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A MAGNETICALLY CONTROLLED QUARTZ FIBER MICROBALANCE

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Abstract

The design, simplified techniques of construction, and uses of an electromagnetically controlled quartz fiber microbalance are described. The balance is capable of weighing directly an unbalanced load as large as 1.2 milligrams, carrying a counter-balanced load of 100 to 150 milligrams, and giving a sensitivity of 0.1 microgram per 6 minutes of arc. The one-piece all-quartz balance unit fits into a 25 millimeter diameter tube 12 centimeters long. The balance may be used under wide conditions of temperature, pressure, and reagents in completely closed systems. The balance is controlled by an external variable electromagnetic field.

I. Introduction

Laboratory microbalances, commercially available, are limited in sensitivity to one microgram. A temperature difference of as little as 0.1°C. has been reported by Lindner⁶ to introduce a weighing error of several micrograms, in the case of a combustion boat and glass pig (total weight of 4 g.). A change in barometric pressure of a few mm. will

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introduce errors due to change in buoyancy. A change in the humidity gives rise to significant variations in the rest point of a commercial microbalance for several reasons discussed by Corwin.²

Quartz fiber microbalances are not as susceptible to temperature changes, because of the low coefficient of expansion of quartz. The effects due to changing barometric pressure and humidity may be eliminated by operating such a balance in a vacuum. The idea of a microbalance constructed of quartz fibers is not a new one and the idea of electromagnetic control goes back to Angström in 1895.^{1,3} Reviews of the developments in these fields have been published by Emich³ and Gorbach,⁴ making unnecessary a detailed discussion here.

Most significant to the development of the balance described in this paper was the work of Steele and Grant,⁶ who first constructed a complete balance, of the central knife-edge type, from fused quartz. Also of significance was the work of Petterson⁷ who improved the design and gave a detailed description of the theory of such instruments. The contributions of Emich,⁴ Stock,^{9,10} and Wiessenberger¹² who used Angström's idea of electromagnetic control in their investigations must be mentioned. We are particularly indebted to the unpublished work of Dr. I. B. Johns* who constructed several balances of a very similar design to the one described in this paper. He used wax or selenium to seal the central axis fiber and pan suspension bows to the beam.

An electromagnetically compensated quartz fiber balance is now more practical and versatile because of the use of improved magnet materials and balance designs. The assembly of the balance described is simplified through the use of unique construction techniques. This balance may be

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used for conventional micro analytical uses, but its compact design with the feature of external control, make it particularly useful as a research tool.

II. Design of Balance

The balance described is an equal-arm lever balance in which the beam is rigidly fastened to a flexible supporting axis fiber. The balance is not a true torsion balance for the force of gravity is only slightly compensated by the torsion of the support fiber. Magnetic compensation is employed to oppose the force of gravity. Every effort has been made to design and construct the balance in such a manner as to combine the features of a high sensitivity quartz fiber microbalance and magnetic compensation, which allows greater load capacity and range of weighings as well as external control.

1) Important Parts of Microbalance

A clearer idea of the principles and terminology involved may be obtained by reference to the perspective drawing in Fig. 1.

a) Beam Form. The beam of the balance is of a braced simple bridge truss design and is constructed of small quartz rods. A light weight beam of maximum strength is possible using this design.

b) Central Axis. The central axis fiber suspends the beam between support posts on a rectangular quartz framework. This axis fiber is fused to the posts of the framework and to the beam. No seals except quartz fusions are used, so that a completed balance unit is an integral piece of quartz. Balances may be constructed by sealing the suspension fibers to the beam and the framework with selenium or wax, however, such balances are less reproducible over periods of time and are much more affected by

temperature changes and chemical reactions than are all quartz balances.

c) Terminal Axes and Fused Thread Suspensions. The terminal axes are placed equidistant from and parallel to the central axis fiber. Quartz thread suspensions are fused to the terminal axes. These bow shaped suspensions are used to support the pans of the balance. They must be in the same plane as, or very slightly below, the central axis fiber.

d) Beam Magnet. A small permanent bar magnet of Alnico or Cunife is mounted below the midpoint of the balance beam and perpendicular to its length. This magnet is sealed in a quartz capillary which in turn is fused to the beam. Use of the newer magnet materials, with their high ratio of magnet strength to weight, make a light weight beam unit possible, and magnetic control more practical. Portions of steel needles may be used, but they have a greater tendency to lose their magnetism thus making numerous calibrations necessary.

e) Quartz Rod Frame and Beam Rests. The quartz rod frame is illustrated in Fig's. 1 and 3. The centrally located posts are used to support the central axis fiber. Beam rests are positioned to limit the swing of the beam.

f) External Case of Balance Unit. A pyrex tube 25 mm. in diameter and 12 cm. long (See Fig. 1) encases the entire balance assembly. This compact unit may be inserted into closed systems for use in a variety of research and analytical problems.

g) Pans. The design of pans is determined by the particular problem for which the balance is to be used. Pans are conveniently shaped from Pt foil and welded to Pt wire hooks. Pans of split mica, suspended on quartz fiber hooks, have also proved satisfactory in some instances.

2. Operating Principles

a) Magnetic Compensation for Weighing. Angstrom's method of magnetic compensation was briefly this.¹ A small permanent bar magnet was attached to the balance beam, below and parallel to the length of the beam. The orientation of this magnet and hence the weight lifted by the balance was controlled by a variable electromagnetic field which was perpendicular to the magnet. This field was produced by current flowing in a solenoid, the end of which was below (or above) the balance magnet. The current passing through the coil was measured with a sensitive galvanometer.

A second method of orienting the permanent magnet and the regulating solenoid was chosen for the balance described in this paper. In this method the permanent magnet is mounted below the midpoint of the beam and perpendicular to its length. Since the field strength, H , within a long solenoid equals $4\pi nI/10$ where n is equal to the number of turns per cm. of length of the solenoid and I the current in amperes, it is apparent that the magnetic field acting on the permanent magnet of the balance is affected only by changes of the current in the solenoid. Furthermore the moment of force, tending to produce rotation on a bar magnet placed at right angles to the lines of a magnetic field, is the product of the strength of the field and the magnetic moment of the magnet. The magnetic moment of a permanent magnet is the product of the pole strength and the distance between the poles; for Alnico or Cunife magnets this quantity is constant. Hence, the rotation of the magnet and correspondingly the weight lifted by the balance is determined by, and is directly proportional to, the current passing through the solenoid. A measure of this current is obtained by placing a fixed resistance in series with the solenoid. The voltage drop over this resistance, and hence the current

through the solenoid, is measured with high precision using a potentiometer.

If the strength of the permanent magnet is not known, then an empirical adjustment of the current, the number of coil turns, and of the type of potentiometer needed for any set-up must be made.

The use of magnetic compensation has a further advantage. The long period oscillations, so disconcerting in a commercial microbalance, or in a torsion balance of the same sensitivity, are eliminated by a magnetic damping effect which permits immediate adjustment of the balance.

b) Electrical Regulating System. The solenoid surrounding the balance consists of 1000 turns of #26 cotton-covered copper magnet wire. To control the current in the solenoid, and hence the magnetic field at its center, three variable resistances (2500 ohms, 25 ohms, 1 ohm) are placed in series in the circuit. Direct current is supplied to the circuit from one or more storage batteries. To measure the current a fixed 3 ohm resistance of #32 Copel wire, which has a negligible temperature coefficient of resistance, is placed in series in the circuit. The IR drop over this resistance is carefully measured with a Leeds and Northrup type K potentiometer. Refinements which may be incorporated in the electrical system include a reversing switch, to reverse the current flow in the solenoid, and a milliammeter, to aid in the adjustment of the potentiometer. A selector switch may be used to successively connect several solenoids, so that several balances may be controlled with one electrical regulating system.

c) Arrestment System. The balance is used as a null instrument and so beam rests are placed to limit the swing of the beam (Fig's 1 and 3). This feature of the design is useful for the following reasons. A very

compact design may thereby be attained. The effective arm length of the balance is more likely to remain constant. Danger of damaging the balance through large accidental swings of the beam is practically eliminated, and there is decreased danger of tipping the pans and spilling a sample.

d) Adjustment of Sensitivity. A stable, sensitive balance must have its center of gravity on, or very slightly below, its central axis fiber. Although during the construction of this balance every effort is made to maintain a weight symmetry, a final adjustment is usually necessary. This is accomplished by fusing bits of quartz to the point at the top of the beam, or to the capillary below the magnet, until the balance is stable and as sensitive as is required.

e) Reading System. The swing of the beam is observed with a reading microscope. The microscope fitted with a cross hair is focused on a pointer fiber drawn from one end of the beam. With the pan empty or tared, current is supplied to the coil until the balance swings free of the beam rests. The pointer fiber is made to coincide with the cross hair in the field of the microscope. This position is used as a zero point position, and then as the equilibrium position for any subsequent weighing. The microscope must remain fixed with respect to the balance during a series of weighings. The fixed positions of the pointer fiber, when the balance is riding the beam-rests, are in the field of the microscope, and thus provide a useful check on the relative orientation of microscope and balance.

III. Construction of Balance

1) Notes on Drawing and Fusing Quartz Fibers

This paper covers only the design and particular construction tech-

niques essential to the preparation of the balance described. Further information on quartz working is contained in Strong's book, Procedures In Experimental Physics.¹¹

With the exception of a micro oxygen torch, little special equipment is necessary. It is important to use a sensitive valve system to regulate the gas and oxygen flow. The micro torch tip may be made from a short length of quartz tubing, so shaped to give a flame of 1 to 2 mm. length.

The quartz fibers from which the balance is constructed are drawn from quartz rods 4 to 8 mm. in diameter. One may draw a fiber of size from 10 microns to 1 mm. in diameter using an ordinary gas-oxygen laboratory hand torch. Bends in quartz fibers may be made by holding one end of the fiber on a graphite plate with a small weight, heating a portion of the fiber with the micro flame, and then bending the fiber by means of tweezers. When the micro burner flame is brought in contact with the graphite plate water condenses and prevents heating to the temperature necessary for bending quartz. This disturbing effect is eliminated by placing the graphite block on a hot plate, and making bends and seals either just over the edge of the block, or over a hole drilled in the surface of the graphite. Quartz fiber construction is easier if the fibers involved are held firmly in position with small weights before the fusing operations are attempted. Quartz fibers are cut to the proper size by using a notched pair of scissors or a tungsten carbide pencil to scratch the fiber before breaking it.

2) Making Quartz Frame and Beam

The quartz frame upon which the balance is mounted (Fig. 3) is made from 3 mm. quartz rod. The support posts for the axis fiber and the beam rests are made from 1 mm. rod.

The beam is constructed of quartz fibers and braced as shown in Fig. 2, in order to keep the beam as light as possible and yet rigid enough to support a total dead weight of 300 to 350 mg. The fibers used for the beam construction are approximately 0.3 mm. in diameter and weigh 1.5 to 2 mg. per cm. of length.

3) Attaching Beam Magnet

The Cunife, or Alnico, magnet sealed in a thin quartz capillary is fused to the beam as in Fig. 2. This magnet weighs about 10 mg., it is 5-7 mm. long, and it has a diameter of about 0.6 mm. Care in selecting a capillary of the proper size, and in sealing the magnet in this capillary, is necessary to eliminate all "play". The position of the magnet below the beam is fixed to counter balance the weight of the quartz bracing and upper span. This places the center of gravity of the beam and magnet unit close to the central axis fiber.

4) Attaching the Three Axes

The three cross arms, corresponding to the three knife edges on an ordinary analytical balance, and consisting of quartz fibers weighing about 1 mg. per cm., are fused to the beam, preparatory to the mounting of the central suspension fiber and the terminal axes suspension fibers (See Fig. 2). Since in a sensitive balance it is essential that these crossarms lie in the same plane, and be mutually parallel, the fusing operation is carried out on a flat block of graphite to insure proper alignment.

5) Mounting the Beam

During the next operations to be described bits of sealing wax or

selenium are used to hold the balance tight to the rests, which are bent upward to hold the beam in an approximation to its final position.

Using a carefully adjusted micro flame, quartz threads of the order of 10 microns in diameter and about 1 cm. long are pulled from the central crossbars as illustrated in Fig. 4. The fusion of these suspension fibers to the support posts of the frame must be carried out with caution to prevent melting them in two (See Fig. 5). If properly completed, the central axis fiber is securely fused to the post. This point of fusion is then carefully heated until the surface tension of the molten ball of quartz pulls the slack in the fine suspension fiber into the post. This same method is used in the mounting of the terminal axes suspension fibers.

It should be noted that, in using these techniques, fusions directly involving the delicate suspension threads are not required. This makes the construction considerably easier than if the quartz threads were drawn in a separate operation and then fused to the larger fibers.

Unless the central suspension fiber is under considerable tension anomalous effects will be observed during operation of the balance. In order to tighten the central suspension fiber, and so remove all slack, the following technique is employed. The frame and balance are oriented with the central axis fiber in a vertical position. The balance beam is freed from the beam rests for these operations. As illustrated in Fig. 6, a hook of quartz fiber is fused to the lower post and a 1 to 2 gm. weight is suspended. The necessary tension is provided by heating the post to the softening point, allowing the weight to pull down. The beam rests are now lowered to allow the beam to rock about 1 mm. Since the swing of the beam is to be observed by a reading microscope, a fine fiber is drawn from a beam end, parallel to the length of the beam, to serve as a pointer.

6) Magnetization

The permanent magnet may be magnetized following completion of the above construction. The entire balance assembly is placed within a pyrex tube 25 mm. in diameter and about 12 cm. long. This unit is placed in a magnetic field created by a magnetizing force of at least 4000 ampere turns per inch of the Alnico or Cunife permanent magnet material. By magnetizing the permanent magnet as a final step in the balance construction, possible demagnetization resulting from heating during the fusing steps is counteracted.

IV. Operation of the Balance

1) Making a Weighing

The operation of the balance is simple, and though separate phases of the procedure have been described above a brief resume will be given. With the pan empty or tared, current is supplied to the coil until the balance is brought to a zero point, using a reading microscope fitted with a cross hair to focus on the pointer fiber. The voltage drop across the standard resistance is measured. Any change in weight will require a second adjustment of current, and thus a second voltage reading. The difference between these readings is directly proportional to the regulating current which in turn is directly proportional to the change in weight.

2) Calibration of Balance

The calibration of the instrument is accomplished by adding to the pan known standard weights such as sections of a weighed length of quartz fiber or fine platinum wire. A known amount of a suitable salt, e.g., potassium chloride solution evaporated to dryness may also be used. The

method and problems of calibration by these methods have been described by Kirk, et al.⁵

For the purpose of illustration of the sensitivity of the balance and of the linearity of the relation, weight vs. voltage, calibration data is listed in Table I and illustrated in Fig. 7. The standard weights used in this calibration were sections of a quartz fiber. No special pains were taken in the preparation of these weights. A length of quartz fiber was weighed and measured giving a factor of 0.087 mg. per cm. of length. One centimeter sections were cut with a razor blade without magnification. As a result the average agreement of the unit weights is of the order of five per cent. The balance pans were initially tared so the right pan was lighter. Upon addition of the second weight unit the right pan became heavier and a reversal of the direction of the coil current was necessary.

Fig. 7 clearly represents the linear relation between the voltage reading and the weight determined.

3) Operating Precautions

As with any microbalance, the system should be protected from mechanical shock, and the usual precautions should be taken against uneven lighting and external electrostatic or magnetic influence.

V. Physical Characteristics of Balance

1) Sensitivity and Reproducibility

The sensitivity of balances of this type can be most exactly defined in terms of the weight required to give a deflection of the balance beam through a definite arc. In this case we have chosen six minutes of arc which corresponds to a displacement of one division on the eyepiece scale.

Table I: Calibration Data

Weight Units	Eye-piece Scale Position	Potentiometer Reading (volts)	Sensitivity (volts per division)	Eye-piece Scale Zero Position (volts)	Weight in Micrograms
0	+4.4	.14456	.00016	.14386	0
	-7.4	.14268			
1	+3.5	.07095	.00015	.07039	87
	-6.9	.06936			
2 ^a	-7.1	.01635	.00014	.01526	174
	+1.7	.01499			
3	-10.9	.09698	.00017	.09505	261
	+4.7	.09431			
4	-2.5	.16520	----- ^b	.16480	348
5	-12.1	.24317	.00016	.24128	435
	+3.3	.24075			

^aDirection of current in regulating coil reversed.^bNo data obtained.

In column 4 of Table I the voltage equivalent of this displacement is tabulated over the weight range 0 to 435 micrograms and is seen to be constant over this range.

The sensitivity of this particular balance is thus about 0.2 microgram per six minutes of arc.

Reproducibility as we choose to use it is a function of the particular operation the balance is used for. If a reaction is carried out without removal of the pans the balance will "reproduce" readings to the same limit as the sensitivity of the balance. However if frequent manipulation of the pans is necessary during the experiment the reproducibility or precision of a weighing may not be the same as the sensitivity. To illustrate what can be done the following experiment was performed. A pan was removed from the balance placed on a platinum foil and then returned to position on the suspension bow. In a series of eleven measurements the balance reproduced the original reading within the sensitivity limit. However more drastic manipulations which involve heating the pans may change the reproducibility to as much as a few micrograms.

2) Load Capacity and Weighing Range

The load capacity of the microbalance, this term describing the counter-balanced weight of a sample and pan, may be as much as 150 milligrams.

The balance will weigh directly, using the magnetic control method, an unbalanced weight difference as large as 1.0 to 1.2 milligrams, if advantage is taken of the reversing of the coil current in the manner illustrated in the calibration procedure, (see Fig. 7).

3) Behavior under Damping

Adjustments and readings may be made in a few seconds, because of

the magnetic damping effect and the use of the balance as a null instrument.

4) Temperature Range

The temperature range of the balance is considerable. Through the use of the special Alnico or Cunife magnet materials the balance unit itself may be used up to 150 to 200°C. At these temperatures the permanent magnet loses some of its residual magnetism. Single pan reactions may be carried out at extremes of temperature if the pan is suspended in a trap, thus protecting the permanent magnet.

5) Stability

The balance is able to withstand reasonable use and is mechanically stable. Balances have been known to maintain their characteristics over a few years time.

VI. Uses of the Balance

The balance may be used as a laboratory microbalance. Because of the nature of its design the balance has many applications to specific analytical and research problems. A few examples from these fields of application will be given.

1) Ash Determinations

Determinations of the metal content of organometallic compounds, or organic complexes with metals may be carried out by direct ignition of the weighed sample on a platinum balance pan. The residue after such an ignition is then weighed as the metal (Ag, Pt, Au), as the oxide (Fe_2O_3 , CuO , Al_2O_3 , SiO_2 , U_3O_8 , etc.), or as the sulfate (Na_2SO_4 , MgSO_4 , BaSO_4 , MnSO_4 , etc.).

2) Determination of Water in Hydrates

The balance is well adapted for moisture content, water of hydration determinations, and similar studies of an equilibrium nature. These are run by following the weight changes of a sample on the balance pan in a closed system. The micro samples required by the fiber balance are desirable, since they reach equilibrium much more quickly than do larger samples. The use of the balance in such a determination is best shown by an example. Fig. 8 is the well known graph of the vapor pressure plotted against water of hydration of the various hydrates of MgSO_4 . To illustrate a use of the balance this hydrate system was studied in the following way. A sample of partially hydrated MgSO_4 was placed on one pan of the microbalance. The balance was inserted into a closed system, the temperature of which was fixed near room temperature. A trap containing water was in the system. By using appropriate baths the temperature of this trap was fixed at values lower than the temperature of the rest of the system. The vapor pressure of water in the closed system was thus established by the temperature of the coldest part of the system, which was the trap. Changing the temperature of the trap changed the vapor pressure of water in the system. Changes in the weight of the sample could be interpreted in terms of hydrate formation as shown in Fig. 9. At point (A) on the curve a dry ice-acetone bath was placed around the trap, the system evacuated and closed. A rapid loss of weight resulted until the anhydrous state was reached. At point (B) an ice bath at a temperature of 0°C . was placed around the trap producing a water vapor pressure of 4.6 mm. inside the system. The weight of the sample increased by an amount corresponding to the monohydrate. In like manner at points (C) and (D) baths of

partially frozen dioxane and acetophenone, having temperatures of 8.6°C . and 16.6°C . respectively, were placed around the trap. Breaks corresponding to the formation of di- and tetra-hydrates were obtained. Of course with a salt of undetermined hydrate composition, a larger number of trap temperatures would be necessary for a complete hydrate study. To extend the temperature range, the system, excluding the trap, can be fitted with jackets through which a heated bath liquid may be circulated.

3) Determination of Gas Density

The balance may be used in the determination of gas densities by mounting a buoyancy bulb on one end of the beam.

4) Carrying out Reactions in Closed Systems

Reactions may be carried out on the pans of the microbalance in closed systems under wide conditions of temperature and pressure and monitored by following the accompanying weight changes. Any gaseous reagent tolerated by the all-quartz construction may be used.*

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BALANCE UNIT

Fig. 1

Fig. 2

QUARTZ BALANCE FRAME

Fig. 3

PULLING AXIS FIBER FROM CENTRAL CROSSARM

Fig. 4

SHRINKING AXIS FIBER

Fig. 5

FINAL TIGHTENING OF AXIS FIBER

Fig. 6

LINEAR RELATION BETWEEN THE VOLTAGE READING AND WEIGHT DETERMINED

Fig. 7

Fig. 8

EXPERIMENTAL CURVE OF WATERS OF HYDRATION OF $MgSO_4$

Fig. 9

END