Thermochimica Acta, 82 (1984) 23—41
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

VACUUM MICROBALANCES AND THERMOGRAVIMETRIC APPARATUS
PART II: TYPES OF RECORDING INSTRUMENTS

E. ROBENS[1], C. EYRAUD[2], M. ESCOUBES[2]

[1] Battelle-Institut e.V., Am Römerhof 35, D-6000 Frankfurt am Main (Federal Republic of Germany)

[2] Université Claude Bernard, Lyon I, B.P. 6010, F-69604 Villeurbanne (France)

ABSTRACT

A survey is given of balances suitable for thermogravimetric and sorption measurements, this survey also covering composited thermogravimetric and sorption measuring apparatus. A bibliography is appended.

BEAM BALANCES

With beam balances the mass difference in the gravitational field between the sample and the counterweight is measured. The relative sensitivity of 10^8 is usually approached, and a sensitivity of 10^9 may be obtained.

Inclination Balances

These balances are characterised by a change in beam inclination when the mass of the sample is varied, until equilibrium has been re-established. This type of balance was often used for thermogravimetry but nowadays is mostly replaced by compensating beam balances. For applications in UHV and corrosive atmospheres bakeable quartz beam balances are sometimes used, with microscopic observation of the inclination (cf. the Rodder balance (ref. 1) shown in Fig. 1).

The beam inclination can be recorded in various ways: Chevenard (ref. 2) used photographic registration (Fig. 2). Chevenard-Duval actuated electrical contacts with the beam, the pulses being recorded. Gordon and Campbell (ref. 3) used a potentiometer, Petersen a magnetic detector (ref. 4), others a differential transformer. Rulfs (ref. 5) performed registration with the aid of photocells, using a diaphragm with varying aperture. Seederer-Feuer (ref. 6) equipped their balance with a

0040-6031/84/$03.00

radium pin, the position of which was determined by two ionisation chambers.

Fig. 1. Rodder's UHV quartz beam balance for optical observati

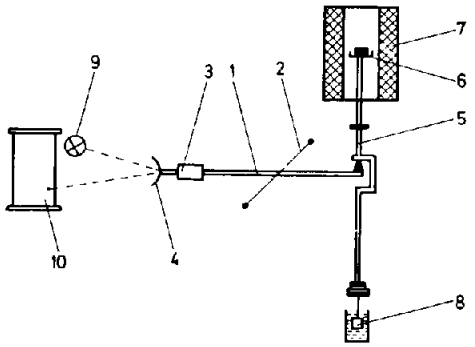


Fig. 2. Guichard's thermobalance
1 beam, 2 taut band, 3 counterweight, 4 mirror, 5 shaft, 6 pan with sample, 7 oven, 8 counterweight and damper, 9 lamp, 10 recorder cylinder with photo-paper

Compensating Beam Balances

With compensating beam balances the momentum due to a change in equilibrium is compensated by a counterforce returning the beam to zero. This counterforce serves as a measure for the mass change. The balance can be made very sensitive and independent of positional variations by locating the centre of gravity in the pivot. Stable position of the sample is advantageous because the temperature field of the thermostat often is not homogeneous. Compensating, equal-armed beam balances are most favourable in terms of the measuring procedure. In balances of this type, sample and counterweight can be kept at the same temperature, so that buoyancy and convection are largely compensated. For the measuring system of the balance a temperature compensation between 0 and 40°C is generally sufficient; for water vapour sorption measurements between 80 and 120°C.

Bartlett and Williams (ref. 7) describe a balance in which the beam is restored by a counteracting pointer of an electrical instrument arranged in Wheatstone bridge. Eyraud's balance (ref. 8,9) is equipped with a metal plate cutting off a light beam and, via a photocell, controlling a d.c. magnet suspended at the balance (Fig. 3). A differential photoelectric detector is described by Mauer (ref. 10). Brockdorff (ref. 11) used a coil at the beam to counteract a permanent magnet and thus compensate the deflection after its photoelectric determination. Similar

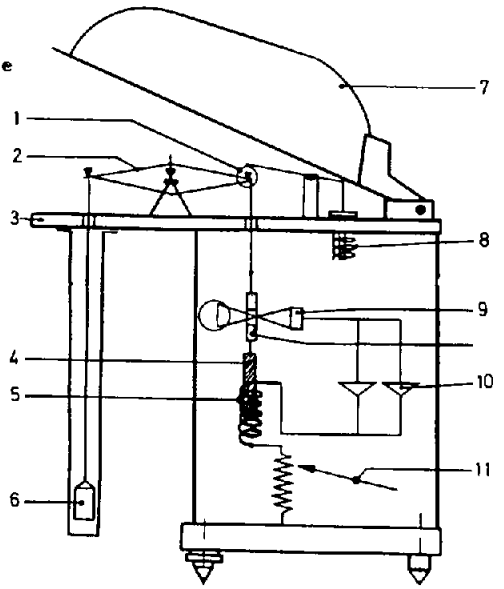
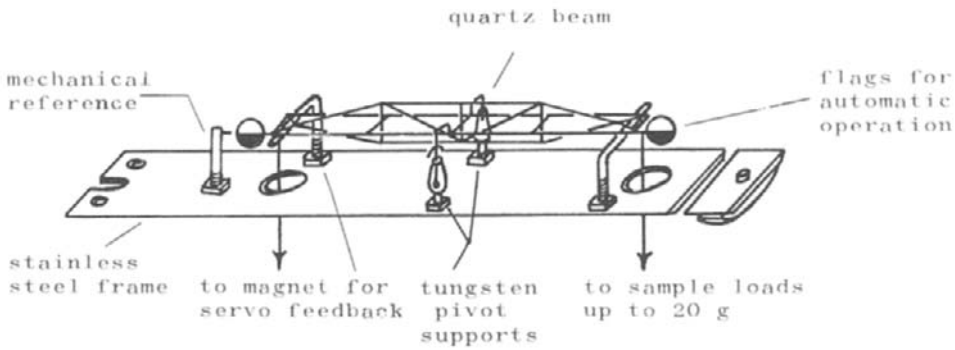
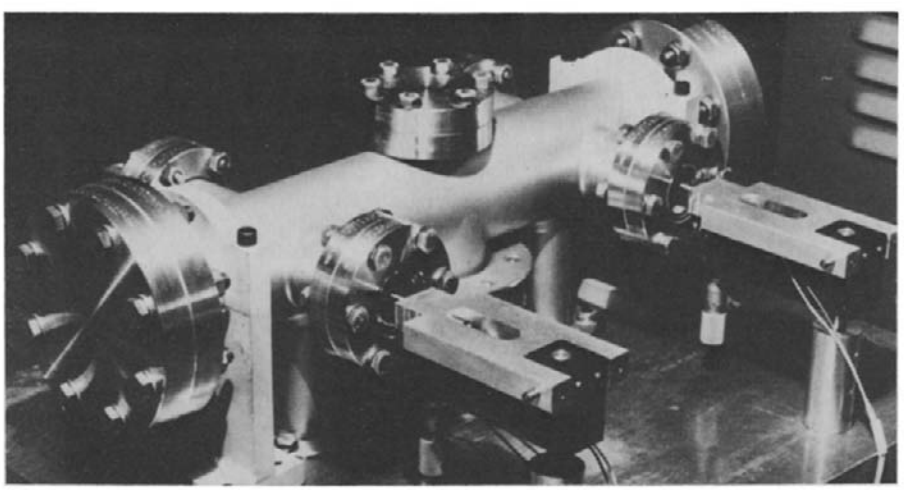


Fig. 3. Eyraud's thermobalance
1 rider, 2 beam, 3 base plate
4 permanent magnet, 5 coil,
6 balance pan, 7 cover,
8 electromagnet, 9 photo cell
10 amplifier, 11 recorder

devices have been described by Cahn (ref. 12), Muller (ref. 13), Hirone and Maeda (ref. 14), and are manufactured by several companies. Manigaut and Tsai (ref. 15) used electromagnetic forces applied to a core of soft iron which was attached to the beam; the current required to compensate the deflection was operated manually. A coil system with controlled d.c. flow was used by Gregg and Wintle (ref. 16), the deflection being observed with a photocell. Similar devices have been developed by many others (ref. 17,18). Czanderna (ref. 19) developed a commercial UHV quartz-beam compensating balance with a relative sensitivity of $2 \cdot 10^{8}$. Photocell and lamp are arranged outside the case, the light beam being introduced through borosilicate windows (Fig. 4, 5).





Figs. 4+5. Czanderna's UHV/high pressure balance

The sensor of Gast's balances (ref. 20,21) (Fig. 6) is composed of coils which are crossed in zero position. After deflection a high-frequency signal is transmitted, which is subsequently rectified and fed back to the beam coil, restoring the beam against a permanent magnet. The d.c. serves as a measure for the mass change.

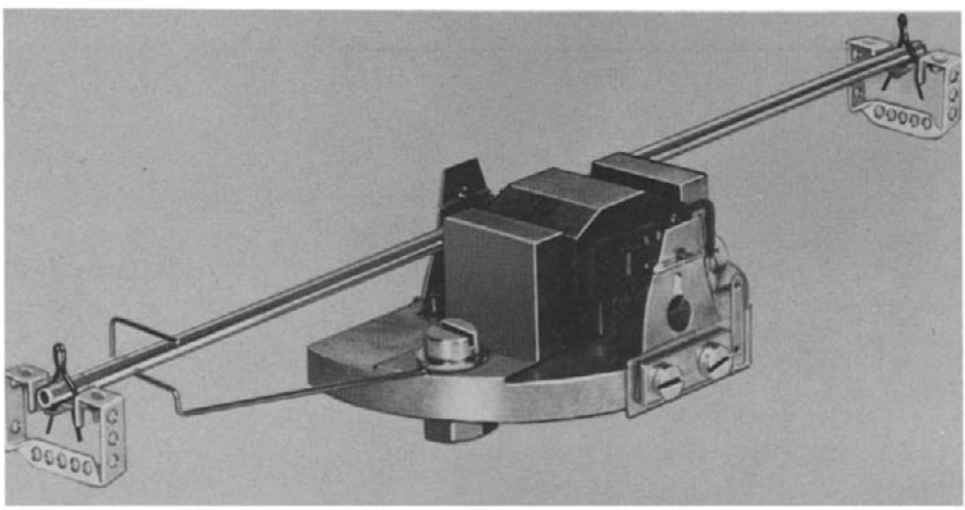


Fig. 6. Gast's electromagnetic balance

Former thermobalances were compensated by chains which could be varied automatically in length (ref. 22). Garn (ref. 23) used a servo-motor controlled by a differential transformer for this (Fig. 7). Waters (ref. 24) described a differential thermobalance, in which the mass change was compensated by electrolytic precipitation of silver from $AgNO_3$. Buoyancy in a liquid is occasionally used to compensate balance deflection. Automatic balances of this kind are described by Paphailhau (ref. 25) and Somet (ref. 26). Dybwad and Zinnow (ref. 27,28) used the force of a light beam as restoring force; the lowest mass change detectable with their balance was 10^{-10} g.

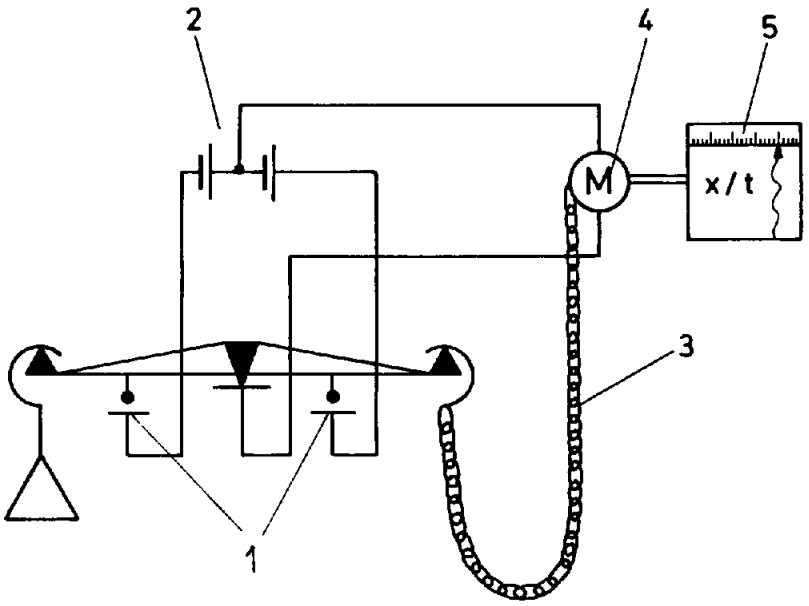


Fig. 7. Chain balance
1 deflection contacts, 2 battery, 3 chain, 4 servo-motor, 5 recorder

Torsion balances where the torsion wire is turned by a servo-motor have been described, a photocell mostly being used as position sensor (ref. 29). The microbalances described above (e.g. Cahn, Gast, Czanderna) can also be regarded as torsion balances because the beam is suspended in taut bands.

SPRING BALANCES

With respect to simplicity of design, quartz spiral balances are particularly favourable. In fact, self-manufacturing is possible. These balances consist of only few materials and thus lend themselves to work in UHV and corrosive atmospheres. However, because of their moderate resolution related to the maximum load of about 10^4, they have largely been displaced by commercial electric beam balances.

Spring Balances with Deflection Measurement

The McBain balance (ref. 30) consists of a quartz spiral in a glass tube. Deflection is observed using a cathetometer. A modification is described by Rhodin (ref. 31). Despite the small coefficient of expansion it is recommended to keep the spiral at constant temperature. Ernsberger (ref. 32) calculated the error

by thermal expansion to be

$$\Delta L = -1.23 \cdot 10^{-4}\ k(M + \frac{m}{2})\ \Delta T$$

where ΔL is the elongation of the spiral (mm), ΔT the temperature difference (K), M the sample mass, m the spiral mass (mg), and k the sensitivity (mm/mg).

The sensitivity of the balance depends on its geometry. For a maximum load of 1 mg it may be 100 mm/mg, and for 10 g about 0.01 mm/mg.

The deflection of the spring balance can be read using a differential transformer (ref. 33,34) (Fig. 8). In an improved version the coil system is automatically guided (ref. 35) to expand the range, which results in a sensitivity of 10 µg for 1 g load. Some spring balances are equipped with a light beam recorder (ref. 36, 37).

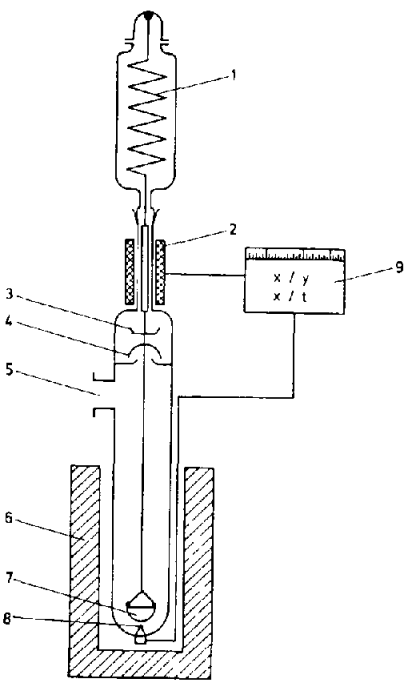


Fig. 8. 'Aminco Thermo-Grav'
1 quartz spring, 2 induction coil
3 tare pan, 4 temperature screen
5 vacuum flange, 6 heater, 7 sample pan, 8 thermocouple, 9 recorder

Compensating Spring Balances

Spring balances can be magnetically equilibrated by attaching a soft iron magnet to the balance pan, as described by Clark (ref. 38). Using a photoelectric control and a d.c. coil system, the elongation can be compensated to zero. A similar balance is described by Beams, Hulburt, Lotz and Montague (ref. 39).

Strain Gauge Balances

The measuring method using strain gauges or stretched resistance wires exhibits similarities to spring balances with respect to the operating principle. This method is increasingly being used for weighing heavy loads. The small maximum load/sensitivity ratio of 10^5 restricts its use in thermo-gravimetry to special tasks.

SUSPENSION BALANCES

Suspension balances are defined as instruments where the sample is freely suspended in the atmosphere without mechanical connection to the measuring system. There are two possibilities of realisation: electrostatic or electromagnetic.

Millikan suspended charged particles to determine the ratio of charge e to mass m. If e is known (and constant during the experiment), m and variations of m - e.g. due to adsorption - can be determined.

Straubel (ref. 40) improved the method by using a capacitor with three circular parallel plates, each with a hole in its centre (Fig. 9). If an a.c.voltage 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. These particles will be kept exactly in the centre of the hole but, according to their mass, somewhat below the horizontal plate. To counterbalance the mass a constant field may be applied across the two outer plates (Millikan experiment). Fig. 10 shows the corresponding experimental set-up. The particles are charged, e.g., in a corona discharge and dusted into the capacitor from above. All particles but one will be removed by varying the a.c.voltage (about 10 kV, 50 Hz). The remaining particle is illuminated from below and observed with a stereo microscope.

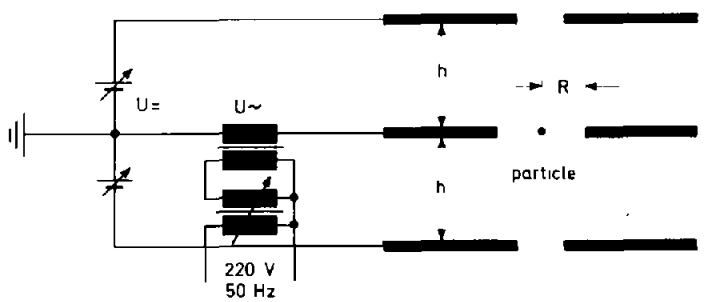


Fig. 9. Straubel's three-plate capacitor

When slowly increasing the voltage, the particle suddenly starts to oscillate. By determining the onset of oscillation it is possible to calculate the ratio e/m. In addition, relative weight changes of the particle are obtained from the relation

$$\frac{\Delta m}{m} = \frac{\Delta U}{U}$$

by repeated determination of the a.c.voltage U at the onset of oscillation. Particles up to milligrams may be used; the smallest mass change observed was 0.1 pg.

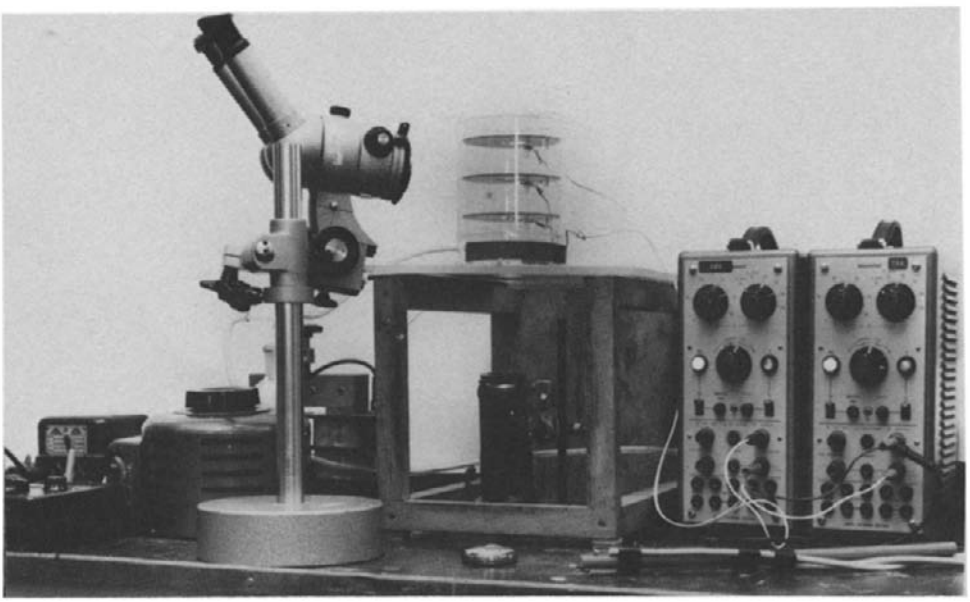
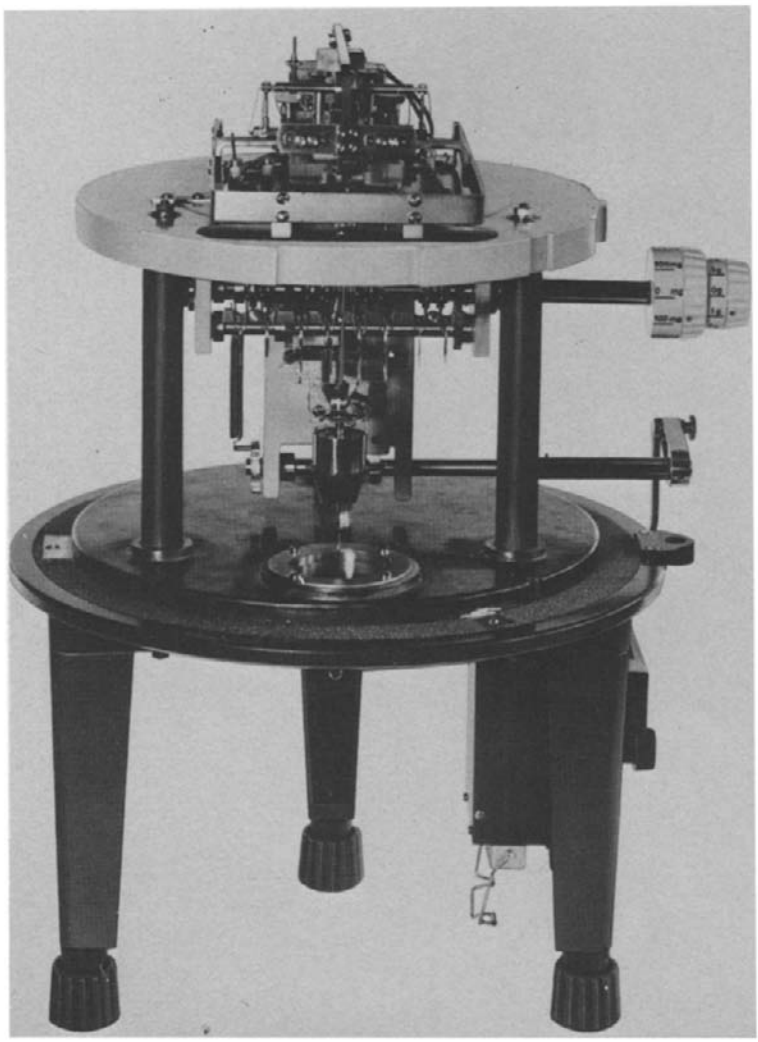


Fig. 10. Arrangement with the particle suspension balance

For studying sorption in a corrosive atmosphere or in ultrahigh vacuum, the electromagnetic suspension balance (Fig. 11) according to Gast (ref. 21) is particularly suitable. This is a single-armed beam balance with electromagnetic compensation in which the sample pan is attached to a permanent magnet which is kept in suspension at a distance of about 10 mm below an electromagnet attached to the hangdown wire, the distance between the two magnets being

controlled electromagnetically. The reaction space, a quartz vessel, thus contains only the sample attached to the permanent magnet. The measuring system of the balance is outside the reaction space, thermostated in air. The sample temperature can be transmitted wireless (ref. 41,42). Special versions for work in corrosive atmospheres (Fig. 12) and at high pressures (up to 150 bar) are available.

Fig. 11. Gast's suspension balance



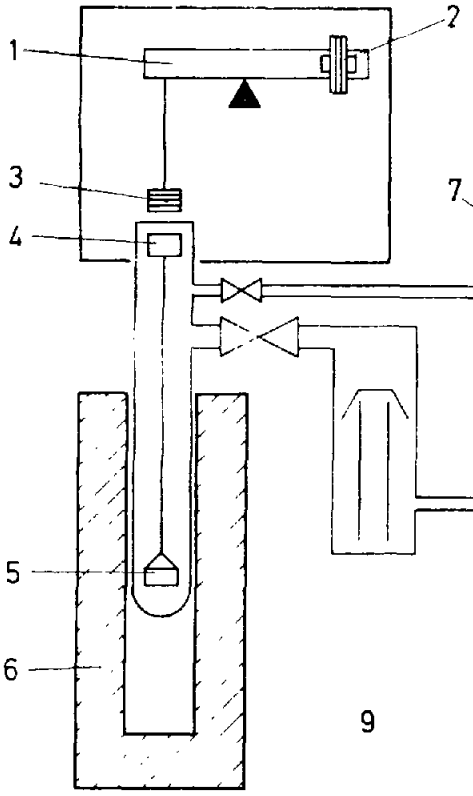


Fig. 12. Apparatus with magnetic suspension balance for measurements with corrosive gases or in UHV
1 balance beam, 2 electromagnetic measuring and compensating system, 3 controlled electromagnet, 4 permanent magnet, 5 sample, 6 oven, 7 pressure gauge, 8 gas cylinder, 9 mercury diffusion pump 10 water jet pump

OSCILLATION BALANCES

Crystal Balances

A change of the mass of the crystal m_o results in a change of it eigenfrequency f_o:

$$\frac{\Delta f}{f_o} = \frac{\Delta m}{m_o}$$

The smallest mass difference observed so far is about 1 pg. It is essential that the sample be firmly connected to the crystal. Otherwise it is not the mass that is measured, but the impedance of a stationary wave within the sample. The application is therefore restricted to the measurement of growing layers (vacuum evaporation, sputtering, etc.; (ref. 43-45)). Some difficulties arise from the temperature dependence of the crystal.

String Balances

The eigenfrequency of strained wires and bands is varied by the deposition of material. This principle has been proposed for weighing (ref. 46,47). A balance pan can be attached to a strained string. This method has been implemented in some technical balances (ref. 48) for g to kg loads, but not yet for thermogravimetric applications.

MULTICOMPONENT BALANCES

Such balances, mostly electromagnetic systems, are used for thermogravimetric applications where additionally to the mass change the impulse of a molecular beam is to be measured.

GRAVIMETRIC APPARATUS

Thermogravimetric instruments are characterised by heating equipment with temperature program.

Gravimetric instruments for investigating physisorption are equipped with pressure and temperature controls and devices for programmable changes of one or both variables. They also include a vacuum apparatus. In addition, simple apparatus for special technical measurements are on the market.

Moisture Meters

A very simple application of gravimetric sorption measurement is in moisture balances. Commercially available moisture balances usually are milligram balances equipped with infrared heaters, where the moisture contained in the sample is vaporized.

Thermogravimetric Instruments

They consist basically of a balance with a program-controlled heater, usually for linear temperature rise. Whereas earlier apparatus were equipped with special milligram balances, microbalances are increasingly being used today. Even small apparatus are equipped with vacuum aggregates. More sophisticated instruments include provisions for working with different gases at controlled pressure and reduced temperatures. Research apparatus of this kind are provided with connections for auxillary instruments. Some typical examples are briefly described in the following.

The 'Derivatograph' (Fig. 13) includes a milligram balance with automatic weight switching. It is an inclination balance

with light beam registration on photo-sensitive paper. The temperature, the mass and the derivative of the mass change are recorded. DTA is built in. The balance can be used alternatively as dilatometer, squeezing the sample between a yoke and the balance beam. The first derivative is here also recorded (ref. 49-53).

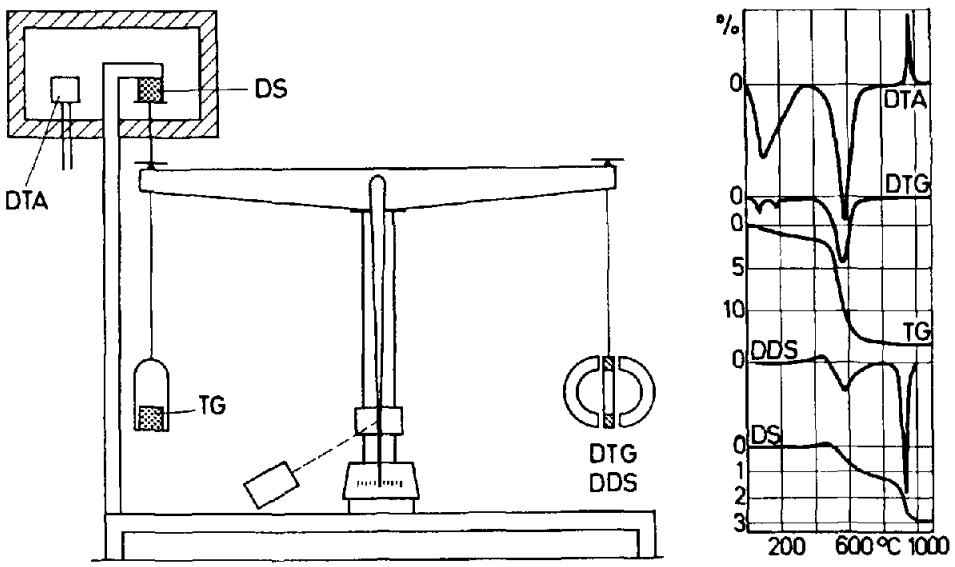


Fig. 13. Combined TG, DTA and dilatometry according to Erdey, Paulik and Paulik; 'Derivatograph'.

The 'Thermomat' (Fig. 12) includes an electromagnetic suspension balance according to Gast (ref. 21, 54). The whole apparatus is made of quartz. An automatic Bodenstein quartz spiral manometer serves for pressure measurement from UHV to 1 bar. Valves are equipped with PTFE seals. A mercury diffusion pump is combined with a water jet pump as forepump. This version is suitable for work in UHV and in corrosive atmospheres. Another version can be used at high pressures up to 150 bar.

The "Thermoanalyzer" (ref. 55, Fig. 14) is equipped with a milligram balance. The sample can be arranged either below or above the beam. The vacuum aggregate includes two diffusion pumps, one for the instrument case, the other for the sample space. DTA at the balance pan is possible.

The "Microthermoanalyseur" (ref. 8,9,56, Fig. 15) is equipped either with an Eyraud balance or a compensating microbalance. The mass and the first derivation of the mass are recorded. DTA is

included. Temperature control is up to 2700 K.

Favourable is the arrangement of the balance on a free stand accessible from all sides, which facilitates the connection of other instruments.

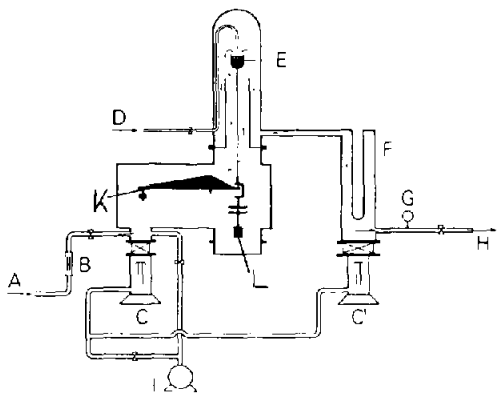


Fig. 14. Mettler Thermoanalyser
A protecting gas supply, B gas dryer C oil diffusion pumps, D reaction gas supply, E sample, F cold trap, G diaphragm pressure gauge, H exhaust, I rotary vane pump

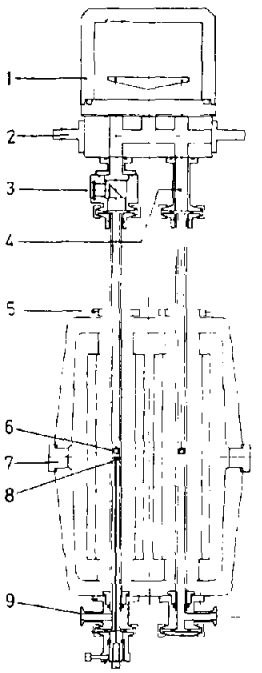


Fig. 15. SETARAM Microthermoanalyser
1 electromagnetic balance in vacuum case, 2 base plate with vacuum manifold, 3 window and mirror for the observation of the sample 4 counterweight suspension, 5 heat shields, 6 sample, 7 oven, 8 DTA thermocouples, 9 gas supply

Sorption Meters

The characteristic feature of sorption measuring instruments is the program-controlled variation of the gas pressure for the measurement of isotherms. Preferably this is performed by stepwise isobaric pressure change, while the temperature is kept constant. Temperature programs are optional. Another typical characteristic of this type of instrument is its being equipped with thermostats for low temperatures: baths of liquid gases, freezing mixtures or cryostats. The 'Gravimat' (ref. 57-59) may serve as an example of an extensively equipped commercial instrument: this apparatus (see Fig. 16) is equipped with several electromagnetic microbalances according to Gast (ref. 20,21). One of these carries a glass bulb and is used for the pressure measurement and control by buoyancy. Depending on the balance type, the balances carry a maximum load of 2.5 or 25 g. In the range of 1 and 10^5 Pa the

pressure is adjusted in 100 stages and maintained for a preselected period of time. The vacuum installation includes a turbomolecular pump. The normal temperature range extends down to 77 K. The 'Thermogravimat' is equipped in addition with a time-controlled temperature program up to 2500 K.

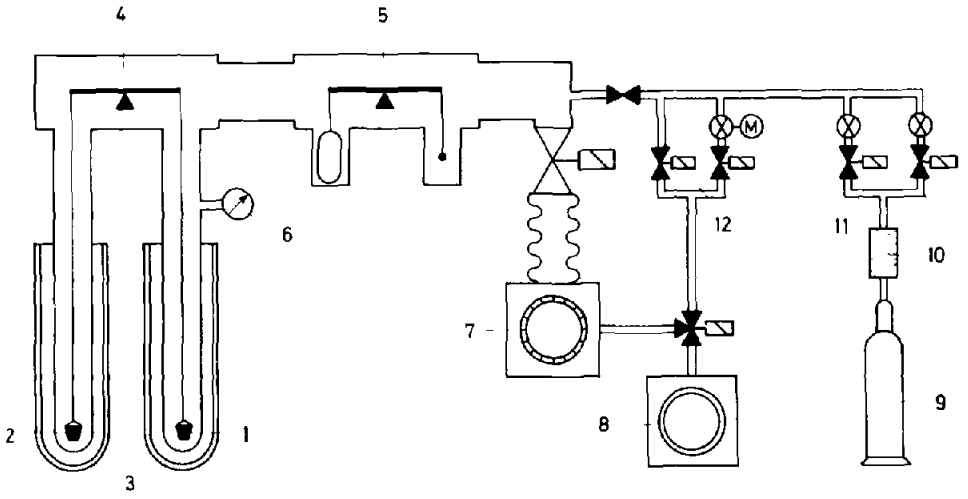


Fig. 16. Netzsch Gravimat
1 sample, 2 counterweight, 3 Dewar vessels 4 electromagnetic balance after Gast, 5 buoyancy pressure gauge, 6 ionisation gauge, 7 turbo molecular pump, 8 rotary vane pump, 9 gas cylinder, 10 gas dryer, 11, 12 pressure control

Composite Instruments

The results of sorption measurements can often be interpreted only with the aid of additional measuring methods. Research apparatus therefore include auxillary instruments.

As mentioned above, a very useful and simple supplement for thermogravimetric investigations is differential thermal analysis (DTA) performed on the sample on the balance pan or on a second sample arranged near the balance pan. Examples are shown in Figs. 13 and 14.

In the setup shown in Fig. 13, dilatometry is used as a supplementary method which is of particular interest for ceramic materials. After completion of the thermogravimetric measurement a second, identical sample is placed on the balance. The sample is inserted between a fixed yoke and the balance beam, and the balance measures the variations in sample length.

Frequently it is of interest to identify the gases which have been released. Because of the small quantities that have to be

analyzed, mass spectrometry or gas chromatography seem to be bes suited. When investigating the adsorption of gas mixtures an additional parameter must be measured. This can be achieved by a simultaneous volumetric determination of the pressure change.

BIBLIOGRAPHY

Books, Surveys

J. Reimpell, W. Bachmann: Handbuch des Waagenbaus; 3 vols., Hamburg: Voigt 1955-1966

A.E.Newkirk: Thermogravimetric Measurements; Analytical Chemistry (1960) 1558-1563

S. Gordon, C. Campbell: Automatic and Recording Balances; Anal. Chem. 32 (1960) 275R

Th. Gast; Bulletin des Schweizerischen Elektrotechnischen Vereins 53 (1962) 1061-1069

Gravimetrie; Techniques de l'Ingénieur K 870

Balances et pesées au laboratoire; Techniques de l'Ingénieur P 270

C. Eyraud, M. Cronenberger, M. Cogniat: Thermogravimetric; Techniques de l'Ingénieur P 880

Vacuum Microbalance Techniques, Bd. 1-8; New York: Plenum Press 1961-1970

C. Duval: Inorganic Thermogravimetric Analysis; 2. ed.; Amsterdam: Elsevier 1963

A.W. Coats d. P. Redfern: Thermogravimetric Analysis; Analyst 88 (1963) 906-924

Surveys under the title "Thermal Analysis" in: Cumul. Rev. Anal. Chem.: C.B. Murphy; 36 (1964) 347 R - 354 R; ... 38 (1966) 443 R; ... 40 (1968) 380 R

W.W. Wendlandt: Thermal Methods of Analysis; New York: Interscience 1974

B. Ke (Ed.): Thermal Analysis of High Polymers; New York: Interscience 1964

J.M. Thomas, B.R. Williams; Quarterly Review 19 (1965) 231-253

J.P. Redfern (Ed.): Thermal Analysis "65"; London: MacMillan 1965

P.D. Garn: Thermoanalytical Methods of Investigation; New York: Academic Press 1965

R.F. Schwenker, Jr. (Ed.): Thermoanalysis of Fibers and Polymers, 1965; New York: Interscience 1966

M. Harmelin, C. Duval; Microchimica Acta (1967) 17-26

E. Robens: Geräte zur Messung der Gassorption, ATM, Abschnitt V 1285 - 1/2 (1968 45-50, 69-74

R.F. Schwenker, Jr., P. Green: Thermal Analysis; 2 Bände, New York: Academic Press 1968

C. Keattch: An Introduction to Thermogravimetry; London: Heyden/Sadtler 1969

E. Robens, G. Walter: Thermogravimetrische Arbeitsmethoden; Sprechsaal 104 (1971) 426-428, 489-492

H.-G. Wiedemann (Ed.): Thermal Analysis, 3 Bände; Zürich: Birkhäuser 1973

Progress in Vacuum Microbalance Techniques, Bd. 1-3; London: Heyden 1973-1975

Recording Differential Balances for Thermogravimetric Analysis; Coke and Gas 20 (1958) Nr. 229, S. 252; Nr. 230, S. 289

C.J. Keattch, D. Dollimore: An Introduction to Thermogravimetry. 2nd Ed., Heyden, London 1975

L. Erdey: Theorie und Praxis der gravimetrischen Analyse. Akademischer Verlag, Budapest 1963

S.P. Wolsky, E.J. Zdanuk (Eds.): Ultra Micro Weight Determination in Controlled Environments. Wiley, New York 1969

A.W. Czanderna, S.P. Wolsky: Microweighing in Vacuum and Controlled Environments. Elsevier, Amsterdam 1980

S. Gál: Die Methodik der Wasserdampf-Sorptionsmessung. Springer, Berlin 1967

R.Sh. Mikhail and E. Robens, Microstructure and Thermal Analysis of Solid Surfaces, Wiley, Chichester 1983

Journals

Thermal Analysis Review; London: Stanton Instrum. Ltd.

Thermochimica Acta; Amsterdam: Elsevier

Journal of Thermal Analysis (E. Buzàgh, J. Simon (ed.)) London: Heyden & Son

Wägen und Dosieren; Mainz: Kirchheim

Thermal Analysis Abstract (J.H. Sharp (ed.)), London: Heyden & Son

REFERENCES

1 J. Rodder in: A.W. Czanderna (ed.): Vacuum Microbalance Techniques, vol. 8; New York: Plenum Press 1970
2 P. Chevenard, X. Waché and R. de la Tullaye; Bull. Soc. Chim. Fr. 10, 31°, 5 (1944) 41
3 S. Gordon, C. Campbell; Anal. Chem. 28 (1956) 124
4 A. Peterson; Instrum. Automation 28 (1955) 1104
5 C.L. Rulfs; Anal. Chem. 20 (1948) 262
6 L. Feuer; Anal. Chem. 20 (1948) 1231
7 E.S. Bartlett, D.N. Williams; Rev. sci. instrum. 28 (1957) No. 11, 919
8 C. Eyraud and I. Eyraud; Laboratoires No. 12 (1953) 13
9 C. Eyraud and I. Eyraud; Catalogue 50° Expos. Soc. Fr. Physique (1953) p. 163
10 Mauer: Analytical and recording balance. Techn. Report Nr. 1762, U.S. Department of Commerce N.B.S., Washington 1953
11 U.V. Brockdorff, K. Kirsch; Elektrotechn. Z. 71 (1950) 611
12 K. Cammann, L. Cahn; Chemie für Labor und Betrieb 18 (1967) 6, 254
13 Müller; Anal. Chem. 29 (1957) 49 A
14 T. Hirone, S. Maeda; Rev. Sci. Instr. (1954) 516
15 P. Manigaut, B. Tsai; C.R. Acad. Sci. 214 (1942) 658
16 S.J. Gregg and M.F. Wintle; J. Sci. Instr. 23 (1946) 259
17 M.J. Pope; J. Sci. Instrum. 34 (1957) 229
18 C. Groot, V.H. Troutner; Anal. Chem. 29 (1957) 835
19 A.W. Czanderna, W. Kollen, J.R. Biegen, J. Rodder; J. Vac. Sci. Technol. 13 (1976) 1, 556
20 Th. Gast; Feinwerktechnik 53 (1949) 167
21 Th. Gast; Vakuum-Technik 14 (1965) 41
22 R. Bauwens, G. Biezunski; Mesures (1957) No. 1, S. 71
23 P.D. Garn; Anal. Chem. 29 (1957) 839
24 P.L. Waters; J. Sci. Instrum. 35 (1958) No. 2, 41
25 J. Papailhau: Appareil d'analyses thermiques pondérales et differentielles simultanées. Französ. Patent No. 1 205 513
26 Lévy-Lebar; Automatisme (1958) 102
27 K.P. Zinnow, J.P. Dybwad in: A.W. Czanderna (Ed.): Vacuum Microbalance Techniques, 8; New York: Plenum Press 1971, 147
28 K.P. Zinnow, J.P. Dybwad in: Th. Gast, E. Robens (eds.) Progress in Vacuum Microbalance Techniques, vol. 1; London: Heyden & Son 1973, 355
29 P.L. Waters; Anal. Chem. 32 (1960) 852
30 J.W. McBain and M.M.Bakr; J. Am. Chem. Soc. 48 (1926) 690
31 T.N. Rhodin in: Advances in Catalysis, vol. 5, Academic Press, New York 1953, p. 53
32 F.M. Ernsberger; Rev. Sci. Instrum. 14 (1953) 998
33 J.G. Hooley; Can. J. Chem. 35 (1957) 374
34 J. Nixdorf, E. Poeschel, R. Skoutajan in: Th. Gast, E. Robens (eds.): Progress in Vacuum Microbalance Techniques; vol. 1; London: Heyden 1972, S. 63
35 Stephenson, Smith, Trantham; Rev. Sci. Instr. 28 (1957) 381
36 P. Barret; Bull. Soc. Chim. Fr. (1958) No. 3, 376
37 G. Fouretier; Usine Nouv. (1957) 1-8
38 Clark; Rev. Sci. Instr. 18 (1947) 915
39 Beams, Hulburt, Lotz, Montague; Rev. Sci. Instr. 26 (1955) 1181

40 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; London: Heyden & Son 1973, 169
41 Th. Gast in: C. Eyraud, M. Escoubes (eds.): Progress in Vacuum Microbalance Techniques, vol. 3; London: Heyden & Son 1975, S. 108
42 Th. Gast, Thermochimica Acta (this volume)
43 W.H. King, Jr. in: A.W. Czanderna (ed.): Vacuum Microbalance Techniques, vol. 8, New York: Plenum Press 1971, 183
44 J.Ph. Termeulen, F.S. van Empel, J.J. Hardon, C.H. Massen, J.A. Poulis in: Th. Gast, E. Robens (eds.): Progress in Vacuum Microbalance Techniques, vol. 1, London: Heyden 1972, 41
45 M.A. Baker in: Th. Gast, E. Robens (eds.): Progress in Vacuum Microbalance Techniques, vol 1; London: Heyden 1972
46 Th. Gast in: C.H. Massen, H.S. van Beckum (Hrsg.): Vacuum Microbalance Techniques, vol. 7; New York: Plenum Press 1970, S. 105
47 R.N. Caffin; Rev. Sci. Instrum. 46 (1975) N. 11
48 H.S. Sacht in: H. Mintrop (eds.): Dosieren, Wägen, Abfüllen; Haus der Technik - Vortragsveröffentlichungen, No. 229; Essen: Vulcan 1970, 16
49 F. Paulik, J. Paulik, L. Erdey; Z.f.anal.Chem. 160 (1958) 241
50 F. Paulik, J. Paulik, L. Erdey; Z.f.anal.Chem. 160 (1959) 321
51 F. Paulik, J. Paulik, L. Erdey; Anal. Chim.Acta 41 (1968) 170
52 L. Erdey, F. Paulik, J. Paulik; Acta Chim. Acad. Sci. Hung. 7 (1955) 27
53 L. Erdey, F. Paulik, J. Paulik; Acta. Chim. Hung. 10 (1956) 61
54 F.B. Hugh-Jones, E. Robens; Lab.Equipm.Digest 11 (1973)3,52
55 H.G. Wiedemann; Chem.-Ing.-Techn. 36 (1964) 1105
56 J. Mercier in: C. Eyraud, M. Escoubes (Eds.): Progress in Vacuum Microbalance Techniques, Vol. 3, Heyden, London 1975
57 E. Robens, G. Sandstede; Z. Instrumentenkunde 75 (1967) 167
58 E. Robens, G. Sandstede; J. Phys. E.: Sci.Instr.Ser.2, 2 (1969) 365
59 H. Fischer, E. Robens, G. Sandstede, R. Sieglen, G. Walter; Meßtechnik 80 (1972) 73