Ion mobility analyzer - quadrupole mass spectrometer system design

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Abstract. Because of their extremely high sensitivity for chemicals with elevated electronegativity or high proton affinity the ion mobility analysers are ideal for the ultra-trace detection of toxic or explosive chemicals, most of these situated often at concentration levels of sub-ppb (parts-per-billion). Ion mobility spectrometers (IMS) can be used to identify illicit drugs or environmental pollutants. Since resolution of an IMS is relatively low, to achieve an accurate identification of target analyte it is recommended to couple the IMS with a quadrupole mass spectrometer (QMS) or a time of flight mass spectrometer, acquiring in this way confirmatory information. This coupling is made through a specific interface. In this paper, an experimental model of such a tandem instrument, IMS-QMS is described. Accomplishment of this general purpose will be done, overcoming a series of specific issues. This implies the solving, using innovative solutions, of a series of complex issues: ensuring the stability of the ions beam generated by ion source; transfer with a good efficiency of the ionic current from IMS analyser to QMS; and realization of a special electronic circuitry which will be able to detect both positive and negative ions.

1. General scheme
The general scheme of the IMS-QMS tandem is given in figure 1. We have proposed us to build a complex detector of tandem type, IMS-QMS, ultra-sensitive and having a fast response, to identify dangerous substances (organophosphoric chemicals). This tandem can be used also for the detection of other compounds, as environmental pollutants.

Positive and negative ions are generated by a corona discharge ionisation source, and are then transported by the electric field and by the carrier gas towards the gap between the two cylinders of the IMS analyser. Depending on the voltages that are applied on those two cylinders (direct compensation voltage and asymmetric wave alternative voltage, respectively), the ions are separated and sent to the interface. From this point, the ions are introduced into the quadrupole analyser, where they are mass analysed. Finally, the ionic current is measured using an electrometer and is further picked up by either an oscilloscope or an analogue-to-digital interface.

Others groups reported results obtained with similar combination of analysers (the level of perchlorate in water matrices) /1/, (the explosive detection) /2/, (isomeric dihalogenated benzenes) /3/.
2. Ion source
The ion source we have designed, manufactured and tested was a corona discharge ionisation source. The well-known corona discharge is, by itself, a gas electrical discharge that reunites the ionisation processes of this gas in the proximity of the active electrode /4/, /5/, where the electric field is strong. Corona discharge implies usually the existence of two electrodes – one having a strong curvature (e.g., a very small diameter needle or wire), and the other having a small curvature (like a plane); therefore, a so-called “point-to-plane” configuration of the corona discharge is used. The strong curvature will ensure a very high gradient of potential around the tip electrode, which shall be enough to generate the necessary plasma.

If the tip electrode is polarised positive, relative to the flat electrode, we will have a positive corona discharge, while by reversing this polarity one shall have a negative corona discharge. The unipolar current density for positive and negative corona discharge is distributed on the plane in accordance with the Waiburg law:

\[ j(\theta) = j_0 \cos^5 \theta \]  \hspace{1cm} (1)
\[ j_0 \sim I / (2d^2) \]  \hspace{1cm} (2)

where \( tg \theta = r/d \), \( I \) is the total corona current and \( d \) is the distance from point to plane. Field lines and ion trajectories are somewhat shifted by the repelling force due to the spatial charge. The unipolar current \( I \) at a certain value \( U_0 \) cannot be larger than the saturation limit.

\[ I_{sat} \sim 2 \mu \varepsilon_0 U_0^2 / d \]  \hspace{1cm} (3)

where \( \mu \) is ionic mobility and \( \varepsilon_0 \) is permittivity.

One can demonstrate that more than 95% of the input electrical energy for an unipolar corona discharge goes to the neutral gas, and only several percent go toward the producing a directional movement of the gas. Thus, the largest part of the energy is used to heating the gas, and the positive ions can strongly excite the atoms and the neutral molecules present in the drift region with low intensity of the field.

3. Cylindrical FAIMS (high-field asymmetric waveform ion mobility spectrometry) analyser
The cylindrical FAIMS /6/ analyser consists of two cylinders, which are denoted electrode I and electrode II. These cylinder electrodes have been manufactured using stainless steel (type
10TiNiCr180) and are concentric, having a gap of 0.5 mm between them. The asymmetric waveform is applied on the external cylinder (5), while on the internal cylinder (6) the direct voltage (compensation voltage) has been applied. This entire system was mounted on a flange made of Teflon PTFE (3). The ions generated by the corona discharge enter the analytical gap between the two cylinders through four holes, and the analysed ions, which were travelling through the gap, exit toward detector through a small hole with 0.5-2 mm diameter (figure 2).

4. Interface IMS – quadrupole MS

Figure 3 presents the above mentioned interface, together with the mounting system for Einzel electrostatic lenses and for the hexapole. Here, one may observe the bodies I (1) and II (17). The Einzel lens is mounted in the body I by using two separator pieces (9) and 10). The lenses (16) are made of non-magnetic stainless steel discs; they are being secured by using a set of bushed bearings (11) and insulating washers (12). Electrical connections are made between the bushed bearing IV (11) to bushed bearing III (7), and from here to the special screw (4), which has a pin to electrical contact. Those pins are also connected to the electrical wires for hexapole’s polarisation. Ion beam is coming from the ion mobility analyser, enters the repelling hole (15) and is accelerated towards the superior hole of body II. From this point, the ion beam is directed toward the Einzel lens, where it is focused, then it is transported through nozzle (19) to the hexapole electrostatic lens mounted in body I (1). This hexapole eliminates the second order image aberration of the ionic beam and sends this beam to be analysed in the quadrupole filter.

According to the theory /7/ a series of relations between the basic parameters of a QMS, which may be used to get a first estimation of their values, have been chosen. Thus, the maximum mass of the ions that could pass through a quadrupole filter is given by:

\[ m_m = \frac{7 \times 10^6 V_m}{f^2 r_0^2} \]  \hspace{1cm} (4)

where \( V_m \cos(2\pi f t) \) represents the radiofrequency voltage applied between the adjacent rods, \( r_0 \) (in meters) is the radius of the rods, and \( m_m \) the maximum mass of the ion (in a.m.u.). For the vast majority of the instruments, choosing of \( V_m \) and \( r_0 \) is relatively limited. Thus, \( V_m \) is on the order of 3,000 V, and \( r_0 \) in the range 3-10 mm. Another useful relation is:

\[ \frac{m}{\Delta m} = \frac{1}{K N^n} \]  \hspace{1cm} (5)

where \( N \) is the number of \( rf \) cycles of the field applied to the ion, and \( \Delta m \) is the width of the peak having the mass \( m \). It was found that "n" has the value n=2, and K=20 /7/.
Figure 3. The assembly of the Einzel lenses within the interface: 1-body I, 2-v. bucea I, 3-v. bucea II, 4-special screw I, 5-washer, 6-screw nut, 7-v. bucea III, 8-screw, 9-distance piece, 10-washer, 11-v. bucea IV, 12-insulating washer, 13-special screw, 14-v. bucea V, 15-ion repeller, 16-disk, 17-body II, 18-O-ring, 19-washer, 20-nozzle.

Equation (5) may be written as:

$$\frac{m}{\Delta m} = 0.05 \left( \frac{fL}{2eVz^2} \right)^2$$  \tag{6}

where "e" is the charge of the electron (C), $m$ the molecular mass and $\Delta m$ mass difference (Kg), $K = 20$ and $n = 2$. From this we will obtain the expression for the maximum resolution:

$$\frac{m}{\Delta m} = \frac{L^2V_m}{570Vz^2r_0^2}$$  \tag{7}

Using cylindrical rods for the electrodes, instead of hyperbolic profile electrodes – as an approximation of the hyperbolic field – represents a factor that degrades the instrument performances, especially its mass resolution. By exploiting the (the above mentioned relation), the following main parameters of the quadrupole analyser were calculated: $r_0 = 4$ mm; $L = 200$ mm; $V_m = 1250$ V; $F = 2.082$ MH$z$; $m_m = 300$ a.m.u.; $R = 300$.

Figure 4. The scheme of the quadrupole analyser: 1-hexapole, 2-screw, 3-O-ring, 5-v. bucea, 6-rod support I, 7-screw, 8-analyser’s housing, 9-rods, 10-rod support II, 11-screw, 12-lid, 13-safety lock, 14-collector grid, 15-screw, 16-grid support, 17-peg.

The length of the rods is 200 mm, and diameter of the rods is $\phi = 8$mm. The alignment of the quadrupole rods has been achieved with an accuracy of the $10^{-3}$ m, being an essential step in generating a symmetric and uniform electric field inside the quadrupole analyser. By exploiting the (the above mentioned relation), the following main parameters of the quadrupole analyser were calculated: $r_0 = 4$ mm; $L = 200$ mm; $V_m = 1250$ V; $F = 2.082$ MH$z$; $m_m = 300$ a.m.u.; $R = 300$.
coming through the interface. From the hexapole the ions enter the quadrupole analyser where they are separated after their m/q ratio and directed to the collector.

5. Vacuum system used for testing the tandem IMS – QMS
This system should ensure a continuous pressure drop, from atmospheric pressure (existent inside the IMS) to a vacuum of at least $10^{-6}$ mbar (inside the quadrupole analyser). Achievement of this goal, combined with the appropriate electrical polarisation, will assure the transport of ions from the IMS to the quadrupole mass analyser, through the interface.

![Diagram of the whole system](image)

**Figure 5.** Diagram of the whole system: 1 - preliminary vacuum pump, 2 - intermediary body, 3 - ion source, 4 - body I, 5 - body II, 6 - blind flange, 7 - body IV, 8 - ion detection system, 9 - preliminary vacuum pump, 10 - diffusion pump, 11 - water trap, 12 - liquid nitrogen trap.

As depicted in figure 5, the IMS has been mounted in section (2) and (3), the IMS-QMS interface in sections (4) and (5), while the quadrupole filter and its associated ion detector were mounted in sections (7) and (8). The preliminary vacuum pump PVP-1 (1), with a flow rate of $24$ m$^3$ h$^{-1}$, will create a vacuum of $10^{-3}$ mbar inside the interface, while the vacuum system (composed of diffusion pump with oil (10) with its preliminary vacuum pump PVP-2 (9) and nitrogen trap (11)) will generate inside the quadrupole filter a vacuum of $10^{-5}$-$10^{-6}$ mbar.

6. Detection and processing of ionic current
Detection and processing of ionic current will be done by using a home-made electrometer, designed and manufactured by our institute, which may be coupled to a fast oscilloscope (TEKTRONIX MSO-4104) or to a National Instruments card (NI SCC-68) interfaced to a personal computer.

7. Conclusions
We succeeded in designing and realising the mechanic and electronic projects of a complex tandem composed of an asymmetric waveform IMS and a QMS. This hyphenated instrument will be used to detect ultra-traces of toxic, pollutants and explosive chemicals. Our solutions for the main components of this tandem were aimed to obtaining the highest possible ionic current (about $10^{-10}$ A), a stable ionic beam and a mass resolution of at least 300.

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