

448. *Magnetochemistry of the Heaviest Elements. Part I. A Sensitive Magnetic Susceptibility Balance for Small Samples.*

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A balance is described by means of which magnetic susceptibilities may be measured on milligram amounts of solids by using a modification of the Faraday method. With a maximum field strength of about 2500 gauss, the susceptibility of a 10-mg. sample of specific susceptibility 1×10^{-6} is measurable to 0.5%. The balance is convenient for general susceptibility measurements even when larger amounts are available.

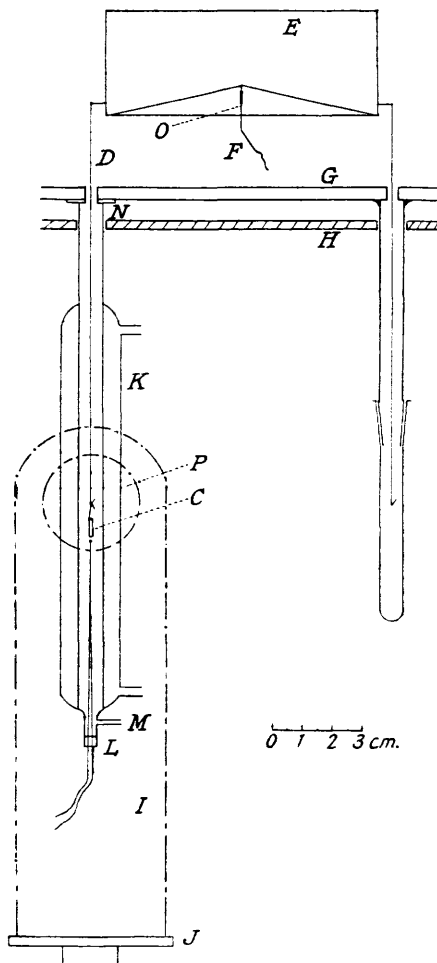
INVESTIGATION of the magnetic properties of compounds of the elements beyond actinium calls for the development of a balance for use with samples of the order of a milligram. When the sample is a solid, such measurements cannot be made by the Gouy method. The non-homogeneous-field method of Faraday has been described in various modifications, but in general these have not been devised for very small samples. The interference balance of Bathnagar and Mathur (*Phil. Mag.*, 1929, 8, 1041) can be used with small samples, but is more elaborate than the present method and is not particularly easily adapted to measurements over a wide temperature range. Temperature control of the sample is easier when the measurements are made by a vertical-force method, as in Sucksmith's balance (*ibid.*, p. 158) and the present apparatus.

The balance now described consists essentially of a quartz torsion fibre microbalance by means of which the changing force on the sample under investigation may be measured as the magnet poles are moved vertically past the sample. Since the sample is small compared with the magnet, the accuracy of the method is not dependent on variations in the packing density. As, moreover, the measurements are all relative to a standard substance, extensive mapping of the field in the vertical direction is unnecessary and mapping in the horizontal plane is avoided by careful alignment of the sample with respect to the magnet pole-pieces, as described below.

The magnetic force as measured per mg. of sample is comparatively high in the present method. This force depends, of course, on the dimensions of the pole-gap as well as on the strength of the magnet; the former cannot be made too small, primarily because the apparatus for temperature control must be accommodated, and, secondly, because if the field gradient is too steep the alignment of the sample becomes too critical. With a magnet of maximum field strength about 2500 gauss, and a pole gap of 28 mm., the difference between the maximum and the minimum force on the sample is about 3×10^{-3} times its weight for a g.-susceptibility of 1×10^{-6} . Consequently the force on a 5-mg. sample of a moderately paramagnetic substance is of the order of 10–100 μ g. and the necessary accuracy was made possible because the balance sensitivity was about 0.01 μ g. The general layout of the balance is shown in Figs. 1 and 2.

The Quartz Beam.—The beam is made of 200- μ . quartz rods and is supported at *O* by two 15- μ . horizontal torsion fibres, *A*, one of these is fixed, through the quartz tensioning bow *Q*, and the other is fused to 1-mm. quartz rod which in turn is cemented to the drive from a reduction gear, *B*. This gear,

FIG. 1.
Susceptibility balance, end view.

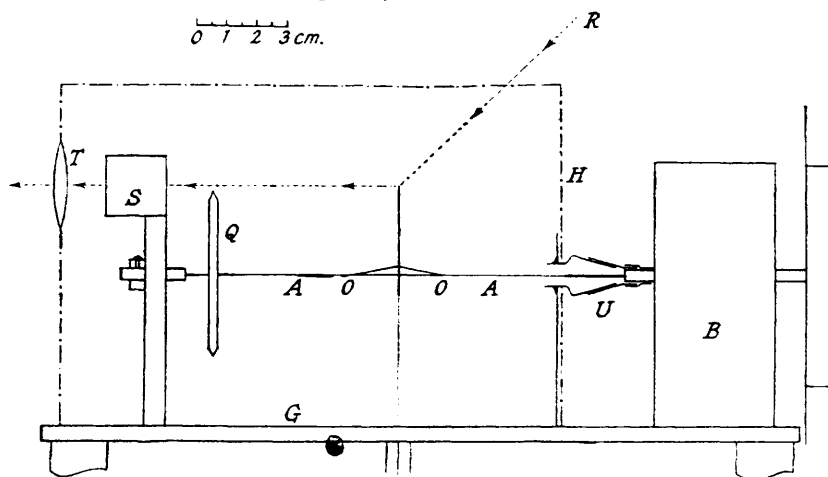


designed to eliminate back-lash, has a ratio of 20 : 1 and carries on its other axle a dial divided into 400 divisions to the full circle. Thus 8000 scale divisions are equivalent to one revolution of the end of the torsion fibre, which in turn corresponds to a change of weight of 60–70 μg . The exact calibration depends on the particular torsion fibre in use, of course, but the average fibre could be turned through $3\frac{1}{2}$ revolutions either way from the relaxed position without breaking, corresponding to full scale deflexion of about 450 μg . The centre of gravity of the beam may be adjusted by bending the rod *F*.

The sample is contained in a fused quartz bucket *C*, 5–6 mm. long and of about 1-mm. internal diameter, having a fused quartz fibre handle and suspended from the beam by a 10- μ . fibre *D*; it is counter-balanced by small pieces of platinum wire hanging from the other arm of the beam.

The Optical System.—A horizontal 5- μ . index fibre *E* is held taut between two upright posts over the top of the beam. The balance is operated by bringing this fibre to a null position by rotation of the torsion head. This null point is determined by observing simultaneously the two ends of *E* by means of an optical system similar in principle to that described by Kirk, Craig, Gullberg, and Boyer (*Ind. Eng. Chem., Anal.*, 1947, 19, 427). The images of the two ends are superimposed by a mirror-and-prism system *S*, of the type employed in microscope comparators, and brought to a focus by an achromatic convex lens *T* at the object position of a low-power microscope. A useful aid in determining the null point is to illuminate the ends of the index fibre with two different coloured lights *R*; when red and green are used there is a noticeable colour change at the exact superposition of the images. The total magnification of the optical system is about 50 \times .

FIG. 2.
Susceptibility balance, side view.



With relatively small loads, the angular motion of the beam caused by turning the torsion head is 0.11 minute of arc per scale division. After magnification, the relative motion in the eye-piece appears to be about 0.15 mm. per scale division; this figure is reduced by perhaps 50% for the largest loads used. Ideally the angular motion of the beam should be sufficient, therefore, to permit weighings to about 2 scale divisions or 1.6×10^{-8} g. This is actually found to be the reproducibility of any one setting, but other, more important errors exist, as will be shown below.

The Case.—The balance, and the optical system, with the exception of the viewing microscope, are attached to a thick brass plate *G* enclosed in a brass box, which in turn is surrounded by a wooden case *H*. Glass windows are inserted in the top of the boxes for the illumination of the index fibre. As far as possible, the inner box is made air-tight, leakage around the torsion head being prevented by the ground joint *U*. The assembly stands on four substantial brass legs attached to a base plate which also supports the screw device *J* for raising and lowering the magnet in the space between the balance legs. Vibrations of the beam are rapidly damped by air resistance, and the balance can be operated on an ordinary laboratory bench; a concrete pillar is not necessary.

The Magnet.—The magnet *I* is of a permanent magnetron type with a field strength at the mid-point between the poles of 2500 gauss. It has parallel circular pole faces *P*, 31 mm. in diameter and 29 mm. apart. For normal operation the maximum vertical travel of the magnet needs to be about 6 cm.

Temperature Control.—Control of the sample temperature is obtained by a set of interchangeable jackets small enough to fit between the magnet pole faces. All the jackets have an inlet *M* for dry nitrogen, which is used to surround the samples for all measurements.

The sample can be maintained at 20° by a water jacket *K* containing water circulated from a thermostat. A tube just wide enough to fit round the freely suspended sample and immersed in a small Dewar flask is used for liquid oxygen and solid carbon dioxide. A thermocouple *L* is incorporated in the tubes just below the sample. For temperatures up to 300° an electrically heated oven is used. This is of glass, wrapped in copper foil, with a non-inductive winding outside the foil and insulated from it by asbestos paper. The winding is tapped at the centre so that the upper and the lower half of the furnace

can be controlled independently. Heat insulation on the outside is provided by more asbestos, and the furnace has two thermocouple inlets about 1 cm. above and below the sample respectively. Each jacket is ground flat at the top, and a seal with the case is effected by the rubber gasket *N*.

Operation of the Balance.—When the sample is on the balance, the magnet is moved vertically past it in steps of 1 mm. At each step the beam is restored to its null position, and the torsion head reading is observed. The magnetic force so measured is given by :

$$F = m\chi H \frac{dH}{dx}$$

for a sample of mass *m* and susceptibility χ in a field of strength *H*, where *x* measures the position of the sample relative to the magnet in a vertical direction. A plot of *F*, measured in balance scale divisions, against sample position shows a maximum and a minimum (Fig. 3).

FIG. 3.

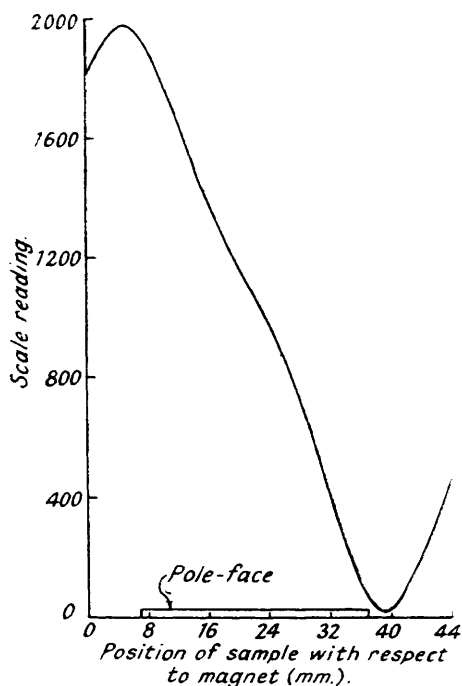
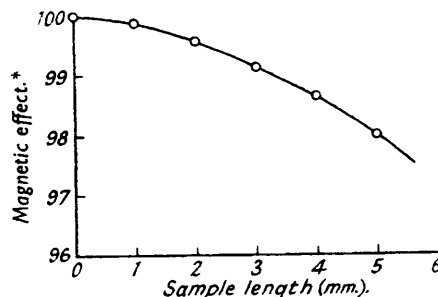


FIG. 4.



* Magnetic effect on the sample compared with zero length (%).

The magnetic effect on the empty sample-container is measured first and then the sample is weighed on an ordinary microbalance. The weight of the sample and container is counterbalanced on the susceptibility apparatus by platinum wire tares, and only the varying magnetic forces are balanced by the torsion head. At the same magnet positions, the scale reading obtained for the empty container are subtracted from those of the sample plus container to give the effect on the sample alone. The exact values of the maximum and minimum on the sample curve are then obtained graphically and the distance between them, in scale divisions, is used to calculate the susceptibility. Since the measurements are made relative to a standard substance, the g.-susceptibility (χ_1) of an unknown is given by :

$$\chi_1 = \frac{(s_1 - s_p)(m_2 - m_p)}{(m_1 - m_p)(s_2 - s_p)} \chi_2 \dots \dots \dots (1)$$

where, χ_2 = g.-susceptibility of the standard, s_1, s_2, s_p = the magnet forces on respectively (i) the sample plus container, (ii) the standard plus container, and (iii) the empty container, m_1, m_2, m_p = the weights respectively of (i), (ii), and (iii).

Since the method depends on comparing the magnetic effects on a sample and on the standard when placed in the same magnetic field, it is pertinent to enquire how reproducible the position of the sample container must be from one measurement to the next

An experiment with a small sample of ferrous ammonium sulphate showed that the magnetic force differed by less than 0.9% over all horizontal positions within 1 mm. of the centre of the field. By moving the magnet the sample is always aligned to within 0.1 mm. of the centre (measured by a travelling microscope) so that errors from this source are negligible.

The alignment of the sample in the vertical direction introduces two possible errors : (i) the length of the sample may not be very small relative to the distance over which $H \frac{dH}{dx}$ is sufficiently close to its maximum value, and (ii) the sag of the torsion fibre under different loads may mean that readings on the sample plus container and on the container alone are not made at precisely the same place.

(i) The correction for the finite length of the sample was found by determining the curve of magnetic force against position for a small piece of platinum foil ($1.5 \times 1.5 \times 0.1$ mm.) hung with its plane horizontal so that its length was negligible. By graphical integration of the curve for various distances round the maximum, the relative force on samples of different lengths was calculated and hence a correction factor for the length. The correction curve is shown in Fig. 4.

(ii) The sag of the torsion fibre increases slightly when the empty sample container is loaded. Direct measurement showed that this introduced no significant error (< 2 scale divisions) into the determination of the magnetic force on the sample alone.

Accuracy of Measurements.—Examination of the accuracy of the measurements yielded the following results.

(1) With the magnet removed, the torsion head was repeatedly turned away from the null position and brought back again. The root mean square deviation (σ) of the readings of the null position was about 1 scale division under a 1-mg. load, and 2.0 scale divisions for a 20-mg. load.

(2) A piece of 50 S.W.G. platinum wire (86.9 μg .) was weighed repeatedly on the balance. This was done at all parts of the torsion head scale by changing the counterweights and also with different total loads on the balance. No detectable difference in sensitivity was found for various parts of the scale up to $3\frac{1}{2}$ fibre revolutions from the relaxed position. It was found, however, that the sensitivity varied slightly with the load as shown below.

Total load, mg.	1.0	20.7	31.3
Relative sensitivity	1	0.9987	0.9982
σ , scale divisions *	3.0	9.7	9.2
No. of weighings	10	10	10

* σ = root mean square deviation in weight found for platinum wire; this weight is the difference of two dial settings and 8000 scale divisions = 1 fibre revolution = 70 μg .

The σ for the mean relative sensitivities is 0.0003. The change in sensitivity for the operating region of the balance (20—30 mg.) was so small that it was ignored.

(3) A sample of a paramagnetic substance (uranium dioxide) was placed on the balance and, with the magnet replaced, the maximum and minimum forces due to the magnet were measured in the usual way. The same sample was measured ten times, and over different regions of the scale by altering the counterweights. The load in each case was about 25 mg.; the results for 3 different samples were:

Difference in scale divisions	2231	9570	20,900
σ	$15\frac{1}{2}$	25	21
σ /difference, %	0.7	0.26	0.10

It was found that merely taking the sample on and off the balance and adjusting the magnet if necessary, but not altering the counterweights, gave a much smaller deviation. It will be seen that altering the counterweights causes a sharp rise in the experimental error, the reason for which is not clear. Part of the extra rise with magnetic measurements is because the maxima and minima are found by graphical interpolation from 5 or 6 readings at successive magnet positions, and it cannot be claimed that these interpolations are better than ± 5 scale divisions for the larger values of the differences.

As regards the total error of the measurements, equation (1) above leads to the following expression, approximately, for σ_x the r.m.s. error in χ_1 .

$$\left[\frac{\sigma_x}{\chi_1} \right]^2 = \frac{1}{n_1} \frac{(\sigma_{S_1}^2 + \sigma_{S_p}^2)}{(S_1 - S_p)^2} + \frac{1}{n_2} \frac{(\sigma_{S_2}^2 + \sigma_{S_p}^2)}{(S_2 - S_p)^2} + \frac{1}{n_1} \frac{(\sigma_{m_1}^2 + \sigma_{m_p}^2)}{(m_1 - m_p)^2} + \frac{1}{n_2} \frac{(\sigma_{m_2}^2 + \sigma_{m_p}^2)}{(m_2 - m_p)^2} \quad (ii)$$

where the subscripts to the various σ show the quantities to which they refer, and n_1 and n_2 are respectively the number of measurements on the unknown and on the calibrating substance. The errors in m_1 , m_2 , and m_p depend on the microbalance on which these weighings are made; a good commercial microbalance should have mean weighing errors not above 2—3 μg . in a sample weight of ca. 5 mg. and a weight of standard substance of 2—3 mg. Thus even if $n_1 = n_2 = 1$, the weighing errors are only 0.15%, *i.e.*, the σ_m parts of (ii) above are about 2.5×10^{-6} . In most cases the weighing error should be less than the errors in magnetic measurements. σ_{S_p} is about 15 as S_p was about -2500 (the container of course is diamagnetic), and σ_1 and σ_2 are between 20 and 25 for reasonable sizes of samples. In the case of the very paramagnetic ferrous ammonium sulphate $S_2 - S_p$ was about 10,000 scale divisions per mg., and for a 2.5-mg. sample the second term on the right hand side of (ii) becomes $1 \times 10^{-6}/n_2$. The first term on the right hand side of (ii) is in general the largest: if 10 mg. of a compound of $\chi = 1 \times 10^{-6}$ are used, $S_1 - S_p = 3750$ approximately, so that S_1 is about 1250. If we put $\sigma_{S_1} = \sigma_{S_2} = 15$, this term in (ii) equals 32×10^{-6} . With these values, and if $n_1 = n_2 = 1$, $\sigma_x/\chi = 0.6\%$; but of course, a number of calibration runs was made and n_2 does not need to be large for σ_x/χ to be considerably below 0.5%. The accuracy for compounds of high susceptibility is considerably better, of course. These estimates naturally include only the random errors of the instrument, though the method is sufficiently simple to make it improbable that other large errors are involved and the estimates agree quite well with experiment. It should however be noted that χ_2 , the susceptibility of the standard substance, is assumed as known. The chief dangers are ferro-magnetic impurities, and if only one magnet is used these are not detected by the magnetic measurements themselves; they have to be avoided by careful preparation and analysis of both the standard substance and the unknown. With two permanent magnets of different strengths or with an electromagnet it is possible to be sure that χ is independent of H .

In the calibration of the present instrument a pure grade of ferrous ammonium sulphate was used as a standard. Analysis gave no measurable deviation from the calculated amount of ferrous ion present. In order to prevent loss of water of crystallisation measurements were made in an atmosphere of nitrogen which had been passed over saturated sodium bromide solution.

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