Non-destructive, Absolute Mass Determination of Sub-micrometer Sized Particles in a Paul-type Trap

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Abstract. A method for non-destructive determination of the mass of a single submicron particle under ultra high vacuum conditions is presented. In an electrodynamic quadrupole trap the eigenfrequencies, ω_r and ω_z, of the particle motion and thus its q/m is measured by recording the scattered light from a laser beam. This allows for online weighing and determination of the particles charge state. Electron bombardment changes the particle charge state in integral steps of elementary charges due to secondary electron emission. The emission yield has been determined event by event at two primary electron energies. In addition the absolute number of charges has been inferred from these measurements and, therefore, the particles absolute mass as well. A relative reproducibility of $3 \cdot 10^{-4}$ over a period of several hours is achieved. Possible applications for this new technique such as the determination of sticking coefficients are mentioned.

Introduction

Localization, long term containment and isolation from disturbing surrounding influences are the prominent features of ion trapping [1]. This confinement technique is the foundation for a number of precision measurements carried out in the last four decades. Mass spectrometry and optical spectroscopy are two important examples. Besides storage of atomic and molecular ions, quadrupole ion traps have also been used for storage of single micrometer size dust particles [2] or droplets [3] since the late 1950's. Whereas in the beginning of these studies the size of the stored droplet was determined via direct observation through a microscope, application of Mie-scattering [4] allowed much more accurate determination of particle radii. In addition, electrostatic balancing of the charged particle was used as a method to measure the particles charge to mass ratio [4]. On the one hand, this technique became known as the electrodynamic balance (EDB) or picobalance, because the balance voltage is a direct measure for relative mass changes, e.g., due to evaporation, as long as the charge state remains the same throughout the experiment. On the other hand, single electron removal by UV-radiation was employed to infer the particle's absolute charge and thus its absolute mass [5]. The accuracy of this method is limited to a few percent due to imperfect determination of the localization by optical means.

Already in the early development of the quadrupole trap, detection of ions was intended to be achieved by resonant excitation at the "eigenfrequency", ω_{res}, of the particular ion in the trap. Since this secular frequency is proportional to the ions charge to mass ratio, resonant detection also serves as an accurate mass analyzer [6]. Unfortunately, this method has not been used for the mass determination of macroscopic particles until very recently [7]. The authors observe a star shape pattern of the particle trajectory in a hyperbolic quadrupole trap using a CCD camera. They determine the secular frequency, ω, and thus also q/m of the particle by adjusting the driving frequency, Ω, to an overtone of ω, since in this case the pattern stabilizes analogous to a Lissajous trajectory.

In this contribution we describe a different laser based non-destructive method of accurate mass determination of sub-micrometer particles in a quadrupole trap. As a first result of this powerful method we present the detection of individual events of secondary electron emission from a single 500 nm in diameter SiO_2 sphere. The inherent precision of the mass determination by a frequency measurement opens up a variety of applications which will be mentioned in the conclusions.

EXPERIMENTAL SECTION

Storage in a Quadrupole Trap

The inhomogeneous electric field
$$\mathbf{E}_0(\mathbf{r},t) = \mathbf{E}_0(\mathbf{r}) \cos(\Omega t) \tag{1}$$
in an electrodynamic trap gives rise to a time-averaged pseudo-potential
$$V^*(\mathbf{r}) = q^2 \, \mathbf{E}_0(\mathbf{r})^2 / 4 \, m \, \Omega^2, \tag{2}$$
where q is the particles charge and m its mass. For a quadrupolar field $\mathbf{E}_0^2$ is harmonic in all directions. Therefore the particle

motion along independent coordinates is separable and V* can be expressed for any direction, e.g., for the z-direction as

$$V_z^* = 1/2 \, m \, \omega_z^2 \, z^2. \tag{3}$$

Here ω_z is the secular frequency of the particles motion in z-direction. For the geometry used in our trap (Paul-type trap) the motion along the x- and y-direction results in a degenerate solution and is therefore characterized by the same frequency ω_r for both coordinates. Using eqs. 2 and 3 one can determine ω_z, which can be solved for

$$q/m = \tfrac{1}{2} \, \omega_z^2 \, / \, (E_{o,z}^2/z^2). \tag{4}$$

For a Paul-trap, $E_{o,z}^2/z^2 = V_0/z_0^2$ is a constant, where V_0 is the amplitude of the applied voltage and $2 z_0$ is the axial distance of the two cap electrodes. Thus for fixed ω, the secular frequency ω_z is measured experimentally and q/m is determined. For a realistic Paul-type trap, $E_{o,z}^2/z^2 = \partial_z E_{o,z}$ is a constant only in the vicinity of the electrical center of the trap and depends on the geometry of the actual electrodes as well as the applied voltage. Numerical values for $\partial_z E_{o,z}$ and $\partial_r E_{o,r}$ have been calculated for the actual trap geometry using an ion optics simulation program, SIMION [8].
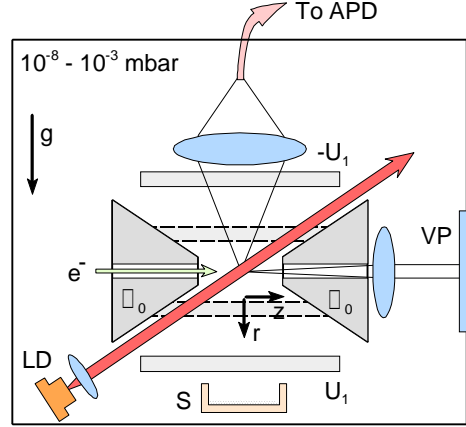

FIGURE 1: Schematic view of the experimental setup. A high voltage at audio frequency ($\Phi_0 = V_0 \cos(\omega t)$) is supplied to the cone electrodes. DC voltages ($\pm U_1$) for compensation of the weight of the stored particle are supplied to the rod electrodes. A reservoir with membrane serves as particle source (S) and a collimated laser diode (LD) for illumination. Scattered light is focused onto a multimode fibre and detected by an avalanche photo diode (APD) outside the vacuum chamber or alternatively, observed through the view port (VP). Electrons (e⁻) from an electron gun are used for changing the charge state of the particle.

Trap-Design and Experimental Setup

Fig. 1 shows a schematic view of the actual trap design and additional features of the experimental setup. The trap consists of two cones, opposing each other at a distance of $2 z_0 = 6.6$ mm with axial bored holes. Their axis of cylinder symmetry defines the z-axis used in the theoretical descritption of the system. They are surrounded by eight rods which form a cage like structure resembling the ring electrode of a Paul-trap. This open design has been chosen in order to obtain a large solid angle for light detection and also to access the trap volume through several ports with additional tools such as the particle source, the laser beam and the electron gun. The potential ($\Phi_0 = V_0 \cos(\omega t)$) for the driving field of the quadrupole trap is applied to the cones only. Pairs of the rods are electrically connected and used to control the position in x- and y-direction by applying symmetrical low DC voltages to opposing pairs. In this way the particle can be steered into the center of the trap where the secular frequency shall be measured.

A small UHV compatible loudspeaker is filled with monodisperse 500 nm diameter SiO_2 spheres and serves as a particle source. For injection, the membrane vibrates and ejects particles into the trap. In order to overcome the problem of the particle being able to settle in the trap when injecting particles from an external source which has been described already in the early paper by E. Fischer [9], the background pressure is increased to several 10^{-4} mbar. Friction due to the buffer gas is sufficient to dissipate kinetic energy of the particle while entering the effective potential given by Eq. 2. Light from a collimated laser diode ($I \approx 2.5$ mW/mm^2) is directed near the center of the trap. Upon storage of a particle scattered light is observed through a view port (VP) using a CCD camera. If several particles are stored at the same time the effective trapping potential is weakened by increasing ω until only a single particle is left. The residual secular motion of the particle leads to a modulation of the scattered light at the eigenfrequencies ω_r and ω_z. This light is collected by a lens, transferred outside the vacuum in a multimode fibre and transmitted to an avalanche photo diode (APD). With the laser intensity given above and a detection angle of 0.013 sr a maximum power of about 4 pW is scattered from a 500 nm SiO_2 sphere. The corresponding APD-signal is further amplified and

filtered electronically, recorded by an AD-converter and Fourier transformed by a computer. The relevant frequency peak for the motion in z-direction, $\omega_z/2\pi$, is found manually and thus the temporal evolution of q/m (Eq. 4) can be followed over a period of hours or even days. Without interfering with the particle we found that the measured q/m remains constant over such long periods of time.

RESULTS

Precision of the q/m Determination

Fig. 2a shows the result of a series of 997 consecutive determinations of ω_z over a period of more than 30 hours. ω_z and therefore q/m remain constant over approx. the first 20 hours. Between two neighboring time steps ω_z increases by a factor of 1.132924(50) and remains again constant for the rest of the measurement. We attribute this step like increase in ω_z to a spontaneous increase in charge of the particle. The measured ratio of the secular frequencies is consistent with an increase from +15 e to +17 e for a single 500 nm in dia. SiO_2 sphere, where +e is the positive elementary charge. Fig 2b illustrates the precision of the experiment. Here the probability of a deviation from the mean value binned in increments of 0.001 Hz is shown for the first 567 data points ($\approx$ 20 h). The envelope of this histogram is fitted to a Gaussian peak shape with a FWHM of 8.7 mHz which corresponds to a precision of 270 ppm for a single q/m determination. Over the period of 20 hours the q/m determination is precise to 4.4×10^{-5} which results in the five significant figures given above for the frequency ratio at the step. The expected ratio (1.13333) deviates significantly (3.6×10^{-4}) from the measured. This is due to imperfections of the quadrupolar field even near the center of the trap where the particle is located [10]. It becomes measurable when the particle is lifted to a slightly different location (r-direction, see Fig. 1) upon charging. Its effect is smaller in ω_z than in ω_r. During this long time measurement we observe also a small drift of about -1 ppm/minute which might be due to minor variations of the distance of the cap electrodes (nm/minute). This drift has been corrected in Fig 2b. Measuring a single step, $\Delta q = + n$ e, of the charge state is not sufficient to unambiguously determine the absolute particle charge state, since an initial charge larger by a factor of 2 and a step with an assumed change in charges twice as big will lead to the same final result.
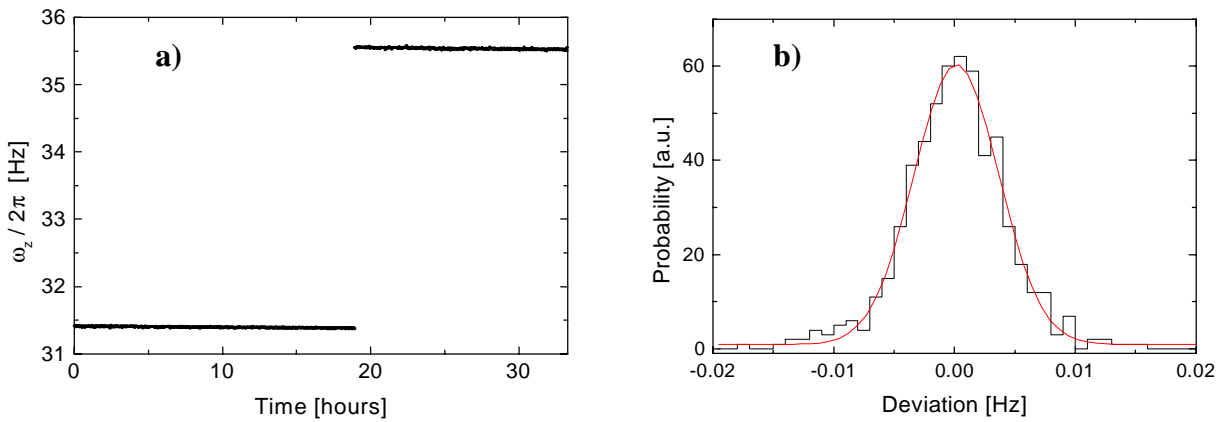

FIGURE 2 a): Repeated determination of the secular frequency ω_z of a single stored particle over a period of more than 30 hours. After approx. 20 h a step in the secular frequency ω_z is observed. The measured ratio of frequencies is consistent with the expected one for one particle carrying +15 e and +17 e before and after the change of charge, respectively. Change of charge of the particle is attributed to the emission of electrons. **b):** Precision of the experiment. The scatter of the individual measurements before the step (13.2 sec integration time, S/N = 25) is shown in a histogram as a probability of deviation from a mean value. The envelope is fitted to a Gaussian with a FWHM of 8.7×10^{-3} Hz. This corresponds to a precision of 270 ppm for a single q/m determination.

Absolute Mass Determination

In order to overcome the problem of determining the absolute particle charge and mass usually the ejection of single photoelectrons is used [5], but in the case of SiO_2 the work function is too large to use a conventional UV-lamp. Therefore we employed an electron gun to charge the particle. Due to the fact that the driving voltage is supplied to the cones only, the kinetic energy of the electrons hitting the particle is modulated by the driving potential, $V_0 \cos(\Omega t)$. We use a repelling grid to allow

injection of electrons only during a time window of several 10 μs. Varying the phase shift of the gate pulse with respect to the driving potential the electron energy can be selected from 0 V up to about 0.8 V_0. Fig. 3 shows $_r$ as a function of time with an electron energy of about 190 eV. Here, thirteen charge steps are observed within 3 hours. It is clearly seen that the steps are at integer multiple of about 0.45 Hz. Since this is the smallest step and since we observed all step sizes between +1 and +5 elementary frequency units we relate this smallest unit to ejection of a single electron. From this we infer that at t=0 the particle carried +31 e. Using Eq. 4 we determine q/m = 30.8 mC/kg for this particle and therefore the absolute mass is m = (1.6±0.3) 10^{-16} kg. A single 500 nm SiO_2 sphere (= 2 g/cm^3 [11]) has a mass of 1.3 10^{-16} kg. Taking into account an uncertainty of 10 % in the radius of the prefabricated SiO_2 spheres [11], the mass determined by the method described here matches well with the manufacturers specifications. However, while the precision of the experiment is very good, the fairly poor absolute accuracy is related to the determination of the values for $_z E_{o,z}$ and $_r E_{o,r}$ which derive from a numerical simulation of a model of the actual trap with a spatial resolution of only 1/25 z_0. More work increasing the resolution as well as taking into account possible misalignments of the electrodes is in progress to improve the accuracy of absolute mass determination.
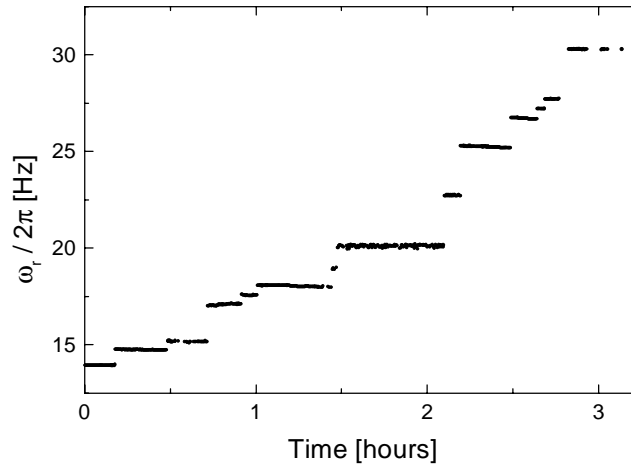

FIGURE 3: Thirteen charging steps of a single particle are induced by use of (190±20) eV electrons. The height of the steps varies between +1 and +5 elementary frequency units of 0.45 Hz which corresponds to charging by +1 e. The net charge is increasing from 31 e to 64 e during this three hour measurement. At the beginning of the measurement q/m was 30.8 mC/kg. From this the absolute mass of the particle has been determined to m = 1.6 10^{-16} kg.
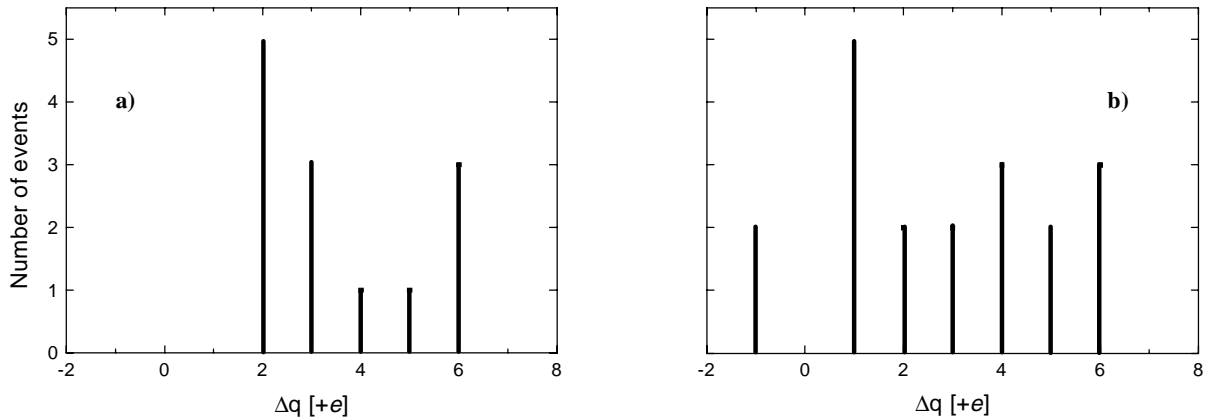

FIGURE 4: Secondary electron emission yields at two different primary electron energies. *a)* 190 eV. *b)* 570 eV. q = 0 events are not detectable.

Secondary Electron Emission Yields

Charging the particle using electron bombardment leads to an increase in positive charge as can be seen in Fig. 3. This charging process can be attributed to secondary electron emission from the surface of the SiO_2 particle. As shown in Fig. 3 this is a statistical process where up to 6 electrons are ejected in a single event. The energetic primary electron penetrates the surface to

a depth up to about 5 [12] and loses energy continuously due to inelastic collisions. Eventually it transfers enough energy to another electron which then might escape from the solid if it can cover the distance to the surface without losing its energy (mean free path also in the regime [12]). For the thirteen steps measured in the experiment shown in Fig. 3 we display the probability of secondary emission yield in Fig. 4a. Although the statistical error is still quite large due to the small total number of recorded events this histogram shows that the probability peaks at a yield of about 2 secondary electrons per primary electron. $q = 0$ events, which signify one primary electron yielding one secondary electron, are undetectable. We repeated the experiment with the same particle at an elevated primary electron energy (570 eV, see Fig. 4b). Here the average yield appears to be slightly increased as well as it is spread over a wider range. This is in agreement with the fact that higher energy electrons produce more secondary electrons. Besides the generally occurring positive charging two events of negative charging (-1 e) have been detected. They are attributed to trapping of the primary electron in the solid with no secondary electron emission. This finding is consistent with the fact that 570 eV electrons penetrate about twice as deep into the solid as 190 eV ones. Therefore the chance of escape for the secondary electron is reduced.

CONCLUSIONS

With the experiments presented here we demonstrate the capability of accurate, non-destructive mass determination of a single very well localized and isolated particle in a mass regime of 10^{-16} kg (10^{11} amu 10^9 SiO_2). At the present stage and for a 500 nm SiO_2 particle the mass resolution is sufficient to resolve molecular adsorption (e.g., H_2O) at a sub-monolayer level. Therefore one of the future applications of this method will be the determination of sticking coefficients at various conditions (e.g., temperatures). Since the mass determination is based on a frequency measurement there is room for further improvement of the resolution (10^{-6}). Especially for much smaller particles (50 nm) single molecule mass resolution is feasible. In that case the secular frequencies are increasing from the Hz- towards the kHz-regime. On the one hand low frequency noise which is hard to be rejected will no longer play a role and gravitational compensation is no longer necessary. On the other hand the time to determine q/m by FFT methods will be reduced and the accuracy will be increased at the same time. In summary it might become feasible to form a macroscopic structure which mass is determined to a single atom accuracy leading to a new reference of absolute mass unit.

The first physical process studied in our new apparatus was the secondary electron emission. This process could be followed online event by event, revealing its statistical nature, and the probability of yields has been measured for two primary electron energies. Due to the small mean free path of primary and secondary electrons this process is related to the outermost shell of the particle. The investigation of further interesting phenomena such as charge transfer from adsorbed molecules can be undertaken. Since the detection scheme is laser based combination of this sensitive method of mass analysis with optical information (e.g., absorption and emission spectra) opens up a variety of additional applications in the fields of aerosol-chemistry (gas/liquid interface), dust-chemistry (gas/grain interface), physics and chemistry of colloidal systems as well as applications in biology.

ACKNOWLEDGEMENT

REFERENCES

1.   M.H. Holzscheiter, Physica Scripta, **T59**, (1995), 69-76.
2.   R.F. Wuerker, H. Shelton, R.V. Langmuir, J. Appl. Phys., **30** (1959) 342.
3.   T.G.O. Berg and T.A. Gaukler, Amer. J. Phys., **37** (1969) 1013; M N.R. Whetten, J. Vac. Sci. Technol., **11** (1974) 515.
4.   E.J. Davis and A.K. Ray, J. Colloid and Interface Science, **75** (1980) 566.
5.   M.A. Philip, F. Gelbard, and S. Arnold, J. Colloid and Interface Science, **91** (1983) 507.
6.   Today this technique is even commercially available as a Paul-trap mass analyzer, e.g. from Finnigan Inc., San Jose.
7.   G. Hars and Z.Tass, J. Appl. Phys., **77**, 4245, (1994).
8.   SIMION 3D, Ion Optics Simulation Program, Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, ID 83415.
9.   E. Fischer, Z. Phys. **156**, (1959), 1.
10.   S. Wellert, Diploma thesis, TU-Chemnitz, March 1998.
11.   Value specified by the manufacturer, Merck Company.
12.   A. Zangwill, physics at surfaces, New York, 1988, ch. 2, p. 21.