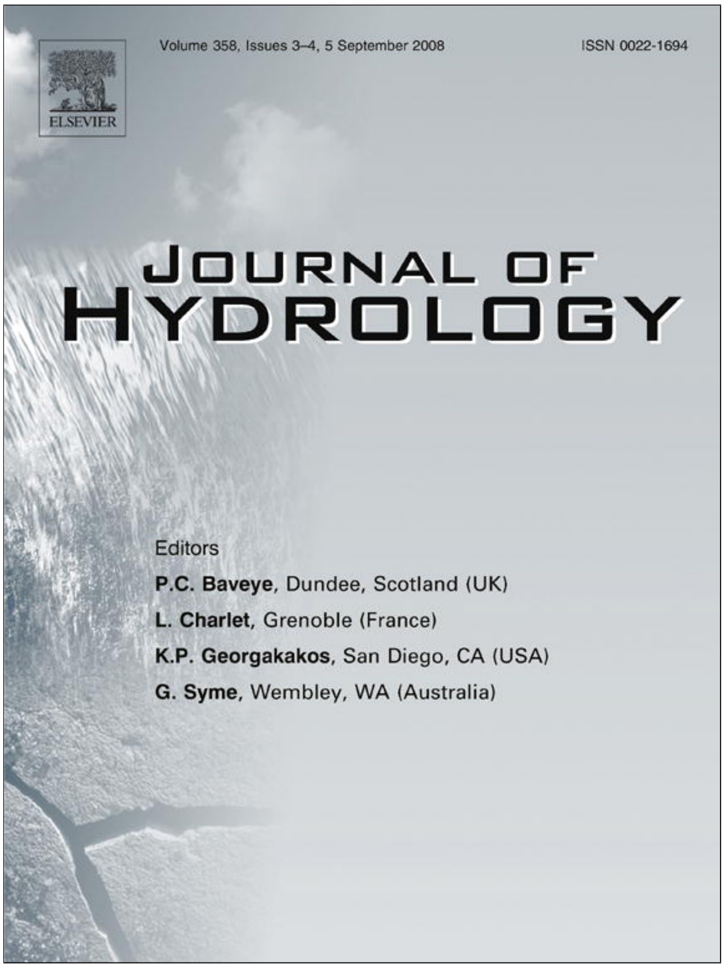
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Controls on water drop volume at speleothem drip sites: An experimental study

Christopher Collister [a], David Mattey [b,*]

[a] *PiTech Research, Red Cottage, Stowell, Dorset DT9 4PD, UK*
[b] *Department of Earth Sciences, Royal Holloway, University of London, Egham, Surrey, TW20 0EX, UK*

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Summary The growth of speleothem under cave drip sites is closely related to local climate events and provides an increasingly important means of deciphering past climate change. Since calcite precipitation rates depend on the water discharge at the drip site, the drip rate and mass of water drops detaching from stalactites are fundamental controls on speleothem growth and we have investigated factors that control the volume of water drops in this environment. The classical investigations on the volume of falling water drops are reviewed but there have been no measurements of the volume of drops detaching from curved surfaces equivalent to tips of stalactites. In this study we have used an acoustic drop counting method to measure the variation of the mass of water drops detaching from tubes (representing 'soda straw' stalactites) and artificial stalactites with spherical terminations (representing massive stalactites) as a function of tube radius or surface curvature and the drip rate. The experimental method corroborates classical measurements of drop mass detaching from tubes and, for massive stalactites, we derive a simple empirical relationship between drop mass and radius of curvature of a spherical surface, based on 100,000 drop counts from artificial stalactites with 19 different radii ranging from 3.6 mm to 500 mm. The results of this study allow discharge to be calculated from drip interval measurements and provide a quantitative basis for theoretical modelling of speleothem growth from drip sites.

Introduction

The growth of speleothem in caves is related to climatic controls such as temperature, precipitation and vegetation cover, and speleothem archives have significant potential in reconstructing past climates (Fairchild et al., 2005; McDermott, 2004; McDermott et al., 2006). The hydrological

* Corresponding author. Tel.: +44 01784 443587; fax: +44 01784 471780.
E-mail address: mattey@gl.rhul.ac.uk (D. Mattey).

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responses of speleothem-forming drips to the rainfall input to the aquifer system has important implications on how climate signals are encoded in speleothem, and there has been growing interest in high resolution monitoring of drip site discharge rates at synoptic, seasonal and inter-annual time scales (Bar-Matthews et al., 1996; Genty and Deflandre, 1998; Tooth and Fairchild, 2003; Cruz et al., 2005; Spötl et al., 2005; Mattey et al., 2006). The discharge characteristics of individual drips have been monitored using a variety of manual and automated logging techniques and these data, in conjunction with geochemical and isotopic studies of cave drip water, provide insight into seepage flow dynamics and the links between climate input and the captured proxy signals recorded in speleothem (Baldini et al., 2006; Tooth and Fairchild, 2003; Mattey et al, 2008).

The drip interval and the volume of drops detaching from roof straws and massive stalactites are the fundamental controls on the growth rate of speleothem and there are no modern studies of the factors that control the volume of water drops in this environment. The most important controls on drop volume are the geometry of the point of detachment — this might be a tubular roof straw or solid stalactite; and the flow rate, which introduces a dynamic component to the detachment mechanism. In addition, temperature (which controls viscosity and surface tension) density (related to dissolved load), the surface properties of the carbonate substrate, and other dynamic effects such as two-phase flow (where air is entrained in the water stream, (Baker and Brunsdon, 2003; Genty and Deflandre, 1998) are also factors that may influence drop volume.

There are several areas in karst research where accurate knowledge of the volume of single water drops is important. One example is modelling of growth of cave deposits where carbonate precipitation takes place from a water film fed by dripping water (Kaufmann, 2003; Kaufmann and Dreybrodt, 2004). Another is the measurement of groundwater discharge rates using drop counting methods (Baker et al., 1997; Baker and Brunsdon, 2003; Genty and Deflandre, 1998; Mattey et al., 2008), where drop interval and drop volume are required to obtain the discharge rate. Although the volume of drops detaching from tubes is well parameterised from classical studies, far less is known about the mass of drops detaching from solid surfaces (i.e. stalactites with different tip radii), or the variability of drop mass at different discharge rates; these are the variables that have greatest relevance in speleothem research and are the subject of this study.

Historical background and previous work

The volume of water drops falling from tubes has been the subject of classical investigations dating back over 200 years and the theoretical basis for the formation and shape of water drops in equilibrium with surface tension and gravity was established in the early 18th Century by Young and Laplace. Tate (1864), a pharmacist by profession, was interested in establishing experimentally what criteria were necessary to ensure that the volume of a given drop was accurately known. Using a limited range of tube diameters, he concluded that ''*Other things being the same, the weight of a drop of liquid is proportional to the diameter of the tube in which it is formed*'', a statement later enshrined as Tate's Law which relates weight w of the drop to the product of the circumference of the tube of radius r and the surface tension of the liquid γ

$$W = 2\pi r\gamma \tag{1}$$

Rayleigh (1899) greatly expanded the scope of Tate's experiments by using a wider range of dropping tube diameters, and was able to show that Tate's law is strictly true only for small tube diameters and modified Tate's expression to

$$w = \rho V g = r\gamma\phi(a^2/r^2) \tag{2}$$

where w is the weight of the drop, r is the radius of the tube, and γ is the surface tension of the liquid; φ is a function to be determined, and a is the 'capillary length' given by $a^2 = \rho\gamma g$ (about 2.7 mm for water). Rayleigh also carried out a series of systematic experiments to establish the form of the function φ, which being dimensionless, should be applicable to any liquid. For a limited range of tube sizes he proposed that Tate's constant of 2π should be replaced by the value 3.8.

Measurement of drop mass is also a means of determining surface tension and the classic paper of Harkins and Brown (1919) describes meticulous experiments to measure the surface tension of water and benzene. In place of Rayleigh's function φ they use the slightly different functions $f(r/a)$ and $\psi rV^{1/3}$, pointing out that the cube root of the drop volume V, having the dimension of length, performs a similar function to the 'capillary length' a. The Harkins and Brown measurements of water drop volume formed at the ends of tubes of varying diameter are reproduced in Fig. 1, which shows that the graph may be subdivided into three distinct regions: a broadly linear part from zero to about 5 mm tip radius, followed by a region of higher slope between 5 mm and 7.5 mm radius. The change of slope occurs when the diameter is approximately equal to the capillary length.

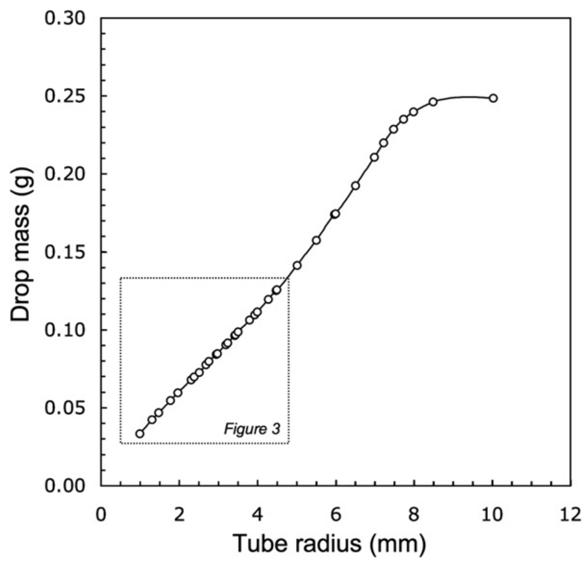

Figure 1 Relationship between drop mass of water at 20 °C and radius of circular tubes (glass and brass) at drip intervals > 3 min using data from Harkins and Brown (1919).

Finally, as the tube radius becomes larger than about 7.5 mm the slope decreases and drop size approaches an asymptotic value around 0.25 g, equivalent to a drop formed on a flat horizontal surface.

Ferguson (1929) further discussed the Harkins and Brown data using dimensional analysis, and expands on the general inapplicability of Tate's law. Padday and Pitt (1973) used the Laplace–Young equations and thermodynamic arguments to predict the volume and shape of circular axisymmetric drops, both stable and critically stable (i.e., at the point of detachment). However, this work does not predict the volume of the drop after detachment, or the dynamic circumstances leading to the formation of satellite drops. The maximum possible volume of drop (one suspended from a horizontal flat ceiling) at the instant of detachment is some 30% greater than what is actually measured, implying that only 2/3 of the volume of suspended fluid actually falls away. Wilkinson (1972) extends the Harkins and Brown measurements using capillary tubes as fine as 0.2 mm, and reported dimensionless constants for a variety of organic liquids. In one of few investigations involving non-axisymmetric geometries, Lorenceau et al. (2004) examine the formation of very small droplets on fine wires. Yildirim et al. (2005) present the results of numerical simulations alongside the Harkins and Brown results. These authors also discuss the effects of density, viscosity and drip rate with their associated dimensionless numbers, Bond, Ohnesorge and Weber, respectively. The drop detachment process may involve formation of secondary and satellite drops along with the detachment of the main drop and the measurements made by early investigators, and in this study necessarily include the masses of any satellite drops which invariably accompany the main drop.

Drop volumes and speleothem research

Measurement of groundwater discharge at drip sites in caves is one of the areas, where knowledge of drop volumes may be important. Water discharge rates at drip sites have been measured using both observational and instrumental methods. Manual timing of drip intervals provides a spot reading of discharge rate in the form of drips/unit time (Spötl et al., 2005; Tooth and Fairchild, 2003). Instrumental logging of volumetric discharge rates have been achieved using tipping bucket devices (e.g. Cruz et al., 2005; Treble et al., 2003) and by automatic drop counting using optical (e.g. Genty and Deflandre, 1998) or acoustic (e.g. Baker and Brunsdon, 2003; Mattey et al., 2006) techniques.

The tipping bucket devices are widely used in logging rain gauges where water drops are collected and fed into a fixed volume container (bucket) configured as a mechanical monostable. An event is recorded and time stamped when the full bucket tips and empties to reset itself. To obtain high temporal and volume resolution the collecting bucket needs to be as small as possible and these devices are therefore at risk of contamination from calcite supersaturated waters which affects long term reliable operation. These devices have a variable time base, and will only record an event and its associated timestamp when the bucket is full so temporal responses to highly variable flows may not be accurately represented.

Automated drip counting is an alternative means of monitoring discharge, and since the time base is constant, both transient events and small fluctuations in driprate can be identified (Collister and Mattey, 2005). Baker and Brunsdon (2003) used a vibrating drum device to count drips falling onto a membrane fitted with an acoustic transducer connected to an event counter, and logged data over five hydrological cycles revealing complex linkages between rainfall input and drip responses. Mattey et al. (2006) used an integrated acoustic drip counter/logger for monitoring seasonal hydrological responses in a Gibraltar cave and this device is described in more detail below.

Drop counting may be a more reliable method for long term logging of drip rates, but requires knowledge of water drop volume at different drip rates to accurately calculate volumetric discharge. The dependence of the volume of water drops forming from the ends of tubes (equivalent to drips forming from roof straws) on tube radius and other parameters has been reviewed above, but for drops detaching from solid surfaces (representing discharge from the tips of massive stalactites) the dependence of drop volume on tip geometry and flow rate has not been studied. In this study we report results of laboratory measurements of water drops forming from tubes, a proxy for hollow roof straws, and from spherical surfaces, a proxy for drips forming from water films detaching from the tips of massive stalactites, as a function of radius and flow rate.

Experimental methods

Acoustic drop counting

The drop counter used in this study records the acoustically generated electrical impulses of drops falling onto the lid of a watertight box (65 mm by 60 mm by 40 mm tall) which contains a signal detector board and an event logger encapsulated in a low modulus polyurethane resin. A water drop falling onto the lid of the instrument is detected and processed for storage as an ''event'' by the data logger. Drop events are stored in 2^{15} preset sampling intervals each having a count capacity of 2^{14} drops. The sampling interval used in these experiments was set to 10 min.

Artificial stalactites

Experiments were performed using a rig that fed either tubes or artificial stalactite tips with a supply of water at a constant flow rate, and the drop numbers were recorded using the acoustic logger. Tubes were made of brass, of wall thickness 0.5 mm with external diameters ranging from 1.58 mm to 5.15 mm. Artificial stalactite tips were machined out of aluminium bar stock to form spherical tips having various radii of curvature between 3.6 mm and 500 mm (Fig. 2). Precise coordinate measurements were made at several points across a diameter using a surface inspection machine, and a least-squares circle applied to the points to obtain the local curvature in the central region of the tip where the drops form. A 1.0 mm diameter hole was drilled in the tip of each stalactite to a depth of a few mm before opening out into a wider hole of between 5 mm and 10 mm diameter, depending on the diameter of

Figure 2 An acoustic drip logger and artificial aluminium stalactite tips with radius of curvature ranging from 3.5 mm to 500 mm used in this study.

the ''stalactite''. The larger hole was loosely packed with cotton wool, and water from a feeder tube was fed onto the cotton wool and allowed to percolate through the capillary hole; this generated a slow growing drop on the external spherical surface, which on detachment would fall and be recorded as a drip event.

All tubes and artificial stalactites were thoroughly cleaned using detergent, solvent degreaser and distilled water. Complete wetting of metal surfaces was enhanced by light abrasion with 400 grade carborundum paper. Water used for the experiments was ordinary tap water which had been allowed to equilibrate for 24 h at room temperature.

Experimental design

Drop mass in each experiment was determined by weighing the quantity of water produced from a known number of drops. Drops were counted using an acoustic drop counter allowing statistically large numbers of drops to be counted in each measurement. Up to four experiments were conducted in parallel where drops from artificial stalactites fell on to acoustic drip loggers placed in 800 ml Tripour® plastic beakers fitted with a tube to allow water to drain away into a second collecting beaker for subsequent measurement. Lids with apertures allowing the drops (or tubes) to pass through inhibited the effects of any loss by splashing and the effects of evaporation. A height of about 1 m between stalactite and the logger provided sufficient potential energy to give reproducible results over a wide range of drip rates and drip volumes. The drip logger was draped with a small strip of fabric to wick water away from the lid, and the insides of the two beakers were pre-wetted before the start of each experiment to minimise errors in water volume measurement. Between 5 and 10 repeated runs were performed to measure drop mass formed from 19 spherical surfaces having radii of curvature ranging from 3.5 mm to 500 mm. A total of 2000–5000 drops were collected per run at a drip interval of between 20 s and 40 s with runs lasting up to 36 h. The mass of water collected on each run varied between 100 and 600 g and was measured to a resolution of 0.01 g. The final value for the drop volume measured at each radius was therefore determined from a data set of at least 10,000 drops.

Flow rate control

Previous studies both in the laboratory (Harkins and Brown, 1919) and at cave drip sites (Genty and Deflandre, 1998) have suggested that drop volumes may vary with drip rate and was further investigated in this work (see below). However, preliminary experiments confirmed that drop volumes are constant within statistical error at intervals greater than about 15 s and for the drop mass measurements using different geometries the drip intervals were constrained to between 20 s and 40 s. This was achieved by passing water from a reservoir through a tube of nominal 20 mm bore and 500 mm length filled with washed sand to constrict the flow. An electromechanical solenoid valve driven by a pulse generator was used to control incoming flow to the sand-filled tube and the outflow was fed to the artificial stalactite. Drip rates were then controlled by varying the period and duty cycle of the pulse generator and a pulse period of 20 s were used, with duty cycles ranging from 0.5% to 2.5% to maintain constant drip rates as the drop volume varied with stalactite geometry. To measure drop volume as a function of drip rate the incremental change in mass was measured as a function of flow rate which was allowed to decrease exponentially and the method is described in Variation of drop volume with drip rate.

Local environmental effects

Temperature was not strictly controlled in these experiments, which were carried out under ambient laboratory conditions. The density of water varies by 0.23%/°C at 20 °C, but drop mass is independent of the liquid density and the temperature dependence of this density does not need to be taken into account, if the quantity of the liquid is measured as a mass. However, drop weight is proportional to surface tension and drop mass will decrease with increasing temperature. Runtime temperatures varied by up to 5 °C, but the temperature dependence of surface tension is very nearly linear at −0.2%/°C between 0 °C and 30 °C (Kaye and Laby, 1995). Temperature at the start and finish of each experiment was recorded and the mean value used to normalise the surface tension and drop sizes to their equivalents at 20 °C. Evaporation from the receiving vessels was measured as 3.3 g per 24 h and a correction to the final mass was applied as a function of time.

Results

Experimental measurement of drops from tubes

In order to validate the experimental technique against the well-corroborated results of historical studies (Rayleigh, 1899; Harkins and Brown, 1919) a series of measurements were made using a variety of square cut circular metal tubes of both brass and aluminium. Results based on measurements of between 3000 and 9000 drops for a range of tube diameters are shown in Fig. 3, where it is seen that the new results are closely similar to the classical measure-

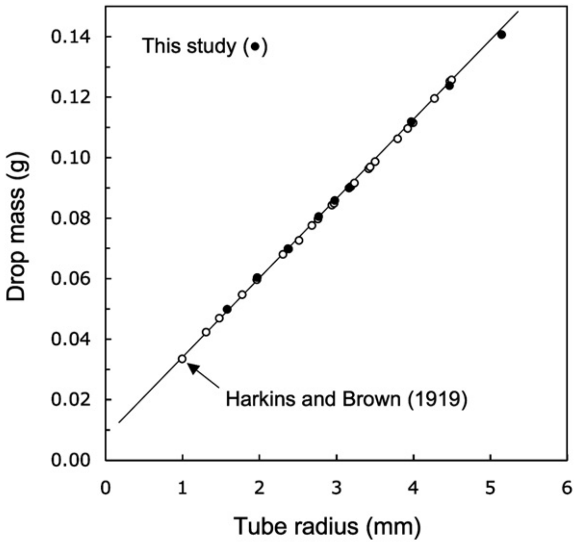

Figure 3 Comparison of the relationship between tube radius and water drop mass measured in this study (closed circles) with data from Harkins and Brown (1919) (open circles and best fit straight line).

ments and, within the range 0 mm < r < 5 mm the drop mass m (for the present measurements) is given by

$$m = 0.0255r + 0.00981 \quad (3)$$

where r the outer tube radius in mm. Over the range 0–5 mm, the rms error between the two predictions is 0.00091 g. The close agreement between the two sets of data shows that the automatic drop counting method is reliable, and may be applied to the main objective of establishing a relationship between drop mass and the radius of curvature of a stalactite tip.

Experimental measurement of drops from spherical tips

The relationship between drop volume and radius of a spherical surface stalactite tip is shown in Fig. 4, and the data define a smooth curve which rises to an asymptote close to 0.25 g. The Harkins and Brown (1919) data for circular tubes are also plotted in Fig. 4, and also show the beginnings of an asymptote at large radii near the same drop mass value as the asymptote obtained for spherical tips. Note also that for small radii the slopes of the two curves appear to be converging to approximately the same value, heading for the origin as $r \to 0$.

A simple function which fits the data with good correlation is of the form

$$m = \frac{m_\infty}{1 + r_0 r^{-1}} \quad (4)$$

where m is the mass of the drop and r is the radius of curvature; m_∞ and r_0 are constants of value 0.245 and 7.74, respectively. This equation fits both extremes at zero and infinite radius of curvature, predicting an asymptotic mass m_∞ = 0.245 g on a flat horizontal surface (infinite radius of curvature). The physical significance of r_0 is that this is the tip radius at which the mass of a drop is exactly one half

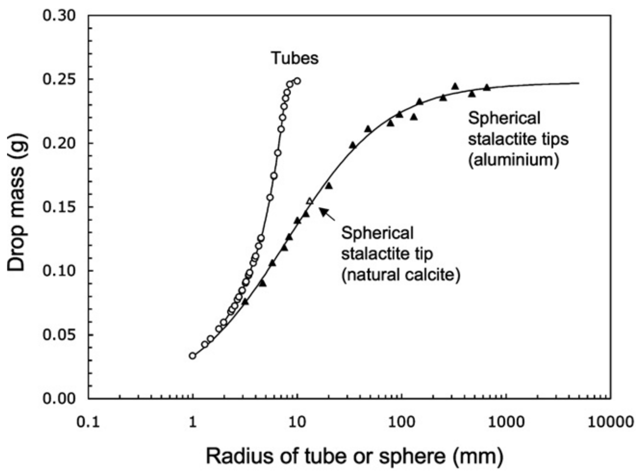

Figure 4 Relationship between drop mass and radius of curvature of the detachment surface for aluminium (closed triangles) and natural calcite (open triangle) stalactite tips. Data for drop mass as a function of tube radius (Harkins and Brown, 1919) is shown for comparison.

of its limiting value of m_∞. Close inspection of the slopes of the tube drop experiments of Fig. 3 suggests that, by comparison with Harkins and Brown's measurements, the surface tension (which controls the slope, since g is constant) of the water used in the present series of experiments may be 2% less than the Harkins–Brown value for pure water (it is assumed for this study that the density of tap water is negligibly different from that of distilled water); in this case m_∞ can be corrected upwards and rises to 0.250 g, which is more in line with the Rayleigh asymptote of Fig. 1.

When the experimental data are fitted to Eq. (4) it becomes

$$m = \frac{0.245}{1 + 7.74r^{-1}} \quad (5)$$

and gives the mass m of a drop forming on the tip of a stalactite based on the effective radius of curvature r at the point of drop detachment. This may be useful in cases where the drip rate is very low, and where it may not be possible to remain on the site long enough to collect enough water for an accurate calibration to be carried out. A physical measurement of the stalactite tip will enable the drop size to be determined within a few percent. This may be achieved by using calipers, a lead (Pb) wire form or a Plasticine cast for subsequent measurement.

Despite the large number of samples collected, some variability appears to still exist in the data, in the sense that all the points do not lie perfectly on a smooth, monotonic curve; this may be due to insufficiently accurate temperature control and compensation, to random vibration or some other natural variability. Differentiating (Eq. (4)) leads to an expression for the relative error in drop mass $\delta m/m$ due to a relative error in tip radius $\delta r/r$:

$$\frac{\delta m}{m} = \frac{r_0 r^{-1}}{1 + r_0 r^{-1}} \frac{\delta r}{r} \quad (6)$$

Genty and Deflandre (1998) measured a drop volume of 0.14 ml over a wide range of drip rates and according to the empirical relation of (Eq. (5)) this corresponds to a stalactite tip radius of curvature of 13 mm, or a roof straw with an outer radius of 5.1 mm (Eq. (3)). If $r = 13$ we get $\delta m/m = 0.38\delta r/r$, so the error in drop mass (and hence in flow rate) is only about 1/3 the error in estimating the tip radius; thus a 10% error here will propagate as an error of just 3.8% in drop volume. This error gets smaller as the tip radius gets bigger, tending to zero as r tends to infinity. Therefore, for large stalactites, it may be sufficient to estimate the curvature by eye. At the other end of the scale, in the limit as $r \to 0$, $\delta m/m \to 1$, i.e. the error is linear in r.

Variation of drop volume with drip rate

The relationship between drop mass and drip interval for an artificial stalactite with tip radius of 34 mm was determined by measuring the incremental change in mass in a collecting beaker placed on an electronic balance. The cumulative mass was recorded as a function of time as the hydrostatic pressure driving the flow through the constricted pipe was allowed to fall gradually to zero, providing an exponentially increasing in drip interval.

Fig. 5 shows the exponential change in cumulative mass over a period of about 20 h. The stepwise increase in cumulative mass can be seen in the enlarged portion of the curve shown as an inset and provides a measure of both drop mass and drip interval. These were calculated for each drop using an algorithm and Fig. 6 shows a typical result from a drop weight experiment, from which some important features are evident. The horizontal banding of the data at 0.19 and 0.20 g, respectively is an artefact of the 0.01 g balance resolution. Data points which indicate a resolution higher than the machine's capability are a result of the mathematical averaging process. The results confirm that drop volumes are essentially constant at drip intervals greater than 10 s. At fast drip rates with drip intervals less than about 10 s drop volumes are seen to increase with a greater degree of scatter in the mass of individual drops. Increasing drop size at high drip rates was observed by Harkins and Brown (1919), and was discussed by Joos (1999), who suggested that drop volume varied with drip rate, because two counteractive effects occur as a result of flow into the drop. One effect is the flow into the drop as the neck thins which increases the drop volume above the volume of the static drop; the other effect is the force imparted by the flow which enhances detachment. As a result the drop volume depends on the interval between consecutive drops, i.e. the flow rate (Joos, 1999). Based on prior work by Brady and Brown (1954), Joos (1999) derives an empirical relationship between drop interval and drop mass m at drop interval T

$$m(T) = m_0 + ST^{-0.75} \tag{7}$$

This function is fitted to the data points in Fig. 6 using $m_0 = 0.192$ and $S = 0.0296$.

Drop size and flow rate into the drop are linked by the Weber number, whose effect is simulated numerically by Yildirim et al. (2005). This dimensionless number represents the ratio of inertial to surface tension forces, and is defined as $We = \rho v2L/\gamma$, where ρ is density, v is fluid velocity, γ is surface tension, and L is an appropriate length scale. In order for inertial forces to be negligible, We must be very small. In the case of a circular tube, it is easy to see that the fluid velocity is proportional to the volume flux Q across the mouth of the tube, and a natural choice for L is the radius R. In this case $We = Q^2/\pi^2R^3$. With such a strong dependence on R it is tempting, for spherical tips, to define R as the radius of curvature to give satisfyingly small values of We at quite moderate curvatures. However, this is likely to give unjustified confidence that the small values of We

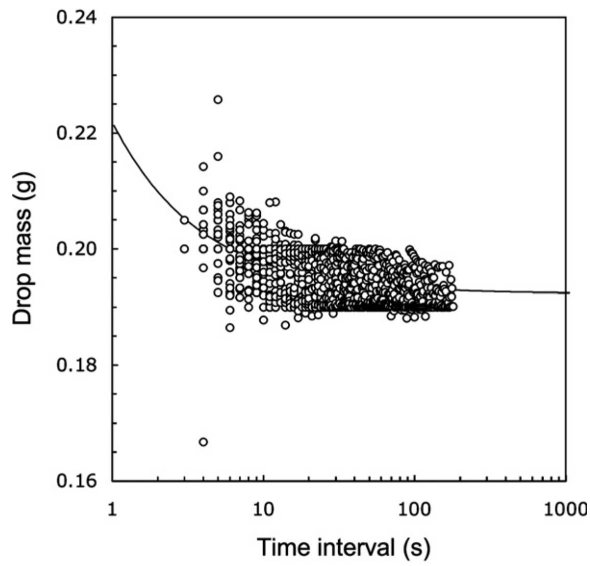

Figure 6 Relationship between drop mass ($r = 34$ mm) and supply flow rate, expressed as a function of interval between drops. The empirical relationship between drop interval and drop mass derived by Joos (1999) is fitted to the data. See text for discussion.

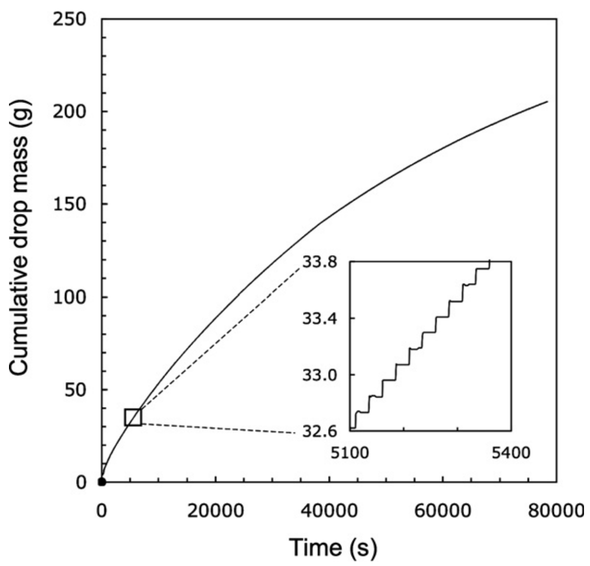

Figure 5 Relationship between cumulative mass of drops falling from an artificial stalactite ($r = 34$ mm), and time, measured for a decreasing water supply rate from a draining reservoir. Inset: enlarged portion of the main curve showing stepped increase from which drop volume and time interval can be inferred. See Discussion.

calculated this way are indicative that inertial forces may be neglected, and a different approach is adopted. For all the stalactite tips examined, the radius of curvature was greater than the capillary length $\sqrt{(\sigma/\rho g)}$, and all of the drops, so formed were pendant shaped rather than the quasi spherical shape characteristic of small Bond numbers. Therefore, it is assumed that the fluid flux passes into a hemisphere whose radius is defined by the volume of the drop (and its satellite). If the interval between drops is T, and a drop volume is V, then

$$We = \frac{2\rho V}{3\pi\gamma T^2} \tag{8}$$

This expression indicates a quadratic advantage to be gained by extending the drop interval. Taking the largest possible (asymptotic) drop volume $V_\infty = 0.25$ ml and an interval $T = 20$ s we get $We = 1.8.10^{-6}$ for water at 20 °C. While the numerical simulations of Yildirim et al. demonstrate that inertial effects disappear when $We < 10^{-7}$, the errors introduced by this means are consistent with the overall precision of the experiment as a whole.

To estimate the error incurred by using a short drip interval of 15 s or less we may use (Eq. (7)) to express the relative error as

$$\varepsilon = \frac{S}{m_0} t^{-0.75} \tag{9}$$

Hence, with $t = 15$ s, we get an error of 2.0%, which is within the limits of all the other sources of experimental error in this investigation.

Observing the central part of the scatter plot between 20 s and 200 s, it is apparent, notwithstanding the resolution of the weighing instrument, that there is a component in the scatter that is not necessarily due to undesirable experimental effects such as vibration or changes in temperature. Is there a good physical reason why falling drops should, or should not, necessarily be completely deterministic, as Harkins and Brown (1919) assumed? Is it possible that, no matter how meticulous the experiment, the factors which determine the point at which a drop detaches will always be subject to unavoidable tiny random fluctuations? If so, then it is important to establish what this variance is in order to attach the appropriate error bars to measurements of flow rates calculated using the falling drop method. The evidence so far suggests that, for drop intervals greater than 15 s the standard deviation is between 2% and 4% of the mean, but this hypothesis remains to be tested. Additionally, a further series of experiments using different tip curvatures to obtain a more accurate estimate of the coefficients in (Eq. (5)) would be desirable.

Discussion: implications for speleothem research

Actively growing stalagmites are fed by water dripping from tubular roof straws or from solid stalactite tips where drops form and detach from a flowing film of surface water. The main result of this study shows that the radius of the roof straw or the solid stalactite tip determines the mass of drops and will vary by an order of magnitude as the roof straw radius increases from 0.8 mm to 8 mm or the solid tip radius varies from 1mm to 100 mm. The mass/volume of water drops is a fundamental parameter in models of carbonate precipitation from carbonate saturated waters used to understand the growth mechanisms of speleothem (Kaufmann, 2003; Kaufmann and Dreybrodt, 2004). Drop volumes of 0.10–0.15 ml have been used in modelling speleothem growth (e.g. (Kaufmann and Dreybrodt, 2004)), which correspond to drops forming from roof straws with radii of 3.5–5.5 mm or detaching from massive stalactites with solid tip radii of 5.3–12 mm. (Eqs. (3) and (5)) can now be used to calculate the drip volume for specific detachment topologies, and develop models where the drip source geometry may evolve over time.

The differences in surface properties between natural calcite and the artificial aluminium stalactites used in this study are not believed to have any significant effect on the geometric controls on drop mass since complete wetting implies that the water contact angle is zero. Differences in rugosity are also not expected to have a significant effect on drop mass provided the scale of rugosity is small relative to the capillary length. To confirm this drip volume was measured for a natural calcite stalactite with a (very nearly) spherical tip of 13.1 ± 0.5 mm radius. Just over 3000 drops were collected at an average temperature of 18.9 °C to give an average temperature-corrected drop mass of 0.155 g. Using (Eq. (5)), the predicted radius of curvature is 13.4 mm, which lies within the measurement tolerance of the natural tip.

Drop volume is also known to be sensitive to changes in flow rate and Genty and Deflandre (1998) showed that although drop volumes remain constant over a wide range of flow rates, they also reported evidence of variance at high and low drip rates. The effects of flow rate on drop volumes are complex and potentially significant in the cave environment where drip rates are known to change rapidly on short timescales. For drip intervals of greater than 10 s the results of this study confirm that drop volumes are essentially constant but at drip intervals less than 10 s drop volumes are seen to increase, but with a greater degree of scatter in the mass of individual drops (Fig. 6). The experimental data are consistent with the empirical analysis by Joos (1999), but Genty and Deflandre (1998) also provide evidence that drop volumes can decrease at fast drip intervals in a cave environment. As variance in drop volume also appears to increase with decreasing drop interval there may be a stochastic component in even the most carefully controlled experiments, with a standard deviation in the order of 2–4% of the mean, and thus drop volumes may not be totally deterministic. These same investigations also suggest that the often quoted minimum drop interval of 3 min for drop volumes to be invariant may be rather conservative in a hydrological context, with 15 s being adequate to achieve a repeat accuracy of 2%.

Summary and conclusions

Following on from early work started over 100 years ago on the mass of water drops detaching from circular tubes, this new study using a drop counting method has been used to corroborate classical measurements, and the technique used to measure the mass of drops that detach from the spherical tips of artificial stalactites. Measurements are based on collecting statistically large numbers of drops, totalling > 10,000 per determination. For circular tubes or roof straws with radii in the range 0 mm < r < 5 mm the drop mass m is given by

$$m = 0.0255r + 0.00981$$

which is very close to the classical study by Harkins and Brown (1919). For tube radii greater than 5 mm the slope increases before starting to decrease at radii greater than 7.5 mm, with the mass asymptotically approaching 0.25 g for very large radii.

For drops detaching from curved solid surfaces, measurements of the mass of drops detaching from 19 different radii of curvature, ranging from 3.5 mm to 500 mm, gives an empirical expression relating drop mass m and the radius of curvature of the point of detachment r as

$$m = \frac{0.245}{1 + 7.74r^{-1}}$$

This expression allows the prediction of drop mass from massive stalactites of known tip radius at the point of drop detachment, and predicts a maximum drop mass of 0.245 g, closely similar to the maximum drop volume from tubes predicted from the classical studies.

These results provide a basis for conversion of drop volumes to discharge rates where the geometry of the drip source is known. Alternatively, information of the physical characteristics of the drip source can be inferred from measurement of drop volumes. Modelling studies assuming drop volumes as a variable also carry an implicit assumption about the physical properties of the drip source, which may change as a function of time with a concomitant change in drop size.

Recommendations for future work

Although the data reported in this paper present a convincing analysis of drop formation from spherical surfaces, there remains some scatter in the data despite using a very large number of drops. Better control of the experiment, particularly with regard to water quality, temperature and relative humidity, is expected to yield tighter results. Where sites exhibit very fast drip rates (T < 10 s), it is also of interest to further investigate evidence for variance of drop mass volume with drip rate. Driven largely by the need to develop accurate methods of measuring surface tension, much useful theoretical work has been done in predicting the sizes and shapes of drops forming on the ends of circular tubes, in particular in the dynamic region where the main and satellite drop(s) separate from the body of the fluid. However, it is believed that little work has been done on the formation of drops on curved surfaces, and this could present an interesting avenue for future research.

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