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VACUUM MICROBALANCES AND THERMOGRAVIMETRIC APPARATUS
PART I: COMMERCIALLY AVAILABLE INSTRUMENTS

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ABSTRACT

Most vacuum balances used today are electromagnetically compensating beam balances with sensitivities down to the nanogram range. Deflection sensors operate either according to the optoelectric or the electromagnetic method. One type of UHV balance is equipped with magnetic sample suspension. For special tasks, quartz spring balances and crystal oscillators are available. Beam balances in the microgram and milligram ranges are also used in thermogravimetric and sorption measuring apparatus. Instruments and manufacturers are compiled in tables.

HISTORICAL REMARKS

Stepwise gravimetric investigation of chemical reactions is a very old experimental practice. The first thermogravimetric assembly seems to have been that described by Nernst and Riesenfeld in 1903 (ref. 1): a quartz balance with electric oven. In 1915 the first thermobalance was developed by Honda (ref. 2), who also created the name. Further developments were made in particular in France by Guichard (ref. 3), Dubois (ref. 4), Chevenard (ref. 5) and Duval (ref. 6). The first thermogravimetric apparatus was manufactured in 1945 by ADAMEL, and C. and I. Eyraud (ref. 7,8) constructed the first commercially available compensating vacuum thermobalance. In 1953 de Kaiser (ref. 9) developed the differential thermogravimetric method.

Another line of development was started as a consequence of the application of gravimetry to sorption measurements. A prerequisite for such measurements was the development of sensitive microbalances, the first one being generally attributed to Warburg and Ihmori (ref. 10) in 1886. Petterson (ref. 11, 12) published the first gravimetric observation of adsorption in 1914.

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Further important developments were made by Rhodin (ref. 13), Gulbransen (ref. 14), McBain and Bakr (ref. 15), Gregg and Wintle (ref. 16), Cahn (ref. 17,18), and Gast (ref. 19-22). One of the most essential steps forward in this development was the introduction of vacuum, which affected the construction of balances.

CURRENT STATE OF THE ART

Today (ref. 23,24) most vacuum balances are electromagnetically compensating balances with sensitivities down to the nanogram range. Deflection sensors operate either according to a photoelectric or electromagnetic method.

Most commercial apparatus are of beam or spring types. Another type is suspension balance where the sample is freely suspended without connection to the measuring system. For special tasks, oscillation balances like crystal balances are available. These commercial balances allow investigations in which vacuum and pressure, atmosphere and temperature are varied.

With respect to the first parameter, commercial vacuum microbalances are suitable for ultrahigh vacuum as well as for pressures up to 500 bar and there seems to be no other limitation to even higher pressures than the vessel of the apparatus. Fast pressure changes mostly are restricted by the nature of the sample, as powdered samples may scatter when evacuated too quickly. Also suspension parts may be affected by rapid gas streams and in such cases the use of crystal balances, vibrating bands or strain gauges may be preferable.

With respect to the atmosphere in which the balance may operate, remarkable progress has been made: many of the commercial types can be used in ultrahigh vacuum and in corrosive atmosphere. With respect to such requirements, spring, torsion and magnetic suspension balances are particularly advantageous.

Sample temperatures down to 4 K and up to 3000 K have been realised, using a liquid helium cryostat and resistance heaters with temperature transmission by radiation or by induction heating of the pan or the sample, respectively. Typical temperature increases are between zero and about 0.5 K per s; in scanning thermogravimetric experiments, temperature rises up to 10^5 K/s have been used.

Sorption and thermobalances are usually designed for maximum loads between 1 mg and 500 g. The maximum load/sensitivity ratio for beam balances amounts to 10^8, and that for spring balances and other types which do not take advantage of mass difference measurements in the gravitational field is 10^5.

FUTURE ASPECTS

Whereas most balances described at the VMT Conferences have been of beam or spring type, one should not underestimate other methods for mass determination, like strain gauges, pressure sensitive semiconductors, piezoelectric crystals, vibrating strings, electromagnetic and capacitive force transducer. With one exception instruments based on these principles are not commercially designed for microbalances and, thus, not mentioned in the appended tables. They are, however, widely used for film thickness, force, pressure, or heavy load measurements. These systems in principle do not need mechanical links and thus they are not exposed to wear. The only small movements of parts having little mass result in a much higher eigenfrequency compared with the beam balance and allows the observation of fast mass changes.

In general, we must observe today a reduced activity of the manufacturers in the development of vacuum microbalances. Whereas in the fiftieth and sixtieth decade such developments were the motor of progress in the balance production, in the seventieth this passed over to the area of higher load laboratory balances, industrial and commerce scales, force and pressure transducers, which, of course, have a much bigger market. Thus, in future new vacuum microbalances may result from developments in this field.

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Table 1. Thermobalances

Manufacturer	Code No.	Model	Method of operation	Deflection sensor	Balance pans top	lateral	suspended	Max. load g	Smallest scale value g	Vacuum	Pressure
Ainsworth	A1		electronic beam balance				2	200	10^{-7}	HV	
Beckman	B1	LM600	compensating beam b.	electro-magnetic			2	2.5	10^{-7}	HV	
		LM500	"				2	5	10^{-7}	HV	
Berkeley	B2		quartz crystal	-	(1)			10^{-4}	$5\cdot10^{-9}$	UHV	possible
Cahn	C1	RG	compensating beam b.	photo-electric			3	2.5	10^{-7}	HV	
		RM 2	"				1	5	$5\cdot10^{-6}$	HV	
		1000	"	"			2	100	$5\cdot10^{-7}$	HV	
Chyo	C2	200H	inclination balance	visual			1	200	10^{-4}		
		SL5	quartz spring balance	visual			1	5	10^{-3}	HV	
		SL1	"	differential transformer			1	1	$5\cdot10^{-4}$	HV	
C.I. Electronics	C3	Mk.1	compensating beam b.	photo-electric			2	0.5	$5\cdot10^{-6}$	HV	
		Mk.2	"				2	5	10^{-5}	HV	
Linseis	L1	L84	substituting beam b.	inductive	(1)	1	(1)	20	10^{-4}		
Netzsch	N1	409E	substituting beam b.	inductive	1			20	10^{-5}	HV	
Perkin-Elmer	P1	Ar-2	compensating beam b.	photoelect.			2	5	10^{-7}	HV	
Sartorius	S1	4401	compensating beam b.	electro-magnetic	(2)		2	25	10^{-6}	HV	
		4431	"		(2)		2	3	10^{-7}	HV	150
		4201	magnetic suspension at compensating beam b.	"			1	16	10^{-6}	UHV	
SETARAM	S2	B70	compensating beam b.	photoelectr.			1	100	10^{-5}	HV	
		MTB10-8	"	electromagn.			2	10/100	$4\cdot10^{-7}$	HV	
Ultramicro-balance	U1		compensating beam b.	photoelectr.			1	20	10^{-8}	UHV	10
Voland	V1	1100-11	compensating beam b.	electromagn.			2	1	$5\cdot10^{-7}$	HV	
Worden	W1	4401	quartz spring b.	visual			1	100	10^{-5}	UHV	
			"	photoelectr.			1	100	10^{-5}	UHV	

Table 2. Thermogravimetric instruments

Manufacturer	Code No.	Model	Balance	Special features	Balance pans			Max. load	Smallest scale value	Temp.		Vacuum	Pressure
					top	lat.	susp.			min	max		
								g	g	K	K		bar
Cahn	C1	Little Gen	compensat. beam balance				2	2.5-100	10^{-6}-10^{-7}		900	HV	
		Gravim. Adsorpt.								77	900	HV	
Chyo	C2	TRDA$_3$-H	" " "	DTA		1		1	10^{-4}		1900	HV	
		TR$_1$-160	inclinat. balance				1	160	10^{-4}		1800	HV	
DuPont	D1	950	compensat. beam bal.			1		0.3	$2 \cdot 10^{-3}$		1500	HV	
Fisher	F1	100 TGA	" " " (Cahn RG)				1	2.5	10^{-6}		1500	HV	
Harrop	H1		(Cahn RG)				3	2.5	10^{-7}	77	1900	HV	
			(Cahn R100)				2						
Heraeus	H2		compensat. beam bal. (C.I. Electronics)				2	1	10^{-6}		1300	-	1
Linseis	L1	L 83	compensat. beam bal. (Sartorius)	DTA at the balance pan	1		(2)	16	$5 \cdot 10^{-5}$		1800	HV	
		L 81	compensat. beam bal.			1		15	10^{-5}	120	1800	HV	
Messtec	M3	Kryo-Heiz-system	compensat. beam bal. (Cahn)	continuously adjust. cooling & heating system			1			83	900	HV	
Mettler	M1	Therm-analyzer	compensat. substitut. beam bal.	DTA at the balance pan	1		1	16/42	$3 \cdot 10^{-5}$	123	1900	HV	
		TA2000C	" "		1			6	10^{-5}		1500	HV	
MOM	M2	Deriva-tograph	beam balance	balance also used as dilatometer	1			10	$5 \cdot 10^{-4}$	293	1800	HV	
		" " Q	" "	" " " " " quasi-isothermal TG	1			1	$2 \cdot 10^{-4}$		1800		

Netzsch	N1	STA 429	compensat. beam bal.	DTA at the balance pan	1		20	10^{-5}	113		HV	
		STA 409	inductive subst.	" " " "					293	1900	HV	
		Thermo-gravimat	compensat. beam bal. (Sartorius)	program-controlled pressure control for the measurement of adsorption isotherms	(2)	2	3/25	10^{-8}	77	2500	HV	
		Thermomat S	magnetic suspens. balance (Sartorius)	corrosion-resist. quartz-PTFE version		1	16	10^{-5}	77	2000	HV	190
Perkin-Elmer	P1	TGS-2	compensat. beam bal.	furnace in vacuum		2	5	10^{-7}	77	1300	HV	
Rigaku	R1	Thermoflex	beam balance	dilatometric and viscosity measurem. by balance	1		450	$2\cdot10^{-7}$	293	1800		
S.A.D.A. M.E.L.	S5	17 AV	substitut. balance	radiation furnace; dilatometer	1		7	10^{-4}	293	1900	HV	
SETARAM	S2	micro-thermo-analyseur	compensat. beam balance B70	combined cryostat/ heater		1	100	10^{-5}	77	2700	HV	
			" " MTB 10-8			2	10/100	$4\cdot10^{-7}$	77	2000	HV	
Shimadzu	S3	TGA-20B	beam bal.	dilatometer	1		0.2	10^{-6}	293	1800	HV	
Stanton Redcroft	S4	TG 750	comp.beam bal. (C.I. Electron.)	DTA		2	1	10^{-5}	293	1300	HV	
		Massflow	analys.bal. with autom. balance of weight	DTA	1		20	10^{-4}	293	1800	HV	
Stone	C4	TGA-5B	comp.beam balance (Cahn - RG)			2	2.5	$2\cdot10^{-6}$	293	1900	HV	
Theta	T1	Gravitronic	comp.beam bal. (Cahn)			2	100	$5\cdot10^{-7}$	120	2000	HV	
Voland	V1	1100-11	comp.beam balance			2	1	$5\cdot10^{-7}$	293	1300	HV	

Table 3. Manufacturer's addresses

A1	Ainsworth Division of Denver Instrument Co., 2050 South Pecos Street, Denver, Colorado 80223, USA
B1	Beckman Instruments, Inc.; Scientific Instruments Div., Fullerton, California 92634, USA
B2	Berkeley Controls Inc.; 2825 Laquna Canyoun Road, Laquna Beach, CA 95652, USA
C1	Cahn Instruments, Div. of Ventron Corp., 16207 South Carmenita Road, Cerritos, Calif. 90701, USA
C2	Chyo Balance Corp., 376-2 Tsukiyama-cho, Kuze, Minami-ku, Kyoto, Japan
C3	C.I. Electronics Ltd., Brunel Road, Churchfields Salisbury, Wilts., England, Großbritannien
C4	Columbia Scientific Industries, Inc., Analytical Instruments Div., 3625 Bluestein Boulevard, Austia, Texas 78762, USA
D1	DuPont de Nemours & Co., Inc., Instruments Product Div., Wilmington Delaware 19898, USA
F1	Fisher Scientific Co. Ltd., 711 Forbes Av., Pittsburgh, Pa. 15219, USA
H1	Harrop Laboratories, 3470 East Fifth Avenue, Columbus, Ohio 43219, USA
H2	W.C. Heraeus GmbH, Postfach 169, D-6450 Hanau
L1	Linseis KG, Vielitzer Str. 43, D-8672 Selb
M1	Mettler Instrumente, CH-8606 Greifensee
M2	MOM, Ungarische Optische Werke, Postfach 52, H-1525 Budapest
M3	Messtec KG, Friesenweg 4, D-2000 Hamburg 50
N1	Netzsch-Geratebau GmbH, Wittelsbacherstr. 42, D-8672 Selb
P1	Perkin-Elmer Corp., Instrument Div., Norwalk, Connecticut 06852, USA
R1	Rigaku Corp., Segawa Bldg. 2-8 Kandasurugadai, Chiyoda-ku, Tokyo, Japan
S1	Sartorius Werke GmbH, Weender Landstr. 96-102, D-3400 Gottingen
S2	S.E.T.A.R.A.M., 101-103 Rue de Sèze, F-69451 Lyon, Cedex 3
S3	Shimadzu Seisakusho Ltd., 1 Nishinokyo-Kuwabaracho, Nakagyo-ku, Kyoto 604, Japan
S4	Stanton Rederoft (Div. of Oertling Ltd.), Copper Mill Lane, London SW 17 0BN, England, Großbritannien
S5	S.A.D.A.M.E.L., CH-2300 La Chaux de Fonds, Rue Jardinière 150
T1	Theta Industries, Inc., 26 Valley Road, Port Washington, N.Y. 11050, USA
U1	Ultramicrobalance Instruments, A.W. Czanderna, P.O. Box 27209, Denver, Colorado 80227, USA
V1	Voland Corp., 27 Centre Avenue, New Rochelle, N.Y. 10802, USA
W1	Worden Quartz Products, Div. of Ruska Instruments, 6121 Hillcroft, Houston, Texas 77036, USA