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A SIMPLE AUTONULL-TYPE SERVO-CONTROLLED ELECTRONIC BALANCE FOR THERMOGRAVIMETRIC APPLICATIONS

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A simple electronic autonull-type recording balance using a helical quartz spring is described. Deviation from the null position is detected by a pair of photoemissive cells. The error signal generated across the cells as a result of weight change is processed by a servo-system which, in turn, produces an electric current in the balancing coil proportional to the force required to restore the null position. This current, recorded as the potential drop across a standard resistor, is a direct measure of the weight change.

The balance has good linear response and can record weight changes up to 150 mg. The performance of the balance was tested in a thermogravimetric set-up, by studying the decomposition in air of the oxalates of copper, nickel and magnesium. The decomposition of nickel oxalate was also studied in flowing hydrogen. The weighing accuracy of the balance, compared against a Mettler model H-15 single-pan balance, was found to be within $\pm 1.5\%$.

Since the pioneering work of McBain and Bakr [1] helical quartz-spring balances have often been used in various research applications [2–7] involving studies such as thermogravimetry, adsorption of vapours and gases, reduction of metal oxide catalysts and magnetochemistry. These balances are simple to use and are inert to corrosive vapours and gases because of the all-glass housing, which also provides a certain degree of flexibility in the modification of the apparatus to suit any required experimental condition. However, these spring balances are basically designed for manual operation in combination with a cathetometer or a micrometer-microscope for the measurement of changes in the spring elongation. This causes difficulty in recording fast weight changes such as those encountered in certain fast chemical reactions like thermal decomposition of organic compounds and reduction of metal oxide catalysts. Automatic recording instruments are best suited for such application. However, commercially available recording balances built around beam, torsion-band or metallic spring weighing elements are expensive and sometimes inconvenient as regards handling corrosive atmospheres. The present paper describes a simple design and construction of a null-type recording balance in an all-glass housing based on the helical quartz-spring element and other components which can readily be procured or assembled. This balance can be operated under dynamic flow conditions and in controlled environments.

Various null-detection systems have been employed by different workers using helical springs. For studying the gravimetric adsorption of vapours. Whalen [8] has used motor-drive Nikkon cameras to record the movement of a reference pointer suspended from the spring. Glaser et al. [9] have described a recording balance based on a quartz-spring element, using a photocell null-detector and vacuum-tube servo-system for the restoration feed-back and weight recording. Wendlandt [10] has described a number of commercial designs which use photocell null-detectors. Nevertheless, these instruments are based on beam-type double-pan balances and are not suitable for use in vacuum or corrosive atmospheres. Moreau [11] used a linear differential transformer as the null-detector for his recording balance. In some types of optical designs [12, 13] the movement of the projected image of an index is amplified and recorded on a photographic plate or a spot-follower.

In the present design a pair of photocells have been used for the null-detection in combination with an electronic servo-system and a feed-back amplifier, built around a helical quartz-spring element. The balance can take a total load of about 2.5 g and has a sensitivity of 0.1 mg. It can record weight changes up to 150 mg in static or dynamic atmospheres.

Description of the balance

The balance design, showing the glass housing, quartz-spring element, sample-jacket, photocell assembly, balancing coil and other components, is given in Fig. 1(a). The quartz spring (manufactured by Worden Quartz Products, Inc., USA) used in the balance has a load capacity of 5 g. The diameter of the helix is 1.5 cm. Total extension of the spring is 500 mm and the sensitivity is 0.1 mm/mg. The spring is suspended from the pulley of the slit-positioner (S.P.) by means of a thin nylon string. The slit-positioner is used to raise or lower the slit, in order to bring it in front of the lamp and photocell assembly, after loading the sample in the quartz bucket. The slit-positioner is also used for balancing the servo-system as will be explained under the section "Setting-up of the balance". Slit (S), made out of a light aluminium foil with a circular pinhole, is suspended from the spring by means of quartz fibre-hooks. A small rectangular ceramic bar-magnet (M) weighing about 1.5 g hangs below the slit. The magnet is coated with a thin film of epoxy resin to make it inert to corrosive and reducing atmospheres. The hemispherical sample pan made of quartz hangs at the end of the suspension assembly. The diameter of the pan is 1.5 cm. Total weight of the suspension assembly, including the aluminium damping cup (D), slit, magnet, sample pan and quartz fibre-hooks, is about 2 g. The pan can therefore take a sample weight of more than 2.5 g. Thus, the total assembly without any sample causes a spring extension of about 200 mm. Further spring elongation for a sample weight of 2.5 g will be 250 mm. However, in practice one can select any sample weight between a few milligrams and 2.5 g, depending on the expected weight change.

The optical assembly consists of a self-focussing lamp (L) positioned in front of the glass window built in the balance housing. The lamp is powered by a 1.5 volt A.C. supply from a filament transformer whose primary is fed from a constant-voltage transformer. Facing the lamp assembly is a pair of photoemissive cells (P), type 51 CLVC (Centralab. U.S.A.), mounted inside a light-proof wooden box on a rack and pinion platform. The box is painted black inside to absorb any stray light. The light from the lamp travels through the first glass-window, the slit and a second glass-window at the opposite end of the optical assembly. The image of the slit falls on the photocells. The position of the photocell mounting can be adjusted along the vertical axis by means of a thumb-screw located on the wooden box. The balancing coil (B) is wound with 36 B.S.W.G. enamelled copper wire on a phenolic resin format. The coil has a D.C. resistance of 800 ohms. It can slide along the glass housing of the balance and its position is so adjusted that about

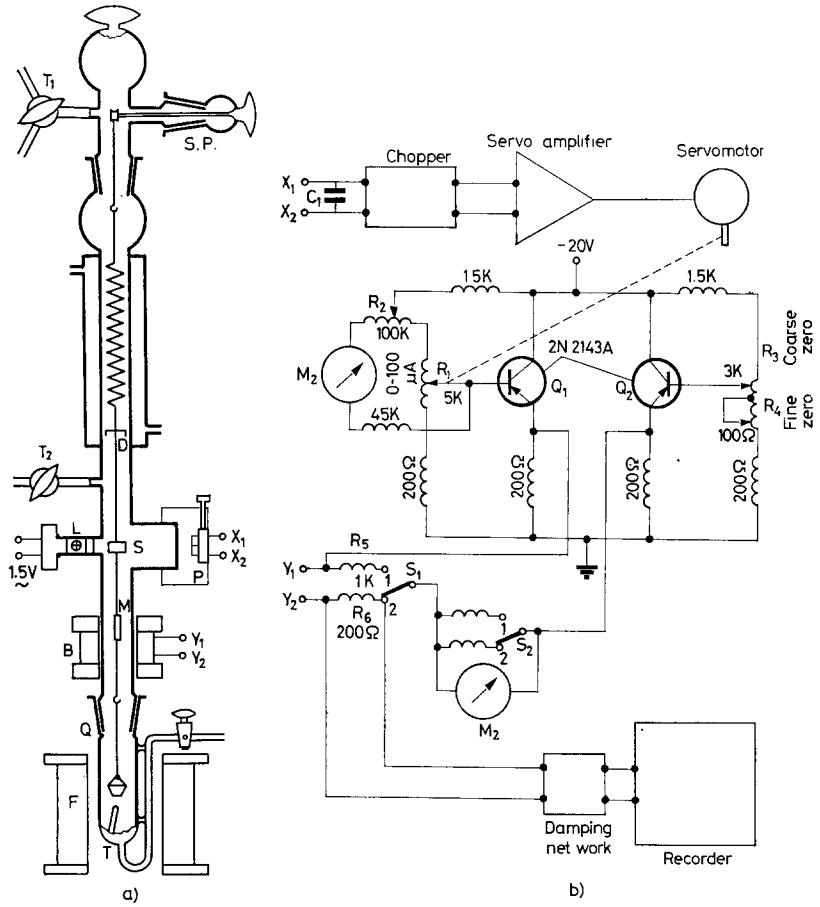

Fig. 1. a) Balance design; b) Electronic circuit

3 – 5 mm of the suspended magnet is exposed above the coil when the balance is at the null position. The length of the coil is 5 cm and that of the magnet 1 cm.

Electronic circuitry

The electronic circuitry is shown in Fig. 1(b). The photocells are connected in opposition and their output is connected to the servo-amplifier through the damping capacitor C_1, and the chopper through contacts X_1 and X_2. Initially, the balance is adjusted to the null position mechanically and electrically. The error signal generated across the photocells due to change in the spring elongation is amplified by the servo-amplifier, which in turn rotates the servomotor. (Both the servo-amplifier and the low-inertia servomotor are reconditioned components of an old Bristol 1 mV recorder.) The servomotor is coupled mechanically to the shaft of the 5 Kohm ten-turn helical potentiometer R_1. The movement of the servomotor therefore produces a current in the balancing coil (B) through R_1 and the rest of the emitter-follower network comprising transistors Q_1, Q_2 and the associated components. This current is equivalent to the force required to attract or repel the suspended magnet in order to hold the slit at the null position. The balancing coil (B) is connected to the emitter follower through contacts Y_1 and Y_2. The current generated in the coil is a direct measure of the weight change, and is recorded as the potential drop across the precision resistor R_6.

Setting-up of the balance

After loading of the sample in the pan, the slit is manually brought approximately in front of the lamp by means of the slit-positioner located at the top right-hand side of the balance. The servo-amplifier is now switched on with S_1 in position 1, thereby connecting the dummy resistor R_5 across the emitters of the restoration amplifier. At this stage the balance may be away from the null point and may cause the servomotor to rotate either clockwise or anticlockwise, depending on the disbalance. Final nulling is achieved by carefully adjusting the slit positioner ($S.P.$) till the movement of the moter stops completely. While the optical system is now at null, some current, as indicated by meter M_2, may be flowing through resistor R_5. This current is zeroed by adjusting the coarse and fine zero potentiometers R_3 and R_4, respectively. High and low ranges of current can be selected on the zero-centre meter M_2 by means of switch S_2. Coarse adjustment is done with S_2 in position 1, which selects the 10 – 0 – 10 mA range, and position 2, for fine zero control, operates in the 25 – 0 – 25 μA range.

Meter M_1 with graduation 0 – 100 indicates the span of the balance or, in other words, the position of the sliding terminal on the helical potentiometer R_1. This span may be adjusted by keeping the pointer of M_1 at any point along the scale, depending upon the expected weight change. This is done by slightly disturbing the balance by rotating the slit-positioner so that the pointer of M_1 moves either up or down the scale as required, and stopping the rotation of the positioner

when M_1 indicates the appropriate position. Electrical zeroing with R_3, R_4 and M_2 may be required once again after the span setting. R_2 is a trimmer potentiometer used for calibrating the meter M_1. The balance is now ready for weight recording, which may be done by throwing switch S_1 to position 2 and S_2 to 1. The balancing coil (B) and R_6 comprise the new emitter load instead of R_5. The potential drop

Table 1

Thermal decomposition data for some oxalates

No.	Sample	Atmosphere	Wt. of sample, mg	Final Wt. loss, mg		Weighing error of the instrument, %
				From thermograms	From wt. of the residue	
I	Ni-Oxalate	Air (i)	100.0	60.5	60.2	+0.5
		Air (ii)	100.2	59.5	59.6	−0.2
II	Cu-Oxalate	Air	103.0	52.5	52.0	+0.9
III	Mg-Oxalate	Air	101.0	75.0	75.3	−0.4
IV	Ni-Oxalate	Hydrogen	103.8	71.0	72.0	−1.4

across R_6 is recorded by a multi-range potentiometric recorder. The 1 volt full scale range was used for recording an expected 100 mg of weight change. Lower recorder ranges may be used if the expected weight changes are of a lower order.

The balancing circuit which comprises the emitter-follower amplifier and the balancing coil (B) is somewhat similar in concept to the vacuum-tube version described by Heal [14]. The present circuit, however, is much simpler and avoids the use of elaborate vacuum-tube power supply and the vacuum-tube amplifier circuitry. In the present design a 20 volt *D.C.* unregulated power supply, using a silicon bridge rectifier and an $R-C$ filter circuit (not shown in Fig. 1b), has been found to be quite adequate for the emitter-follower amplifier.

Servo-amplifier gain adjustment

The servo-amplifier gain adjustment is very critical for this instrument. High gain may result in the so-called "hunting" phenomenon, while with very low gain the balance response becomes sluggish, resulting in "stepped" recorder traces. For gain adjustment, the balance is set to null after sample loading. The dummy resistor R_5 is connected across the emitters of the balancing amplifier by throwing switch S_1 to position 1. The servo gain is slowly increased from the lowest setting while adjusting the null by means of the slit-positioner. The gain is increased till the servomotor shaft resists with equal force its rotation in either direction, when turned manually.

Linearity of balance response

Linearity test and weight calibration were carried out as follows. The balance was set up without any sample, as described in the earlier sections. Known weights of approximately 10 mg denominations were loaded on the pan, one at a time. The corresponding deflections of the recorder pen were noted. The results are shown

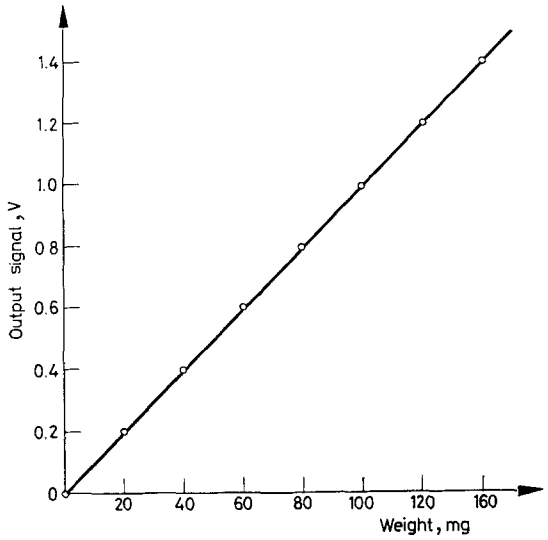

Fig. 2. Balance calibration

in Fig. 2. Good linearity is observed between the recorder input voltage, that is the voltage drop across *R6*, and the weight change up to about 150 mg. The current in the balancing coil corresponding to 150 mg was about 6 mA, as read from meter M_2.

Balance performance

Balance performance was examined by using it in a thermogravimetric set-up and by studying the decomposition of the oxalates of copper, nickel and magnesium in air. Decomposition of nickel oxalate was also studied in flowing hydrogen atmosphere to evaluate the performance under dynamic conditions. Temperature programming was done manually by controlling the heating of the sample jacket (A) by means of the furnace (F) and a calibrated variable auto-transformer. The heating rate employed was about 8°/min. Hydrogen was admitted through stopcock T_2 while stopcock T_3 served as the vent point. The thermal curves which have been replotted from the original recorder traces are shown in Fig. 3.

It is seen from the curves that, except in the case of copper oxalate, all the curves represent two-step decomposition, involving dehydration and decomposition of

the anhydrous salt [15]. In the case of copper oxalate the dehydration and decomposition occur simultaneously. The curves for copper and nickel oxalates in air register a slight increase in weight towards the end of the experiment, which is due to the oxidation of the metal particles formed during the decomposition (3). This feature is absent in the curve for nickel oxalate decomposition in hydrogen and also in the curve for the decomposition of magnesium oxalate in air.

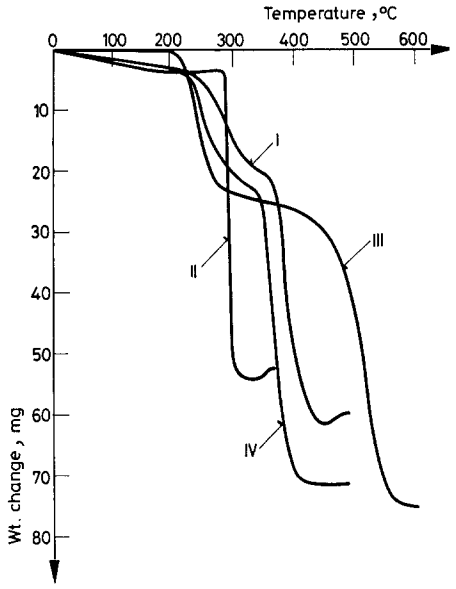

Fig. 3. Thermal decomposition of oxalates: I: Nickel oxalate in air, II: Copper oxalate in air, III: Magnesium oxalate in air, IV: Nickel oxalate in hydrogen

Table 1 shows the decomposition data for the samples studied. Two sets of data for the decomposition of nickel oxalate in air have been included to show the repeatability of the experiments. Final residues from all the experiments were weighed in a Mettler Model *H*-15 single-pan balance and these weights have been taken as standards for calculating the weighing error of the instrument shown in the last column. It is seen that this error is within $\pm 1.5\%$.

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RÉSUMÉ — On décrit une balance électronique enregistreuse simple du type auto-zéro, à hélice de quartz. La déviation de la position zéro est décelée par une paire de cellules photoémissives. Le signal de déséquilibre décelé par les photocellules et résultant d'un changement de poids, est reçu par un système asservi qui, à son tour, produit un courant électrique dans la bobine de la balance, proportionnel à la force nécessaire pour rétablir la position zéro. Ce courant, enregistré comme chute de potentiel dans une résistance étalon, est une mesure directe du changement de poids.

La balance donne une bonne réponse linéaire et peut enregistrer des changements de poids allant jusqu'à 150 mg. Ses caractéristiques ont été examinées dans un montage thermogravimétrique, en étudiant la décomposition dans l'air des oxalates de cuivre, nickel et magnésium. La décomposition de l'oxalate de nickel a aussi été étudiée sous courant d'hydrogène. L'exactitude de la balance, comparée à celle d'un modèle Mettler monoplateau (type H-15), coïncide à $\pm 1.5\%$.

ZUSAMMENFASSUNG — Eine einfache elektronische registrierende Quartz-Spiralfeder Kompensationswaage wird beschrieben. Die Abweichung von der Nullposition wird durch zwei Photoemissionszellen angezeigt. Das infolge der Gewichtsänderung durch die Zellen erzeugte Fehlersignal wird durch ein Servosystem empfangen, das seinerseits in der Ausgleichsspirale einen elektrischen Strom erzeugt, der proportional zur für die Wiederherstellung der Nullposition benötigten Kraft ist. Dieser Strom, der als Spannungsgefälle in einem Standardwiderstand registriert wird, ist eine direkte Maßzahl der Gewichtsänderung.

Die Waage zeigt ein gutes lineares Verhalten und kann Gewichtsänderungen bis zu 150 mg registrieren. Die Leistung der Waage wurde in einer thermogravimetrischen Vorrichtung durch Untersuchungen der Zersetzung der Oxalate von Kupfer, Nickel und Magnesium in Luft geprüft. Die Zersetzung von Nickeloxalat wurde auch in strömendem Stickstoff untersucht. Die Meßgenauigkeit der Waage, vergleichen mit der Einschalenwaage Mettler H-15 wurde im Bereich von $\pm 1.5\%$ gefunden.

Резюме — Описаны простые электронные регистрирующие весы с автоматической установкой нуля, используя спиральную кварцевую пружину. Отклонения от нулевого положения детектируется двумя фотоэмиссионными ячейками. Сигнал ошибки, генерируемый через ячейки в результате изменения веса, обрабатывается серво-системой, которая в свою очередь вызывает электрический ток в балансной катушке пропорциональный силе, требуемой для восстановления нулевого положения. Этот ток, регистрируемый как падение потенциала через стандартный резистор, является непосредственно мерой изменения веса. Весы обладают хорошим линейным откликом и регистрируют изменение веса до 150 мг. Работа весов была проверена в термогравиметрической установке при изучении разложения оксалатов меди, никеля и магния в атмосфере воздуха. Разложение оксалата никеля было также изучено в проточной атмосфере водорода. Точность взвешивания весов по сравнению с одночашечными весами Меттлер Н-15 была в пределах $+1.5\%$.