Thermochimica Acta, 103 (1986) 33-38 Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

INFLUENCE OF THERMAL NOISE ON THE ACCURACY OF MASS DETERMINATION ACCORDING TO THE STRAUBEL METHOD

C.H. MASSEN<sup>1</sup>, J.A. POULIS<sup>1</sup>, E. ROBENS<sup>2</sup> and H. STRAUBEL<sup>3</sup>

<sup>4</sup>Physics Department, Eindhoven University of Technology (The Netherlands)

<sup>2</sup>Institut für Anorganische und Analytische Chemie der Johannes-Gutenberg-Universität, Mainz (Federal Republic of Germany)

<sup>3</sup>Bergweg 7, D-8973 Vorderhindelang (Federal Republic of Germany)

#### ABSTRACT

According to Straubel's method, a small, charged particle is suspended in a three-plate condensor, connected with d.c. and a.c. voltages. Using this arrangement, mass variations can be measured because the particle **retains** its charge for hours even when reactions with the surrouding gas take place. It was possible to measure mass changes of particles 3 /um in diameter as a result of adsorption or desorption down to 0.1 pg. This paper deals with the influence of Brownian motion on the particle. The acting force, and hence, the weighing accuracy is calculated to be of the same order of magnitude and this seems to be the limit of resolution.

## INTRODUCTION

Straubel (ref. 1) described a method of localizing charged particles suspended in air. At the conferences at Uxbridge (ref. 2,3) and Lyon (ref. 4) the use of that method to measure mass changes of small particles and droplets, respectively, was presented. Using this method it was possible to observe mass variations due to sorption, condensation or evaporation processes and - in combination with the Stokes drop experiment or optically - to determine simultaneously the particle mass.

The device (Fig. 1) consists of a capacitor with three circular plates, e.g. 40 mm in diameter, spaced at intervals of 12 mm and arranged in a transparent plastic tube. Each plate has a cen-0040-6031/86/\$03.50 © 1986 Elsevier Science Publishers B.V.



Fig. 1. Arrangement of a three-plate-capacitor, particle observation by means of a lateral stereomicroscope.

tral bore hole, in the intermediate plate 12 mm in diameter. Another version is equipped with a slit-shaped bore hole. If an a.c. voltage of about 2 kV, 50 Hz is applied between the intermediate plate and the ground, small particles carrying a sufficiently high charge will be trapped in the inhomogeneous field of the hole, exactly in its center but, according to its mass, somewhat below the plate. The mass can be counterbalanced applying a d.c. field across the outer plates - so called Millikan plates - in such a way that the particle is centered in the level of the middle plate. The particles or droplets can be illuminated by a lamp and observed through a lateral stereomicroscope (Fig. 1) or, as shown in Fig. 2, by a laser beam and the diffraction patterns recorded on a film.



# Fig. 2. Schematic drawing of a three-plate-capacitor. Illumination of a suspended droplet by a laser beam, **recorded photographically**

The trapped particle remains in a stable position and - damped by the surrounding air - unmoving. If the a.c. voltage is raised above a certain value, the particle suddenly starts to oscillate. For further determinations the voltage is increased just below that voltage. Because the particle retains its charge for many hours, various measurements including the determination of mass changes are possible.

Different methods may be used to measure variations of the mass of the the suspended particle:

- Most suitable for this arrangement is the Millikan method: counterbalancing the particle mass  $m_p$  by a d.c. field acting on the charge Q of the particle. We obtain a value for  $Q/m_p$  or - in case of subsequent observations at constant Q directly the mass variation  $\Delta m_p/m_p$ . Mass variations up to 1/20000 may be determined (ref. 1).
- Also the onset of oscillation in function of the applied a.c. field depends on the ratio  $\Omega/m_p$  and may be used to determine the mass variation in some cases. Relative mass changes of the particle are obtained from the relation  $\Delta m_p/m_p = \Delta U_{\sim}/U_{\sim}$  by repeated determination of the voltage  $U_{\sim}$  at which oscillation

starts. Because of the dependence on the square of friction coefficient only relative determinations can be made neglecting changes of particle diameter and mean density. Thus, only little mass variations can be measured. Using this method we measured sorption isotherms of water vapour on calcium chloride and magnesium perchlorate particles of about 3 /um in diameter corresponding to a mass of 40 pg. Mass variations down to 0.1 pg were observed (ref. 2).

- By switching-off the condensor it is possible to measure the constant rate of fall of a spherical particle and to calculate the particle mass according to Stokes law.

More convenient is the measurement using the condenser with slit shaped boring. The condensor tilts and the fall velocity, reduced according to the inclination is measured without losing the particle. The method is limited to particles bigger than 100 /um in diameter.

Optically, the diameter of spherical particles can be determined by measuring the distances between diffraction rings. In some cases spheres can be generated by melting the suspended particle. If the density of the material is known the particle mass can be calculated. The unknown density can be measured at two different air pressures in the condenser.

Fractical limitations of these methods result from the optical observation of the suspended particle, that means from size and reflexivity. For diameters below 2 /um the **particle** is shown only as diffraction pattern. Furthermore, particles below, let us say, 3 /um may be hardly stimulated to oscillate and to stabilize (refs. 1,7). Particles of high mass particles can no longer be suspended because the corresponding high voltages generate gas discharges. As a consequence, investigations of high density material is limited to some respect. Using the condensor with

36

slit-shaped bore hole the measuring range can be increased to particle diameters of more than 100 /um.

### THERMAL NOISE

For the estimation of the effect of thermal noise we can calculate the stochastic forces influencing the localization or the motion of the particle and compare it with the weight of the particle. The assessment is valid for both, the Millikan method and the a.c.-experiment.

Let us consider one spherical particle (radius r) suspended in air. This particle will be hit by air molecules both from above and from below. The number of each these collisions **is** submitted to statistical fluctuations which cause the Brownian motion. The average number N of gas molecules, mass m, colliding from above or from below can be estimated by:

$$N = \mathcal{T}r^{2}\frac{n}{6} v_{th} t_{m}$$
<sup>(1)</sup>

where n =  $\frac{P}{kT}$  is the number of molecules per m<sup>3</sup>, T the absolute temperature (K), p the pressure (Pa), k = 1.4 × 10<sup>-23</sup> J/K the Boltzmann constant and  $v_{th} = \left(\frac{kT}{m}\right)^{t/2}$  is the mean vertical component of the thermal velocity of the gas molecules in m/s. The uncertainity of the force acting on the particle is  $\frac{N^{t/2} 2 m V_{th}}{t_m}$ 

The resulting force  $\Delta F$  on the particle becomes:

$$\Delta F = \frac{2 (2 N)^{\frac{1}{2}} m v_{eh}}{t_m}$$
(2)

Replacing N and v<sub>th</sub> results in:

$$\Delta F = 2r \left(\frac{\pi}{3} \frac{r}{t_m}\right)^{\prime \prime \prime} \left(\frac{M}{N_a} kT\right)^{\prime \prime \prime}$$
(3)

where M stands of the molar mass and  $N_a$  for Avogadro's number 6.0 x  $10^{26}$  kmol<sup>-1</sup>. The disturbing force  $\Delta$ F is proporional to the particle radius. For the numerical assessment of the resolution

limit of the method we insert the smallest particle radius which can be used for practical reasons as discussed above:  $3 \times 10^{-6}$  m. We take the ambient pressure, p = 10 Pa, and the temperature T = 300 K, M (air) = 29 kg/m. We chose a reasonable time  $t_m = 10$  s for **observing** the falling or oscillating particle, and we obtain:  $\Delta F \approx 2 \times 10^{-45}$  N. This estimation of the disturbing force due to Brownian motion yields for the uncertainty in the mass changes of  $\approx 0.2$  pg and this is close to the value mentioned before (ref. 2).

### REFERENCES

 H. Straubel, Technisches Messen 48 (1981) 6, 199-210.
 G. Böhme, E. Robens, H. Straubel, G. Walter, in S.C. Bevan, S.J. Gregg, N.D. Parkyns (Eds.): Progress in Vacuum Microbalance Techniques, Vol. 2; Heyden, London 1973, pp. 169-174.
 R.Sh. Mikhail, E. Robens: Microstructure and Thermal Analysis. of Solid Surfaces; Wiley, Chichester 1983, pp. 319-321,337-338.
 H. Straubel, in C. Eyraud, M. Escoubes: Progress in Vacuum Microbalance Techniques, V.3; Heyden, London 1975, pp. 319-323.
 H. Straubel, J. Electrostatics 10 (1981) 223-228.
 H. Straubel, in: Atmospheric Pollution 1978, Studies in Environmental Science Vol. 1, Elsevier, Amsterdam 1979.

7 E. Straubel, H. Straubel, J. Aerosol Sci. 15 (1984) 6, 301-305