

A novel thermogravimetric analyser

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Abstract

This paper describes the design and development of a novel vibrating-reed technique for thermogravimetric analysis (TGA). The system can provide thermogravimetric data for samples in a well-mixed state, thus overcoming the heat transfer problems associated with conventional instruments. Other advantages include low cost of manufacture, robustness and ease of operation. Preliminary data are reported for the thermal dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in the range 20–500°C. A typical mass resolution for 0.5 g samples is better than $\pm 1.5\%$.

INTRODUCTION

Thermogravimetry involves the continuous monitoring of the mass of a substance as a function of temperature. The sample may be heated or cooled at a particular rate or the temperature may be isothermally maintained. This method of sample characterisation has found applications in almost all areas of chemistry and its allied fields. Some specific examples include the study of the thermal decomposition of substances, the corrosion of metals in aggressive environments and reaction kinetics.

The main types of thermogravimetric balances are classified into two main categories: null-type and deflection-type instruments. The majority of the commercially available instruments are capable of measuring mass with a high degree of resolution. However, they have the disadvantage of being either expensive or non-robust.

A common problem is associated with the unavoidable presence of temperature gradients in the samples during heating cycles which is believed to be partly responsible for the discrepancies in the reported thermogravimetric literature. In some cases, the resulting temperature gradients produce different results for the same sample depending on the heating rate, sample size or indeed the type of instrument employed [1]. In cases where gases are evolved in thermal decompositions, the trapping of gas in the material may

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result in a build-up of gas partial pressure and, hence, in a decrease in the reaction rate [2]. These problems have been partly alleviated by using smaller samples for which, unfortunately, greater sensitivity and hence more expensive instruments are required. An additional complication is associated with the fact that for most of the devices described, the sample weight changes can be affected by phenomena such as buoyancy [3], gas flow effects [4], free gas convection [5], electrostatic effects [4], zero drift [6], and any changes in inclination [7].

This paper describes the design and development of a novel technique for TGA in which the sample mass is used to modify the resonant frequency of a remotely driven vibrating reed. The instrument is inexpensive to manufacture, robust and capable of operating in aggressive environments provided the reed is constructed from a corrosion-proof, non-oxidisable material. The problems associated with the presence of temperature gradients are also largely eliminated, as the rate of heat transfer in a well-mixed bed of particles is several times higher than that in a stationary packed bed [8]. In the present case, sample mixing is obtained as a consequence of the vibration of a cavity partly filled with the test powder which is attached at the free end of the reed. The instrument also has the advantage of providing a rapid digital output response which may be easily interfaced to a computer.

THE VIBRATING-REED THERMOGRAVIMETRIC ANALYSER

Design and operational features

Figure 1 is a basic schematic representation highlighting the principle of operation of the TGA unit. Basically, the transducer comprises a stiff elastic reed securely clamped at an intermediate point along its length, thus effectively isolating its two free spans. The system is driven into resonance

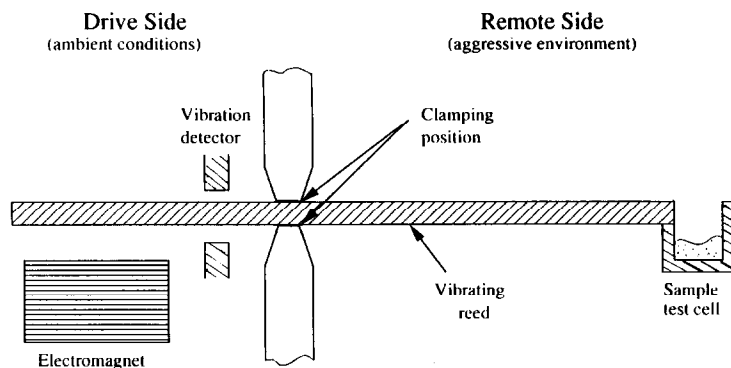


Fig. 1. A schematic representation showing the main features of the remote drive system.

at one end using an electromagnet. With careful choice of the ratio of the lengths of the reed at either side of the clamp, it is possible to transmit vibrations through the clamp and at the same time detect the vibrational characteristics of the remote side of the reed using a suitable detector positioned at the drive end. This in turn allows operation in aggressive environments as the drive and the detection components may remain under ambient conditions. The remote side is mounted with a test cell which is in turn partially filled with the test powder for TGA.

As may be appreciated, the stability and sensitivity in response are a function of a number of operating and design parameters. These factors have been identified and optimised using a computer-aided finite-element analysis technique [9].

The electromagnet is constructed from a laminated rectangular soft iron core, wound with approximately 2000 turns of 0.1 mm diameter copper wire.

Heat is supplied using a specially constructed 110 V, 150 Watt-rated coaxial epoxy resin embedded heater built by Electrothermal. This is in the form of a 21 mm i.d., 33 mm o.d. and 30 mm long cylinder which is supported by a suitably machined phyrophyllite tube which also serves as thermal insulation. The heater is positioned so that it completely surrounds the sample container at close proximity (approx. 2 mm). Temperatures up to 500°C are achievable using this type of heater.

The remote side of the reed is enveloped by a cylindrical brass cover with a suitably sized (approx. 2 mm diameter) aperture drilled at the top in order to allow the insertion of a temperature probe near (approx. 2 mm) the cavity. Temperature is measured and controlled using a calibrated Comark digital thermometer (type 3001) incorporating a chromel–alumel (Ni/Cr, Ni/Al) thermocouple with $\pm 0.1^\circ\text{C}$ resolution and accuracy. The 250 Ω heating circuit is powered from a 5 kW-power Stanton Redcroft temperature controller via a deflection ammeter (10 amp full-scale).

The measurement of the actual sample temperature during TGA unfortunately presents a practical difficulty. Temperature probes cannot be inserted into the test cell as these severely compromise the system's performance by mechanically interfering with the vibration.

For the present case, the temperature of the sample is derived by applying a correction to the temperature of the probe located near the outer wall of the test cell. For calibration, a second probe is attached to the inner wall of the (stationary) test cell so that it is fully covered by the contained powder, in this case sand. The required correction is the difference between the temperatures monitored by the two probes. The improved heat transfer brought about by the vibration-induced mixing during TGA means that the second probe closely indicates the powder temperature.

Temperature calibration experiments performed at typical heating rates of about $2.5\text{--}10^\circ\text{C min}^{-1}$, indicate that the maximum temperature differ-

ence between the two probes and, hence, the correction required is about 5°C. Such differences are not uncommon in thermogravimetric measurements [10].

The sample test cell is constructed from mild steel in the form of a 12 mm i.d. and 10 mm long cylinder. This is permanently closed at one end whilst the other end is threaded to take on a cap incorporating a 63 μm stainless steel wire mesh gauze. This arrangement allows the escape of any gases or vapours produced as a result of thermal decompositions.

The test cell is normally one third filled with the powder under test and the typical amplitude and frequency of vibration are 2 mm and 60 Hz respectively, thus providing ample vibration-induced mixing. The corresponding sensitivity, constant over a wide mass range, is 3.847 Hz g^{-1} (see below).

The electronic drive and detection circuit

The electronic drive and detection system is a more sophisticated version of the circuit described by Briscoe et al. [11]. Basically, the reed is mechanically excited by a magnetic flux generated via a solenoid driven by a pulsating alternating current supplied from an oscillator (Philips type PM 5190; $\pm 1 \times 10^{-3}$ Hz resolution) incorporated in a 30 W power amplifier. The pulsed drive signal attracts the reed towards the electromagnet for only part of a full cycle, thus minimising the degree of interaction between the drive and the oscillator [12]. This is manifested in a more stable and efficient mode of operation as compared to a continuously driven system. The duration and the phase lag of the drive pulse relative to the reed signal may be adjusted at will via suitable arrangements incorporated in the power amplifier. It is found from experiment that optimum conditions in terms of reed stability correspond to a pulse signal with a duration approximately one eighth of the reed's period of oscillation together with a 90° phase lag as dictated by resonant criteria [13, 14].

The resonant frequency may be determined either manually or by automatic tuning. In the former case, the system is simply driven into resonance by varying the frequency of the induced vibration using the oscillator and observing the frequency corresponding to the maximum amplitude of vibration as monitored by a suitable detector.

This mode of operation is useful for studying the system's characteristics but is of limited value for the monitoring of transient responses. The automatic tuning system overcomes this problem. The appropriate circuit diagram is shown in Fig. 2. This is operated by feeding back the detected signal to the driving system thus forming a closed loop. The system then automatically tunes to the primary resonant frequency, operating on the basis of a regenerative feedback loop [15].

Various means of detecting the vibrations, including strain gauge [16], inductance [17, 18] and optical [19] transducers were considered. These were

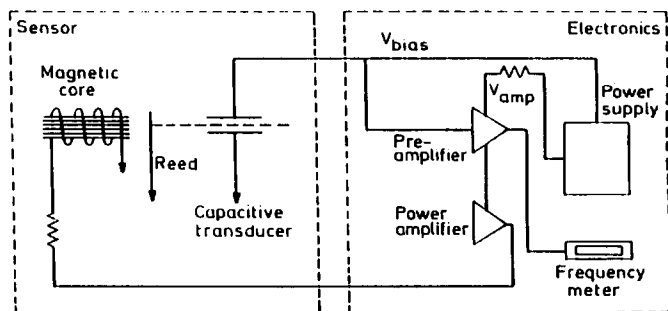


Fig. 2. TGA unit electronic circuit diagram.

found to be unsuitable as they either relied on direct contact with the reed, were non-linear in response, or possessed low resolution. Unfortunately, the use of a tapered reed required the positioning of the vibration detector at the remote end; the amplitude of vibration at the drive span was simply too low to be monitored. This in turn prevented the use of an optical detector as it may not be exposed to high temperatures. The problem was overcome by using a differential capacitance transducer positioned at the remote side. This detector was simply configured by sandwiching the reed between two fixed copper plates (18 mm × 7 mm × 0.5 mm thick) and measuring the electrical capacitance in between. Each copper plate was positioned at approx. 0.2 mm from the earthed reed. The sensitivity was enhanced largely by using two plates as these doubled the output signal which was in differential mode. In addition, any extraneous noise was cancelled out using the two-plate arrangement. The appropriate circuit diagram required for converting the detected capacitance into a voltage signal, which is subsequently monitored and displayed as both frequency and amplitude of vibration, is shown in Fig. 3. The magnitude of the sensed capacitance is only a few picofarads, its precise value being proportional to the plate area and inversely proportional to the separation. Hence, higher sensitivities result from using larger plate sizes and minimal gaps (approx. 0.2 mm) between each of the plates and the vibrating reed.

This system is capable of detecting amplitudes of vibration as low as 1×10^{-3} mm, operating linearly up to a maximum displacement of 0.4 mm. The frequency of the vibration may be measured with $\pm 1 \times 10^{-3}$ Hz resolution at approx. 2 s intervals. The sample mass is then simply obtained from the resonant frequency using the procedure described in the next section. Data acquisition may be performed by means of a personal computer by using a data translation interface which may also in principle be further refined to allow programming of the furnace temperature.

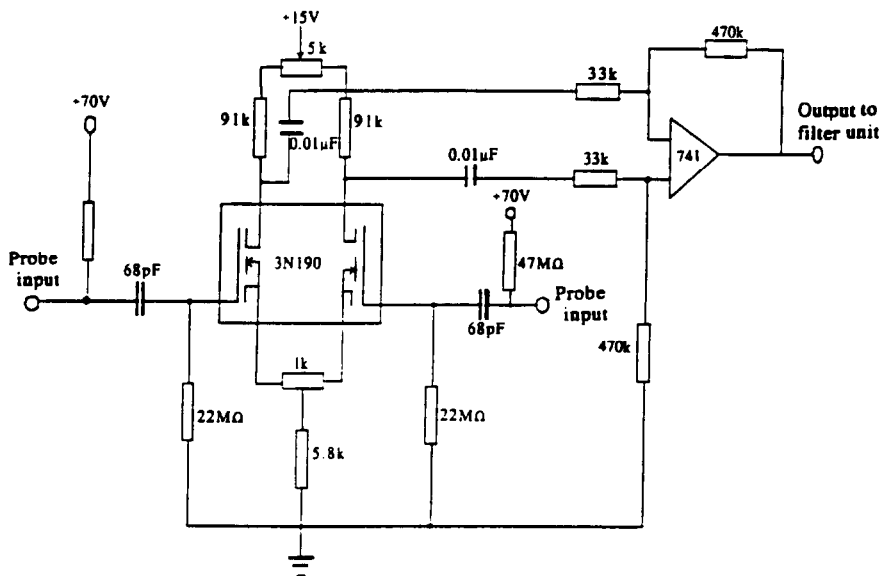


Fig. 3. Electrical circuit for measuring displacement using a capacitance transducer.

Frequency/mass calibration and system resolution

Figure 4 shows the experimentally measured mass/frequency calibration response for the tapered reed obtained at room temperature. As may be observed, the response is linear and the sensitivity is $\pm 3.847 \text{ Hz g}^{-1}$.

The system's frequency stability which is considered to be the major source of error is $\pm 5 \times 10^{-3} \text{ Hz}$. The maximum error associated with the measurement of the sample temperature is assumed to be $\pm 5^\circ\text{C}$. For a temperature calibration sensitivity of $1.245 \times 10^{-3} \text{ Hz } ^\circ\text{C}^{-1}$, the above may be translated into $\pm 6.2 \times 10^{-3} \text{ Hz}$ error in frequency.

For a system sensitivity of $\pm 3.847 \text{ Hz g}^{-1}$ at room temperature (Fig. 4) and a total frequency uncertainty of about $\pm 0.01 \text{ Hz}$, the maximum detec-

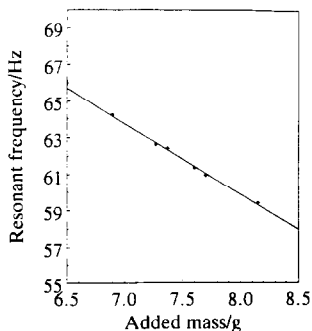


Fig. 4. The variation of the resonant frequency with added mass for a typical operating mass range obtained at room temperature.

tion limit of the system at the operating temperature range is approx. ± 3 mg. For a typical sample mass of 0.6 g, the maximum estimated error is therefore $\pm 1.3\%$.

Materials

The test powders were obtained in the form of 0.5 g samples in the size range 90–120 μm corresponding to an average particle size of about 100 μm as measured using an optical microscope. The powders included copper(II) sulphate pentahydrate (99% purity), cobalt(II) sulphate heptahydrate (97% purity) and nickel(II) sulphate heptahydrate (99% purity). All compounds were supplied by BDH Chemicals and were used as manufactured. These samples were selected because of their marked transitions at a convenient range of temperatures and because their thermal decomposition products are non-toxic gases. In addition, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ offers the possibility of testing the instrument in conjunction with a material in the molten state at 97°C [20].

Experiments with different sizes of glass Ballotini spheres and irregular coal fragments have shown that the resonant frequency is independent of particle size and shape. The corresponding data obtained at room temperature for 1 g samples are shown in Fig. 5. The maximum deviation is about $\pm 1 \times 10^{-3}$ Hz which is of the same order of magnitude as the system's stability in response.

THERMOGRAVIMETRIC STUDIES

Figures 6–8 show thermal curves for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at a constant heating rate of $2.5^\circ\text{C min}^{-1}$, and for $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ at a heating rate of approx. $10^\circ\text{C min}^{-1}$ using the thermogravimetric unit up to a maximum temperature of 500°C. The appropriate sample masses employed are given in the figure legends. Different heating rates down to $1.5^\circ\text{C min}^{-1}$ did not appear to have an appreciable effect on the data. This is believed to

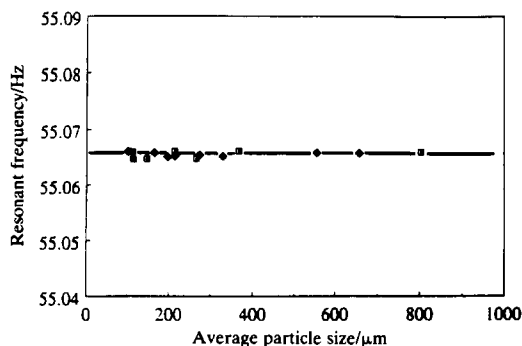


Fig. 5. The variation of the resonant frequency with particle size: \square , glass Ballotini; \blacklozenge , coal particles.

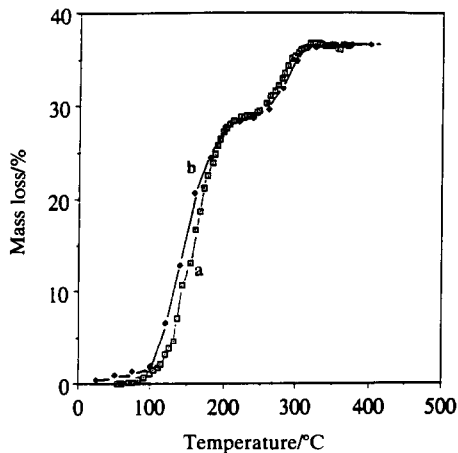


Fig. 6. Thermogravimetric data for the dehydration of 0.742 g of copper(II) sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$: curve a, data using the optimised instrument; curve b, published data [22].

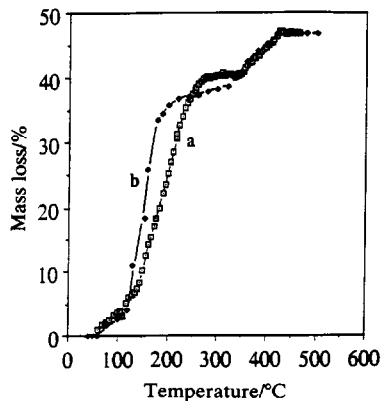


Fig. 7. Thermogravimetric data for the dehydration of 0.613 g of cobalt(II) sulphate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$: curve a, data using the optimised instrument; curve b, published data [23].

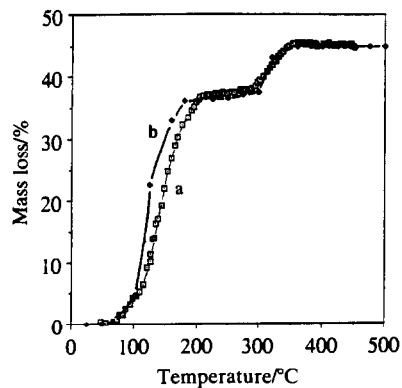


Fig. 8. Thermogravimetric data for the dehydration of 0.650 g of nickel(II) sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$: curve a, data using the optimised instrument; curve b, published data [23].

be largely a consequence of improved heat transfer due to vibration-induced particle agitation. However, it is appreciated that the heating rate may directly affect the reaction kinetics, thus resulting in an inevitable shift in the TG thermal curves [21]. For the present range of heating rates, the above effect was found to be insignificant.

Also included in the figures are the corresponding results reported by Liptay [22, 23] obtained at the same heating rates. All experiments, including those reported by others, were performed under a static air atmosphere.

Referring to the TG thermal curves, it is evident that the data obtained using the present technique are in good agreement with those reported by other workers. Various factors believed to be responsible for the observed finite discrepancies are discussed below.

Sources of error in the data

It is difficult and perhaps unsafe to attempt to identify and quantify categorically the causes for the observed finite discrepancies in the present data as compared to published values. The problems associated with the production of consistent results in thermogravimetric measurements are well documented [1]. This is due to the large number of variables affecting these types of measurements. Apart from the errors associated with the finite sensitivity of the instrument (see above) the most important sources of error are discussed below.

The effect of sample mass

Dense samples of larger mass are expected to give rise to more pronounced temperature gradients and, hence, to a delayed response [24]. However, the vibration-induced mixing of the sample is believed to largely eliminate the above effect (approx. 0.7 g test samples were used in the present experiments as smaller masses require greater system sensitivity). In addition, kinetics will cause larger samples to decompose over a wider range of temperatures, i.e. 'low resolution'.

Self-generated pressure and atmosphere in the test sample

An increase in pressure increases dissociation, boiling and hydration temperatures [25]. This situation may occur in the test cell due to the hindered escape of gaseous products as a consequence of the partial blocking of the wire gauze with solid particles. In addition, a self-generated atmosphere composed of the reaction products which is in intimate contact with the sample in the test cell may affect the rate of the decomposition [26] and, hence, affect the mass/temperature response.

Sample temperature

The precise temperature of the sample is unknown as this relies on the prior calibration of an external temperature probe. It is believed that in the

present work, the dehydration temperatures may not be measured to better than $\pm 5^{\circ}\text{C}$.

CONCLUSION

The TGA unit developed has the advantage that it is robust: the only components exposed to the high-temperature environment are a steel reed mounted with a cavity containing the test sample. Furthermore, the vibration-induced mixing feature overcomes most of the problems associated with poor heat transfer experienced with other conventional instruments. Relatively larger samples may be used here at the expense of resolution. Faster heating/cooling rates may also be employed in cases where the kinetics of the reactions are not significantly affected by the heating rate.

Analysis of samples containing liquids may be possible provided no loss of material occurs due to spillage.

The instrument is relatively cheap to manufacture because simple and inexpensive ancillary control and monitoring units are used.

Substitution of the steel reed by a ceramic one would increase the present maximum operating temperature of about 500°C to a minimum of 1000°C , and at the same time dramatically improve the system performance. Theoretical modelling verified by experimental evidence supports this view [9] as materials with the highest ratio of Young's modulus to density produce the most sensitive and stable response. Results of preliminary experiments with simply shaped ceramic reeds indicate a 20-fold increase in sensitivity as compared to a steel reed of identical geometry. Unfortunately, it was not possible to experiment with more complicatedly shaped ceramic reeds due to machining difficulties associated with this type of material.

In conclusion, it is believed that with more careful engineering design and better machining procedures such as those available in a commercial environment, significant improvements in the system's stability and sensitivity in response may be obtained. Under these circumstances, the finished product is expected to offer a new and exciting way of performing thermogravimetric analysis.

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