaturization). We have also to underline here another serious advantage of IMS: it is an analytical technique which fits perfectly to field applications and to process applications.

Ion Mobility Spectrometry is based upon the separation of ions (obtained by the ionization of the neutral chemical species in the gaseous phase, at atmospheric pressure, by collisional charge exchanges and ion-molecule reactions),

which occurs because of their mobility differences in a relatively low intensity electrical field.

It can be stated today that Ion Mobility Spectrometry is practically the backbone of defense systems against chemical warfare agents in many NATO countries, that it helps real-time detection of explosives and illicit drugs and that, last but not least, it contributes to industrial hygiene standards observance and to environment protection.

The development of this technique after its discovery in 1970 was not at all simple or straightforward. The initial enthusiasm due to the extremely low detection limits (at part-per-billion levels), versatility and very fast response fell down when disadvantages were also made evident: low selectivity, relatively low resolution and severe memory effects. However, the biggest part of all these drawbacks were surpassed by major improvements in the instrumentation design, but also by application of knowledge due to the better understanding of the ionic mobility theory and of the processes involved in atmospheric pressure chemical ionization.

This paper aims to demonstrate the advantages of Ion Mobility Spectrometry. It is quite sure so far that IMS will be soon an usual and widely accepted analytical technique, especially in several particular niches. In fact, it is obvious that the latest trends in IMS field (including the commercial market) predict a very interesting evolution, of course if the IMS experts and users will focus upon solving the problems remained unclear.

2. Theoretical basis of IMS

2.1. Principle of IMS

When an ion (at atmospheric pressure and in gaseous phase) is placed in a constant electric field, it will be accelerated until collides a neutral molecule, then it is re-accelerated and suffers another collision, and so forth. This chaotic sequence of accelerations/collisions at molecular level is translated, at the macroscopic level, in a constant speed of the ion. The ratio between the ion speed and the electric field intensity is called *"ionic mobility"*, and the analytical technique that uses ions' separation upon different mobilities was consequently named ***ion mobility spectrometry*** *[3,4]*.

Ion mobility spectrometry is actually ruled by two distinct processes:

a) the ionization in the gaseous phase, at atmospheric pressure, by collisional charge transfer and ion-molecule reactions;
b) the separation of the resulted ions due to their different mobilities in a neutral gas (usually purified air or nitrogen are used), in a relatively small electric field (up to 300 V/cm).

In the last two decades Ion Mobility Spectrometry developed practically in an explosive manner, so that IMS is now a powerful and quite less expensive tool for the detection and even quantitation of a very large number of chemical compounds at trace levels (directly or after a chromatographic preseparation). It is worthy to mention that currently IMS is extensively used to monitor directly several chemical categories, such as chemical warfare agents, explosives and illicit drugs *[3,4]*.

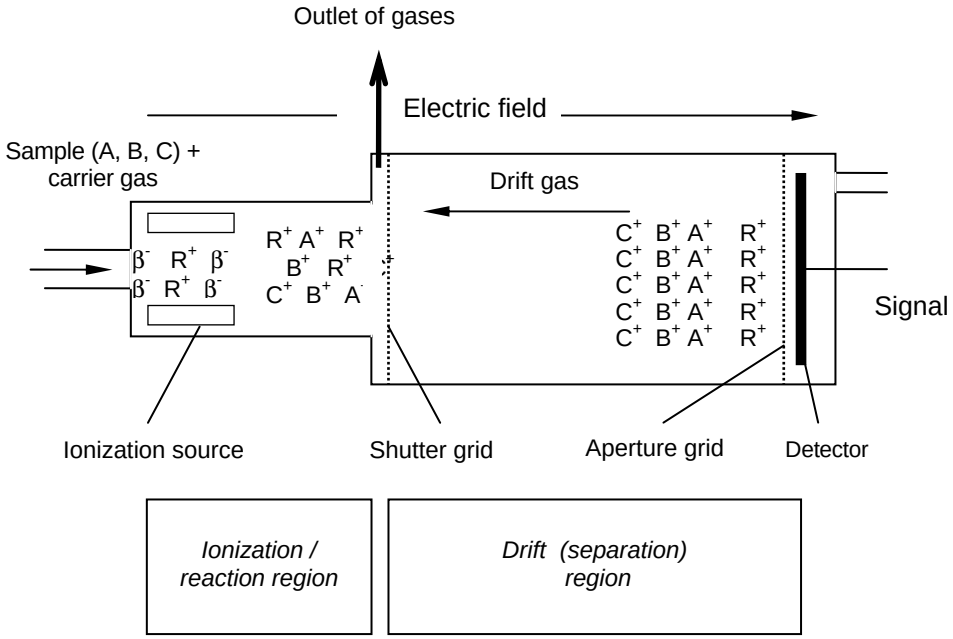


Fig. 1. Schematic of an ion mobility spectrometer

As a conclusion, Ion Mobility Spectrometry is, first at all, a vapors' identification technique by measuring their ionic mobilities in the gaseous phase.

In IMS, chemical separation and detection are accomplished by:

1. Ionization of a gas (or vapors).
2. Separation of ionic species resulted in a drift tube, under the driving influence of an electric field with low intensity, at (or near) atmospheric pressure.
3. Conversion of ionic clouds in ionic current at the detector (placed at the end of the drift tube), after traveling down the drift tube.
4. Signal processing, in order to extract the useful analytical information (qualitative and quantitative) *[4,5]*.

A typical ion mobility spectrometer is illustrated schematically in Figure 1. After their separation inside the drift tube the ions strike the detector, resulting a so-called "ion mobility spectrum", named also "plasmagram" or pure and simple "signature" (Figure 2). In Figure 2, R^+ represent the RIP (reactant ions peak) and A^+, B^+ and C^+ are product ions peaks (PIP).

The IMS information is contained in the IMS signal, which represents the variation of ionic current in time, averaged for a number of scans (Figure 2). The ion cloud formed in the reaction region varies continuously, together with the concentration of chemical compounds which enter the instrument. The ions with suitable polarity are sent, due to the electric field, to the drift tube. Meanwhile, the shutter grid (made by closely spaced, parallel metallic wires) is periodically pulsed

open so that the ions are allowed to pass into the drift region, where they suffer collisions with the neutral drift gas molecules and consequently their separation occurs. Finally, at the end of the drift tube the ion clouds will be converted into ion currents (with very low intensity, of the order of picoampers pA) by a Faraday plate (the detector).

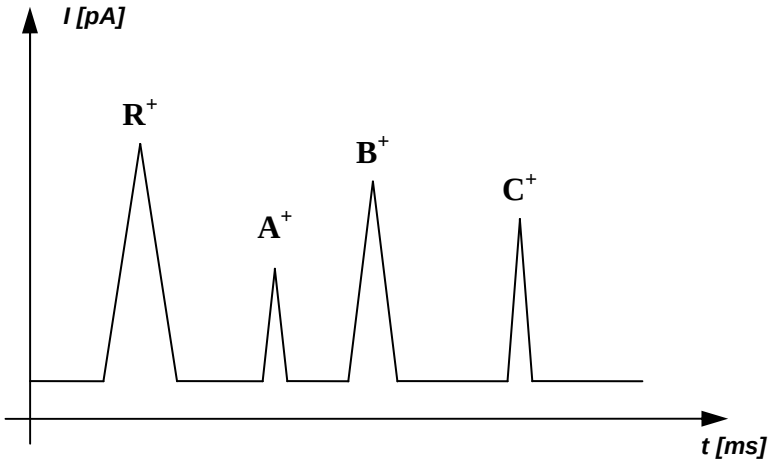


Fig. 2. A typical ion mobility spectrum (plasmagram; signature)

Ion Mobility Spectrometry has a number of similarities with several analytical techniques: electrophoresis, chromatography and mass spectrometry (time-of-flight MS and chemical ionization MS). The resemblance of Ion Mobility Spectrometry with MS-TOF is quite evident, because both analytical techniques rely on ions separation in a drift tube, and the resemblance with CI-MS could be seen in the ionization processes (which imply ion-molecule reactions with generation of the primary reactant ions, then formation of secondary product ions) *[3]*. It is now usual to say that in IMS the ions are subject of the time-of-flight measurements at atmospheric pressure.

Ion Mobility Spectrometry has several advantages:

- analytical flexibility, because it can be applied to analyze both organic and inorganic vapors, and also either positive or negative ions can be monitored
- very fast response (the drift times are in the millisecond range, up to several dozens ms); so, a complete analysis cycle will take only several seconds, and consequently we can speak here about real-time response
- very good sensitivity, in the parts-per-billion (ppb) and even parts-per-trillion (ppt) range without any preconcentration
- good selectivity; it can be improved by using dopants and/or different ionization sources

- the analysis is done at (or near) atmospheric pressure, and not in vacuum like in mass spectrometry
- the instrumentation is very robust and can be easily miniaturized.

Of course, IMS has a number of major drawbacks:

- the theoretical concepts concerning ion mobility spectrometry were not yet perfectly defined
- there are not comprehensive models for the response characteristics
- the dynamic range is quite limited, which in turn don't encourage the quantitation.

2.2. Theory of ionic mobility

In this section the theory of gaseous ions, with emphasis on most important characteristics for IMS *[6,7,8]* is shortly reviewed. The main applications of the IMS theory include: the effects of temperature variation, the effects of electric field intensity and drift gas pressure *[6]*, the effect due to the drift gas change *[9,10]*, the behavior of the multiple charged ions, mass-mobility correlations *[11,12,13]*, the correlation with vapor diffusion coefficients, peak width and shape analysis *[14,15]*, and IMS resolution *[16]*.

The essential theoretical relations which govern in IMS are the following:

- *drift rate equation:* The average rate of an ion moving in a neutral drift gas is called *drift rate*, v_d, and is proportional to the electric field E, if E is not too large:

$$v_d = KxE = l_d/t_d \qquad (2.1).$$

This proportionality constant ***K*** is exactly *ionic mobility*, l_d is the drift length, and t_d is the drift time of an ion.

- *reduced mobility equation:* The mobility $K=l_d/t_d$ could be normalized (reduced), to eliminate the effects of pressure and temperature:

$$K_0 = (273/T)(P/760)K \qquad (2.2)$$

where K_0 is the reduced mobility, T is the absolute temperature of the drift gas, and P is the atmospheric pressure.

- *low field condition:* At that electric fields normally used in IMS at atmospheric pressure, the mobility K is independent on E. A semiquantitative criterion for low field operation (at room temperature) could be written as follows:

$$\frac{E}{N} \langle \left(\frac{m}{m+M} \right)^{1/2} \cdot \frac{d^2}{z} \qquad (2.3)$$

where m represents ion mass, M is the mass of neutral molecules (of the drift gas), d is the sum of ion and neutral molecule radii (in Angstroms), and z is the charge of the ion. The parameter E/N is measured in Townsends (Td): 1 Td=10^{-17} Vxcm^2. It is important to note here that in IMS the typical values for E/N ratio are 1...2 Td.

- *relationship between ionic mobility and diffusion coefficient:* This equation has many names: Einstein equation, Nernst-Einstein equation or Nernst-Townsend-Einstein equation:

$$K = qD/kT \qquad (2.4)$$

where *q=zxe* is the electrical charge of an ion, and *k* is the Boltzmann constant. This equation is very useful in connecting the results obtained in IMS with those obtained about air diffusion of uncharged vapors. It also gives a connection between the measured transit times and shapes and widths of the detected ionic pulses, which means an additional information about the studied ion.

- *Mason-Schamp equation:* Because the collisions between particles are controlled by forces occurring between them, the mobility should clearly depend on the force between ion and neutral molecule. Because in fact the collisions between particles are controlled by their interaction forces, the mobility will depend finally on the force between ion and neutral molecule. This kind of dependence appears as an integral of diffusional collision, or the average collision section, Ω_D:

$$K = \frac{3}{16} \cdot \frac{q}{N} \cdot \left(\frac{1}{m} + \frac{1}{M} \right)^{1/2} \cdot \left(\frac{2\pi}{kT} \right)^{1/2} \cdot \frac{1}{\Omega_D} \qquad (2.5)$$

Mason-Schamp equation

where *q* is the electric charge of the ion, *N* is the drift gas density, *m* is the mass of the ion, *M* is the mass of drift gas molecule, *k* is the constant of Boltzmann, and *T* is the temperature.

The whole dependence of ionic mobility on ion-molecule interaction is included in the collision integral Ω_D. Because of the fact that Ion Mobility Spectrometry wants to use the measured ionic mobility to characterize a specific ion, it is important to know in detail how Ω_D (and consequently the mobility) depends on ion-neutral molecule forces.

The detailed theoretical approaches show that mobility depends in a well-defined way on ion-neutral interactions. An ion mobility spectrum contains information about these ion-molecule interactions, and this information can help to interpret that spectrum. In addition, not only the measured mobilities can be used successfully to study the ion-molecule potentials, but also the independent cognition of these potentials could be used to check the mobility measured. The relationship between ion-molecule forces and mobility is very well represented by the temperature dependence of ionic mobility.

The mobility definition equation underlines as well an inverse relationship between *K* and *N* (drift gas density). So, an increase of *N* will lead to an increase of the collision number, to a lower drift rate and to a lower mobility. The variation of *E* (electric field) and of *N* (the drift gas density) produce similar effects, and the mobility depends in fact on the variable *E/N*.

Another useful parameter that can be easily modified in IMS is the neutral drift gas itself. In this way, making experiments with different drift gases may be a good test of the agreement between results and theory and also may offer some valuable additional information about ion-molecule interactions. Moreover, using another drift gas or a mixture of gases in the drift cell is a good opportunity to test if a studied ion changes its chemical identity by forming clusters or complex ions. To calculate how mobility changes with the drift gas, the masses and polarizabilities of neutral molecules are needed.

The values of the reduced mobility K_0 for different drift gases were already compared, and it was found that generally K_0 changed with the drift gas polarizability. For example, using drift gases with a large polarizability, the attractive forces between the product ions and the induced dipole moment will increase, we will have a greater number of collisions and finally a lower mobility.

Usually the ions produced in the IMS spectrometer are single charged, but it can be expected that larger, bulky ions (for example, those formed by large biomolecules) will have many electrical charges. The additional charge leads to an increase of the interaction energy between ion and neutral molecule, and also will increase the collision probability. However, the diffusion coefficient decreases with charge increase if K is a constant, according to the Einstein equation. So, the mobility could be greater or lower, but for large ions the effect will be very probable a slight increase of ionic mobility due to the multiple charge.

The equation (2.5) is very important, because it shows us that drift time t_d (which is proportional with K^{-1}) depends on mass and size of the ion:

$$K^{-1} \sim \mu^{1/2}.\Omega_D \qquad (2.6)$$

, where μ is the reduced mass ($1/\mu=1/m+1/M$), and the size is measured by Ω_D.

For a series of small ions in the same drift gas, Ω_D is almost a constant, and hence the mobility is controlled by reduced mass μ. For heavy ions, the reduced mass μ is practically equal with drift gas molecule mass, and the separation property is the ion size (reflected by Ω_D).

Of course, for those ions that are between the above two extreme categories (and that form the majority of ions), the mobility is function both of ion mass and size/conformation of that ion. For instance, the analysis of mass-mobility correlations *[11]* has indicated a dispersion of about ±20% for the compounds that were not structurally related, but only of ±2% in a homologous series of aromatics. We can clearly observe that mass measurement using IMS is indeed a very inaccurate process.

The Einstein equation (2.4) suggests the existence of the relationship between drift times and diffusion coefficients, so that the diffusion coefficients could be seen as equivalent mobilities.

Concerning the shape and width of the ionic pulse, it should be emphasized that the main characteristics of an ionic pulse reaching the detector are imposed by four factors:

1. initial width and initial shape of the pulse which enters drift region
2. pulse broadening by coulombian mutual repulsion between ions
3. diffusional broadening, as ionic pulse travels in the drift tube
4. ion-molecule reactions with drift gas and/or with impurities.

Resolution R measures the ability of an instrument to distinguish between two very closed peaks. In IMS, resolution is given by the equation:

$$R = t_d/(2.T_{1/2}) \qquad (2.7)$$

where t_d represents drift time, and $T_{1/2}$ is the temporal broadening at 1/2 of peak height.

From an experimental point of view, the parameter $T_{1/2}$ and also peak shape are governed by many factors:

1) shape and width of the initial pulse
2) diffusional broadening
3) coulombian repulsion
4) capacitive coupling between ionic pulse and detector
5) gradients of the electric field
6) gradients of the temperature
7) emptying of the gate (shutter grid) and dynamic drains
8) pressure variations
9) ion-molecule reactions inside the drift tube.

Experimental data suggested several trends concerning IMS resolution, which can be easily explained only when the initial width of ionic pulse, t_0, was introduced in the equation of resolution:

1. Resolution increases with drift time t_d.
2. Resolution depends on electric field E.
3. In most cases, a lower drift potential generates a better resolution.
4. There is a linear relationship between R and $T^{1/2}$.

At high initial width of ionic pulse, the peak's shape is gaussian, having $T_{1/2}$ proportional with $t_d^{1/2}$.

The values of H_{TT} (theoretical plate height) for IMS are several orders of magnitude lower that H_{TT} in gas chromatography. The mass resolution ($R=M/\Delta M$) is in IMS only about 10...50, comparing with values of 400...70000 in mass spectrometry. All these considerations let us to the conclusion that Ion Mobility Spectrometry has modest resolutions comparing with mass spectrometry, and also that its separation power is lower that in chromatography.

In conclusion, the mobility of ionic species is connected with collision processes which occur in the drift tube. In the theoretical analyses of IMS, the reaction region and the drift region are usually treated separately, being supposed that in the reaction tube separation of the ions don't occurs, and that in the drift tube we don't have any ion-molecule reactions.

The most important ideas concerning the theory of ionic mobility are:

(1) The information contained in the ion mobility spectrum can be extracted by measuring the drift time and peaks' area.
(2) The mobility K depends on environmental variables; K is inversely proportional with pressure in the IMS cell.
(3) The reduced mobility K_0 depends also on average transversal collision section Ω_D, which has a very complex form.
(4) Theoretical treatment of small ions and of macro-ions is quite different.
(5) Changing the neutral drift gas has a great effect on ionic mobilities.

3. Ionization processes in IMS

The first step in a measurement involving IMS consists in ionization of neutral molecules present in the vapor sample. These ionization processes occur in gaseous phase, at atmospheric pressure, by a series of very fast ion-molecule reactions

between neutral molecules of analyte and the reactant ions. Therefore, it is easy to understand that ionization is a crucial event in IMS.

The ionization involves proton transfer (or electron transfer, for the negative mode of operation) reactions between reactant ions and neutral analytes, and the final ions that result by these processes are called "product ions".

Atmospheric pressure chemical ionization which occurs in IMS differs from other type of ionization processes by two essential characteristics:

1. A gentle energetic of product ions formation, which implies the absence of any fragmentation of the molecules ionized (even if there are few exceptions, such as the butylacetates for example).
2. The available charge is competitively and preferentially distributed between the different types of neutral molecules co-existing in the vapor sample, as a function of their proton affinities (for the positive ions) or electron affinities (for the negative species) *[4]*.

In IMS the reactant ions' composition depends on composition of the gas in the reaction region and may be easily altered by temperature, humidity and dopants adding *[17,18,19]*. The complex nature of reactant species, as well as the very complex equilibria between them is not at all a disadvantage for IMS analyses, if the gas that enters the reaction region (usual air) has a constant composition and is purified *[20-23]*.

On the other hand, this complexity of the reactant ions mixture was leading to the impossibility to effect physico-chemical studies using exclusively IMS, and exactly this absence of such studies has obstructed the development of a predictive & interpretative model of this atmospheric pressure ionization chemistry. However, the increasing number of studies (conducted especially in the last two decades) is definitely a positive aspect concerning the ionization chemistry elucidation in the ion mobility spectrometer.

The results of main reactions leading to the positive and negative reactant ions, with emphasis on ionization processes that occur using the radioactive source with β isotope ^{63}Ni (which is by far the most common ionization source in IMS) *[24,25]* are summarized as follows:

Positive reactant ions:	*Negative reactant ions:*
$(H_2O)_xH^+$; $(H_2O)_yNO^+$; $(H_2O)_zNH_4^+$	$(H_2O)_xO_2^-$; $(H_2O)_yO^-$; $(H_2O)_zO_4^-$
predominant species: $(H_2O)_xH^+$	predominant species: $(H_2O)_xO_2^-$

Product ions are formed in the reaction region, mainly by collisional charge transfer reactions between the reactant ions and analyte neutral molecules from the sample. They could be also generated by attachment reaction of a reactant ion to the neutral species. At the first sight, product ions formation seems to be quite simple, at least from a qualitative point of view. However, all the efforts undertaken to study product ions generation using IMS coupled to mass spectrometry (IMS/MS) did not lead to a comprehensive quantitative model so far.

There are several main processes that generate positive product ions: proton transfer reactions, charge transfer reactions, electrophilic addition reactions, hydride ion transfer, dimer formation, cluster formation *[26,27]*. These processes are summarized below:

$$(H_2O)_xH^+ + M \longrightarrow MH^+ + xH_2O$$
$$(H_2O)_yNO^+ + M \longrightarrow M^+ + NO + yH_2O$$
$$(H_2O)_yNO^+ + M \longrightarrow MNO^+ + yH_2O$$
$$(H_2O)_yNO^+ + C_nH_{2n+2} \longrightarrow [C_nH_{2n+1}]^+ + HNO + yH_2O$$
$$MH^+ + M \longrightarrow M_2H^+$$
$$MH^+ + nL \longrightarrow MH^+(L)_n .$$

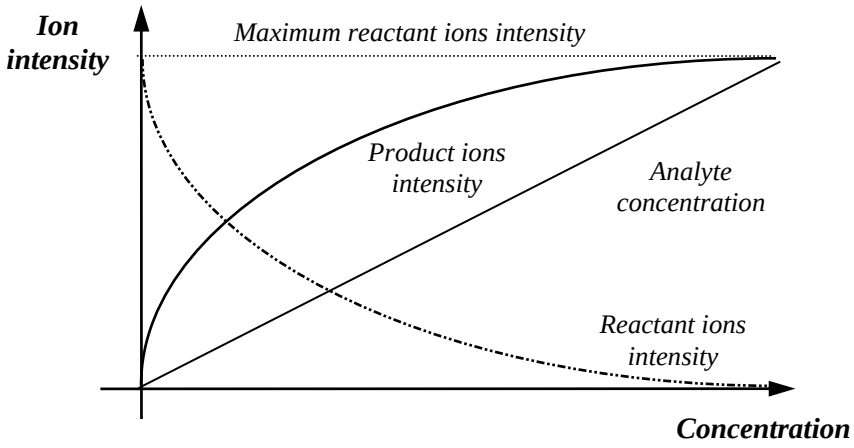
The negative product ions are generated by: associative electron capture, dissociative electron capture, proton extraction processes, as follows:

$$M + e^- \longrightarrow M^-$$
$$MX + e^- \longrightarrow M(\cdot) + X^-$$
$$MH + e^- \longrightarrow M^- + H^+ .$$

We shall remind here that in the radioactive ionization source -which is by far the most used source used in IMS- the distribution of available charge is done in a competitive way. The consequence is that the apparition of an ion should lead, because of the charge conservation, to a decrease in intensity of another ion (or ions).

In a first approximation, the charge seems to be distributed proportionally with the concentration of each component in the sample and with its proton (or electron) relative affinity.

The charge will distribute virtually to any compound present in the vapor sample, and this is exactly the cause of the IMS extraordinary versatility. However, because most of drift tubes used currently have a low resolution, they can't be used to separate complex mixtures of ions.



The IMS response could be shortly defined as the intensity change of the product ions with the change of analyte's concentration (as seen in Figure 3).

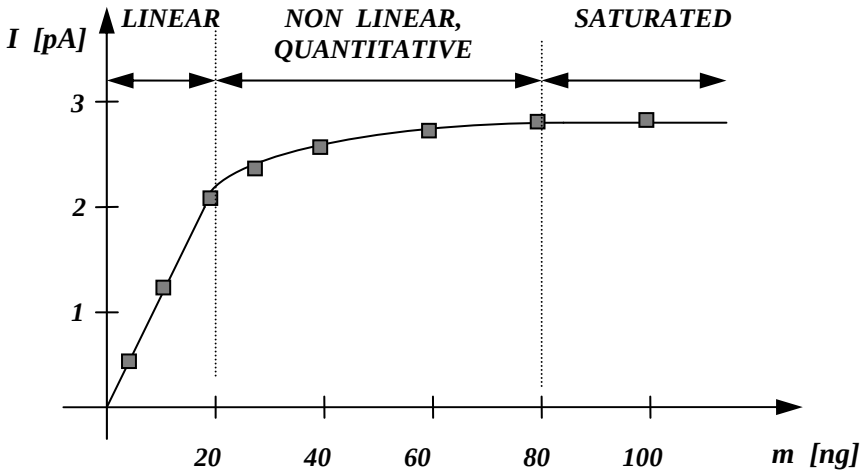


Fig. 3. Typical quantitative IMS response

Fig. 4. The dependence of reactant and product ions intensity upon concentration of the analyte in the vapor sample

This particular kind of response is bound on concentration profiles of reactant and product ions correlated with sample concentration; Figure 4 illustrates well the variation of both reactant and product ion peaks' intensity with analyte concentration.

There were many attempts to control the separation/resolution in IMS, and one of these attempts is based exactly on changing ions' selectivity by modifying the atmospheric pressure ionization chemistry. More specifically, this change of the selectivity implies to continuously add a chemical compound called *dopant* (at a constant concentration level, usually in the parts-per-million range) into the carrier gas flow *[4,22,28]*. Even water could be seen as a dopant, but the "real" dopants most used in IMS are acetone, carbon tetrachloride and ammonia.

Depending on the origin of the reactant ions, the competitive charge exchange would be an advantage or a disadvantage for a given application. The critic parameters are here the complexity of the sample, sample composition and the relative ionization properties of the target analyte comparing with those of the other compounds present in that sample.

If the target analyte has a greater proton/electron affinity than any other sample component, then it will present a strong IMS response on the expense of the rest of compounds. If all the compounds have approximately the same

proton/electron affinity, then the resulting IMS spectrum will contain all the product ions generated by these compounds. Finally, if the proton/electron affinity of our target analyte is much lower than the affinities of all other components, the detection by IMS becomes very problematic, because it is quite sure that this analyte will not catch the charge; in that case, one should take into consideration a preseparation of the sample (using gas chromatography, for example) or the use of an alternative ionization chemistry (with a dopant).

Nowadays Ion Mobility Spectrometry can be successfully used to the identification of chemical vapors, and even to their quantitation in a complex matrix. Unfortunately IMS poses a number a problems, so that it is an analytical tool often difficult to use. As a matter of fact, because of these drawbacks IMS is not a real challenge for mass spectrometry or other usual laboratory analytical techniques *[29-32]*. It must specify here that an absolute identification of the ions can be made only by coupling the IMS spectrometer to a quadrupole mass spectrometer, using a micrometric circular aperture driven in the detector plate of the ion mobility spectrometer (IMS/MS).

Many IMS applications are not laboratory applications but field applications, which do have totally different specifications. For instance, IMS has became attractive as a field technique due to its physico-mechanical simplicity of instrumentation and also to its low cost electronics, comparing with other bulk and complex systems (such as vacuum pumps used in mass spectrometers).

Using an ion mobility spectrometer one can made some separations very easily, but the other are impossible. For example, some anesthetic gases were separated (even if they were isomers !), but hexane can’t be separated from carbon dioxide (because none of them is "seen" in IMS).

We can expect that the IMS spectrometer can be used as a chemical analyzer only if the target analyte has very different ionization characteristics as compared with the other sample components. At this stage of knowledge, the IMS technology has not predictive or interpretative properties when it analyzes mixtures which contain compounds with similar ionization parameters.

4. The instrumentation: ion mobility spectrometer

The diagram of an ion mobility spectrometer is presented in Figure 5.

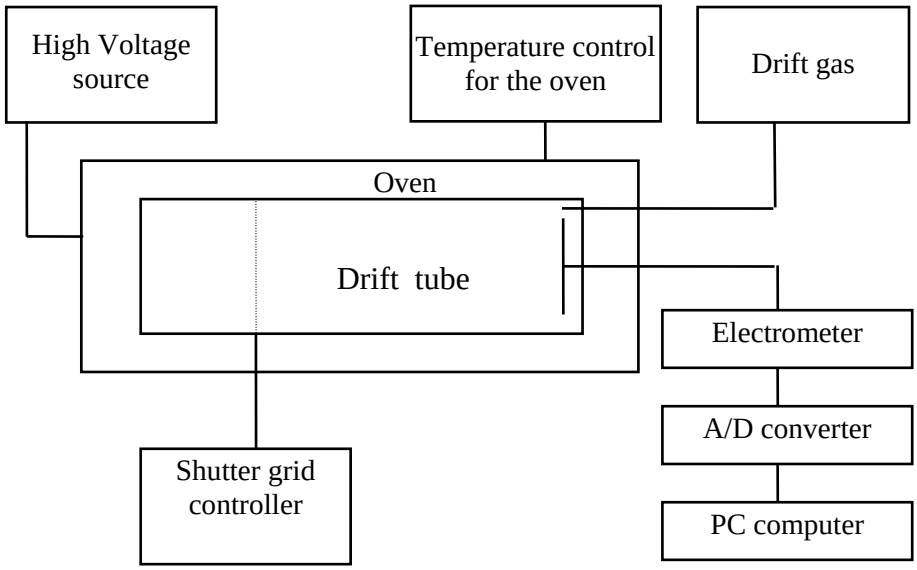


Fig. 5. Schematic diagram of an IMS spectrometer

The essential parts of an IMS spectrometer are the following:

1) a sample inlet system
2) an ionization source
3) a reaction region
4) an ion gate (shutter grid)
5) a drift region
6) a detector (ion collector).

The ancillary equipment necessary for an IMS spectrometer includes:

1) a high voltage source, which creates the electric field along the drift tube
2) a gate controller
3) a drift (and carrier) gas source
4) temperature control instrumentation
5) a fast electrometer
6) data collecting and processing devices, which usually include a computer.

Figures 6 and 7 depict these components of the IMS spectrometer for the two main different configurations of the IMS cell - stacked ring design and compact (ceramic tube) design.

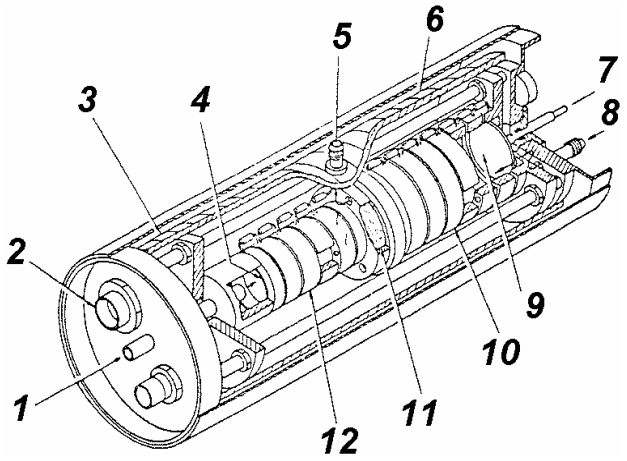


Fig. 6. IMS cell with stacked rings

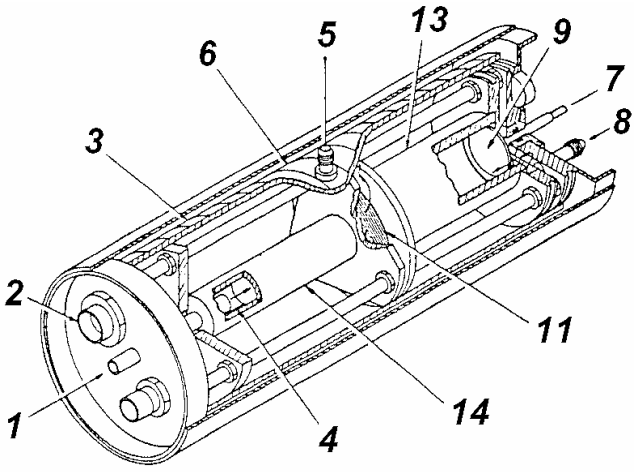


Fig. 7. IMS cell with ceramic tube

The corresponding legend for Figures 6 and 7 is:

1 = Carrier gas + sample inlet
2 = High voltage connectors
3 = Heating strips
4 = Ionization source
5 = Gas exit
6 = Sealed and heated housing
7 = Electrometer
8 = Drift gas inlet
9 = Faraday plate (detector)
10 = Drift region
11 = Shutter grid
12 = Reaction region
13 = Ceramic drift tube + resistive coating
14 = Ceramic reaction tube + resistive coating

There are many methods for the introduction of sample vapors into the ionization/reaction region of an IMS spectrometer. Among these are: metal wire sample introduction *[33]*; syringe injection *[34]*; exponential dilution flask *[35]*; permeation tubes *[36]*; diffusion tubes *[36,37]*; thermal desorption ovens *[38]*; laser desorption *[39]*; sample introduction into the instrument (directly or via a membrane) *[40,41]*; introduction of the efluent from a chromatographic column (gas, liquid or supercritical) *[42,43]*.

It must be underlined that if the main role of these sample introduction systems is to vaporize and/or carry the vapors into the ionization source, a secondary role is to control the size of the sample, to avoid instrument's overloading.

Sample inlet systems could be classified, according to the initial form of the sample, as follows *[3]*:

A. *Gaseous samples:* direct introduction (with or without preheating); syringe injection; exponential dilution flask; permeation tubes; diffusion tubes; introduction from gas chromatographic columns; membrane systems.
B. *Liquid samples:* mobile metallic wire systems; syringe injection; electrospra & coronaspray systems; introduction from liquid chromatographic columns.
C. *Solid samples:* thermal desorption ovens; laser desorption.

Membrane-based sample introduction systems are currently mounted on the majority of IMS spectrometers operated at ambient temperature *[44,45,46]*. The final conclusion concerning these sample introduction systems is that membrane inlets are not useful for the heated IMS cells (where cluster formation is minimized); moreover, a membrane inlet will affect negatively detection limits. However, because membrane inlets are very effective in maintaining a constant low level of water vapors concentration inside the IMS cells operated at ambiant temperature (20°C...35°C), they are now the most used systems for portable and hand-held IMS spectrometers.

Vapors ionization is the initial event in the IMS spectrometer, and will define the species that are observed in the mobility spectrum. The ionization of different molecules could be made in many ways:

1. Radioactive ionization *[1,2,47]*, which is by far the most used method in IMS
2. Photoionization *[48-50]*
3. Laser ionization *[51-53]*
4. Surface ionization *[54,55]*
5. Electrospray and coronaspray ionization *[56-58]*.

The IMS cell is the heart of an ion mobility spectrometer. It contains the drift tube (with reaction region and drift region), the grids (ion gates), the detector and optionally a heating system.

Drift tubes could be classified according to the manner of drift field generation, or according to the gas flow through the cell. There are many types of drift tubes *[18,33,59-61]*:

- stacked ring drift tube (the classical and still most used IMS drift tube)

- compact drift tube - ceramic tube with resistive internal coating
- unidirectional drift tube
- non-conventional drift tubes.

Ion mobility spectrometers contain entrance grids (called also shutter grids) *[12,62]* and aperture grids (located very close near detector plate) *[63]*.

Shutter grids introduce (inject) periodically the ions from reaction region into drift region. They are pulsed open and closed by a specialized electronic circuit (grid controller); sometimes the opening time can be set by the operator (between 0.1 and 1 milliseconds). The usual opening time is 0.2 ms.

The aperture grid dramatically reduces the capacitive response of the detector when ion clouds are approaching (capacitive decoupling). Without an aperture grid, the ion cloud is coulombically detected before it really strikes the detector plate; the result is the peak broadening and consequently a serious loss in resolution.

In ion mobility spectrometry a gas source (for drift and carrier gases) *[3,64,65]* is needed. These gases have many functions:

1. To introduce the sample inside ionization/reaction region (carrier gas).
2. To continuously supply neutral molecules for ion-molecule collisions (carrier gas; in the unidirectional IMS cells this function is accomplished by drift gas).
3. To clean the drift tube by continuous purging, avoiding its contamination and memory effects (drift gas).
4. To supply molecules for reactant ions formation.

Usually as carrier and drift gases are used purified air or purified nitrogen. Their purification is done by filtering through molecular sieve cartridges (13X molecular sieve), which retain the impurities and also maintain a very low water vapor level (several ppm). Activated charcoal is also used to retain the organic impurities.

Drift gas may differ from carrier gas. For example, one can use air as carrier gas and nitrogen, air, or sulfur hexafluoride as drift gas. The restrictive condition is the following: drift gas must be chemically inert toward product ions injected into drift region. This requirement is necessary to avoid any ion-molecule reaction in the drift region.

For portable IMS spectrometers the most convenient gas source is in fact a closed loop which filters the air using molecular sieves, coupled with a membrane inlet. Fixed point and laboratory/desktop ion mobility spectrometers can be supplied with compressed air (from air cylinders or from a compressor), after drying and purification.

To collect and process ion mobility spectra one can use many methods: single scan, signal averaging, second gate moving, Fourier transform method *[4,66-68]*. Currently, the most used is signal averaging method.

Ion mobility spectrometers have been used successfully in many applications involving vapors detection: industrial hygiene, quality control in semiconductor industry, drugs and explosive detection and chemical warfare agents detection.

There is a rule of paramount importance: when all reactant ions were consumed (so the reactant ion peak disappeared from the spectrum), any possibility to

quantitatively interpret the IMS response was also lost. Consequently, to have quantitative information from the IMS spectra an excessive consumption of reactant ions (also called saturation; see Figure 4) must be avoided, and the reactant ion peak must be observed in the spectrum.

Although there are still many unknown aspects, there is a continuously increasing amount of experimental data and studies which assess the quantitative performances of the IMS spectrometers. Several basic consideration regarding the response of ion mobility spectrometers *[4,5]* are:

- detection limits are very low (in the range 10^{-15}...10^{-12} mol/s)
- precision is good (in accordance with some studies, the relative standard deviation RSD of a modern IMS instrument is between 5% and 25%)
- stability of the IMS response is excellent over very long periods of time
- the response sensibility and linear range
- separation efficiency (in IMS, the number of theoretical plates is several thousands)
- resolution (to have an IMS separation, two ions must have at least a difference of 3% in their reduced mobilities K_0).

Ion Mobility Spectrometry has suffered tremendous progresses after the appearance, in the late 1980s, of hand-help portable, small, lightweight and relatively low cost IMS spectrometers issued from the military research & development programs. The problems related to chemical warfare agents detection lead to a large number of very valuable studies and to a great development of IMS instrumentation, but IMS units used in environmental applications appeared only after 20 years from IMS invention. There are several IMS instrumentation manufacturers, most of them being located in USA and Canada: *Graseby Dynamics Ltd.* (United Kingdom); *Bruker GmbH* (Germany); *PCP Inc.* (USA); *Ion Track Instruments Inc.* (USA); *Barringer Research Ltd.* (Canada/USA); *Molecular Analytics Inc.* (USA); *Environmental Technologies Group Inc.* (USA); *CPAD Technologies Inc.* (Canada) and *FemtoScan Corporation* (USA).

Commercial IMS instruments could be classified according to their size and specific applications *[3]* in: laboratory instruments - stationary or desktop (transportable in a vehicle), fixed-point field instruments and hand-held portable instruments.

5. Conclusions

Most important trends in the evolution of Ion Mobility Spectrometry are the following:

- continuous simplification and miniaturization of the IMS cells
- use of selective techniques for sampling
- implementation of new signal processing techniques for IMS signal (such as neural networks) *[69]*

- use of new designs of the IMS cells, such as non-conventional field control
- building of portable heated IMS cells
- manufacturing of portable GC/IMS and IMS/MS instrumentation
- use on a larger scale of the non-radioactive ionization sources *[70]*
- ultraminiaturization of the IMS instrumentation *[71]*.

As a final conclusion, we can say that after 1980 Ion Mobility Spectrometry has developed very fast and passed the boundary from an "exotic" laboratory technique to a simple technique for ultra-trace analysis, alone or coupled with another analytical technique (like mass spectrometry or chromatography).

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