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# Numerical study of segmented-electrode planar Orbitraps

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ABSTRACT

This study proposes a planar geometry mass analyzer which has fields and performance like that of a reference Orbitrap.

The planar geometry taken up for investigation consists of two planar surfaces with concentric ring electrodes on each facing surface. Appropriate potentials are applied to the individual rings for effecting trapping of ions. The study used both single particle and multi-particle simulations. In the multi-particle simulations spatial and energetic distribution as well as space charge effects in the ion ensemble have been incorporated. The performance of this planar geometry has been compared to that of a reference Orbitrap by computing (1) the variation in potential along the principle directions, (2) ion trajectories and (3) induced image currents in the two geometries. The potentials applied to the ring electrodes were optimized to improve the electric field inside the planar geometry.



## 1. Introduction

This study proposes a planar geometry mass analyzer which has fields and performance similar to that of a reference Orbitrap.

The Orbitrap geometry was first proposed by Makarov in 1999 [1] and a commercial instrument based on the Orbitrap was reported in 2005 [2–4]. The geometry consists of two axially symmetric electrodes, an inner spindle shaped electrode and an outer barrel shaped (split) electrode. The profile of these electrodes, $z_{1,2}$, are given by [5],

$$z_{1,2} = \sqrt{\frac{r^2}{2} - \frac{R_{1,2}^2}{2} + R_m^2 \ln \frac{R_{1,2}}{r}} \tag{1}$$

Here, $z_1$ and $z_2$ refer to the profile of the inner and the outer electrodes, respectively; $r$ is a the radial coordinate; $R_1$ and $R_2$ are the radii of the inner and the outer electrodes, respectively; $R_m$ is known as the Orbitrap's characteristic radius. The operation of the Orbitrap is based on electrostatic orbital trapping of ions [6,7,3]. For its operation, a negative DC potential is applied to the inner electrode and the split outer electrode is kept at ground potential. Due to the special shapes of these electrodes, the potential inside the Orbitrap has a logarithmic variation in radial ($r$) direction and quadratic variation in axial ($z$) direction. The potential at a point $(r, z)$, $U(r, z)$, is expressed as [5],

$$U(r,z) = \frac{k}{2}\left(z^2 - \frac{r^2}{2}\right) - \frac{k}{2}(R_m)^2 \ln\left(\frac{R_m}{r}\right) + C \tag{2}$$

Here, $k$ and $C$ are the constants related to the Orbitrap geometry defined later in Eqs. (4) and (5).

Ions of an analyte, which are pulsed into the Orbitrap from an external ion source, undergo a (near) circular motion in the $r$ direction and a simple harmonic motion in the $z$ direction (because of the linear field in this direction). The frequency of ion motion in $z$ direction, $\omega_{axial}$, is related to the mass-to-charge ratio of ions by [5],

$$\omega_{axial} = \sqrt{k\frac{q}{m}} \tag{3}$$

Here, $q$ is the charge and $m$ is the mass of an ion. The mass-to-charge ratios of fragment ions of an analyte gas are determined by first measuring the induced image current waveform across the split outer electrode and then computing its Fourier transform to obtain the frequencies of the ion's axial motion, similar to what is done in the FT-ICR [5,8].

The Orbitrap mass analyzer is known for its ability to provide accurate mass analysis with high resolution [5]. The use of Orbitrap mass spectrometer was demonstrated in the research areas such as proteomics and metabolomics [9]. Simulation exercises were carried out to study the ion motion inside the Orbitrap under the influence of different excitations on the electrodes [10,11] as well as space charge effects [12].

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A few studies are available in the literature which have attempted to modify the geometry of the Orbitrap for improving its performance. In the first modification known as high-field Orbitrap, Makarov [13] reduced the gap between the inner and the outer electrodes by increasing the radius of the inner electrode, keeping the radius of the outer electrode unchanged. This geometry was found to be useful for providing higher field strength which resulted in higher resolution as well as lesser effect of space charge on mass shifts. Denisov et al. [14] suggested another design of the Orbitrap in which radii of the inner and the outer electrodes were scaled down by the factors of 1.2 and 1.5, respectively. These modified Orbitrap designs demonstrated very high mass resolution. A recent study which modified the geometry of the Orbitrap was that of the Sonalikar et al. [15] which presented segmented geometries of Orbitraps having simplified, easily machinable electrodes. This last study was motivated by both the initial suggestion of Makarov [16] and a more recent study of segmented electrode geometries for the CIT [17].

Planar geometry mass analyzers are not new in mass spectrometry. Planar ion traps typically consist of one or two planar substrates on which the number of metallic electrodes are printed by micro-fabrication techniques [18]. Planar geometries typically use a large number of segmented electrodes with appropriate potential applied on them in order to satisfy the boundary values of a desired field profile [19]. Planar ion traps have been used for a variety of applications in the literature. Austin et al. [20] presented a geometry consisting of two planar substrates with concentric ring electrodes lithographically printed on them. This geometry was demonstrated to create toroidal trapping volume by applying the optimized values of potentials to the ring electrodes as well as a quadrupolar electric field of the Paul trap [21–24]. Hansen et al. [25] and Zhou et al. [26] presented planar geometries consisting of a combination of grounded, RF and DC potentials applied to the electrodes to create an electric field similar to that of Linear Ion Trap. Chaudhary et al. [27] reported a design of planar ion funnel for miniature ion optics by applying a gradient of electrostatic potentials to the concentric ring electrodes printed on a planar substrate. Such planar geometries of ion traps are suitable for micro-fabrication and hence suitable for miniaturization [19]. Also, planar geometries provide a comparatively large trapping volume as well as an easier access to trapped ions [20].

In the present study, we have taken up for numerical investigation a planar geometry mass analyzer consisting of two planes, each plane having a number of concentric ring electrodes. Appropriate potentials are applied to the individual rings for effecting trapping of ions. This geometry has been named as PORB ('**P**lanar **ORB**itrap'). Both single particle and multi-particle simulations are performed. The multi-particle simulations are carried out on an ensemble of 1000 ions. These simulations incorporate spatial and energetic distributions as well as space charge effects. The performance of the PORB will be compared with that of a reference Orbitrap. The following comparative studies will be undertaken: (1) potential variation in the principle directions, (2) ion trajectories and (3) image currents in the PORB and the reference Orbitrap.

The following section describes the geometries considered in this study. Section 3 briefly summarizes the numerical methods used in this work. Section 4 presents the results and discussion. A few concluding remarks are presented in Section 5.

## 2. Geometries considered

The geometry and geometry parameters of the reference Orbitrap and the PORB geometry taken up for investigation in this study are presented below.

**Table 1**
Geometry parameters of the reference Orbitrap and the PORB. All dimensions are in millimeter.

| Parameter | Reference Orbitrap | PORB |
|---|---|---|
| $R_1$ | 7.0 | 7.0 |
| $R_2$ | 80.0 | 80.1 |
| $Z_{max}$ | 100.0 | 15.0 |
| $g$ | – | 0.2 |
| $h$ | – | 2.47 |

### 2.1. Reference Orbitrap

The geometry of the reference Orbitrap used in this study is shown in Fig. 1(a). While outer electrode of the practical Orbitrap is symmetrically split into two at $z=0$ for ion entry as well as for the measurement of the image current, in our present numerical study, no split has been incorporated. $R_1$ and $R_2$ are the radii of the inner and the outer electrodes of the Orbitrap, respectively. The Orbitrap is truncated in axial direction at $z=Z_{max}$. The characteristic radius of the Orbitrap is $R_m=\sqrt{2}R_2$ [5]. The dimensions of the geometry parameters used in our study are listed in Table 1 under the column Orbitrap.

The values of geometry parameters $R_1$, $R_2$ and $R_m$ of our reference Orbitrap are used to compute the values of constants $k$ and $C$ by using equations,

$$k=\frac{2V_0}{\left((R_2^2-R_1^2)/2\right)-R_m^2\ln\left(R_2/R_1\right)} \tag{4}$$

$$C=\frac{k}{2}\left(\frac{R_2^2}{2}+R_m^2\ln\left(\frac{R_m}{R_2}\right)\right) \tag{5}$$

These have been derived from Eq. (2). Here, $V_0$ denotes the potential applied to the inner electrode of the Orbitrap. The value of $V_0$ is generally kept negative for trapping positive ions. The values of $k$ and $C$ are used to compute potentials applied to the different ring electrodes of the PORB geometry.

The length of the Orbitrap is arbitrarily truncated at $Z_{max}=100$ mm. This length is sufficient since we have restricted the maximum distance of ion motion in $z$ direction to 10 mm in our simulations. $R_2$ of 80 mm chosen in our reference Orbitrap is much larger than the $R_2$ values in practical traps reported in the literature. The reason for this choice of large $R_2$ will be discussed in Section 4.1.

### 2.2. PORB

The geometry of the PORB consists of two planar surfaces, each consisting of $N_R$ concentric metallic ring electrodes. The cross section of the PORB geometry is shown in Fig. 1(b). Fig. 1(e) and (f) shows the top and 3D views of the PORB, respectively. Both the planes of PORB share the same central $z$ axis. The distance between the two planes is $2Z_{max}$. The radius of the outermost ring electrode is denoted by $R_2$. $h$ denotes the width of each ring electrode and $g$ denotes the width of an air gap separating neighboring electrodes. The values of these geometry parameters are listed in Table 1 under the column PORB.

The potential applied to each ring electrode of the PORB is computed by putting the $r$ and $z$ coordinates corresponding to the center of each ring electrode in Eq. (2). The values of constants $k$, $C$ and $R_m$ used in this computation correspond to the parameters of the reference Orbitrap (Section 2.1).

The value of $R_2$ used for the PORB geometry is 80.1 mm. The value of $Z_{max}$ used for the PORB is 15 mm, which is much smaller than the $Z_{max}$ in the reference Orbitrap. The reason for this will be discussed in Section 4.1. In addition to this geometry, the PORB